THERMAL, OXIDATIVE AND HYDROLYTIC DEGRADATION STUDIES OF POLY(ETHYLENE NAPHTHALATE)

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A thesis submitted to the Department of Pure and Applied Chemistry, University of Strathclyde, in part fulfilment of the requirements for the degree of Doctor of Philosophy

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DECLARATION

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ABSTRACT

Degradation of PEN is a particular problem above its melt temperature and is generally inevitable during synthesis and processing as the material is subjected to high thermal and mechanical stress. Whilst the literature is replete with studies on the degradation of PET, PEN has received little attention. In our research, we report on the thermal, thermal-oxidative and hydrolytic degradation of PEN, in comparison to PET, with particular emphasis on degradation under model processing conditions.

Despite evidence of increased thermal stability of PEN in contrast to PET, thermal degradation studies of PET and PEN highlighted strong similarities in their degradation behaviour. Identical primary and secondary thermal degradation mechanisms have been proposed for PET and PEN, with radical processes thought to dominate at high temperatures. Under thermo-oxidative conditions, the dominant degradation reaction in PEN has been revealed as oxidative cross-linking with more extensive chain scission thought to occur in PET. A reduction in the formation of cross-linked species in both polyesters has been demonstrated only in the presence of significant levels of moisture due to competing thermo-oxidative and hydrolytic degradation reactions. Cross-linking reactions in PET and PEN have been proposed to result in the formation of interconnected rings, with a high degree of conjugation, contributing to the extensive discoloration observed following thermo-oxidative degradation, particularly in PEN.

Finally, the extent of degradation has been shown to differ quite significantly during low temperature ageing studies of PET and PEN. Degradation of PET was largely influenced by the ageing environment and temperature with the dominant degradation reaction shown to differ with ageing temperature. However, all ageing environments and temperatures were found to have no detrimental effect on the physical properties of PEN. Embrittlement of both PET and PEN after ageing has been proposed to originate from secondary crystallisation developed upon ageing, causing remarkable changes to mechanical properties.

TABLE OF CONTENTS

ABBREVIATIONS

PET	Poly(ethylene terephthalate)
PEN	Poly(ethylene naphthalate)
NDC	Dimethyl-2,6-naphthalenedicarboxylate
DTF	DuPont Teijin Films
LED	Light emitting diode
T_g	Glass transition temperature
T_m	Crystalline melt temperature
DCA	Dichloroacetic acid
TFA	Trifluoroacetic acid
HFIP	Hexafluoroisopropanol
BHET	Bis-hydroxyethyl terephthalate
DMT	Dimethylterephthalate
EG	Ethylene glycol
TA	Terephthalic acid
M_n	Number average molar mass
IV	Intrinsic viscosity
DEG	Diethylene glycol
UV	Ultraviolet
SSP	Solid-state polymerisation
$\mathrm{M_n}$	Number average molar mass
ISBM	Injection stretch blow moulding
BHEN	Bis-hydroxyethyl naphthalate
NMR	Nuclear magnetic resonance
GPC	Gel permeation chromatography
NDA	2,6-naphthlaene dicarboxylic acid
PMMA	Poly(methylmethacrylate)
PVC	Poly(vinyl chloride)
MALDI	Matrix assisted laser desorption ionisation
TVA	Thermal volatilisation analysis
FTIR	Fourier transform infrared

GC	Gas chromatography
GC-MS	Gas chromatography - mass spectrometry
TGA	Thermal gravimetric analysis
DTG	Differential thermal gravimetry
PBT	Poly(butylene terephthalate)
EDB	Ethylene dibenzoate
BDB	Butylene dibenzoate
DSC	Differential scanning calorimetry
SEC	Size-exclusion chromatography
EDN	Ethylene dinaphthoate
BDB	Butylene dinaphthoate
DC	Direct current
DMF	Dimethylfuran
CSA	Chemical shift anisotropy
MSA	Magic-angle spinning
TOSS	Total suppression of sidebands
MS	Mass spectrometry
TMS	Tetramethylsilane
CEG	Carboxyl end group
T_c	Peak maximum temperature for crystallisation
TIC	Total ion chromatogram

1 INTRODUCTION

Synthetic polymers continue to play a significant role in society today due to their extensive applications. Modern lifestyles would be impossible without synthetic polymers used to produce valuable products such as protective packaging, insulated materials, medical devices and key components for diverse applications such as renewable energy production. Polyesters, in particular, are amongst the most industrially important synthetic thermoplastics in use today, with applications ranging from bottles for carbonated soft drinks to fibres for clothing and polyester based film for use within the packaging and electronic industries.

The synthesis of linear, fibre-forming aliphatic polyesters originally commenced in the 1930s by Carothers at DuPont USA, however these aliphatic polyesters did not succeed commercially due to their low melting temperatures and poor hydrolytic stability. [1] This research did, however, inspire other scientists to attempt the synthesis of polyesters from ethylene glycol and terephthalic acid monomers, leading to the synthesis of the first linear aromatic polyester, poly(ethylene terephthalate) (PET), by Whinfield and Dickson of Calico Printers Association UK, in 1941. [2,3] Whilst searching for a replacement for silk, Whinfield and Dickson identified PET as an excellent fibre forming polymer due to its thermal and mechanical properties and low cost, resulting in rapid expansion in the production of PET fibres. The development of polyester based films from PET followed thereafter.

PET is now one of the leading commercial polymers, accounting for 6.5% of the total world plastic demand in 2011. [4] Its major commercial uses remain as a textile fibre, material for blow molded bottles and biaxially oriented film for packaging, advanced photo systems, electrical and electronic applications. [5]

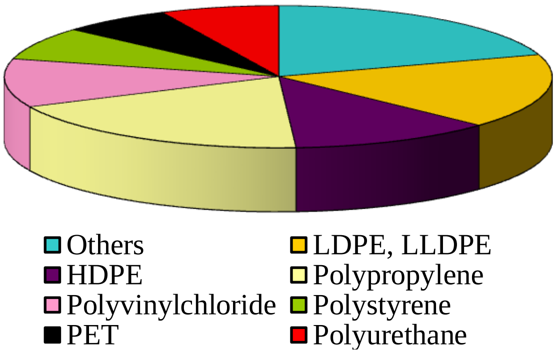


Figure 1.1 World plastic material demand 2011 [4]

Although the demand for PET remains strong, applications exist which often require improved properties that PET cannot provide. These include increased mechanical strength for motor substrates, high temperature resistance for electronics and improved gaseous barrier properties for food packaging applications. One polymer that can provide such properties is poly(ethylene naphthalate) (PEN). PEN incorporates naphthalene rings into the polymer backbone as opposed to phenyl rings in PET. The naphthalene units stiffen the polymer backbone resulting in a higher glass transition temperature and improved thermal, mechanical, electrical and barrier properties, in comparison to PET. [6,7] Although PEN was first produced in 1948, it is now only beginning to make a major appearance into the market place due to the lack of availability of the starting monomer, dimethyl-2,6-naphthalenedicarboxylate (NDC). Large-scale production of NDC was only introduced in the early 1990s leading to a significant increase in the raw material feed stocks for the production of PEN, reducing the overall cost of PEN resin. [1,5] This led to a substantial increase in the production and applications of PEN, with PEN now competing with PET in certain performance-driven markets based on its superior strength, heat stability and barrier properties.

DuPont Teijin Films (DTF) is currently the world’s largest supplier of PET and PEN polyester films, producing a wide range of versatile and adaptable polyester films with outstanding performance. Their broad portfolio of products, suitable for the specialty, industrial, packaging, electrical and electronic markets, enables them to compete in many diverse and challenging markets. [8] DTF also continuously research new uses for their current brands of PET and PEN polyester films and develop new and improved grades of polyester film in order to meet high performance expectations of new and existing customers. Recently, a great deal of research has been conducted into the development of PEN films for use in flexible electronic applications, such as high performance touch screens, flexible organic light emitting diode (LED) displays, high-density data cartridges and advanced photo systems. This has resulted in a sharp increase in the interest and demand for PEN polyester film, and therefore the need for extensive research at DTF to ensure customer needs are satisfied and their current market position is maintained.

DTF are particularly interested in the underlying degradation chemistry of PEN, in comparison to PET. For example, degradation related issues during processing such as the generation of colour, gels and white oligomeric material are of interest. Whilst these issues and the influence of environmental factors such as temperature, time, moisture and oxygen content have been well understood and modelled by DTF for PET, their exact effect on PEN is poorly understood. Although the fundamental degradation chemistry of PEN is believed to be similar to that of PET, there is little literature evidence to support this.

This research programme therefore focuses on developing a greater understanding of the degradation of PEN, in comparison to PET, to enable DTF to re-parameterise their existing and successful PET degradation/processing model for PEN. Particular emphasis is placed on the thermal, thermo-oxidative and hydrolytic degradation of PEN under model processing conditions.

1.1 Overview of Polyesters

1.1.1 PET

PET is a linear, semi-crystalline, aromatic polyester with a glass transition temperature, T_g ~80 °C and a crystalline melt temperature, T_m ~250 °C. The presence of aromatic rings in the backbone of the polymer, alongside carboxylate groups, results in a rigid and highly planar structure. However, segmental motion is increased with the presence of flexible ethylene glycol chains. The repeat unit of PET is illustrated in *Figure 1.2*. By rapid quenching of PET from its melt to below T_g, a “glassy/amorphous” material forms. Alternatively, on heating PET above its T_g, rapid crystallisation can occur resulting in the formation of an opaque “semi-crystalline” material with spherullitic morphology.

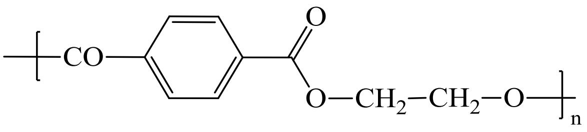


Figure 1.2 Repeat unit of PET

Generally speaking, PET has an excellent balance of physical, chemical and mechanical properties, providing many benefits over the use of other polymers, in the fibre, film and packaging sectors. These properties include its excellent clarity, high mechanical strength, high melting point and good thermal and hydrolytic stability. PET also has good barrier properties in O_2 and CO_2, a non-toxic nature and a lack of influence on flavour. [9,10] Such properties are obviously most advantageous in the bottling sector and have led to increasing interest in the use of PET in new applications such as bottles for beer or cosmetics. Additionally, the thermoplastic nature of PET is beneficial as this enables the polymer to be recycled.

PET is resistant to many chemicals, bleaches and solvents and is insoluble in all common solvents. Expensive polyhalogenated acetic acids such as dichloroacetic acid (DCA), trifluoroacetic acid (TFA) and fluorinated solvents such as hexafluoroisopropanol (HFIP) are required for solution studies of PET.

1.1.1.1 Industrial Synthesis of PET

PET is a saturated polyester produced by the step-growth polycondensation of bis-hydroxyethyl terephthalate (BHET). BHET is formed by the condensation reaction of ethylene glycol (EG) with dimethylterephthalate (DMT) or terephthalic acid (TA). Industrial synthesis of PET can be achieved in two reactions: (1) esterification and (2) polycondensation. The polycondensation stage is identical for both DMT and TA monomers, however the esterification reaction differs. PET can be esterified via transesterification or direct esterification routes.

1.1.1.2 Transesterification Reaction

The formation of the premonomer BHET can be achieved by the transesterification reaction of DMT and EG, resulting in the by-product methanol. This transesterification reaction, illustrated in *Figure 1.3*, occurs under atmospheric pressure at temperatures between 170 and 210 ^{o}C, in the presence of a metal acetate catalyst (generally Mg, Pb, Co or Zn acetate). [11,12]

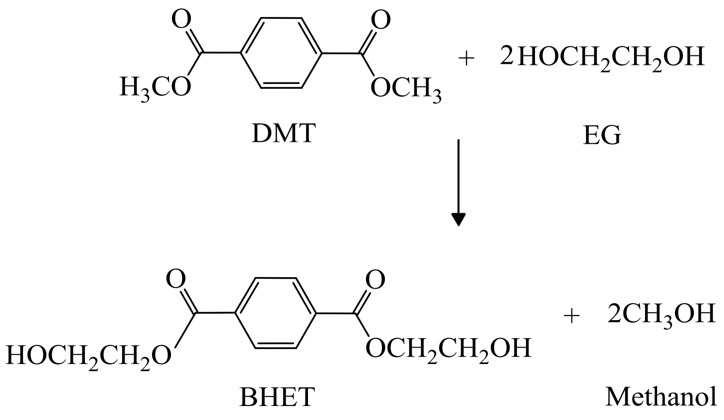


Figure 1.3 Transesterification reaction of DMT and EG

In practice, the transesterification reaction of DMT and EG must proceed with a large excess of diol. This excess diol compensates for the loss of diol as a result of volatilisation and leads to an increase in the overall rate of reaction, ensuring all methyl ester groups are converted to glycol end groups. The addition of phosphorus based stabilisers is also necessary at the end of the transesterification reaction to neutralise the activity of the catalyst used. Often the catalysts used in transesterification reactions are also active in degradation processes and therefore if the catalyst is destroyed prior to storage or processing, the risk of degradation occurring can be minimised. [13] On completion of transesterification, a relatively small quantity of low molar mass oligomers can form alongside BHET. As a result of this, the second stage of the reaction (polycondensation) can often be hindered due to the presence of unreacted methyl ester end groups. [1]

1.1.1.3 Direct Esterification Reaction

For many years, DMT was used as the starting material due to the lack of availability of pure TA. However, in the late 1960s, the first successful industrial scale production of TA was performed and thereafter the majority of PET production plants replaced DMT with TA feedstock. [1]

During this direct esterification reaction, purified TA is esterified with EG to form the premonomer BHET, as illustrated in *Figure 1.4*. This reaction is carried out under pressure (~3 bar) and high temperature (230 - 260 ^{o}C) to assist in the elimination of water formed. Any EG vaporised with the water evolved is separated in a distillation column and recovered back into the reaction vessel. Metal catalysts are not required, in contrast to the transesterification route, as the carboxyl groups in TA catalyse the reaction. [1,14]

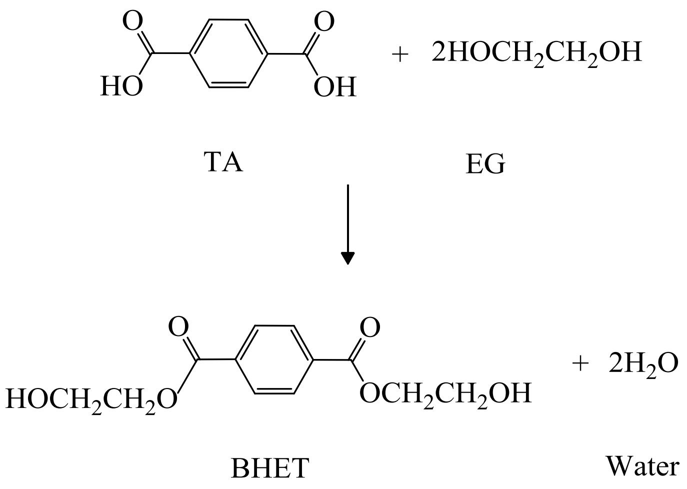


Figure 1.4 Direct esterification reaction of TA and EG

Many advantages exist for producing BHET via the direct esterification route. Excess EG is not required in the direct esterification reaction due to the nature of the starting monomer, TA, reducing the overall cost. The absence of methyl ester groups eliminates the risk of unreacted methyl ester groups disrupting the polycondensation reaction to form PET. The high pressure utilised throughout the reaction also lowers the consumption of EG and due to the absence of catalysts, no phosphorus-based stabilisers are required. Finally, the by-product water is removed easier from the reaction mixture in comparison to methanol, generated from the transesterification reaction of EG and DMT.

The monomer, BHET, produced from either the transesterification reaction or direct esterification reaction then acts as the monomer for polymerisation to yield PET. This is referred to as the polycondensation reaction.

1.1.1.4 Polycondensation Reaction

In stage two of the synthesis of PET, shown in *Figure 1.5,* polycondensation of BHET occurs in the melt phase leading to the coupling of monomers and the evolution of EG. This polycondensation reaction is carried out under high vacuum and elevated temperatures up to 290 ^{o}C, ensuring the successful evolution of EG and lengthening of polymer chains. In contrast to the esterification stage, this reaction is catalysed using antimony catalysts such as antimony trioxide (Sb_2O_3) or antimony acetate ($Sb_2(CH_3CO_2)_3$). [1,15] Titanium alkoxides have also been reported as successful catalysts in polycondensation reactions of PET, however they are no longer used as they result in discolouration of the final product. [12]

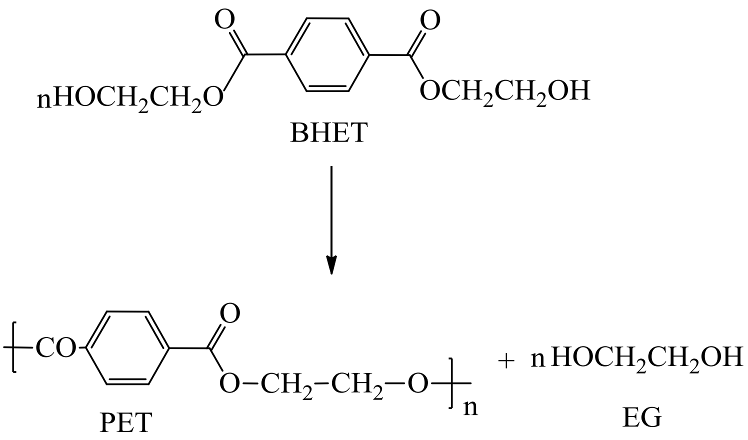


Figure 1.5 Polycondensation reaction of PET

Throughout the polycondensation reaction, the melt viscosity and the overall molar mass of PET increases as EG is eliminated. The number average molar mass (M_n) of PET produced by a melt polymerisation reaction is typically 16,000 to 19,000 g mol^{-1} (therefore an intrinsic viscosity (IV) between 0.58 and 0.68 dL g^{-1}). [1]

As highlighted previously, a relatively small quantity of low molar mass oligomers, with unreacted methyl esters groups, can form when synthesising BHET from DMT and EG. The presence of unreacted methyl ester groups can hinder the polycondensation reaction of PET as methyl ester groups are less reactive towards nucleophilic substitution than hydroxyethyl ester groups from BHET. This problem is not encountered in the TA route as carboxylic acids groups are even more susceptible to nucleophilic substitution and therefore more likely to undergo esterification than hydroxyethyl ester groups in BHET. However, it must be noted that although excess carboxylic acid groups can survive the polycondensation reaction, they are reported to have an adverse effect on the thermal stability of the final product. [13]

1.1.1.5 Side Reactions

The quality of the final polymer product can be impaired by side reactions that occur during the synthesis of PET. Two important side reactions result in the formation of diethylene glycol (DEG) and PET oligomers.

- ***Diethylene Glycol***

Different mechanisms have been published for the formation of DEG, [16,17] however most recent publications favour the formation of DEG by direct etherification. [18,19] This acid-catalysed reaction, illustrated in *Equation 1.1*, occurs during the initial esterification step in the synthesis of PET and involves condensation of two hydroxyl groups to form DEG and water. Once DEG is formed, it is preferentially incorporated into the polymer due to its identical reactivity to EG and lower volatility. Therefore, despite great efforts to reduce this side reaction, DEG cannot be eliminated from the polymer melt and 1 - 3% of DEG is incorporated into PET as a co-monomer, independent of the preparation route. [12,15,18]

$$R^1\text{-OH} + R^2\text{-OH} \longrightarrow R^1\text{-O-}R^2 + H_2O$$

Equation 1.1 Typical direct etherification reaction

The presence of DEG moieties in PET is known to impact the physical properties and chemical behaviour of PET, potentially leading to serious problems. The DEG ether bonds introduce more flexibility into the main polymer chain, subsequently reducing the melt temperature of the polymer. For every weight per cent increase in DEG incorporated, the melt temperature of PET decreases by 5 ^{o}C. [15,18] Other properties such as the glass transition, crystallisation behaviour, thermal and ultraviolet (UV) stability, melt viscosity and thermal/thermo-oxidative/hydrolytic degradation behaviour are also reported to vary with increasing DEG content. [1,10,18,20,21,22]

- ***Oligomeric Material***

PET is also known to contain approximately 2 - 3% of short chain linear and cyclic oligomers that form via several mechanisms during the synthesis of PET. Firstly, degradation of the polymer chains as a result of heating, processing, drying or recycling can result in the formation of oligomeric species. [23,24,25] During the polycondensation reaction in the synthesis of PET, oligomers can also be formed due to the presence of methyl ester groups, limiting growth of the polymer chains. These methyl ester groups are present due to an incomplete esterification step, discussed previously, and allow only one end of the polymer chain to grow slowly, limiting the final polymer chain length. Intramolecular cyclisation can also result in the formation of cyclic oligomers, as illustrated in *Figure 1.6*. Cyclic oligomers are most likely to form when access to the reactive end groups on the polymer chain is limited, preventing the access of monomers into the polymer network. [1]

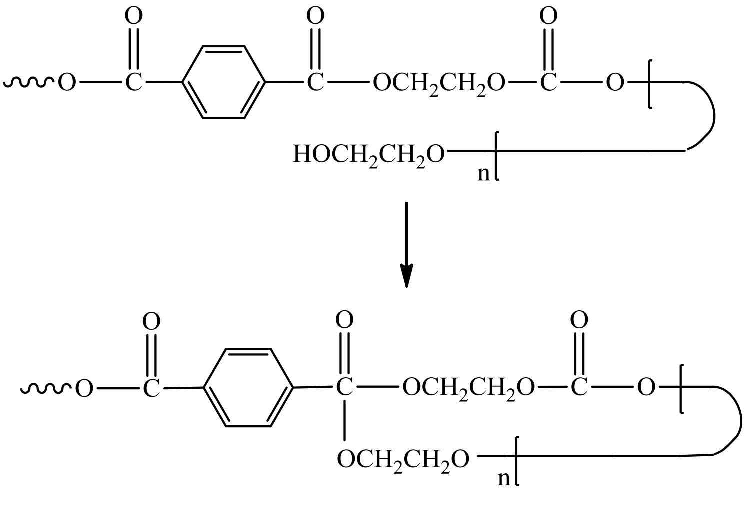


Figure 1.6 Formation of cyclic oligomers in PET [1]

1.1.1.6 Post-Polymerisation Treatment of PET

On completion of the melt polymerisation reaction, PET can be formed into laces through a rough die and cooled using a stream of water, prior to being chopped into small chips. The polymer chips are then dried and crystallised before being packaged - the highly compact chain packing in crystalline material results in a reduction in the diffusion of water into the polymer, reducing the rate at which hydrolytic degradation can occur. Alternatively, the PET melt can be directly fed into the extruder and processed into its final shape. This process completely eliminates the risk of hydrolytic degradation as the polymer does not come into contact with water.

1.1.1.7 Solid-State Polymerisation of PET

Although the average molar mass grade of PET, produced by melt polymerisation reactions, is suitable for numerous applications, it is often necessary to produce PET of a higher molar mass for applications such as soft drink bottles, tire cord filaments and industrial fibres. High molar mass PET cannot be feasibly synthesised by melt polymerisation as the melt viscosity is too high and degradation reactions can overtake the polycondensation reactions, limiting the overall molar mass. [12] Solid-state polymerisation (SSP) is a process in which the molar mass of polyesters can be further increased in the solid-state. The M_n of SSP PET can reach up to 27,000 g mol^{-1} (IV = 0.90 dL g^{-1}) for bottle grades and 38,000 g mol^{-1} (IV = 1.20 dL g^{-1}) for technical fibre applications. [1]

The first step in SSP of PET is to crystallise the low molar mass polymer chips, synthesised via melt polymerisation, around 160 ^{o}C to prevent sintering. The polymer chips are then heated above their T_g and approximately 20 ^{o}C below their T_m. This temperature for SSP has to be as high as possible to maximise the reaction rate, by increasing the mobility of the end groups, but below the melting point to prevent sticking of the polymer chips. SSP is carried out either in high vacuum or in a hot inert gas and the volatile by-products of the reaction escape from the surface of the polymer chip by diffusion. The chemistry of SSP is identical to that of melt phase polycondensation and generally raises the degree of polymerisation from approximately 100 to 140 repeat units. [12,26,27] *Figure 1.7* illustrates the different steps involved in the SSP of PET.

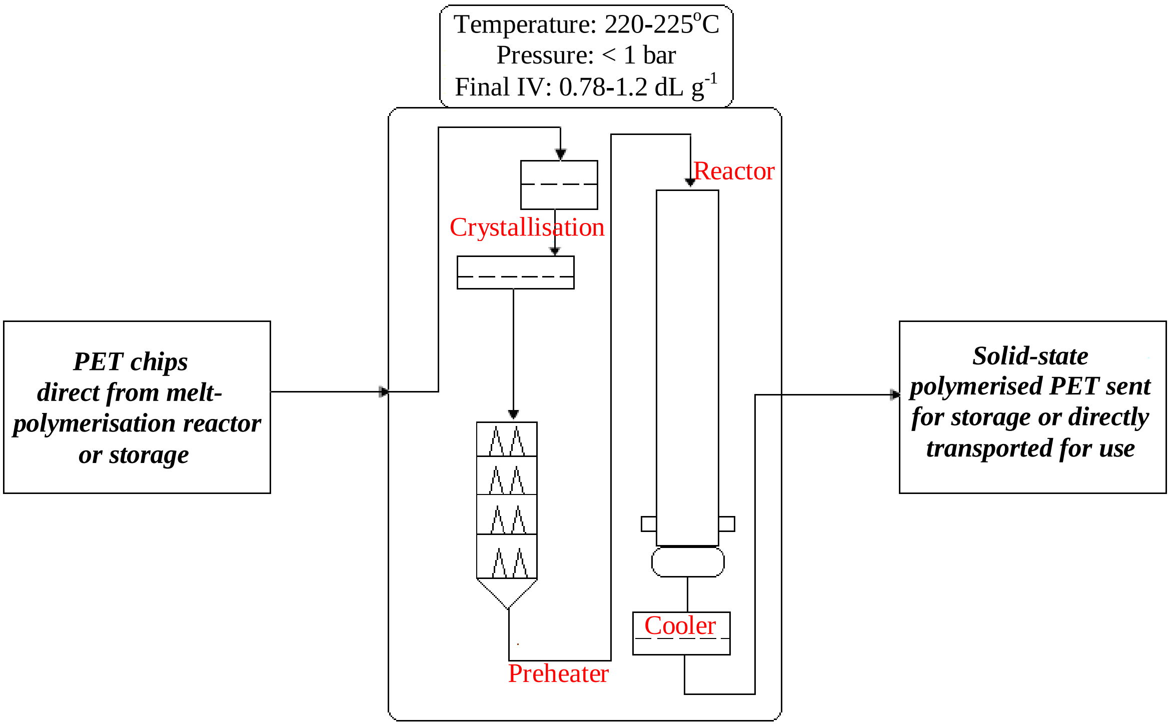


Figure 1.7 Solid-state polymerisation of PET [1]

SSP enables high molar masses to be reached which are either technically or commercially infeasible in the melt phase. The main advantages of SSP compared to melt phase polymerisations are: [1,26]

- The problems associated with stirring a highly viscous melt, as the molar mass increases, are eliminated in the solid-state.
- The running costs are lower as high temperature and vacua are not required.
- Degradation and side reactions are limited in the solid-state due to the low operating temperatures used.
- No environmental pollution as no solvent is required in SSP.

- The existing polycondensation catalyst present in PET remains active during SSP, therefore no additional or new catalysts are required.

It must also be noted that the reaction rate is slower in SSP compared to melt polymerisation reactions. This is due to the reduced mobility of the reacting end group species and the slow diffusion/removal of the by-products, ethylene glycol and water. Furthermore, as SSP is occurring in a solid polymer matrix constantly undergoing crystallisation, the mobility of the end groups and by-products are further restricted. The SSP reaction rate is also influenced by factors such as temperature, time, particle size and end group concentration, resulting in no two PET materials having the same SSP behaviour. [1,26,28]

1.1.1.8 Pre-Processing Treatment of PET

Hydrolytic degradation of PET chips is inevitable during storage and post-polymerisation cooling processes. The hydroxyl chain ends and the ester groups within the polymer network are likely to retain water and therefore if the polymer chips were to be processed directly, the molar mass of the polymer would significantly decrease as a result of hydrolytic degradation. For this reason, PET chips are crystallised, again to avoid sintering during drying, and then dried for several hours to reduce the moisture content, prior to processing. DuPont Teijin Films recommend drying PET under air for a period of 4 hours at 160 ^{o}C.

The effect of this pre-processing treatment on the thermal degradation of PET pellets has been investigated. Villain *et al.* [29] studied the overall mass loss of PET when dried under air and nitrogen at 160 ^{o}C for 800 minutes, prior to thermal degradation at processing temperatures of 280 ^{o}C and 310 ^{o}C. The most significant mass loss was reported when drying and degradation were performed under air, due to oxidative and hydrolytic degradation leading to a reduction in the overall length of the polymer chains. These observations are not entirely surprising as the drying temperature is above the glass transition temperature of PET and therefore the polyester chains are more mobile and subsequently more likely to enable the penetration of oxygen and water into the polymer network.

1.1.1.9 Processing PET

PET is a strong, flexible thermoplastic that readily crystallises, can be oriented and also heat stabilised. It has many different applications as an amorphous, partially crystalline, or highly crystalline material and can be processed into a variety of products. However, its major commercial uses remain within the textile fibre, biaxially oriented film and packaging industries.

a) Fibres

After development of the process of stretching and uniaxially orienting PET fibres in the early 1950s, demand increased significantly resulting in PET fibres becoming more cost-competitive with other materials. PET is a suitable material for textile fibre applications due to its linear, unbranched structure and its ability to crystallise to a high extent. Grades of PET typically used for the production of fibres have M_n values between 15,000 and 20,000 g mol^{-1} (therefore an IV between 0.55 and 0.67 dL g^{-1}). [1] Higher molar mass grades are available for higher mechanical strength applications such as fibres for industrial yarn and tyre cords, however the melt viscosity of these materials are often extremely high resulting in great difficulties during processing.

The processing of PET into fibres is an economical process whereby dry polymer chips are initially melted in an extruder. The polymer melt is then extruded through a die, with the assistance of a pumping system, and spun around cylinders as semi-crystalline fibres at temperatures around 285 - 300 ^{o}C. The semi-crystalline fibres formed then undergo a drawing process. This process aligns the polymer chains in a parallel fashion along the fibre axis, increasing the intermolecular forces and restricting the chains into a crystalline fibre structure, forming fibres of a very high mechanical strength. [1,30] A schematic diagram of the melt-spinning process, used to produce PET fibres, is illustrated in *Figure 1.8*.

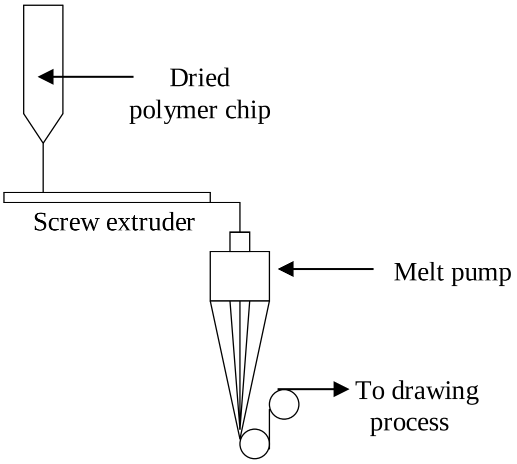


Figure 1.8 Schematic of the melt-spinning process used to produce PET fibres

b) Biaxially Oriented Film

PET was first identified as a suitable polymer for the formation of biaxially oriented film in the late 1950s by DuPont and ICI. [5] Developments in previous years have focused on improving gas barrier and thermal properties of PET film for food and beverage applications, however as PET film has found acceptance in a number of different markets, a good balance of thermal, physical, chemical and mechanical properties is essential. [5,30] A highly intricate drawing and heat setting process, known as extrusion, is performed in order to achieve such high quality films with the required properties.

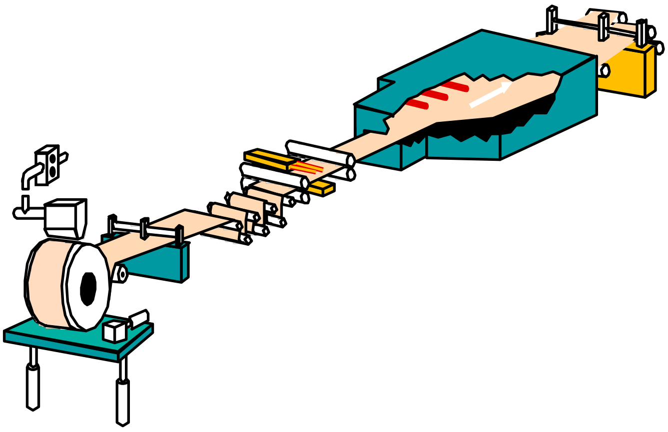


Figure 1.9 A biaxially oriented film processing line

Biaxially oriented film, with high mechanical strength, can be produced from grades of PET with a typical IV of 0.64 dL g^{-1} and therefore a number average molar mass of less than 20,000 g mol^{-1}. The main sequence of events, which occur during the processing of PET into biaxially drawn film, is illustrated in *Figure 1.10*.

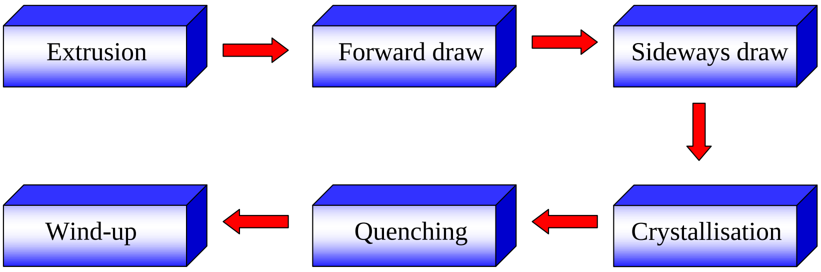


Figure 1.10 Schematic representation of the processing steps involved in the production of biaxially drawn PET film

Dry PET chips are initially melted in a screw extruder between 270 - 300 ^{o}C and fed through a horizontal slot die. This die is a stainless steel shaping tool, mounted onto the end of the extruder, to provide the required shape to the melt. [30,31] On exiting the die, the molten PET is then cast onto a water chilled roll, known as the casting drum, which quenches the film into the amorphous state. If the film is not quenched rapidly, nucleation and crystal growth will occur, resulting in a film with increased haze and brittleness which can create problems during subsequent drawing stages. Therefore the aim of casting is to produce a uniform, non-crystalline, thick film free from surface blemishes which can then undergo a drawing process known as biaxial orientation. [5,31]

The process of biaxial orientation involves drawing the film initially in the direction of the machine i.e. in the forward direction using heated rollers. These heated rollers are temperature programmed to operate approximately 15 ^{o}C above the T_g of PET, enabling the material to be physically stretched in the machine direction, resulting in improved tensile properties. Subsequently this process is followed by drawing the film in the transverse direction i.e. sideways to the direction of travel in a heated stenter oven comprising of a series of heated zones between 90 ^{o}C and 110 ^{o}C. The edges of the film are clipped along diverging rails in the stenter oven enabling the material to be stretched by a factor of three or four. This transverse drawing process increases the overall crystallinity and extent of orientation (on a molecular level) within the polymer. [5,31]

Once the drawing process is complete, the film is then "heat set" or crystallised under tension in the oven at temperatures typically above 200 ^{o}C. This process further stabilises the film into its oriented state by use of heat. As the polymer is oriented and annealed, the size and number of crystallites increase, enabling chains that are in an aligned position to lock into place. This provides the film with further dimensional stability during storage or use as the chains have restricted mobility, preventing the film from shrinking back to its original, unstretched shape. Finally, the film is quenched in air on water cooled rollers and uneven edges are cut off prior to wind-up. These edges are then glycolysed back to monomer and recycled back into the film process. [1] The thermal and mechanical properties of biaxially oriented polyester film can be varied depending upon the stretching and heat set conditions used during production. [30] This enables a wide variety of polyester films to be generated for different applications.

Great care is taken in the design and operation of PET plants to produce film with the highest degree of purity, often required for applications within the packaging and electronic industries. However, this high degree of purity is often difficult to maintain due to the high processing temperatures and subsequent degradation of the polymer as it is processed. The degradation reactions that PET can undergo are influenced by both the polymer recipe and the extrusion conditions – the resulting degradation products are often deposited on the rollers and often on the product itself, leading to processing issues and product defects.

c) Blow Moulded Objects

Injection stretch blow moulding (ISBM) is the most common process for producing PET objects such as bottles commonly used for water, juice and a variety of other products. Grades of PET specifically produced for blow-moulded bottle applications are typically of a higher molar mass (M_n values range between 24,000 and 36,000 g mol^{-1}) than film and fibre grade PET and must meet specific colour requirements and regulations for food packaging. [1]

ISBM can be achieved in one single step by simply extruding dry PET chips into preform moulds which are then directly fed into the blow-moulding device, encompassed on the same machine. Alternatively two-stage stretch blow moulding can be carried out. This procedure involves the use of pre-prepared preforms in contrast to the online synthesis of preforms in the one-step process. The two-stage moulding procedure introduces more flexibility in the choice of preforms used in the production of blow moulded objects. [1,30]

Even after more than fifty years, the future still holds great potential for PET across all market sectors. With its excellent balance of properties, suitable for a broad array of applications in the specialty, industrial, packaging, electrical and electronic markets, continuous demand for PET is likely for the foreseeable future.

1.1.2 PEN

PEN is a structurally related aromatic polyester to PET, produced by the step-growth polycondensation of bis-hydroxyethyl naphthalate (BHEN). The repeat unit of PEN is illustrated in *Figure 1.11*. The two condensed aromatic rings in PEN result in overall improvements in the thermal, mechanical, chemical, hydrolytic, electrical and barrier properties of PEN, in comparison to PET. [1,6,7,32,33]

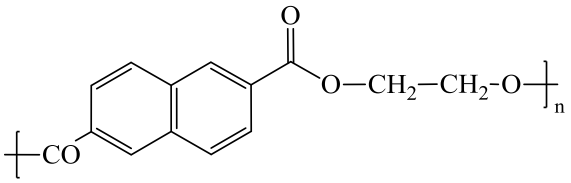


Figure 1.11 Repeat unit of PEN

Teijin first introduced semi-commercial quantities of the improved polyester, PEN, into the market place in the early 1970s as an extruded film. Owing to its superior properties, many other companies then expressed an interest in PEN and it quickly found use in numerous applications such as audio and video tapes, electrical insulation and fibre for belts in radial tyres. [32] PEN film is particularly well suited for electrical applications such as flexible printed circuits, wiring applications and flexible heaters. [33,34] Furthermore, because of its superior permeability and thermal properties, there has been large interest in PEN for packaging applications. Plastic beer bottles, improved carbonated beverage containers and hot fill containers are some examples of PEN packaging applications.

Despite the superior properties of PEN, in comparison to PET, there are two major drawbacks that must be considered before selecting PEN as a suitable polyester for specific applications. Firstly, PEN has a higher melt viscosity than PET which can lead to great difficulties when processing the polymer, particularly in fibre spinning and injection moulding processes. Secondly, PEN is a great deal more expensive than PET due to the high costs of starting materials. Therefore, it may not always be feasible in some high volume applications. There have been many attempts to combine the superior performance of PEN and the economic aspects of PET through polymer blending, [34,35,36,37] however DuPont Teijin Films have developed a cost-effective biaxially oriented PEN film, with enhanced properties in comparison to PET.

1.1.2.1 Important Properties of PEN

PEN is a semi-crystalline, aromatic polyester with a T_g of 122 ^{o}C and T_m of 267 ^{o}C. The chain structure in PEN is close to that of PET, but PEN has naphthalene groups instead of phenyl groups, resulting in a more rigid macromolecular system. This rigidity is not only due to the size of the naphthalene rings in PEN but also the non-collinear attachments of the ester groups to the naphthalene rings, [38] reducing the polymers rate of crystallisation in comparison to PET. Finally, the overall thermal stability of PEN is improved in comparison to PET. This is thought to be a result of the enhanced delocalisation of charge across the naphthalene ring units in PEN, increasing the stability of the ester linkages. The differences in the physical and chemical properties of PET and PEN can therefore be attributed to the presence of highly rigid naphthalene rings, with the remaining portion of the repeat units i.e. EG units terminated by ester bonds, common to both PET and PEN. *Figure 1.12* illustrates improved properties of PEN, in comparison to PET.

PEN exhibits increased tensile strength as well as elasticity modulus and elongation at break. The gas barrier properties in CO_2 and O_2 are also greatly improved in PEN compared to PET. The naphthalene ring in PEN has an extended chromophore that absorbs light up to 380 nm in comparison to absorption up to 313 nm in PET. This increased UV absorption further expands applications of PEN to products where the screening from UV light is desirable e.g. food and medical packaging. The increased thermal stability of PEN, together with its good hydrolytic resistance, chemical resistance and electrical properties earn its strong position in high temperature applications. [1,35]

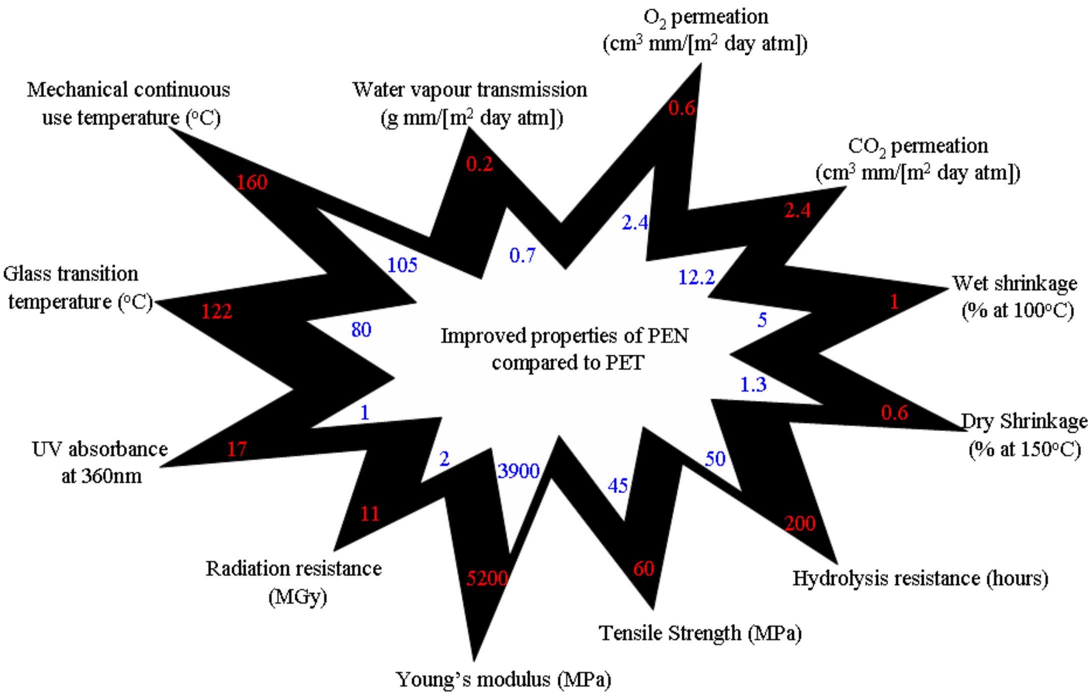


Figure 1.12 Differences in physical properties of PET and PEN [1]

PEN also has greater chemical resistance than PET, which is an extremely desirable property for household, chemical and cosmetic packaging. However, this can create difficulties for analytical testing where dissolution is required i.e. NMR, GPC, particularly as the crystallinity of PEN escalates.

1.1.2.2 Industrial Synthesis of PEN

PEN is synthesised by the step-growth polycondensation of BHEN, which is produced via the condensation reaction of EG with NDC or 2,6-naphthlaene dicarboxylic acid (NDA). Identical to PET, industrial synthesis of PEN is achieved in two reactions; esterification followed by polycondensation.

1.1.2.3 Transesterification Reaction

Although the literature on the synthesis of PEN is limited, the most preferred route appears to be via the transesterification process. As illustrated in *Figure 1.13*, the formation of the premonomer BHEN can be achieved by the transesterification reaction of NDC with EG, resulting in the by-product methanol.

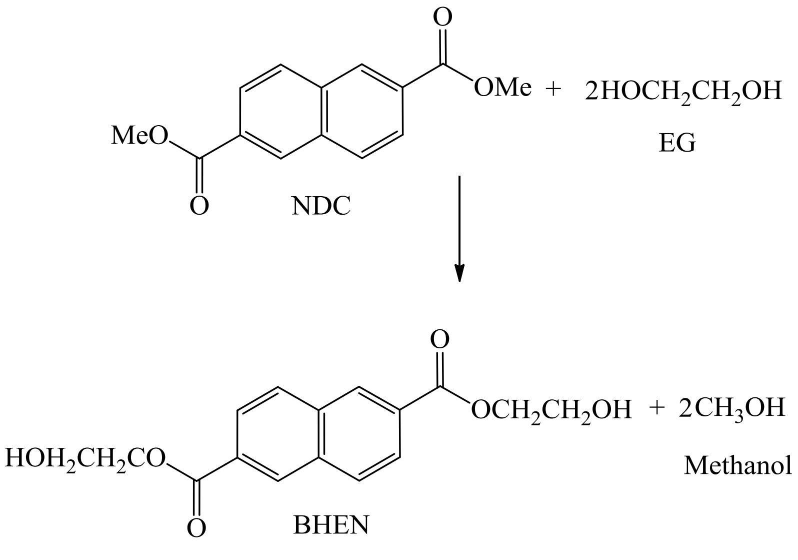


Figure 1.13 Transesterification reaction of NDC and EG

The transesterification reaction to produce BHEN occurs under atmospheric pressure and temperatures of 190 - 230 ^{o}C in the presence of a metal acetate catalyst (generally Pb, Zn, Co, Mg acetate). [33] This process is very similar to the transesterification reaction for the synthesis of PET, with identical practical issues as described previously for PET in *Section 1.1.1.2*.

1.1.2.4 Direct Esterification Reaction

PEN can also be synthesised via the direct esterification route using NDA and EG. However, this route is rarely adopted due to the poor commercial availability of pure NDA. The monomer, NDA, is also less soluble in the reaction system and more difficult to handle in comparison to TA, used in the direct esterification reaction of PET, leading to a more challenging, less economical polymerisation process. [1,32]

1.1.2.5 Polycondensation Reaction

In stage two of the synthesis of PEN, illustrated in *Figure 1.14*, polycondensation of BHEN occurs in the melt phase leading to the coupling of monomers and the evolution of EG. This polycondensation reaction is very similar to that of PET and is carried out under reduced pressure and elevated temperatures up to 300 ^{o}C, ensuring the successful evolution of EG and lengthening of polymer chains. The most active catalyst for the polycondensation reaction of BHEN is reported to be antimony trioxide. [33]

Throughout the polycondensation reaction, the melt viscosity of PEN increases and thus the overall molar mass of the system increases as EG is eliminated. However, due to the increased melt viscosity of PEN in comparison to PET, the achieved molar mass of PEN obtained from the melt polymerisation is reduced. The M_n of PEN, after melt polymerisation, is typically 15,000 g mol^{-1} (IV of 0.5 - 0.55 dL g^{-1}) in comparison to 16,000 to 19,000 g mol^{-1} (IV of 0.58 - 0.68 dL g^{-1}) for PET.

Therefore SSP of PEN is often performed in order to substantially increase the molar mass of the polymer. [1]

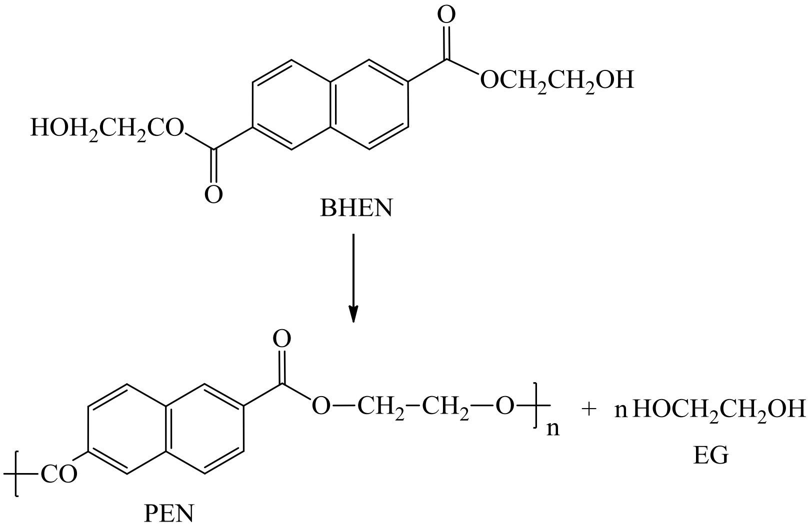


Figure 1.14 Polycondensation reaction of PEN

In addition to the increased melt viscosity of PEN, the monomers used to synthesise PEN also have higher melt temperatures in comparison to those used to synthesise PET. High temperatures must therefore be maintained during the synthesis of PEN in order to account for these properties and ensure that the polycondensation reaction is successful. Unfortunately, this increases the overall manufacture costs of PEN, in comparison to PET, and increases the risk of thermal and thermo-oxidative degradation during manufacture.

1.1.2.6 Side Reactions

Although the side reactions that occur during the synthesis of PEN are not covered in the literature, these are thought to be identical to PET due to the similar nature of the starting monomers and final polymers. The two important side reactions are the formation of DEG and oligomeric material, outlined for PET in *Section 1.1.1.5*.

1.1.2.7 Post-Polymerisation Treatment of PEN

On completion of the melt-polycondensation reaction, PEN can then undergo an identical process to PET whereby the polymer is formed into chips. To form the polymer chips, PEN is processed into laces through a rough die before being cooled using a stream of water and then chopped into chips. As highlighted previously for PET, the chips are then dried and crystallised by heat setting in order to reduce the diffusion of water into the polymer matrix, decreasing the risk of hydrolytic degradation. Despite the fact that PEN is reported to have increased hydrolytic resistance in comparison to PET, [1] no studies exist with an explanation to account for this difference. Therefore, the same post-polymerisation treatment must be performed for PEN, as for PET, in order to minimise the risk of hydrolytic degradation occurring during processing and storage.

Similar to PET, PEN can be directly extruded from the melt and processed into its final shape. Once again, this process can be problematic due to the high melt viscosity of PEN and can lead to the polymer being exposed to high temperatures for long periods of time, subsequently increasing the risk of thermal and thermo-oxidative degradation.

1.1.2.8 Solid-State Polymerisation of PEN

In order to synthesise PEN with a M_n greater than 15,000 g mol^{-1}, it is necessary to perform SSP. Melt polymerisation processes cannot synthesise PEN of a high molar mass as the melt viscosity of the material is too high and due to the high temperatures used in the synthesis reactions, degradation reactions limit the overall molar mass. SSP of PEN can be performed using a similar procedure described in *Section 1.1.1.7* for PET. However, the process conditions for SSP of PEN differ slightly due to the higher thermal transitions and gaseous barrier properties of PEN.

Prior to processing PEN in a SSP column, crystallisation and annealing stages are completed. The crystallisation process is slightly more complicated for PEN than PET due to the higher glass transition and crystallisation temperature of PEN. Significant crystallisation of PEN does not occur until 180 ^{o}C, with the rate of maximum crystallisation occurring around 210 ^{o}C. However, above temperatures of 200 ^{o}C, PEN has a tendency to stick very strongly and in the presence of high moisture content can expand and burst known as “pop-corning”. Subsequently, this results in a very limited temperature range in which to crystallise PEN.

The environment in which PEN is crystallised must also be carefully controlled. Although the SSP pre-crystallisation step of PET can be conducted in a dry air environment, inert atmospheres must be used for pre-crystallisation of PEN due to the higher operating temperatures involved. This reduces the risk of oxidation occurring on the surface of the polymer. [1]

In an identical process to SSP of PET, the polymer chips must then be heated to a temperature above the glass transition temperature and approximately 20 ^{o}C below the melt temperature. PEN has a melting temperature around 267 ^{o}C. Therefore, in order to prevent the polymer particles from sticking to one another, but still achieve significant SSP reaction rates, the SSP reactor must be heated to a minimum temperature of 220 ^{o}C. Higher SSP temperatures of 230 - 240 ^{o}C are preferred to increase the reaction rate and decrease the reaction time, however considerable care must be taken at these high temperatures in order to minimise thermal degradation. Similar to PET, SSP must be carried out either under high vacuum or in a hot inert gas. This reduces the risk of thermo-oxidative degradation and is particularly important in SSP of PEN due to the high operating temperatures involved. The SSP by-products, EG and water, are removed in a diffusion controlled manner. [1,26]

Prolonged reaction times are required for SSP of PEN due to the rigidity of the naphthalene system. This rigidity reduces the mobility of the end groups and the diffusion of by-products from the polymer matrix, therefore increasing reaction times. Approximately 22 hours is required in order to increase the IV of PEN from

0.55 to 0.75 dL g^{-1} using SSP, at a temperature of 235 ^{o}C. [1] Similar to PET, particle size and end group concentration also influence the SSP reaction rate of PEN.

1.1.2.9 Processing PEN

PEN can be processed into many different shaped products, however its major commercial use lies within the film industry as a substrate for flexible electronics. Biaxial oriented PEN film is typically manufactured from resin with a molar mass lower than that required for fibre or blow moulded applications.

The pre-processing treatment for PEN is identical to that described for PET in *Section 1.1.1.8*. The main sequence of events that occur when manufacturing PEN film are also similar to those outlined for PET in *Section 1.1.1.8,* however the entire process for PEN is carried out at higher temperatures (typically 320 ^{o}C). This is due to the increased T_m and increased melt viscosity of PEN compared to PET. The temperature of the screw extruder must be increased above 300 ^{o}C in order to melt the PEN polymer chips and enable the polymer to flow through the horizontal die. If temperatures are too low, the melt viscosity will be too high in order to extrude the melt successfully, however if the processing temperature is too high, significant thermal degradation of the polymer may occur. Therefore a suitable processing temperature must be determined whereby an appropriate melt viscosity is achieved but the risk of significant thermal degradation is minimised.

PEN also has the ability to be stretched at higher draw ratios, in comparison to PET, resulting in improved mechanical properties. This is a result of the slow rate at which PEN crystallises, producing highly ductile cast film which can be stretched at high draw ratios to produce highly oriented film. With increasing temperature, the mechanical strength of PEN increases - a property particularly useful for high temperature packaging applications. [1,39]

1.2 Overview of Polymer Degradation

Polymer degradation is the collective name given to the different processes which polymers degrade, leading to the loss of crucial properties. [40] Degradation plays an important role in every life phase of a polymer and usually occurs under the influence of one or more of the following environmental factors; **heat** (thermal/thermo-oxidative degradation), **light** (photo-degradation), **oxygen** (oxidative degradation) or **weathering** (UV, hydrolytic degradation). In this research, the processes of thermal, thermo-oxidative and hydrolytic degradation of PET and PEN are of most interest.

1.2.1 Thermal Degradation

Thermal degradation of a polymer can be defined as the molecular deterioration as a result of overheating. [40] This form of degradation can occur during polymer synthesis, processing or use. In particular, a degree of thermal degradation is generally inevitable during processing as the material is subjected to very high thermal and mechanical stress. These stresses can initiate a variety of polymer degradation processes resulting in physical and chemical changes to the polymer, leading to the deterioration of its most desirable properties. The degradation of polymers by heat can be classified into two sections: purely thermal (under an inert atmosphere) or thermo-oxidative (in the presence of oxygen).

Thermal degradation occurs solely in the presence of heat and in the absence of air, or any other oxidising species. Preferentially, this type of degradation is studied under vacuum, and not inert gases such as nitrogen or argon, to prevent primary degradation products from becoming trapped in the polymer network. Under vacuum, all primary thermal degradation products are pumped out of the system with no further secondary reactions occurring. Although this type of degradation is not very realistic in an oxygen-free environment, it still provides a useful insight into the degradation pathways of polymers and can be very useful when attempting to solve more complex thermo-oxidative degradation pathways.

Numerous different types of degradation reactions may be induced thermally in polymers. However, the two most important classes are depolymerisation and substituent reactions.

- ***Depolymerisation Reactions***

Depolymerisation is essentially the reverse of the polymerisation process and involves a reduction in the main polymer chain length by the elimination of monomer units. The resultant low molar mass degradation products from the chain scission process are said to resemble that of the parent material i.e. the fragments are typically made up of the monomer units of the starting polymer. Depolymerisation reactions can take place either via a radical or non-radical based mechanism. [40,41]

The simplest radical based depolymerisation reaction is that of poly(methylmethacrylate) (PMMA), whereby 80 - 100% of the original monomer is regenerated. As illustrated in *Figure 1.15*, the process is initiated by scission of the polymer at random points along the chain to form radicals. These radicals then unzip and undergo termination to form the monomer units.

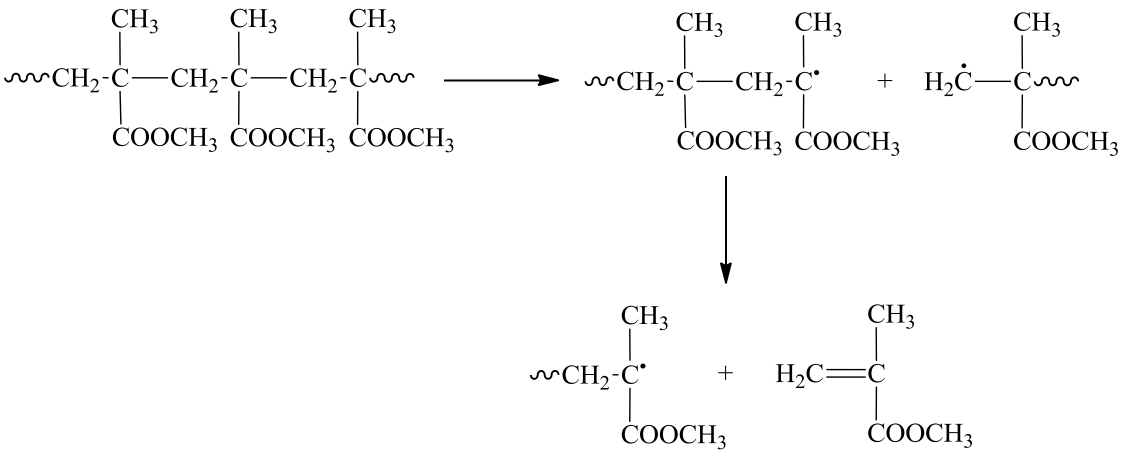


Figure 1.15 Radical depolymerisation of PMMA [41]

In addition to monomer producing depolymerisation degradation reactions, there is also another reaction that is in direct competition, referred to as an intramolecular transfer reaction. This reaction can involve a simple intramolecular transfer such as the transfer of α-hydrogen atoms in the degradation of polystyrene. As illustrated in *Figure 1.16,* this competitive degradation reaction leads to the production of styrene oligomers alongside that of styrene monomer units (~40%) formed by depolymerisation.

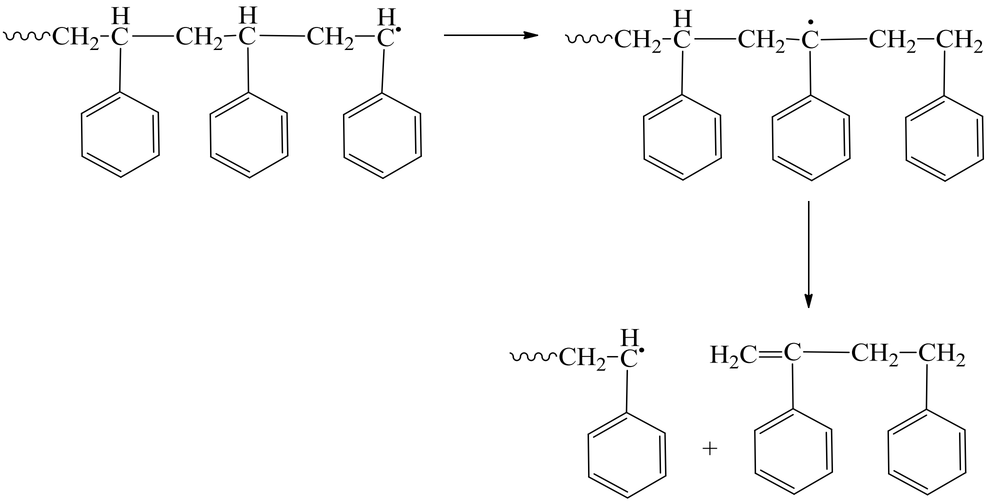


Figure 1.16 Intramolecular transfer of α-hydrogen atoms during the degradation of polystyrene [41]

Degradation, via radical depolymerisation reactions, can therefore differ quite significantly for different polymers. Therefore, in an attempt to simplify matters, Grassie [41] devised a single mechanistic scheme for the representation of radical based depolymerisation reactions, shown in *Figure 1.17.* The nature of the depolymerisation reactions which occur within any one polymer i.e. depolymerisation or intramolecular transfer reactions can be predicted by the relative amounts of monomer and non-monomer products generated.

Random Initiation $M_n \rightarrow M_j^{\cdot} + M_{n-j}^{\cdot}$

Terminal Initiation $M_n \rightarrow M_{n-1}^{\cdot} + M^{\cdot}$

Depropagation $M_i \rightarrow M_{i-1}^{\cdot} + M$

Intermolecular transfer and scission $M_i \rightarrow M_{i-z}^{\cdot} + M_z$

Intermolecular Transfer $M_i^{\cdot} + M_n \rightarrow M_i + M_n^{\cdot}$

Scission $M_n^{\cdot} \rightarrow M_j + M_{n-j}^{\cdot}$

Termination $M_i^{\cdot} + M_j^{\cdot} \rightarrow M_i + M_j$ or M_{i+j}

Where n = chain length of starting material, i, j and z = fragment lengths,
M_i, M_j, M_z = ‘dead’ polymer molecules and $M_i^{\cdot}$, $M_j^{\cdot}$, $M_z^{\cdot}$ = long chain radicals.

Figure 1.17 General mechanism for radical depolymerisation

In contrast, non-radical depolymerisation reactions are recognisable as the chain scission occurs randomly at the functional group linkages in the polymers. For example, in the degradation of polyesters where β-hydrogen atoms are present, scission is reported to take place at the alkyl-oxygen of the polyester linkage. The ester decomposition occurs at random intervals along the polymer chains and involves a six-membered ring transition state. Successively, the overall molar mass of the polymer is reduced, resulting in the formation of vinyl and carboxylic acid end groups, as illustrated in *Figure 1.18*.

- ***Substituent Reactions***

Another very important type of polymer degradation consists of processes that take place without necessarily breaking the main polymer chain i.e. degradation without substantial chain scission. Degradation of this sort involves participation of the side substituents attached to the backbone of the polymer, hence the name substituent reactions. [40] The general types of decomposition processes in substituent reactions are elimination and cyclisation.

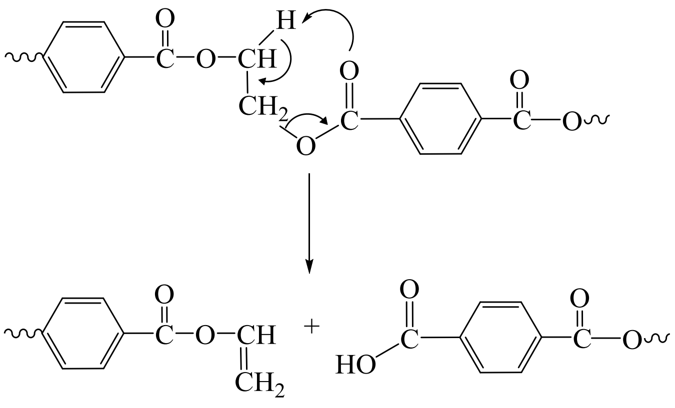


Figure 1.18 Alkyl-oxygen scission in polyesters [41]

Elimination reactions can proceed at lower temperatures than depolymerisation reactions and will occur if one of the bonds within a chain substituent group or that attaching it to the backbone is weaker than the carbon-carbon backbone. As the side groups participate in the reaction, often low molar mass degradation products are produced. However, the products formed do not in any way resemble that of the parent material i.e. in contrast to depolymerisation reactions, the fragments produced are not similar to the monomer units of the original polymer. For example, in poly(vinyl chloride) (PVC), the elimination of pendant Cl groups produces an unsaturated polymer chain and HCl gas. [41]

Cyclisation reactions generally occur between adjacent substituents on polymers that are located in close proximity. The potential reactants, at elevated temperatures, can undergo intramolecular cyclisation resulting in the elimination of a small molecule. An example of a cyclisation reaction is the elimination of methylamine from poly(N-methyl methacrylamide). [41]

Figure 1.19 presents a summary of the main pathways in the thermal degradation of polymers. These reactions produce a variety of degradation products from volatile gases and liquids to tars and waxes.

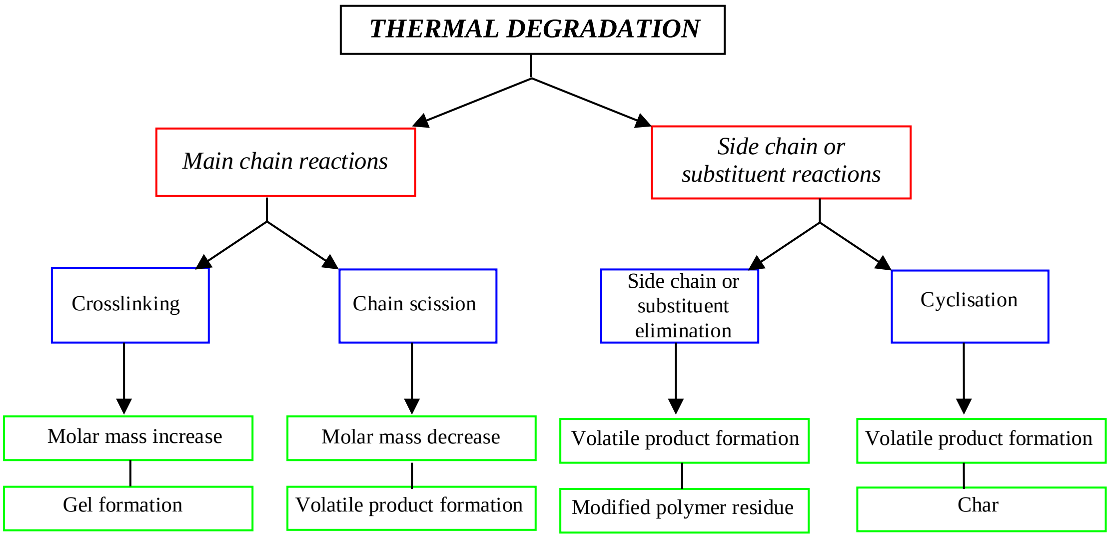


Figure 1.19 Main pathways in the thermal degradation of polymers [42]

1.2.2 Thermo-Oxidative Degradation

Although all polymers degrade at high temperatures in the absence of air, degradation is very common and almost always faster in the presence of oxygen. [41] This type of thermal degradation in the presence of oxygen is termed "thermo-oxidative degradation" and is most common during polymer synthesis and processing. The thermo-oxidative degradation process begins at lower temperatures and proceeds at a faster rate than purely thermal degradation (i.e. oxidation is an auto-accelerating process) and generally leads to a mixture of degradation products containing both similar species to the ones found in thermal degradation and newly oxidised species from reaction with O_2. [43]

The oxidative degradation of polymers proceeds via a free radical chain reaction involving separate initiation, propagation and termination steps. The key reactive species involved are hydroperoxides (ROOH) which are considered as both initiators and intermediates. The general oxidation scheme for the degradation of polymers, summarised by Grassie, [41] is outlined in the simplified reaction sequence shown in *Figure 1.20.*

Initiation $\mathrm{RH} \rightarrow \mathrm{R}^{\cdot} + \mathrm{H}^{\cdot}$

Propagation $\mathrm{R}^{\cdot} + \mathrm{O}_2 \rightarrow \mathrm{ROO}^{\cdot}$

$\mathrm{ROO}^{\cdot} + \mathrm{RH} \rightarrow \mathrm{ROOH} + \mathrm{R}^{\cdot}$

Termination $\mathrm{R}^{\cdot} + \mathrm{R}^{\cdot} \rightarrow \mathrm{RR}$

$\mathrm{R}^{\cdot} + \mathrm{ROO}^{\cdot} \rightarrow \mathrm{ROOR}$

$\mathrm{ROO}^{\cdot} + \mathrm{ROO}^{\cdot} \rightarrow \mathrm{ROOR} + \mathrm{O}_2$

Figure 1.20 General oxidation scheme for polymer degradation

The first initiation step involves the formation of polymer radicals. The exact nature of initiating reactions are not fully understood, however it is assumed that primary radicals are formed through the action of physical factors such as heat, light, mechanical stress or chemical factors such as the presence of catalysts. [44] Polymer radicals formed during the initiation reaction then react rapidly with oxygen to produce peroxy radicals ($\mathrm{ROO}^{\cdot}$). Each peroxy radical is sufficiently reactive to abstract hydrogen from another polymer molecule to yield a hydroperoxide species, ROOH and a polymeric radical, $\mathrm{R}^{\cdot}$. These hydroperoxide species are the key reactive species and are considered as initiators and intermediates in thermo-oxidative degradation reactions of polymers. [44] Following the formation of hydroperoxide species, the radical $\mathrm{R}^{\cdot}$ can then react rapidly with oxygen to produce another peroxy radical and the cycle repeats itself many times. This propagation reaction will determine the rate of oxidation of the polymer, the rate being a function of the bond strength of the R-H bond broken and the stability of the polymer radical formed.

The hydroperoxides, formed as a result of propagation, are unstable and therefore undergo a series of complex chain scission reactions leading to decomposition of the polymer chains. The two most common chain breaking reactions are unimolecular and bimolecular homolysis, as illustrated in *Figure 1.21.* The homolytic chain scission reaction that occurs is dependent on the concentration of hydroperoxides species present within the polymer. [44]

Unimolecular homolysis $\mathrm{ROOH \rightarrow RO^{\cdot} + HO^{\cdot}}$

Bimolecular homolysis $\mathrm{2ROOH \rightarrow RO^{\cdot} + ROO^{\cdot} + H_2O}$

Figure 1.21 Chain scission reactions of hydroperoxides [44]

Following the oxidative chain scission reactions, the highly reactive alkyl and alkyl peroxy radicals can finally undergo termination reactions, leading to a variety of degradation products such as aldehydes, ketones and esters.

Polymers of different chemical structures vary quite significantly in their resistance to oxidative degradation. The rate and course of an oxidation reaction is strongly affected by factors such as light, oxygen concentration, moisture and the presence of trace impurities, which can act as either catalysts or inhibitors. [45] Individual properties of a polymer, such as the degree of crystallinity, molar mass and sample thickness can also affect the rate at which oxidation occurs. [40]

1.2.3 Hydrolytic Degradation

In addition to degradation at high temperatures, degradation in the presence of water can also occur. This type of degradation is termed “hydrolytic degradation” and is very common during the synthesis and processing of polymers.

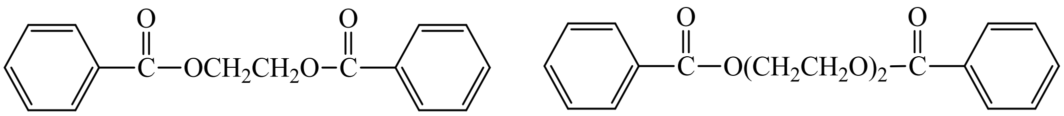
Hydrolysis is the scission of susceptible molecular functional groups by reaction with water. It may be catalysed by acids, bases, salts or enzymes and generally occurs at temperatures above the polymers glass transition. A polymer’s susceptibility to hydrolysis is very much dependent on its chemical structure, morphology, dimensions and surrounding environment. The rate of hydrolytic degradation is reported to be several orders of magnitude faster than that of degradation at high temperatures and can lead to the most significant loss of polymer properties. [46,47,48]

1.3 Degradation of PET

During the manufacture and processing of PET, the polymer is exposed to temperatures as high as 300 ^{o}C, both under non-oxidative and oxidative conditions in the presence of moisture. These conditions can result in a combination of thermal, thermo-oxidative and hydrolytic degradation reactions leading to the evolution of volatile degradation products and significant loss of crucial polymer properties. The degradation processes of PET are controlled by both ***physical*** (e.g. processing temperature, residence time, drying temperature, melt and drying environment, moisture content) and ***chemical*** (e.g. IV or molecular weight, catalyst system, method of polymerisation, starting monomer, polymerisation conditions) factors. Despite the relatively high thermal stability of PET, only a small amount of thermally initiated decomposition is substantial to lead to variations in the macromolecular properties. All three major degradation reactions in PET are discussed in more detail below.

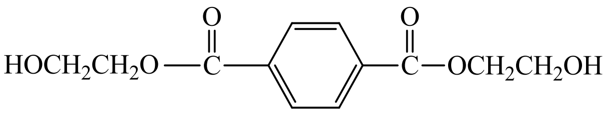
1.3.1 Thermal Degradation of PET

The mechanism for the thermal degradation of PET has been studied over many years, with the polyester itself and with model compounds which correspond to segments of the polyester chain and end groups. These model compounds, illustrated in *Figure 1.22*, include ethylene glycol dibenzoate, [49,50] diethylene glycol dibenzoate, [17,51] bis-hydroxyethyl terephthalate and bis-benzoyloxyethyl terephthalate. [29] When analysed under the same conditions, the degradation products of the model compounds and hence their degradation mechanisms assist in understanding the degradation processes in PET.

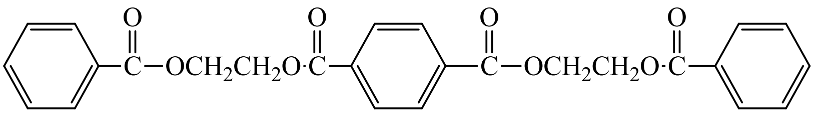


Ethylene glycol dibenzoate

Diethylene glycol dibenzoate



Bis-hydroxyethyl terephthalate



Bis-benzoyloxyethyl terephthalate

Figure 1.22 Typical model compounds used to study the thermal degradation of PET

- ***Primary Thermal Degradation Process in PET***

The primary thermal degradation process in PET is still very much a subject for debate. There is good agreement that the principal reaction involves the thermal cleavage of the ester bonds resulting in the formation of vinyl ester end groups and carboxylic acid end groups, as illustrated in *Figure 1.23.* However, it has not been possible to determine whether this mechanism proceeds via a radical or ionic process.

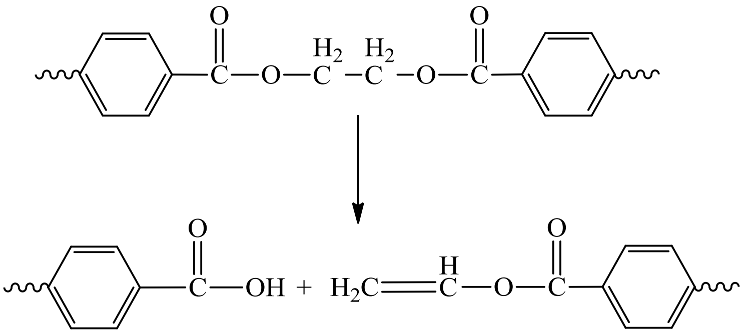


Figure 1.23 Scission at ester linkage in PET

One ionic mechanism proposed for the thermal degradation of PET involves random chain scission of ester linkages, resulting from an intramolecular β-hydrogen abstraction reaction through a six-membered transition state. This leads to β-scission of the polymer backbone at ester sites and yields carboxylic acid and vinyl ester end groups, as illustrated in *Figure 1.24.* [41]

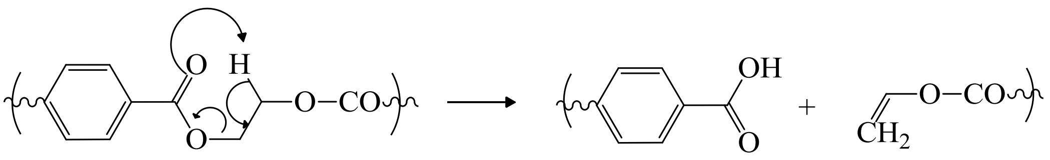


Figure 1.24 β-Scission of ester bonds in PET

This mechanism was first proposed in 1951 by Pohl [52] on completion of a thermal degradation study on PET and β-substituted polyesters. The thermal stability of PET was reported to be lower in comparison to β-substituted polyesters, indicating that the problematic and thermally weak component in PET was the presence of β-hydrogen atoms. Identical results were observed during a study on the role of β-hydrogen atoms in the degradation of polyesters by Sivasamy *et al.* [53] Decreasing the β-hydrogen atom content in the polymer backbone was found to increase the thermal stability of the polyester. Many authors [13,17,41,50] appear to be in support of this mechanism over any other ionic or radical mechanism proposed.

Although in agreement that this chain scission reaction occurs, via an ionic intramolecular β-hydrogen abstraction reaction, Montaudo *et al.* [24] report that this scission process occurs only after an intramolecular cyclisation reaction (otherwise known as back-biting). This cyclisation reaction, illustrated in *Figure 1.25*, leads to the formation of cyclic oligomers that then undergo β-scission at ester linkages.

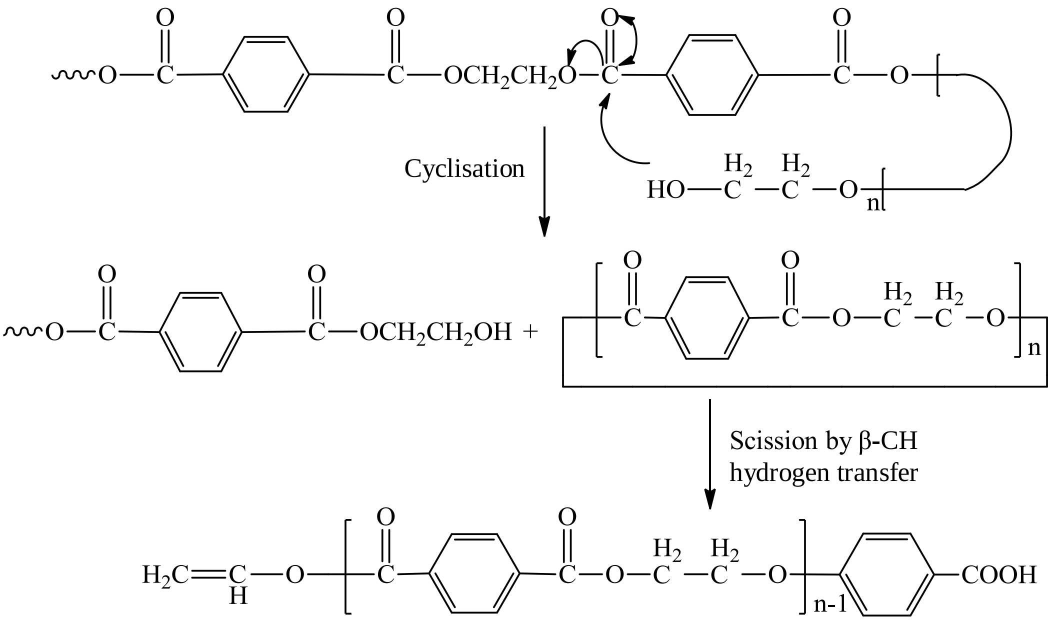


Figure 1.25 Intramolecular cyclisation of PET followed by scission via β-CH hydrogen transfer [23,24]

More recently in another publication by Samperi *et al.*, [54] the thermal degradation of PET was monitored isothermally at temperatures between 270 °C and 370 °C using matrix assisted laser desorption ionisation (MALDI) mass spectrometry. Interestingly in this study, no vinyl ester end groups were detected. Instead, linear PET oligomers bearing two carboxyl chain ends were detected at temperatures above 320 °C, alongside oligomers containing terephthalic anhydride units. These anhydride containing oligomers were thought to originate from unimolecular extrusion of acetaldehyde from PET chains, as shown in *Figure 1.26.*

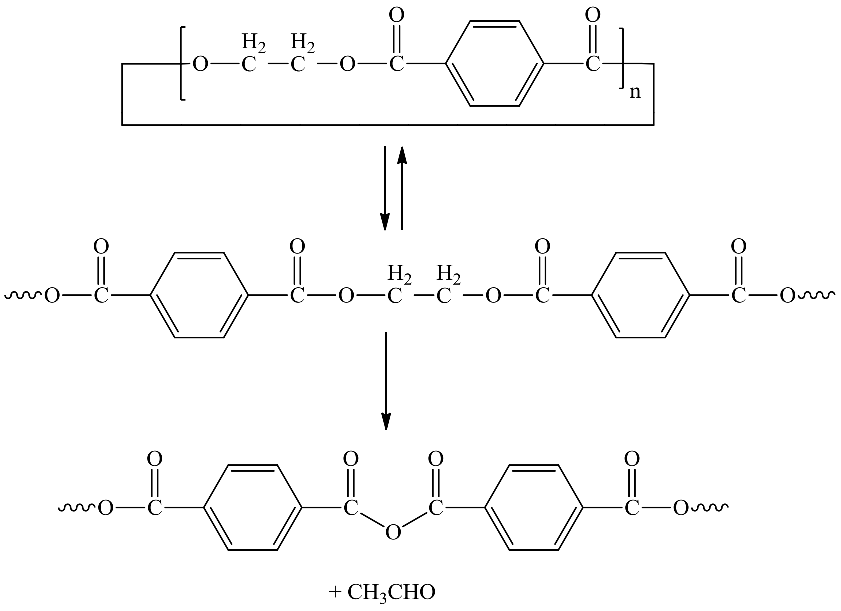


Figure 1.26 Formation of terephthalic anhydride oligomers in PET [54]

In contrast to the global opinion on the primary degradation process of PET, McNeill *et al.*[55] published a homolytic mechanism for the degradation of PET. McNeill *et al.* examined the degradation products of PET using isothermal thermal volatilisation analysis (TVA) studies at temperatures ranging from 300 - 500 °C and suggested that only a homolytic mechanism can explain the whole range of degradation products observed. This was supported on the basis that products such as CO and CO_2 are formed throughout the main temperature range of decomposition, whereas by a non-homolytic route, such products would only be formed at the highest degradation temperatures. Zimmermann [56] argued that homolysis is not the main chain scission process as it is not inhibited by free radical trapping agents. However, McNeill *et al.* commented that free radical trapping reagents would only inhibit a chain reaction mechanism, whereas the mechanism proposed involves only homolysis followed by H-abstraction mainly by disproportionation of the pair of radicals formed as a result of homolytic scission. The radical scission process is illustrated in *Figure 1.27.*

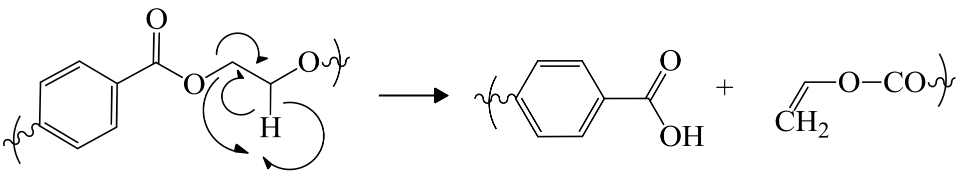


Figure 1.27 Homolysis and radical abstraction of H from β-scission of ester bonds in PET

Despite the disagreements over the mechanism for the primary thermal degradation of PET, the reaction principally involves the random chain scission of ester linkages, yielding carboxylic acid and vinyl ester end groups. It is possible that a combination of both ionic and homolytic reactions occur during the degradation of PET, with radical processes thought to dominate at higher degradation temperatures.

- ***Secondary Thermal Degradation Processes in PET***

After the initial chain scission of ester bonds at random points in the polymer backbone, a series of reactions known as secondary thermal degradation processes generally occur at higher temperatures. These reactions result in the production of volatile species and non-volatile residues. Over many years, the secondary degradation processes in PET have been studied using a variety of different techniques. Volatile degradation species are most commonly analysed using gas-chromatography [57,58,59,60] or mass spectrometry [24,55] instruments directly attached to degradation lines. Solution or solid-state NMR, FTIR and elemental analysis can be employed for the analysis of non-volatile residues.

A wide variety of products have been identified from thermal degradation studies of PET, such as carbon oxides, aldehydes, hydrocarbons and aromatic acids and esters. *Figure 1.28* provides an overview of the main degradation products reported from only a few studies on the thermal degradation of PET. [17,55,59] The composition of degradation products depends very much on the degradation temperatures studied. The degradation products illustrated in *Figure 1.28* are separated into volatile gases that are condensable and non-condensable at -196 ^{o}C and products which are condensable at room temperature.

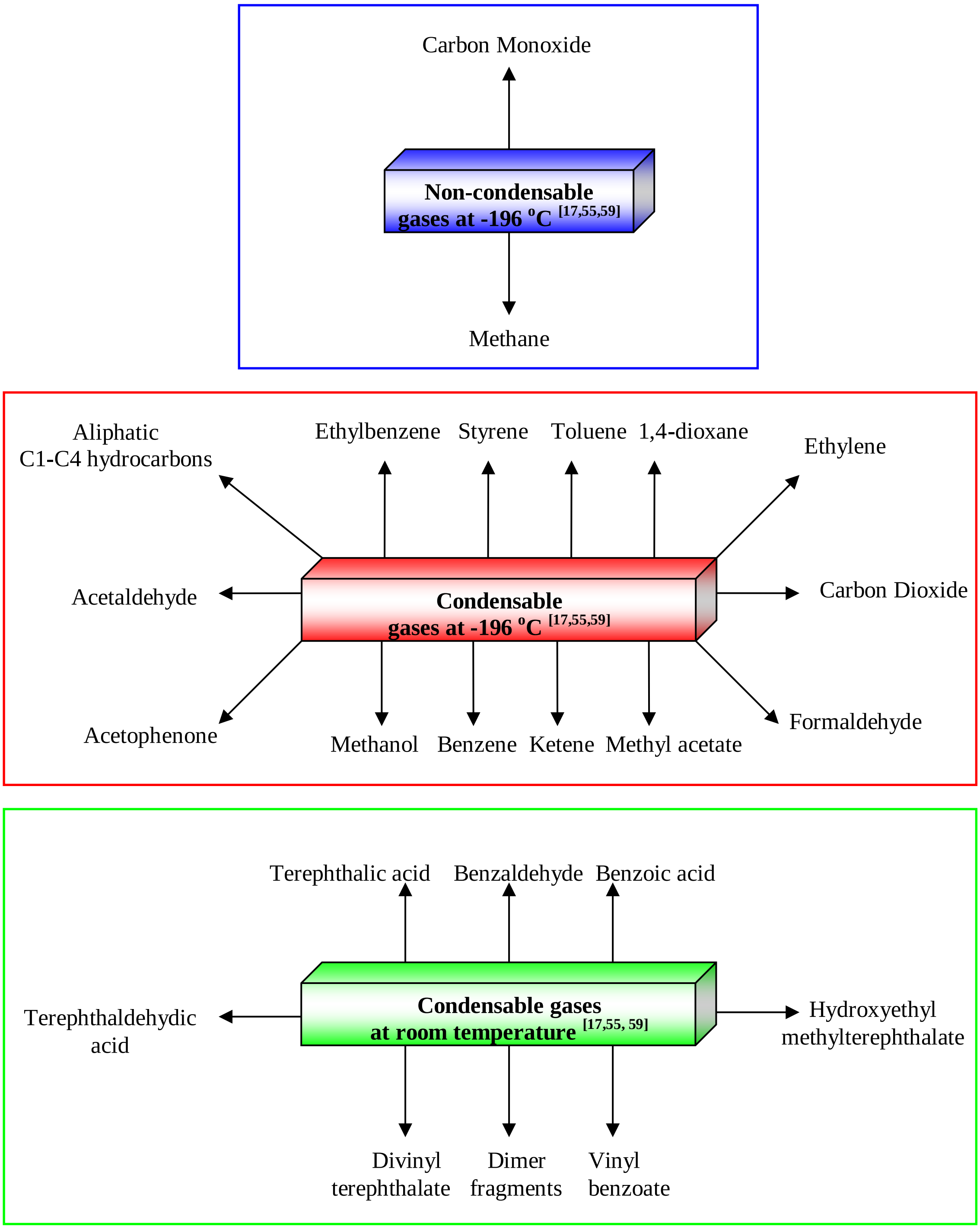


Figure 1.28 Major products reported from the thermal degradation of PET

Acetaldehyde, carbon dioxide, carbon monoxide and terephthalic acid have been identified as the major volatile products formed during the degradation of PET. Acetaldehyde is the most problematic degradation product as it is known to migrate into food packaging, resulting in changes in product flavour. For this reason, bottle-grade and food packaging grades of PET must be produced with special care to minimise the generation of acetaldehyde. [1,60]

Acetaldehyde is reported to form at temperatures as low as 200 - 300 °C [29,58,60] by three distinctively different ionic mechanisms, [1,50,57] all of which are illustrated in *Figures 1.29 - 1.31.* Scission of a hydroxyl chain end group in PET can result in the formation of a vinyl alcohol, which rearranges instantaneously to acetaldehyde.

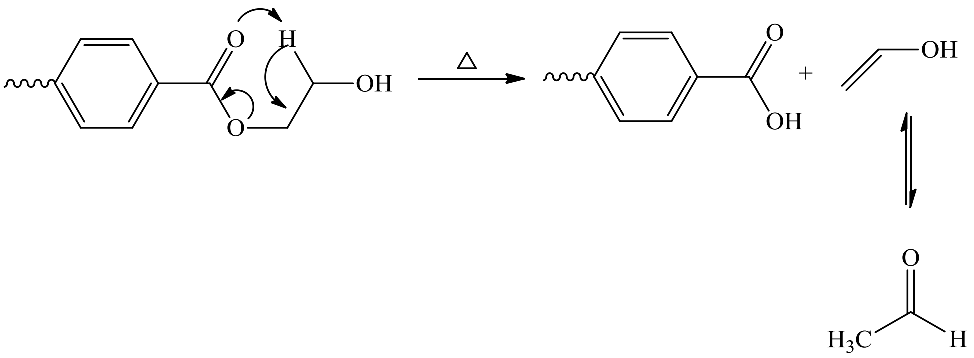


Figure 1.29 Formation of acetaldehyde from hydroxyl end groups in PET [57]

Alternatively, acetaldehyde can be formed by the transesterification reaction of terminal vinyl groups, liberating vinyl alcohol and thus acetaldehyde. In this reaction, the polyester chains are regenerated by reaction with a hydroxyl end group and the average degree of polymerisation is maintained. This reaction can be very difficult to monitor as the molar mass of the polymer is maintained, even although the polymer is undergoing thermal degradation. A decrease in the molar mass of the polymer will only be observed when the majority of hydroxyl end groups have been consumed and carboxyl and vinyl end groups have accumulated.

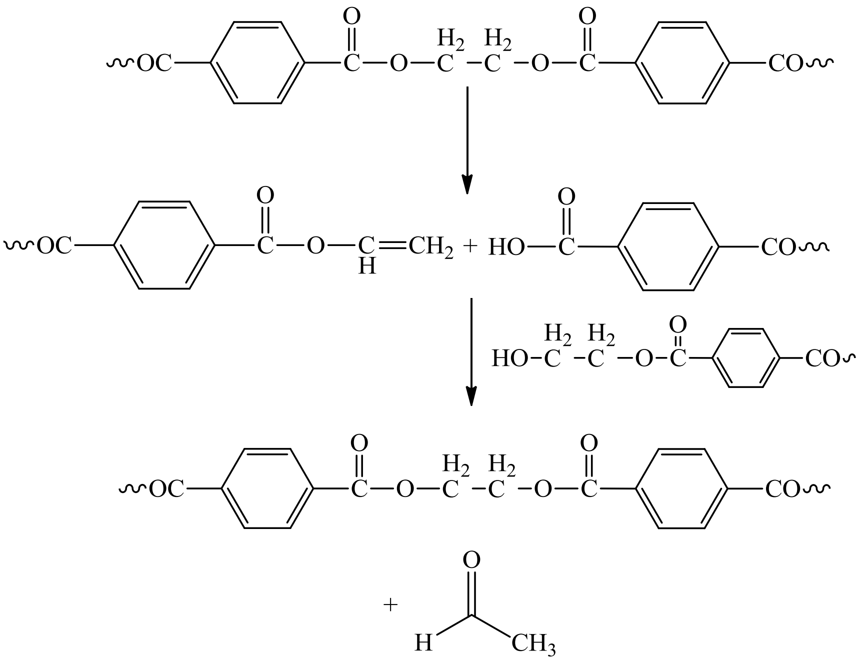


Figure 1.30 Formation of acetaldehyde from vinyl end groups in PET [50]

The third mechanism proposed for the formation of acetaldehyde is reported to involve the addition of carboxyl end groups to the olefinic double bond of vinyl end groups. This reaction is thought to be slower than the other two reactions discussed and will occur only when the hydroxyl end group content in the polymer is low. [17] The addition of the acid and vinyl chain ends results in the formation of an acylal which can then decompose further to generate an anhydride and acetaldehyde. The anhydride group can then react further with water to generate two carboxyl groups or alternatively it can react with hydroxyl groups to form one ester and one carboxyl group.

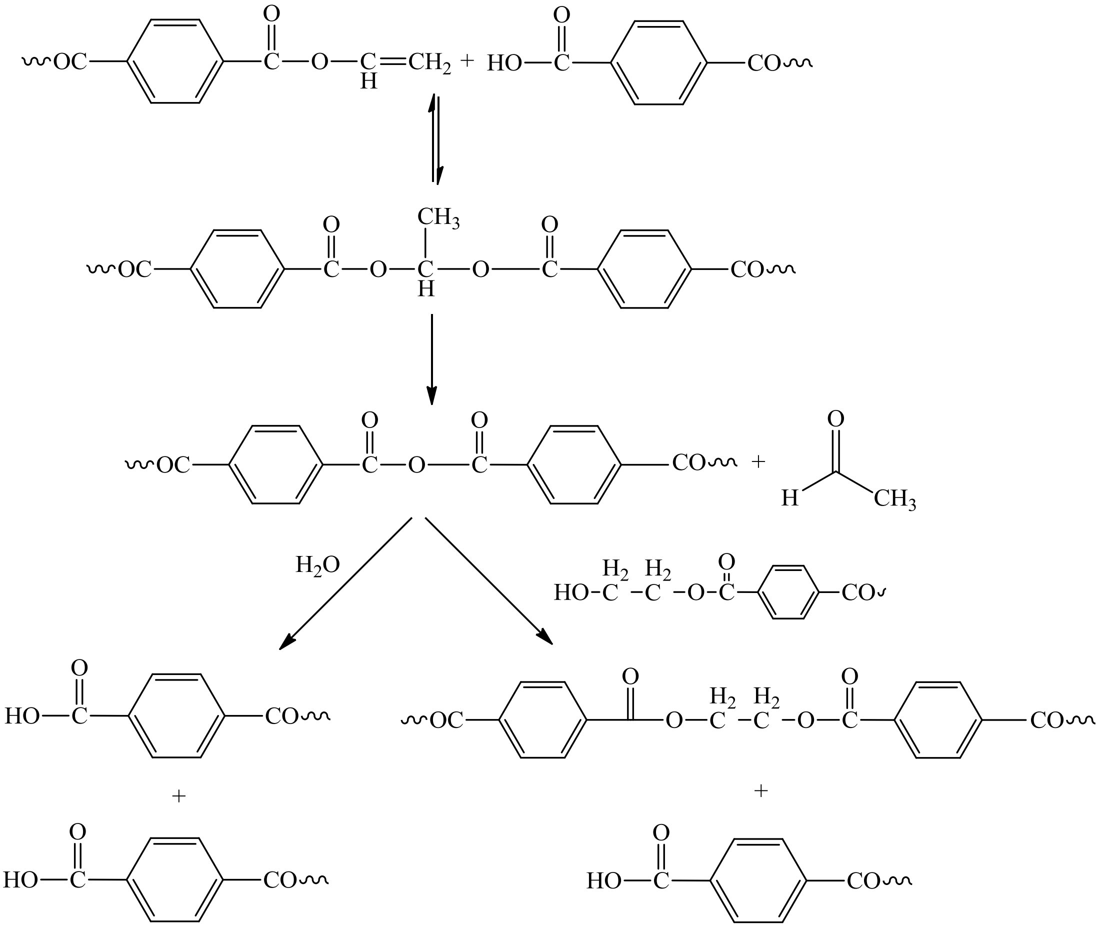


Figure 1.31 Formation of acetaldehyde from addition of carboxyl and vinyl groups in PET [1,50]

Khemani [57] studied the amount of acetaldehyde evolved during the degradation of PET over extended periods of time using gas chromatography (GC). A gradual decrease in the amount of acetaldehyde generated was reported after approximately 60 minutes at 280 °C, with the decline in acetaldehyde eventually reaching an asymptotic value. This plateau of acetaldehyde evolved is thought to be an indication that the acetaldehyde generated after 1 hour is mainly arising from mid-polymer chain scission and not degradation of polymer end groups (e.g. hydroxyl end groups). As mid-polymer chain scission does not generate acetaldehyde directly and relies solely on identifying another reactive group (such as a hydroxyl or acid end group), the asymptote indicates a state of equilibrium within the molten polymer.

Carbon dioxide, carbon monoxide and terephthalic acid have also been identified as major volatile products formed during the degradation of PET. CO and CO_2 can be produced by the breaking of a combination of bonds in various different degradation products. However, the simplest degradation reaction to produce CO_2 involves the decarboxylation of carboxyl groups as shown in *Figure 1.32.*

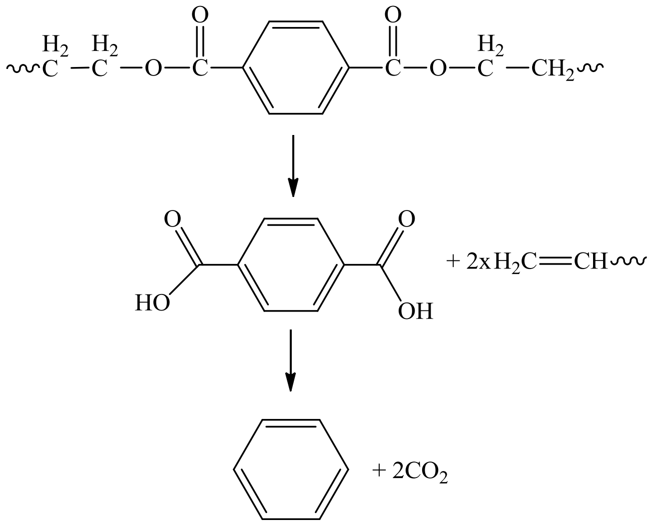


Figure 1.32 Degradation of PET to produce terephthalic acid, benzene and CO_2

Terephthalic acid is reported to form at degradation temperatures in the region of 400 - 550 °C by the double scission of ester groups in PET. Separate studies performed by Sakata *et al.* [61] and Chui *et al.* [9] on the thermal degradation of PET at temperatures of 430 °C and 550 °C respectively, reported the formation of a mixture of terephthalic acid and benzoic acid. This mixture of terephthalic acid and benzoic acid was identified as a yellow solid residue within the reactor vessels used to thermally degrade the polymer.

In support of the homolytic mechanism proposed for the primary thermal decomposition process in PET, McNeill *et al.* [55] proposed a radical mechanism to explain all the products observed during thermal degradation studies of poly(alkylterephthalates), including the large quantities of CO and CO_2 generated.

The thermal degradation of three poly(alkyl terephthalates) with 2, 4 and 10 alkyl groups, were studied under temperature-programmed and isothermal heating conditions in an inert atmosphere using TVA, thermal gravimetric analysis (TGA) and differential thermal gravimetry (DTG). From TGA, PET was reported to degrade in a single step above 300 ^oC. The maximum rate of mass loss was found to be in the region of 400 - 450 ^oC, corresponding to degradation of the polymer backbone. In agreement with the TGA findings, the TVA degradation curve also illustrated that the evolution of volatile products in PET occurs in a one-stage degradation process in the temperature regime up to 550 ^oC. The non-condensable degradation products of PET were found to consist mainly of carbon monoxide and traces of methane. CO_2, acetaldehyde, vinyl benzoate and dioxane were identified as the main condensable degradation products of PET at liquid nitrogen temperatures with traces of ethene, ketene, benzaldehyde, toluene and divinyl terephthalate. Condensable volatile products at room temperatures were found to consist mainly of terephthalic acid and short chain fragments terminated by $–COOH$ or $–CH=CH_2$ groups, alongside traces of benzoic acid, terephthaldehydic acid and hydroxyethylmethyl terephthalate.

During this study, McNeill *et al.* also carried out isothermal TVA degradation studies at lower temperatures (300 - 405 ^oC) to establish if the nature of degradation products differed with temperature. The principal degradation products such as CO, CO_2 and acetaldehyde were all formed at the low isothermal degradation temperatures, indicating that the nature of the products and the mechanism for the thermal degradation of PET does not differ significantly with increasing temperature. Only the relative amounts of degradation products were found to vary with increasing temperature. As poly(butylene terephthalate) (PBT) was found to have an essentially similar thermal degradation mechanism to PET, McNeill *et al.* proposed a general degradation mechanism for both polymers, illustrated in *Figure 1.33.*

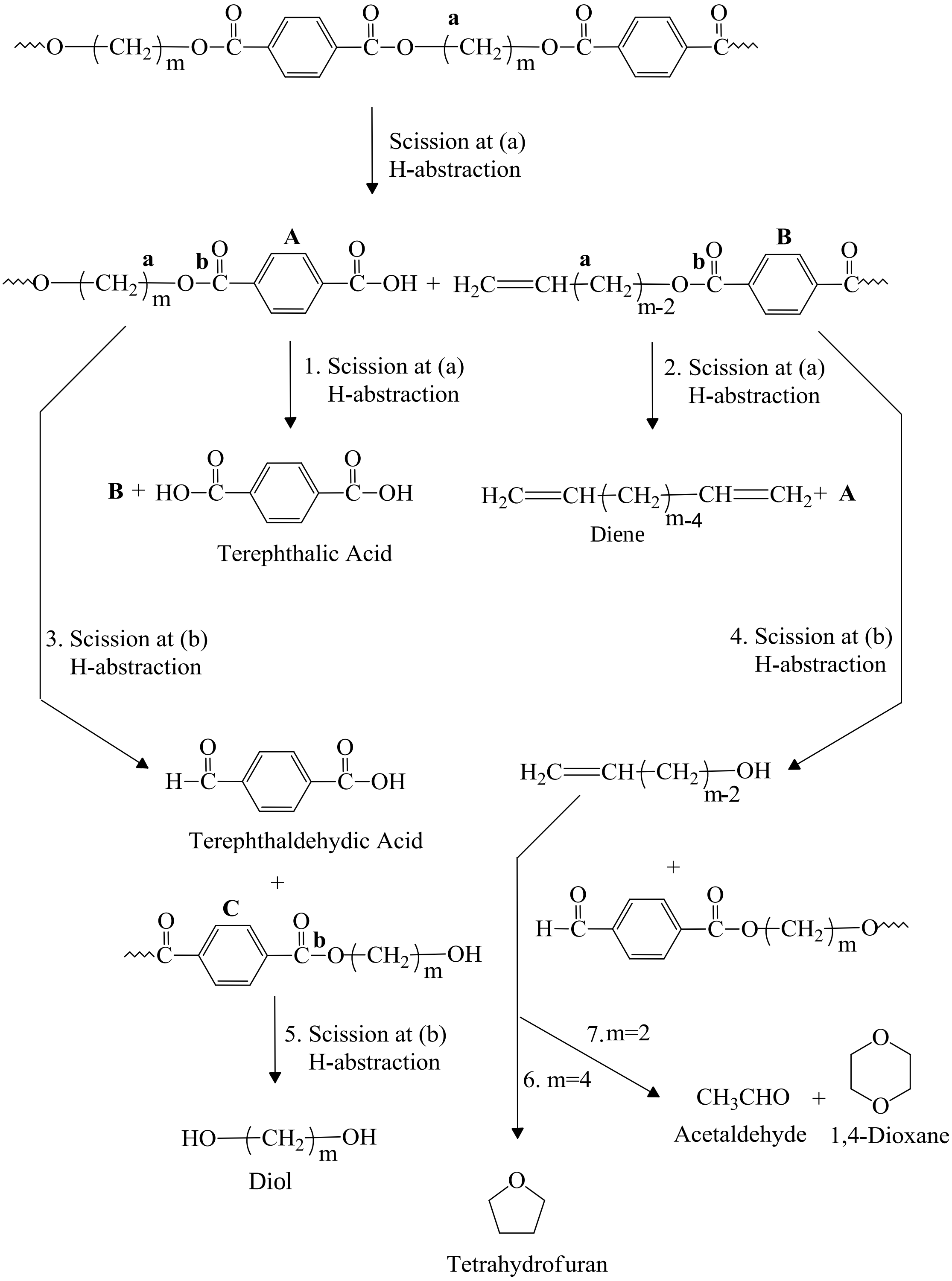


Figure 1.33 Thermal degradation pathway for PET (m=2) [55]

Variations in this basic degradation scheme, proposed by McNeill *et al.*, [55] can be derived resulting in the formation of a variety of products with carbonyl, vinyl, aldehyde or hydroxyl groups at one or both ends of the polymer chain. CO and CO_2 can be formed by homolytic degradation reactions at the alkyl-oxygen or acyl-oxygen link respectively, followed by H-abstraction by the radicals formed. The benzoate ends (**D**) formed provide a source for the formation of other products such as benzoate esters, benzene, benzaldehyde, and benzoic acid. The chain scission reactions illustrated in *Figure 1.34* accounts for the formation of carbon oxides throughout the thermal degradation of PET.

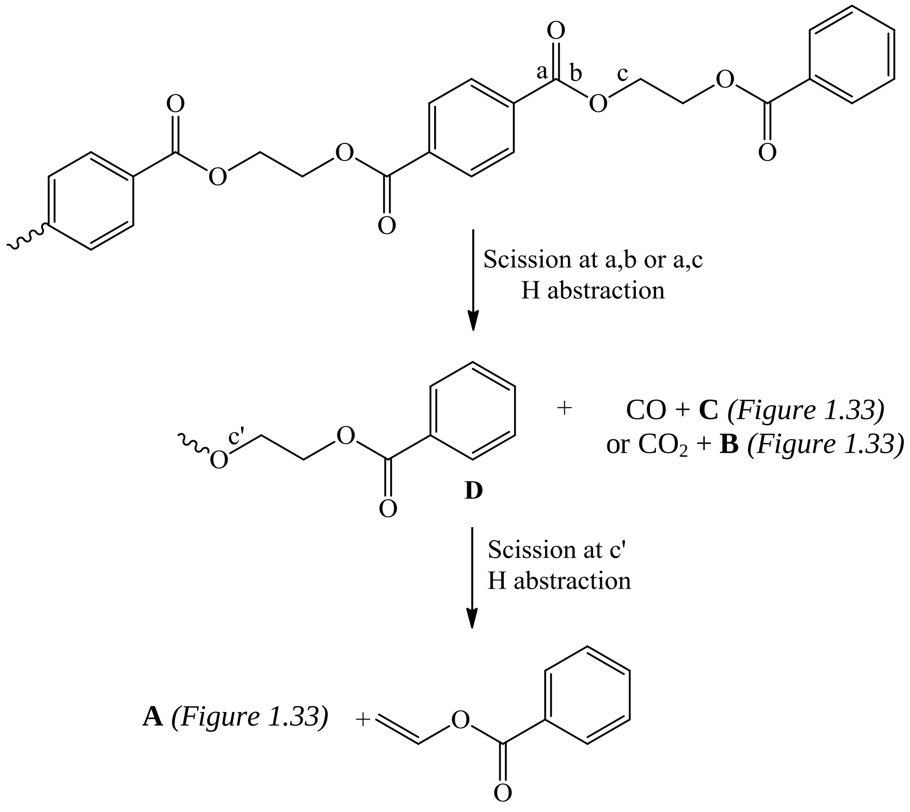


Figure 1.34 Homolytic degradation reactions in PET [55]

The basic reaction mechanisms, presented in *Figures 1.33* and *1.34,* are thought to occur via homolytic degradation processes. McNeill *et al.* [55] believe that homolytic processes are the most satisfactory mechanism to explain the formation of CO and CO_2, alongside a range of other products, at all degradation temperatures studied between 300 and 550 °C. The authors report that the degradation mechanism would only be non-homolytic in nature if CO and CO_2 were formed only at the higher degradation temperatures.

A wide variety of degradation products can therefore form as a result of the thermal decomposition of PET from temperatures as low as 200 °C. The formation of these degradation products is dependent on many factors such as the degradation conditions (e.g. time, temperature, humidity) and the sample of interest. The effects of temperature, time, particle size and humidity on the thermal degradation of PET have all been studied. As mentioned previously, the effect of temperature on the thermal degradation process has been reported to influence the quantity [29,55,57,59,60] and nature of degradation products formed. [54,58,59] Chui *et al.* [9] studied the effects of degradation time and particle size on the degradation of PET. Particle size was found to have little influence on the overall production rate of volatile degradation species, with the overall % mass loss identical for all three different samples sizes examined. The effect of time on the degradation of PET was found to be very much dependent on the degradation temperature. At 400 °C, the % mass loss of degradation products from PET was reported to increase with degradation time prior to levelling off around 45% after 9 hours. The initial rates of thermal degradation were substantially increased with an increase in degradation temperature to 450 °C and 500 °C. The % mass loss of PET was reported to approach a steady value of approximately 80% within a shorter period of time.

1.3.2 Thermo-Oxidative Degradation of PET

Thermo-oxidative degradation is inevitable during the synthesis and processing of PET as the polymer is exposed to air at elevated temperatures. This can lead to a decrease in the molar mass and the formation of undesirable degradation products, significantly impairing the polymer properties. Studies on the thermo-oxidative degradation of PET have been carried out by various authors over several decades, however the radical based reactions are complex due to the participation of heat and oxygen. Most mechanisms refer to or adopt the reactions schemes described by Bolland *et al.* [43] in 1946 for the thermal oxidation of rubbers and polyolefins.

The thermo-oxidative degradation of PET is thought to be initiated by heat and oxygen leading to the formation of hydroperoxides at methylene sites within the polymer chains. *Figure 1.35* illustrates the early oxidation scheme for the formation of hydroperoxides in PET by Buxhaum. [17] Buxhaum deduced that the hydrogens most vulnerable to abstraction, and thus initiation of free radical processes, were those alpha to the ester group in the polyester backbone. In the presence of oxygen, the alkyl radical formed will then react rapidly with oxygen to result in a peroxy radical, which can abstract hydrogen from the same or another polymer chain, to form a hydroperoxide. The remaining radical can then be recycled back into the process in order to initiate another oxidation cycle. Due to the conjugated action of heat and oxygen, the hydroperoxide species are formed auto-catalytically in the polymer.

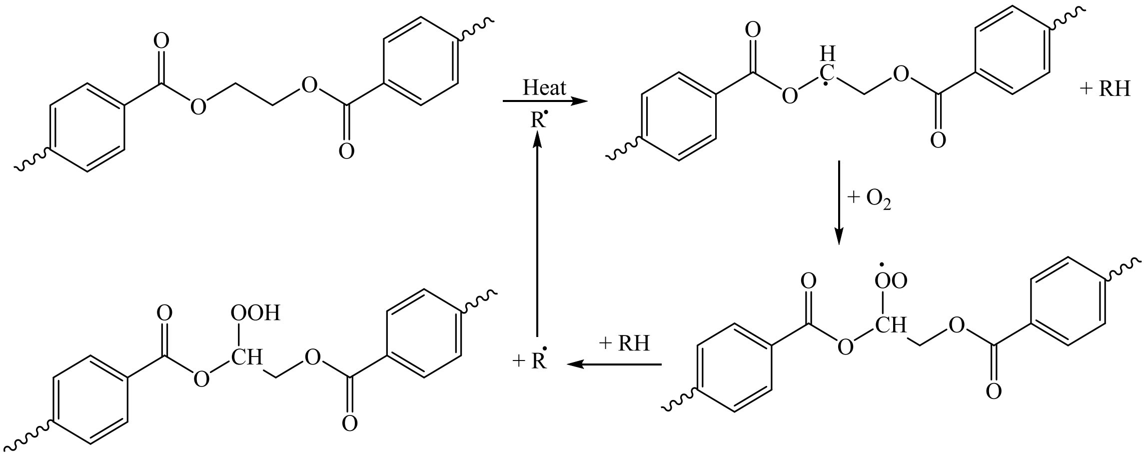


Figure 1.35 Formation of hydroperoxides in PET

The second stage in the thermo-oxidative degradation of PET is reported to involve homolytic chain scissions of the unstable hydroperoxide species. This decomposition is illustrated in *Figure 1.36* and can occur in two different ways:

(1) O-O bond scission to form an alkoxy macroradical and OH•

(2) C-O bond scission to form an alkyl macroradical and HOO•

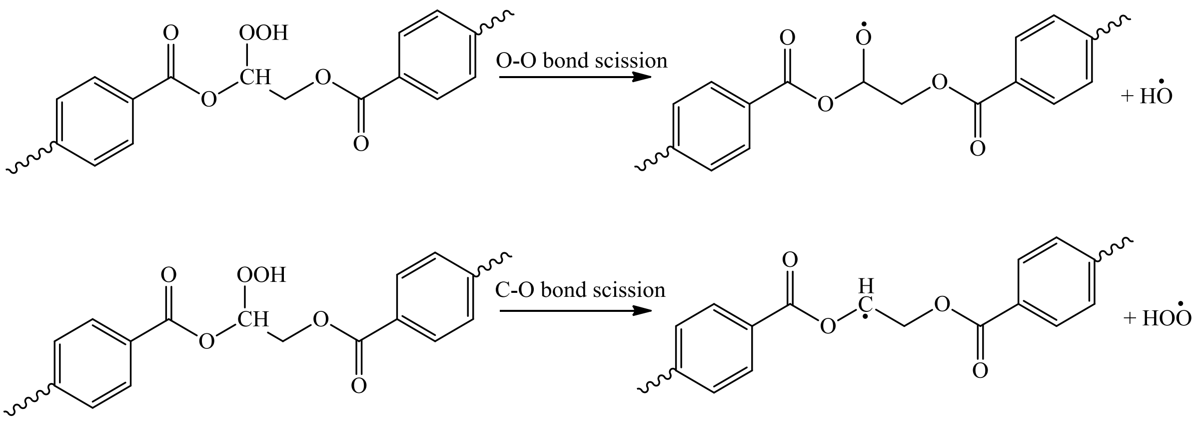


Figure 1.36 Homolytic chain scission of hydroperoxides in PET [17]

The radicals formed from the homolytic chain scission reactions of PET are just the beginning of a series of further degradation reactions. Extensive chain scission reactions follow, leading to the formation of chain fragments with oxygen and carbon radicals, vinyl ester and carboxyl end groups. Unimolecular and bimolecular homolytic chain scission reactions can occur in PET, however the reaction that occurs will depend on the concentration of hydroperoxides. A high concentration of hydroperoxides in PET will result in bimolecular homolysis, while a low concentration of hydroperoxides will result in unimolecular homolysis. A general scheme for the thermo-oxidative degradation of PET is illustrated in *Figure 1.37.*

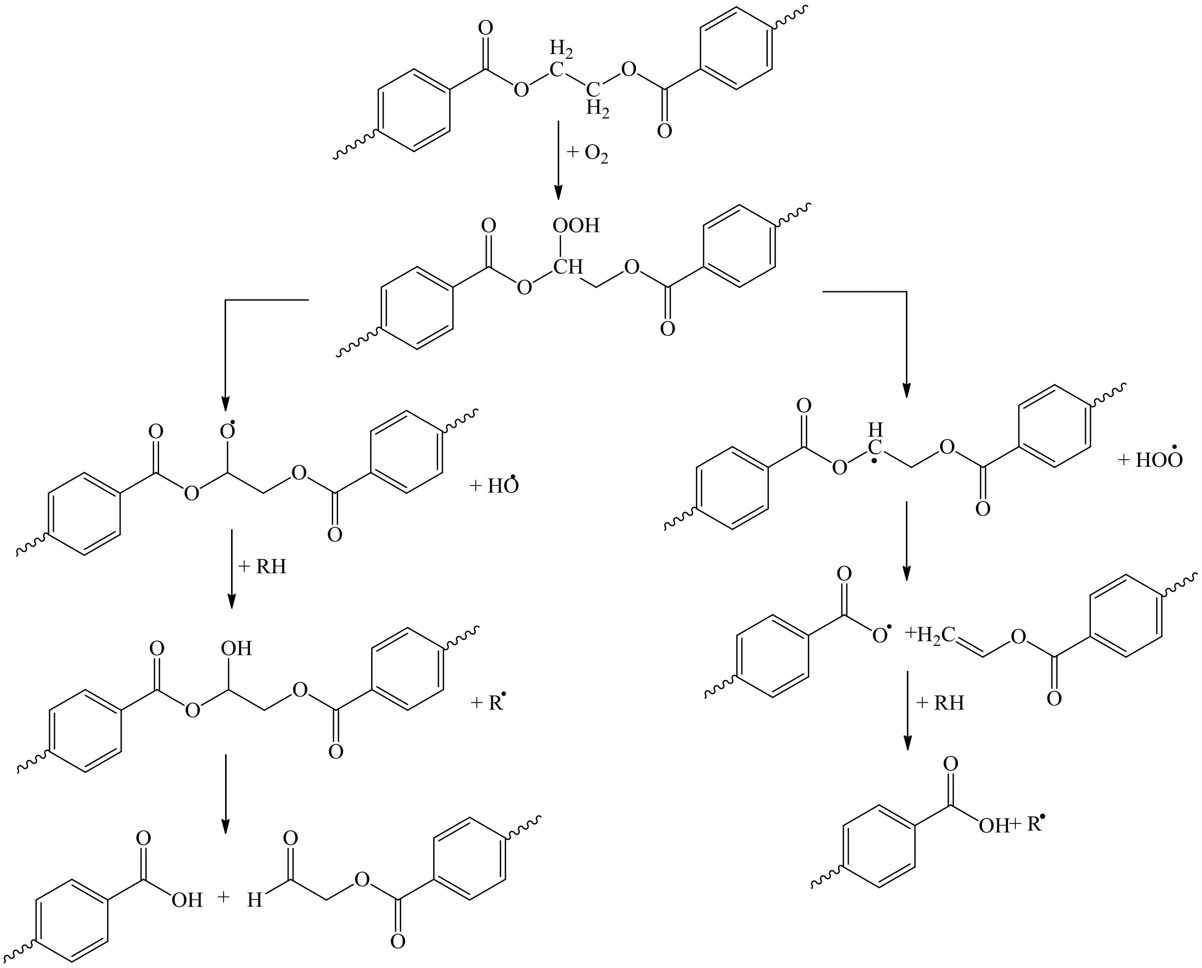


Figure 1.37 Mechanism for the thermo-oxidative degradation of PET [17]

The above reaction scheme in *Figure 1.37*, devised by Buxhaum, [17] is purely based on thermo-oxidative processes. However Botelho [49] and co-workers showed that the thermo-oxidative degradation of PET involves non-oxidative thermal degradation processes, especially in the early stages. Therefore, the overall thermo-oxidative process in PET is much more complex than shown. The thermo-oxidative stability of PET is additionally complicated by the presence of catalysts. Various catalysts, used during the synthesis PET, are reported to increase thermo-oxidative degradation, the extent of degradation being dependent on the type of catalyst used. [56]

Degradation products, formed as a result of thermo-oxidative degradation of PET, are thought to consist of a mixture of degradation products containing both similar species to the ones found in thermal degradation and newly oxidised species from reaction with O_2. However, McNeill and co-workers [55] reported that the same products were found in thermal and thermo-oxidative degradation studies of PET and model compounds. They reported that the only difference between the thermo-oxidative and thermal degradation of PET was the increase in quantity of degradation products produced from thermo-oxidative studies. These findings were strongly criticised by Botelho *et al.* [49] during a similar study comparing the thermal and thermo-oxidative degradation of PET and PBT with their respective model compounds, ethylene dibenzoate (EDB) and butylene dibenzoate (BDB). PET degraded under oxygen was found to produce a large quantity of degradation products, some identical to those observed in the thermal degradation, as well as some additional products. *Figure 1.38* summarises the degradation products reported from two separate studies by Dzieciol *et al.* [58,62] over a temperature regime of 200 - 600 °C. The principal volatile degradation products at lower temperatures were found to be acetaldehyde, formaldehyde and CO. However, the composition of volatile degradation products identified was very much dependent on the degradation temperature studied.

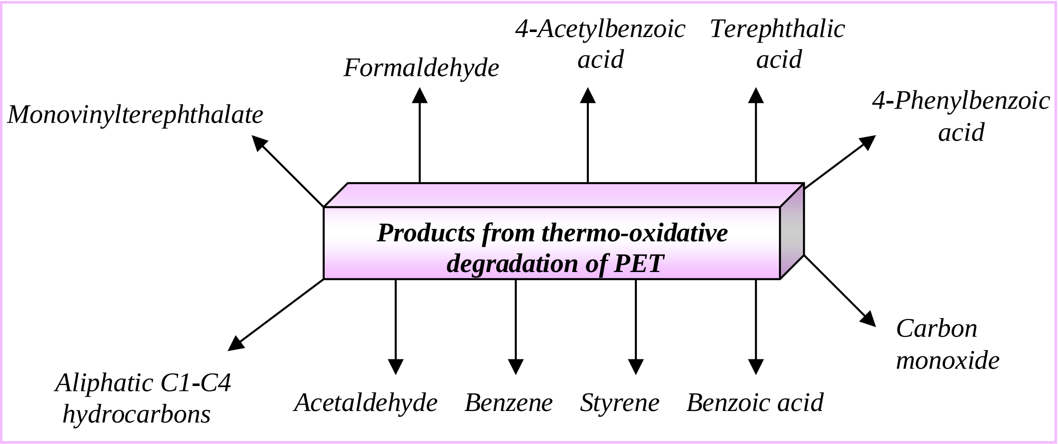


Figure 1.38 Summary of thermo-oxidative degradation products of PET [58,62]

The solid residue remaining from the thermo-oxidative degradation of PET is reported to comprise of a gel-like material. The presence of such gels indicates the formation of cross-linked material. Yoda *et al.* [63] reported on network formation in

PET under thermo-oxidative conditions at processing temperatures and discovered that degraded PET comprised of 38.5% and 52.6% gel structures at temperatures of 280 ^{o}C and 300 ^{o}C, respectively after a period of 4 hours. With increased degradation time and temperature, an increase in gel content and increased volatilisation was observed. Yoda *et al.* [63] therefore deduced that the primary degradation reaction leading to volatilisation of PET and formation of cross-linked species occurs as the concentration of vinyl ester groups, formed as a result of chain scission reactions, accumulates within the polymer. These vinyl ester groups are then thought to react with radical species to form network structures, most likely connected via aliphatic bridges.

In contrast to the views of Yoda, Holland *et al.* [23] reported that the formation of cross-linked structures were unlikely to derive from vinyl esters. Under the extreme conditions of thermal oxidation, the vinyl ester groups are thought to undergo a series of further reactions leading to the formation of interconnected aromatic rings. Despite the contrasting opinions, both authors are in agreement that the formation of cross-linked material predominates in aerobic zones due to the absence of radical polymer species during purely thermal ionic degradation reactions.

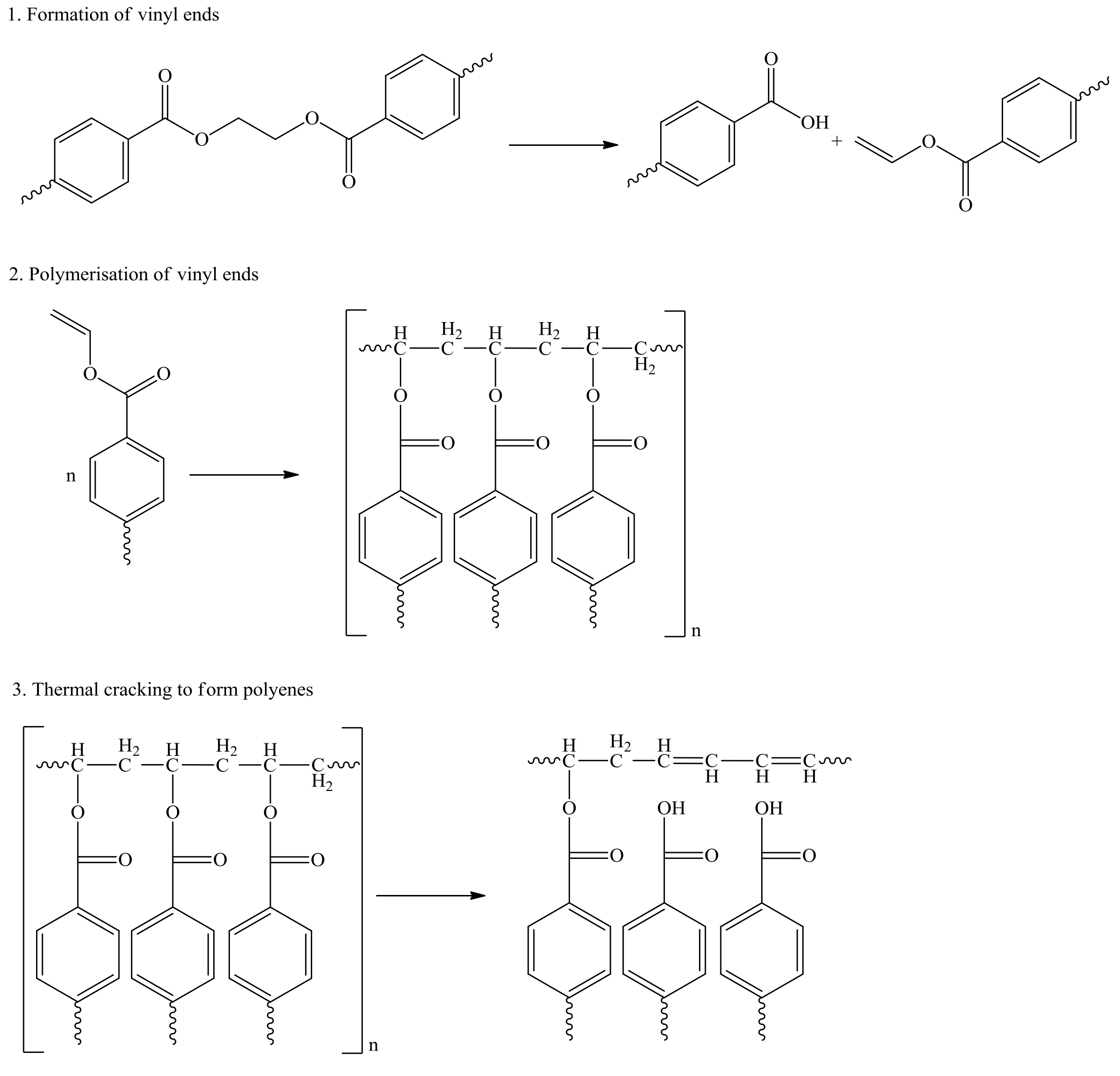
Conveniently, the solubility of PET in hexafluoroisopropanol can provide an indication of the presence of cross-linked material within the polymer. If the polymer is soluble in halogenated solvent, no cross-linked material exists. However, if the polymer is not fully soluble, it is possible to separate the gel-fraction for subsequent analysis. Gel content, which can be defined as a ratio of the portion of polymer that is not dissolved in solvent i.e. gel to the total weight of the polymer (excluding filler) would typically be measured according to the international standard procedures. [64,65,66] However, these tests methods are not always practical due to the hazardous solvents involved and the length of time required to perform the procedure. Therefore, new techniques to measure and detect cross-linking are highly desirable. Currently, new DSC and FTIR methods for the determination of gel content in polymers are being researched. [67] DSC is reported as a useful technique as cross-linking can result in non-uniformity within the crystal lattice, shifting the crystalline melt temperature. Therefore, for a higher degree of cross-linking, a broader melt peak and a lower onset temperature should be observed in comparison to samples which have little or no cross-linked chains. The degree of cross-linking in polymer samples has also been monitored using FTIR. Using this technique, changes in the degree of cross-linking can be monitored by changes in the absorbance intensities of the functional groups involved in the cross-linking process, such as esters and substitutes of benzene.

From this short review provided on the thermo-oxidative degradation of PET, it should be evident that the mechanisms involved are extremely complex. Despite extensive research efforts to study the degradation products and various factors influencing the degradation, the mechanism by which the polymer degrades in the presence of oxygen is still not fully understood.

1.3.2.1 Discolouration of PET

In addition to the significant decrease in molar mass and subsequent loss in mechanical, physical and chemical properties during the degradation of PET, discolouration of PET is also inevitable. Yellowing of the polymer can be caused by both thermal and thermo-oxidative degradation and is a severe problem during synthesis and melt processing. [1,68,69] The transparency of PET renders it a suitable material for the production of blow moulded bottles and packaging materials, therefore discolouration can adversely affect the end use of the product. Similarly, some manufacturers use PET film as a substrate in white consumer goods therefore must maintain a brilliant white colour specification. [17]

As PET degrades, its colour is reported to change first to yellow, then brown, and finally black. [17,68] An understanding of the reactions that result in discolouration of PET is therefore necessary if any attempts are to be made to minimise the yellowing of the polymer. Only a few attempts have previously been made to identify the species responsible for the discolouration in PET, particularly during melt processing. This is due to the great difficulty associated with isolating the chromophoric substances thought to be responsible for discolouration. Initially it was suggested that the discolouration of PET was due to the formation of polyene species. Under thermal degradation conditions, β-scission of PET results in the formation of vinyl ester and carboxyl end groups. These vinyl ester end groups were then thought to undergo further reactions, one of which included the polymerisation of the vinyl groups to polyvinyl esters and then the elimination of carboxylic acids to form polyenes. The absorption energy state of polyene structures is low enough to be detected in the visible region of the spectrum, resulting in coloured species. This mechanism for the formation of polyenes, originally proposed by Buxhaum *et al.* and later supported by Zimmermann *et al.* is illustrated in *Figure 1.39*. [1]



1. Formation of vinyl ends

2. Polymerisation of vinyl ends

3. Thermal cracking to form polyenes

Figure 1.39 Formation of polyenes from vinyl end groups [1,12]

A lack of experimental evidence for the formation of polyenes was later highlighted by MacDonald [12] and additional studies were completed to look for evidence of polyene species using Raman spectroscopy. Measurement of the conjugated $-(C=C)_n-$ stretching frequency, using resonance Raman spectroscopy, enabled precise information to be generated on the value and polydispersity of the conjugation length 'n', even in the presence of very low levels of polyenes. However, no evidence was found to indicate the presence of polyenes in any degraded PET samples studied, even when the samples were extensively degraded and therefore highly coloured. This led the author to believe that such species are not responsible for the colour formation in PET.

Studies on colour formation in PET were also completed by Edge *et al.* [70,71,72] who focused on investigating discolouration in degraded samples of PET at 280 - 300 ^oC in nitrogen and air by fluorescence, phosphorescence and IR spectroscopy. From these studies it was highlighted that the formation of coloured species was much greater in air than in nitrogen, indicating that thermo-oxidative conditions contribute more to the discolouration of PET than thermal degradation conditions. Chromophores present in the samples degraded under thermo-oxidative conditions were compared relative to model compounds and were proposed to arise from hydroxylation of the terephthalate ring and formation of unsaturated ester and quinonoid species. The degradation mechanism, giving rise to these species, is illustrated in *Figure 1.40.*

From *Figure 1.40,* direct decarboxylation, followed by radical recombination and oxidation is thought to result in the formation of stilbenequinones (route **b)**. Decomposition of hydroperoxides are proposed to yield hydroxyl radicals which abstract hydrogen from the aromatic rings to form hydroxylated aromatics, as illustrated in route **a**. Edge *et al.* commented that although oxidation of the hydroxylated aromatics to form quinones may seem unlikely, changes in the luminescence spectra of PET and model compounds were observed, therefore it does appear feasible under the conditions studied. Other researchers [73] are also in agreement that colour formation in PET begins with hydroxylation of the terephthalate ring. The formation of conjugated chromophoric species is then thought to follow, completing the colour formation. It is reported that these compounds need only to be present in ppm amounts for PET to be discoloured. [12]

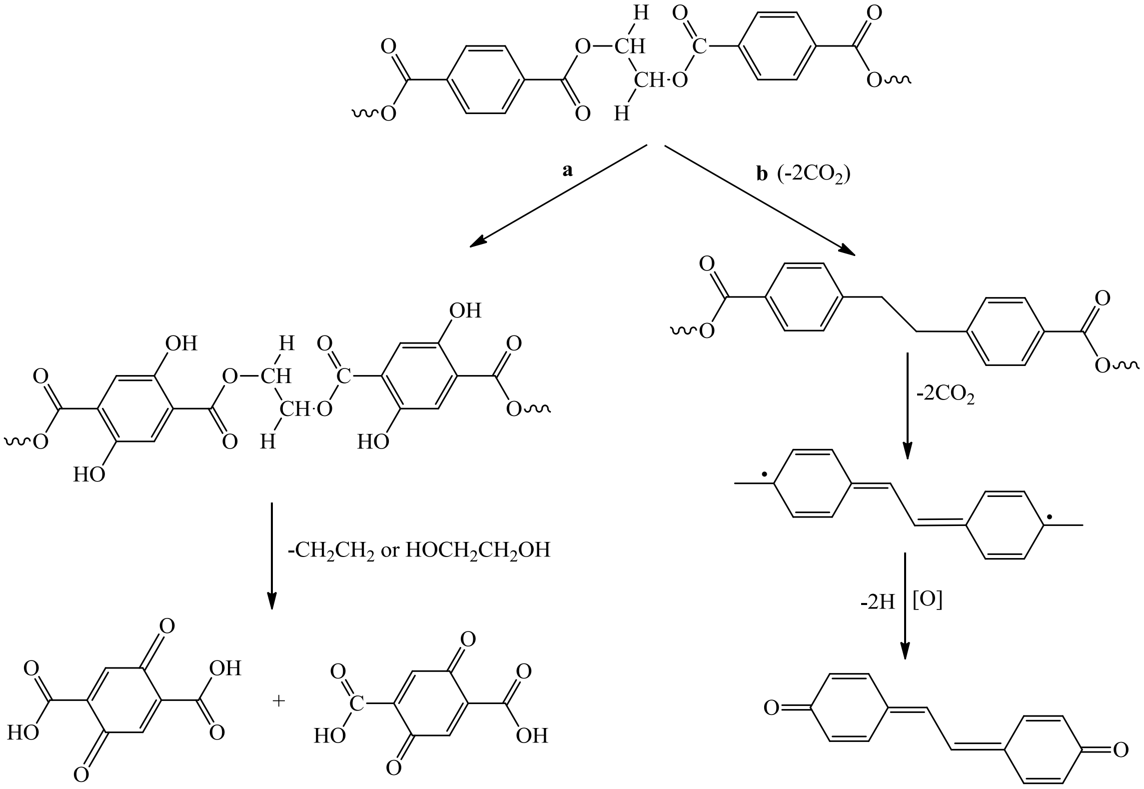


Figure 1.40 Formation of quinonoid species during thermo-oxidative degradation of PET [70,72]

Reactions leading to the discolouration of PET currently remain of great interest. As the chromophoric species involved in such reactions are very difficult to isolate, contradictory reports exist on their nature and composition. Further investigation is therefore still required to continuously improve our understanding on the discolouration reactions in PET.

1.3.3 Hydrolytic Degradation of PET

The hydrolytic degradation processes that occur in PET have received continuous attention in the literature [56,74,75,76,77,78] for many years due to their problematic nature. PET polymers are extremely hygroscopic and will absorb moisture rapidly up to saturation level in moist, wet or humid environments. This absorbed moisture is known to cause hydrolytic degradation of the polyester at temperatures above its glass transition, and most significantly at melt processing temperatures. The rate of hydrolytic degradation is reported to be several orders of magnitude higher than that of thermal degradation, resulting in severe loss of mechanical properties. [46,47,48]

The hydrolytic degradation of PET involves chain scission at the ester linkages. During this process, each water molecule breaks down one ester bond, leading to the formation of one carboxyl and one hydroxyl end group. Such degradation reactions are not accompanied by the evolution of volatile degradation products or discolouration. However, as the degree of hydrolytic degradation increases and the molar mass decreases, an increase in the concentration of carboxyl end groups is expected. The rate of hydrolytic degradation in PET can therefore be monitored using end group analysis. [75] Zimmermann *et al*. [56] used an increase in carboxyl end groups as a measure of the chain scission per unit time. Changes in the molar mass of polyesters as a result of hydrolytic degradation can also be monitored by various other techniques including gel-permeation chromatography (GPC), size-exclusion chromatography (SEC), viscometric analysis, FTIR, x-ray diffraction and differential scanning calorimetry (DSC). *Figure 1.41* illustrates the general hydrolytic degradation mechanism for PET summarised by Pirzadeh *et al*. [46]

The rate of hydrolytic degradation of PET is enhanced under acidic and basic conditions. General mechanisms for the hydrolytic degradation of polyesters in acidic, neutral, and alkaline environments are illustrated in *Figure 1.42*. Hydrolysis under acidic conditions involves protonation of the in-chain oxygen atom of the ester groups, followed by reaction with water to produce equal quantities of hydroxyl and carboxyl end groups. Under alkaline conditions, the hydroxide anion attacks the carbonyl oxygen atom to produce equivalent amounts of hydroxyl and carboxyl end groups. [46,47,75,79]

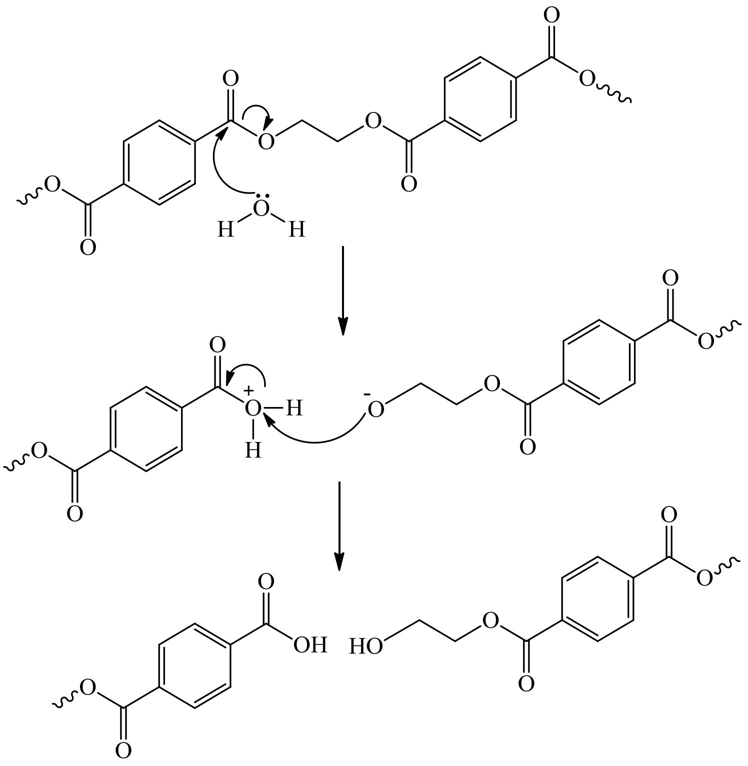


Figure 1.41 Chain-scission mechanism for hydrolytic degradation of PET [46]

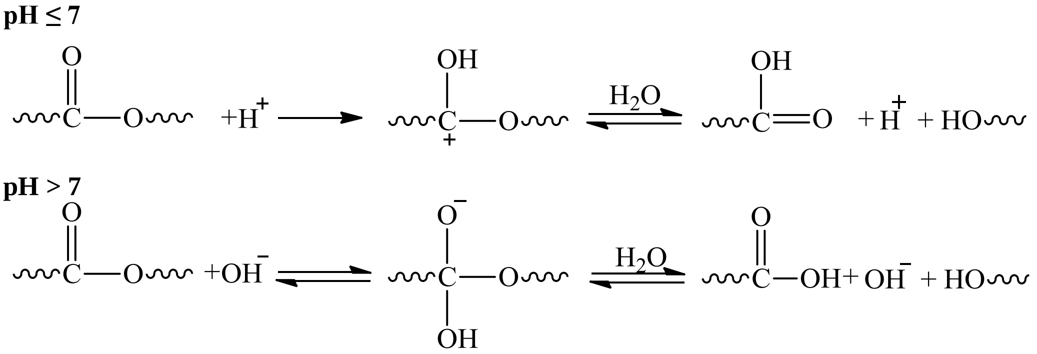


Figure 1.42 General mechanisms for the hydrolytic degradation of polyesters in acidic, neutral and alkaline environments [47,76]

Despite the simplicity of the mechanism, the hydrolysis of polyesters is a complex process which is not fully understood, even in the simplest case of the linear polyester, PET. An important source of difficulty is the role of chain ends. Some researchers [56,74,80,81] have proposed that hydrolytic degradation of PET is an autocatalytic reaction and that the concentration of carboxyl end groups controls the hydrolytic degradation. They suggest that an increase in the number of end groups during degradation leads to an increase in hydrophilicity and the penetration of more water into the system. This provides the conditions for an autocatalytic reaction, in contrast to random chain scission reactions.

During the hydrolysis of PET, it is thought that water diffuses into the amorphous regions of the polymer where hydrolysis occurs at a rate which depends on the shape, morphology and degree of crystallinity of the sample, the relative humidity and temperature. [56,75,79,80,82,83,84] At temperatures below the glass transition temperature of PET, hydrolytic degradation is negligible. However, above the glass transition temperature, increased mobility in the polymer chains enables penetration of water into the amorphous regions, increasing the rate of hydrolytic degradation. The rate of hydrolytic degradation of PET is strongly influenced by the crystallinity of the polymer as crystallites are impermeable to water and therefore act as barriers to moisture and oxygen diffusion. A high degree of crystallinity hinders the hydrolysis reaction as the crystalline phase is inaccessible to water. Thus, initial degradation is restricted to the amorphous regions and crystalline edges. [74-76] As water molecules diffuse into the amorphous regions of PET, chain scission occurs in these regions only. This provides mobility to small chain segments and enables them to realign in the polymer media, increasing the polymer crystallinity and reducing the amorphous fraction. This phenomenon is known as chemi-crystallisation and is reported to result in the incorporation of 5 - 6 monomer units into the crystalline phase per chain scission. [47,74] Chemi-crystallisation can be detected by changes in the polymer density during hydrolytic ageing and is also reported to occur during thermo-oxidative degradation of PET. [74] These changes in the morphology of PET will obviously affect the processability and the physical and mechanical properties of the polymer.

Hosseini *et al.* [47] studied the hydrolytic degradation of PET using gravimetric, FTIR and microcalorimetric techniques. Virgin PET granules were exposed to demineralised water within a bath at 85 °C and sampled at 5 day intervals for a period of 25 days. An increase in exposure time was reported to decrease the IV as a result of hydrolytic degradation. Subsequently, the molar mass was reported to decrease exponentially with the hydrolysis exposure time. The trends of IV and molar mass were found to decrease towards an asymptotic value highlighting restrictions on the extent of hydrolytic degradation possible in PET. This phenomenon was explained by PET morphology using a chain folded model, proposed by Miyagi *et al.*, [85] to represent the semi-crystalline structure of PET.

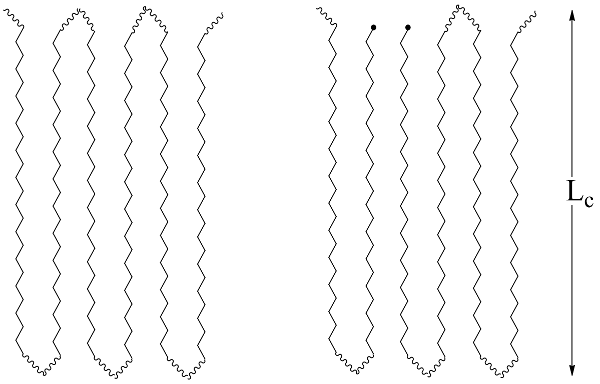


Figure 1.43 Chain folded model of PET - lamellar thickness indicated by L_c

On the basis of this model, illustrated in *Figure 1.43*, the structure of PET is represented as segments of crystalline and amorphous regions. In the regular, crystalline sections of the chain segments, water molecules cannot access the ester linkages minimising hydrolytic degradation. Water molecules are only able to access ester linkages in the amorphous regions and chain folds at the crystalline border, therefore limiting the extent of hydrolytic degradation. Consequently IV and molar mass values decrease toward an asymptotic value with increasing hydrolytic degradation. Unsurprisingly, the amount of moisture content in the samples analysed was reported to increase with the exposure time. However, there were no significant changes in the moisture content of samples exposed for longer than 5 days, indicating no further penetration of water into the samples due to saturation. It was therefore thought that hydrolytic degradation occurred simultaneously with the penetration of water molecules during the initial 5 days. Thereafter, the polymer was saturated with water and no further penetration of water could occur. Degradation reactions were then thought to continue as a result of temperature and time, for the remaining 20 days, due to the water already present in the polymer media.

Reports from many other publications on the hydrolytic degradation of PET all agree that the extent of hydrolysis increases with increasing moisture content. The rates of hydrolytic degradation of PET are only reported to be significant at temperatures above the T_g and found to increase with increasing temperature. Therefore humid and high temperature conditions induce hydrolytic degradation, subsequently resulting in an increase in carboxyl terminal polyester chains and a decrease in molar mass. To reduce the degree of hydrolytic degradation, it is necessary to dry the polymer chip to moisture levels below 40ppm, and preferably to less than 25ppm, prior to melting. The effective removal of moisture is dependent upon both the level and rate of diffusion of water through the material. Careful control of these key variables is essential to produce the best physical and mechanical properties for the end product.

1.4 Degradation of PEN

During manufacture and processing, PEN is exposed to higher temperatures than PET, due to its high melt temperature and high melt viscosity. Therefore, despite increased thermal stability of PEN, in comparison to PET, degradation reactions at high processing temperatures will occur. These degradation reactions will lead to a drop in molar mass, evolution of volatile degradation products and loss of crucial polymer properties. Although the fundamental degradation chemistry of PEN is believed to be similar to that of PET, there is very little evidence in the literature to support this. A small number of studies exist on the photo-degradation of PEN and PET/PEN polymer blends, however no reports exist on the thermal degradation of PEN. Botelho *et al.* [86] published the first thermo-oxidative degradation study of PEN in the year 2000.

Botelho *et al.* focused on the thermo-oxidative degradation of PEN and polybutylene naphthalate (PBN) using the model compounds ethylene dinaphthoate (EDN) and butylene dinaphthoate (BDN). These model compounds were studied alongside PEN and PBN to determine their thermo-oxidative degradation mechanisms. FTIR studies indicated the presence of anhydride groups in PEN, thought to originate from the processing of films. Carboxylic acid groups were also detected alongside hydroperoxide species indicating that thermal degradation of PEN occurs simultaneously with thermo-oxidative degradation. Furthermore, GC-MS analysis indicated the formation of naphthoic acid alongside that of ethyl and butyl naphthoate. The formation of such compounds were explained by the homolytic cleavage of the C-O ester linkage followed by abstraction of a hydrogen radical, as illustrated in the proposed mechanism in *Figure 1.44.*

Trace quantities of additional degradation products were observed from thermo-oxidative degradation studies of the model compound ethylene dinaphthoate. These degradation products led Botelho to believe that the thermo-oxidative degradation mechanism of PEN involves the oxidation of the methylene group in the α-position to the ester group. This mechanism is identical to that described previously for PET in *Section 1.3.2* (*Figures 1.35 - 1.37*).

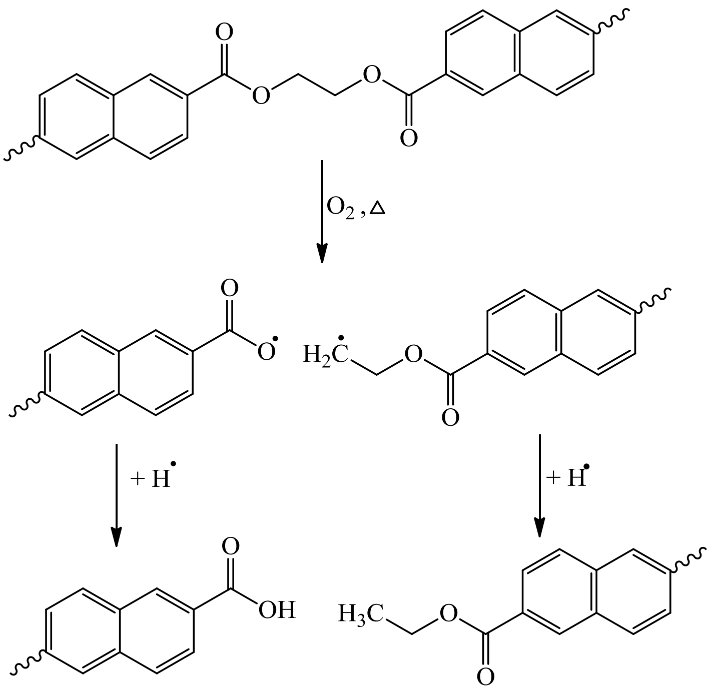


Figure 1.44 Chain scission of ester linkages in PEN

Similar to PET, the thermo-oxidative degradation of PEN leads to discolouration of the polymer. Botelho *et al.* [86] report that PEN discolours more rapidly than PET, suggesting that the naphthalene ring is involved in the discolouration reactions. These findings were supported by Scheirs *et al.* [87] during a study to monitor the photo-oxidation and photolysis of PEN and its blends/copolymers with PET and PBN. Thin film samples were irradiated for set periods of time under UV light and the discolouration of the polymers monitored by UV spectroscopy. As the naphthalene content within the polymer blends increased, discolouration increased. The extent of discolouration in PEN was found to be greater than any other aromatic polyester, indicating that the photo-yellowing of PEN is related to the presence of highly conjugated and highly absorbing naphthalene structures. The yellowing of PEN samples was also found to be accompanied by gel formation, indicative of the presence of cross-linked species. It has been proposed that these cross-linking reactions, illustrated in *Figure 1.45*, lead to the formation of highly conjugated bis-naphthalene structures, thought to be responsible for yellowing in PEN.

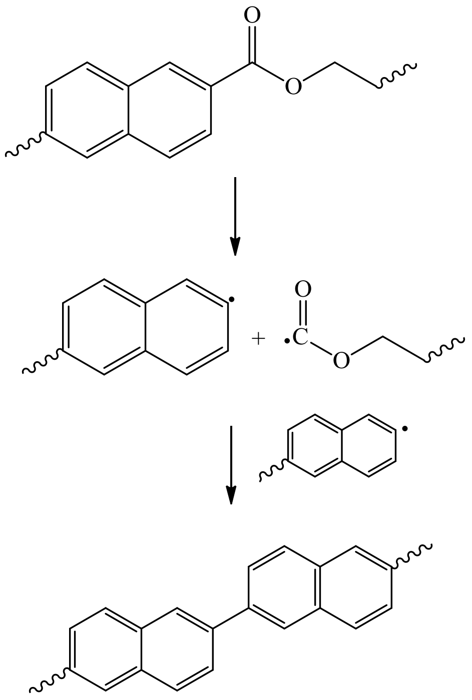


Figure 1.45 Cross-linking reaction during the degradation of PEN

The hydrolytic degradation of PEN has also been briefly covered in one study performed by Zhang *et al.* [88] on the hydrolytic degradation kinetics of PEN. Although PEN is thought to hydrolyse in an identical manner to PET, the relative rates of hydrolytic degradation are unknown. Zhang *et al.* studied the hydrolytic degradation of PEN, in comparison to PET, in a saturated steam environment at 120, 140 and 160 ^{o}C. The film samples were hydrolysed for various times and analysed using IR end group analysis to measure the change in the number of end groups in PET and PEN. PET was reported to hydrolyse at a much faster rate than PEN and the hydrolytic degradation was rapidly accelerated with an increase in temperature for both PET and PEN.

Other than the above evidence, mechanistic details for the degradation of PEN are very limited. This research will therefore focus on studying the thermal, thermooxidative and hydrolytic degradation of PEN, in comparison to PET, in an attempt to elucidate further mechanistic details.

1.5 Focus and Aim of Research

During the synthesis and processing of PET and PEN, a variety of thermal, thermo-oxidative and hydrolytic degradation reactions are likely to occur. The impact of these degradation reactions are very specific to the part of the process where they occur. However, generally speaking, degradation leads to the evolution of volatile and residual degradation products resulting in crucial changes to the thermal, mechanical, colour and optical properties of the final product.

DuPont Teijin Films are particularly interested in the underlying degradation chemistry of PEN, in comparison to PET, including processing issues such as the generation of colour, gels and oligomers. Whilst these degradation issues and the influence of environmental factors such as temperature, time, moisture and oxygen content have been well understood and modelled by DuPont Teijin Films for PET, their exact effect on PEN is less understood. This research programme therefore focuses on developing a greater understanding of the degradation pathways of PEN, in comparison to PET, particularly under processing environment and temperature regimes. Particular emphasis is placed on the thermal, thermo-oxidative and hydrolytic degradation of PEN under model processing conditions. The specific objective is to generate data that is directly applicable to a film manufacturing process to enable DuPont Teijin Films to identify any operational improvements and re-parameterise their existing PET degradation/processing model for PEN. A summary of the different research areas covered throughout this three year research programme is illustrated in *Figure 1.46*.

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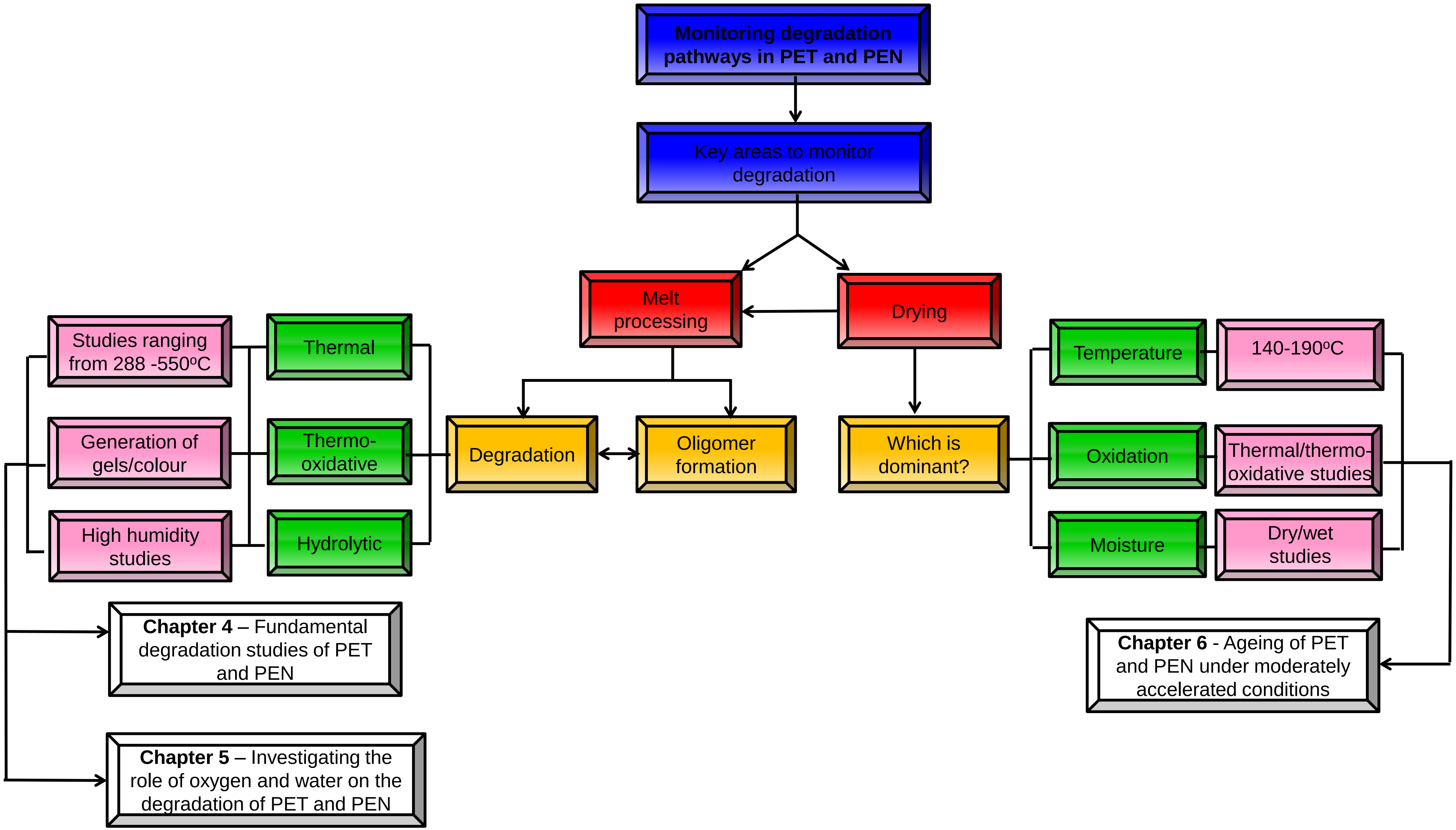

Figure 1.46 Summary of PET/PEN degradation programme

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2 INSTRUMENTAL TECHNIQUES

A relatively broad range of spectroscopic and thermal analysis techniques were employed throughout this research. The author will therefore assume that the reader will be familiar with the theory of common spectroscopic techniques such as FTIR, solution NMR and GC-MS. Less common techniques, used for the analysis of polymers, will be discussed in some detail in this section.

2.1 Thermal Analysis

The thermal stability of polymers can be determined with the use of thermal analysis techniques such as differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA). These methods of analysis determine the physical and chemical properties of a material as a function of temperature. Both techniques are complimentary to one another and can be used together to establish the thermal degradation behaviour of a material of interest. The third thermal analysis technique used is called thermal volatilisation analysis (TVA). This technique identifies the volatile products generated when a material thermally degrades, thus complementing the DSC and TGA data to identify thermal degradation mechanisms.

2.1.1 Differential Scanning Calorimetry

2.1.1.1 Theory

DSC is a technique used to measure the energy required to establish a zero temperature difference between a substance and an inert reference material, as both are subject to identical temperature programmes in a controlled atmosphere. [1] This method of thermal analysis enables the detection of both chemical (oxidation, degradation) and physical (glass transition, crystallisation, melting) processes occurring within a material.

The basic underlying principle of DSC involves disruption of the equilibrium established between a sample and reference when a change of heat capacity, phase transition or reaction occurs. The sample temperature will therefore be higher (exothermic process) or lower (endothermic process) than the reference. This difference in temperature, ΔT is detected by the temperature controlling system and the differential heat flow between the sample and reference is calculated. The temperature difference, ΔT is given by the following equation:

$$\Delta T = K\Delta\left(mC_p\right)R$$ **Equation 1.1** [2]

where $\Delta(mC_p)$ is the difference in total heat capacity between reference and sample, R is the heating rate (^{o}C min^{-1}) and K is the calibration constant. This temperature difference, sensed by the detectors, is directly proportional to the difference in heat flow into or out of the sample and reference. The heating rate in DSC must be carefully selected in order to minimise thermal lag and physical ageing effects. A heating rate that is too high will result in a thermal lag effect as the sample temperature will continuously lag behind the target temperature. However, if the rate is too low, physical ageing may occur. Both physical ageing and thermal lag events can result in subsequent changes in a materials response in later DSC cycles.

The results obtained from a DSC study are generally displayed as a thermogram where the instrument signal (i.e. heat flow) is plotted against temperature for dynamic studies, or time for isothermal studies. A typical dynamic DSC trace is shown in *Figure 2.1*. The important temperatures from a thermal analysis curve are generally represented as the maximum peak temperature, T_p and the extrapolated onset temperature, T_{onset} for the transition of interest. The onset temperature can be defined as the temperature of intersection between the extrapolated initial base line and the tangent through the linear section of the leading edge of the peak. The area under a DSC peak can also be used to estimate the enthalpy of the transition, ΔH and the T_g is often measured as the half-height of the step change in baseline. [1,2]

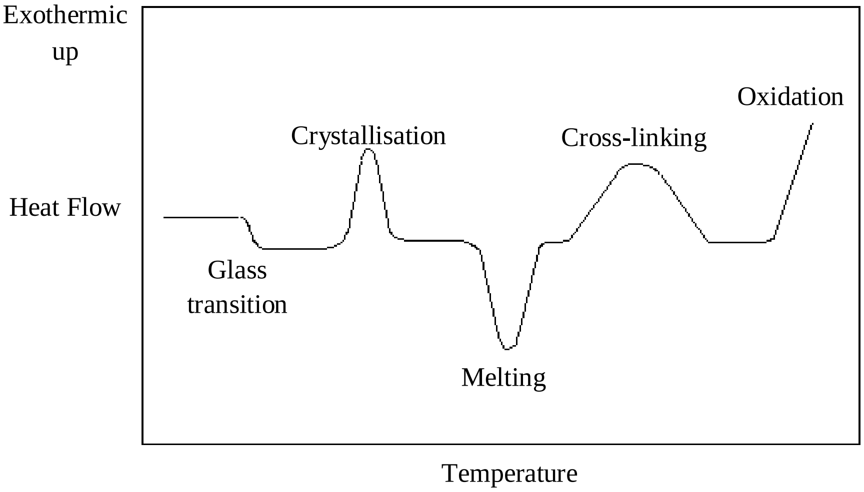


Figure 2.1 Typical events on a DSC thermogram

2.1.1.2 Instrumentation

The majority of differential scanning calorimeters fall into one of two categories depending on their operating principle. The two DSC systems are known as the power compensation DSC and the heat flux DSC. Throughout this research, only the heat flux method was utilised, therefore it will be the only method described.

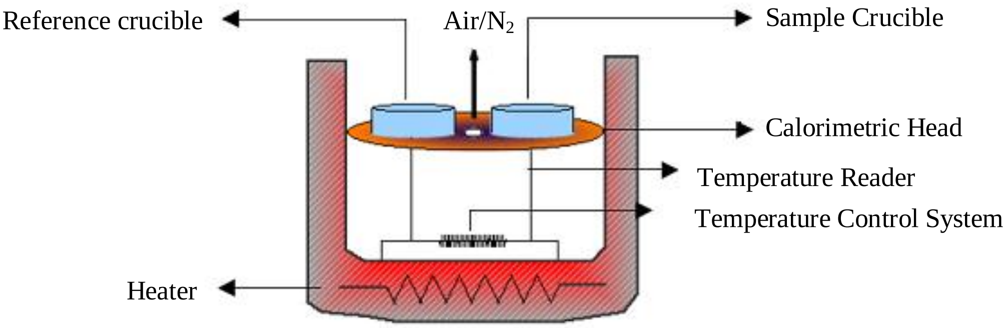


Figure 2.2 Heat flux DSC system

In heat flux DSC, both the sample and reference are connected by a low resistance heat flow path. The instrument signal is derived from the temperature difference (measured by temperature sensors) established when the sample and reference are heated in the same furnace. A typical heat flux DSC system is shown in *Figure 2.2*.

Heat flux DSC systems make use of an aluminium pan to contain the sample. The reference is either an inert material in a pan of the same type as that used for the sample or simply an empty pan.

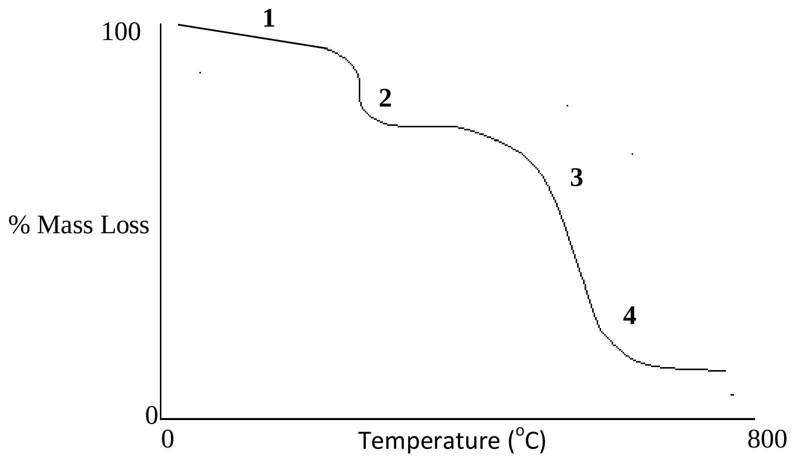
2.1.2 Thermal Gravimetric Analysis (TGA)

2.1.2.1 Theory

The second technique used in conjunction with DSC, when investigating the degradation behaviour of polymers, is TGA. This technique records the mass of a material as a function of temperature when the material is subjected to a controlled temperature programme. [2] Therefore it provides a quantitative measurement of any mass change in a sample associated with a transition or degradation process. Isothermal studies can also be performed, recording the mass loss of a material as a function of time. All samples can be heated under an inert or oxidative atmosphere.

Thermal events that may result in a change in the mass of a sample include desorption, absorption, sublimation, oxidation and decomposition. [3] TGA is most commonly used to characterise the thermal stability and decomposition of materials under various conditions and can therefore monitor the mass loss of a polymer as a result of the evolution of volatile species. However, TGA cannot identify the volatile degradation species evolved unless the instrument is connected to a mass spectrometer. *Figure 2.3* illustrates some of the common characteristics of a TGA profile for a polymer. The information generated from a TGA provides not only a quantitative measure of the mass loss but also an indication of the number of degradation processes occurring within a polymer.

Alternatively, the TGA results can be presented by taking the derivative of the original experimental curve to produce a curve representing the rate of mass loss as a function of temperature i.e. dm/dT. The generation of such curves is called derivative thermogravimetry, where the area under the derivative peak is directly proportional to the mass loss. [1]



1 - Small mass loss typically from impurities and low molar mass volatiles

2 - Sharp increase in mass loss often due to degradation of the polymer

3 - Mass loss decreases as carbonaceous char forms

4 - Increasing mass loss as the carbonaceous char is completely oxidised

Figure 2.3 Typical events on a TGA profile

2.1.2.2 Instrumentation

The TGA apparatus primarily consists of a sensitive balance, a furnace and a thermocouple. The sample of interest is placed into a small inert crucible that is attached to a microbalance and surrounded by a furnace. The temperature in the TGA system is measured by a thermocouple positioned only a few millimetres away from the sample in the furnace. As the sample pan is part of the sensitive electronic balance and the thermocouple is so close to the sample crucible, both the mass and the temperature of the sample can be continuously and accurately recorded. A schematic diagram of a typical TGA system is shown in *Figure 2.4*. Both the magnitude of the event measured and the overall sensitivity of the microbalance dictate the amount of sample required for TGA; however typical sample sizes range from 5 - 20 mg.

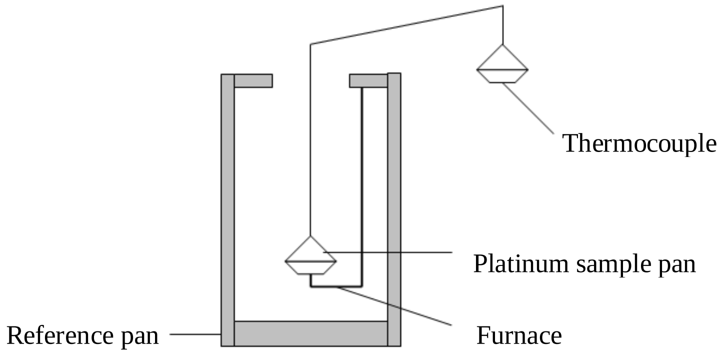


Figure 2.4 Schematic diagram of a typical TGA system

2.1.3 Thermal Volatilisation Analysis (TVA)

2.1.3.1 Theory

Thermal volatilisation analysis is a technique useful for studying the degradation behaviour of polymers that breakdown to give some proportion of volatile products when heated under vacuum. The system, originally designed by I.C. McNeill [4] and co-workers in 1966, consists of a continuously evacuated system with a cold trap located a good distance away from the sample of interest. As the sample is heated at a linear rate and subsequently degrades, a small pressure develops due to the time taken for the volatile degradation products to distil from the hot degrading surface of the sample to the cold surface of a liquid nitrogen cooled trap. The magnitude of this pressure developed ranges between the orders of 10^{-5} to 10^{-1} Torr and depends on the rate of volatilisation of the sample. Pirani gauges are used to record the pressure changes between the heated sample and the cold trap and results are represented in the form of thermograms, representing the pressure changes as a function of temperature or time.

In addition to the collection of condensable volatile species, differential distillation of the degradation products is achievable, which greatly facilitates the identification of degradation products. Once again, the pressure changes can be monitored during the differential distillation as products are separated according to their volatility and collected for subsequent analysis. Accurate measurement of the pressure changes as volatile components are evolved during degradation processes and subsequent collection of these degradation products can provide useful information on the mechanisms of polymer degradation. [4]

2.1.3.2 Instrumentation

The TVA apparatus consists primarily of a glass sample chamber connected to a primary liquid nitrogen cooled sub-ambient trap and a series of secondary liquid nitrogen cooled cold traps, as illustrated in *Figure 2.5*. The entire system is pumped to a vacuum of ~1x10^{-4} Torr by the use of a two-stage rotary pump and an oil diffusion pumping system. As the sample is heated at a linear rate, using a programmable tube furnace, the water jacket cooled 'cold ring' condenses high boiling point degradation materials. These high boiling point materials, such as high molar mass degradation products, are volatile at elevated temperatures but condense within the 'cold ring' under vacuum at ambient temperatures. High boiling point degradation species, with a molar mass of approximately 200 to 1000 g mol^{-1} are often referred to as 'oligomeric fractions'. [5] These oligomeric, 'cold-ring', products are not detected by Pirani gauges as they condense prior to exiting the degradation tube.

In contrast, the volatile degradation species with lower boiling points are collected in a primary liquid nitrogen cooled sub-ambient trap, maintained at a temperature of –196 ^{o}C. These 'condensable' fractions are volatile at room temperature but involatile at –196 ^{o}C, hence collect within the primary sub-ambient trap. They generally consist of materials ranging from C_2H_2 up to species with a molar mass of 200 g mol^{-1}. [5] Linear response Pirani gauges, positioned at both the entrance and exit of the primary sub-ambient trap, allow the evolution of both condensable and non-condensable volatiles to be continuously monitored as a function of pressure versus temperature.

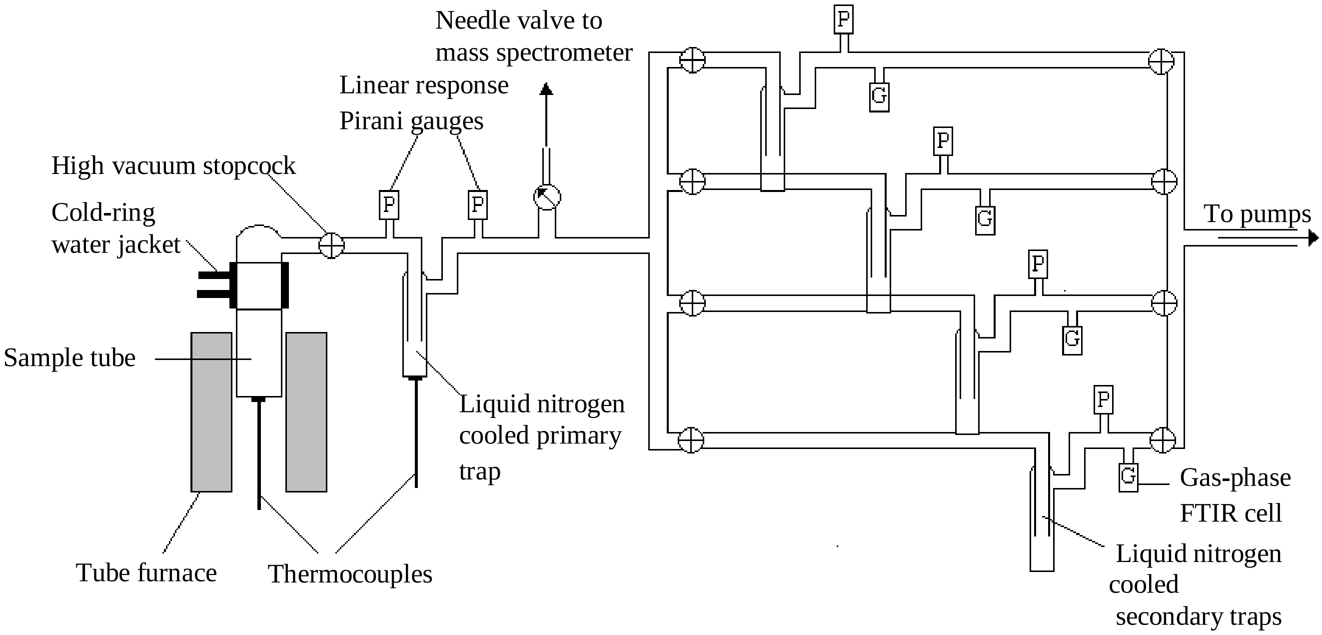


Figure 2.5 Schematic diagram of TVA system

The low boiling point species, trapped within the liquid nitrogen cooled primary trap, can then be separated and isolated into four separate secondary traps. This process is known as differential distillation and involves heating the primary sub-ambient trap up to ambient temperatures. This separation depends ultimately on differences in volatility between the degradation species present. If two species of the same volatility are present, separation will not occur. Strong hydrogen bonding effects can also hinder separation. The primary sub-ambient trap is composed of a steel can with a double-U tube glass trap as illustrated in *Figure 2.6*.

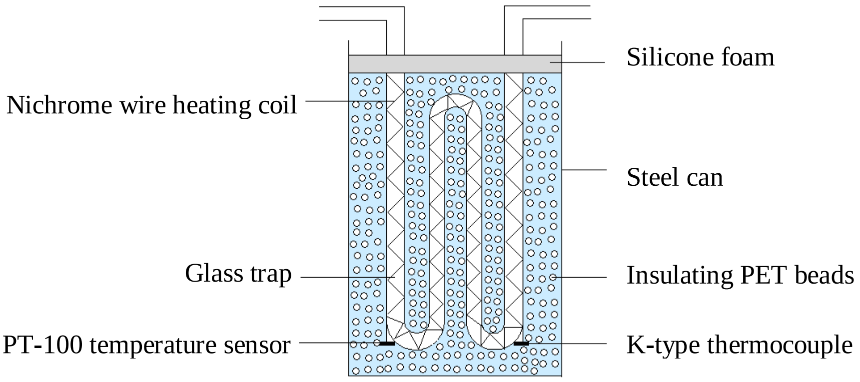
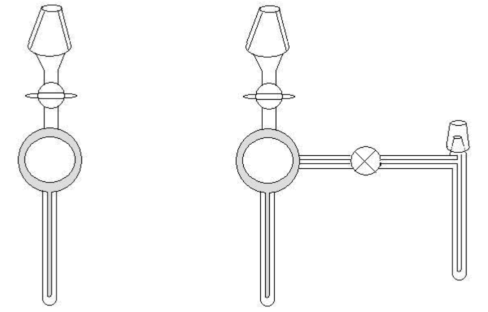


Figure 2.6 Schematic diagram of primary sub-ambient trap

The glass trap is coiled with nichrome heating wire and connected to a direct current (DC) power supply to enable heating. A PT-100 resistor acts as a temperature sensor for the power supply control unit and a K-type thermocouple monitors the temperature of the primary sub-ambient trap throughout the analysis. PET beads are packed into the trap as a thermal insulation material. On heating, the degradation products will evaporate at specific temperatures and pressure changes will occur as the products distil from the trap. The resolution of pressure peaks depends on the rate at which the trap is allowed to warm up on removal of the liquid nitrogen vessel.

After separation, volatile degradation products can then be transferred from the secondary traps into gas-phase cells for offline FTIR and GC-MS analysis. The transfer of the isolated fraction into the gas-phase cells is performed by isolating the fraction from the remainder of the vacuum system and cooling the cold finger on the gas-phase cells using liquid nitrogen. The liquid nitrogen from the secondary trap is then removed allowing the trap to heat up to room temperature and Pirani gauges positioned at the secondary trap exit, monitor the transfer of the isolated fraction to the gas-phase analysis cell. The two main types of gas cells employed for the analysis of fractions collected from the differential distillation process are illustrated in *Figure 2.7*.



Standard IR gas cell Combined GC-MS/IR cell

Figure 2.7 Main types of gas-phase cells employed in TVA

The standard, sealed glass IR cell is composed of two NaCl disks enabling direct IR analysis of the volatile degradation products. However, FTIR alone is often unable to provide explicit information about an analyte. The sensitivity of the technique is comparatively low and the technique is often unable to identify high molar mass and thus high boiling point volatiles. Therefore, the combined FTIR/GC-MS cell is often used to enable direct IR analysis subsequently followed by solvent trapping of the volatile product in a secondary limb for GC-MS analysis of large, high-boiling volatiles.

Throughout the entire thermal volatilisation procedure, the gas stream is continuously monitored at the exit of the primary subambient trap by an online quadrupole mass spectrometer. This is particularly useful for the identification of non-condensable degradation products such as carbon monoxide and methane in addition to condensable degradation products collected from the differential distillation procedure.

2.2 Molar Mass Determination of Polymers

2.2.1 Gel Permeation Chromatography

2.2.1.1 Theory

In addition to thermal analysis to characterise degradation of polyesters, it is fundamentally important to monitor the molar mass of polymers. Gel permeation chromatography (GPC) is now one of the most useful methods for routine determination of the molar mass distribution and the average molar mass of polymers and is recognised as a useful aid in studies of polymer degradation and/or quality control during polymer production and processing.

The molar mass of a polymeric system is a fundamental characteristic that significantly influences the properties of a polymer and consequently a polymer’s end use. However, there is great difficulty associated with assigning an accurate molar mass to any one polymer system. This is due to the entirely random events that occur during a polymerisation reaction producing a polymer with a mixture of chains of different lengths and thus a distribution of molar masses. The molar mass of a polymer is therefore most appropriately expressed as an average molar mass.

GPC, otherwise known as size exclusion chromatography, is a rapid, efficient and reliable method that can provide an indication of the molar mass distribution of a polymer. There are many different methods used to calculate an average molar mass for a given distribution of molar masses. Two of the most common methods involve the determination of a number average or mass average of the total number of chains within any one polymeric system. [6]

1. Estimation of the number of chains with a particular length to define a 'number average molar mass' (M_n) where n_i is the number of polymer molecules with mass M_i.

$$M_n = \frac{\sum n_i M_i}{\sum n_i}$$ **Equation 2.2**

2. Estimation of the number of chains of a particular mass to define a 'weight average molar mass' (M_w) where $w_i = \left(n_i M_i / N_a\right)$ and N_a is Avogadro's constant.

$$M_w = \frac{\sum w_i M_i}{\sum w_i}$$ **Equation 2.3**

GPC is a liquid-liquid chromatographic technique in which molecules are separated according to their molecular size. The GPC method generally involves injecting a dilute solution of a polydisperse polymer into a continuous flow of carrier solvent passing through a tightly packed column. The column, or stationary phase, is generally composed of microporous gel particles such as cross-linked polystyrene or porous silica microspheres, which are not prone to swelling in the carrier solvent. The non-ionic gel stationary phase particles exist in a range of pore sizes from 0.5 to 10^5 nm, which correspond to the effective size range of polymer molecules. Separation of polymer molecules occurs by preferential penetration of different sized polymer molecules into different sized pores. When a solution of polymer is injected to be analysed, the polymer molecules tend to diffuse from the mobile phase into the stationary phase, to the extent that the molecules are small enough to be accommodated within the “gel”. As a sample progresses through the column with the carrier solvent, larger molecules, which occupy the greatest effective volume in solution, have minimal interaction and remain excluded from the smaller pore sizes in the stationary phase. Larger molecules therefore progress most quickly through larger channels between gel particles, resulting in premature elution. In contrast, small molecules are more likely to penetrate through the small pores easily, slowing their time of passage through the column, resulting in longer elution times. The time or the volume of elution is inversely proportional to the molecular size. [2,7]

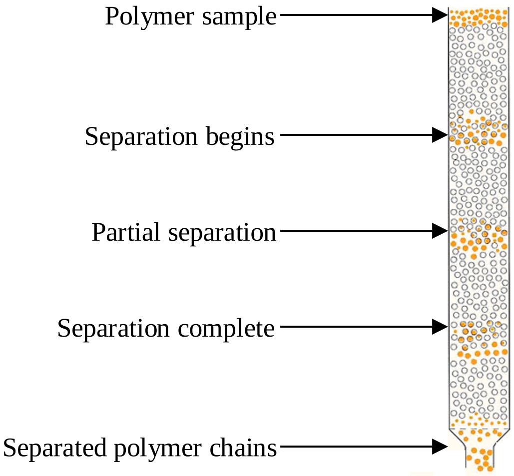


Figure 2.8 GPC column

Therefore by choosing a series of gel columns with a wide range of pore sizes, an efficient and effective separation of polymer molecules can be obtained. The solute molecules eluted are finally passed through a detector to monitor their concentrations and enable qualitative analysis of the various different components within the polymer sample analysed.

Different molar mass fractions eluted from the GPC column can be characterised by elution volume or peak retention volume, V_R. V_R is defined as the volume of solution eluted from the time of sample injection into the GPC column to the peak of the chromatogram for that fraction. V_R can be calculated from the interstitial volume, V_O and the volume of liquid within the pores, V_i as shown by *Equation 2.4*.

K represents the distribution coefficient which corresponds to the ease at which the solute molecules can penetrate into the porous stationary phase. When $K = 0$, no penetration occurs and when $K = 1$, there is unrestricted penetration.

$$V_R = V_O + KDVi \qquad \textbf{Equation 2.4}$$

Although GPC separates molecules according to their molecular size, resulting in a size distribution curve, the technique itself cannot give absolute values of molar mass from calculation of V_R without calibration with polymer standards of a known molar mass. Polystyrene calibration standards and the universal calibration method are most commonly used. The universal calibration method relates V_R and the molar mass, by assuming that the hydrodynamic volume (or effective molecular size) of a macromolecule is proportional to the product of the intrinsic viscosity of the polymer in the GPC eluent, $[\eta]$ and the molar mass of the solute, M. A universal calibration curve can then be obtained for different polymer calibration standards by plotting log $[\eta]M$ against V_R for a given carrier solvent at a fixed temperature. Once the calibration curve is obtained, the gel permeation chromatogram of any other polymer can be obtained in the same solvent and the average molar masses (M_n and M_w) and the complete molar mass distribution for the polymer can be determined. Repeat GPC chromatograms usually agree within 1 - 2%, but chromotograms are sensitive to experimental parameters such as the resolution of columns used, flow rate, porosities of column packing etc. [2,7]

2.2.1.2 Instrumentation

The essential components of a GPC instrument are illustrated in *Figure 2.9* and include:

- A solvent system capable of maintaining a constant flow.
- A column containing microporous gel particles of a suitable size for effective separation.

- An injection system capable of delivering appropriate volumes of the polymer solutions without disturbing the solvent flow.
- A detection system to monitor the output from the GPC column in order to provide quantative and qualitative data on the fractions being eluted.
- A recorder to produce continuous output traces.

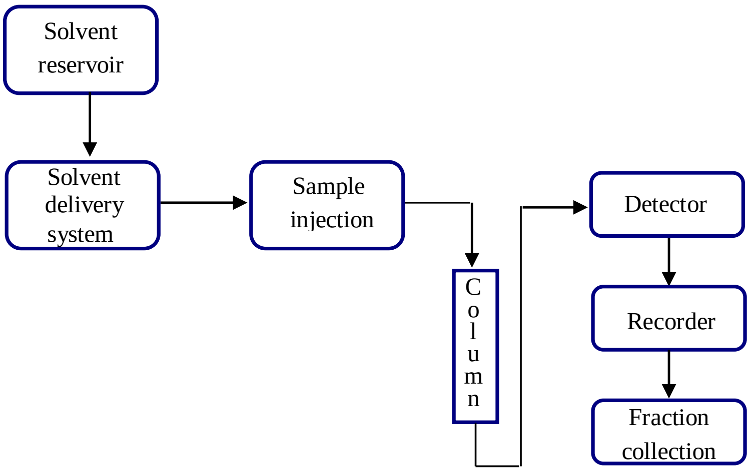


Figure 2.9 Typical components of a GPC instrument

As the retention time has a logarithimic relationship with the molar mass, it is essential that the flow remains constant. Flow rates between 0.1 and 10 mL min^{-1} are typically selected. The columns are generally packed with microporous cross-linked polystyrene gels or porous glasses or silica. Inorganic packing materials are most suitable for aqueous solution work, while styrene gels are generally employed for non-polar organic solvents such as toluene. However, a recent improvement in the stability of cross-linked polystyrene gels now allows the use of polar solvents such as dimethylfuran (DMF) and ortho-chlorophenol. This enables GPC analysis of polymers such as nylon and PET to be performed at ambient temperatures rather than elevated temperatures. The detector is required to monitor the concentration of the solute molecules in the solvent continuously and allow qualitative analysis of the various components in the sample. The most common types of detector are differential refractometers, which can be used for all types of molecules.

UV-visible absorption instruments can also be advantageous for the identification of components which may absorb in the UV or visible spectral regions. IR absorption detection systems are also suitable detectors, producing spectra rapidly. [2,7]

2.3 Viscosity Measurements of Polyesters

2.3.1 High - Temperature Melt Rheology

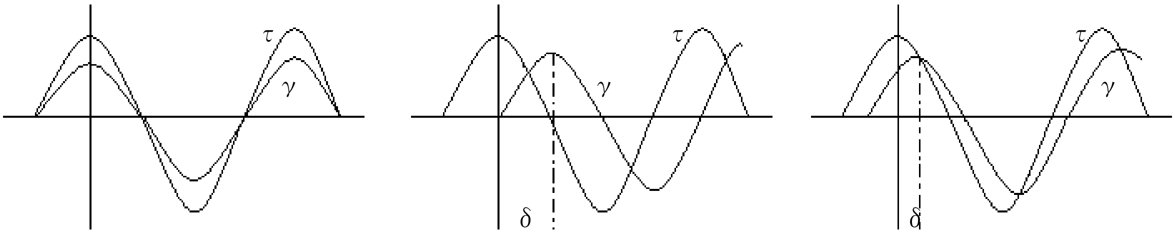
Rheology is the science that deals with the way materials deform upon application of force. [8] The technique is applicable to all types of material from gases to solids, however is most commonly used to study the viscosity of liquids and liquid-like materials such as paints, polymer solutions and molten plastics, often as a basis for understanding extrusion and injection moulding processes. In this research, the melt rheology of both PET and PEN has been examined as a method of monitoring the chain mobility following ageing in inert and oxidative environments.

Many different rheological methods exist for measuring the viscosity of a material. However, only the oscillation method performed using a rotation rheometer will be described in more detail for this research.

2.3.1.1 Theory

Viscosity, η is defined as the measure of resistance to flow that a fluid offers when it is subjected to stress. [9] Oscillation rheometry is often used to measure the viscosity of a material. This oscillation technique involves applying a sinusoidal oscillating stress wave, τ and measuring the resulting strain wave, γ.

The differences observed between the oscillating stress wave and the resultant strain wave, measured in oscillation rheometry, are very much dependent on the material being analysed. For example, if a material is purely elastic it will retain all of the energy applied to it and will produce a phase difference (i.e. phase angle) of zero degrees between the imposed stress and the resultant strain. In contrast, a purely viscous material will lose all the applied energy resulting in a phase difference, δ of 90^o. Polymeric materials are generally visco-elastic and therefore have phase angles that lie between 0^o and 90^o as illustrated in *Figure 2.10*. It is these phase angles together with the amplitude of the imposed and resultant strain waves that are used to determine the viscous and elastic properties of a material.



Pure elastic response
Phase angle = 0°

Pure viscous response
Phase angle = 90°

Visco-elastic response
Phase angle = 0-90°

Figure 2.10 Variations in phase difference in oscillation rheometry with elastic, viscous and visco-elastic materials

Generally oscillation strain controlled measurements are performed with variations in the temperature or frequency. A temperature sweep involves measuring the viscosity of a material at various temperatures with constant frequency. In contrast, a frequency sweep involves viscosity measurements at a constant temperature when altering the frequency. The data derived from these oscillation strain controlled measurements are (i) complex viscosity, η^* (ii) phase angle and (iii) storage, *G'* (elastic component) and loss modulus, *G"* (viscose component). The following relationship of *G'* and *G"* is used to describe the viscosity response of the material where the oscillation frequency is defined by ω:

$$\eta^* = \frac{\left[(G')^2 + (G'')^2\right]^{1/2}}{\omega} \qquad \textbf{Equation 2.5}$$

Many different factors can exert an effect upon the measured viscosity of a material. The rheological behaviour can be influenced by the structure and composition of the material and the temperature and pressure at which the measurements are performed.

For example, fluids with a high molecular weight generally have higher viscosity due to molecular branching and entanglement of the chains within the material. However, by increasing the temperature it is possible to reduce the viscosity by increasing chain mobility. [8]

2.3.1.2 Instrumentation

Rotational rheometers are generally used to record the oscillation measurements of a material in order to measure viscosity. The most common rotational rheometers include cone and plate, parallel plate and concentric cylinders designs, all of which possess advantages and disadvantages for their use when analysing different materials. Rotational parallel-plate rheometers are most common for the study of rheological properties in polyesters.

Rotational rheometers have two main plates, known as geometries, with the fluid under study separating them. During oscillation strain controlled measurements, the bottom plate in a parallel plate rheometer remains fixed and the top plate oscillates at a known frequency. As the top plate is rotated, the fluid exerts a resultant stress on the other plate which is measured. The parallel-plate geometry is illustrated in *Figure 2.11*.

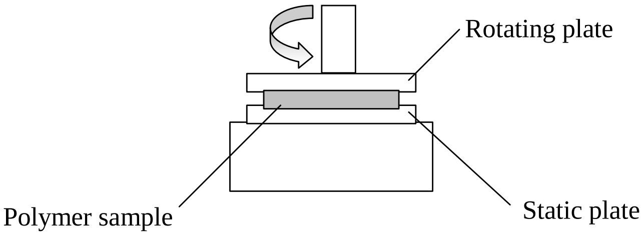


Figure 2.11 Parallel-plate geometry in a rotational rheometer

The parallel-plate geometry is often favoured due to its flexibility under testing conditions. Generally, the parallel plate rheometer is programmed with a heating profile (from room temperature up to polymer degradation temperatures of ~400 ^{o}C), oscillating frequency and stress to produce strain within a sample. The instrument computer then compares this material strain to the input stress and mathematically derives viscosity information.

2.4 ^{13}C Solid-State NMR Spectroscopy [10-21]

Nuclear magnetic resonance (NMR) is a physical phenomenon based upon the magnetic properties of an atom's nucleus. It primarily detects the absorption or emission of electromagnetic radiation, within the system under investigation, resulting from transitions between different energy levels. As the energy levels are directly influenced by the environment of nuclei, the resulting spectrum provides direct evidence regarding the chemical nature of the interacting atoms.

Although solution NMR is frequently used for the characterisation of polymers due to its high resolution and sensitivity, solid-state NMR has become a powerful tool for studying crystalline, semi-crystalline and amorphous materials. Solid-state NMR is particularly useful as most polymers are now utilised in the solid-state, enabling the NMR properties to be directly related to their macroscopic properties.

The NMR spectrum of a solid is fundamentally different from solution and more challenging to obtain due to restricted atomic mobility from the presence of nearby chains. Local interactions that generally result in line broadening, such as chemical shift anisotropy (CSA) and dipolar coupling cannot be averaged by molecular motion in solid-state NMR and therefore result in poor resolution spectra. The overall sensitivity and resolution of solid-state NMR spectra is also very much dependent on several sample related factors, in contrast to solution NMR where the initial form of the material is irrelevant to the quality of the final spectrum. Therefore, artificial means of obtaining high-resolution solid-state NMR spectra have to be obtained, by means of complicated acquisition methods, in comparison to straightforward solution NMR.

Solid-state NMR is fundamentally different than solution NMR as the NMR spectra of solids consists of very broad bands with no resolved structure. This behaviour is a result of three major factors:

(a) ***Dipole-dipole interactions*** - the nuclear dipoles in a solid interact with each other by direct coupling through space. The strength of the dipolar coupling depends on distance, and is especially large for nuclei that are directly bonded to each other i.e. ^{13}C-H fragments.

(b) ***Chemical shift anisotropy*** - as the movement of atoms is severely restricted or even prevented altogether in solids, this can result in extensive broadening as the chemical shift is dependent on the orientation of the molecule or fragment relative to the external magnetic field. Therefore molecules in different orientations will resonate at different frequencies.

(c) ***Long relaxation times*** - nuclei in solids generally possess long relaxation times and therefore require a considerable amount of time to relax back to equilibrium magnetisation after each pulse. If this is not permitted, then the signal-noise ratio and overall resolution of the spectrum will be poor. These long relaxation times are particularly problematic for nuclei with dilute spins i.e. ^{13}C.

Both dipole-dipole interactions and chemical shift anisotropy effects do occur in solution but they are generally averaged to zero as a result of the rapid motion of the molecules, resulting in narrow resonances. However, due to limited motion in solids, both these factors lead to substantial line-broadening and must be overcome in order to obtain high quality solid-state NMR spectra.

A series of techniques can be used to overcome the problems outlined above, enabling high resolution spectra to be obtained in the solid-state. These include magic-angle spinning (MAS), high power decoupling and cross-polarisation, described in more detail below.

2.4.1 Dipolar Interactions and High Power Decoupling

In most polymer samples, the nuclei of interest experience dipolar interactions from nearby NMR-active nuclei. Under such conditions, the observed line-shape results from the sum of all dipolar interactions, often leading to extensive broadening. Dipole-dipole interactions are therefore a major source of line broadening in solids and must be removed if high-resolution spectra are to be obtained.

The field experienced by a nucleus is the sum of the external magnetic field and the local fields from nearby nuclei. The separation between the energy levels due to dipolar couplings depends on both the distance r between the nuclei and the angle θ that the internuclear vector makes with the magnetic field, as expressed in *Equation 2.6*:

$$\Delta E = B_0 \pm \frac{3\mu}{r^3}\left(3\cos^2\theta - 1\right) \qquad \textbf{Equation 2.6}$$

The positive and negative signs arise as the spins generating the local field may be oriented with or against the applied field. The splitting of the signal depends upon the nucleus producing the field, the internuclear separation and the orientation of the internuclear vector with respect to the magnetic field.

As mentioned previously, dipole-dipole interactions are not averaged out in the solid-state and therefore must be removed in order to reduce the extent of line broadening. This can be performed using a heteronuclear decoupling technique provided the observed nucleus is a “dilute spin” i.e. ^{13}C and both nuclei are different (i.e. ^{13}C and ^{1}H). By applying a sufficiently powerful decoupling radiofrequency field at the ^{1}H larmor frequency, rapid transitions occurs between the spin states, resulting in the ^{13}C spins becoming decoupled from the ^{1}H spins. Provided the magnitude of the radiofrequency field is larger than the dipolar coupling, then efficient line narrowing should occur.

2.4.2 Chemical Shift Anisotropy and Magic Angle Spinning

The second major source of line broadening in solid-state NMR spectra is chemical shift anisotropy. When a molecule is placed in uniform magnetic field, the electrons circulate and produce a secondary magnetic field, which contributes to the chemical shift of nuclei in the molecule. The chemical shifts are averaged over the different orientations of the molecule, due to the different magnetic susceptibility of the molecule in different orientations. In solution, these molecular orientations vary rapidly resulting in a chemical shift anisotropy contribution that is averaged to zero. However, in the solid-state, groups of molecules may appear in different, fixed orientations with respect to the applied magnetic field due to a lack of molecular mobility. Therefore the chemical shift anisotropy term is not averaged, resulting in a range of contributions to each different nuclear shift and thus a broad appearance of spectral lines. One means of averaging the chemical shift anisotropy in solids, and thus obtaining high resolution spectra is by MAS.

Any factors that change molecular orientation, including molecular motion, diffusion or rotation will lead to changes in the chemical shifts. Therefore MAS is a method based on rapid spinning of the sample at an angle, θ to the applied magnetic field, resulting in time dependent orientations and thus chemical shifts. Like dipole-dipole interactions, CSA contains an angular dependence of the form ($3\cos^2\theta-1$), where θ is the angle between the magnetic field and the principal axis about which the chemical shift is defined. When $\theta = 54^{\circ}$, $3\cos^2\theta-1 = 0$ and thus all nuclei are contained on a common axis. This angle is known as the “magic-angle” as it is the only angle that results in complete averaging of the chemical shift anisotropy, yielding spectra comparable with those of solutions. The geometry of the sample with respect to the applied field in MAS is illustrated below in *Figure 2.12.*

In order for the MAS experiment to succeed in narrowing the resonance lines, the rotation frequency must be at least the order of the CSA linewidth. If the rate of the sample rotation is fast compared to the CSA linewidth, then a single peak will be observed at the isotropic chemical shift. However, if the spinning speed is slower than the CSA linewidth, then the chemical shift pattern will be broken up into a number of sidebands that are separated from the isotropic shift by the spinning speed. As the spinning speed increases, the isotropic peak increases in intensity, while all of the spinning sidebands become less intense.

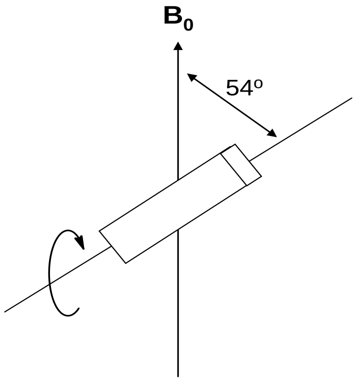


Figure 2.12 Schematic diagram of a sample spinning at the magic angle in an applied field

Spinning sidebands can present problems for high-resolution analysis of polymers as they can often overlap with the NMR peaks of interest. The easiest solution to this problem is to spin the sample fast enough to ensure that the sidebands have negligible intensity. However, it is not always possible to spin the samples fast enough to remove all the effects of CSA spinning sidebands. As the spinning sidebands can easily be identified due to their change in position with different spinning frequencies, it is possible to vary the spinning speed to ensure that the peaks of interest do not overlap with spinning sidebands. Alternatively, the sidebands can be eliminated using a solid-state spectral editing method known as total suppression of sidebands (TOSS). This method involves applying a 180° pulse at specific points during sample rotation, causing destructive interference between sidebands.

It is finally important to note that in most organic molecules, the ^{13}C lines are often too broad to permit only MAS to generate quality spectra. This is due to the limitations in rotation speeds discussed previously. Although MAS can also sharpen dipolar broadened lines, it is most effective to perform both CAS and dipolar broadening to produce spectra comparable to those generated from solution NMR.

2.4.3 Long Relaxation Times and Cross-Polarisation

Long relaxation times are particularly problematic for low sensitivity nuclei such as ^{13}C, resulting in very inefficient normal pulse fourier transform NMR studies. However, a double resonance pulse regime, known as cross-polarisation can overcome this sensitivity difficulty.

The cross-polarisation pulse sequence works by forcing the insensitive nuclei (e.g. ^{13}C) and protons to precess at the same frequency in the rotating frame, even although they differ significantly in frequency. Exchange of polarisation then occurs between the highly polarisable, abundant proton spins and dilute ^{13}C spins, resulting in the overall ^{13}C spectra being enhanced due to the greater sensitivity of protons. Cross-polarisation was first demonstrated in 1962 by Hartmann and Hahn, who illustrated that energy transfer between nuclei with differing Larmor frequencies can occur when nuclei are simultaneously irradiated with identical radiofrequency fields. This can occur for carbon and protons when the Hartmann-Hahn condition, outlined in *Equation 2.7*, is satisfied:

$$\gamma_C B_{1C} = \gamma_H B_{1H} \qquad \textbf{Equation 2.7}$$

When the above expression in *Equation 2.7* holds, the nuclei have the same Larmor frequency in the rotating frame and therefore transfer of energy between the spins may take place. As γ_H is four times γ_c, the strength of the applied carbon field B_{1c} is four times the strength of the applied proton field B_{1H} and thus the enhancement of the ^{13}C spin signal is approximately four times greater.

The protons are initially prepared for cross-polarisation by application of a short 90^o pulse (B_{1H}) which rotates the protons in the x-y plane. The pulse intensity of B_{1H} is then reduced and its phase is changed by 90^o so that the B_{1H} vector lies parallel to the spins. This process effectively locks the spins in the x-y plane i.e. the ^{1}H spins remain in the x-y plane precessing about B_{1H} and is therefore known as the spin locking phase. At the same time, a long 90^o pulse is then applied at the ^{13}C frequency with an amplitude B_{1C}, resulting in both protons and ^{13}C nuclei precessing at the frequency. Energy transfer can then occur and the intensity of the ^{13}C increases to a maximum, enhancing the overall signal strength.

It is important to note that the cross-polarisation technique is only useful for insensitive nuclei in close proximity to protons i.e. it relies on dipolar coupling between the abundant nuclei and thus is potentially selective. Cross-polarisation is also not quantitative and therefore the intensities of the peaks cannot be directly compared.

2.5 References

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3 EXPERIMENTAL

Various polyester chip and film samples have been examined throughout this research programme. Therefore, further details of the samples selected for each of the studies and more detailed experimental conditions can be found in the relevant results and discussion chapters. Details of the general experimental procedures, common to all research studies, are outlined below.

3.1 DSC Analysis

3.1.1 Apparatus

All samples were analysed using a TA Q1000 differential scanning calorimeter capable of analysing samples between –90 ^{o}C and 750 ^{o}C. A RC90 refrigerated cooling system was attached adjacent to the instrument and an autosampler was also used to ensure a high throughput of samples. The instrument was calibrated with a standard of indium and all DSC data processed using TA software.

3.1.2 Sample Preparation

Samples weighing 6 mg were prepared for analysis. Standard aluminium DSC pans were selected only for thin film samples and large hermetic aluminium pans for polyester chip samples to ensure excellent thermal contact with the furnace platform. Based on the sample pan of choice, the appropriate aluminium lid was used in addition to an empty aluminium pan as a reference. All sample pan edges were crimped prior to analysis and when preparing DSC samples for degradation studies, two evenly spaced holes were pierced in the centre of the DSC lid using a pin to ensure both purge gas flow to the sample as well as enabling the release of any volatile materials generated during analysis.

3.1.3 Experimental Conditions

3.1.3.1 Degradation Programme

Dynamic DSC degradation experiments were performed by heating samples from 30 - 550 ^{o}C, at a heating rate of 10 ^{o}C min^{-1}. Analyses were performed either under air (oxidative) or nitrogen (inert) atmospheres with gas flow rates of 60 mL min^{-1}.

All temperature values quoted from the DSC thermograms were rounded to the nearest integral value, with an error of ± 1 ^{o}C.

3.1.3.2 Heat-Cool-Reheat Programme

The effect of previous heat treatments (i.e. thermal history) can significantly affect the DSC response for semi-crystalline materials, often making comparisons difficult unless a similar thermal history has been applied to every sample. Therefore, it is important to destroy the thermal history of the material prior to studying morphological changes and/or changes in the thermal transitions of different polymer samples. The simplest method for achieving this is a heat-cool-reheat DSC method.

The heat-cool-reheat method adopted throughout this research initially involved heating the samples from 25 ^{o}C to 320 ^{o}C, at a rate of 10 ^{o}C min^{-1}, to destroy the thermal history of the sample of interest. The samples were then cooled from 320 ^{o}C to 25 ^{o}C, at a rate of 10 ^{o}C min^{-1}, to impose a known thermal history on all samples prior to a second heating cycle ramping from 25 ^{o}C to 320 ^{o}C, at a rate of 10 ^{o}C min^{-1}. The heat-cool-reheat DSC method was conducted on 6 mg samples under a flow of dry nitrogen (20 mL min^{-1}) to limit thermo-oxidative degradation at high temperatures. All DSC data was processed using TA software and temperature values quoted from the DSC curves rounded to the nearest integral value, with an error of ± 1 ^{o}C.

3.2 Thermal Gravimetric Analysis (TGA)

3.2.1 Apparatus

TGA studies were carried out using a Perkin Elmer Thermogravimetric Analyser (TGA7), controlled using Windows based software on a bench-top PC.

3.2.2 Sample Preparation

All experiments were carried out using 10 mg of sample.

3.2.3 Experimental Conditions

3.2.3.1 Degradation Programme

Prior to analysis, the TGA system was purged with the atmosphere of interest (i.e. helium for inert studies and air for oxidative studies) and a 5 minute isothermal hold was performed at 50 ^{o}C. A heating profile from 50 ^{o}C to 800 ^{o}C was then generated at a heating rate of 10 ^{o}C min^{-1} under a thermal or thermo-oxidative environment. From the data obtained, the % mass loss was recorded as a function of temperature and the onset temperatures of degradation were determined at 5% mass loss. All data was processed using Origin software and the temperature values quoted from the TGA curves rounded to the nearest integral value, with an error of ± 1 ^{o}C.

3.3 Thermal Volatilisation Analysis (TVA)

3.3.1 Apparatus

All TVA studies performed throughout this research programme were carried out using a TVA line, specifically designed and built in-house for degradation studies. The apparatus and techniques are based on those described in *Section 2.1.3*.

3.3.2 Sample Preparation

The preferred sample type for TVA analysis was thin film samples cast from solution. Due to both the size and shape of standard polyester chip, degradation reactions can often be limited by diffusion due to the increased path length by which volatiles must escape. This can often result in increased condensed phase chemistry as volatile degradation products remain trapped within the polyester chip. Therefore standard polyester chip samples were preferably dissolved in solvent and cast from solution, prior to TVA analysis, to minimise the effects of diffusion limited reactions.

50 mg of polyester chip was found to be the optimum sample mass to achieve the desired quality of gas-phase IR spectra, GC-MS chromatographs and resolution of TVA chromatograms. After accurate weighing, the selected polyester chip sample was dissolved in 1 mL of HFIP for a minimum of twelve hours. Upon dissolution, the sample solution was then transferred to a TVA tube and the solvent left to evaporate in standard laboratory conditions for a period of 24 hours. Finally, prior to analysis, the sample tube was placed in a vacuum oven for 4 hours at 10 ^{o}C above the polymer's T_g to remove as much solvent as possible. Despite extensive drying, a considerable volume of solvent still remained trapped within the polyester matrix and could not be completely removed until temperatures of approximately 135 ^{o}C were achieved during TVA analysis. All solvent was completely removed as furnace temperatures approached 300 ^{o}C. *Figure 3.1* illustrates the total solvent and non-condensable volatiles collected for a thin solvent cast film sample of PEN. Due to the lack of degradation activity within the solvent evaporation regime of 135 ^{o}C to 300 ^{o}C, all TVA curves presented throughout this report illustrate the degradation sections of each TVA curve only to avoid repetition. A MS of the volatile solvent being extracted using TVA is also illustrated in *Figure 3.2*.

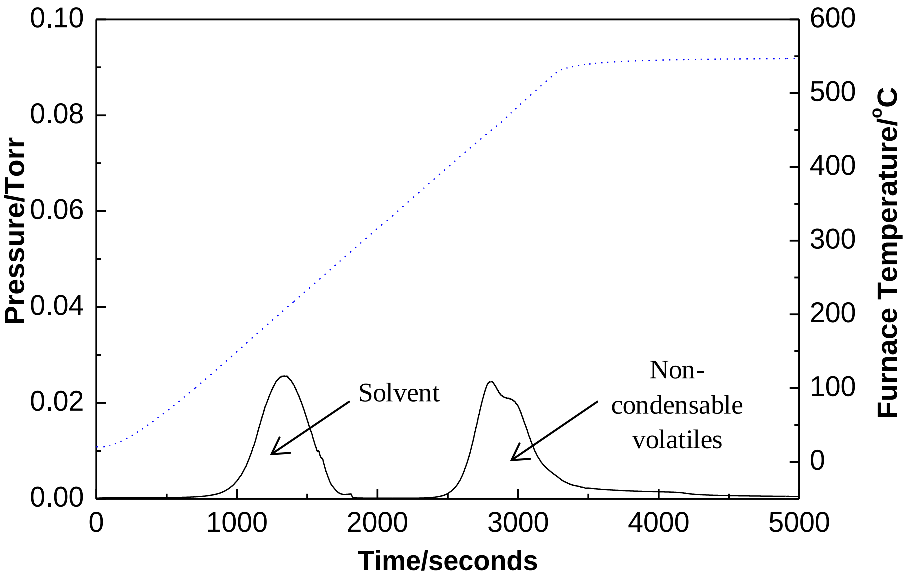


Figure 3.1 Typical TVA curve of PEN illustrating solvent and non-condensable volatiles, furnace temperature illustrated in blue

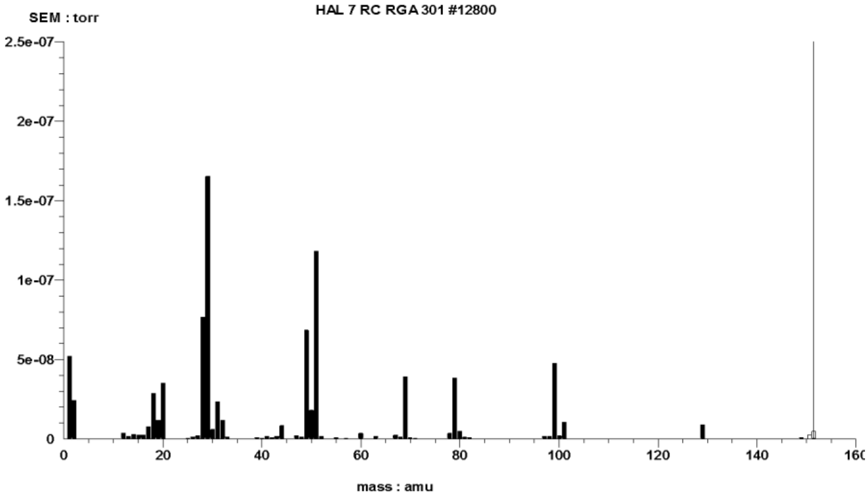


Figure 3.2 Typical MS of HFIP solvent generated during TVA degradation analysis of PEN

3.3.3 Experimental Conditions

Prior to analysis, the polymer of interest was placed in a degradation tube and the entire TVA system was left to pump down to vacuum (approximately 6 x 10^{-3} Torr) overnight. This procedure was performed in order to reduce the background level of water and CO_2 within the apparatus.

3.3.3.1 Dynamic Degradation Programme

A dynamic heating programme was applied to heat the sample of interest to 550 ^{o}C at a rate of 10 ^{o}C min^{-1}. The sample was then isothermally held at 550 ^{o}C for a period of 30 minutes as the pressure was recorded at the cold trap to monitor continual cryogenic trapping of the evolved volatiles. Following the collection of volatile materials within the liquid nitrogen cooled primary trap, the sub-ambient distillation was then performed. This involved reheating the primary sub-ambient trap at a rate of 4 ^{o}C min^{-1} from –196 ^{o}C to 40 ^{o}C. The separated volatiles were subsequently analysed by a combination of MS, FTIR spectroscopy and GC-MS as outlined in *Sections 3.3.3.3 to 3.3.3.5.*

3.3.3.2 Isothermal Degradation Programme

In an attempt to investigate the degradation chemistry of polyesters at typical processing temperatures, isothermal TVA experiments were conducted by heating the sample of interest to the target temperature followed by an isothermal hold for a period of 60 minutes. The target temperatures of interest were 288, 300 and 320 ^{o}C. Sample size remained at 50 mg to ensure volatile species could be detected with the low degradation temperatures selected.

3.3.3.3 Mass Spectrometry

MS analysis was performed using an online 1 - 300 amu Hiden single quadrupole RGA mass spectrometer operated in continual scan mode. During TVA degradation, the instrument enabled online identification of both non-condensable and condensable volatile materials of a low molecular mass.

3.3.3.4 FTIR Spectroscopy

FTIR analyses were performed using a Perkin Elmer Spectrum 100 FTIR Spectrometer in transmission mode. The instrument was programmed to perform

32 scans over a wavenumber range of 4000 - 500 cm^{-1}. Prior to analysis a background scan was performed with no cell in the sample area. Data was collected as a plot of % transmission against wavenumber.

The low boiling volatile species collected from TVA were directly analysed in the gas-phase using the gas-phase IR cells outlined in *Section 2.1.3.2*. The gas-phase cells were directly placed in the optical path of the IR spectrometer, allowing the gas contained within the cells to be analysed. The cold-ring fractions collected from TVA were dissolved in chloroform and then filtered using a syringe filter. The samples were then cast onto NaCl discs for analysis.

3.3.3.5 GC-MS

All GC-MS measurements were carried out using a Finnigan Thermoquest capillary column trace GC and Finnigan Polaris Quadrupole Mass Spectrometer. The capillary column consisted of a fused silica column with a silicone oil stationary phase and was programmed to perform a temperature ramp from 40 to 320 ^{o}C at a rate of 20 $^{o}C\ min^{-1}$. The carrier gas used was helium and the mass spectra were obtained over a m/z range of 30 - 600.

All cold-ring fractions analysed by GC-MS were dissolved in chloroform and filtered using a syringe filter. These samples were then further diluted with chloroform prior to analysis. Any high boiling fractions collected from TVA were also initially dissolved in chloroform, however these fractions were treated as more dilute solutions and were not further diluted prior to GC-MS analysis. All solvents used throughout this research were obtained from Sigma-Aldrich Chemical Company.

In addition to GC-MS analysis of the samples of interest, analysis was performed on solvent blanks to examine the background spectra obtained as a result of column contamination and impurities e.g. phthalates and/or plasticisers. *Figure 3.3* illustrates an example of a GC trace obtained on analysing $CHCl_3$ and *Figure 3.4* presents the compounds identified from the GC-MS analysis of solvent only.

Fortunately, computer background correction enables the removal of background ions from the analyte spectrum and was applied to all spectra when analysing samples. This reduced the risk of misinterpretation and cross-contamination when attempting to identify degradation analytes.

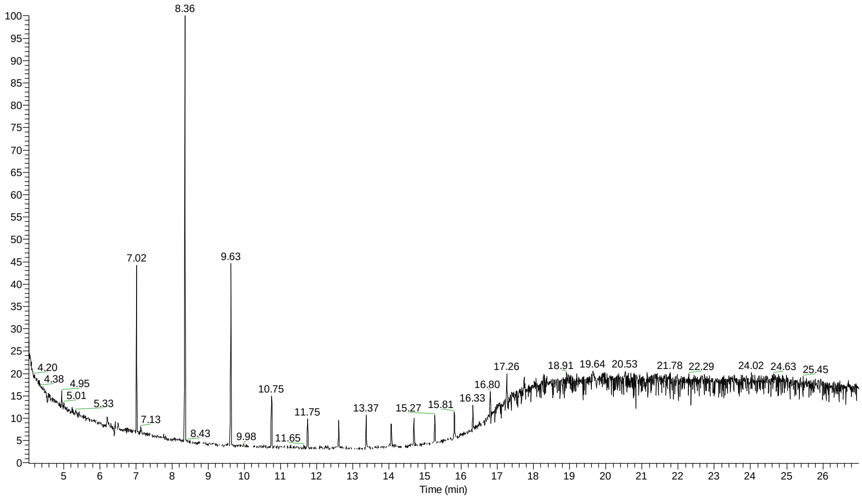
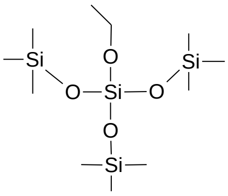
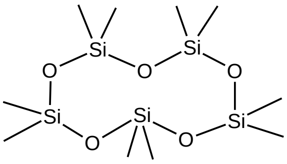


Figure 3.3 Typical GC trace of $CHCl_3$



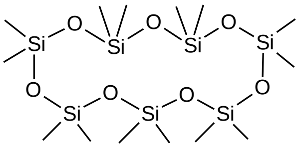
3-Ethoxy-1,1,1,5,5,5-hexamethyl-3-(trimethylsiloxy)trisiloxane

Retention time – 7.02



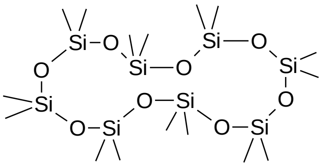
Decamethylcyclopenta-siloxane

Retention times – 8.36, 9.63



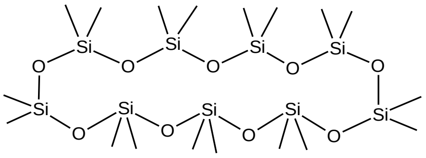
Tetradecamethylcycloheptasiloxane

Retention time – 10.75



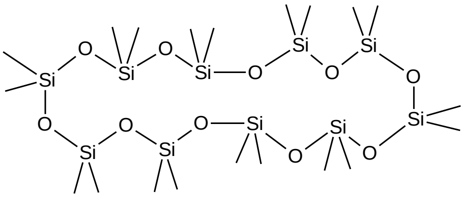
Hexadecamethyl-cyclooctasiloxane

Retention time – 11.75



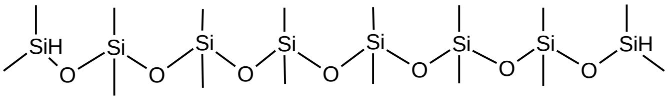
Octadecamethylcyclononasiloxane

Retention time – 12.61



Eicosamethylcyclodecasiloxane

Retention times – 13.37, 14.06, 14.69,15.27



Hexadecamethyloctasiloxane

Retention times – 15.81, 16.33, 16.80, 17.26

Figure 3.4 Typical column analytes detected from GC-MS trace of $CHCl_3$

3.3.4 TVA Tube Calibrations

Historical TVA studies have monitored furnace temperature by use of an external thermocouple placed directly in contact with the outside base of the TVA sample tube. However, it is believed that a significant temperature differential can exist between the outside base and inside base of the sample tube due to the insulating effect of borosilicate glass. This is thought to result in lower temperature readings by the external thermocouple than observed if monitoring sample temperature on the inside of the sample tube. Ideally, the sample temperatures should be measured by the use of a permanent thermocouple positioned directly in contact with the sample; however this can be problematic and result in air leaks within the high vacuum system in addition to sample contamination. Therefore, a method was developed by which the sample temperature could be measured with increased accuracy by a series of internal tube calibrations. This was achieved by permanently placing a K-type thermocouple into a modified TVA tube head, as illustrated in *Figure 3.5*, for the series of internal tube calibrations. A temperature calibration curve could then be devised from these studies to enable the sample temperature to be deduced from the temperature measurement recorded on the outside of the sample tube.

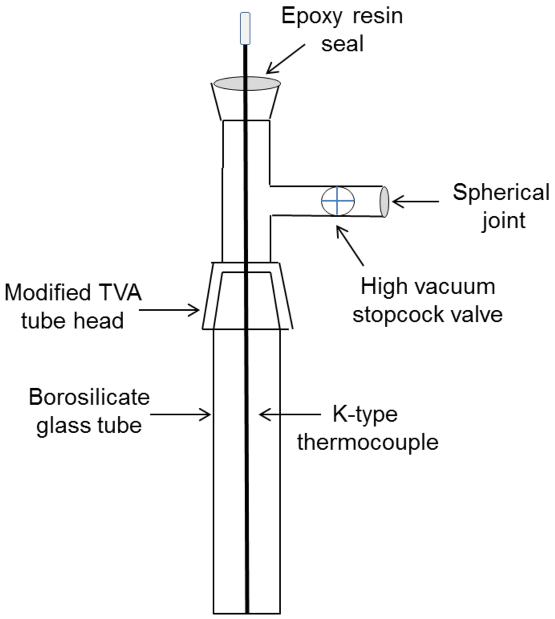


Figure 3.5 Modified TVA apparatus used for internal tube temperature calibrations

The K-type thermocouple, used in the apparatus outlined in *Figure 3.5*, was carefully positioned to ensure direct contact was established with the centre base of the sample tube. The TVA system could then be pumped to high vacuum followed by heating the sample of interest from room temperature to the target temperature at a rate of 10 ^{o}C min^{-1}. Throughout the thermal programme, measurements from both the external furnace and internal sample thermocouples were monitored to produce a calibration curve, typical to that illustrated in *Figure 3.6*. This process was repeated for each sample tube utilised throughout all TVA studies, enabling the internal sample temperature to be deduced for any furnace temperature recorded by use of the appropriate calibration curve.

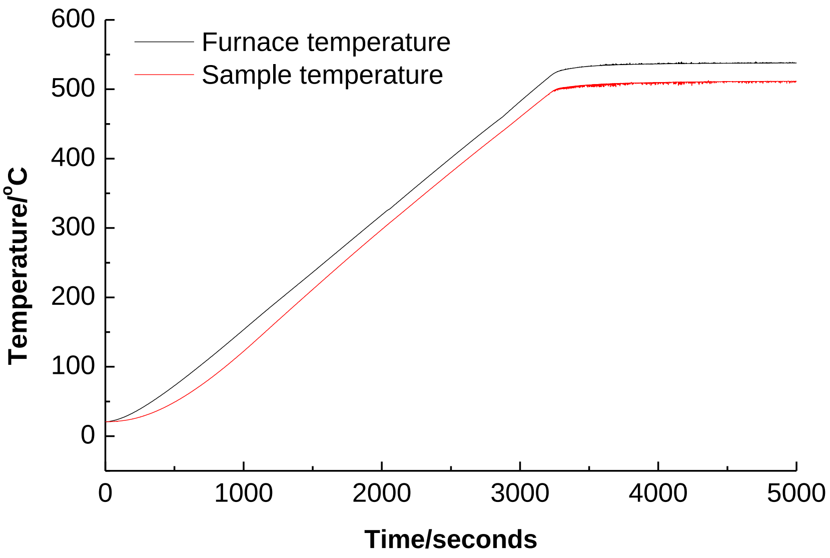


Figure 3.6 Typical TVA tube calibration curve

Throughout this report, all TVA curves are presented as pressure versus furnace temperature. An accompanying table is then presented to represent both the external furnace temperature and internal sample temperature. The error for the TVA temperature measurements has been calculated as ± 3 ^{o}C and takes into account both the sample reproducibility and tube calibrations. Both temperatures for the onset of volatile evolution and maximum peak of volatile evolution are reported for each sample. The onset of volatile evolution can be defined as the temperature at which the pressure increases by 5×10^{-4} Torr from the initial baseline pressure.

3.3.5 TVA Reproducibility Studies

The casting of thin films from polyester solutions can be problematic as the polyester must be fully dissolved and transferred into the analysis tube. Therefore, it was essential to ensure that the method developed for TVA analysis was reproducible. Reproducibility of the TVA method was examined by performing three repeat runs on 50 mg polyester samples dissolved in 1 mL of HFIP for a minimum of 24 hours. *Figures 3.7* and *3.8* illustrate the degradation profile and sub-ambient distillation profiles, respectively, for each of the repeat runs.

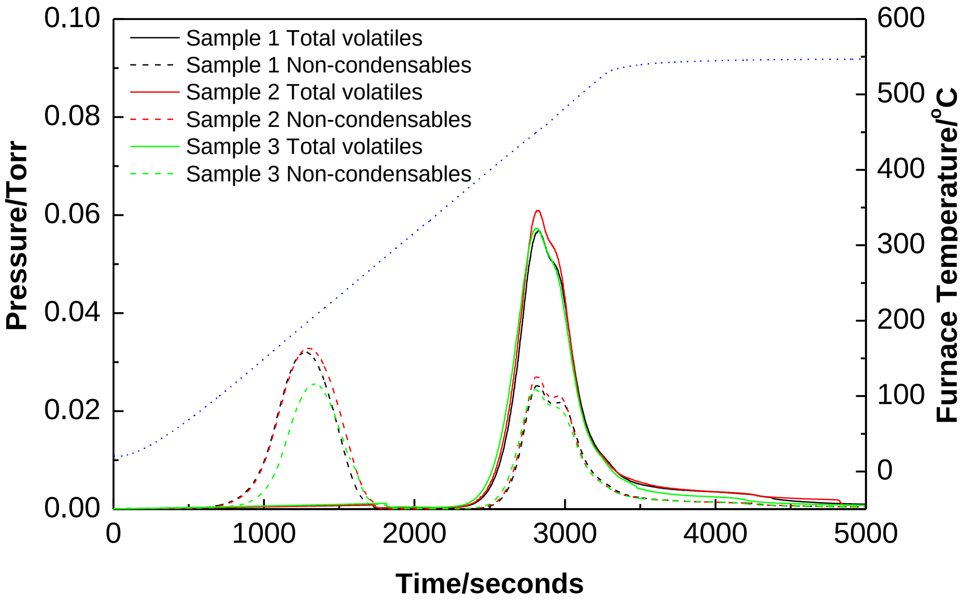


Figure 3.7 TVA degradation curves of PEN showing the rate of volatile evolution as a function of pressure vs. time, furnace temperature illustrated in blue

Figure 3.7 illustrates two separate events; firstly HFIP solvent evolution occurs within the first 2000 seconds followed by degradation of PEN from 2000 seconds onwards. The degradation of PEN can be seen to be very reproducible between samples, despite minor differences in the solvent evolution traces from each sample as expected. Similarly, the levels of reproducibility within the sub-ambient distillation traces of PEN, illustrated in *Figure 3.8*, were also excellent. Identical component peaks can be observed in all three samples, highlighting the excellent reproducibility of the sub-ambient distillation process with only small variation observed in the levels of each volatile species. The TVA technique can therefore yield reproducible results for the analysis of thin polyester films.

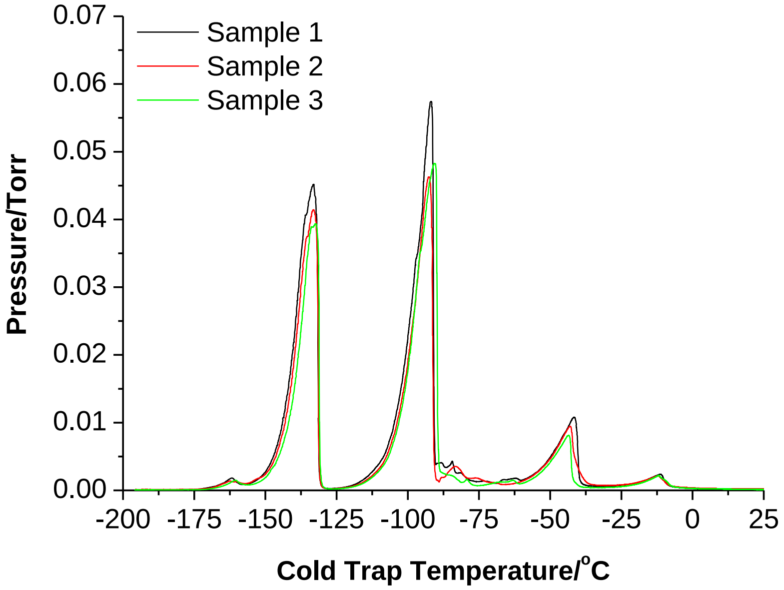


Figure 3.8 TVA sub-ambient differential distillation curves of PEN

3.4 Gel Permeation Chromatography

All practical GPC work was kindly undertaken by Smithers Rapra based in Shrewsbury, UK.

3.4.1 Apparatus

The molar mass and molar mass distribution of the polyester samples were determined on a Viscotek TDA model 301 GPC, equipped with PL HFIP gel guard columns and a refractive index detector.

3.4.2 Sample Preparation

Duplicate solutions of each sample were prepared by adding 10 mL of solvent to 20 mg of polymer and leaving overnight to dissolve. The solutions were thoroughly mixed and filtered through a 0.45 μm poly(tetrafluoroethylene) (PTFE) filter prior to analysis.

3.4.3 Experimental Conditions

Measurements were carried out at 40 ^{o}C, using HFIP with 25 mM sodium trifluoroacetate (NaTFAc) as the eluent, at a rate of 0.8 mL min^{-1}. The GPC system was calibrated using poly(methylmethacrylate) (PMMA), therefore results are expressed as 'PMMA equivalent' molar masses. Data was collected and analysed using Polymer Laboratories 'Cirrus' software. For all samples, integration limits were selected to exclude any material with a PMMA equivalent molar mass of less than 400 g mol^{-1}. The results are summarised as the calculated molar mass averages and polydispersities (M_w/M_n) and the graphs are all plotted to the same area, the y-axis being a function of mass fraction.

3.5 High - Temperature Melt Rheology

3.5.1 Apparatus

All materials were characterised using a Rheometrics rotational rheometer, in dynamic oscillation mode, at Wilton Research Centre by Intertek Measurement Science Group. The instrument was fitted with parallel plates with a diameter of 25 mm.

3.5.2 Sample Preparation

All samples analysed were dried under vacuum at room temperature to remove any surface water prior to analysis.

3.5.3 Experimental Conditions

Polyester samples were placed in the rheometer between two 25 mm diameter parallel plates and heated to the required measurement temperature. Any residual material at the edges was removed prior to commencing measurements.

The rheometer was operated in two different modes; time sweep and temperature sweep modes. For temperature sweep measurements, PET was heated from 250 to 390 °C at a ramp rate of 10 °C min^{-1}, whilst PEN was heated from 270 to 390 °C at an identical ramp rate. The stacked film samples were then squeezed to remove any voids until a gap of 0.5 - 1.0 mm was achieved. All temperature sweep studies were performed at a constant oscillation frequency of 10 rad s^{-1} and a constant amplitude strain of 25%, under N_2 and air atmospheres. Similarly, for time sweep measurements, identical strain and oscillation frequencies were applied, but the temperature remained constant.

Measurements were made on both PET and PEN at typical processing temperatures under nitrogen and air atmospheres for a period of 60 minutes. From the measured torque response, the phase storage modulus, G' (elastic component), out of phase loss modulus, G" (viscous component) and complex viscosity, ETA* were calculated.

3.6 ^{13}C Solid-State NMR Spectroscopy

All ^{13}C solid-state NMR analysis was kindly undertaken by Dr David Apperley of the Solid-State NMR Research Group at Durham University.

3.6.1 Apparatus

All ^{13}C NMR spectra were obtained using a Varian VNMRS spectrometer, operating at 100.56 MHz with a 6 mm (rotor outer diameter) magic angle spinning probe. An external sample of neat tetramethylsilane (TMS) was employed as the spectral reference.

3.6.2 Sample Preparation

Polyester residues were cut into thin strips or small squares to enable them to be placed inside the rotor. No sample pre-treatment was required and approximately 50 mg of sample was sufficient to perform the measurements.

3.6.3 Experimental Conditions

All ^{13}C NMR spectra were obtained using cross-polarisation with a 6 mm magic angle spinning probe. The average acquisition time was 30 - 40 milliseconds with an overall spectral width of 40322.6 Hz. Each sample was mounted into the rotor of a small air driven turbine whose axis was inclined at the magic angle of 54° to the magnetic field direction. 6mm rotors used in this research could accommodate up to 0.2 g of sample, providing good sensitivity for insensitive ^{13}C nuclei. Maximum rotor spinning rates of 6800 Hz were applied, however these spinning rates were not high enough to completely eliminate spinning sidebands. Therefore, a TOSS spinning sideband suppression pulse sequence was applied in an attempt to remove these signals. It is finally important to note that all ^{13}C NMR spectra were obtained at room temperature.

3.7 Quantification of Carboxyl End Groups in Polyesters

Rapid determination of the carboxyl end group (CEG) concentration was performed on selected polyester residues after ageing to examine the extent of degradation. The titration technique adopted was the method used by Pohl [1] to determine the carboxyl end group concentration in solution. Polyester samples were dissolved in hot benzyl alcohol, diluted with chloroform, and titrated with a sodium hydroxide solution in benzyl alcohol.

3.7.1 Apparatus

The apparatus consisted of a thermostatically controlled block heater capable of reaching temperatures of 300 ^{o}C ± 1 ^{o}C.

3.7.2 Sample Preparation

Polyester residue:

0.1 g of polyester film was dried and finely chopped into small pieces prior to analysis.

Preparation of benzyl alcohol:

Benzyl alcohol was dried prior to analysis using 0.4 nm molecular sieve pellets. This reduced the risk of hydrolytic degradation occurring at high temperatures during dissolution of the polyester film. 10 g of molecular sieves per 100 mL of benzyl alcohol were pre-dried in a fan-assisted air oven at 200 ^{o}C for 30 minutes prior to use.

Preparation of phenol red indicator:

Phenyl red indicator was prepared as a neutral solution of 0.1% in ethanol.

Preparation of 0.1N sodium hydroxide solution in benzyl alcohol:

0.41 g NaOH pellets were initially added to 0.4 mL H_2O to form a paste. This paste was then rinsed into a 100 mL volumetric flask using 10 mL of methanol and then diluted with benzyl alcohol to 100 mL. After mixing thoroughly, the exact concentration of the NaOH solution was determined by titration using standard hydrochloric acid and two drops of phenol red indicator.

3.7.3 Experimental Conditions

The titration procedure was performed as follows: 1 g of polyester film was initially added to 5 mL of pre-dried benzyl alcohol preheated to 215 ^{o}C ± 1 ^{o}C. After addition of the polyester film, the solution was maintained at 215 ^{o}C and continuously stirred for 108 seconds. The glass tube containing the sample was then immediately immersed into a beaker containing cold water for 6 seconds to subsequently quench the sample. Upon quenching, the sample solution was added to 10 mL of chloroform, creating a clear meta-stable polymer solution, capable of reacting rapidly and quantitatively with base and indicator. Before proceeding with the titration, an additional 5 mL rinsing of hot benzyl alcohol was added to the empty sample tube to wash off any gels remaining on the walls of the tube. This sample solution was once again heated at 215 ^{o}C ± 1 ^{o}C for 1 minute before carefully combining with the remainder of the sample. In preparation for titration, 150 μL of phenol red indicator was added to the sample solution using a 50 - 200 μL micropipette and a magnetic stirrer bar utilised to enable thorough mixture during titrations.

On completion of the sample preparation, the titration was performed by gradual addition of 2 μL aliquots of 0.1N sodium hydroxide solution in benzyl alcohol to the sample solution using a micro syringe. This was continued until the first discernible pink colour persisted for a period of 10 seconds. A blank titration was also performed on the benzyl alcohol-chloroform mixture to calculate the correction factor described below. As the alcohol itself may be acidic, it is important to perform a blank titration to calculate the volume of base required to neutralise any acid that may be present.

3.7.4 Calculations

The concentration of carboxyl end groups was calculated by the formula given in *Equation 3.1.* [2,3]

$$[COOH] = \left(\frac{(V_t - V_0) \times 10^6 \times C_{tir}}{m} \right) - [COOH]_{CORR} \qquad \textbf{Equation 3.1}$$

Where *[COOH]* is the amount of carboxyl end groups (Meq/kg), V_0 is volume of NaOH titre consumed (μL) for a blank run of heated benzyl alcohol with chloroform,

V_t is the total volume of titre for the sample titration (µL), C_{tir} is the molar concentration of NaOH, m is the mass of polyester sample (g) and $[COOH]_{CORR}$ is the correction factor. The results are expressed in equivalents per 10^6 grams with standard correction of 1.6 equivalents per 10^6 grams to account for degradation and thus formation of carboxyl groups during dissolution at high temperature.

3.8 Gel Quantification in Polyesters

Gel quantification studies were performed on PET and PEN samples using a method similar to that described in the international standard procedures. [4,5,6] Gel content can be defined as the percentage by mass of polymer insoluble in a specified solvent after extraction under specified conditions. As discussed previously in *Section 1.3.2*, the solubility of polyesters in HFIP can provide an indication of the presence of gels and thus cross-linked material within a sample.

3.8.1 Sample Preparation

All gel quantification studies were performed using 0.2 g of polyester residue.

3.8.2 Experimental Conditions

Specimens of aged polyester films were weighed out accurately and immersed in 10 mL of the extracting solvent mixture, at room temperature for a period of 48 hours. The chosen solvent system was a 50:50 v/v% mixture of HFIP and chloroform. After extraction, the samples were filtered through a buchner vacuum and the gel specimens collected and dried on Fisherbrand QL100 filter paper. To ensure all solvent was removed from each gel residue prior to weighing for quantification, the samples were all dried in a vacuum oven 10 ^{o}C above their T_g for a minimum of 4 hours. This drying temperature was selected to increase the mobility of the polymer chains subsequently enabling easier removal of solvent. After drying, samples were accurately reweighed to quantify the gel material extracted. Blank and solvent controls were also performed alongside each sample set to ensure no degradation of the filter system was occurring due to high drying temperatures or exposure to solvent.

3.8.3 Calculations

The % gel content within aged polyester films was calculated using the following equations:

$$\begin{array}{c}\textit{\% Gel content}\\ \textit{(residual)}\end{array} = \left({W_r}/{W_f} \right) \times 100 \qquad \textbf{Equation 3.2}$$

$$\begin{array}{c}\textit{\% Gel content}\\ \textit{(original)}\end{array} = \left(\frac{\left({W_r}/{W_f} \right) \times W_a}{W_0} \right) \times 100 \qquad \textbf{Equation 3.3}$$

Where W_0 is the original mass of the specimen being studied prior to ageing, W_a is the mass of the residue remaining after ageing, W_f is the original mass of the polyester residue before gel extraction and W_r is the mass of the dried gel sample after extraction. It is equally important to calculate the gel content using both *Equations 3.2* and *3.3* as the former expresses the gel content as a % of the starting residual mass of polyester sample, in contrast to the latter which expresses the gel content as a % of the original sample mass prior to ageing.

This method for the quantification of gel content has proven only to be suitable for materials with gel content greater than 5%. If the method is not carefully performed, the PET can crash out of solution and will not filter, thus resulting in false, increased gel content figures.

3.9 References

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[4] ASTM D 2765-01, ASTM International, West Conshohocken, PA, **2006**.

[5] ASTM D 7567-09, ASTM International, West Conshohocken, PA, **2009**.

[6] ISO 10147:2004, International Organisation for Standardisation: Geneva, Switzerland, **2004**.

4 FUNDAMENTAL DEGRADATION STUDIES OF PET AND PEN

4.1 Background to Research

Basic degradation studies were performed on PET and PEN in an attempt to compare the fundamental degradation pathways of both polyesters, under different environmental and temperature regimes. To enable the degradation properties of PET and PEN to be directly compared, both PET and PEN polyester chip analysed throughout this study had not experienced any further drying or processing treatment. Both polymers were extracted directly after melt polymerisation, prior to crystallisation and solid-state polymerisation treatment.

4.2 Experimental Details

4.2.1 Materials

The PET and PEN polyester samples analysed throughout this study were obtained from DuPont Teijin Films as polymer chip. Transparent polyester chip samples of PET (IV = 0.615) were obtained from the direct esterification reaction of EG and TA, followed by the polycondensation reaction of BHET (as outlined in *Sections 1.1.1.3 and 1.1.1.4*). The polycondensation catalyst mixture was based on Sb_2O_3 and GeO_2. PEN polyester chip (IV = 0.50) was synthesised via the transesterification reaction of NDC and EG followed by the polycondensation reaction of BHEN. The catalysts used in the transesterification and polycondensation reactions to produce PEN were $Mn(OAc)_2$ and Sb_2O_3, respectively. Phosphoric acid stabiliser and a colour adjusting reagent, $Co(OAc)_2$ were also added during the polymerisation reaction of PEN.

4.3 Results and Discussion

4.3.1 Thermal Properties of PET and PEN

To characterise the thermal transitions in both polyesters, heat-cool-reheat DSC experiments were performed. A known thermal history was imposed on PET and PEN to identify any differences in their morphology and/or thermal transitions. *Figures 4.1* and *4.2* illustrate the second DSC heating cycle of PET and PEN (cycle 3). The DSC thermograms for the first heating cycle (cycle 1) and cooling cycle (cycle 2) for both materials, can be viewed in *Chapter 8 Supplementary Material*.

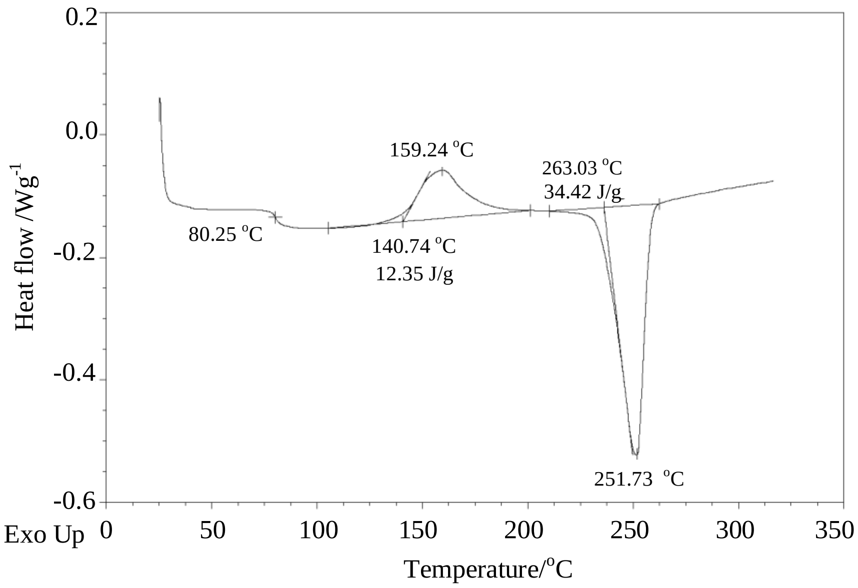

Figure 4.1 DSC of PET in N_2, heat-cool-reheat programme, cycle 3

From *Figures 4.1* and *4.2,* it can be observed that the T_g of PET and PEN are 80 °C and 122 °C, respectively. This significant difference in the T_g of PET and PEN can be attributed to the presence of rigid naphthalene groups in PEN, in contrast to phenyl groups in PET. The presence of bulky, sterically hindered naphthalene groups in PEN results in increased rigidity within the polymer backbone, generating the need for increased thermal energy to enable chains to move more freely.

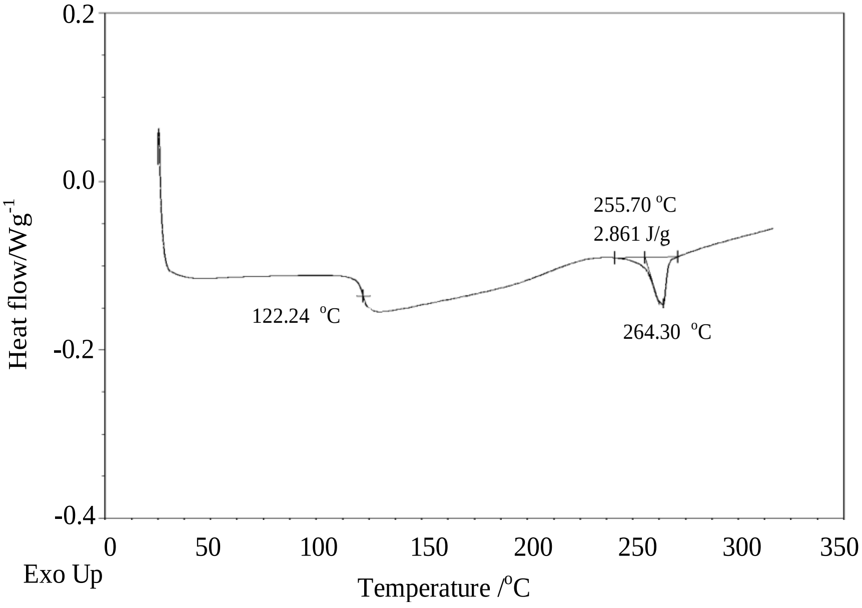

Figure 4.2 DSC of PEN in N_2, heat-cool-reheat programme, cycle 3

The overall crystallisation behaviour of PET and PEN also differs. The onset and peak maximum temperature for crystallisation (T_c) of PET can be observed at 141 °C and 159 °C respectively, with an overall crystallisation enthalpy of 12 J g^{-1}. However, the crystallisation process for PEN is more complex. The enthalpy, onset and peak maximum temperatures of crystallisation are very difficult to define due to the very slow nature of the PEN crystallisation process. From approximately 140 °C to the crystalline melt temperature, crystallisation of PEN is occurring, with most significant crystallisation occurring between 180 °C and 220 °C. These differences in the rates of crystallisation between PET and PEN can once again be attributed to the presence of naphthalene groups in PEN. The ease at which PEN can arrange its polymer chains into regular domains is reduced due to the presence of the bulky naphthalene rings. Additionally, the non-linear 2,6-substitution pattern of aromatic rings in PEN, compared to a 1,4 linear substitution of the phenyl group in PET, reduces its tendency to crystallise.

The reduced extent to which PEN crystallises, in comparison to PET, is also evident in the crystalline melt peaks illustrated in *Figures 4.1* and *4.2*. The enthalpy of the crystalline melt peak for PET and PEN are 34 J g^{-1} and 3 J g^{-1}, respectively. This reduction in the enthalpy of the crystalline melt peak of PEN is due to the low levels of crystallinity. PEN melts at approximately 264 °C in comparison to 252 °C for PET and the onset temperatures of the crystalline melt peaks in PET and PEN are shown to be 236 °C and 256 °C, respectively. The presence of additional, sterically hindered phenyl rings in PEN therefore results in a higher onset and crystalline melt temperature due to increased rigidity in the polymer backbone. Due to the presence of one crystallisation peak and one crystalline melt peak, only one crystalline form is thought to exist in both PET and PEN.

4.3.2 Thermal Degradation Studies of PET and PEN

Thermal degradation studies on PET and PEN were conducted in an oxygen-free nitrogen atmosphere. This enabled an insight into the thermal processes occurring in the absence of oxygen.

4.3.2.1 Dynamic DSC Results

Figures 4.3 and *4.4* illustrate the DSC thermograms obtained for the degradation of PET and PEN. Endothermic melting and degradation peaks can be observed in both DSC profiles, with the degradation processes being endothermic under nitrogen. The spikes on both thermograms around the degradation region (typically above 400 °C) are linked to the evolution of volatile species from the degrading sample, leading to sudden changes in heat flow.

Serious endothermic degradation of PET is seen to occur from approximately 385 °C onwards, where the major endothermic peak is observed. The minimum heat flow, corresponding to this one major degradation event, can be observed at 441 °C. Similarly, serious endothermic degradation of PEN begins around 384 °C and the minimum heat flow, corresponding to this endothermic degradation event can be observed at 446 °C.

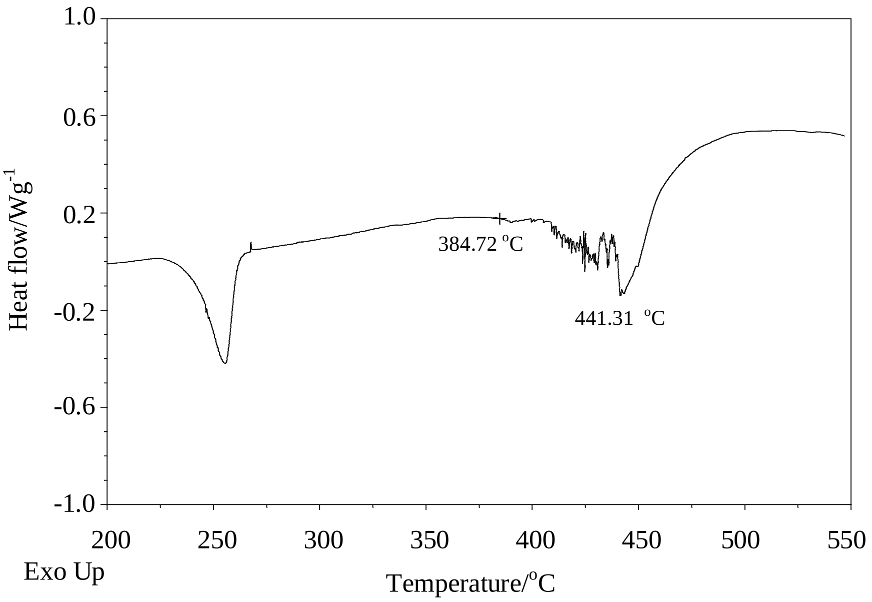

Figure 4.3 DSC of PET in N_2, 30 - 550 °C, 10 °C min^{-1}

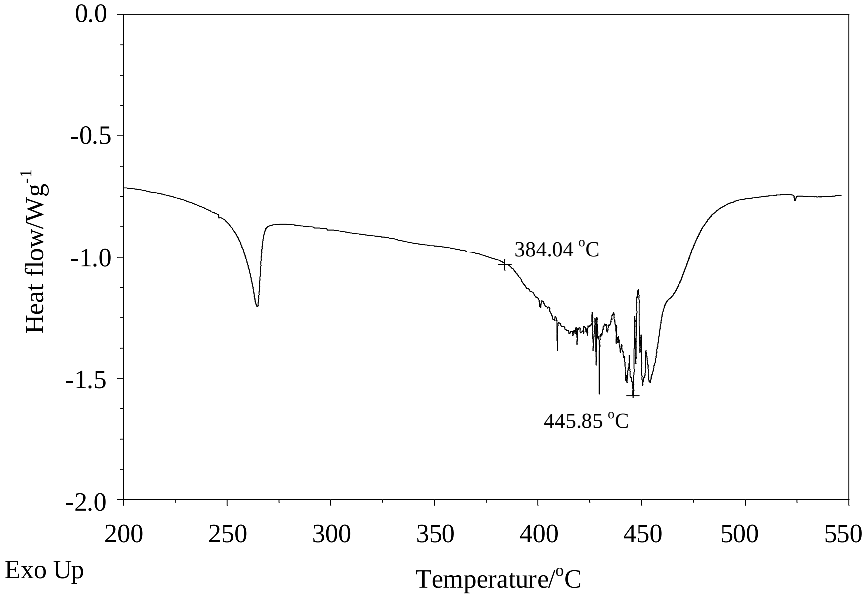

Figure 4.4 DSC of PEN in N_2, 30 - 550 °C, 10 °C min^{-1}

4.3.2.2 Dynamic TGA Results

The thermogravimetry and differential thermogravimetry curves for the non-oxidative degradation of PET and PEN are shown in *Figure 4.5*. Comparison of the TGA traces reveal only small differences in the mass loss behaviour of PET and PEN.

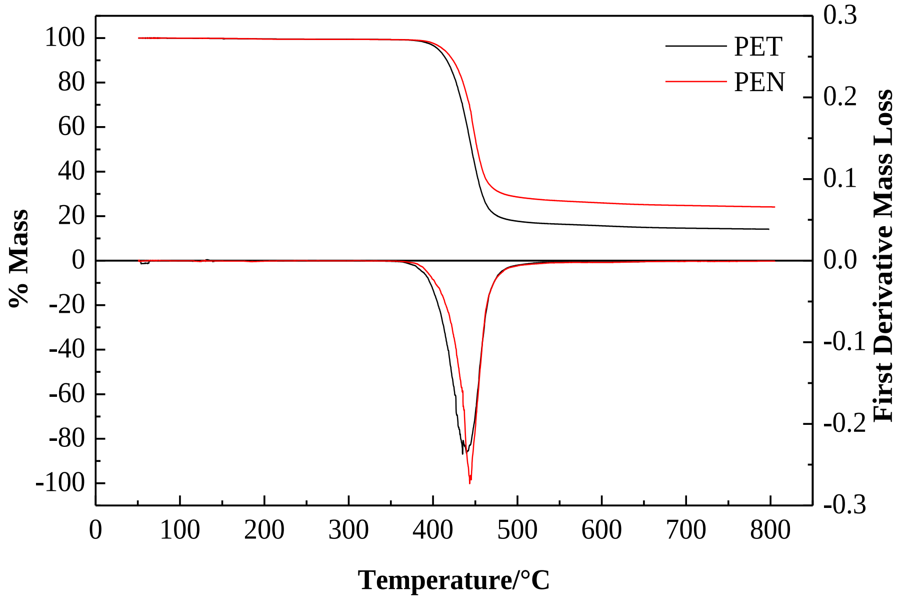

Figure 4.5 Thermogravimetry and differential thermogravimetry curves of PET and PEN in helium, 30 - 800 °C, 10 °C min^{-1}

Both PET and PEN appear to undergo only one significant mass loss step in an inert environment. However, the temperature at which this mass loss step occurs differs between both polymers. In PET, significant mass loss (i.e. 5% mass loss) is not evident until 406 °C. Above this temperature, one significant mass loss event occurs stretching to approximately 520 °C. As seen in the differential thermogravimetry curve, the maximum rate of mass loss for PET is observed at 441 °C. This maximum mass loss is thought to be due to thermal degradation of the polymer backbone i.e. chain scission of the ester bonds. Finally, at temperatures above 520 °C, the thermogravimetric curve of PET indicates a slow continuous mass loss up to 800 °C. 14% of the original mass of PET was found to remain after TG analysis.

In contrast to PET, a delay in the initial release of volatiles can be observed for PEN. Significant mass loss of PEN is not evident until 412 ^{o}C. This is thought to be a result of the enhanced delocalisation of charge across the naphthalene ring units in PEN, increasing the stability of the ester linkages and thus the overall thermal stability of the polymer. The major mass loss event in PEN occurs between 412 ^{o}C and 520 ^{o}C and the maximum rate of mass loss from the differential thermogravimetry curve can be observed at 443 ^{o}C. Slow, continuous mass loss of PEN then proceeds from 520 ^{o}C up to 800 ^{o}C, yielding a final residue of 24%.

Finally, it is noteworthy that the overall % mass of carbonaceous residue remaining from the degradation of PEN is significantly increased in comparison to PET. This is not entirely surprising as the majority of the carbonaceous residue originates from graphitisation of aromatic sequences. The overall % mass fraction of aromatic sequences present in the repeat units of PET and PEN are 41% and 52% respectively. This higher % mass fraction of aromatic sequences in PEN therefore results in an increase in the overall carbonaceous residue remaining after TG analyses.

The above DSC and TGA results presented in *Figures 4.1 – 4.5* appear to correlate well. Both techniques indicate that PET and PEN undergo only one major thermal degradation process, with maximum degradation activity occurring above 440 ^{o}C for both PET and PEN. This degradation activity, resulting in one major mass loss process, can be associated with the principal primary thermal degradation reaction illustrated previously for PET in *Figure 1.23*. This reaction involves the thermal cleavage of ester bonds in the polymer chains resulting in the formation of vinyl ester and carboxylic acid end groups. The variations observed in the transition and degradation temperatures also highlight differences in the morphology and thermal stability between PET and PEN. The T_g, T_c, T_m are all higher in PEN than observed in PET, due to the presence of bulky naphthalene rings, increasing the overall rigidity of the macromolecular system. The temperatures of degradation for PEN are also marginally increased, emphasising the increased thermal stability of PEN over its terephthalate counterpart.

4.3.1 Thermo-Oxidative Degradation Studies of PET and PEN

In addition to thermal degradation studies, preliminary thermo-oxidative degradation studies on PET and PEN were conducted under air. This provided an insight into the thermo-oxidative degradation behaviour of PEN in comparison to PET.

4.3.1.1 Dynamic DSC Results

The DSC degradation profiles obtained for PET and PEN are illustrated in *Figures 4.6* and *4.7.*

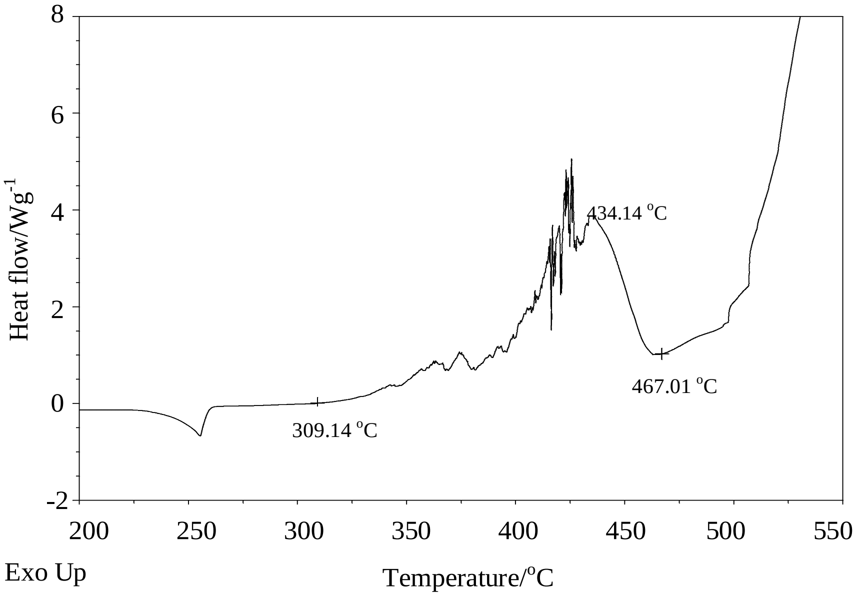

Figure 4.6 DSC of PET in air, 30 - 550 °C, 10 °C min^{-1}

In the presence of air, the onset temperature of degradation for PET is significantly reduced, in comparison to thermal degradation, with a major exothermic DSC signal slowly arising from 309 °C onwards. This indicates that discrete exothermic degradation processes are occurring at much lower temperatures in PET, in the presence of oxygen. PEN does not exhibit any marked differences in degradation temperatures on changing from a thermal to thermo-oxidative environment, in contrast to PET. The major exothermic degradation signal in PEN is not observed until a higher temperature of 377 °C, with the maximum heat flow, corresponding to exothermic degradation, observed at 436 °C in PEN and 434 °C in PET. Between the onset temperature for oxidative degradation and the temperature of maximum heat flow, the heat flow signal is spiked and characteristic of the evolution of volatile species.

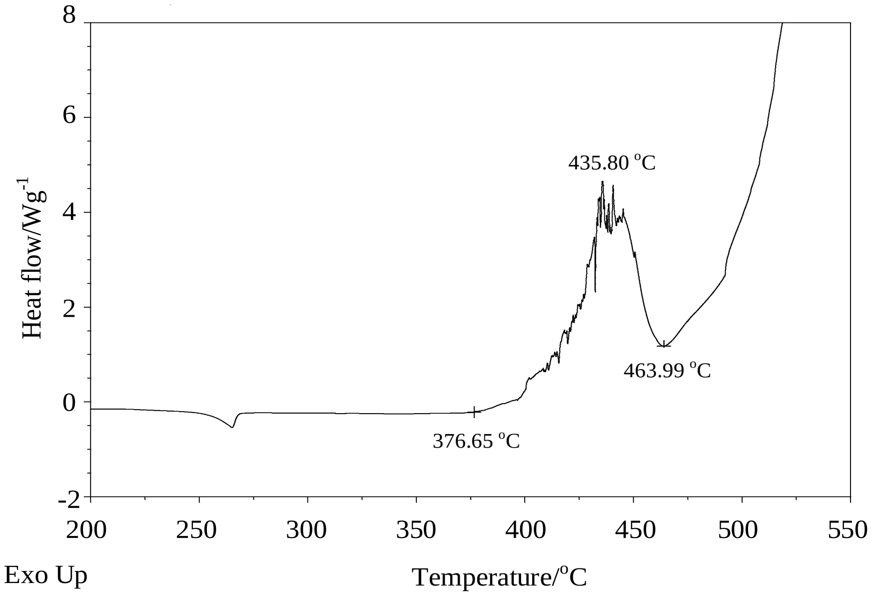

Figure 4.7 DSC of PEN in air, 30 - 550 °C, 10 °C min^{-1}

Comparison of the degradation temperatures quoted for the onset of major exothermic/endothermic degradation for oxidative and non-oxidative studies of PET and PEN, reveals that PET is very susceptible to thermo-oxidative degradation. The onset temperature for the thermo-oxidative degradation of PET is considerably lower than that observed for thermal degradation, indicating that the presence of oxygen rapidly accelerates the degradation process. However, interestingly there were no significant differences between the onset temperatures of thermal and thermo-oxidative degradation in PEN. This behaviour indicates that PEN is no more susceptible to degradation in the presence of oxygen than in an inert atmosphere.

4.3.1.2 Dynamic TGA Results

The thermogravimetry and differential thermogravimetry curves for the thermo-oxidative degradation of PET and PEN are illustrated in *Figure 4.8*. Both PET and

PEN undergo one major mass loss event, prior to a second minor degradation step occurring at very high temperature. Again, the difference in the mass loss behaviour of PET and PEN remains in the temperatures at which the major mass loss event occurs.

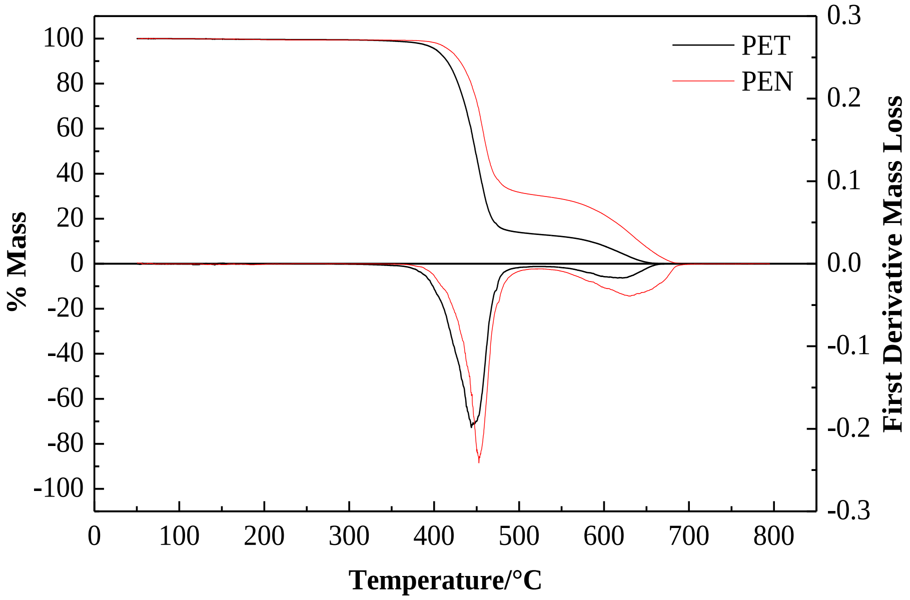

Figure 4.8 Thermogravimetry and differential thermogravimetry curves of PET and PEN in air, 30 - 800 °C, 10 °C min^{-1}

In agreement with the thermo-oxidative DSC results, volatile species are evolved at a marginally lower temperature for PET in the presence of oxygen. Significant mass loss of PET begins at 402 ^{o}C and finishes at approximately 505 ^{o}C. Although the onset temperatures of degradation do not show significant differences, DSC is an increasingly sensitive technique in comparison to TGA. Therefore, it is of no surprise that the DSC results indicate far more thermo-oxidative degradation activity for PET at lower temperatures in comparison to the TGA results. As seen in the differential thermogravimetry curve in *Figure 4.8*, the maximum rate of mass loss in PET occurs at 444 ^{o}C. A smaller degradation step, not observed in the thermal degradation studies, is then evident from 505 ^{o}C to 665 ^{o}C. This second mass loss stage is due to extensive thermo-oxidative degradation of PET, resulting in 100% mass loss as the polymer is fully oxidised.

The mass loss profile obtained for PEN under thermo-oxidative conditions proved to be very similar to that of PET, despite the initial delay in the release of volatiles due to the increased thermal stability of PEN. Significant mass loss of PEN is not evident until 417 ^{o}C, with the maximum rate of mass loss observed on the differential thermogravimetry curve at 453 ^{o}C. A second slower mass loss stage, observed in PET, then proceeds in PEN from 510 ^{o}C to 680 ^{o}C, leaving no residual mass as the polymer is fully oxidised.

The TGA and DSC results for the thermo-oxidative degradation of PET and PEN therefore appear to correlate well. Results indicate that PET is more sensitive to degradation in the presence of oxygen in contrast to degradation under purely thermal conditions. Interestingly, this marked decrease in the thermo-oxidative stability of PET was not observed in PEN. PEN does not exhibit any marked changes in degradation temperatures on changing from a thermal to thermo-oxidative environment. The sensitivity of PET and PEN to both temperature and oxygen will be investigated further in *Chapter 5*.

4.3.2 Thermal Volatilisation Studies of PET and PEN

From DSC and TGA studies of PET and PEN, it has been illustrated that the thermal degradation behaviour of both polymers is similar. However, in order to gain further insight into the processes involved in the thermal degradation of both polyesters, thermal volatilisation analysis (TVA) was performed. TVA is a powerful tool useful for studying the degradation behaviour of polymers that breakdown to give some proportion of volatile products when heated under vacuum. The identification of volatile degradation products may lead to a better understanding of the processes by which PET and PEN thermally degrade.

- ***Degradation Profiles of PET and PEN***

During degradation of the polymer samples, the Pirani gauge positioned at the entrance of the primary sub-ambient trap monitored the evolution of all volatile species i.e. all condensable and non-condensable species. The second Pirani gauge, positioned at the exit of the primary sub-ambient trap monitored the evolution of non-condensable volatile species i.e. any volatile species that could not condense within the liquid nitrogen cooled primary trap. The resultant thermogram profiles for PET and PEN are shown in *Figures 4.9* and *4.10*. *Tables 4.1* and *4.2* represent both the furnace and corresponding sample temperature for each major degradation event.

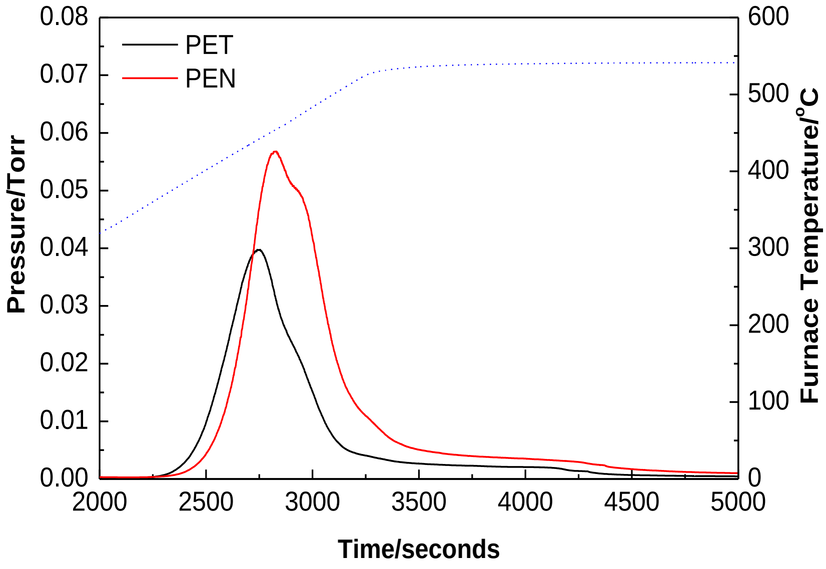

Figure 4.9 TVA thermograms showing total evolution of volatile species in PET and PEN, furnace temperature/°C illustrated in blue

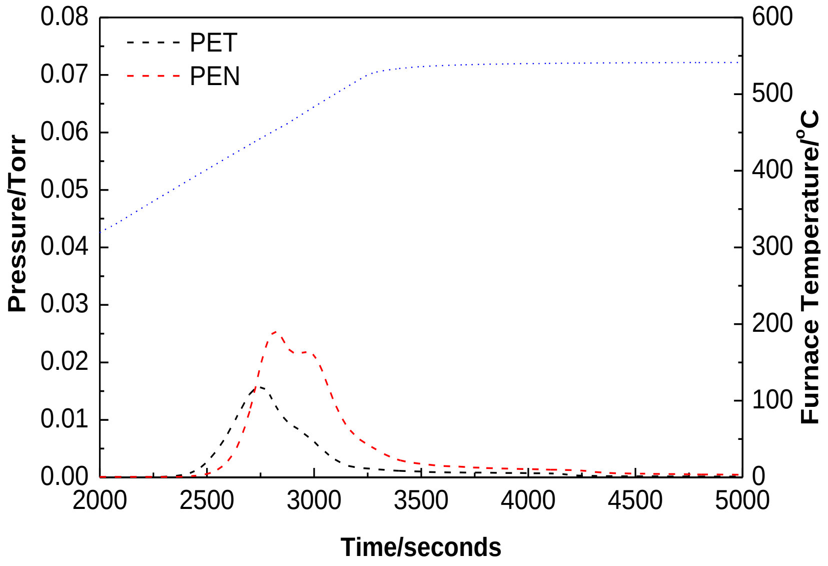

Figure 4.10 TVA thermograms showing total evolution of non-condensable species in PET and PEN, furnace temperature/°C illustrated in blue

Event	Furnace Temperature/^{o}C	Sample Temperature/^{o}C
Onset of volatile evolution	386	365
Peak 1 maximum rate of volatile evolution	441	420

Table 4.1 TVA degradation temperatures of PET

Event	Furnace Temperature/^{o}C	Sample Temperature/^{o}C
Onset of volatile evolution	399	380
Peak 1 maximum rate of volatile evolution	452	433
Peak 2 maximum rate of volatile evolution	468	448

Table 4.2 TVA degradation temperatures of PEN

In PET, the evolution of volatile species starts around 365 ^{o}C where a rapid increase in pressure is observed. The peak maximum for the evolution of volatile species in PET is observed at 420 ^{o}C. In contrast, the initial evolution of volatile species in PEN is not evident until a higher temperature of approximately 380 ^{o}C. Similarly, the peak maximum for the evolution of volatile species in PEN is observed at a slightly higher temperature of 433 ^{o}C. As discussed previously, this increased thermal stability is thought to be a result of the enhanced delocalisation of charge across the naphthalene ring units in PEN, increasing the overall stability of the ester linkages within the polymer chains.

Almost 50% of the total volatile species detected in PET and PEN are non-condensable species. These non-condensable degradation species were detected using online mass spectrometry and were found to consist mainly of carbon monoxide in both PET and PEN. Traces of methane and hydrogen were also detected in both polymers using the mass spectrometer in multiple ion detection mode. The MS for carbon monoxide, detected in substantial quantities in both PET and PEN, is illustrated in *Figure 4.11* alongside the MS product distribution for the non-condensable species detected in multiple ion detection mode in *Figure 4.12*.

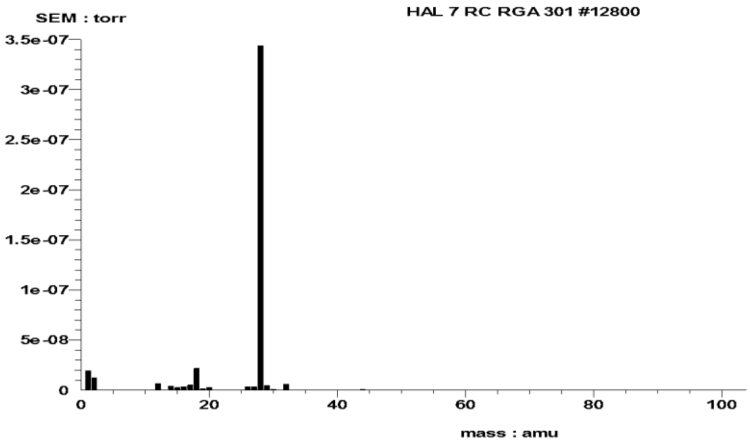

Figure 4.11 Mass spectrum of carbon monoxide, detected in PET and PEN

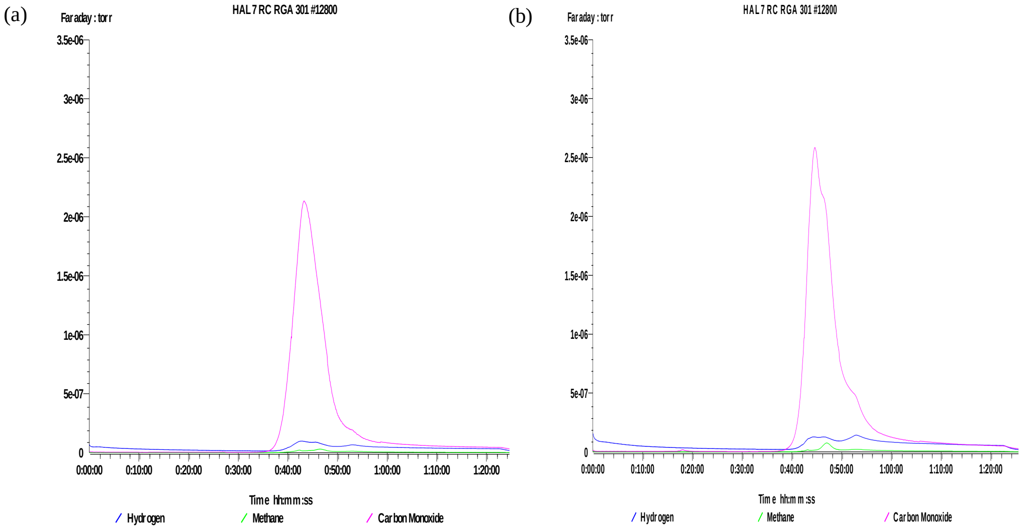

Figure 4.12 MS non-condensable product distribution in (a) PET and (b) PEN

A small shoulder on the degradation curve of PEN at 448 ^{o}C, suggests the possibility of a two-step degradation process occurring in PEN, in contrast to one major degradation process in PET. This is also evident in the mass spectrum for the evolution of non-condensable volatiles in PEN. In order to deduce if this two-step degradation process is valid or simply a diffusion limited effect, isothermal TVA studies were performed at temperatures of 400, 450 and 500 ^{o}C, encompassing either side of the small shoulder on the degradation curve. However, the degradation products, at all temperatures, were found to be identical to those reported below for degradation up to 550 ^{o}C. Only the relative amount of degradation products were found to vary with temperature. This demonstrates that the mechanism of degradation does not differ on either side of the small shoulder on the degradation curve of PEN. Instead, it is thought that this small shoulder is due to the increased melt viscosity of PEN, inhibiting the diffusion of volatile degradation products from the polymer melt.

On completion of the degradation process, the sub-ambient distillation was then performed to collect all condensable volatile species. This was then followed by collection of the cold ring fractions for both polyesters.

- ***Sub - Ambient Distillation Data for PET and PEN***

During the sub-ambient distillation of PET and PEN, four separate fractions were collected from both polymers. The sub-ambient distillation profile, illustrated in *Figure 4.13*, provides a qualitative indication of the distribution of condensable volatile species produced during degradation. Only small differences are evident in the product distribution, highlighting the strong similarities in thermal degradation of PET and PEN.

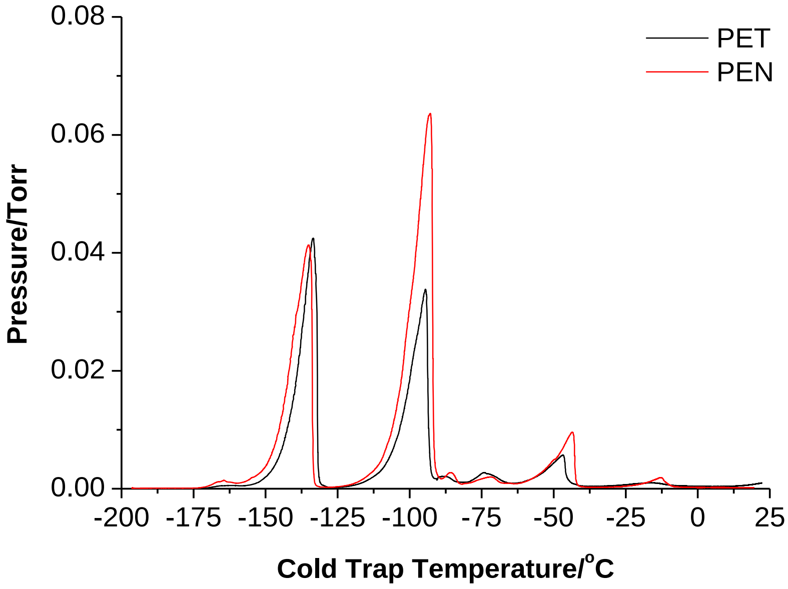

Figure 4.13 Sub-ambient TVA curve for degradation products of PET and PEN

- ### *Degradation Products Isolated from PET*

Table 4.3 illustrates the degradation products collected from PET. The composition of degradation products was identified using IR, online-MS and GC-MS analysis.

Fraction	*Temperature range collected*	*Major degradation product(s)*
1	-196 °C to -125 °C	Carbon dioxide, Ethylene, Acetylene
2	-124 °C to -90 °C	Acetaldehyde
3	-89 °C to -37 °C	Benzene, Toluene, Water
4	-36 °C to 40 °C	Benzaldehyde, Benzoic acid

Table 4.3 Sub-ambient distillation products collected from the degradation of PET

Fraction 1 from PET was found to consist mainly of carbon dioxide with traces of ethylene and acetylene. The mass spectra for these three degradation species are illustrated in *Figures 4.14*. The gas-phase IR spectrum for fraction 1 can also be seen in *Figure 4.15*. The asymmetric stretch of carbon dioxide gives a strong absorption band at ~2330 cm^{-1} with the assymmetric stretch of bending vibrations observed above 600 cm^{-1}.

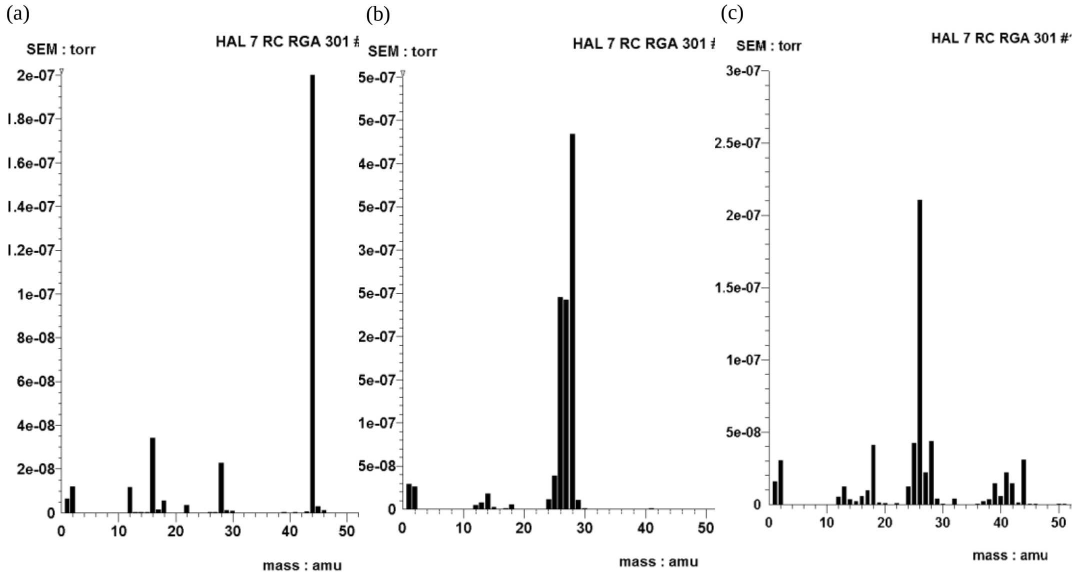

Figure 4.14 Mass spectrum of (a) carbon dioxide (b) ethylene and (c) acetylene – PET fraction 1

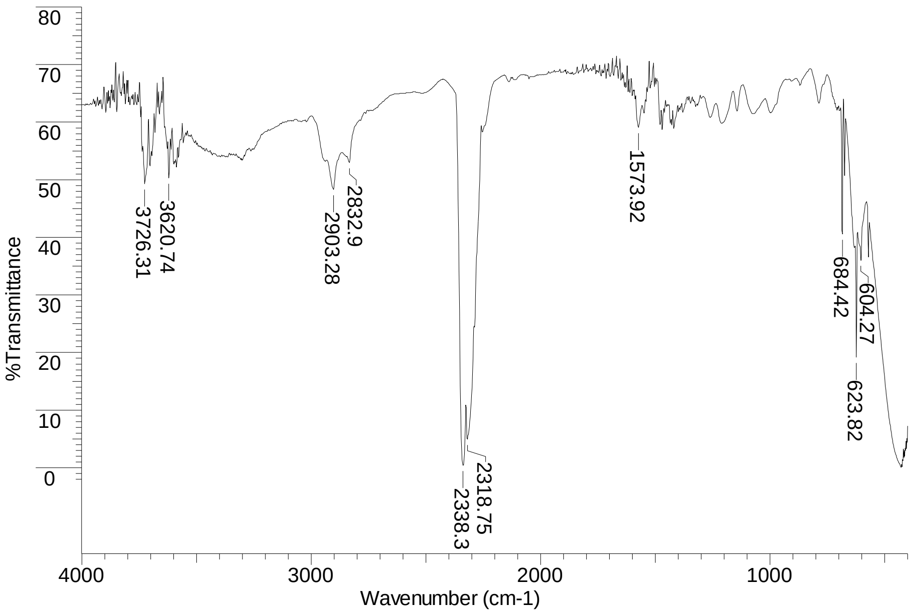

Figure 4.15 IR spectrum of carbon dioxide, ethylene and acetylene - PET fraction 1

One degradation species was identified in fraction 2 from PET. This second fraction was identified as acetaldehyde from the MS and IR spectra shown in *Figures 4.16* and *4.17*, respectively. The high intensity carbonyl stretch of the saturated aliphatic aldehyde is evident in the IR spectrum of acetaldehyde at 1760 cm^{-1} alongside the distinct O=C-H stretching vibrations observed between 2706 - 2822 cm^{-1}. The presence of such large amounts of carbon dioxide and acetaldehyde, identified from fractions 1 and 2, highlight the extent of degradation occurring under thermal conditions.

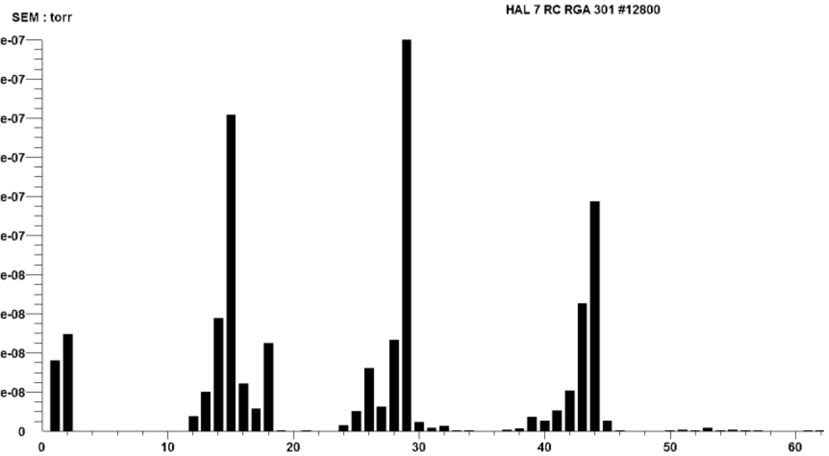

Figure 4.16 Mass spectrum of acetaldehyde - PET fraction 2

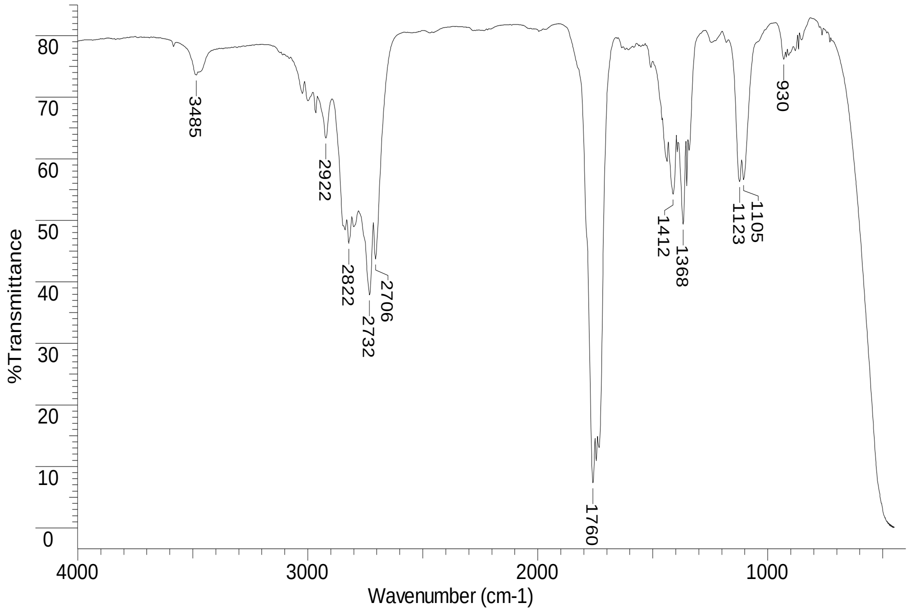

Figure 4.17 IR spectrum of acetaldehyde - PET fraction 2

Online mass spectrometry was of key importance in the identification of degradation species present in fractions 3 and 4 from PET. This was due to the predominantly weaker IR spectra obtained in comparison to fractions 1 and 2. The IR and mass spectra obtained for fraction 3 from PET are illustrated in *Figures 4.18* and *4.19.*

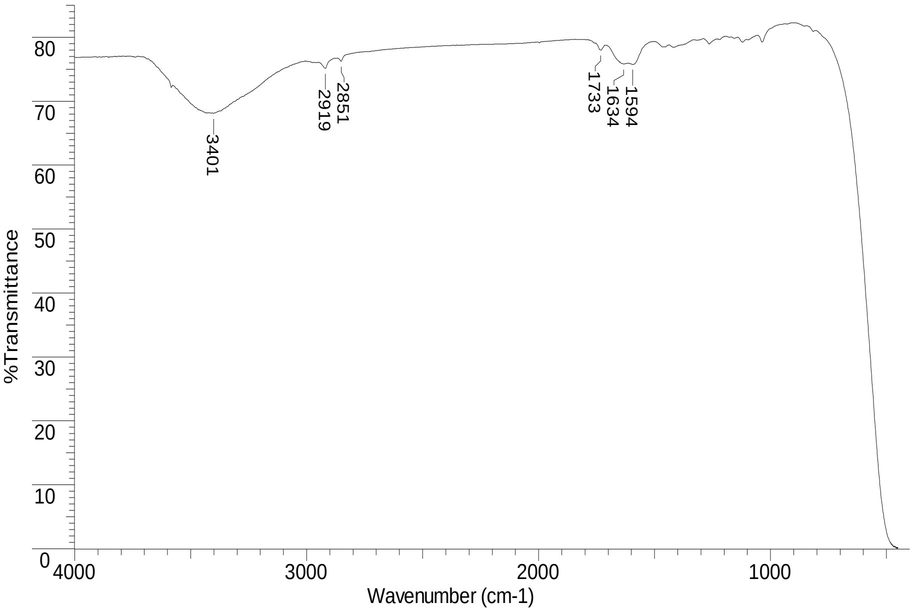

Figure 4.18 IR spectrum of benzene, toluene and water - PET fraction 3

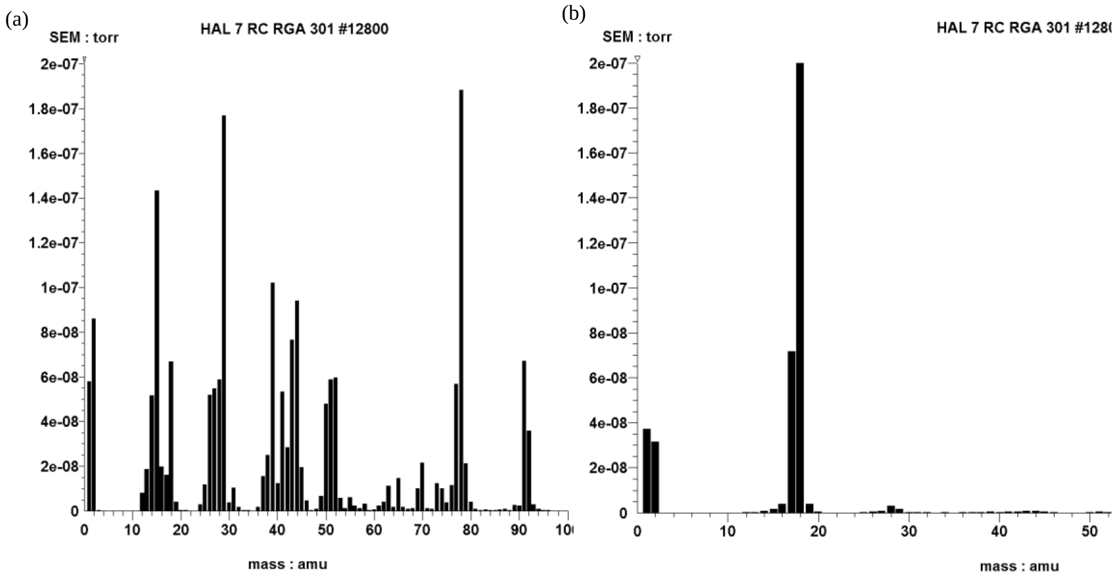

Figure 4.19 Mass spectrum of (a) benzene and toluene and (b) water - PET fraction 3

The mass spectra illustrated for PET fraction 3 indicate the presence of benzene, toluene and water. This is confirmed from the IR spectrum by the presence of weak aromatic C-H stretching observed around 1600 cm^{-1} and one broad O-H band at 3401 cm^{-1}. Stretching vibrations can also be seen at 1733 cm^{-1} and indicate the presence of an aromatic aldehyde. This aldehyde is most likely to be benzaldehyde, the majority of which was collected in fraction 4.

From online MS, fraction 4 from PET was found to consist of benzaldehyde and trace amounts of benzoic acid. The mass spectra of benzaldehyde and benzoic acid are shown in *Figures 4.20* and *4.21*. Trace quantities of other high molar mass aromatic ketones and esters were also thought to exist. However due to the small quantities and overlap in the mass spectra, positive identification of these species proved difficult.

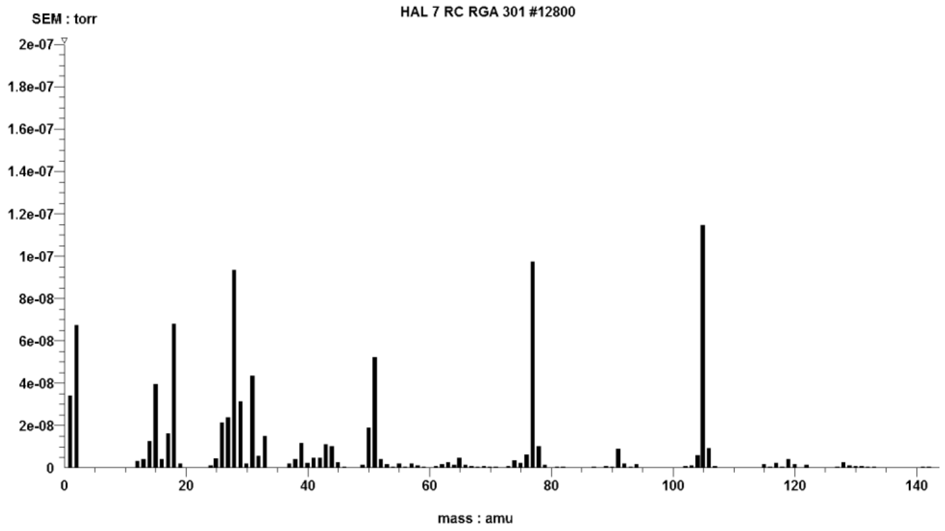

Figure 4.20 Mass spectrum of benzaldehyde - PET fraction 4

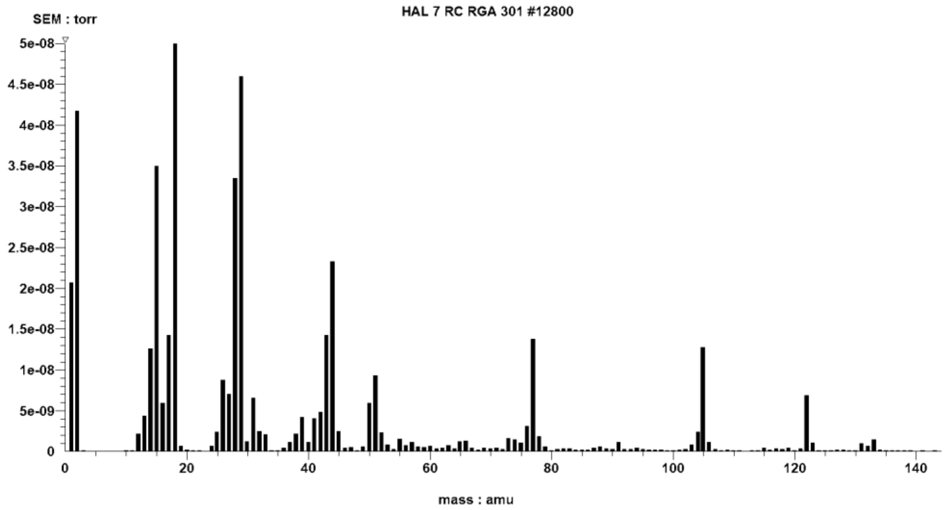

Figure 4.21 Mass spectrum of benzoic acid - PET fraction 4

Due to the inherently weaker IR spectrum obtained from fraction 4 of PET, additional solvent trapping of the volatile product in a secondary limb enabled GC-MS analysis to be performed. GC-MS analysis confirmed the presence of both major degradation products benzaldehyde and benzoic acid. Due to the improved detection limits of GC-MS, toluene, ethyl benzene, 4-formylbenzoic acid and biphenyl were also detected as illustrated in *Figures 4.22 - 4.24*. The presence of such degradation products in fraction 4 from PET indicates extensive fragmentation of the polyester chain, most likely to be a result of radical degradation processes.

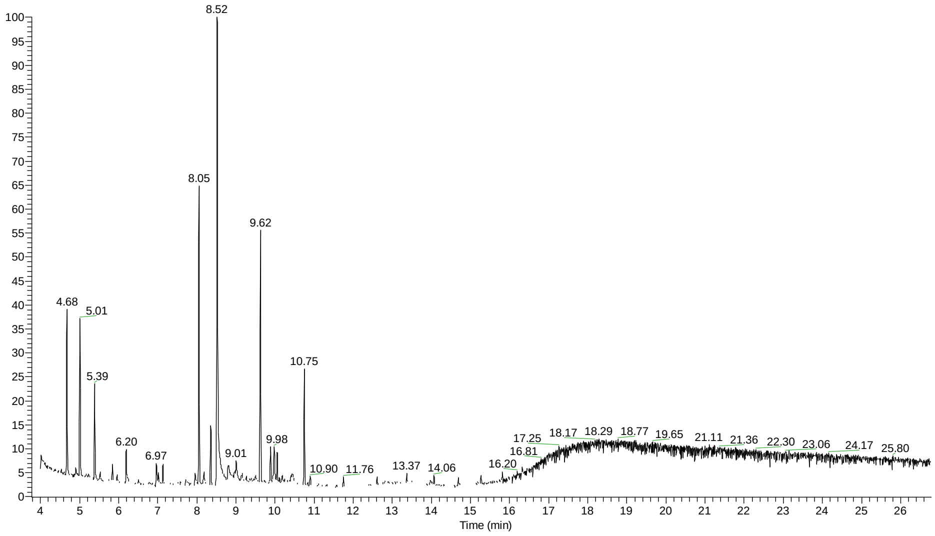

Figure 4.22 GC-MS total ion chromatogram (TIC) - PET fraction 4

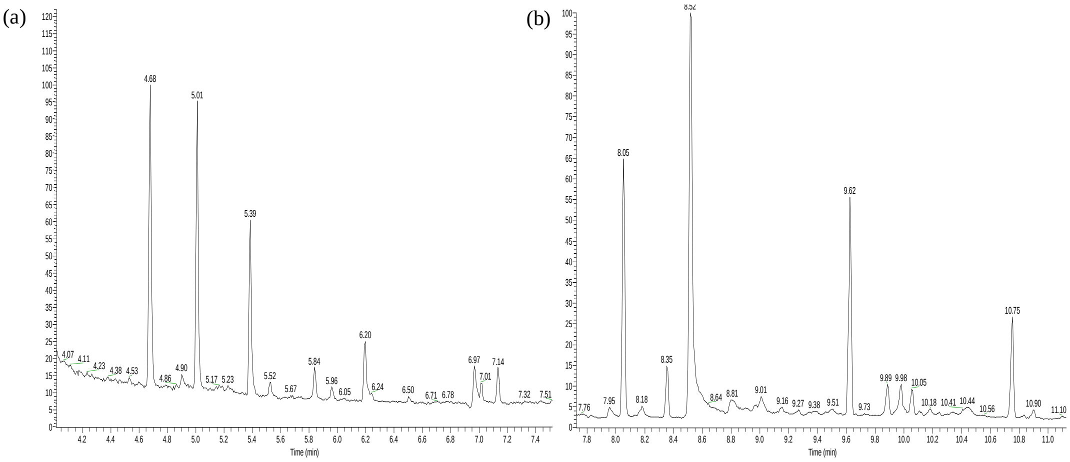

Figure 4.23 GC TIC chromatogram - PET fraction 4, retention times (a) 4.0 – 7.5 mins, (b) 7.5 – 11.0 mins

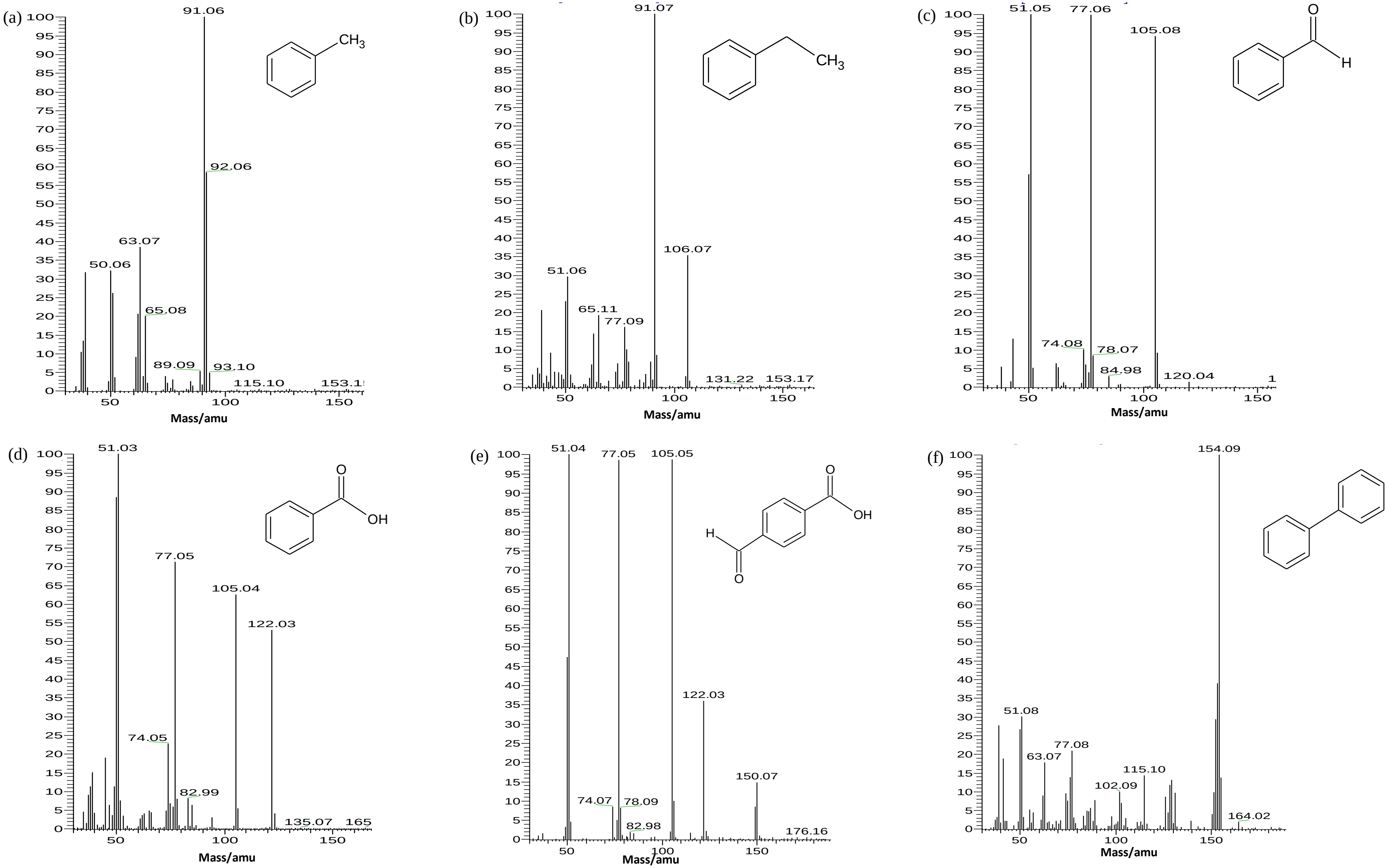

Figure 4.24 MS of (a) toluene - 4.68 mins (b) ethyl benzene – 5.84 mins (c) benzaldehyde – 7.95 mins (d) benzoic acid – 8.52 mins (e) 4-formylbenzoic acid - 8.81 mins and (f) biphenyl – 10.44 mins from GC-MS analysis of PET fraction 4

- ***Degradation Products Isolated from PEN***

The TVA sub-ambient distillation curves, shown in *Figure 4.13,* highlight the strong similarities in the thermal degradation of PET and PEN. Only small differences are evident in the product distribution, with PEN producing slightly higher quantities of condensable volatile products. *Table 4.4* illustrates the degradation products collected from PEN during the sub-ambient distillation process. Once again, the composition of degradation products were identified using IR, online-MS and GC-MS analysis.

Fraction	***Temperature range collected***	***Major degradation product(s)***
1	-192 ^{o}C to -119 ^{o}C	Carbon dioxide, Ethylene, Acetylene
2	-118 ^{o}C to -82 ^{o}C	Acetaldehyde
3	-81 ^{o}C to -40 ^{o}C	Water
4	-39 ^{o}C to 40 ^{o}C	Naphthalene, Methyl naphthalene

Table 4.4 Sub-ambient distillation products collected from the degradation of PEN

The first two fractions, collected from PEN, were found to be identical to those found in PET. The main degradation products were identified as carbon dioxide and acetaldehyde with smaller quantities of ethylene and acetylene. The IR and MS spectra obtained for these fractions have not been illustrated to avoid repetition.

In fractions 3 and 4, the degradation products were found to differ between PET and PEN. This is thought to be due to the distinct differences in volatility between benzene and naphthalene. Degradation products from PEN, containing naphthalene rings, have increased molar mass and are therefore less volatile. Fraction 3 in PEN was therefore found to consist only of water, with less volatile, higher molar mass fragments, such as naphthalene and methyl naphthalene identified in fraction 4. The MS and IR spectra, of fraction 3 from PEN can be found in *Chapter 8 Supplementary Material. Figure 4.25* illustrates the MS spectra obtained for fraction 4 from PEN. The major products identified were naphthalene and methyl naphthalene.

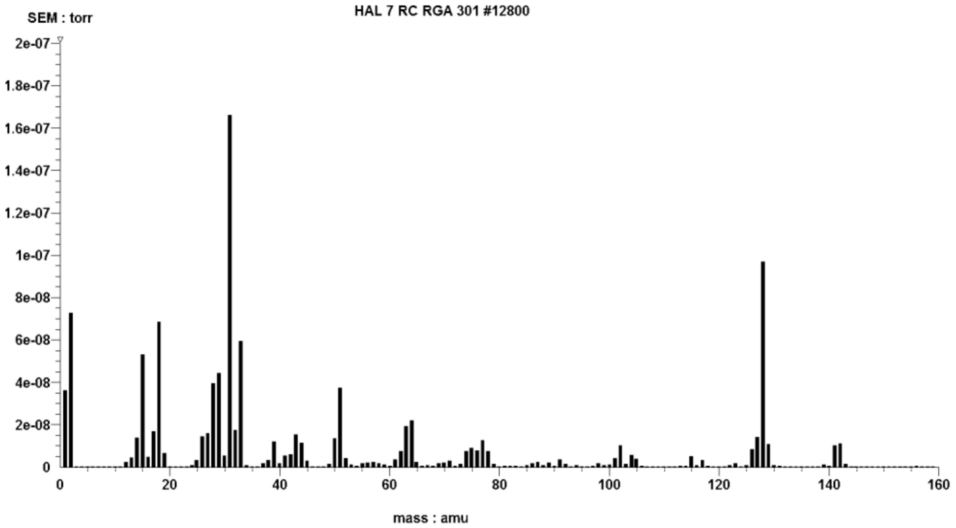

Figure 4.25 Mass spectrum of naphthalene and methyl naphthalene - PEN fraction 4

In addition to mass spectrometry, solvent trapping of the volatile products in a secondary limb enabled GC-MS analysis to be performed on fraction 4 from PEN. GC-MS analysis confirmed the presence of both naphthalene and methyl naphthalene as illustrated in *Figures 4.26* and *4.27*.

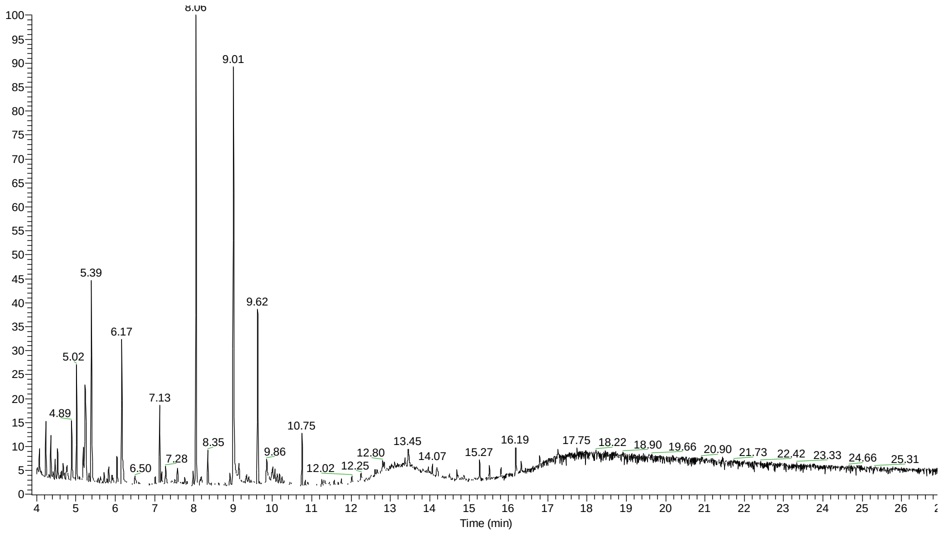

Figure 4.26 GC-MS total ion chromatogram (TIC) - PEN fraction 4

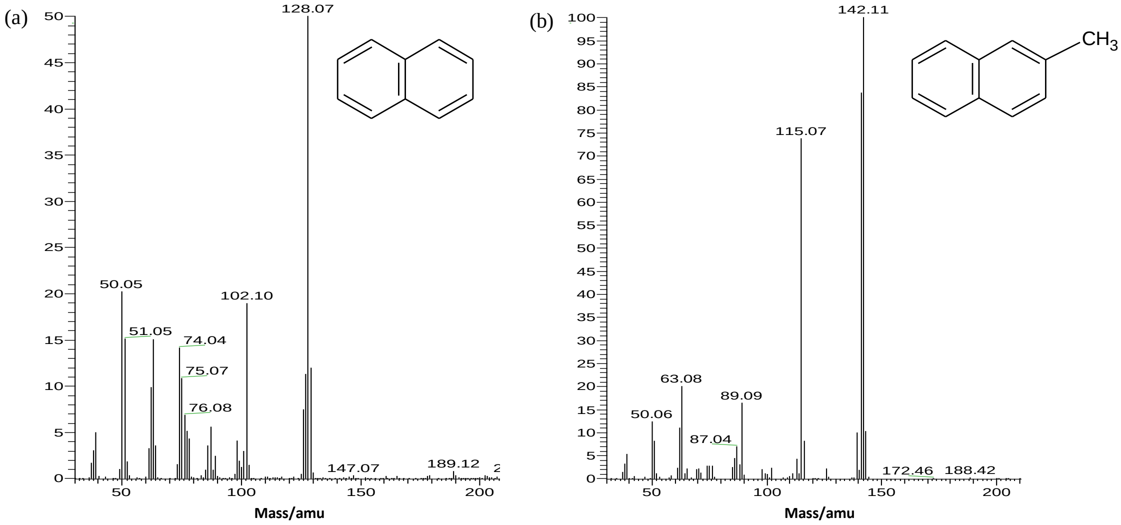

Figure 4.27 MS of (a) naphthalene - 9.01mins (b) methyl naphthalene - 9.86mins from GC-MS analysis of PEN fraction 4

- ***Cold Ring Fractions of PET and PEN***

The cold ring fractions of PET and PEN, containing high boiling point degradation products condensable at room temperature, were found to consist of a mixture of white powdery solid and a yellow coloured solid. As the material was extracted into chloroform it became apparent that the majority of the material was insoluble. The material was dissolved in a number of other common laboratory solvents with little success, indicating that the bulk of the cold ring fraction of PET and PEN is likely to consist of oligomeric polyester.

- ***PET Cold Ring Fraction***

The IR spectrum, obtained from the cold ring fraction of PET, is illustrated in *Figure 4.28*. *Table 4.5* displays the IR bands observed on analysis of the PET cold ring fraction with the general assignment for each absorption band. The IR results presented indicate the presence of a mixture of species within the PET cold ring fraction containing acidic, ester and vinyl functionalities. However, the predominant species, in terms of the relative intensity of the IR peaks, is the PET repeat unit and terephthalic acid. PET is most likely to be encountered as short oligomeric PET, due to the chain scission processes occurring during thermal degradation.

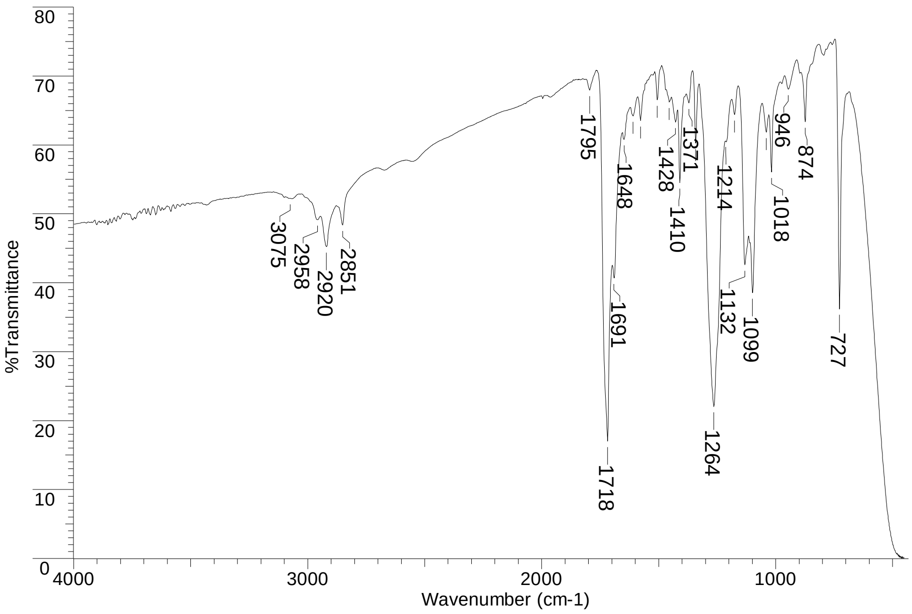

Figure 4.28 IR spectrum of PET cold ring fraction

Wavenumber/cm^{-1}	Absorption mode
3075	Aromatic C-H stretching
2958, 2920, 2851	Aliphatic C-H stretching (saturated C-H)
1795	C=O absorption of vinyl ester
1718	C=O absorption of ester
1691	C=O absorption of aryl carboxylic acid
1648-1342	Aromatic skeletal C-H stretching
1264, 1132	C(O)-O stretching of ester
1176, 1099, 1018	Bands in skeletal region indicate 1,4-substitution of aromatics
948	O-CH_2 stretching of EG
874	C-H out-of-plane deformations of para-substituted benzene ring
727	Out of plane deformations of two carbonyl substituents on aromatic ring

Table 4.5 IR peak assignments from TVA cold ring fraction of PET [1,2,3]

In addition to IR, the soluble component of the cold ring fraction of PET was analysed by GC-MS. *Figures 4.29 – 4.31* illustrate the GC chromatograms and mass spectra obtained. In agreement with the IR results presented above, the GC-MS analysis of the cold ring fraction of PET highlights the presence of different degradation species containing acidic, aldehydic, ester and vinyl functionalities due to the extent of chain fragmentation. In contrast to the degradation species collected in fraction 4 for PET, the degradation products found within the cold ring fraction were of a higher molecular weight and thus reduced volatility as expected. *Figure 4.31* highlights a variety of these degradation species identified from GC-MS analysis.

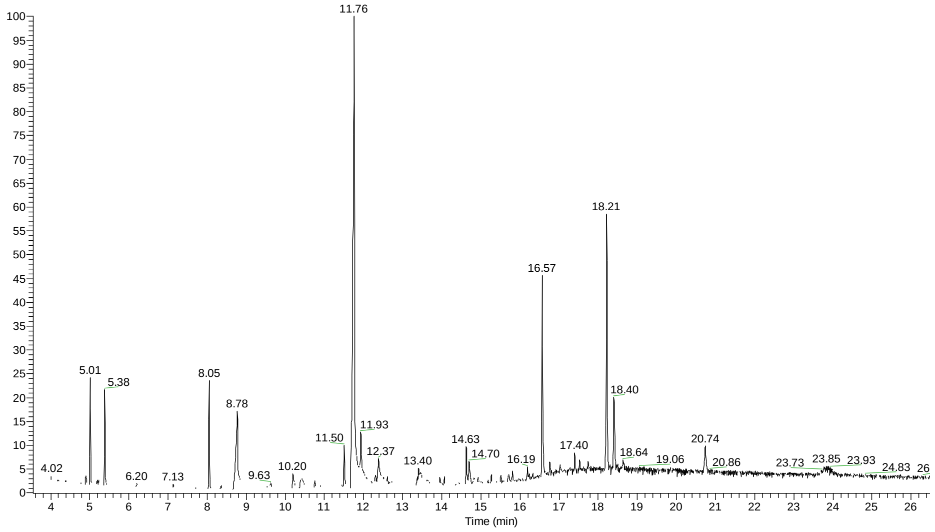

Figure 4.29 GC-MS total ion chromatogram (TIC) - PET cold ring fraction

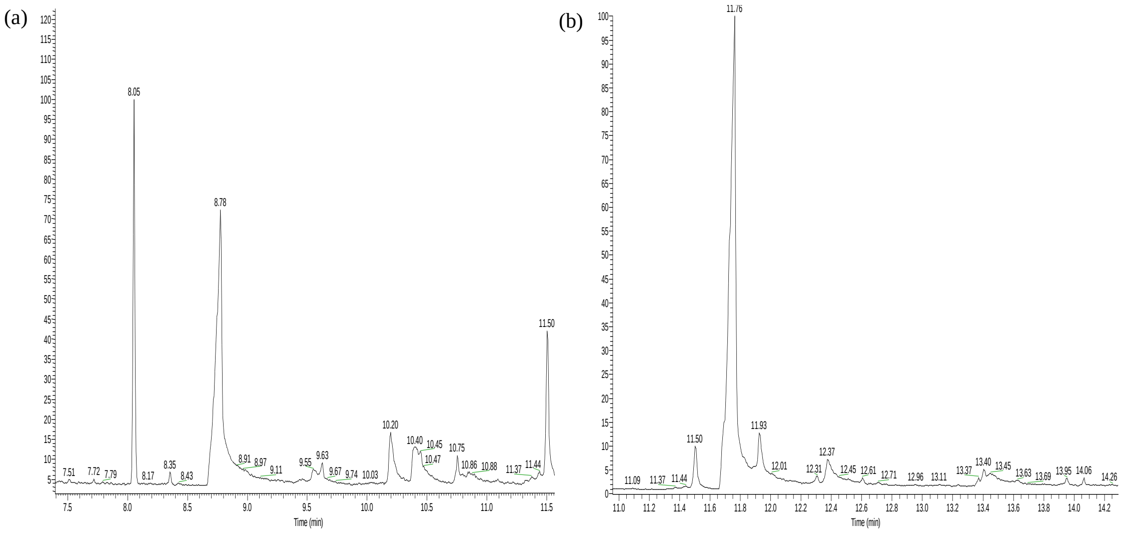

Figure 4.30 GC TIC chromatogram - PET cold ring fraction, retention times (a) 7.4 – 11.6 mins and (b) 11.0 – 14.3 mins

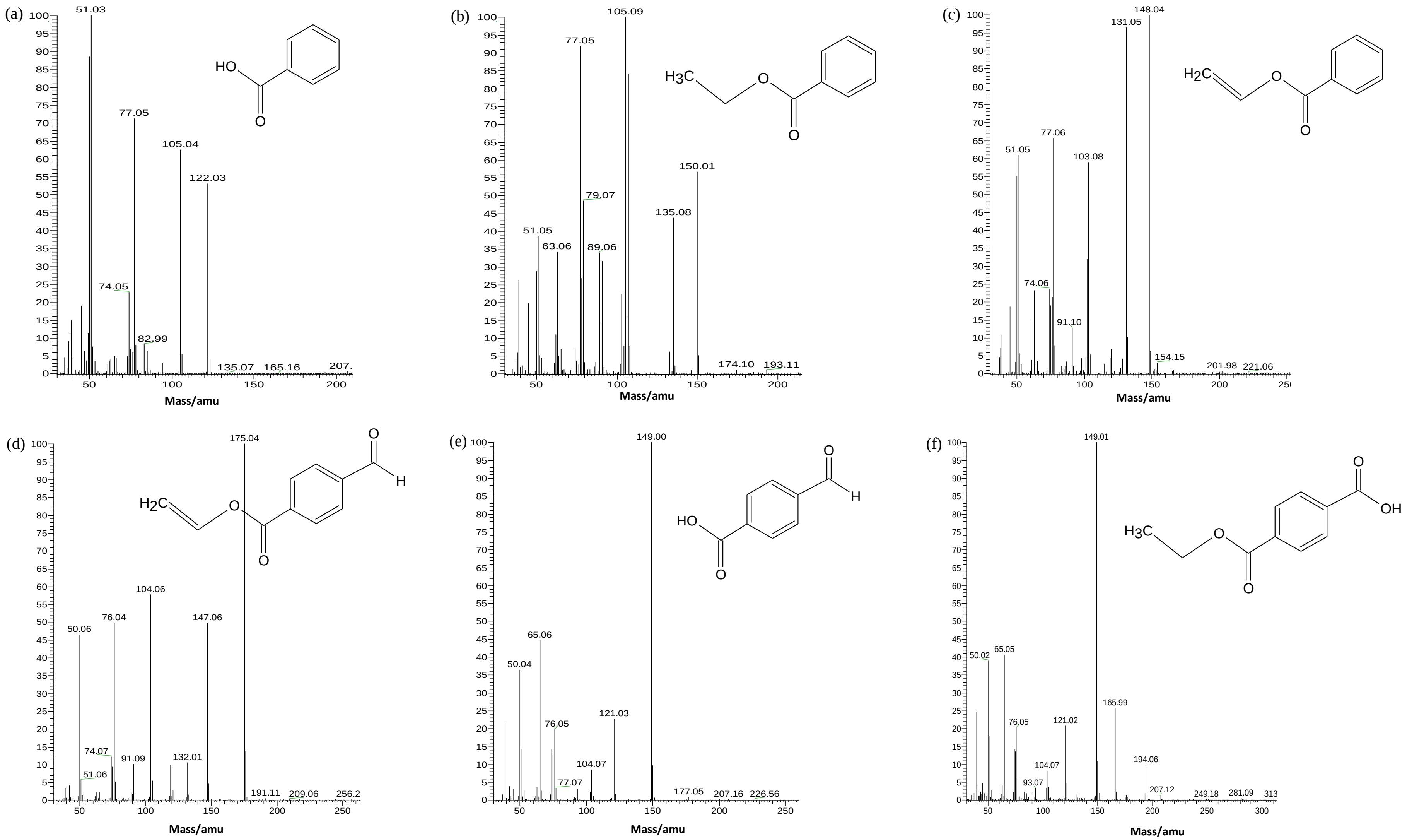

Figure 4.31 MS of (a) benzoic acid - 8.78 mins, (b) ethyl benzoate - 10.20 mins (c) vinyl benzoate - 10.40 mins (d) ethenyl 4-formylbenzoate - 11.50 mins (e) 4-formylbenzoic acid - 11.72 mins and (f) 4-(ethoxycarbonyl) benzoic acid - 11.96 mins from GC-MS analysis of PET cold ring fraction

On the basis of the TVA results presented above, it can be concluded that PET thermally degrades above temperatures of 365 °C, subsequently leading to the release of volatile species. Of the volatile species evolved, those condensable within the cold ring fraction comprise of mainly PET oligomers, terephthalic acid and a number of mono- and disubstituted chain fragments constituting acidic, aldehydic, ester and vinyl functional groups. The volatile degradation species, capable of condensing at –196 °C, were positively identified as carbon dioxide, ethylene, acetylene, acetaldehyde, toluene, benzene, water, benzaldehyde and benzoic acid. Large amounts of carbon monoxide were also detected as a non-condensable gas alongside traces of methane and hydrogen.

- ***PEN Cold Ring Fraction***

The results presented in *Figure 4.32* and *Table 4.6* indicate the presence of mainly oligomers within the cold ring fraction of PEN. Unfortunately, due to the weak intensities of the absorption bands in the spectrum, the identification of other degradation species proved difficult.

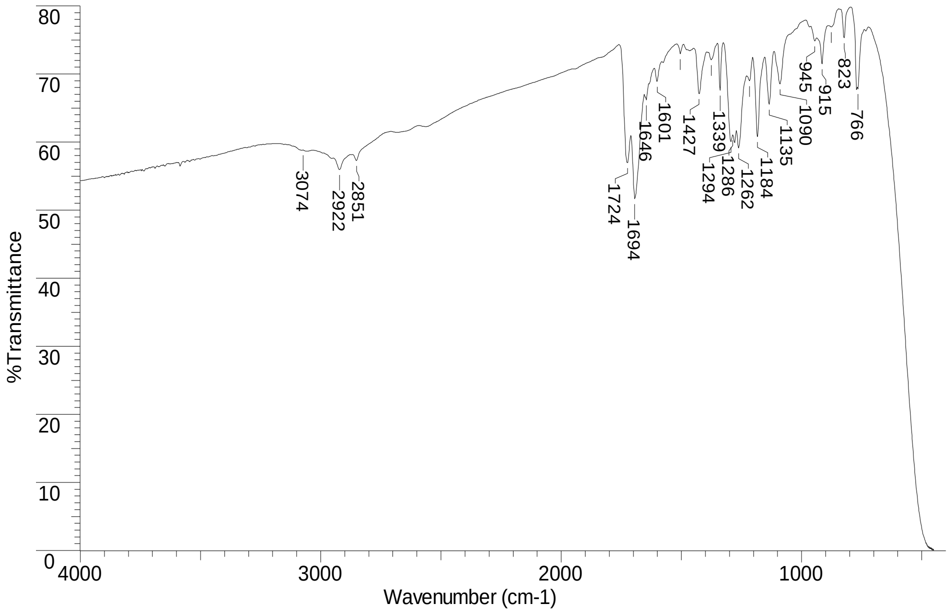

Figure 4.32 IR spectrum of PEN cold ring fraction

Wavenumber/cm^{-1}	***Absorption mode***
3074	Aromatic C-H stretching
2922, 2851	Aliphatic C-H stretching (saturated C-H)
1724	C=O absorption of ester
1694	C=O absorption of aryl carboxylic acid
1646 - 1339	Aromatic skeletalC-H stretching
1294, 1262, 1184	C(O)-O stretching of ester
1217, 1135, 1090	Bands in skeletal region indicate 1,4-substitution of aromatics
915	O-CH$_2$ stretching of EG
823	C-H out-of-plane deformations of para-substituted benzene ring
766	Out of plane deformations of two carbonyl substituents on aromatic ring

Table 4.6 IR peak assignments from TVA cold ring fraction of PEN [1-3]

The GC-MS analysis of the cold ring fraction of PEN highlights the presence of different degradation species containing acidic, aldehydic, ester and vinyl functionalities as observed previously in the cold ring fraction of PET. In addition to the functional groups already mentioned, binaphthalene was also identified in the cold ring fraction of PEN. The reduced volatility of binapthalene in contrast to biphenyl results in identification of the degradation species within the cold ring fraction rather than fraction 4 as observed for PET. *Figures 4.33 – 4.35* illustrate a variety of the degradation species identified from GC-MS analysis of the PEN cold ring fraction.

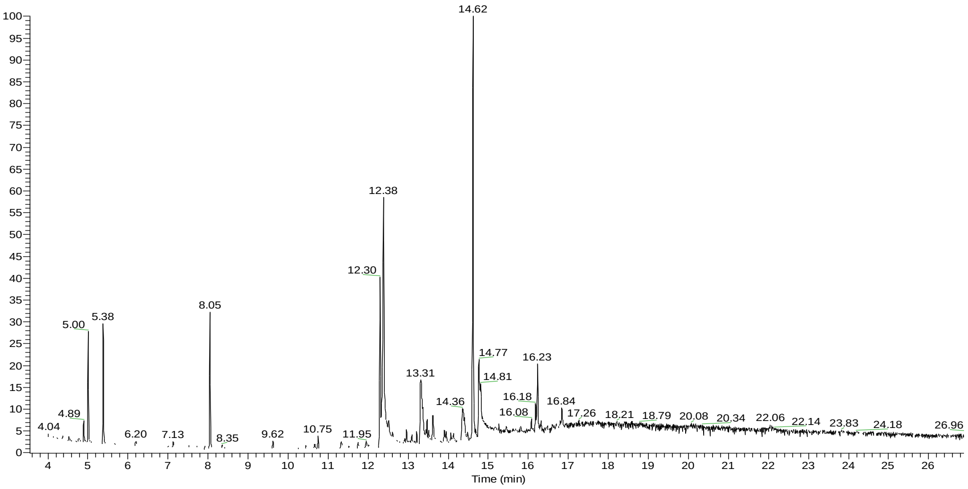

Figure 4.33 GC-MS total ion chromatogram (TIC) - PEN cold ring fraction

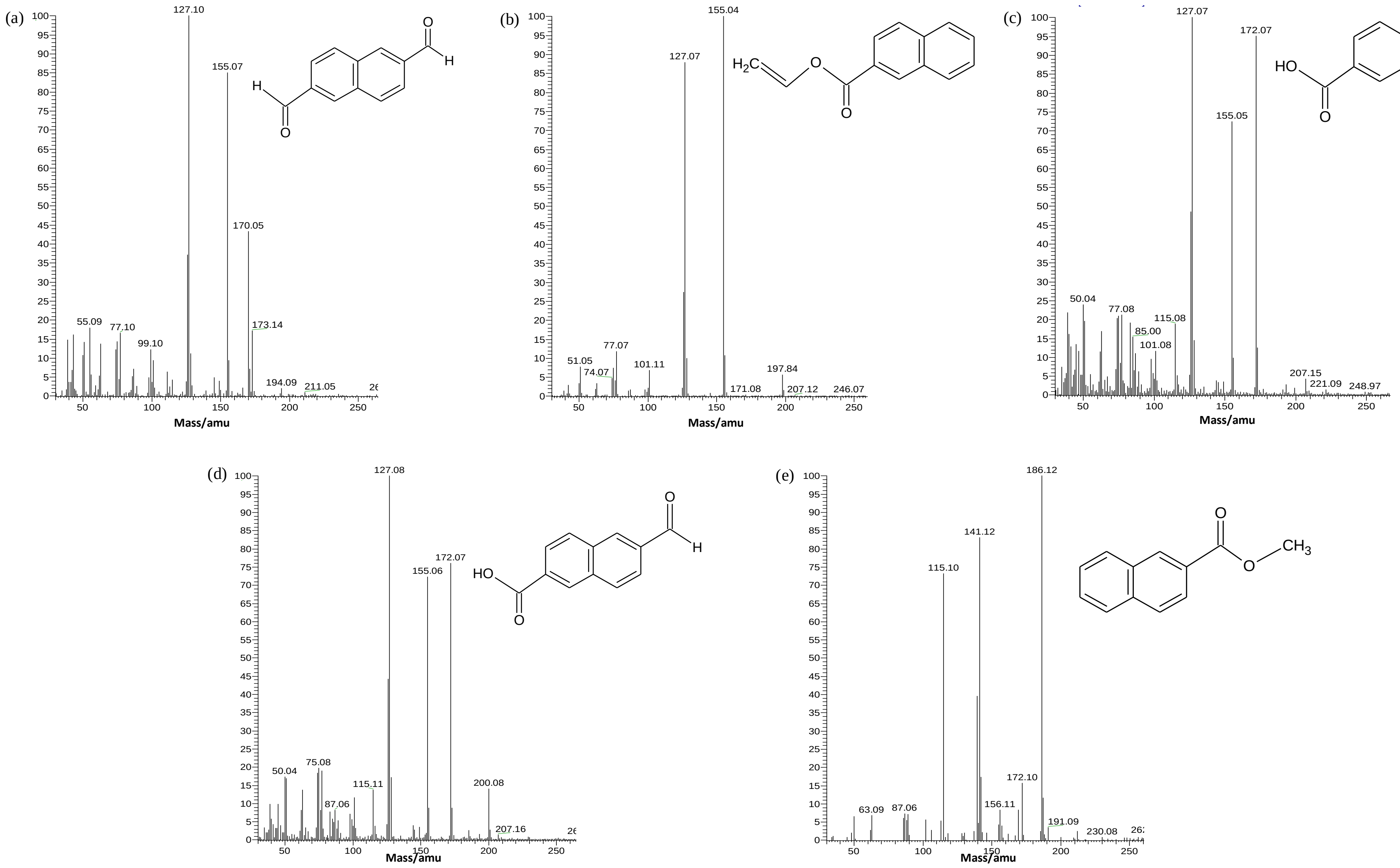

Figure 4.34 MS of (a) naphthalene-2,6-dicarbaldehyde - 11.95 mins (b) ethenyl naphthalene-2-carboxylate - 12.30 mins (c) naphthalene-2-carboxylic acid - 12.36 mins (d) 6-formylnaphthalene-2-carboxylic acid - 12.51 mins (e) methyl naphthalene-2-carboxylate - 13.03 mins from GC-MS analysis of PEN cold ring fraction

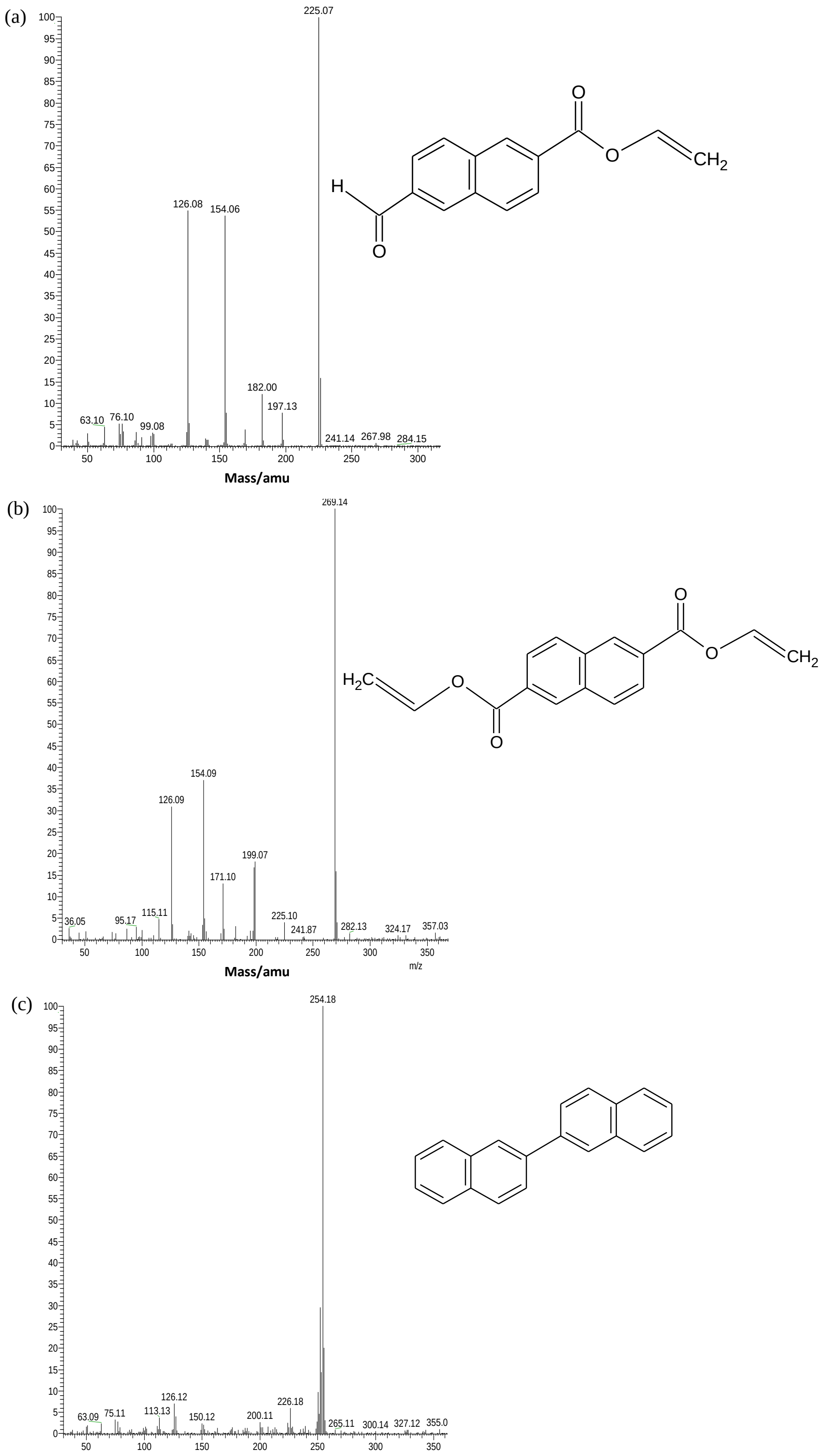

Figure 4.35 MS of (a) ethenyl 6-formylnaphthalene-2-carboxylate - 14.62mins (b) diethenyl naphthalene-2,6-dicarboxylate - 16.08mins (c) binaphthalene - 16.23, 16.84mins for GC-MS analysis of PEN cold ring fraction

From the TVA results discussed above, it can be concluded that PEN thermally degrades at a higher temperature of 380 °C, in comparison to 365 °C for PET. Of the volatile species evolved, those condensable within the cold ring fraction were identified as mainly PEN oligomers with small molecular chain fragments containing acidic, aldehydic, ester and vinyl functionalities. The condensable volatile species collected in the first two fractions from PEN were found to be identical to the volatile species collected from PET; namely carbon dioxide, ethylene, acetylene and acetaldehyde. Water, naphthalene and methyl naphthalene were also identified as condensable volatile degradation species. Similar to PET, large quantities of carbon monoxide and traces of methane and hydrogen were detected as non-condensable species during the thermal degradation of PEN. The formation of these degradation species from PEN indicates that the major thermal degradation mechanism is identical to PET, involving random chain scission of ester linkages in the polymer backbone.

4.3.2.1 Discussion of the Thermal Degradation Mechanisms of PET and PEN

DSC, TGA and TVA results all indicate that both PET and PEN undergo one major degradation process. This is most likely to involve the thermal cleavage of ester bonds in the polymer backbone resulting in the formation of vinyl ester and carboxylic acid end groups. This primary thermal degradation reaction is thought to be identical for both polymers, however it has yet to be determined whether this reaction proceeds via an ionic or radical mechanism.

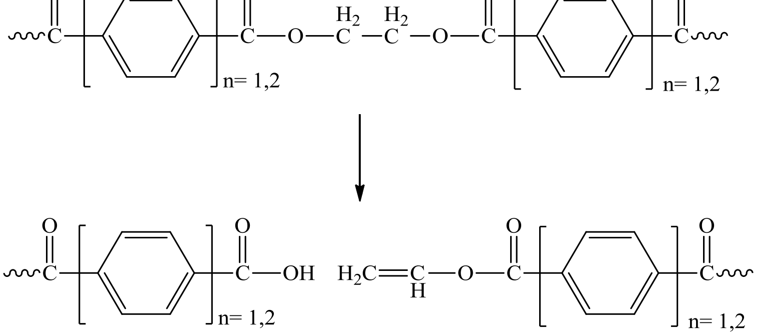

Figure 4.36 Scission at ester linkages in PET (n=1) and PEN (n=2)

PET oligomers, alongside small chain fragments containing acid, aldehydic, ester and vinyl functionalities were the largest, high boiling point degradation species identified from PET. Condensable species including ethylene, acetylene, acetaldehyde, toluene, benzene, water, benzaldehyde and benzoic acid were also identified as well as copious quantities of carbon monoxide and carbon dioxide. These degradation products obtained from PET appear to correlate well with the degradation mechanism devised by McNeill *et al.* [4] which provides a good explanation for the continuous formation of CO and CO_2.

The homolytic mechanism, published by McNeill *et al.*, [4] accounts for the wide range of degradation products observed from TVA studies of PET at temperatures ranging from 300 - 500 °C. McNeill *et al.* believe that only a homolytic mechanism can explain the whole range of degradation products formed, in particular the large quantities of CO and CO_2 formed throughout the main temperature range of decomposition. If the main chain degradation process of PET were to proceed via a non-homolytic degradation mechanism, continuous formation of CO and CO_2 would only be observed at the highest degradation temperatures. However, from the results presented above, copious amounts of both CO and CO_2 were formed alongside other degradation products at a range of degradation temperatures between 400 and 550 °C. Although Zimmermann [5] argues that a homolytic degradation reaction is not possible, as it is not inhibited by free radical trapping agents, the mechanism thought to occur involves only homolysis followed by H-abstraction, mainly by disproportionation of the pair of radicals formed as a result of homolytic scission. Only chain reaction mechanisms are reported to be inhibited by radical trapping reagents.

Therefore, the predominant reaction in the thermal degradation of PET is likely to involve homolytic bond scissions in the polymer backbone as illustrated in *Figure 4.37*. The resultant radicals can then abstract hydrogen from elsewhere in the system or undergo disproportionation reactions with other radicals formed as a result of homolytic scission. These chain scission reactions account for the products identified, in particular the significant formation of CO and CO_2.

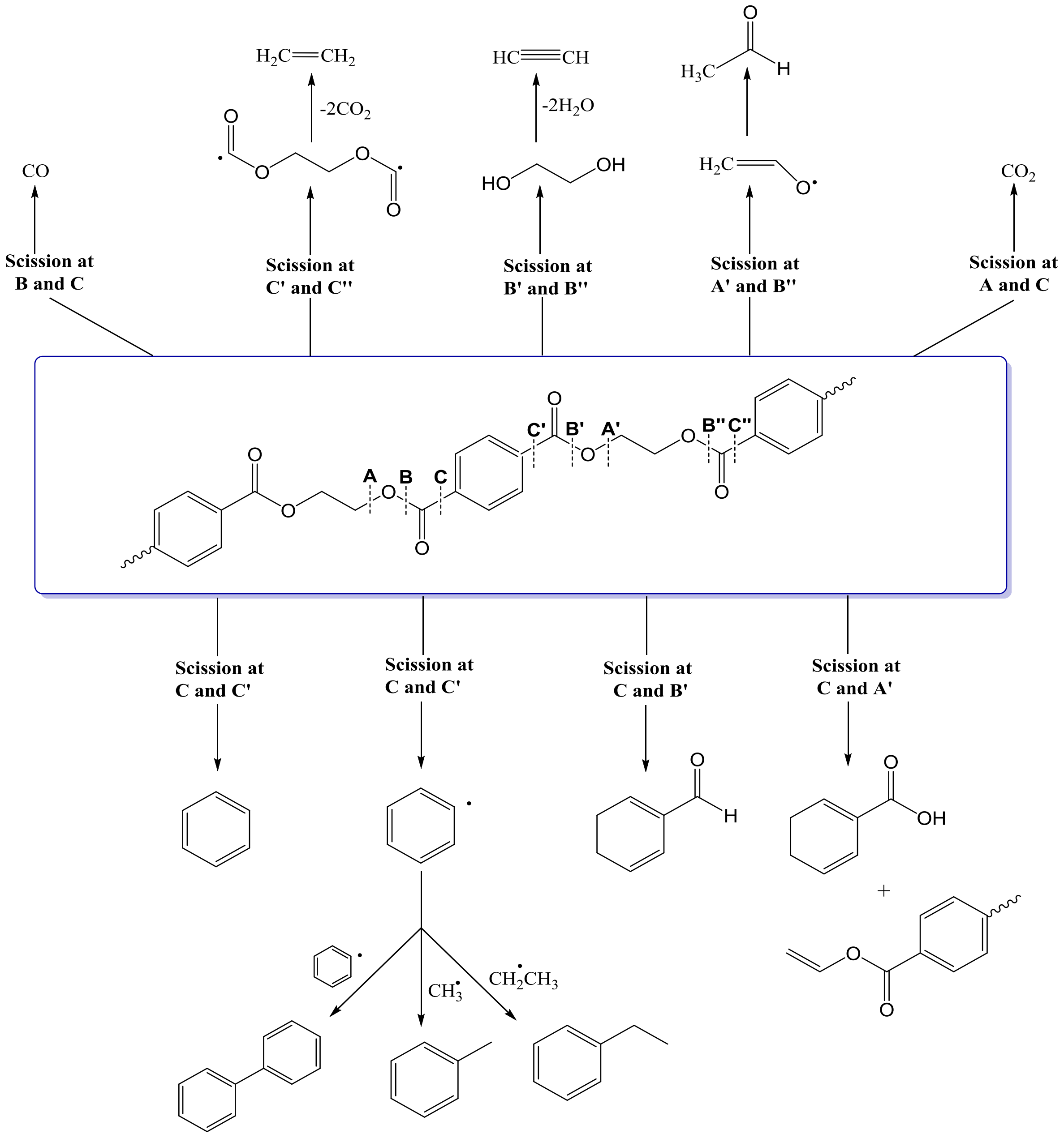

Figure 4.37 Basic homolytic mechanism for the thermal degradation of PET

Variations in this basic homolytic degradation scheme proposed in *Figure 4.37* can be derived resulting in the formation of a variety of products often containing alkyl, acidic, aldehydic or vinyl groups at one or both ends of the polymer chain. CO and CO_2 are continuously formed by homolytic degradation reactions at the alkyl-oxygen or acyl-oxygen link respectively, followed by H-abstraction by the radicals formed.

Identical homolytic chain scission reactions are thought to occur during the degradation of PEN, leading to the formation of volatile degradation products such as ethylene, acetylene, acetaldehyde, naphthalene and methyl naphthalene alongside large quantities of carbon monoxide and carbon dioxide. High molar mass degradation products including oligomeric PEN and degradation fragments containing alkyl, acidic, aldehydic, ester and vinyl functionalities on the naphthalene rings were also identified in the cold ring fraction from PEN, with similar end group nature to those observed for PET. Minor differences in the product distribution between volatile species of PET and PEN were highlighted; however these variations are thought to be due to the distinct differences in volatility between benzene and naphthalene. Therefore, it is possible to suggest an essentially similar mechanism of decomposition for both polyesters.

Figure 4.38 summarises the homolytic bond scissions likely to occur during the thermal degradation of PEN. Scission of different bonds in the polymer backbone, followed by H-abstraction or disproportionation reactions, account for the products identified, in particular the large quantities of CO and CO_2.

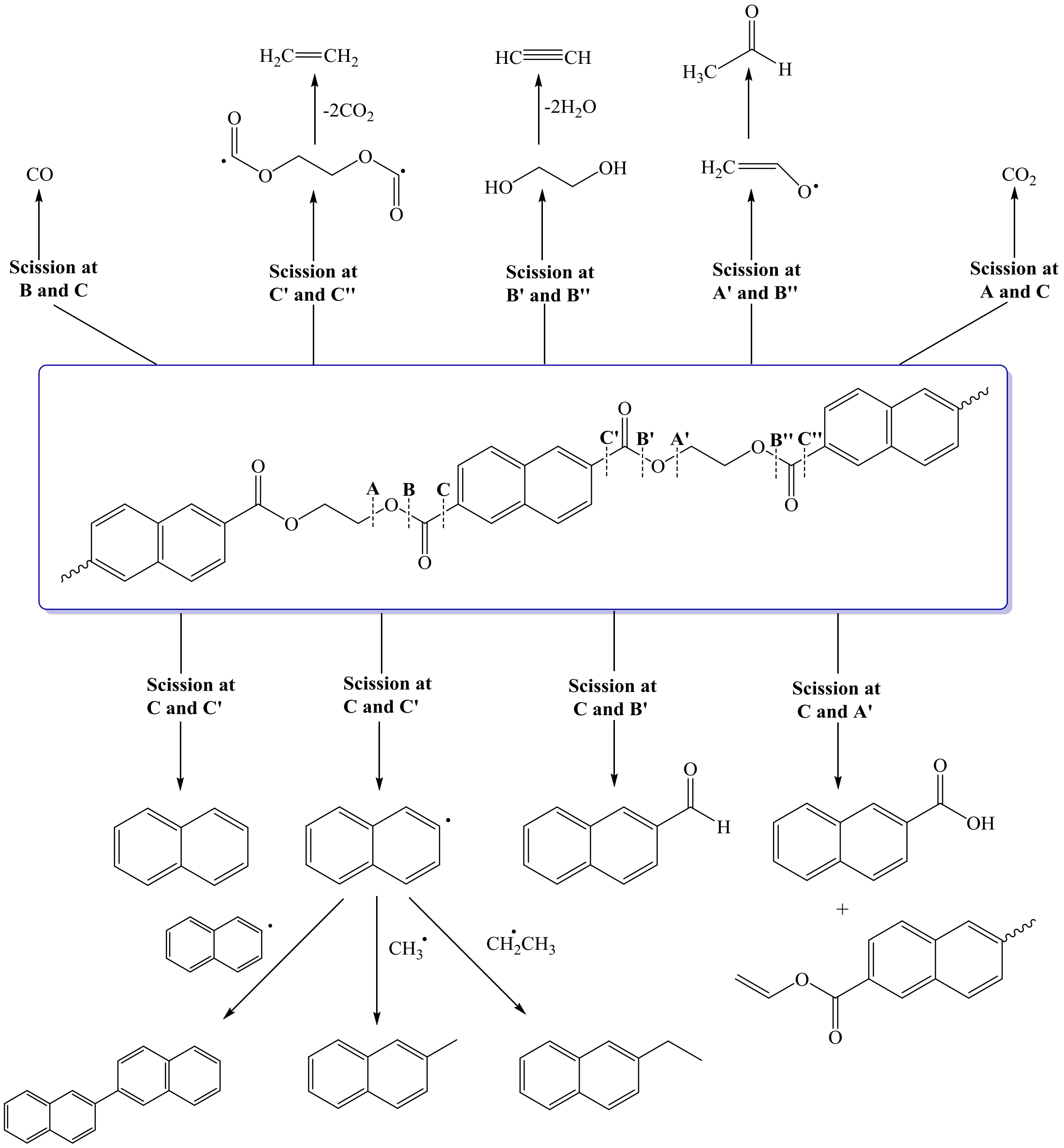

Figure 4.38 Basic homolytic mechanism for the thermal degradation of PEN

4.3.2.2 TVA of PET and PEN at Processing Temperature

During the processing of PET and PEN into biaxially oriented polyester film, both polymers are subject to high temperatures under inert and oxidative environments. Processing temperatures in the order of 320 ^{o}C are often required due to the high melt temperatures and melt viscosity of both polyesters. However, such high processing temperatures can often lead to thermal/thermo-oxidative degradation leading to the evolution of volatile degradation products and significant loss of crucial polymer properties. DuPont Teijin Films are particularly interested in the underlying degradation chemistry of PEN, in comparison to PET, in the processing temperature regime of 288 – 320 ^{o}C. The following study therefore focuses on developing a basic understanding of the degradation of PET and PEN, at typical processing temperatures, using TVA. Previously, TGA and DSC degradation studies have shown that very little degradation occurs around 300 ^{o}C for both polymers, however as TVA is conducted under vacuum, this enables the degradation products to be directly removed from the polymer melt, prior to participating in secondary degradation reactions.

- ***Degradation Profiles of PET and PEN at Processing Temperature***

The TVA thermogram profiles, for the degradation of PET and PEN at processing temperatures, are presented in *Figure 4.39*. Due to lower degradation temperatures, the pressure changes, corresponding to the presence of both condensable and non-condensable degradation species are significantly reduced in comparison to those shown previously for degradation studies up to 550 ^{o}C. The TVA furnace temperatures appear higher than 288 ^{o}C to 320 ^{o}C, as the furnace temperatures were increased to ensure the samples were sustained at the correct isothermal temperatures.

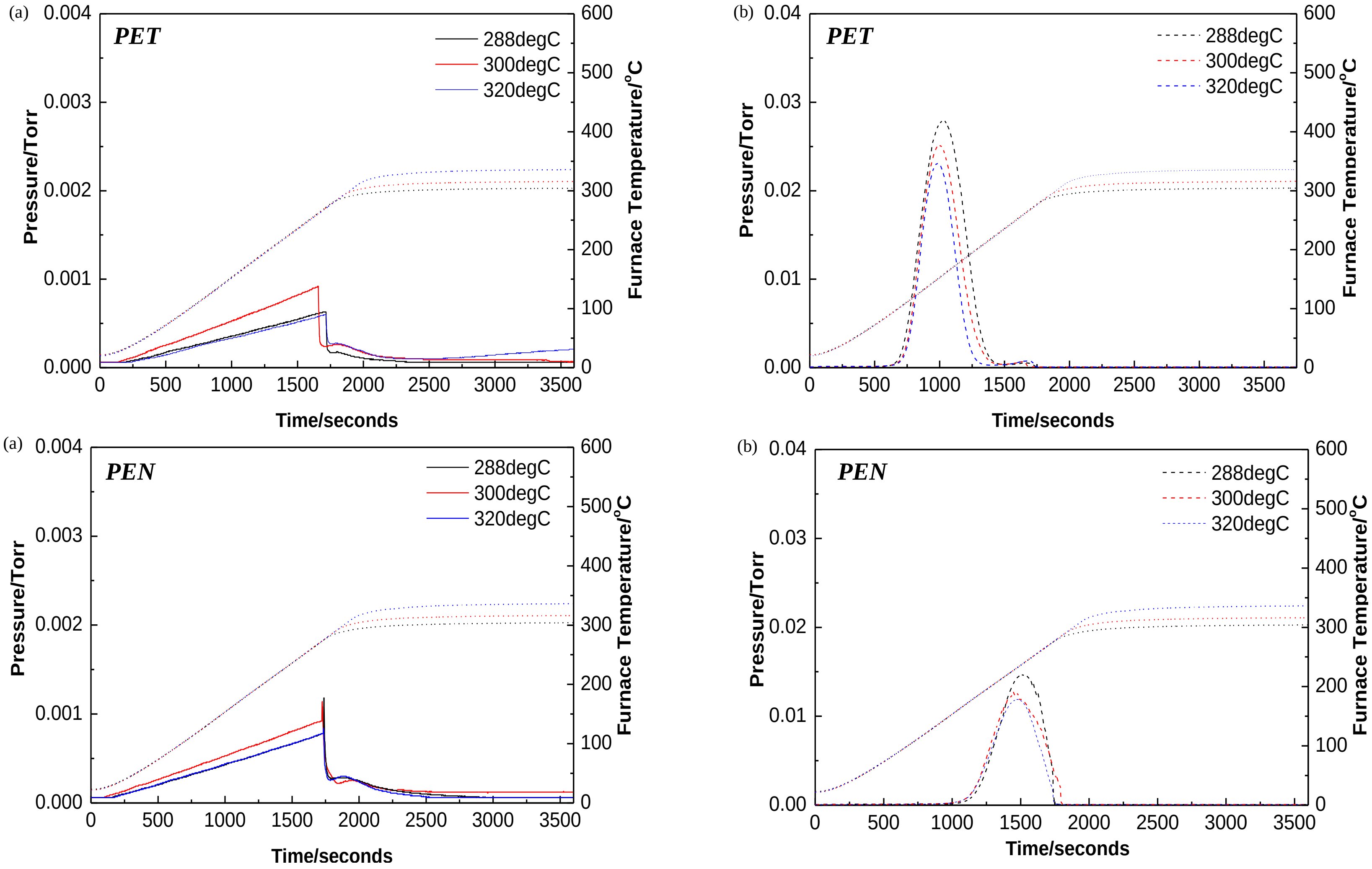

Figure 4.39 TVA thermograms showing total evolution of (a) all volatile species and (b) non-condensable species in PET and PEN at 288 °C, 300 °C and 320 °C

The TVA degradation profiles for both PET and PEN at typical processing temperatures were found to be swamped by the presence of solvent. As thin film samples were cast from solution, trapped solvent was found to volatilise at temperatures between 135 ^{o}C and 300 ^{o}C, resulting in rapid pressure changes. Besides the major pressure changes as a result of volatilisation of solvent, only minor pressure changes were observed, thought to be a result of polyester degradation. From isothermal TGA studies of PET polymer chip, completed as part of a separate research programme, mass loss for PET was found to be as low as 1% over a 60 minute period (see *Chapter 8 Supplementary Material* for TGA data). Minimal TVA pressure changes, at such low degradation temperatures, are therefore not particularly surprising and contributed to the difficulties that arose in deducing accurate onset temperatures of degradation.

Online mass spectrometry did not detect any non-condensable degradation species such as CO, methane or hydrogen from PEN. However, small traces of CO were detected from the degradation of PET at isothermal temperatures of 300 ^{o}C and 320 ^{o}C. This supports previous data suggesting PEN has increased thermal stability in contrast to PET.

On completion of the degradation process, the sub-ambient distillation was then performed to collect all condensable volatile species. This was followed by collection of cold ring fractions for both polyesters.

- ***Sub-Ambient Distillation Data for PET and PEN at Processing Temperatures***

During the sub-ambient distillation of PET and PEN, four separate fractions were collected from both polymers. The sub-ambient distillation profiles for PET and PEN, following isothermal holds at 288 ^{o}C – 320 ^{o}C, are illustrated in *Figure 4.40* and *4.41*. Significant differences are evident in the levels of condensable volatile products at the three temperatures of interest for both PET and PEN.

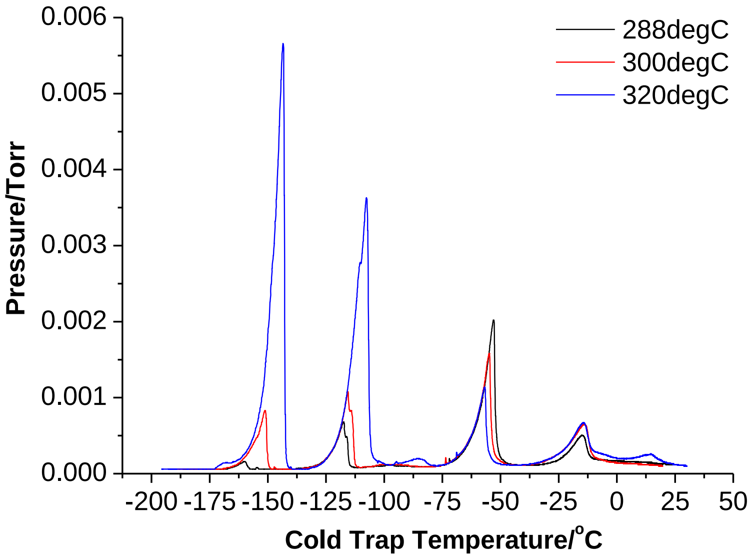

Figure 4.40 Sub-ambient TVA curves for degradation products of PET from isothermal studies at 288 °C, 300 °C and 320 °C

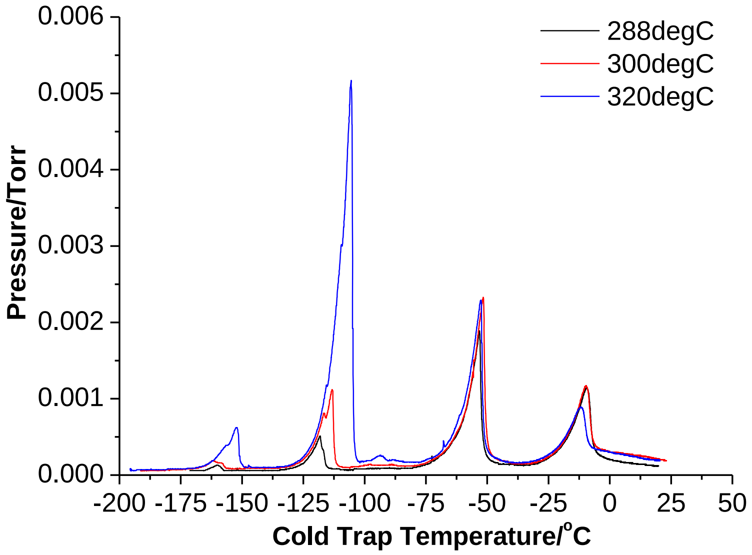

Figure 4.41 Sub-ambient TVA curves for degradation products of PEN from isothermal studies at 288 °C, 300 °C and 320 °C

Table 4.7 illustrates the degradation products isolated from PET and PEN at processing temperatures of 288 °C – 320 °C. The composition of degradation products, identified by online MS, were found to be identical for PET and PEN at all three temperatures of interest, highlighting the strong similarities in the mechanisms by which both polyesters thermally degrade. IR analysis was also performed on all fractions collected from PET and PEN, and GC-MS analysis for fraction 4 species, however due to the very small quantity of degradation products produced, identifying the exact nature of degradation products proved difficult. The IR and GC-MS spectra, generated during isothermal TVA studies for all fractions of PET and PEN, can be found in *Chapter 8 Supplementary Material*.

Fraction	***Temperature range collected***	***Major degradation product(s)***
1	-196 °C to -137 °C	Carbon dioxide
2	-136 °C to -78 °C	Acetaldehyde
3	-77 °C to -40 °C	Water
4	-39 °C to 25 °C	Ethylene Glycol

Table 4.7 Sub-ambient distillation products collected from the degradation of PET and PEN at temperatures of 288 °C, 300 °Cand 320 °C

On increasing the temperature from 288 °C to 320 °C, the generation of CO_2 was found to increase in both polyesters. Generation of CO_2 in PET at 320 °C was found to be significantly increased in contrast to PEN, indicative that extensive degradation, leading to the production of secondary degradation products, is increased for PET in comparison to PEN. Both PET and PEN were found to generate similar quantities of both acetaldehyde and water, identified in fractions 2 and 3, respectively. On increasing the temperature from 288 °C to 320 °C, increasing quantities of acetaldehyde were generated from both PET and PEN. In addition to CO_2, acetaldehyde and water, previously identified from degradation studies of PET and PEN up to temperatures of 550 °C, ethylene glycol was identified in fraction 4 from PET and PEN. The mass spectrum of ethylene glycol is illustrated in *Figure 4.42*. The levels of ethylene glycol formed in PET and PEN were similar at all isothermal temperatures.

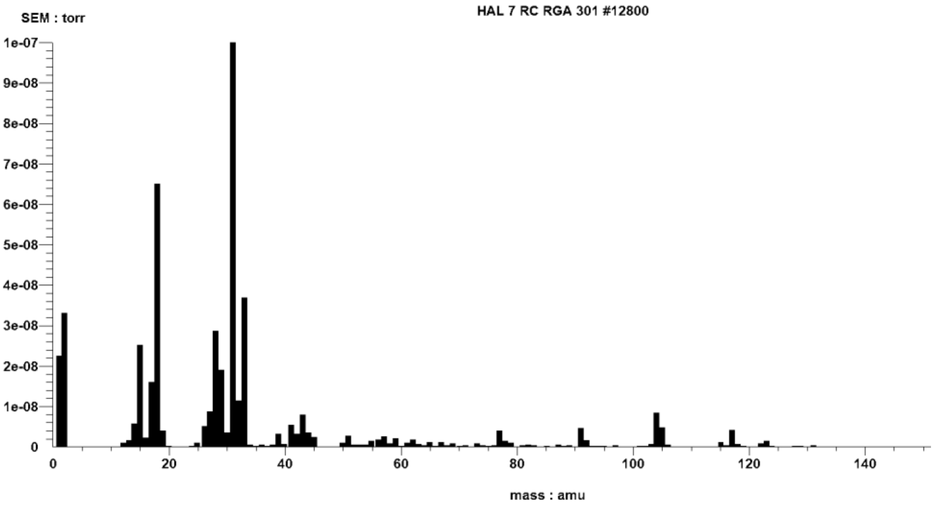

Figure 4.42 Mass spectrum of ethylene glycol - isolated from PET and PEN fraction 4 at isothermal degradation temperatures of 288 °C, 300 °C and 320 °C

▪ *Cold-Ring Fractions of PET and PEN at Processing Temperature*

The cold ring fractions from PET and PEN, containing high boiling point degradation products condensable at room temperature, were found to consist of a very small amount of white solid. Once again, due to the poor solubility of the cold ring fractions in chloroform and many other common laboratory solvents, the samples were primarily suited for IR analysis. The IR spectra obtained for the cold ring fractions of PET and PEN are illustrated in *Figures 4.43* and *4.44*. GC-MS analysis was performed on all cold ring fractions of PET and PEN, however no degradation species could be identified and all spectra consisted of peaks eluting as a result of column contamination and/or impurities. The GC-MS spectra for all PET and PEN cold ring fractions can be found in *Chapter 8 Supplementary Material.*

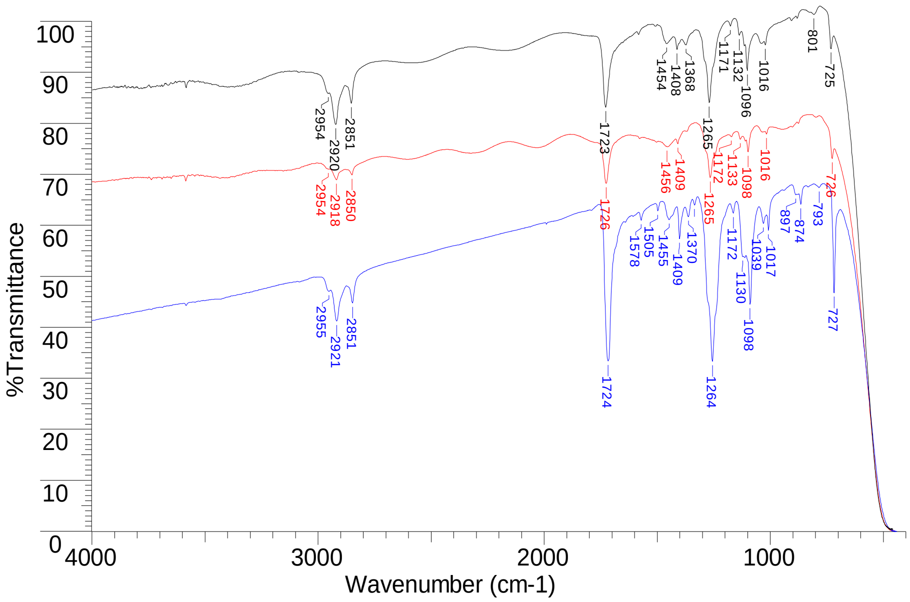

Figure 4.43 IR spectra of PET cold ring fraction at isothermal degradation temperatures of 288 °C, 300 °C and 320 °C

The results presented in *Figure 4.43* indicate the presence of mainly oligomers within the cold ring fractions of PET. The IR spectra are particularly weak at the lower isothermal temperatures of 288 °C and 300 °C due to the small quantity of cold ring fraction generated; however as the concentration of cold ring fraction increases at 320 °C, the intensity of the IR absorption bands improves. For all PET cold ring fractions, aliphatic C-H stretching of CH_2 units in PET can be observed around 2954 cm^{-1}, 2920 cm^{-1} and 2851 cm^{-1} alongside a weak C=O absorption band at 1725 cm^{-1} for ester groups present in oligomeric PET. Aromatic skeletal C-H stretching from the phenyl rings in PET are evident from 1578 cm^{-1} to 1368 cm^{-1} and the C(O)-O stretching and bending vibrations of ester groups in PET can be observed at 1265 cm^{-1} and 1130 cm^{-1}, respectively. Aromatic bands in the skeletal region of 1172 cm^{-1} to 1016 cm^{-1} indicate 1,4 substitution of aromatics, in addition to IR absorption bands in the region of 874 cm^{-1} representing C-H out-of-plane deformations of para-substituted benzene rings in PET. The aromatic C-H bending mode from disubstituted benzene rings in PET can be observed at 727 cm^{-1}. A lack of carboxylic acid or vinyl ester absorption bands must be highlighted from this IR analysis indicative that the oligomers of PET generated at typical processing temperatures are most likely to be cyclic rather than linear oligomers.

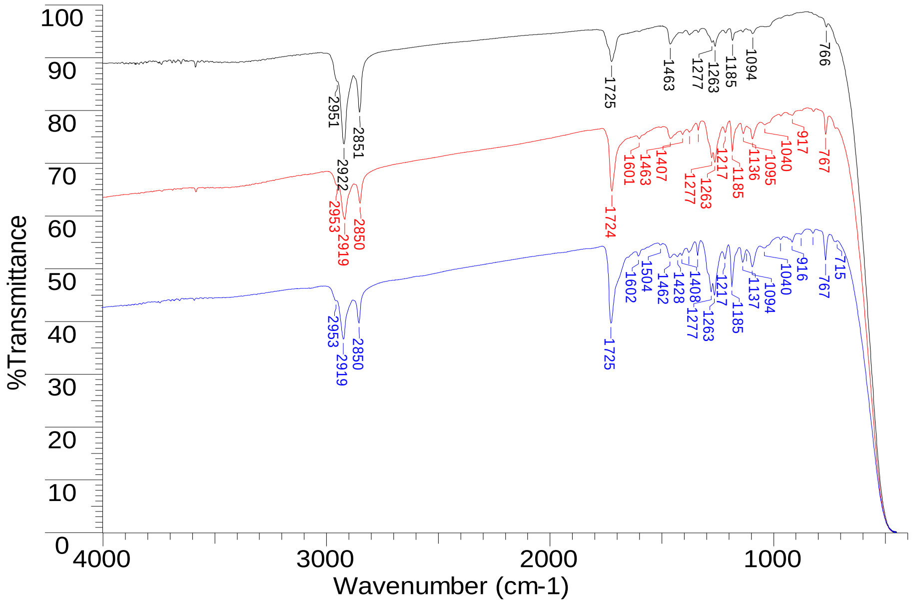

Figure 4.44 IR spectra of PEN cold ring fraction at isothermal degradation temperatures of 288 °C, 300 °C and 320 °C

Similarly, the cold ring fractions collected from the isothermal degradation studies of PEN were also found to contain short chain oligomers of PEN. Once again, the IR absorption bands are weak due to the small quantity of cold ring fraction obtained from each analysis, however distinct IR absorption bands can still be observed in *Figure 4.44*. Aliphatic C-H stretching of the CH_2 units in PEN can be observed at 2920 cm^{-1} and 2850 cm^{-1} alongside a C=O absorption band at 1725 cm^{-1} for ester groups present in oligomeric PEN. Aromatic skeletal C-H stretching from the naphthalene rings in PEN are evident from 1601 cm^{-1} to 1408 cm^{-1} and the C(O)-O stretching vibrations of ester groups can be observed at 1277 cm^{-1}, 1263 cm^{-1} and 1185 cm^{-1}. C(O)-O bending vibrations of ester groups in PEN are also evident at 1137 cm^{-1} and 1095 cm^{-1} with out of plane deformations of two carbonyl substituents on aromatic rings visible around 767 cm^{-1}. These IR bands, observed at all three isothermal temperatures, are all identical to those observed in the cold ring fractions of PEN when degraded up to 550 °C. However, key IR absorption bands are absent for carboxylic acid and vinyl end groups indicating that the cold ring fractions of PEN are most likely to consist of cyclic oligomers rather than linear oligomers, as previously highlighted for isothermal cold ring fractions of PET.

4.3.2.3 Discussion of the Thermal Degradation Mechanisms in PET and PEN at Processing Temperature

From the degradation studies of PET and PEN at typical processing temperatures, it is evident that few degradation species reach the main cold trap, in comparison to the significant quantity of degradation species reported from TVA studies performed at temperatures upto 550 ^{o}C. This highlights a significant reduction in the extent of thermal degradation in both PET and PEN.

The formation of significant quantities of CO and CO_2, formed from secondary chain scission reactions of the polymer chains, was found to be absent during the degradation of PEN at temperatures of 288 ^{o}C to 320 ^{o}C. However, traces of CO and CO_2 were detected from the degradation of PET at 300 ^{o}C and 320 ^{o}C. This is not entirely surprising due to the reduced thermal stability of PET, in comparison to PEN. The formation of CO and CO_2 from the degradation of PET indicates that the overall extent of thermal degradation occurring in PET is increased in comparison to PEN.

Despite the limited evolution of condensable volatile degradation species in the main cold trap during the isothermal degradation studies of PET and PEN, oligomers were identified in the cold ring fractions of both PET and PEN at all three temperatures. Due to the absence of carboxylic acid or vinyl end groups in the IR spectra for the cold ring fractions of PET and PEN, it is thought that these oligomers are cyclic and not linear oligomers. These observations are in agreement with the degradation mechanism proposed by Montaudo *et al.* [6] who studied the degradation products of PET at processing temperatures (270 - 370 ^{o}C) using Matrix – Assisted Laser Desorption Ionisation (MALDI) spectrometry. Montaudo *et al.* report that the main degradation products observed from PET are cyclic oligomers which only open and degrade after prolonged exposure to heat and increased temperatures (i.e. greater than 370 ^{o}C). Therefore it is thought that the formation of cyclic oligomers is the dominant degradation reaction in PET and PEN at temperatures of 288 - 320 ^{o}C. These cyclic oligomers are then thought to undergo a series of further degradation reactions after prolonged exposure at this temperature to produce degradation species such as acetaldehyde and ethylene glycol, with more extensive degradation occurring in PET than PEN. The formation of these degradation products is thought to occur via ionic processes, and not radical chain scission reactions due to the absence of significant quantities of CO and CO_2. A mechanism for the formation of cyclic oligomers in PET is proposed in *Figure 4.45*. This reaction mechanism proposed is thought to be identical for the formation of cyclic oligomers in PEN, however the extent of cyclic oligomer formation is expected to be reduced in PEN, in comparison to PET, due to the presence of bulky naphthalene species reducing the ease at which such back-biting mechanisms can occur.

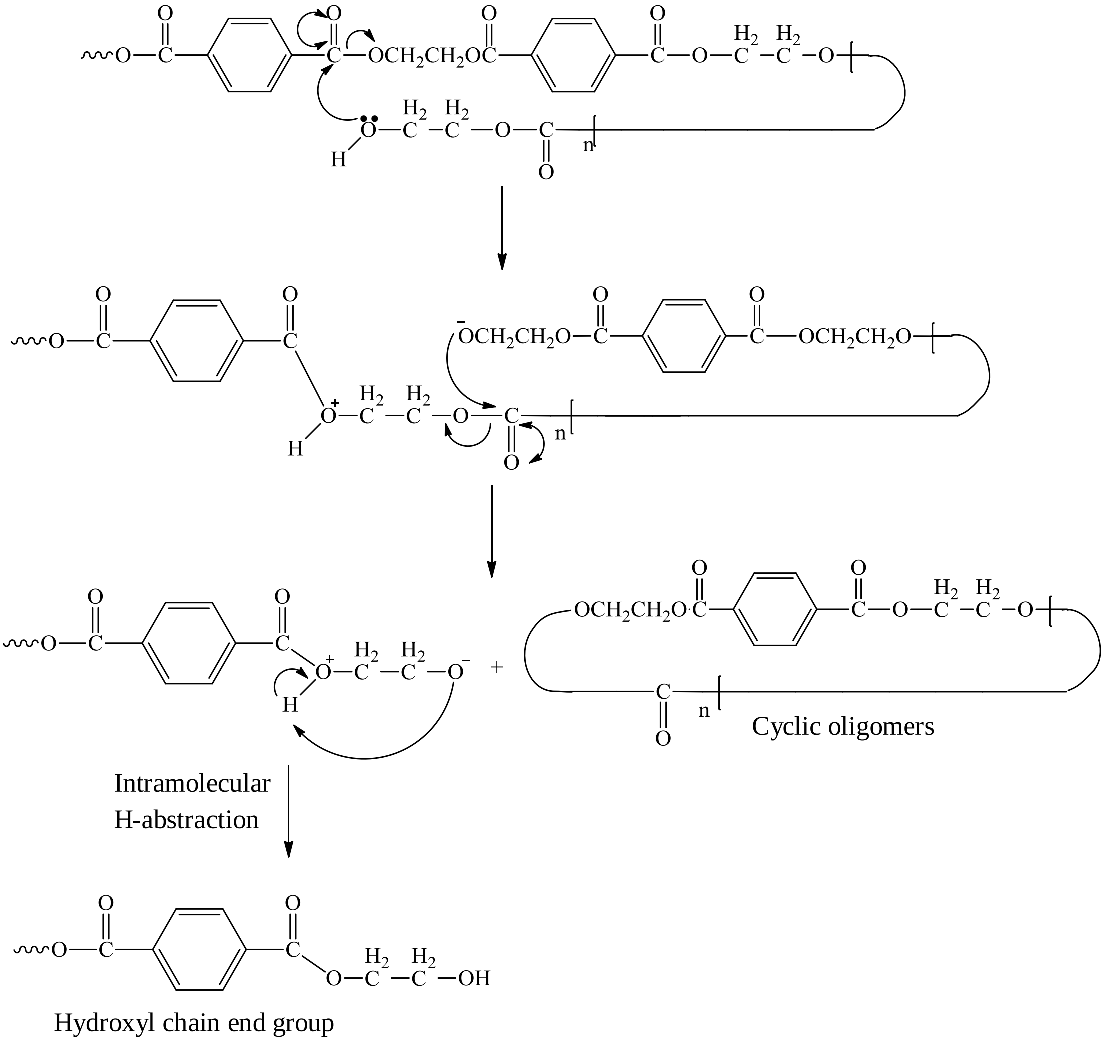

Figure 4.45 Mechanism for the formation of cyclic oligomers in PET and PEN

The intramolecular cyclisation reaction, illustrated in *Figure 4.45*, results in the formation of cyclic oligomers and hydroxyl chain end groups. These hydroxyl chain end groups can then undergo scission to result in the formation of vinyl alcohol, which can rearrange instantaneously to form acetaldehyde. This reaction is illustrated in *Figure 4.46*.

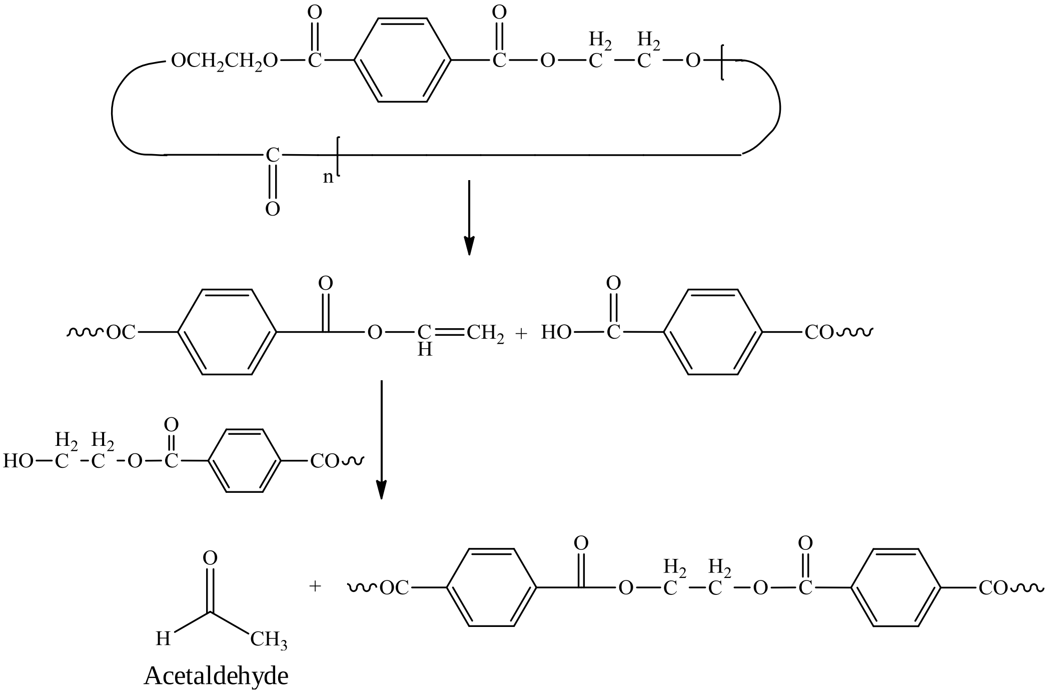

Figure 4.46 Mechanism for the formation of acetaldehyde in PET and PEN

Additionally, it is proposed that the hydroxyl chain end groups undergo another intramolecular cyclisation reaction with oligomeric PET to result in the formation of ethylene glycol. This reaction is illustrated is *Figure 4.47*. Both reaction mechanisms proposed in *Figures 4.46* and *4.47* are thought to be identical for PET and PEN.

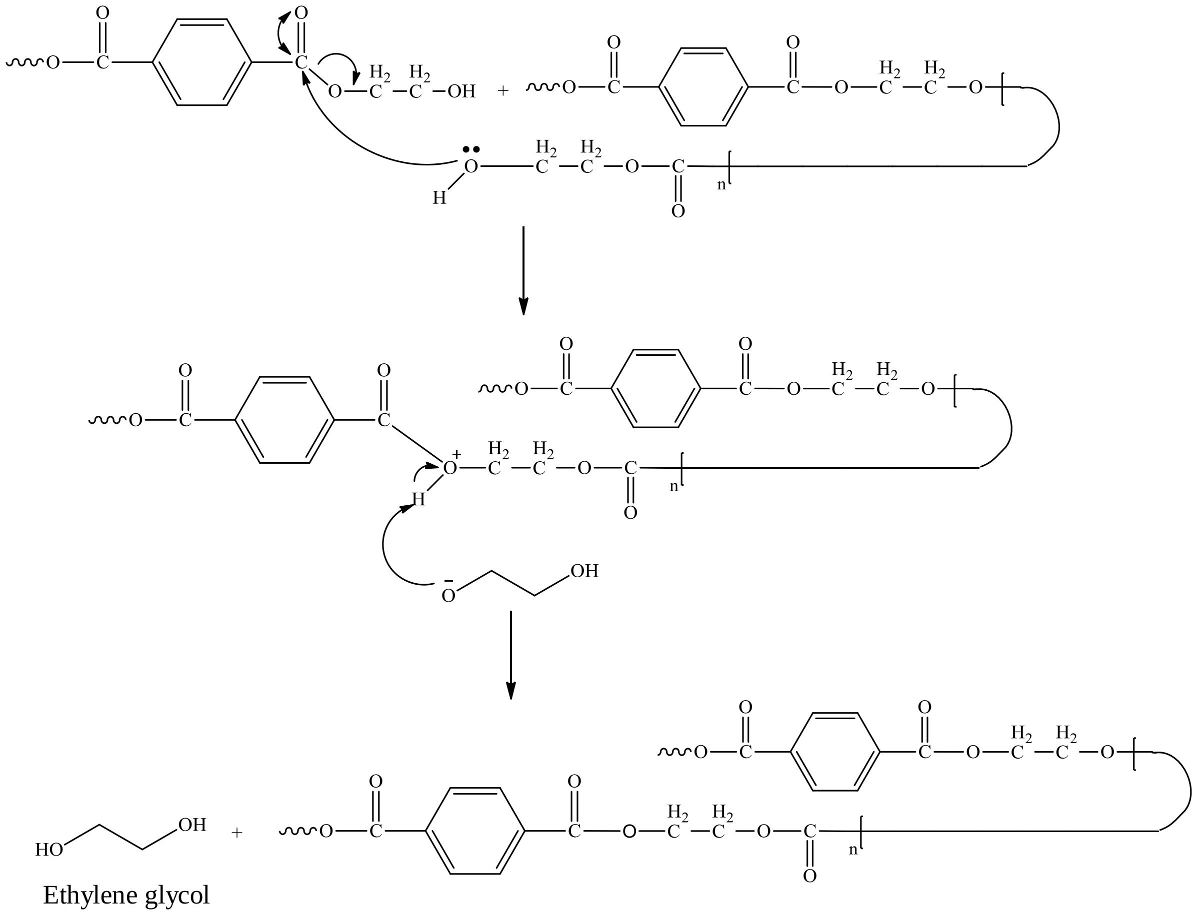

Figure 4.47 Mechanism for the formation of ethylene glycol in PET and PEN

Although the reaction schemes proposed in *Figures 4.45 – 4.47* are predominately based on ionic mechanisms, a combination of both ionic and homolytic degradation reactions are thought to occur over the temperature range of degradation i.e. 288 - 550 °C. It is very unlikely that the degradation mechanism of PET and PEN is predominately homolytic at processing temperatures due to the negligible quantities of CO and CO_2 produced from PET and the absence of CO and CO_2 from PEN. However, as the degradation temperature increases, radical chain scission processes are thought to dominate, leading to the production of copious quantities of CO and CO_2. The absence of CO and CO_2 from PEN suggests that the overall extent of thermal degradation occurring in PEN is reduced in comparison to PET. As highlighted on many occasions previously, this is thought to be due to the increased thermal stability of PEN.

4.4 Conclusions

Degradation studies have been performed on PET and PEN in an attempt to compare the fundamental degradation pathways of both polyesters under different environmental and temperature regimes. All DSC, TGA and TVA studies highlight strong similarities in the degradation behaviour of both polyesters.

From DSC, TGA and TVA results, both PET and PEN are thought to undergo one major thermal degradation process. This thermal degradation reaction involves thermal scission of ester bonds in the polyester chains resulting in the formation of vinyl ester and carboxylic acid end groups. This primary thermal degradation reaction is thought to be identical for both polymers; however it is still unknown whether this reaction proceeds via an ionic or radical mechanism.

TVA studies highlight that thermal degradation of PET occurs above temperatures of 365 ^{o}C subsequently leading to the release of volatile species. PET oligomers and small chain fragments containing acid, aldehydic, ester and vinyl functionalities were the largest, high boiling point degradation species identified. Copious quantities of carbon monoxide and carbon dioxide were also identified alongside condensable species such as ethylene, acetylene, acetaldehyde, toluene, benzene, water, benzaldehyde, benzoic acid. A mechanism for the thermal degradation of PET has been proposed, to account for the generation of all degradation species.

An essentially similar mechanism of decomposition has been proposed from TVA degradation studies of PEN. Identical random chain scission reactions are thought to occur at temperatures above 380 ^{o}C for PEN, highlighting the increased thermal stability of PEN over its terephthalate counterpart. Such reactions lead to the formation of volatile degradation products including ethylene, acetylene, acetaldehyde, naphthalene and methyl naphthalene alongside large quantities of non-condensable carbon monoxide and condensable carbon dioxide. High molar mass degradation products including oligomeric PEN and degradation fragments containing alkyl, acidic, aldehydic, ester and vinyl functionalities on the naphthalene rings were also identified. Minor differences in the product distribution between volatile species of PET and PEN have been highlighted, proposed to be a result of the distinct differences in volatility between benzene and naphthalene species.

On degrading PET and PEN at typical processing temperatures, few degradation species were detected, highlighting a significant reduction in the extent of thermal degradation of PET and PEN up to temperatures of 320 °C. Significant quantities of CO and CO_2, formed from secondary chain scission reactions of the polymer chains, were absent during the degradation of PEN at temperatures of 288 °C to 320 °C. However, traces of CO and CO_2 were detected from the degradation of PET at 300 °C and 320 °C thought to be due to the reduced thermal stability of PET and thus increased thermal degradation activity, in comparison to PEN.

Despite limited evolution of condensable volatile degradation species during isothermal degradation studies of PET and PEN, the dominant degradation reaction appears to be the formation of cyclic oligomers at temperatures between 288 – 320 °C. These cyclic oligomers are then thought to undergo a series of further degradation reactions after prolonged exposure to produce degradation species such as acetaldehyde and ethylene glycol, with more extensive degradation observed in PET than PEN. An identical reaction mechanism for the formation of cyclic oligomers in PET and PEN has been proposed, however the extent of cyclic oligomer formation is expected to be reduced in PEN, in comparison to PET, due to the presence of bulky naphthalene species reducing the ease at which such back-biting mechanisms can occur. The formation of these degradation products is thought to occur via ionic processes, and not radical chain scission reactions due to the absence of significant quantities of CO and CO_2.

Finally, TGA and DSC results for the thermo-oxidative degradation of PET and PEN indicate that PET is more sensitive to degradation in the presence of oxygen in contrast to degradation under purely thermal conditions. Interestingly, this marked decrease in the thermo-oxidative stability of PET was not observed in PEN. PEN is therefore thought to be more resistant to thermo-oxidative degradation in comparison to PET.

4.5 References

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5 INVESTIGATING THE ROLE OF OXYGEN AND WATER ON THE DEGRADATION OF PET AND PEN AT PROCESSING TEMPERATURES

5.1 Background to Research

From the TVA evidence presented in *Chapter 4*, the fundamental thermal degradation mechanisms for PET and PEN do not appear to significantly differ. However, as TVA is conducted under vacuum, these conditions do not mimic a typical processing environment for polyesters, with degradation products having the ability to rapidly escape from the polymer melt, leaving little opportunity for secondary degradation reactions. This research will therefore examine the degradation of PET and PEN under controlled processing conditions. Thermal, thermal-hydrolytic, thermo-oxidative and thermo-oxidative-hydrolytic studies have been completed to investigate the role of oxygen and water on the degradation of PET and PEN at typical processing temperatures.

In contrast to many research studies, looking to examine degradation behaviour as a means of prevention, the overall aim of this research is to identify die lip atmospheric conditions best suited to promoting volatilisation of PEN and thus minimising die streaks within PEN films. As PEN is extruded through the film process, a stagnant zone is known to exist at the die lip exit whereby polyester debris collects. This debris continues to degrade with each subsequent processing cycle, at high processing temperature, often resulting in the formation of gels and inorganic residues which can either flow out with the melt curtain or wet-along the die face subsequently resulting in die streaks. By identifying suitable die lip atmospheric conditions, which reduce the extent of polyester debris by means of promoting volatilisation, it is hoped that a substantial reduction in the extent of die streak formation will result.

Volatilisation studies were initially completed at processing temperatures to examine the impact of different environmental conditions on the extent of degradation in

PEN, in contrast to PET. Structural information on these polyester residues aged under dry, wet, inert and oxidative environments were gained using ^{13}C solid-state NMR and gel quantification studies. Melt-rheology studies also monitored the viscosity changes of PET and PEN, under both inert and oxidative environments at the processing temperatures of interest. Finally, high humidity studies of PET and PEN were completed to examine the effects of high moisture levels on the degradation of both polyesters. Together, these results enabled the effects of thermal, thermal-hydrolytic, thermo-oxidative and thermo-oxidative-hydrolytic degradation to be evaluated in PET and PEN at typical processing temperatures.

5.2 Experimental Details

5.2.1 Materials

All PET and PEN film samples analysed throughout this study were provided by DuPont Teijin Films. All chlorinated solvents used were obtained from Sigma-Aldrich Chemical Company and 1,1,1,3,3,3-Hexafluoroisopropanol was obtained from Apollo Scientific Ltd.

PET was supplied as A4 sheets of Melinex OD, at a thickness of 125 μm. This sparkling, clear grade of PET film is most suitable for applications where very high transparency is required. PEN was supplied as A4 sheets of 125 μm Q65FA film. Q65FA is a highly transparent, biaxially oriented PEN film suitable for optical and optoelectronic applications. In contrast to Melinex OD, this grade of PEN is treated on one side during processing to provide enhanced adhesion, winding and handling properties. The film is also further processed in comparison to PET to reduce thermal shrinkage levels and maintain dimensional stability and reproducibility through high temperature processing steps.

Basic physical and degradation properties of PET and PEN polyester film used throughout this study were investigated. The thermal and degradation properties were found to be identical to those discussed previously in *Chapter 4* for PET and

PEN polyester chip. The data can therefore be found in *Chapter 8 Supplementary Material*. From these preliminary examinations of the polyester films of interest, it can be expected that PET will degrade and result in a higher extent of volatilisation than PEN, particularly in the presence of air. However, promoting volatilisation of PEN may be more problematic due to the polymers increased thermal stability and reduced sensitivity to degradation in the presence of oxygen.

5.2.2 Ageing Apparatus

The purpose of this experimental study was to age samples under contrasting environments to examine the impact of different environmental conditions on the extent of degradation in PEN, in comparison to PET. With the overall aim of identifying die lip atmospheric conditions best suited to promoting volatilisation of PEN and thus minimising die streaks within PEN films, polyester film samples were aged under dry, wet, inert and oxidative environments at elevated processing temperatures for various different time intervals. Careful design of such a system, that could examine the degradation of polyester samples under both dry and wet environments, was vital to ensure that the data produced was directly applicable to the polyester film manufacturing process conducted at DuPont Teijin Films. Schematic representations of the main ageing apparatus are illustrated in *Figures 5.1 - 5.3* and discussed below.

The ageing apparatus consisted of a Lenton ARF 7/22 recirculating air furnace capable of reaching temperatures of 750 ^{o}C ± 1.0 ^{o}C. The sample chamber was composed of glass with a flat stainless steel lid, designed to withstand high ageing temperatures. Flexible stainless steel tubing was attached to the gas inlet and outlet of the sample chamber via Swagelok bulkhead unions and the lid was clamped down using spherical joint metal clips to ensure the chamber was airtight. With a large sample chamber in use, large polyester film samples could be aged, resulting in the formation of increased residual material for post-ageing analysis.

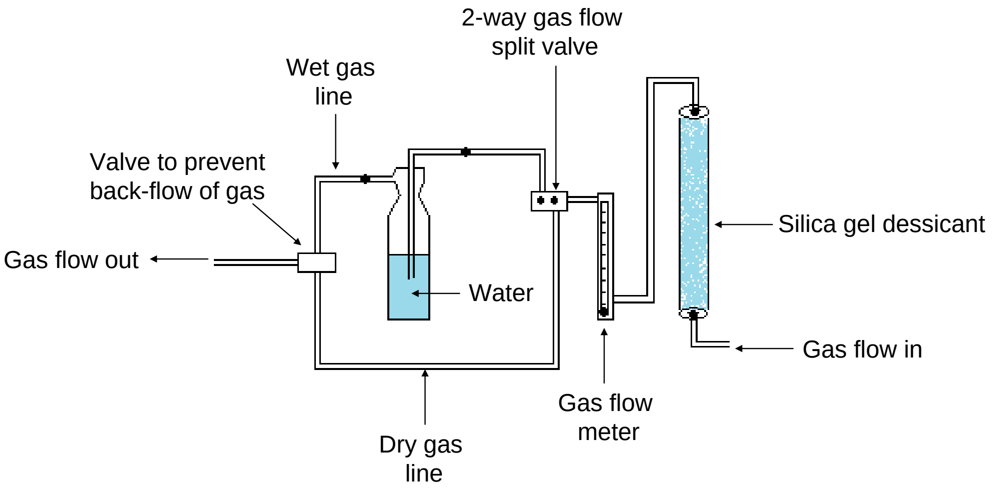


Figure 5.1 Schematic diagram of ageing equipment used to create dry and wet (1.5 - 2% AH) environments

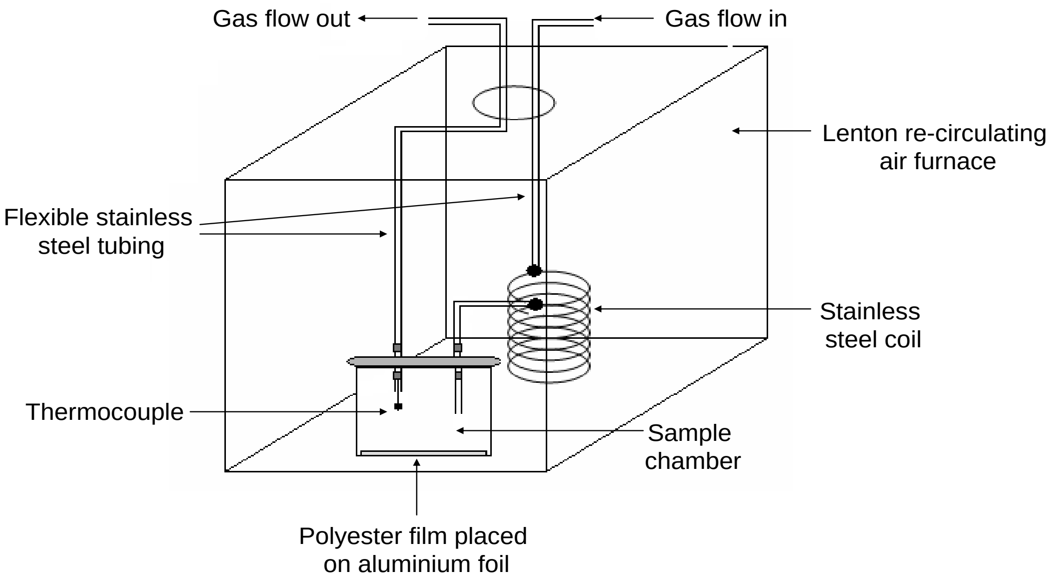


Figure 5.2 Schematic diagram of experimental apparatus for ageing

Prior to entering the sample chamber, all gases were pretreated. Gases were initially dried by passing through silica gel desiccant before reaching the gas flow controller. Separate gas lines were then created using a 2-way valve system to avoid contamination of both the dry and wet gas lines. A dreschel containing water created a wet atmosphere of 1.5 - 2% absolute humidity. On entering the oven, the selected gas was preheated by the use of a stainless steel coil, ensuring that the temperature of the sample was maintained during ageing. A thermocouple, placed 2 cm above the sample, monitored the sample temperature continuously during ageing.

To promote degradation of PET and PEN, beyond that observed during studies at low moisture levels, high humidity studies were also conducted at processing temperatures. Such studies were performed using the apparatus illustrated in *Figure 5.3*. Dry gas was purged into a large round bottomed flask placed in a DrySyn heating block on a IKA RCT classic hot plate. A known mass of H_2O was placed into the flask and a condenser was fitted with a stopper to ensure that the wet gas could only purge into the oven and thus sample chamber.

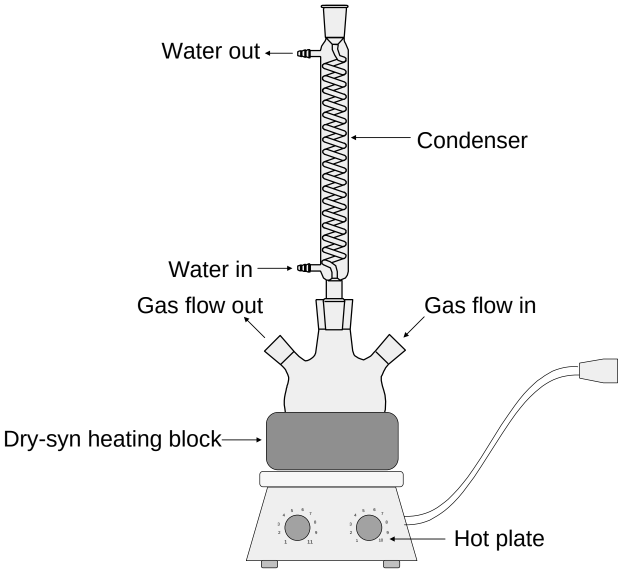


Figure 5.3 Schematic diagram of high-humidity apparatus

Upon completion of ageing, the mass of water remaining was then measured to enable the absolute humidity (AH) to be calculated. By simply varying the temperature of the hotplate (capable of reaching temperatures up to 275 ^{o}C ± 1 ^{o}C), samples were aged under different humid conditions. As the temperature of the hot plate increased and the temperature of water increased, the water levels present in the gas approached saturation.

5.2.3 Sample Preparation

Prior to ageing the polyester films, all samples were dried in a vacuum desiccator at room temperature for a minimum of 24 hours, ensuring that any residual water which may have been picked up during storage was removed. Films samples were then cut into a circular shape and placed on aluminum foil bases. To ensure maximum residual material was obtained for post-ageing analysis, maximum coverage of the surface area of the sample chamber was utilised, with sample masses of up to 1 g analysed. Accurate volatilisation calculations were performed by careful weighing of the film and aluminum foil bases before and after ageing.

5.2.4 Experimental Conditions

5.2.4.1 Gas flow rate

An optimum gas flow rate of 400 mL min^{-1} was selected for all ageing studies. This flow rate was selected to maximise the extent of volatilisation and prevent cooling of the sample. A variety of ageing studies were performed on both polyesters to select the optimum gas flow rate, based on the extent of volatilisation under typical ageing conditions. *Figures 5.4* and *5.5* illustrate the impact of gas flow rate on the extent of volatilisation of PET and PEN.

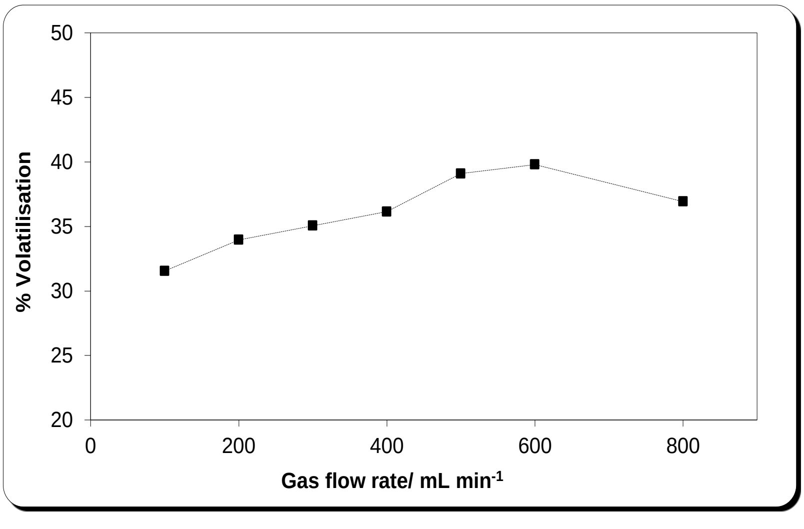


Figure 5.4 Influence of gas flow rate on volatilisation of PET aged at 320°C for 4 hours under dry air

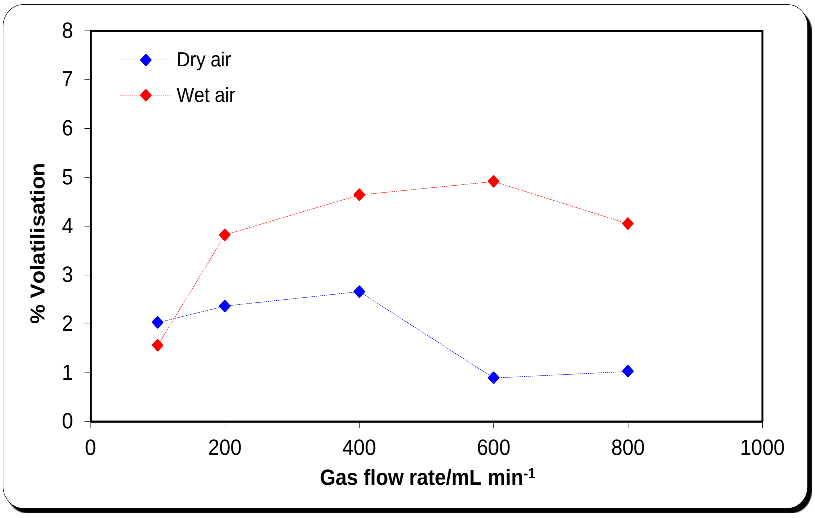


Figure 5.5 Influence of gas flow rate on the volatilisation of PEN aged at 300°C for 4 hours under dry and wet (1.5 - 2% AH) air

From *Figures 5.4* and *5.5*, it can be observed that volatilisation of both PET and PEN increases up to a gas flow rate of 400 - 600 mL min^{-1} before decreasing on approach of the highest flow rates. This decrease in volatilisation at high flow rates is due to a reduction in the temperature of the gas and subsequent cooling of the polyester sample, reducing the overall extent of volatilisation. By selecting a gas flow rate of 400 mL min^{-1}, confidence is attained that the residence time of the gas preheating in the stainless steel coil is long enough to ensure that the gas is sufficiently heated, lowering the probability of a decrease in sample temperature and thus volatilisation during ageing.

Prior to commencing all ageing experiments, the gas flow was left to purge at a rate of 400 mL min^{-1} for 15 minutes. This was particularly important for samples aged under an inert atmosphere, ensuring that all air was removed from the sample chamber. A positive gas flow, exiting the sample chamber, was monitored at the start of each ageing study to ensure the sample chamber was entirely sealed. Throughout the ageing studies, the gas flow was regulated using a flow meter programmed at 400 mL min^{-1}.

5.2.4.2 Ageing Temperatures

As this research examines the impact of different environmental conditions on the extent of degradation in PET and PEN, with the overall aim of promoting degradation for the purpose of reducing die streaks, the ageing temperatures of interest were selected based around the processing temperatures of both polyesters. Although the operating temperature of the extrusion die can be increased, the lower temperatures are obviously more economical and practical to implement. The three ageing temperatures of interest, selected by DuPont Teijin Films, were 288, 300 and 320 ^{o}C, however studies were also performed at temperatures from 270 - 380 ^{o}C. All samples were heated at a rate of 10 ^{o}C min^{-1} from room temperature up to the ageing temperature of interest. As stated previously, the sample temperature was monitored throughout every ageing study using a thermocouple positioned approximately 2 cm above the sample.

5.2.4.3 Ageing Times

All samples were aged for a period of 4 hours, with some samples selected for volatilisation studies over different time intervals between 60 minutes and 24 hours. The ageing times stated exclude an additional, 60 minute hold necessary to ensure all samples reached their target temperature.

5.2.4.4 Atmospheres of interest

A variety of ageing atmospheres were selected to enable to the effects of thermal, thermal-hydrolytic, thermo-oxidative and thermo-oxidative-hydrolytic degradation to be studied in both PET and PEN. Both dry and wet atmospheres were generated using nitrogen, air, 3% oxygen and 42% oxygen.

5.2.5 Calculations

5.2.5.1 Extent of Volatilisation

The extent of volatilisation in PET and PEN was analysed via mass loss studies. Prior to ageing, the mass of the polyester film and aluminum foil base were recorded accurately, enabling the overall % mass loss (otherwise expressed as % volatilisation) to be calculated after ageing using the following equation:

$$\% \ Volatilisation \ = \left(\left(IW_0 - AW_1 \middle/ IW_0 \right) \right) \times 100 \qquad \textbf{Equation 5.1}$$

Where IW_0 is the initial mass of the polyester film before ageing and AW_1 is the mass of the polyester film after ageing. Unfortunately, it was impossible to repeat every ageing studies due to the extensive number completed. Therefore, only an average error on the volatilisation measurements can be quoted. This error was based on the standard deviation calculated from five repeat volatilisation studies completed on PET and PEN under dry air at all three temperatures of interest. From the average volatilisation results presented in *Figures 5.6* and *5.7*, the maximum standard deviation on volatilisation measurements was calculated to be 1.5%.

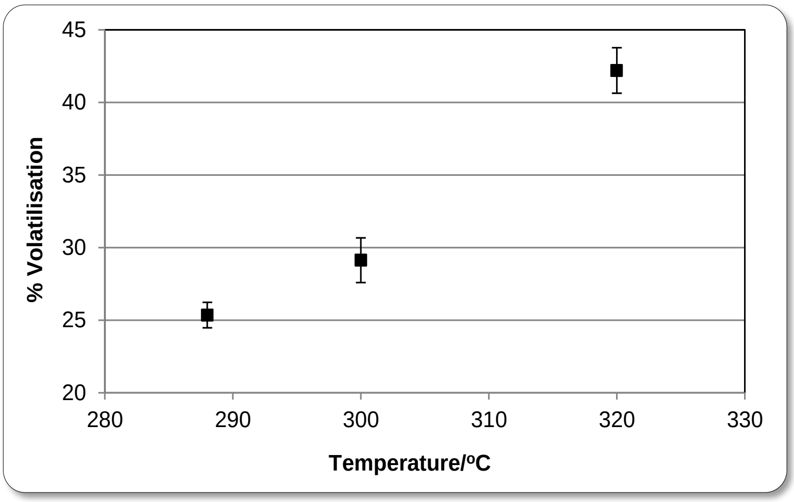


Figure 5.6 Average % volatilisation of PET aged for 4 hours under dry air at 288 °C - 320 °C. Each data point represents the average % volatilisation from five repeat studies

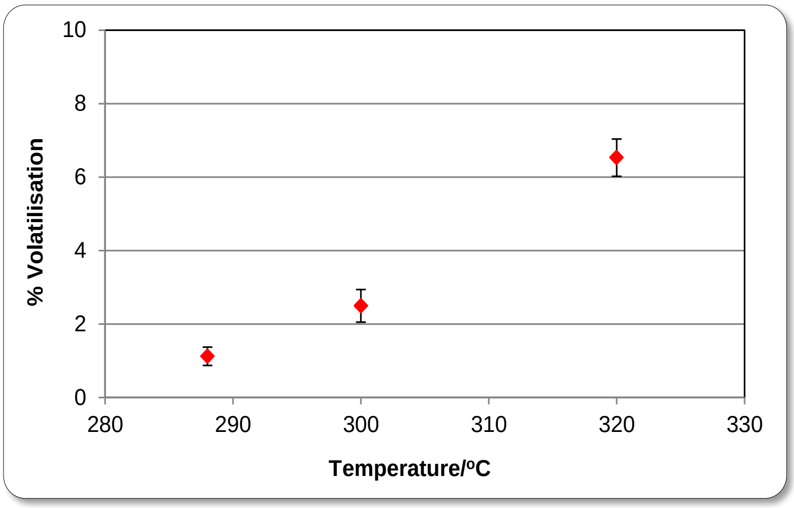


Figure 5.7 Average % volatilisation of PEN aged for 4 hours under dry air at 288 °C - 320 °C. Each data point represents the average % volatilisation from five repeat studies

5.2.5.2 Humidity Calculations

Humidity is defined as the quantity of water vapor that is present in the atmosphere and can be measured in several forms such as absolute humidity and relative humidity. In this research, all humidity ageing studies of PET and PEN were measured as % absolute humidity.

Absolute humidity (AH) is the exact quantity of water present in a given volume of air. It can be calculated on a volume basis as the mass of dissolved water vapor, M_w, per cubic meter of total moist air, V_{net} as described in *Equation 5.2*.

$$\%\ Absolute\ Humidity = \left({}^{M_w}\!/_{V_{net}} \right) \times 100 \qquad \textbf{Equation 5.2}$$

Throughout this research, % AH levels were calculated using *Equation 5.2* by measuring the mass loss from the water reservoir (*Figure 5.1*) and determining the total gas flow through the sample chamber for the period of ageing run. Absolute humidity levels of 0 - 80% were achieved using the high humidity apparatus outlined in *Section 5.2.2*.

5.2.6 Post-Ageing Methods of Analysis

A combination of analysis techniques were employed on the polyester residues in order to characterise any physical or chemical changes that may have occurred as a result of ageing. In addition to mass loss studies to examine the extent of volatilisation in PET and PEN, solid-state NMR and FTIR studies were performed to identify any structural changes as a result of ageing. Titrations, determining the concentration of acid end groups, were performed to provide an indication as to the extent of degradation alongside melt rheology studies to examine any viscosity changes at typical processing temperatures. Finally, colour changes were monitored in the polyester residues and gel content studies performed to compare and contrast the extent of discolouration and gel formation in PET and PEN when aged under different environments. All methods of analysis are outlined in *Chapter 3 Experimental*.

5.2.7 Influence of Coating on Degradation and Volatilisation Properties of PEN

In contrast to PET (Melinex OD), the grade of PEN film supplied for this research was coated on one side to enhance adhesion, winding and handling properties. The film was also further processed to reduce thermal shrinkage levels and maintain dimensional stability and reproducibility through high temperature processing steps. Therefore, prior to commencing volatilisation studies of PET (Melinex OD) and PEN (Q65FA), it was vital to ensure that the coating had no influence on the volatilisation results for PEN. This was particularly important when presenting a direct comparison to uncoated PET. Q65FA PEN was initially selected as the most suitable polyester film for volatilisation studies as it could be sourced as 125 μm film, allowing a direct comparison to be made with the 125 μm PET film supplied. However, Q65FA PEN could not be sourced in this thickness without the additional coating, not present on PET. Therefore, comparative degradation studies were performed on the coated grade of PEN film (Q65FA) and an uncoated grade of PEN film (Q71), supplied as 5 µm polyester sheets, to ensure that the coating had no influence on the volatilisation results.

Thermal and thermo-oxidative degradation studies were conducted on the two different grades of PEN using DSC and TGA. This enabled the onset temperatures of degradation to be compared under both environments, using two different techniques. The DSC and TGA degradation profiles obtained for Q71 and Q65FA PEN are illustrated in *Figures 5.8* and *5.9*, respectively.

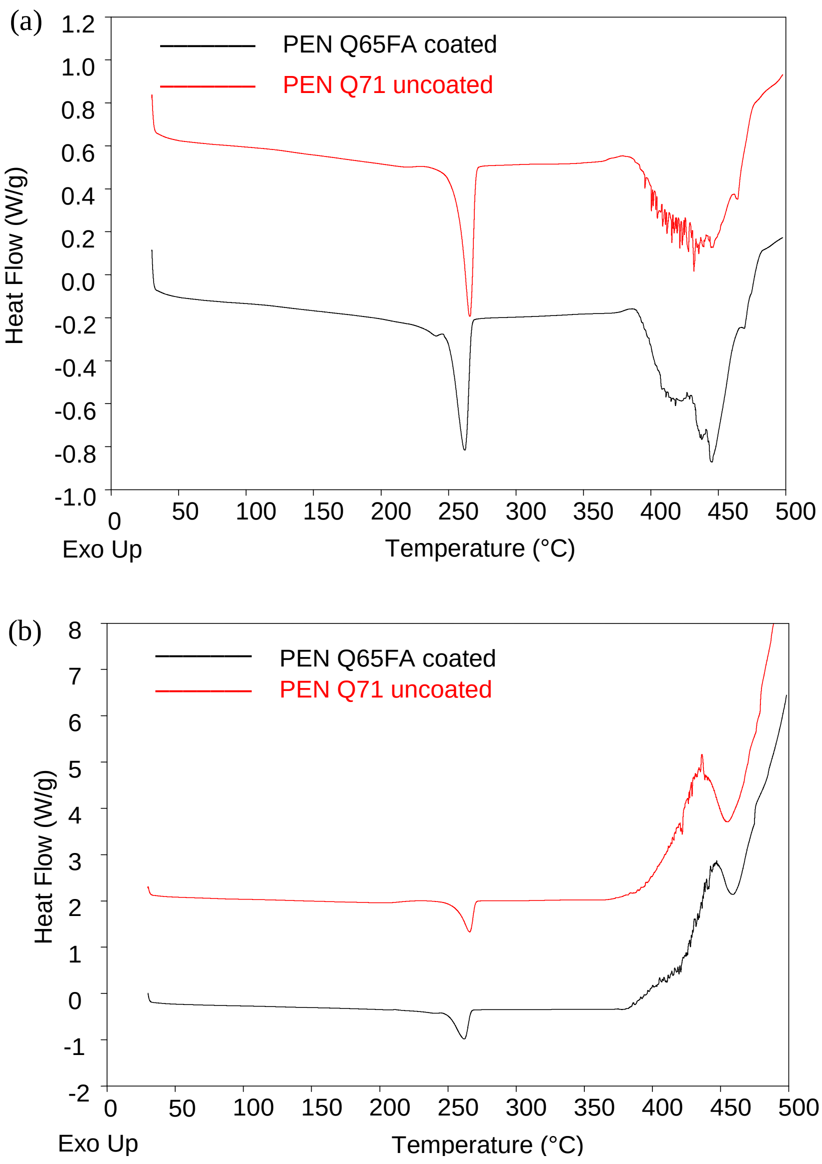


Figure 5.8 DSC degradation curves of Q65FA PEN and Q71 PEN, 30 - 500 °C, 10 °C min^{-1} under (a) nitrogen and (b) air

From *Figure 5.8*, it can be observed that both grades of PEN have similar melting temperatures and degradation behaviour. Endothermic melting can be seen to occur at 265 °C for Q71 uncoated PEN and 262 °C for Q65FA coated PEN. Degradation of PEN by DSC appears to be identical for both samples, with similar onset temperatures of degradation noted. Under an inert atmosphere, the onset temperatures of degradation are 384 °C and 388 °C for uncoated and coated PEN, respectively. As observed previously for PEN, the onset temperatures of degradation do not vary significantly in the presence of air. Uncoated PEN begins to degrade around 382 °C in air, with an onset of degradation observed at 380 °C for coated PEN.

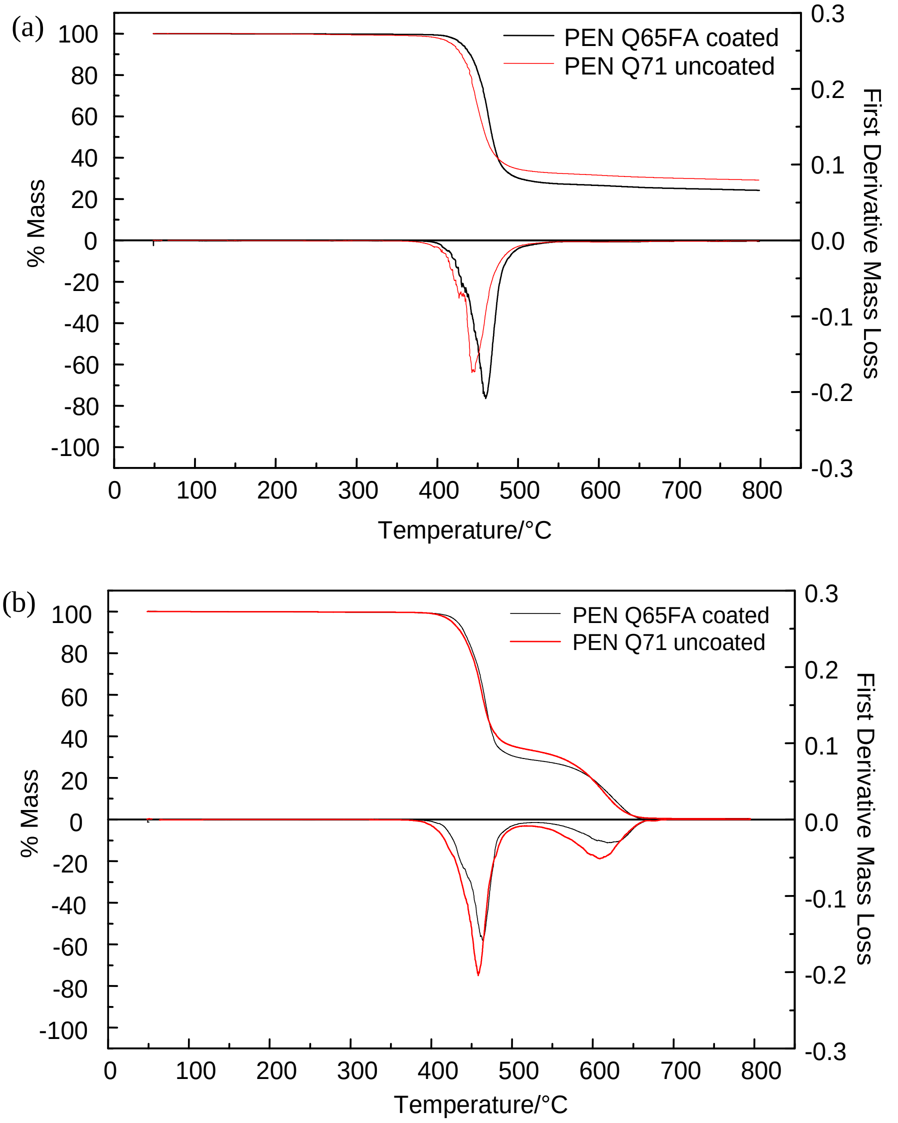


Figure 5.9 Thermogravimetry and differential thermogravimetry curves of Q65FA PEN and Q71 PEN, 50 - 800 °C, 10 °C min^{-1} under (a) helium and (b) air

Despite insignificant differences observed in the DSC curves for coated and uncoated grades of PEN, small changes are evident in the TGA profiles, illustrated in *Figure 5.9* for both materials. Both grades of PEN appear to undergo identical mass loss events. However, the temperatures at which these mass loss events occur differ slightly between the two different grades of PEN. From *Figure 5.9*, it can be observed that under both non-oxidative and oxidative environments, the uncoated grade of PEN appears to degrade marginally faster with earlier onset temperatures and temperatures of maximum mass loss.

Under an inert environment, significant mass loss from coated PEN occurs around 430 ^{o}C, with the maximum rate of mass loss observed at 460 ^{o}C on the differential thermogravimetry curve. These temperatures are decreased in uncoated PEN with an onset of degradation observed around 418 °C and a temperature of maximum mass loss at 441 °C. Once again, the temperatures of degradation for PEN scarcely change on degrading the material under air. The onset temperature for thermo-oxidative degradation of coated PEN can be observed at 432 ^{o}C, with the maximum rate of mass loss observed at 463 ^{o}C on the differential thermogravimetry curve. Uncoated PEN degrades faster again, in comparison to coated PEN, with the onset of degradation observed at 424 °C. Finally, the maximum rate of mass loss can be observed at 454 °C for uncoated PEN degraded in air.

Although these results indicate that the overall thermal stability of uncoated PEN is marginally decreased, in comparison to coated PEN, it is thought that the variation in film thickness may be a contributing factor. Both grades of PEN were analysed directly by DSC and TGA, resulting in analysis of 5 μm samples of Q71 uncoated PEN and 125 μm samples of Q65FA coated PEN. This significant reduction in film thickness could contribute to the small decrease in degradation temperatures observed for uncoated PEN by TGA. On decreasing the film thickness, the rate at which gases can diffuse both in and out of the polyester film significantly increases due to a marked reduction in the diffusion path length. Therefore, on analysis of 5 μm film samples of uncoated PEN, it is thought that the earlier onset of mass loss is due to the fast diffusion of degradation products from the polyester melt. In thicker film samples i.e. 125 μm Q65FA coated PEN, the degradation products will take longer to diffuse from the polyester melt and will therefore result in a slight delay in the onset temperatures of degradation.

Therefore, due to the small changes observed in the TGA temperatures of degradation for uncoated and coated grades of PEN, it was deemed necessary to complete a small set of volatilisation ageing studies under typical processing conditions. It was hoped from the volatilisation results, that any differences due to the presence of the coating on Q65FA PEN could be identified. To eliminate any diffusional effects prior to commencing volatilisation studies, 5 μm uncoated PEN film was melt-pressed into 125 μm PEN coupons of identical dimensions and mass to 125 μm Q65FA coated PEN samples. This melt-pressing technique was performed at a temperature of 240 °C and enabled a direct comparison to be obtained between uncoated and coated grades of PEN. The results from the volatilisation studies of PEN are illustrated in *Table 5.1*.

Sample	***Ageing Temperature/ °C***	***% Volatilisation***
125 μm Q65FA coated PEN as supplied	288	1.0
	300	2.4
	320	5.1
125 μm melt-pressed Q71 uncoated PEN	288	0.9
	300	1.8
	320	5.1

Table 5.1 Volatilisation results for PEN samples aged under dry air for 4 hours

At all three temperatures of interest, the volatilisation results were not found to differ significantly between uncoated and coated grades of PEN. The residual materials were also found to be identical for all uncoated and coated samples of PEN at all three ageing temperatures, the images of which can be viewed in *Chapter 8 Supplementary Material*. The results therefore indicate that the coating present in Q65FA PEN has minimal impact on the degradation of PEN at processing temperature, deeming it suitable for all remaining ageing studies.

5.3 Results and Discussion

Volatilisation studies of PET and PEN were completed to investigate the role of temperature, water and oxygen on the degradation of PEN, in comparison to PET, at typical processing temperatures. From these studies, it was hoped that the optimum conditions, to promote volatilisation of PEN, could be deduced to reduce build-up of degraded material on the die hardware. Implementation of such conditions would result in a reduction in die streaks and thus vital operational improvements for PEN processing.

Although similar volatilisation studies have been completed previously at DuPont Teijin Films research facilities, the experimental data was limited due to the experimental apparatus. Firstly, the maximum operating temperature of the ageing oven at DuPont Teijin Films was 288 °C. Although this is within the temperature range for processing PET, it is too low to mimic processing conditions of PEN. In addition to low ageing temperatures, the maximum absolute humidity level that could be achieved with the equipment was 15%. The experimental studies, outlined in this research, enabled a more comprehensive data set to be obtained for PET and PEN over a range of processing temperatures and environmental conditions. This enabled the effects of thermal, thermal-hydrolytic, thermo-oxidative and thermo-oxidative-hydrolytic degradation to be evaluated in both polyesters.

5.3.1 Volatilisation Studies of PET and PEN

5.3.1.1 Thermal and Thermal-Hydrolytic Volatilisation Studies

Figure 5.10 and Table *5.2* illustrate the volatilisation data obtained for PET and PEN after ageing in dry and wet inert atmospheres for 4 hours. Volatilisation results reveal noticeable differences in the mass loss behaviour between PET and PEN under thermal and thermal-hydrolytic conditions.

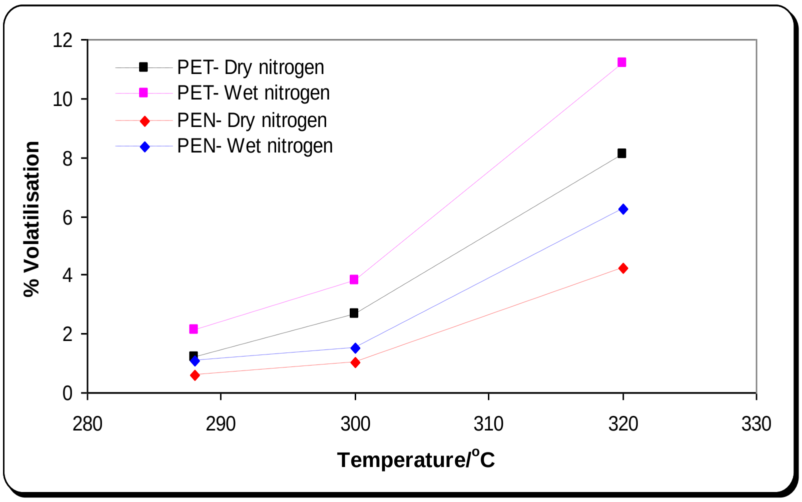


Figure 5.10 Volatilisation results for PET and PEN samples aged in dry and wet (1.5 - 2% AH) nitrogen for 4 hours

Polymer	*Ageing Environment*	*Ageing Temperature/ °C*	*% Volatilisation*
PET	Dry nitrogen	288	1.2
PET	Wet nitrogen	288	2.1
PET	Dry nitrogen	300	2.7
PET	Wet nitrogen	300	3.8
PET	Dry nitrogen	320	8.1
PET	Wet nitrogen	320	11.2
PEN	Dry nitrogen	288	0.6
PEN	Wet nitrogen	288	1.1
PEN	Dry nitrogen	300	1.0
PEN	Wet nitrogen	300	1.5
PEN	Dry nitrogen	320	4.2
PEN	Wet nitrogen	320	6.2

Table 5.2 Volatilisation data for PET and PEN samples aged in dry and wet (1.5 - 2% AH) nitrogen for 4 hours

On analysis of the thermal volatilisation data illustrated in *Figure 5.10*, a significant decrease in the extent of volatilisation is evident for PEN in comparison to PET. The extent of volatilisation for PEN is approximately 50% lower than observed for PET.

As discussed in *Chapter 4*, this is thought to be a result of the enhanced delocalisation of charge across the naphthalene ring units, increasing the overall stability of the ester linkages and thus thermal stability of PEN. On increasing the ageing temperature, an increase in thermal volatilisation can be observed for both PET and PEN. Volatilisation is particularly low at temperatures of 288 °C, however on increasing the temperature to 320 °C, the extent of volatilisation increases in agreement with the TVA results presented in *Chapter 4*. Therefore, as expected, the extent of volatilisation in PET and PEN is temperature dependent, although the overall extent of volatilisation remains low. As the temperature increases and the number of chain scissions in the polyester backbone increases, significant formation of additional vinyl ester and carboxylic acid end groups will result, due to primary chain scission reactions as illustrated for PET and PEN in *Figure 4.36*. These primary degradation reactions are then thought to be followed by secondary degradation reactions leading to the formation of volatile degradation products.

In an attempt to promote volatilisation and thus degradation of PEN, beyond that observed under purely thermal conditions, water was introduced into the ageing system of PET and PEN. Hydrolytic degradation of PET and PEN involves chain scission at the esters linkages. Each water molecule breaks down one ester bond, leading to the formation of one carboxyl and one hydroxyl end group, as illustrated in *Figure 1.41*. Therefore, as the degree of hydrolytic degradation increases and the molar mass decreases at typical processing temperatures, an increase in the extent of volatilisation of PET and PEN is expected. However, the results shown in *Figure 5.10* reveal only a marginal increase in volatilisation of both polyesters on introduction of low moisture content (1.5 - 2% AH) into the thermal ageing system.

At all three ageing temperatures of interest under thermal-hydrolytic conditions, PET and PEN exhibit identical volatilisation trends to those observed previously under thermal conditions. An increase in volatilisation can be observed for both polyesters with increased ageing temperature, with a slightly higher extent of volatilisation observed for all samples aged in the presence of low moisture content. This is not entirely surprising as water is expected to rapidly penetrate into the polyester melt systems at such high temperatures, resulting in competing thermal and hydrolytic degradation reactions. However, as the rate of hydrolytic degradation is reported to be several orders of magnitude higher than that of thermal degradation [1,2,3], it was hoped that the extent of volatilisation in PET and PEN would increase more significantly than observed.

More extensive thermal and thermal-hydrolytic degradation of PET and PEN can be observed on increasing the ageing time, at all three temperatures of interest. *Figures 5.11* and *5.12* illustrate the volatilisation data for PET and PEN samples aged in dry nitrogen and wet nitrogen for 1 - 24 hours, respectively.

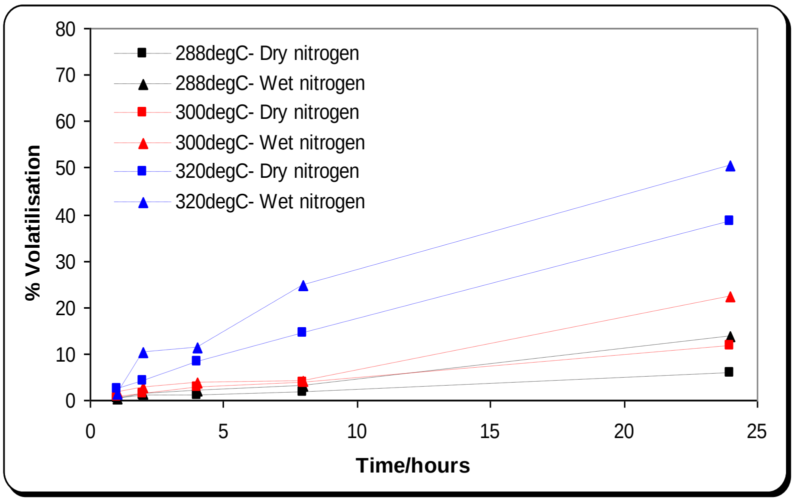


Figure 5.11 Volatilisation results for PET samples aged in dry and wet (1.5 - 2% AH) nitrogen for 1 - 24 hours

At temperatures of 288 °C and 300 °C, extremely low levels of volatilisation were detected for PET and PEN samples aged in wet nitrogen up to 8 hours. However, on increasing the ageing time to 24 hours, degradation increased and therefore the extent of volatilisation also increased. At an ageing temperature of 320 °C, the impact of low moisture on the volatilisation of PET and PEN can be observed most significantly. In contrast to thermal ageing conditions, the extent of volatilisation was found to increase from 38.4% to 50.4% in PET and 20.4% to 36.1% in PEN after ageing for 24 hours at 320 °C in the presence of low moisture levels. Volatilisation of both polyesters, in dry and low moisture conditions, also appears to increase in a reasonably linear manner with increased ageing time, providing no indication of slowing degradation rates even after ageing for 24 hours. All raw volatilisation data for PET and PEN samples, aged in dry and wet nitrogen for 1 - 24 hours, can be found in *Chapter 8 Supplementary Material.*

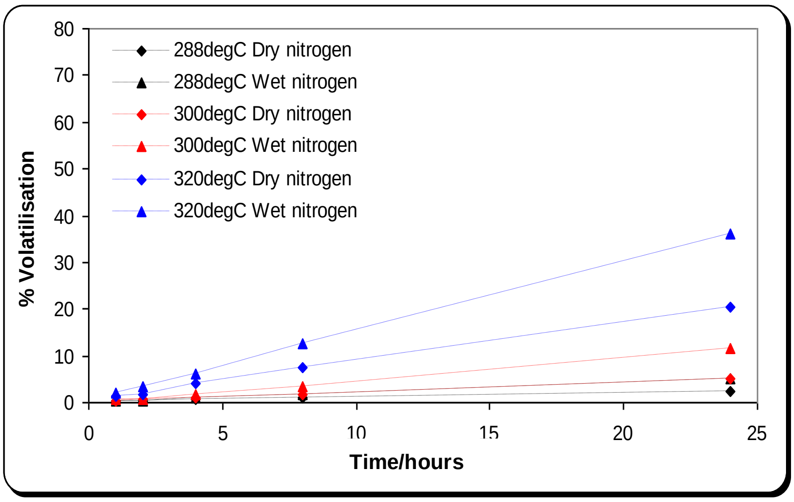


Figure 5.12 Volatilisation results for PEN samples aged in dry and wet (1.5 - 2% AH) nitrogen for 1 - 24 hours

5.3.1.2 Thermo-Oxidative Volatilisation Studies

Although polyesters degrade at high temperatures in the absence of air, degradation is most common and almost always faster in the presence of oxygen. Thermo-oxidative degradation typically commences at lower temperatures than thermal degradation and generally leads to a mixture of degradation products containing both similar species to those formed during thermal degradation and newly oxidised species from reaction with O_2. During synthesis and processing of polyesters, thermo-oxidative degradation is inevitable as the polymers are exposed to air at elevated temperatures. The rate and course of these thermo-oxidative degradation reactions are obviously strongly influenced by factors such as oxygen concentration and moisture.

In an attempt to promote degradation of PEN, beyond that observed under thermal and thermal-hydrolytic conditions, oxygen was introduced into the ageing system of PET and PEN. It was hoped that thermo-oxidative degradation of PEN would promote volatilisation over short ageing periods, creating ideal conditions that could be replicated under processing conditions for the control of die streaks. Three different oxygen containing environments were employed throughout these studies; 3 % oxygen, air and 42% oxygen.

Figure 5.13 and *Table 5.3* illustrate the volatilisation data obtained for PET samples aged in dry, oxidative environments for 4 hours. As expected, the results reveal a significant increase in volatilisation of PET on increasing the oxygen concentration and temperature. Even at low oxygen concentration, the extent of volatilisation in PET is found to be approximately double that observed previously for samples aged under thermal conditions. With an increase in oxygen concentration to 21% and 42% on ageing in air and 42% oxygen, respectively, volatilisation of PET increased considerably more. These results highlight once again that PET is increasingly susceptible towards thermo-oxidative degradation. *Figure 5.14* illustrates this relationship described between oxygen concentration and volatilisation in PET. Under all oxidative environments, the extent of volatilisation can be seen to increase with ageing temperature.

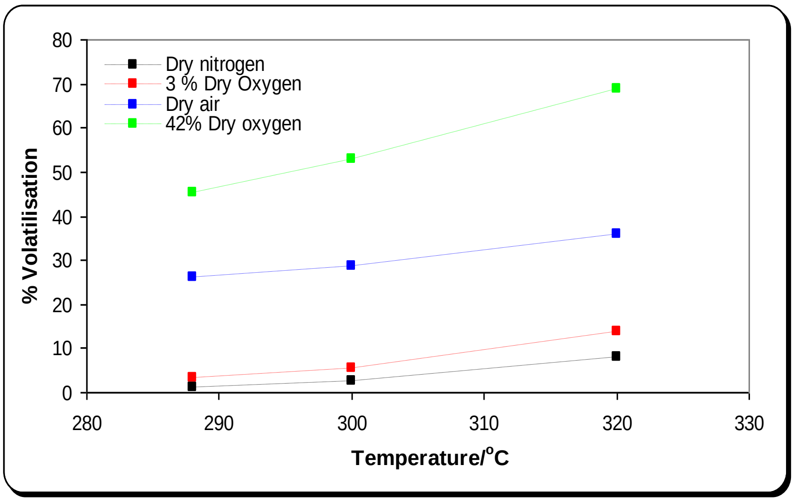


Figure 5.13 Volatilisation results for PET samples aged in dry oxidative environments for 4 hours

Ageing Environment	***Ageing Temperature/ °C***	***% Volatilisation***
Dry 3% oxygen	288	3.2
Dry air	288	26.1
Dry 42% oxygen	288	45.1
Dry 3% oxygen	300	5.2
Dry air	300	28.5
Dry 42% oxygen	300	53.0
Dry 3% oxygen	320	13.6
Dry air	320	35.7
Dry 42% oxygen	320	68.7

Table 5.3 Volatilisation data for PET samples aged in dry oxidative environments for 4 hours

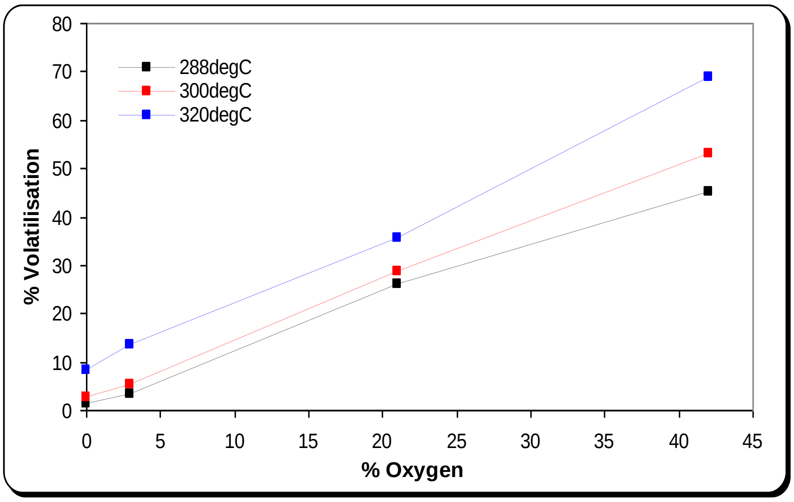


Figure 5.14 Impact of oxygen level on volatilisation of PET samples aged in dry oxidative environments, 288 - 320 °C, 4 hours

As degradation of PET in 42% oxygen is not particularly practical to implement in a processing environment, a similar extent of volatilisation can be achieved by simply increasing the ageing period in the presence of air. 74.4% volatilisation of PET was achieved on ageing PET for 24 hours in dry air at 320 °C, in comparison to 68.7% volatilisation on ageing in 42% oxygen for 4 hours. *Figure 5.15* illustrates the volatilisation results obtained for PET samples aged in dry air for 1 – 24 hours at temperatures of 288 - 320 °C. All corresponding volatilisation data for PET aged in dry air for 1 - 24 hours can be found in *Chapter 8 Supplementary Material.*

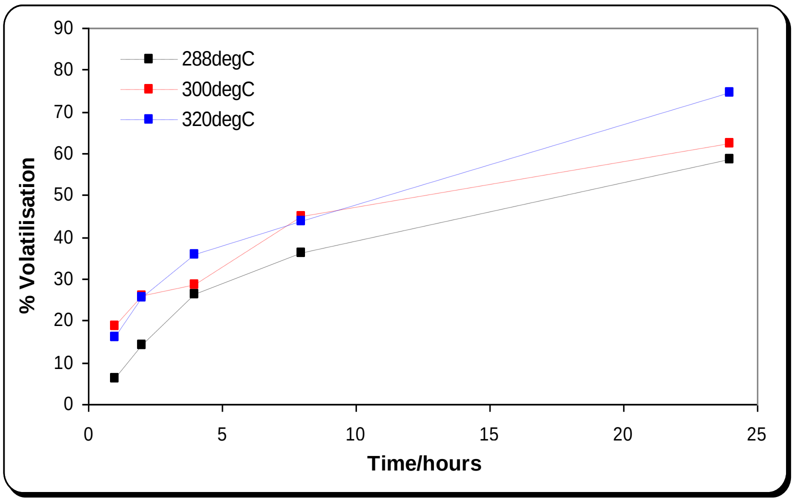


Figure 5.15 Volatilisation results for PET samples aged in dry air for 1 - 24 hours

With increased ageing time and temperature, a subsequent increase in volatilisation can be observed for PET on ageing in a dry air environment. However, the volatilisation trends appear to be non-linear with increased ageing time, in contrast to the reasonably linear relationship observed previously for thermal and thermal-hydrolytic degradation of PET. These results demonstrate that the extent of volatilisation is beginning to plateau in PET, suggesting that the overall rate of thermo-oxidative degradation is rapidly decreasing after 24 hours, possibly due to exhaustion of reactive end groups.

Oxidative degradation is therefore proposed to be the dominant reaction occurring in PET on ageing in thermo-oxidative conditions. This can be deduced from the poor extent of volatilisation observed on ageing PET in thermal conditions, in comparison to thermo-oxidative conditions, and increase in volatilisation observed with increased ageing temperature under thermo-oxidative conditions. Typical oxidation reactions of PET are well outlined in the literature [4,5,6,7,8,9], with heat and oxygen thought to initiate formation of hydroperoxides at methylene sites within polyester chains, as illustrated in *Figure 1.35*. These unstable hydroperoxide species are then believed to undergo homolytic chain scission reactions, resulting in the formation of chain fragments with oxygen and carbon radicals, vinyl ester and carboxyl end groups. Various radicals finally participate in a series of further degradation reactions leading to a variety of volatile degradation products including aldehydes, ketones and esters.

With high levels of volatilisation observed in PET on ageing in oxidative environments, it was hoped that similar volatilisation levels could be achieved for PEN. *Figure 5.16* and *Table 5.4* present the volatilisation data obtained for PEN samples aged in dry, oxidative environments for 4 hours.

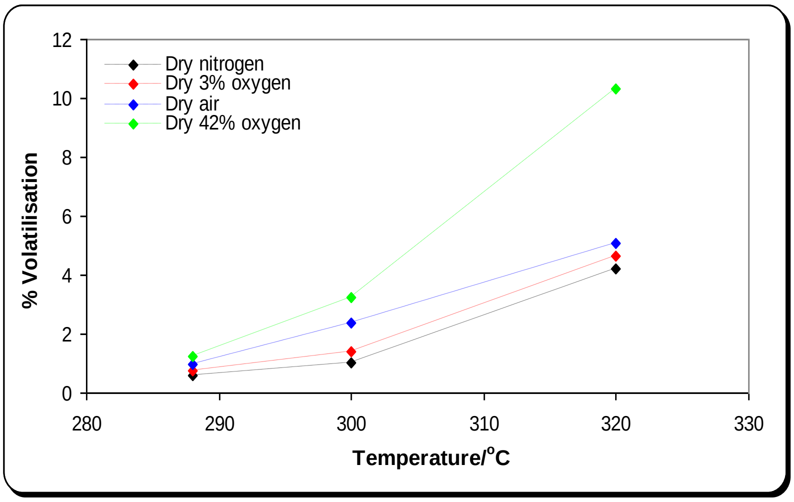


Figure 5.16 Volatilisation results for PEN samples aged in dry oxidative environments for 4 hours

Ageing Environment	*Ageing Temperature/ °C*	*% Volatilisation*
Dry 3% oxygen	288	0.8
Dry air	288	1.0
Dry 42% oxygen	288	1.2
Dry 3% oxygen	300	1.4
Dry air	300	2.4
Dry 42% oxygen	300	3.2
Dry 3% oxygen	320	4.7
Dry air	320	5.1
Dry 42% oxygen	320	10.3

Table 5.4 Volatilisation data for PEN samples aged in dry oxidative environments for 4 hours

Unfortunately, the extent of volatilisation in PEN is particularly low, with only a small volatilisation increase observed on increasing oxygen concentration. PEN is therefore thought to be increasingly less sensitive towards thermo-oxidative degradation, in comparison to PET. These observations are in agreement with DSC and TGA results discussed previously for PEN, in *Section 4.1.3*. *Figure 5.17* illustrates this relationship described between oxygen concentration and volatilisation in PEN. As observed for PET, the extent of volatilisation in PEN can be seen to increase with increased ageing temperature, under all oxidative environments.

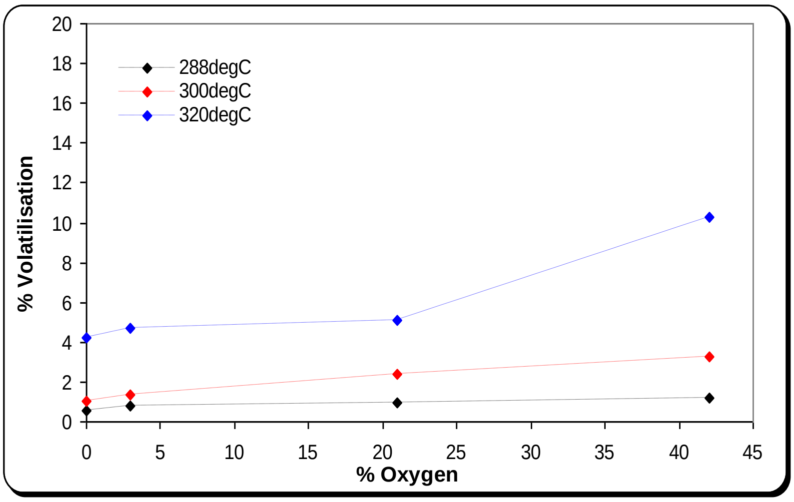


Figure 5.17 Impact of oxygen level on volatilisation of PEN samples aged in dry oxidative environments, 288 - 320 °C, 4 hours

A significant increase in the extent of volatilisation in PEN can also be observed on simply increasing the ageing time in the presence of air, as previously illustrated for PET. After ageing PEN for a period of 24 hours at 320°C in dry air, volatilisation levels were found to increase to 38.3%, in comparison to just 10.4% observed for PEN aged for 4 hours at 320 °C in dry 42% oxygen. *Figure 5.18* illustrates the volatilisation data obtained for PEN samples aged in dry air for 1 - 24 hours at temperatures of 288 - 320 °C. All corresponding volatilisation data can be found in *Chapter 8 Supplementary Material.*

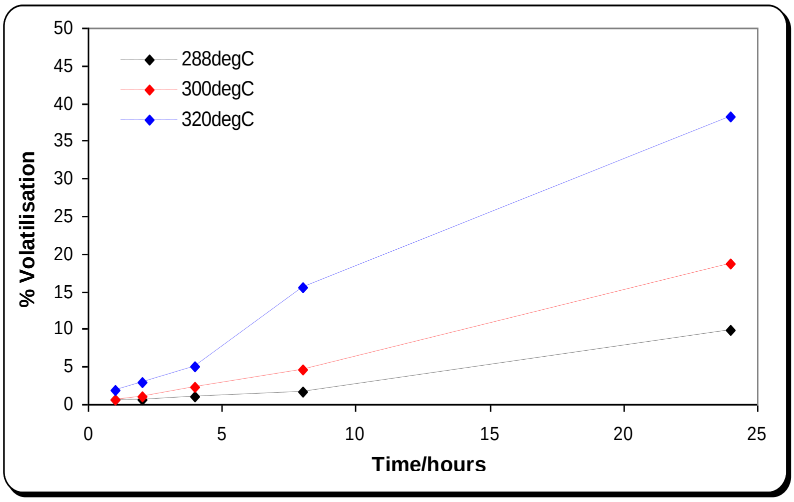


Figure 5.18 Volatilisation results for PEN samples aged in dry air for 1 - 24 hours

With increased ageing time and temperature, a subsequent increase in volatilisation can be observed for PEN on ageing in a dry air environment. However, the overall rate and extent of volatilisation in PEN appears to be significantly reduced, in comparison to PET. Volatilisation of PEN is particularly low at ageing periods of up to 8 hours, with an overall linear relationship observed between volatilisation and ageing time. Therefore, a 24 hour ageing period is unlikely to promote maximum degradation and thus volatilisation of PEN. In contrast to this, volatilisation of PET exhibited a non-linear relationship with ageing time, suggesting degradation is near to completion after ageing for 24 hours. Significantly higher levels of volatilisation were observed at all ageing times in PET, in comparison to PEN. Such observations suggest that PET and PEN may undergo different chemical processes, which result in, or prevent volatilisation from occurring during thermo-oxidative degradation.

Due to the reduced extent of volatilisation observed in PEN samples aged in the presence of high oxygen levels, it is thought that PEN may be acting as a barrier for the penetration of oxygen, leading to a significant reduction in oxidative-sensitivity and thus volatilisation in comparison to PET. If this is occurring, then thermal degradation must be the dominant reaction occurring in PEN under thermo-oxidative ageing conditions, resulting in only a small increase in volatilisation with increased ageing temperature. Alternatively, PEN could simply be restricting the diffusion of bulky, volatile degradation products from the polyester melt, as discussed previously for thermal degradation of PEN. This is feasible due to the higher melt viscosity of PEN, in comparison to PET, at all ageing temperatures of interest.

5.3.1.3 Thermo-Oxidative-Hydrolytic Volatilisation Studies

In a final attempt to promote volatilisation of PEN, low levels of water were introduced into a thermo-oxidative ageing system. This enabled the extent of degradation in PET and PEN to be analysed under one final set of ageing conditions; thermo-oxidative-hydrolytic ageing. By combining moisture, high temperature and oxygen, it was hoped that significant degradation of PET and PEN would result due to competing thermal, thermo-oxidative and hydrolytic degradation reactions.

Figure 5.19 and *Table 5.5* illustrate the volatilisation data obtained for PET samples aged in a wet, oxidative environment for 4 hours. Volatilisation results for PET samples aged in 3% oxygen and air reveal only a small increase in volatilisation on introduction of low moisture content (1.5 - 2% AH) into the ageing system, similar to the increase observed on ageing in wet, inert conditions. PET samples aged in dry air obviously exhibit greater levels of volatilisation due to more extensive thermo-oxidative degradation than samples aged in 3% wet oxygen, however all exhibit a small increase in volatilisation with increased ageing temperature. These results indicate that thermo-oxidative degradation remains the dominant reaction despite the presence of moisture.

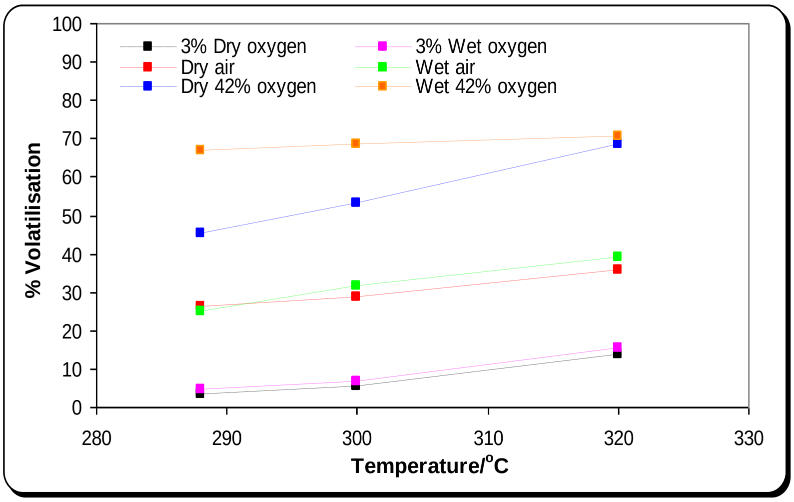


Figure 5.19 Volatilisation results for PET samples aged in dry and wet (1.5 - 2% AH) oxidative environments for 4 hours

Ageing Environment	*Ageing Temperature/ °C*	*% Volatilisation*
Wet 3% oxygen	288	4.7
Wet air	288	24.8
Wet 42% oxygen	288	66.9
Wet 3% oxygen	300	6.6
Wet air	300	31.7
Wet 42% oxygen	300	68.7
Wet 3% oxygen	320	15.3
Wet air	320	38.8
Wet 42% oxygen	320	70.4

Table 5.5 Volatilisation results for PET samples aged in wet (1.5 - 2% AH) oxidative environments for 4 hours

On ageing PET in a 42% wet oxygen environment, the extent of volatilisation can be seen to increase significantly at 288 °C and 300 °C, in comparison to ageing in 42% dry oxygen. This is thought to be due to increased rates of hydrolysis at the two lowest ageing temperatures. On reaching 320 °C, similar volatilisation results were obtained for PET samples aged in dry and wet 42% oxygen, indicating that water has little impact on the extent of volatilisation at the highest temperature. In contrast to

PET samples aged in 3% wet oxygen and wet air, the extent of volatilisation in PET samples aged in 42% wet oxygen does not increase with increased ageing temperature. Instead, the overall extent of volatilisation appears to plateau around 70 % at all ageing temperatures. This indicates that the maximum extent of volatilisation has been approached on ageing PET in 42% wet oxygen.

Once again, as degradation of PET in 42% wet oxygen is not particularly practical to implement in a processing environment, a similar extent of volatilisation can be achieved by simply increasing the ageing period in the presence of air. 85.9% volatilisation of PET was achieved on ageing PET for 24 hours in wet air at 320 °C, in comparison to 70.4% after ageing in wet 42% oxygen for 4 hours. *Figure 5.20* compares the volatilisation data obtained for PET samples aged in dry and wet air for upto 24 hours at temperatures of 288 - 320 °C. Identical trends to those observed in dry air can be seen for PET samples aged in wet air, with only a small increase in volatilisation on switching from a dry to wet ageing environment. Therefore, the presence of low moisture levels during thermo-oxidative degradation of PET has only small impact on the overall extent of volatilisation due to the dominant reaction being thermo-oxidative degradation. All volatilisation data for PET aged in wet air for 1 - 24 hours can be found in *Chapter 8 Supplementary Material.*

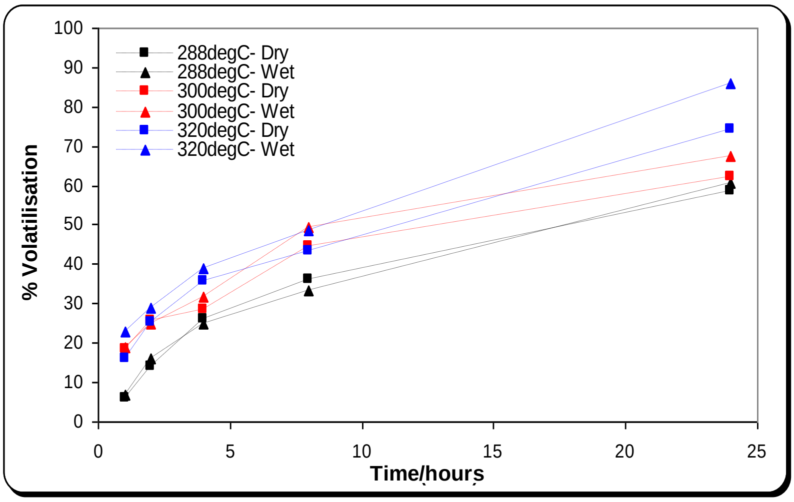


Figure 5.20 Volatilisation results for PET samples aged in dry and wet (1.5 - 2% AH) air for 1 - 24 hours

Figure 5.21 and *Table 5.6* illustrate the volatilisation results obtained for PEN samples aged in wet, oxidative environments for 4 hours. Once again, a significant reduction in the overall extent of volatilisation in PEN can be observed, in comparison to PET. Even in the presence of low moisture content and high oxygen concentration, volatilisation of PEN is particularly low, indicating that both oxygen and low moisture levels have little impact on the volatilisation of PEN.

At all three ageing temperatures of interest, PEN exhibits identical volatilisation trends to those observed previously under dry thermo-oxidative conditions. An increase in volatilisation can be observed for PEN samples with increased ageing temperature, with a slightly higher extent of volatilisation observed for all samples aged in the presence of low moisture content. Although the overall extent of volatilisation still remains low, volatilisation does appear to increase more significantly on ageing PEN in a wet oxidative environment at 320 °C, than ageing at 288 °C and 300 °C. Water is therefore thought to begin to interfere more extensively with oxidative/radical chemistry of PEN at 320 °C, resulting in a more significant increase in volatilisation. If competing degradation reactions are occurring in PEN, then the extent of oxidative cross-linking should also decrease on ageing under wet oxidative environments at 320 °C.

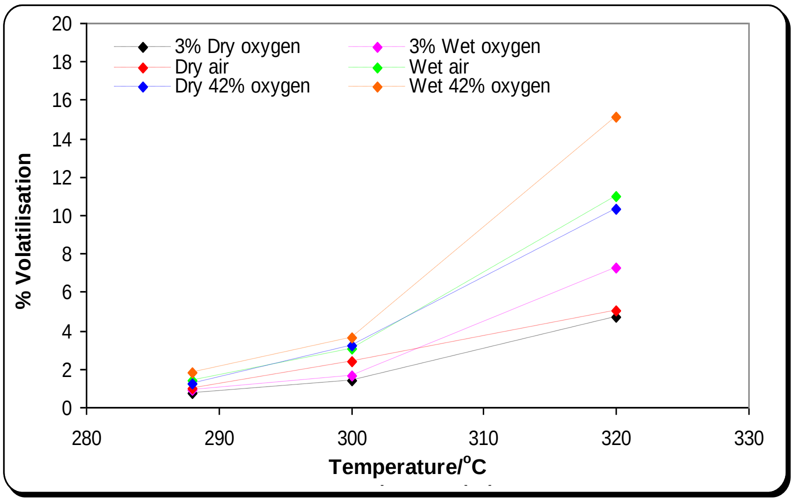


Figure 5.21 Volatilisation results for PEN samples aged in dry and wet (1.5 - 2% AH) oxidative environments for 4 hours

Ageing Environment	*Ageing Temperature/ °C*	*% Volatilisation*
Wet 3% oxygen	288	0.9
Wet air	288	1.4
Wet 42% oxygen	288	1.8
Wet 3% oxygen	300	1.7
Wet air	300	3.1
Wet 42% oxygen	300	3.6
Wet 3% oxygen	320	7.3
Wet air	320	11.0
Wet 42% oxygen	320	15.1

Table 5.6 Volatilisation results for PEN samples aged in wet (1.5 - 2% AH) oxidative environments for 4 hours

As observed previously for PET, an increase in the overall extent of volatilisation in PEN can be observed on simply increasing the ageing time in wet air. After ageing PEN for a period of 24 hours at 320°C in wet air, volatilisation levels were increased to 40.0%, in comparison to just 15.1% observed for PEN aged at 320 °C in 42% wet oxygen for 4 hours. *Figure 5.22* compares the volatilisation data obtained for PEN samples aged in dry and wet air for 1 - 24 hours at temperatures of 288 - 320 °C. All volatilisation data for PEN aged in wet air for 1 - 24 hours can be found in *Chapter 8 Supplementary Material.*

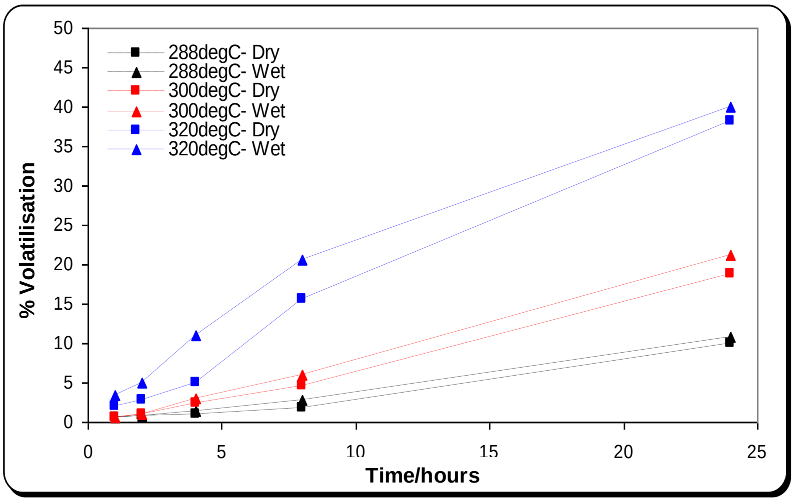


Figure 5.22 Volatilisation results for PEN samples aged in wet (1.5 - 2% AH) air for 1 - 24 hours

With increased ageing time and temperature, a subsequent increase in volatilisation can be observed once again for PEN on ageing in a wet air environment. Due to the increased thermal and hydrolytic stability of PEN and its low susceptibility to degrade in the presence of oxygen, volatilisation is low at temperatures of 288 °C and 300 °C. However, on reaching 320 °C, volatilisation is more pronounced, particularly on ageing for 8 hours or longer due to increased thermo-oxidative and hydrolytic degradation of the polyester.

The above results indicate that water only has a small impact on promoting volatilisation in both polyesters, as discussed previously for PET and PEN samples aged in thermal-hydrolytic conditions. Hydrolytic degradation does occur resulting in an increase in volatilisation for both PET and PEN at low moisture levels, however thermo-oxidative degradation appears to remain the dominant degradation reaction. Higher moisture levels appear necessary in order to promote hydrolytic degradation of PET and PEN and thus increase the extent of volatilisation beyond that observed so far.

5.3.2 Discolouration of Residual PET and PEN Film Samples

5.3.2.1 Visual Examination of Residual Samples from Thermal and Thermal-Hydrolytic Studies

Following ageing of the polyester samples, the residual film samples were examined for discolouration. Although some samples were aged for up to 24 hours, post-analysis studies and degradation discussions focus solely on samples aged for only 4 hours. This is simply due to the fact that these experimental conditions are most practical to implement on the PEN processing line. *Figure 5.23* illustrates the residual film samples obtained from PET and PEN after ageing in dry nitrogen for 4 hours.

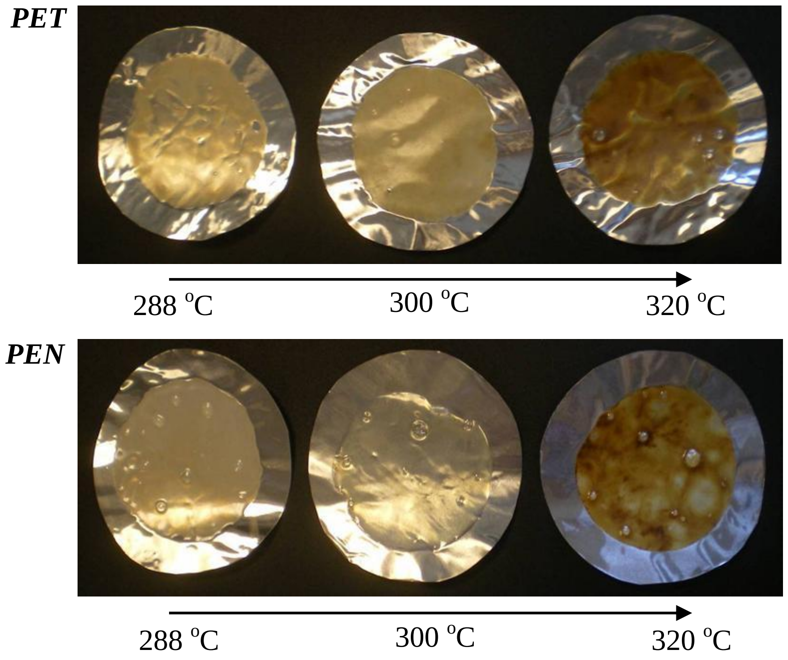


Figure 5.23 Residual film samples from (a) PET and (b) PEN aged in dry nitrogen for 4 hours

Only marginal discolouration is evident in samples of PET aged in thermal conditions at 288 °C and 300 °C. From *Figure 5.23*, it can be observed that the residual samples of PET marginally discolour on increasing temperature from 288 °C to 300 °C, coinciding with increased degradation. In contrast to PET, residual samples of PEN appear identical in colour after ageing in dry nitrogen at 288 °C and 300 °C.

On increasing the ageing temperature to 320 °C, discolouration is more pronounced in both PET and PEN. The residual film samples, aged at 320 °C, are orange in colour and identical for PET and PEN. Discolouration is therefore thought to result from the increase in ageing temperature, resulting in increased degradation, in comparison to samples aged under thermal conditions at 288 °C and 300 °C. This increase in discolouration coincides with the significant increase in volatilisation observed for both polyesters at 320 °C.

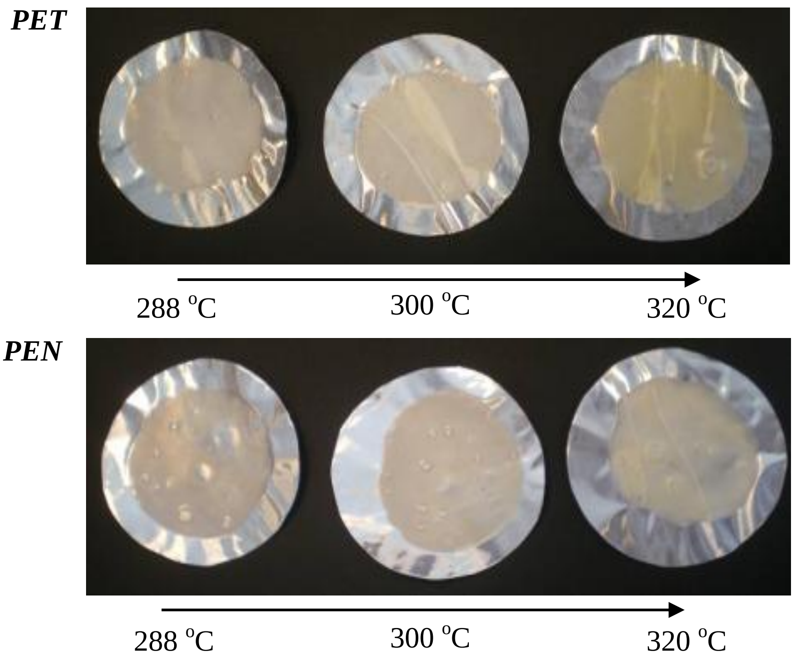


Figure 5.24 Residual film samples from PET and PEN aged in wet (1.5 - 2% AH) nitrogen for 4 hours

Significant discolouration is not evident in any samples of PET and PEN aged under thermal-hydrolytic conditions at 288 - 320 °C. From *Figure 5.24*, it can be observed that all residual PET and PEN film samples are off - white in colour with no obvious differences in the appearance of their residual polyester melts. These observations appear to contradict those discussed previously for samples aged under thermal conditions, where significant discolouration was observed in PET and PEN at 320 °C. In the presence of low moisture content, the discolouration in PET and PEN samples aged at 320 °C does not exist highlighting that the degradation species, responsible for discolouration during thermal degradation of PET and PEN at 320 °C, are simply not formed in the presence of water.

5.3.2.2 Visual Examination of Residual Samples from Thermo-Oxidative Studies

Unsurprisingly, extensive discolouration of both polyesters was observed under thermo-oxidative ageing conditions. These results are in agreement with the observations noted by Edge *et al.* [10,11,12] during degradation studies of PET, with the formation of coloured species reported to be much greater in the presence of air, than nitrogen. *Figures 5.25 – 5.27* illustrate the residual film samples obtained from PET and PEN samples after ageing in a range of different dry oxidative environments.

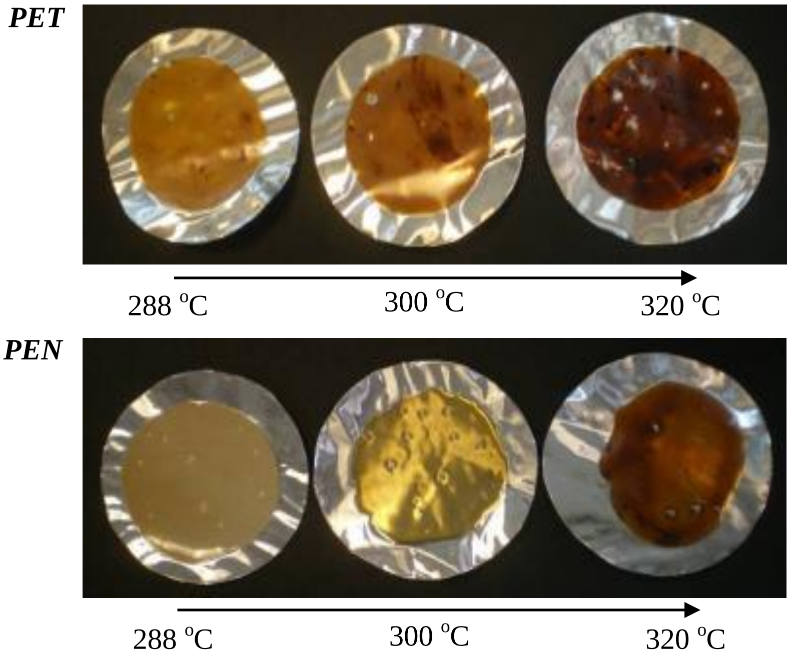


Figure 5.25 Residual film samples from PET and PEN aged in dry 3% oxygen for 4 hours

The extent of discolouration in PET and PEN aged in 3% dry oxygen can be seen to differ quite significantly between both polyesters, at all three ageing temperatures. Such observations indicate that the degradation chemistry is likely to differ in PET and PEN under thermo-oxidative conditions. With increased ageing temperature, the discolouration can be seen to increase in both polyesters. This is simply thought to be due to an increase in thermo-oxidative degradation activity with increased ageing temperature. The overall extent of discolouration in PET appears to be increased at all three ageing temperatures, in comparison to PEN. This discolouration is accompanied by increased volatilisation, and once again highlights the increased sensitivity of PET towards thermo-oxidative degradation. At lower ageing temperatures, discolouration in PEN is minimal highlighting increased thermo-oxidative stability of PEN in comparison to PET, resulting in an overall reduction in degradation and subsequent reduction in volatilisation. However, on reaching the highest ageing temperature of 320 °C, the extent of discolouration in PET and PEN samples appears to be very similar.

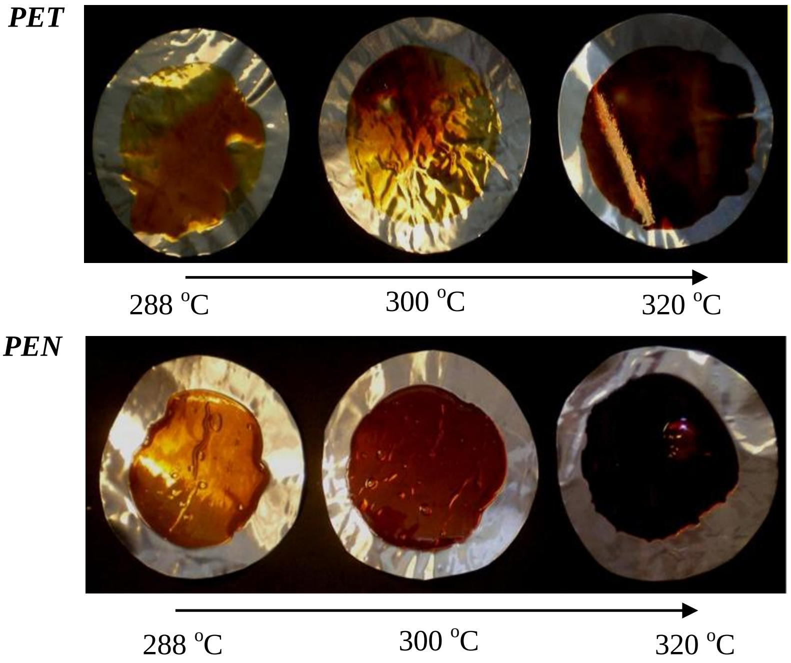


Figure 5.26 Residual film samples from PET and PEN aged in dry air for 4 hours

With increased ageing temperature, the discolouration can be seen to increase in both polyesters aged in dry air. Discolouration of PEN was found to be more extensive than PET, suggesting that the nature of the thermo-oxidative degradation species, responsible for discolouration, differ between PET and PEN. These observations are in agreement with those noted by Botelho *et al.* [13] and Scheirs *et al.* [14] during photo and thermo-oxidative degradation studies of PEN. Both studies report increased discolouration in PEN, in comparison to PET, suggesting that the naphthalene ring is involved in the discolouration reactions. On increasing naphthalene content, discolouration was found to increase due to the presence of highly conjugated and highly absorbing naphthalene species.

In addition to discolouration of PET and PEN samples aged under air, the extent of surface coverage can be seen to differ in both polyesters from *Figure 5.26*. The overall surface area of PEN was observed to decrease after ageing at all temperatures, in contrast to an increase in surface area observed for PET samples. An increase in surface area will obviously increase volatilisation by virtue of increased exposure area, irrespective of the degradation chemistry. In a similar manner, shrinking of the sample will decrease volatilisation due to a reduction in exposure area and increase in sample density. Therefore, this variation in surface coverage may be one contributory factor to the increase and reduction in volatilisation observed for PET and PEN, respectively.

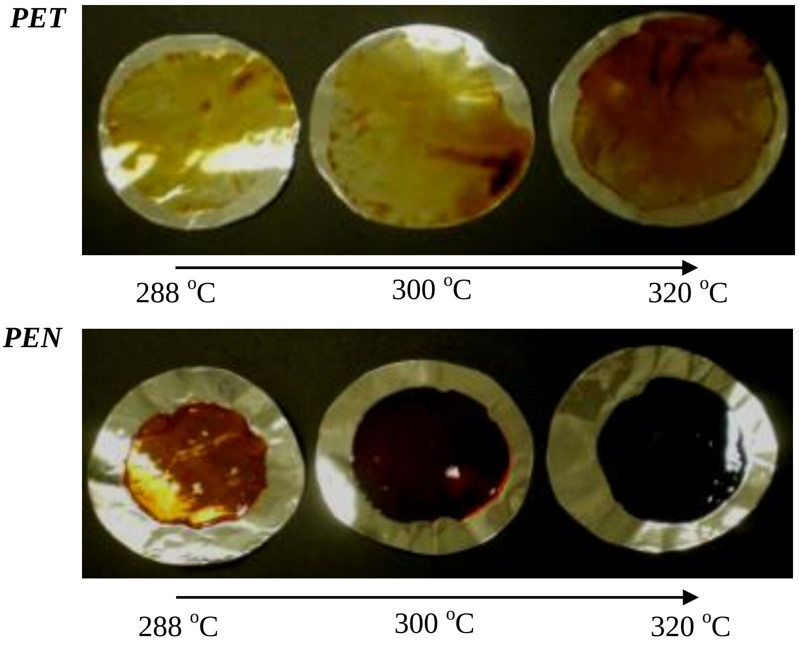


Figure 5.27 Residual film samples from PET and PEN aged in dry 42% oxygen for 4 hours

Figure 5.27 illustrates the residual film samples obtained from PET and PEN samples after ageing in 42% dry oxygen for 4 hours. Once again, the extent of discolouration in PEN was found to be greater than that observed in PET. Interestingly, the extent of discolouration in PET does not appear to vary significantly with increased ageing temperature. This is thought to be due to the high extent of volatile product formation, accompanied by increased surface spreading, reducing the overall residual deposit thickness. Such ageing conditions are therefore beneficial to encourage flow of PET from the extrusion die under processing conditions and promote degradation. In contrast to these observations noted for PET, discolouration of PEN still deteriorates on increasing the ageing temperature from 288 °C to 320 °C on ageing in 42% dry oxygen. Once again, this highlights differences in the oxidation chemistry between PET and PEN.

On ageing samples of PEN, in 42% oxygen, at typical processing temperatures of 320 °C, the residual samples were found to be completely black. Therefore, despite low volatilisation of PEN in high oxygen concentrations, thermo-oxidative activity contributing to the formation of discoloured species is still thought to remain high. In contrast to the previous observations noted for PET aged in 42% dry oxygen, volatilisation of PEN still remains low and the samples appear to shrink rather than spread under the combined influence of high temperature and high oxygen concentration. From *Figure 5.27* it can be observed that shrinking is most evident in samples aged at 288 °C, at least providing the benefit of reduced deposit thickness when processing at higher temperatures. Despite significant differences observed in the extent of discolouration between PET and PEN after thermo-oxidative ageing, the nature of the degradation species causing the discolouration still remain unknown.

5.3.2.3 Visual Examination of Residual Samples from Thermo-Oxidative-Hydrolytic Studies

Unsurprisingly, extensive discolouration of both polyesters was observed on ageing under thermo-oxidative-hydrolytic conditions. However, the overall extent of discolouration was not found to differ significantly between PET and PEN samples aged in dry and wet thermo-oxidative environments. *Figures 5.28 – 5.30* illustrate the residual film samples obtained from PET and PEN samples after ageing under a range of different wet oxidative environments for 4 hours.

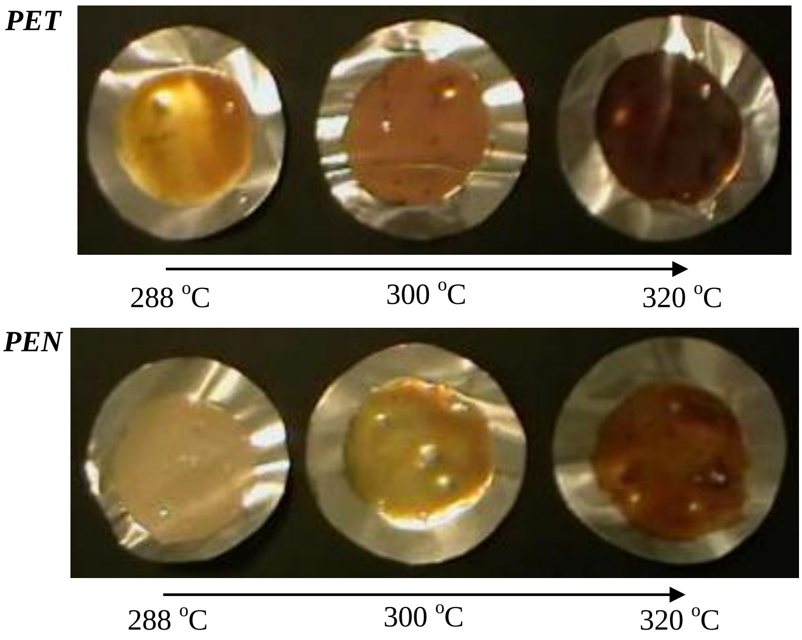


Figure 5.28 Residual film samples from PET and PEN aged in wet (1.5 - 2% AH) 3% oxygen for 4 hours

As reported previously for PET and PEN samples aged in dry 3% oxygen, the extent of discolouration in PET and PEN aged in 3% wet oxygen differs quite significantly between both polyesters at all three ageing temperatures. With increased ageing temperature, the discolouration can be seen to increase in both polyesters due to further oxidation. However, the overall extent of discolouration in PET is increased at all three ageing temperatures, in comparison to PEN, highlighting the increased sensitivity of PET towards thermo-oxidative degradation. Due to a lack of significant differences noted between residual PET and PEN samples aged in 3% dry and 3% wet oxygen, it can be concluded that thermo-oxidative degradation is the dominant reaction occurring in both polyesters during thermo-oxidative-hydrolytic ageing at temperatures between 288°C and 320 °C.

On ageing both polyesters in wet air and wet 42% oxygen, the extent of discolouration in PEN was found to be more extensive than observed in PET. This is thought to be due to the formation of highly conjugated, cross-linked bis-naphthalene structures, discussed previously for thermo-oxidative degradation of PEN.

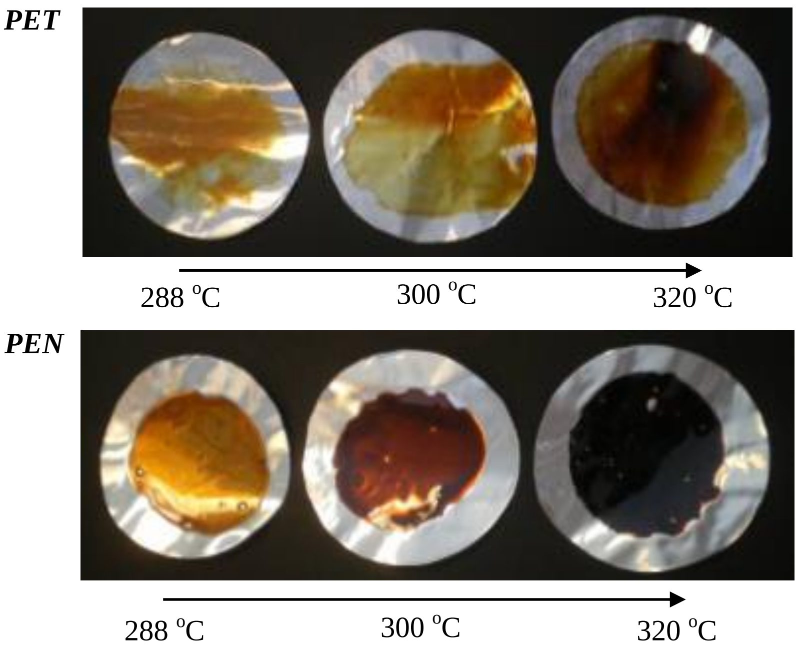


Figure 5.29 Residual film samples from PET and PEN aged in wet (1.5 - 2% AH) air for 4 hours

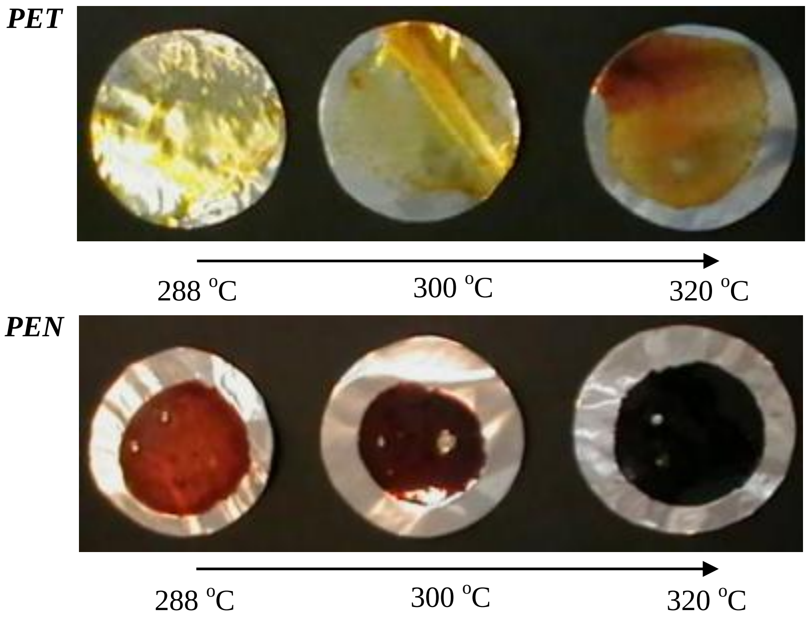


Figure 5.30 Residual film samples from PET and PEN aged in wet (1.5 - 2% AH) 42% oxygen for 4 hours

With increased ageing temperature, the discolouration in PEN can be seen to increase, resulting in the formation of black residual material after ageing at 320 °C in 42% wet oxygen. Even with a marginal increase in volatilisation, after ageing in the presence of low moisture, PEN samples still appear to shrink during ageing. This is likely to result in a reduction of PEN melt flow and problematic build up of residual material in the die. In contrast to PEN, discolouration of PET is not so extreme after ageing in wet air and wet 42% oxygen at all ageing temperatures. These observations are identical to those noted previously under thermo-oxidative conditions and are thought to be due to the high extent of volatile product formation, accompanied by increased surface spreading, reducing the overall residual deposit thickness. Once again, these conditions are advantageous to encourage flow of PET from the die, preventing build up of residual material and die-streaks.

As discolouration of PET and PEN was found to be similar on ageing in dry and wet oxidative environments, it can be concluded that thermo-oxidative degradation is the dominant reaction occurring in PET and PEN. The impact of low moisture levels on the discolouration of PET and PEN has been shown to be minimal during thermo-oxidative-hydrolytic ageing at temperatures between 288°C and 320 °C.

5.3.2.4 UV-Visible Spectroscopy Studies on Solvent Cast PET and PEN Films

In addition to visual examination of the residual ageing material, a small set of studies examined solvent cast thin films exposed to identical thermal ageing conditions to illustrate the changes in the UV-visible absorption spectra before and after ageing. Although the UV-visible spectra are not directly comparable to the residual samples due to differences in the nature of the starting material (i.e. film thickness, sample size), the spectra still illustrate significant differences in the absorption properties of degradation species of PET and PEN. *Figures 5.31 and 5.32* illustrate the changes in the UV-visible spectra before and after ageing under thermal, thermal-hydrolytic, thermo-oxidative and thermo-oxidative-hydrolytic environments at temperatures of 288, 300 and 320 ^{o}C. By monitoring the degree of absorption at 400 nm, the extent of yellowing can be compared upon ageing PET and PEN. Also evident on the spectra are the highly absorbing regions evident around 300nm for PET which can be attributed to the π-π^* transition absorption structure of the terepthalate group and ester carbonyl on the polymer chain. Similarly, this

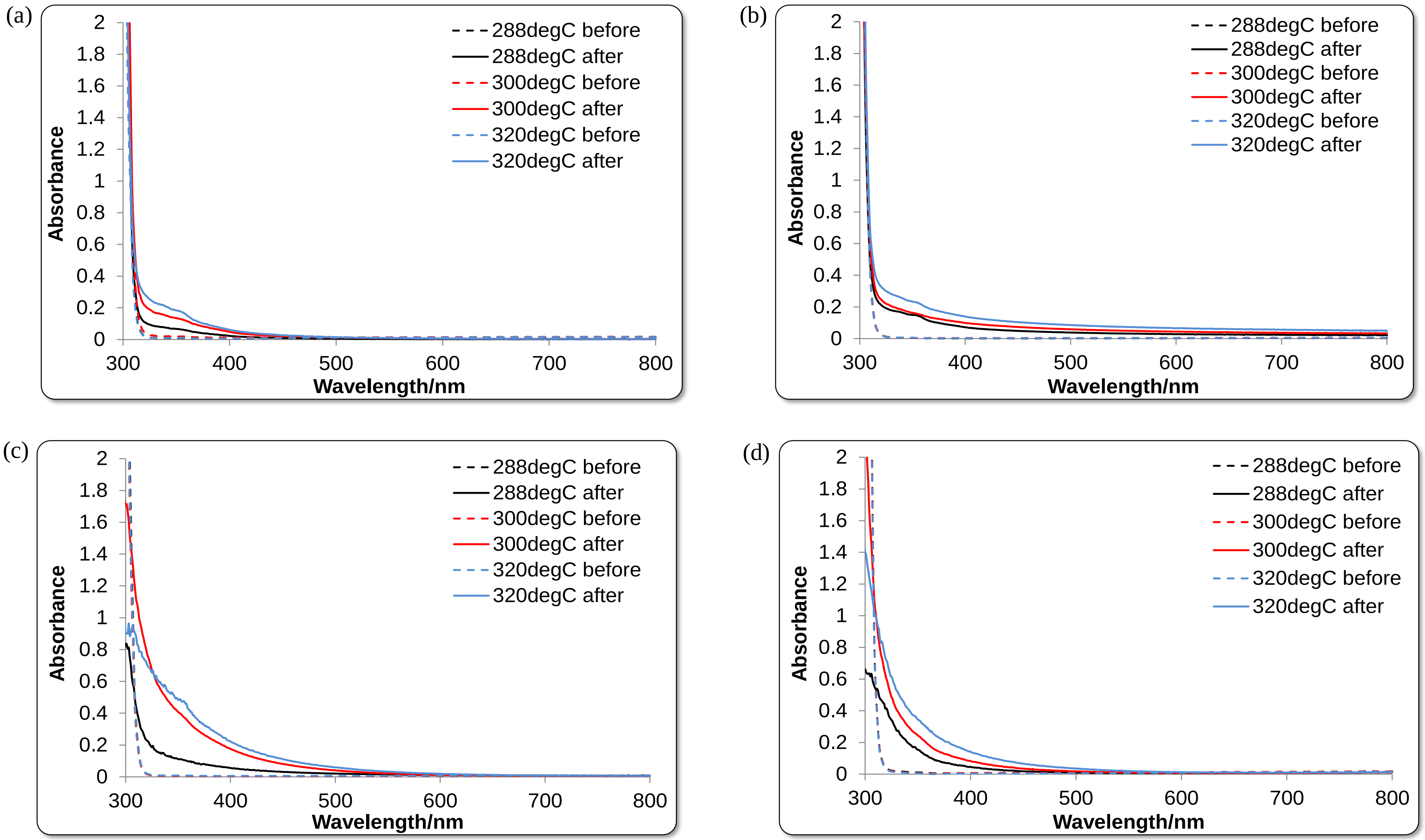


Figure 5.31 Changes in UV-visible absorption spectra of thin cast PET film sampled before and after ageing in (a) dry nitrogen (b) wet nitrogen (c) dry air (d) wet air for 4 hours

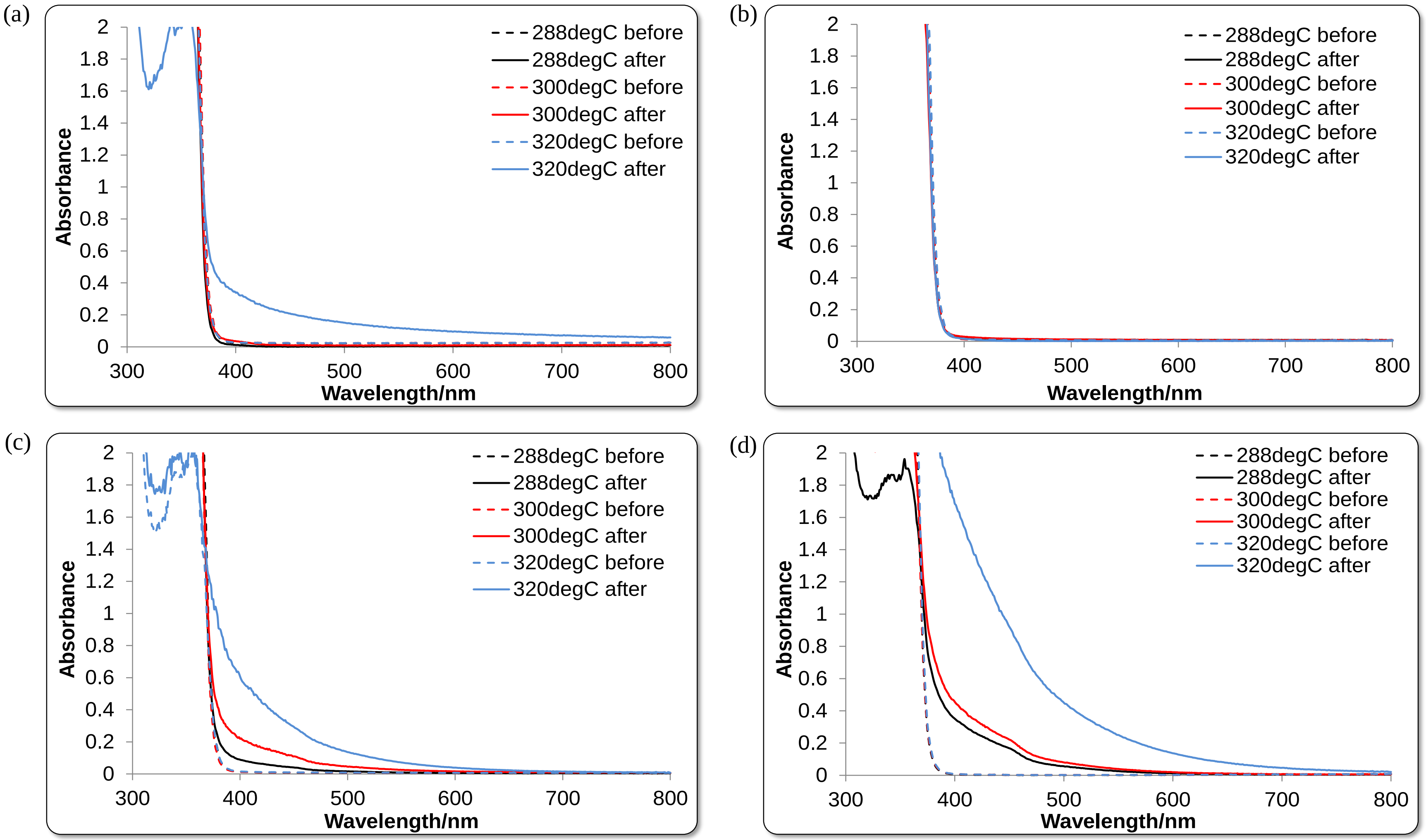


Figure 5.32 Changes in UV-visible absorption spectra of thin cast PEN film sampled before and after ageing in (a) dry nitrogen (b) wet nitrogen (c) dry air (d) wet air for 4 hours

absorption for PEN can be observed at a higher wavelength between 320 and 380nm for the π-π* transition absorption structure of the naphthalate group and ester carbonyl on the PEN polymer chain.

Similar trends to those discussed on visual examination of the residual samples can be observed from the UV-visible spectra illustrated in *Figures 5.31* and *5.32*. On ageing PET under thermal conditions, a gradual increase in the extent of discolouration can be observed with increased ageing temperature, in contrast to PEN which shows no discolouration until 320 °C. Only at 320 °C can extensive yellowing be observed in PEN on ageing in a thermal environment. As observed from the residual polyester material, this extent of discolouration in PET and PEN at 320 °C cannot be observed on ageing in the presence of low levels of moisture. Again, this highlights that the degradation species, responsible for discolouration during thermal degradation of PET and PEN are simply not formed to the same extent in the presence of water. On introducing oxygen into the ageing system, a significant increase in absorption can be observed for PET and PEN at all ageing temperatures, with the most highly absorbing species formed in PEN. *Figures 5.33* and *5.34* summarise the UV-visible spectroscopy results by plotting the absorption of PET and PEN at 400 nm as a function of ageing temperature, emphasising this increased extent of absorption and thus discolouration of PEN in contrast to PET.

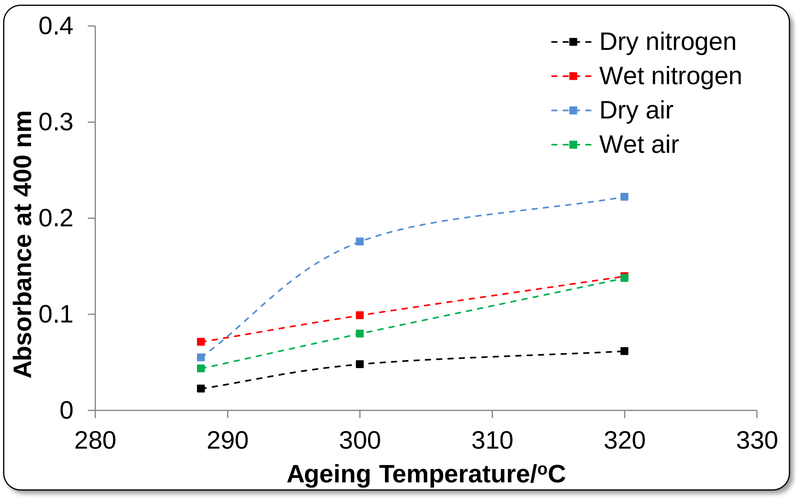


Figure 5.33 Absorption of PET at 400 nm as a function of ageing temperature for samples aged under dry and wet (1.5 - 2% AH) atmospheric conditions

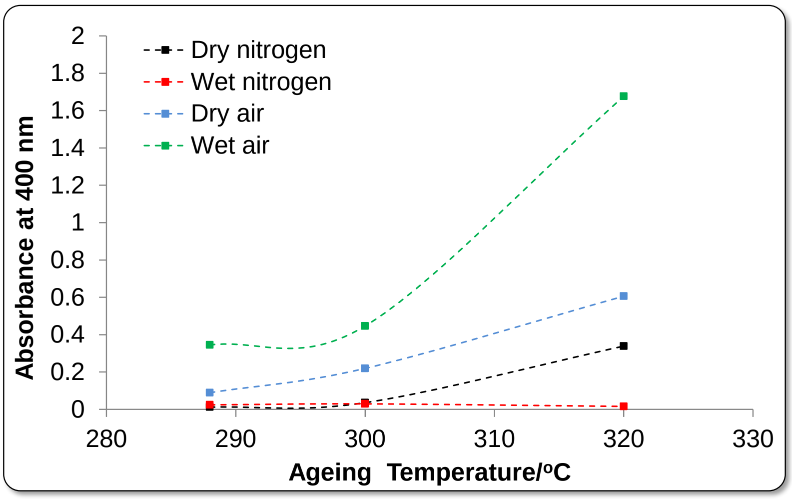


Figure 5.34 Absorption of PEN at 400 nm as a function of ageing temperature for samples aged under dry and wet (1.5 - 2% AH) atmospheric conditions

5.3.3 Gel Formation in Residual Film Samples of PET and PEN

The solubility of PET and PEN in hexafluoroisopropanol provides an indication as to the extent of gel formation and thus cross-linked material formed as a result of processing and/or ageing. If the polyester is soluble in halogenated solvent, no cross-linked material exists. However, if the material is not fully soluble, it is possible to separate the gel-fraction for subsequent analysis. Although, cross-linked species in PET are only reported to form in the presence of oxygen, [15,16] it is important to ensure that this is identical for PEN. Therefore, the solubility and thus gel content of all PET and PEN samples aged under all degradation environments was investigated.

5.3.3.1 Residual Samples Aged Under Thermal and Thermal-Hydrolytic Conditions

As it is very difficult to eliminate oxygen during processing of PET and PEN, it is not entirely surprising that cross-linked species form, resulting in a low residual gel content in the final PET and PEN polyester films (virgin materials) and thus thermally aged samples of PET and PEN. Control samples of virgin/unaged material and all samples of PET and PEN, aged under thermal and thermal-hydrolytic conditions, appeared fully soluble in the selected solvent mixture prior to extraction.

However, the presence of small quantities of gels (<5%) were still detected in all samples. These low quantities of gels detected did not appear to vary significantly between PET and PEN samples aged between 288 and 320 °C and are likely to originate from the virgin film materials as a result of processing.

5.3.3.2 Residual Samples Aged Under Thermo-Oxidative Conditions

The solubility of both PET and PEN film samples, aged in dry oxidative environments were found to differ quite significantly, in comparison to the results reported previously for ageing in inert environments. All samples of PET and PEN were found to be insoluble in the selected solvent mixture, in contrast to the high degree of solubility observed for samples aged in dry/wet nitrogen. These observations are not entirely surprising as thermo-oxidative degradation is reported to result in the formation of cross-linked species, otherwise known as gels. [15,16] *Figure 5.35* illustrates the % gel recovered from PET samples aged in dry oxidative conditions. Two charts are shown to provide an understanding of the overall gel content as a % of the original and residual sample mass. *Table 5.7* summarises the gel content data for PET samples aged in dry oxidative environments for 4 hours.

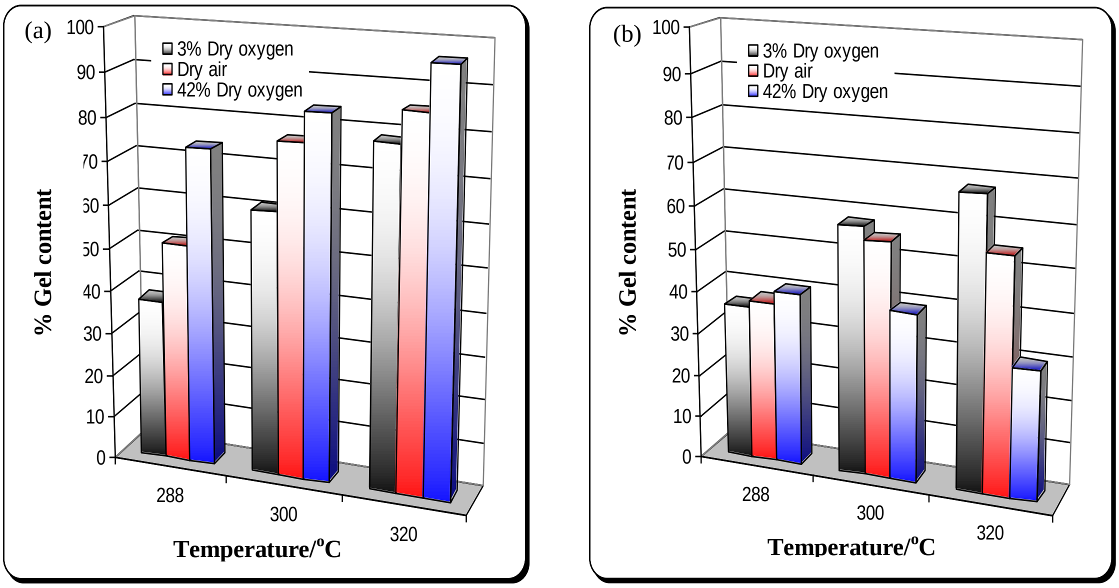


Figure 5.35 % Gel content in PET samples aged in dry oxidative environments for 4 hours - expressed as (a) % of residual sample mass (b) % of original sample mass

On expressing the gel content within PET as a function of the % residual sample mass, it can be observed that the overall gel content increases with increased ageing temperature and oxygen concentration. This highlights that both high temperature and high oxygen concentration promote cross-linking reactions in PET. On ageing PET in the most extreme environment i.e. 320 °C, dry 42% oxygen, over 95% of the residual material was found to be composed of insoluble gels.

Ageing Environment	***Ageing Temperature/ °C***	***% Gel Content (residual)***	***% Gel Content (original)***
Dry 3% oxygen	288	37.3	36.1
Dry air	288	51.0	37.7
Dry 42% oxygen	288	73.8	40.5
Dry 3% oxygen	300	61.0	57.8
Dry air	300	76.9	55.0
Dry 42% oxygen	300	83.8	39.4
Dry 3% oxygen	320	78.5	67.8
Dry air	320	85.5	55.0
Dry 42% oxygen	320	96.1	30.1

Table 5.7 Gel content data for PET samples aged in dry oxidative environments for 4 hours

Different trends are evident on presenting the gel content data, for PET samples aged in thermo-oxidative environments, as a % of the original sample mass. This is a consequence of the gel content calculation taking into account the overall product formation, including volatile and soluble degradation products. From *Figure 5.35,* we observe a significant increase in gel formation with increased temperature on ageing PET in 3% dry oxygen. Similarly, on ageing PET in dry air, the % gel content can be seen to increase on increasing the ageing temperature from 288 °C to 300 °C. However, at an ageing temperature of 320 °C, the gel content appears to plateau, signifying that no further thermo-oxidative cross-linking reactions are occurring within the polyester melt. This exact effect is illustrated most significantly for PET samples aged in dry 42% oxygen. On increasing the ageing temperature in dry 42% oxygen, the gel content in PET appears to decrease. This is thought to be due to an overall reduction in the formation of oxidative cross-linked degradation species due to a significant increase in the formation of volatile degradation products. Therefore by increasing the volatilisation of PET under extremely oxidative ageing environments, the overall extent of gel formation can be reduced. However, any residual material that does remain will not be soluble, and will essentially be composed entirely of cross-linked gels. These observations discussed, regarding the extent of gel formation in PET, are in agreement with previous studies reported by Yoda *et al.* [16] and Holland *et al.*. [15] Yoda *et al.* report that PET degrades to 38.5% and 52.6% gel structures during thermo-oxidative degradation at temperatures of 280 ^{o}C and 300 ^{o}C, respectively after 4 hours. With increased degradation times and temperatures, increased gel formation and volatilisation were reported.

On determining the extent of gel formation in residual PEN samples, aged in oxidative environments, the % gel content was found to be significant, particularly in samples aged in dry air and dry 42% oxygen. *Figure 5.36* illustrates the % gel content recovered from PEN samples aged in dry oxidative conditions for 4 hours, with the corresponding data presented in *Table 5.8.*

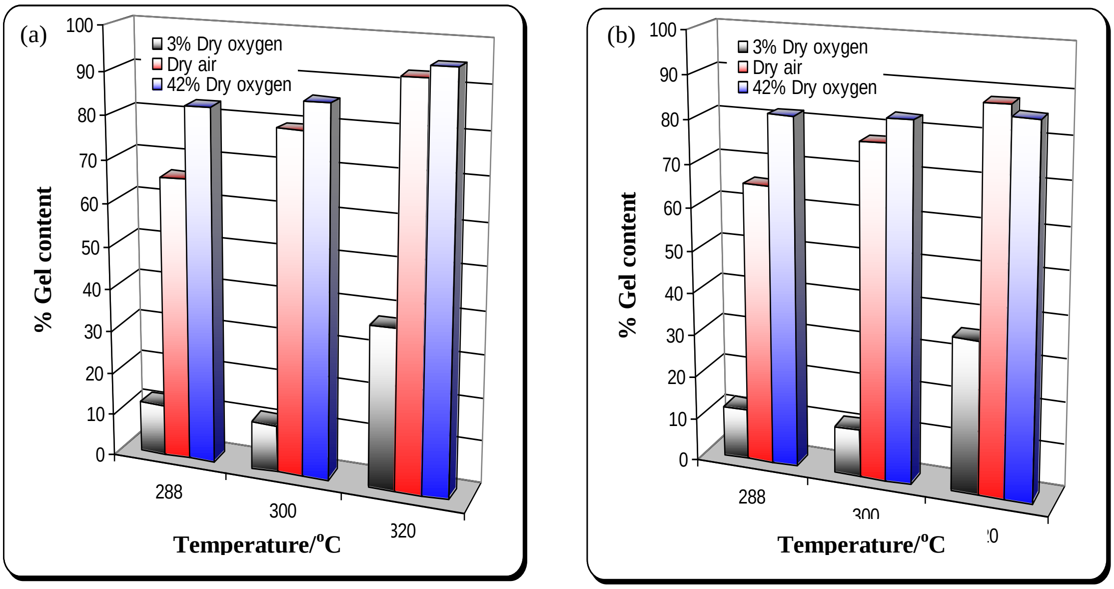


Figure 5.36 % Gel content in PEN samples aged in dry oxidative environments for 4 hours - expressed as (a) % of residual sample mass (b) % of original sample mass

Ageing Environment	*Ageing Temperature/ °C*	*% Gel Content (residual)*	*% Gel Content (original)*
Dry 3% oxygen	288	11.9	11.8
Dry air	288	66.0	65.4
Dry 42% oxygen	288	82.7	81.7
Dry 3% oxygen	300	11.2	11.0
Dry air	300	79.3	77.4
Dry 42% oxygen	300	85.6	82.8
Dry 3% oxygen	320	39.5	35.8
Dry air	320	92.6	87.9
Dry 42% oxygen	320	95.1	85.3

Table 5.8 % Gel content data for PEN samples aged in dry oxidative environments for 4 hours

When expressing the gel content of PEN as a % of the residual sample mass, we can observe that the formation of cross-linked species is minor in samples aged in 3% oxygen. This is thought to be due to the reduced sensitivity of PEN towards thermo-oxidative degradation, particularly at such low levels of oxygen. On increasing the oxygen concentration and temperature during ageing of PEN, a significant increase in thermo-oxidative activity becomes apparent, highlighting once again that both high temperature and high oxygen concentration promote cross-linking. Identical results were obtained on expressing the gel content results as a % of the original sample mass due to the poor extent of volatilisation observed in all samples of PEN. These results highlight that the dominant degradation reaction in PEN, on ageing in air and 42% oxygen, is oxidative cross-linking. Such reactions result in the formation of mainly cross-linked species, limiting the overall production of volatile degradation products.

Another interesting observation from the gel content results is the overall increase in gel formation observed in PEN, in comparison to PET, when ageing in air and 42% oxygen. Despite low levels of volatilisation observed for PEN during thermo-oxidative degradation studies, the overall extent of gel formation remains higher in PEN than PET. Such results highlight that oxygen must have the ability to diffuse into the highly viscous PEN melt in order to enable these thermo-oxidative cross-linking reactions to occur. This suggests that the overall levels of volatilisation in PEN are likely to be limited by restricted diffusion of bulky degradation products from the polyester melt. These trapped degradation products of PEN are then likely to undergo further reactions, possibly leading to formation of cross-linked species. Of course, once the PEN system has cross-linked the subsequent volatilisation of degradation products will become even more restricted.

This increase in the overall extent of gel formation in PEN, in comparison to PET is emphasised further in *Figure 5.37* summarising the overall proportion of volatile, gel and soluble degradation products formed in both polyesters after ageing in dry oxidative environments. By increasing the volatilisation of PET under extremely oxidative ageing environments, the overall extent of gel formation and soluble products can be reduced. However, as we appear unable to increase the levels of volatilisation in PEN, on ageing at high temperature and high oxygen concentrations, the overall extent of gel formation remains very high, with only a low proportion of soluble products.

Despite observing high gel formation in both polyesters after ageing in thermo-oxidative conditions, structural information on the nature of these cross-linked species in both PET and PEN remains limited. FTIR analysis was performed on the extracted gels aged under the most extreme dry oxidative environments using an Agilent 5500a FTIR spectrometer containing a diamond ATR cell. However, all spectra of the PET and PEN gels appeared identical to the virgin, unaged samples, indicating that the absorption bands for cross – linked gels are not abundant enough to be detected. All ATR data can therefore be found in *Chapter 8 Supplementary Material*. Yoda *et al.* [16] report that vinyl ester groups, formed from primary thermo-oxidative chain scission reactions participate in the formation of cross-linked species. As the concentration of vinyl end groups increase with degradation and accumulate within the polymer, the vinyl groups are thought to react with radical species to form network structures, most likely to be connected via aliphatic bridges. In contrast to this mechanism proposed, Holland *et al.* [15] report that the formation of cross-linked structures is unlikely to derive from vinyl esters.

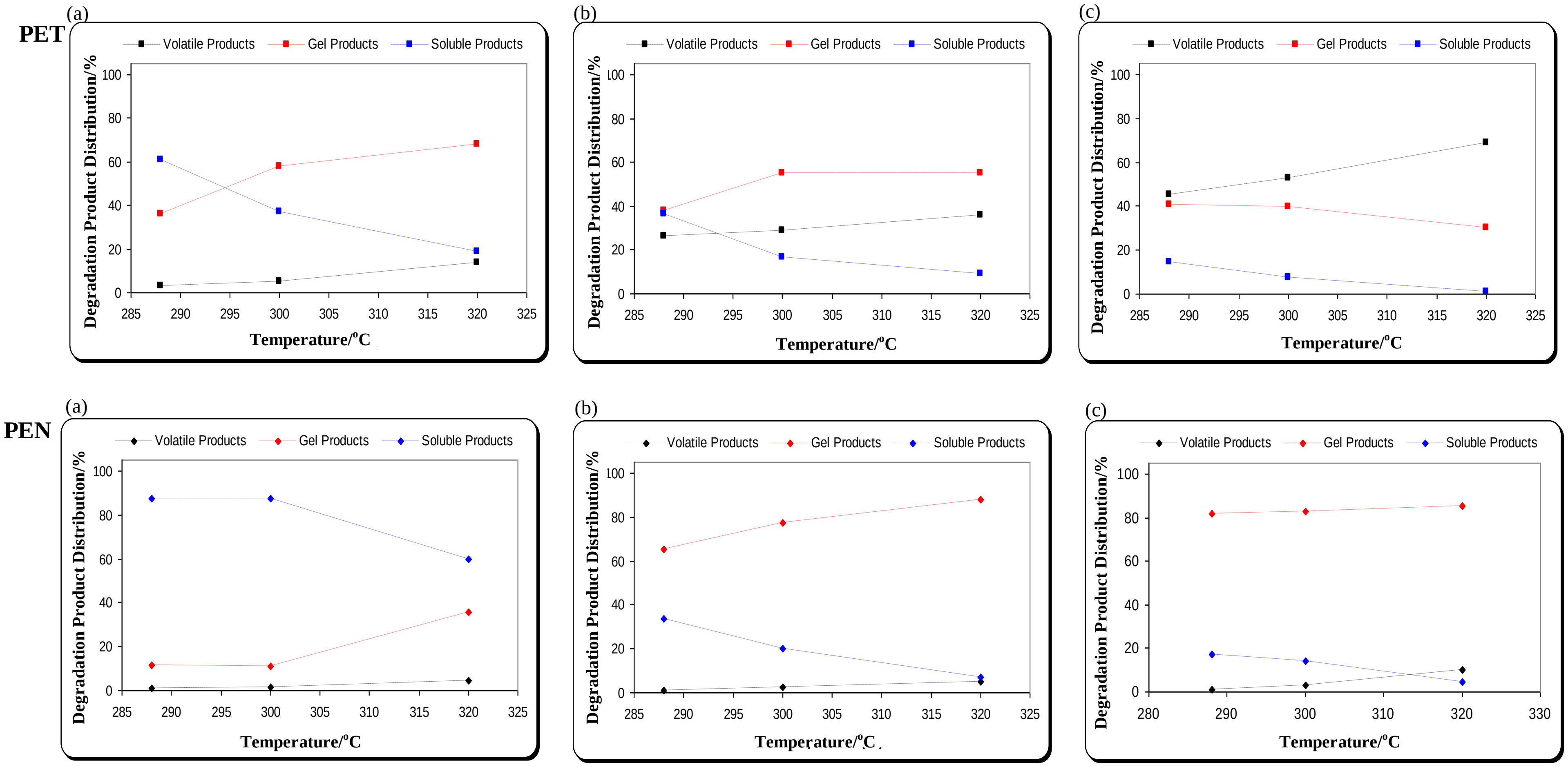


Figure 5.37 Degradation product distribution for PET and PEN samples aged in dry (a) 3% oxygen (b) air and (c) 42% oxygen for 4 hours

Under the extreme conditions of thermo-oxidation, the vinyl ester groups are thought to undergo a series of further reactions leading to the formation of interconnected aromatic rings. However, no structural evidence was presented in either study to prove such degradation species are responsible for cross-linking in PET and PEN.

5.3.3.3 Residual Samples Aged Under Thermo-Oxidative-Hydrolytic Conditions

The solubility of PET and PEN film samples, aged in wet oxidative environments, were found to be similar to samples aged in a dry oxidative environment. All samples of PET and PEN were found to be insoluble in the selected solvent mixture, in contrast to the high degree of solubility observed for samples aged in dry and wet nitrogen. *Figures 5.38 – 5.40* compare the % gel content recovered from PET samples aged in dry and wet oxidative conditions. Two charts are shown for each oxidative environment to provide an understanding of the overall gel content as a % of the original and residual sample mass. *Table 5.9* summarises the gel content data for PET samples aged in wet oxidative environments for 4 hours.

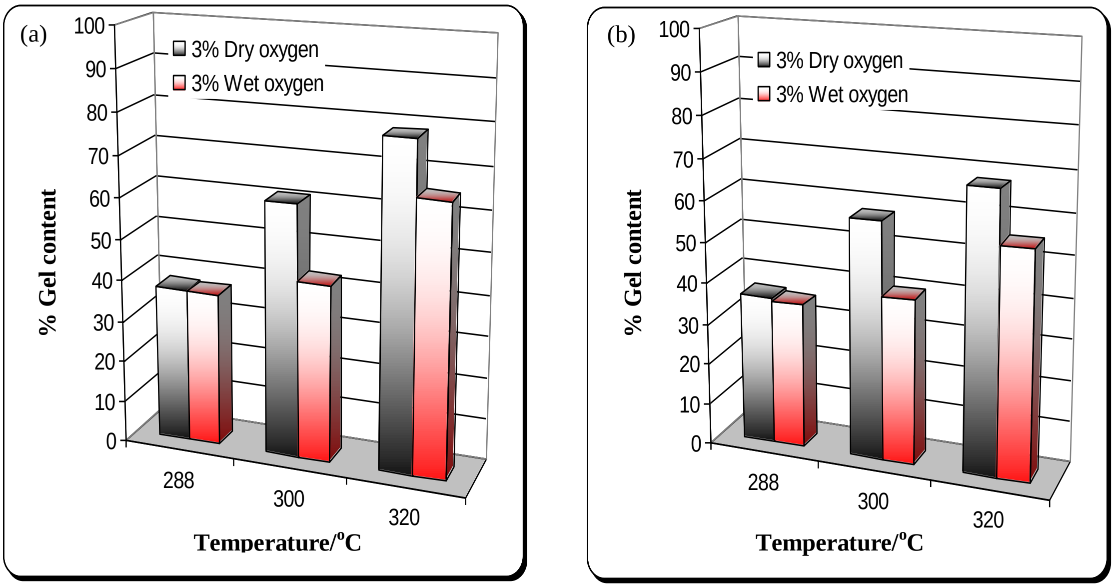


Figure 5.38 % Gel content in PET samples aged in dry and wet (1.5 - 2% AH) 3% oxygen for 4 hours - expressed as (a) % of residual sample mass (b) % of original sample mass

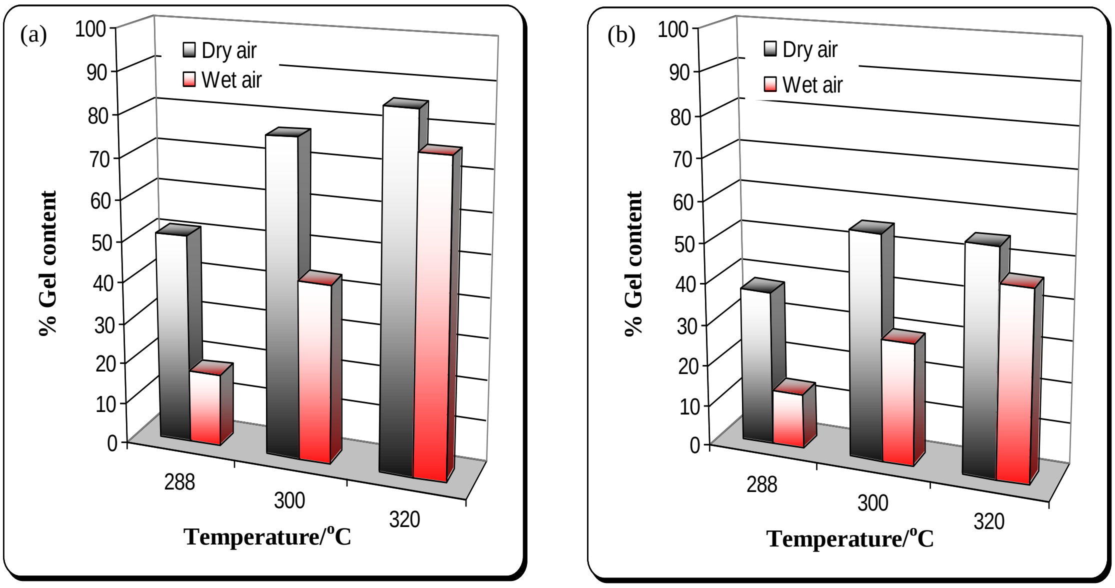


Figure 5.39 % Gel content in PET samples aged in dry and wet (1.5 - 2% AH) air for 4 hours - expressed as (a) % of residual sample mass (b) a % of original sample mass

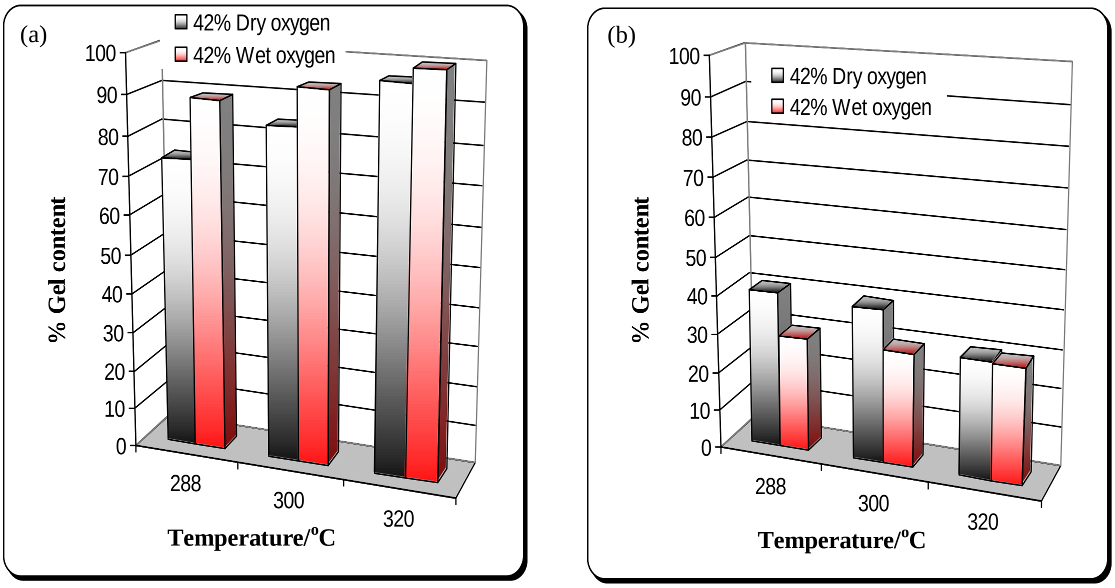


Figure 5.40 % Gel content in PET samples aged in dry and wet (1.5 - 2% AH) 42% oxygen for 4 hours - expressed as (a) % of residual sample mass (b)% of original sample mass

Ageing Environment	*Ageing Temperature/ °C*	*% Gel Content (residual)*	*% Gel Content (original)*
Wet 3% oxygen	288	37.0	35.3
Wet air	288	17.7	13.3
Wet 42% oxygen	288	88.9	29.4
Wet 3% oxygen	300	42.7	39.9
Wet air	300	43.5	29.7
Wet 42% oxygen	300	93.4	29.3
Wet 3% oxygen	320	65.0	55.1
Wet air	320	75.8	46.4
Wet 42% oxygen	320	99.6	29.5

Table 5.9 % Gel content data for PET samples aged in wet (1.5 - 2% AH) oxidative environments for 4 hours

On expressing the gel content within PET as a % of the residual sample mass, it can be observed that the overall gel content increases with increased ageing temperature and oxygen concentration, on ageing in wet oxidative environments. This highlights that both high temperature and high oxygen concentration promote cross-linking reactions in PET. However, on comparing the % gel content of PET between samples aged in dry and wet oxidative conditions, a general decrease in % gel content can be observed for samples aged in the presence of low moisture levels. This is most significant under 3% oxygen and air and is thought to be due to competing oxidative and hydrolytic degradation reactions. As hydrolysis competes with thermo-oxidative degradation during ageing, the overall extent of cross-linking is reduced, with an increase in the extent of chain scission resulting in a marginal increase in volatilisation, as observed for PET samples aged in wet oxidative environments.

As observed previously for PET samples aged in dry oxidative environments, the % gel content appears to be significantly reduced when expressing as a % of the original sample mass. This is a consequence of the gel content calculation taking into account the overall product distribution, including volatile and soluble degradation products. On ageing PET in 3% wet oxygen and air, a significant increase in gel formation can be observed from *Figures 5.38* and *5.39* on increasing the ageing temperature. However, the overall extent of gel formation in PET samples aged in wet oxidative conditions still remains considerably lower than the % gel content reported after ageing in dry oxidative conditions due to competing hydrolytic and thermo-oxidative degradation reactions. PET samples aged in 42% wet oxygen also exhibit this decrease in % gel formation on ageing in the presence of moisture; however the % gel content does not appear to increase with temperature. Instead, the % gel content plateaus around 30%, coinciding with an identical plateau observed from the volatilisation results reported previously for PET samples aged in wet 42% oxygen. These results indicate that the maximum extent of thermo-oxidative degradation and thus volatilisation has been approached on ageing PET in wet 42% oxygen.

On determining the extent of gel formation in residual PEN samples, aged in wet oxidative environments, the % gel content was found to be considerably large, particularly in samples aged in 42% wet oxygen. *Figures 5.41 – 5.43* compare the % gel content recovered from PEN samples aged in dry and wet oxidative conditions. *Table 5.10* summarises the gel content data for PEN samples aged in wet oxidative environments for 4 hours. In contrast to PET, similar results were obtained on expressing the gel content as a % of the residual and original sample mass due to the low volatilisation levels observed in all samples of PEN.

From *Figure 5.41*, it can be observed that the formation of cross-linked species is minor in PEN samples aged in 3% wet oxygen. This is thought to be due to the reduced sensitivity of PEN towards thermo-oxidative degradation, particularly at low oxygen concentrations. Competing hydrolytic degradation reactions will also contribute to a reduction in gel content, in comparison to PEN samples aged in dry 3% oxygen.

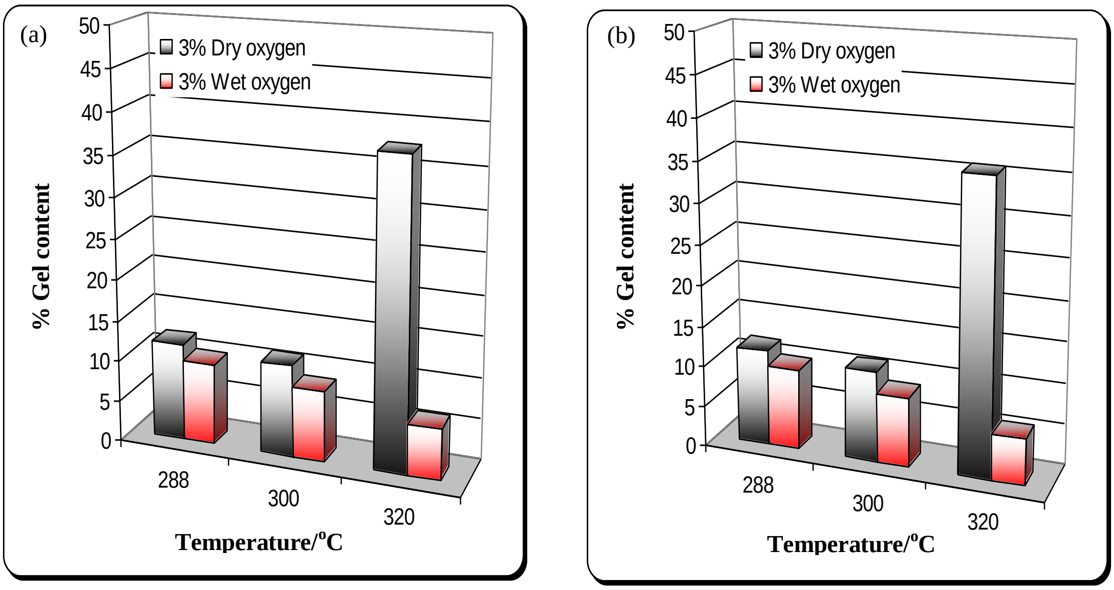


Figure 5.41 % Gel content in PEN samples aged in dry and wet (1.5 - 2% AH) 3% oxygen for 4 hours - expressed as (a) % of residual sample mass (b) % of original sample mass

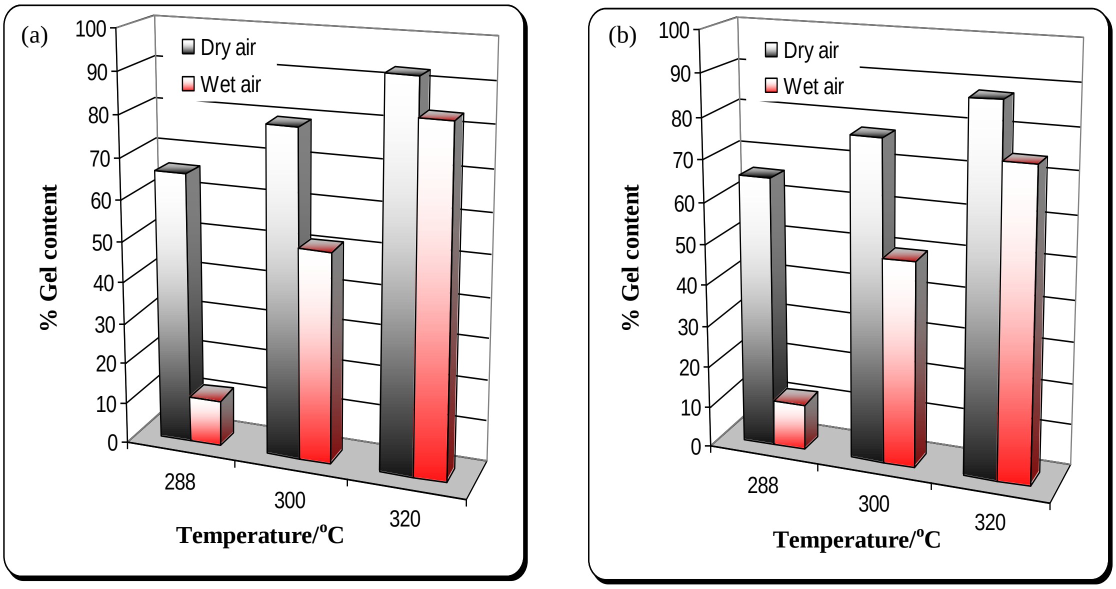


Figure 5.42 % Gel content in PEN samples aged in dry and wet (1.5 - 2% AH) air for 4 hours - expressed as (a) % of residual sample mass (b) % of original sample mass

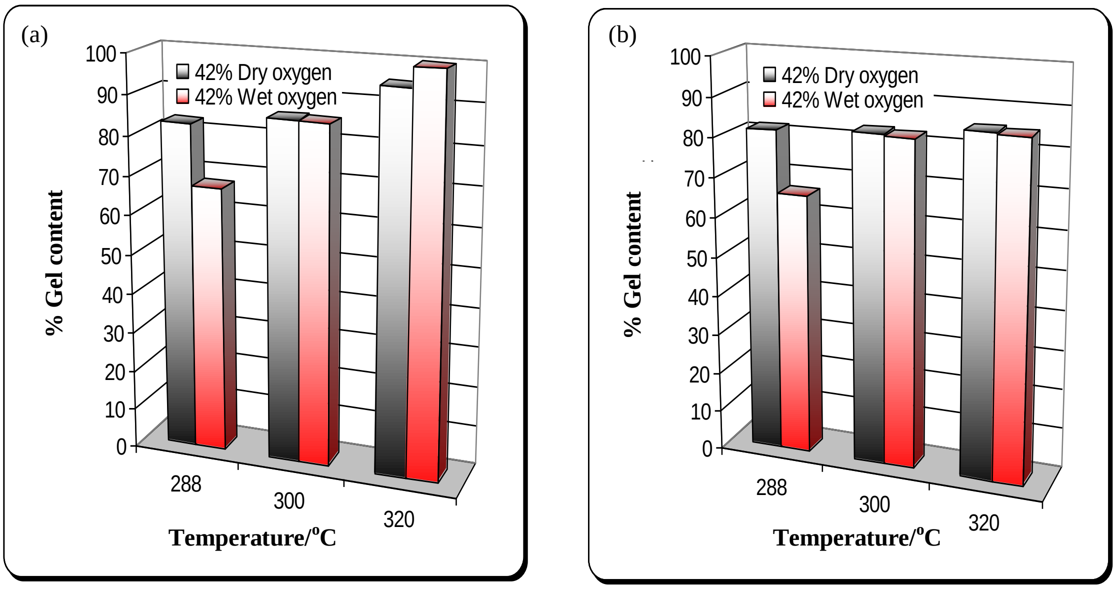


Figure 5.43 % Gel content in PEN samples aged in dry and wet (1.5 - 2% AH) 42% oxygen for 4 hours - expressed as (a) % of residual sample mass (b) % of original sample mass

Ageing Environment	*Ageing Temperature/ °C*	*% Gel Content (residual)*	*% Gel Content (original)*
Wet 3% oxygen	288	10.0	9.9
Wet air	288	11.4	11.2
Wet 42% oxygen	288	67.2	66.0
Wet 3% oxygen	300	8.7	8.5
Wet air	300	51.1	49.5
Wet 42% oxygen	300	85.4	82.3
Wet 3% oxygen	320	6.2	5.7
Wet air	320	83.5	74.3
Wet 42% oxygen	320	99.9	84.8

Table 5.10 % Gel content data for PEN samples aged in wet (1.5 - 2% AH) oxidative environments for 4 hours

On increasing the oxygen concentration and temperature during ageing of PEN, a significant increase in gel formation prevails, highlighting once again that both temperature and high oxygen levels promote cross-linking. However, once again a reduction in the extent of gel content and thus formation of cross-linked species can be observed for PEN samples aged in the presence of water. This is most pronounced in wet air, highlighting the competitive thermo-oxidative and hydrolytic degradation reactions ongoing in PEN. On reaching an oxygen concentration of 42% and ageing temperatures of 300 °C and 320 °C, this difference in the extent of gel formation between PEN samples aged in dry and wet 42% oxygen decreases. Hydrolysis is therefore thought to have more impact on the overall extent of degradation at lower oxygen concentrations, resulting in an overall reduction in gel formation. However, in highly oxidative environments, thermo-oxidative cross-linking reactions are thought to dominate, resulting in a high rate of formation of cross-linked species in PEN.

Identical to the observations previously reported for PET and PEN aged in dry oxidative environments, an overall increase in gel formation was observed in PEN, in comparison to PET, on ageing in wet air and wet 42% oxygen. As discussed previously, this is thought to be due to extensive cross-linking reactions involving bulky aromatic degradation products which are unable to volatilise from the polyester melt. Subsequently, the extent of gel formation is increased and the extent of volatilisation is decreased, in comparison to PET. Once again, ATR spectra provided little indication as to the nature of the gel species formed in either PET or PEN, the data of which can be found in *Chapter 8 Supplementary Material.*

This increase in the overall extent of gel formation in PEN, in comparison to PET, is further emphasised in *Figure 5.44* summarising the overall product distribution of volatile, gel and soluble degradation products formed in both polyesters after ageing in wet oxidative environments. By increasing the extent of volatilisation in PET on ageing in extremely oxidative-hydrolytic ageing environments, an overall reduction in the extent of gel formation and soluble products can be observed. However, as we appear unable to increase the levels of volatilisation in PEN beyond 15%, on ageing in high temperature and high oxygen concentrations, the overall extent of gel formation remains very high, with a low proportion of soluble products. These trends are very similar to those observed previously for PET and PEN aged under thermo-oxidative conditions.

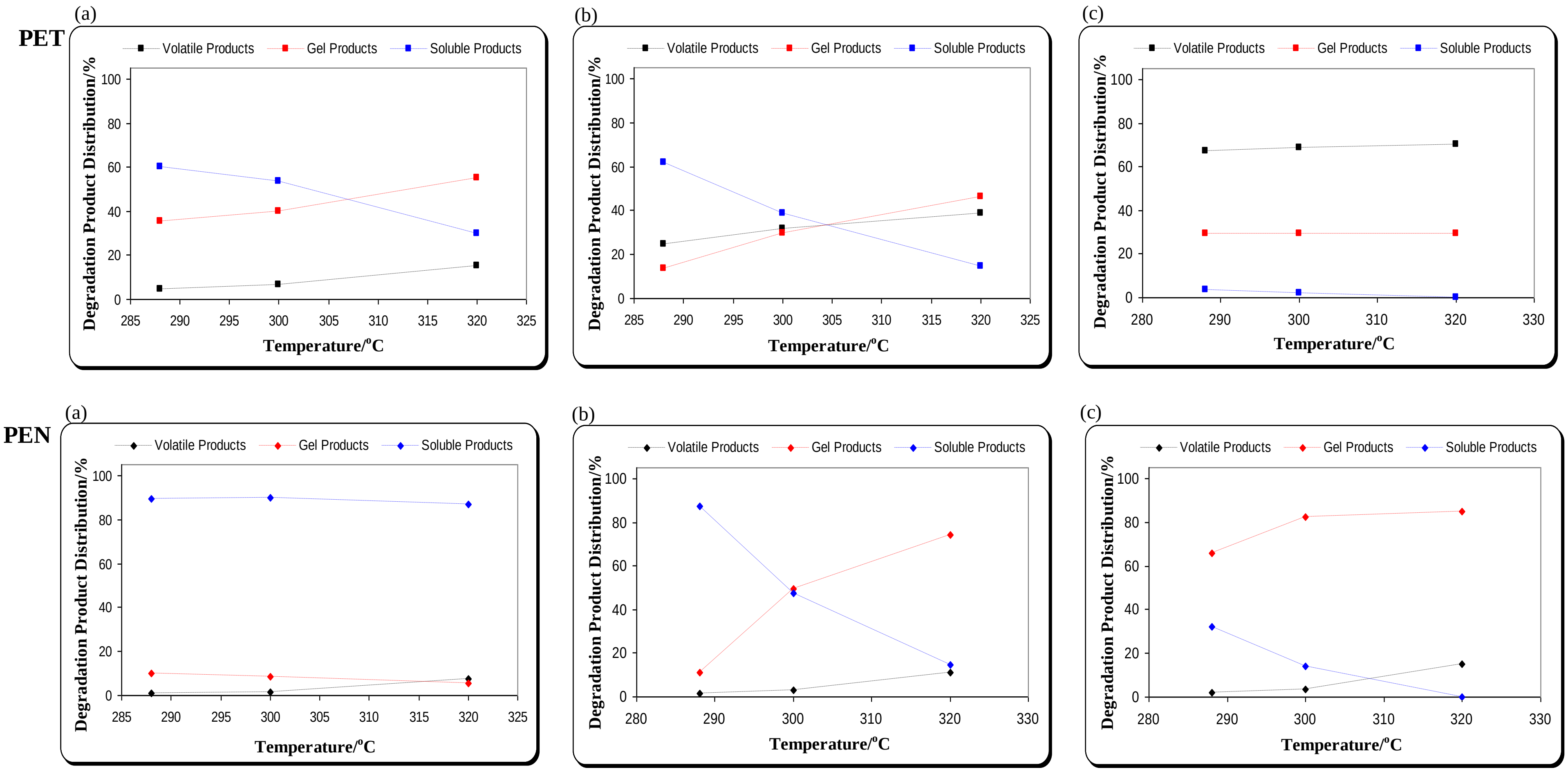


Figure 5.44 Degradation product distribution for PET and PEN samples aged in wet (1.5 – 2% AH) (a) 3% oxygen (b) air and (c) 42% oxygen for 4 hours

5.3.4 Carboxyl End Group Determination of Aged Samples of PET and PEN

As the residual film samples from PET and PEN aged under dry and wet nitrogen were composed of soluble material, rapid determination of the carboxyl end group (CEG) concentration was performed on all residual samples to examine their extent of degradation. At lower ageing temperatures i.e. below the polyester melt temperature, where extensive degradation does not occur, the CEG concentration is expected to decrease in both PET and PEN with increasing temperature due to further polymerisation i.e. polymerisation of unreacted acid chain ends increasing the overall polymer chain length. This concept is illustrated in *Figure 5.45* for samples of PET and PEN aged under typical solid-state polymerisation conditions. Additional volatilisation and CEG concentration data for PET and PEN samples aged at solid-state polymerisation temperatures can be found in *Chapter 8 Supplementary Material*.

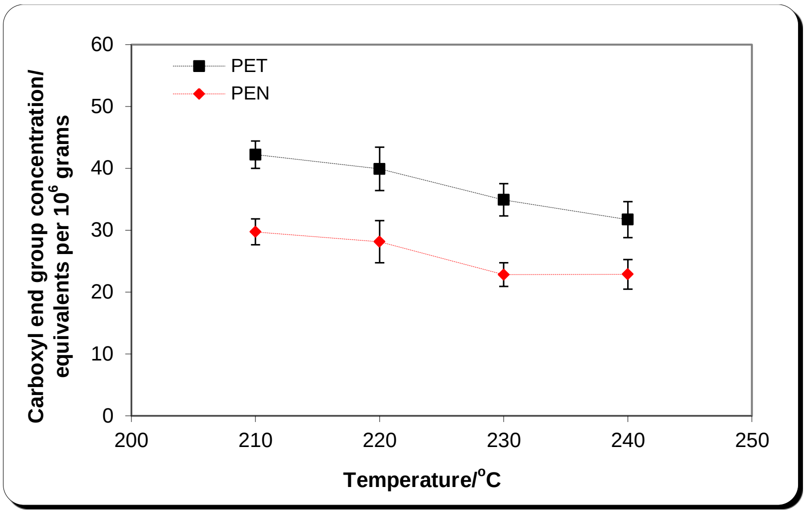


Figure 5.45 Average CEG concentrations for PET and PEN samples aged at solid-state polymerisation temperatures in dry nitrogen for 4 hours

With increased ageing temperature and thus increased degradation, it is expected that an increase in the CEG concentration will be observed due to the presence of additional acid end groups formed from primary chain scission reactions. *Figure 5.46* and *Table 5.11* present the CEG concentrations determined for PET and PEN film samples aged in dry nitrogen.

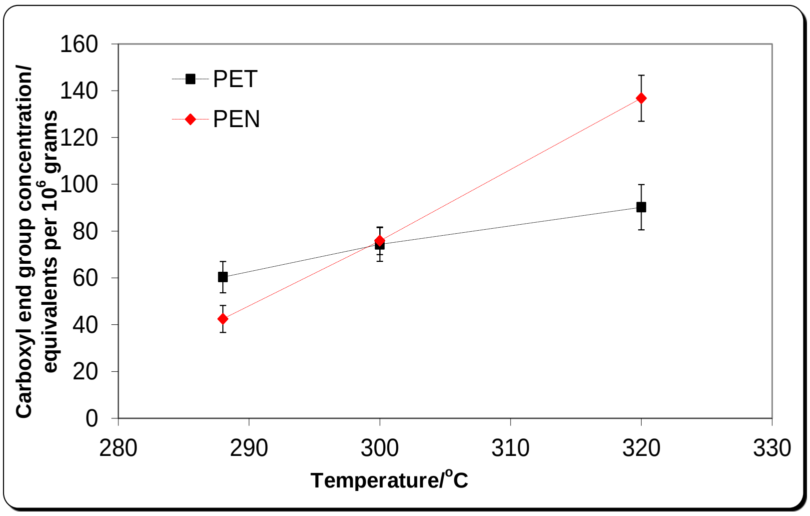


Figure 5.46 Average CEG concentrations for PET and PEN samples aged in dry nitrogen for 4 hours

Polymer	*Ageing Temperature/°C*	*Average[COOH]/equiv. per 10^6 grams*
PET	Virgin	38.9 ± 2.3
PEN	Virgin	36.5 ± 4.9
PET	288	60.3 ± 6.7
PEN	288	42.5 ± 5.8
PET	300	74.3 ± 7.2
PEN	300	75.9 ± 5.9
PET	320	90.2 ± 9.7
PEN	320	136.8 ± 9.8

Table 5.11 Average CEG concentrations for PET and PEN samples aged in dry nitrogen for 4 hours

As predicted, an increase in the CEG concentration can be observed for both PET and PEN as the ageing temperature increases from 288 °C to 320 °C. On ageing PET at 288 °C, the extent of thermal degradation appears to be significant with a higher concentration of acid end groups detected, in comparison to the virgin material. In contrast to this, the difference in acid end group concentration between virgin PEN and PEN aged at 288 °C appears to be minor, indicating few chain scission reactions are ongoing. These results are in agreement with the volatilisation data presented previously, for PET and PEN, in *Table 5.2*.

On increasing the ageing temperature above 288 °C, the acid end group concentration for PEN appears to rise more rapidly than PET. A considerably higher CEG concentration for samples of PEN, aged under thermal conditions at 320 °C, can also be observed in *Figure 5.46*, in comparison to PET. This observation is surprising as one would initially hypothesise that aged samples of PET would exhibit increased CEG concentrations, in comparison to PEN, due to the overall reduction in thermal stability and increased degradation activity observed for PET. However, it is feasible that secondary degradation reactions in PEN, which result in the formation of volatile degradation products, could simply be occurring at a much slower rate than those in PET. This would result in CEG's in PEN being consumed at a slower rate than those in secondary degradation reactions of PET, resulting in an overall higher concentration of CEG's. This hypothesis agrees with the decrease in volatile degradation products observed for PEN (4.2 %) in comparison to PET (8.1 %) after ageing at 320 °C in dry, inert conditions. Alternatively, the nature and volatility of the degradation products in PEN may differ and limit volatilisation from the polyester melt. This would lead to the decrease in volatilisation observed for PEN, in comparison to PET and possibly an increase in the CEG concentration. However, the increase in the CEG concentration would very much depend on the nature of the degradation products trapped within the PEN polyester melt.

Under thermal hydrolytic ageing conditions, it is expected that both PET and PEN would exhibit an increase in CEG concentration due to hydrolytic degradation from the presence of low moisture levels. As discussed previously, during hydrolytic degradation, each water molecule breaks down one ester linkage resulting in the formation of one carboxyl and one hydroxyl end group. Therefore, as the degree of thermal and hydrolytic degradation increases, an increase in the CEG concentration should be observed. *Figure 5.47* illustrates the CEG concentrations for PET and PEN film samples aged in dry and wet nitrogen. *Table 5.12* presents the CEG concentration data for PET and PEN samples aged in wet nitrogen.

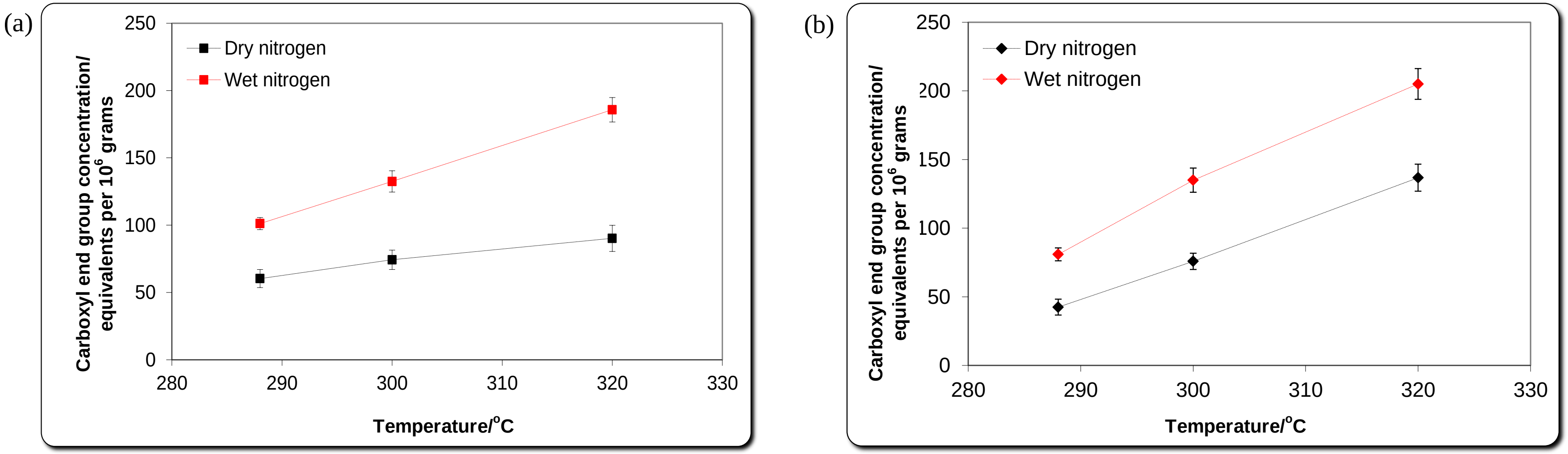


Figure 5.47 Average CEG concentrations for (a) PET and (b) PEN samples aged in dry and wet (1.5 - 2% AH) nitrogen for 4 hours

Polymer	*Ageing Temperature/ °C*	*Average[COOH]/ equiv. per 10^6 grams*
PET	Virgin	38.9 ± 2.3
PEN	Virgin	36.5 ± 1.9
PET	288	101.2 ± 4.5
PEN	288	80.9 ± 4.7
PET	300	132.5 ± 7.9
PEN	300	134.9 ± 8.8
PET	320	185.8 ± 9.1
PEN	320	205.0 ± 11.2

Table 5.12 Average CEG concentrations for PET and PEN samples aged in wet (1.5 - 2% AH) nitrogen for 4 hours

As predicted, a higher concentration of carboxyl end groups can be observed for PET and PEN samples aged in thermal-hydrolytic conditions, in comparison to thermally aged samples. This indicates that both thermal and hydrolytic degradation reactions are ongoing in both PET and PEN resulting in an increase in the extent of degradation and thus increased formation of carboxyl end groups. As the ageing temperature increases under thermal-hydrolytic conditions, the CEG concentration continues to increase, with the highest CEG concentration observed in PET and PEN samples aged at 320 °C in a wet, inert environment.

On close examination of the CEG data illustrated in *Table 5.12*, for PET and PEN samples aged at 288 °C in wet nitrogen, it can be observed that extensive chain scission reactions are ongoing in both materials. This is evident from the rapid increase in CEG concentration observed, in comparison to the virgin materials. These results therefore differ considerably from those observed under thermal conditions, particularly in PEN. After thermal ageing at 288 °C, degradation of PEN was shown to be minimal with no change in the concentration of CEG's observed, in comparison to the virgin material. However, upon ageing in thermal-hydrolytic conditions, the CEG concentration was shown to be much larger than that of virgin PEN. This indicates that hydrolytic degradation is the dominant degradation reaction ongoing in PEN at temperatures of 288 °C, resulting in rapid formation of CEG's and an overall higher CEG concentration. Thermal degradation of PEN is then thought to become significant in relation to hydrolytic degradation at temperatures above 300 °C.

Due to the insolubility of PET and PEN residues recovered from thermo-oxidative and thermo-oxidative-hydrolytic ageing studies, studies to determine the CEG concentration could not be performed.

5.3.5 Melt Rheology Studies of PET and PEN

Due to the reduced extent of volatilisation observed in PEN samples aged in the presence of under thermal and thermo-oxidative environments, it is thought that PEN may be restricting the diffusion of bulky, volatile degradation products from the polyester melt limiting volatilisation and thus promoting cross-linking reactions. It is therefore vital to examine the melt rheology behaviour of PET and PEN in an attempt to understand the degradation chemistry of PEN in comparison to PET.

At an ageing temperature of 288 °C, under thermal ageing conditions, experimental evidence presented thus far suggests that very little degradation is ongoing in PEN, in comparison to PET. The extent of volatilisation observed in PEN is very low, even after an ageing period of 24 hours, suggesting that the increased thermal stability of PEN leads to a reduction in the extent of chain scission reactions occurring, in comparison to PET. This evidence is supported by melt rheology studies of PEN completed at all ageing temperatures of interest, over a short 60 minute period. *Figure 5.48* illustrates complex viscosity measurements of PEN as a function of time at all three ageing temperature of interest.

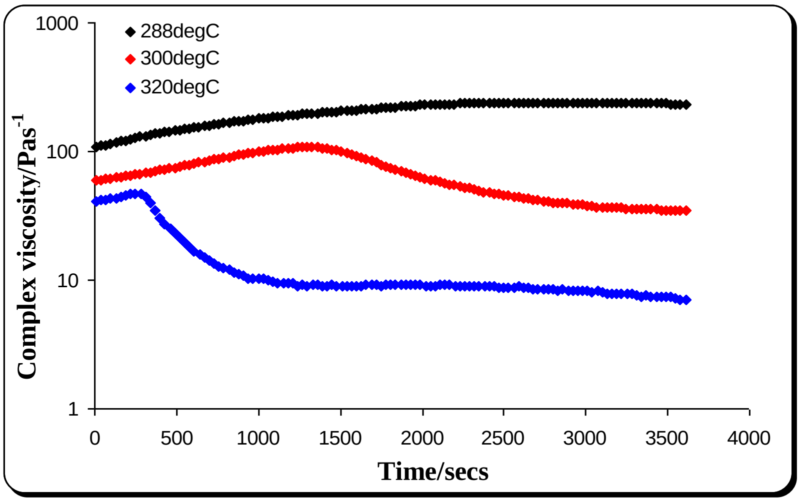


Figure 5.48 Complex viscosity measurements of PEN as a function of time, at ageing temperatures of 288 – 320 ^{o}C, in a dry inert environment

From *Figure 5.48*, the melt viscosity of PEN at 288 °C can be seen to increase over the entire period of the study. This indicates that the main activity ongoing within the PEN polyester melt is chain extension i.e. further polymerisation of the polyester chain ends and not chain scission. Further polymerisation results in an increase in the overall length of the polymer chains and increase in molar mass. In contrast to the results observed for PEN, evidence suggests that more significant degradation of

PET occurs on ageing at 288 °C under thermal conditions. From *Figure 5.49*, the melt viscosity of PET at 288 °C can be seen to increase initially over the first 30 minutes, prior to decreasing for the remaining 30 minutes. This illustrates that chains composed of free acid end groups initially polymerise, prior to degrading after 30 minutes, resulting in a decrease in melt viscosity. The starting melt viscosity values for PET samples aged at 288 °C were also recognised to be lower in comparison to PEN, providing beneficial, increased flow of the polyester from the extrusion die.

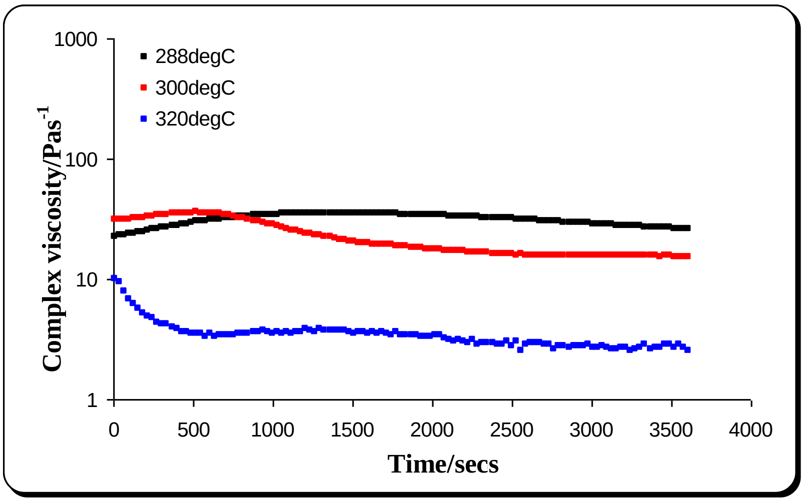


Figure 5.49 Complex viscosity measurements of PET as a function of time, at ageing temperatures of 288 – 320 ^{o}C, in a dry inert environment

On increasing the ageing temperature to 300 °C, a reduction in chain extension and an increase in chain scission can be observed from the melt viscosity data presented in *Figures 5.48* and *5.49*. As the ageing time progresses, both PET and PEN exhibit an initial increase in melt viscosity as polymerisation takes place, prior to degradation resulting in a decrease in melt viscosity. This time period within which polymerisation occurs and the melt viscosity increases is extended in PEN, in comparison to PET. On increasing the ageing temperature to 300 °C, a lower melt viscosity was observed for both polyesters, indicating increased flow from the extrusion die. Once again, the starting melt viscosity was higher in PEN than PET. Finally on measuring the viscosity at temperatures of 320 ^{o}C under thermal condtions, a constant decrease in melt viscosity of PET and PEN can be observed with time, illustrating that the dominant reaction is thermal degradation.

Figures 5.50 and 5.51 illustrate the changes in melt viscosity of PET and PEN as a function of temperature. With increased ageing temperature, the melt viscosity decreases in both polyesters examined under thermal and thermo-oxidative environments. The overall melt viscosity of PEN is higher than that of PET at all temperatures. Therefore, as the nature and thus volatility of the degradation products in PEN differ due to the presence of bulky naphthalene groups, in comparison to phenyl groups in PET, it is feasible that this could limit their volatilisation from the polyester melt.

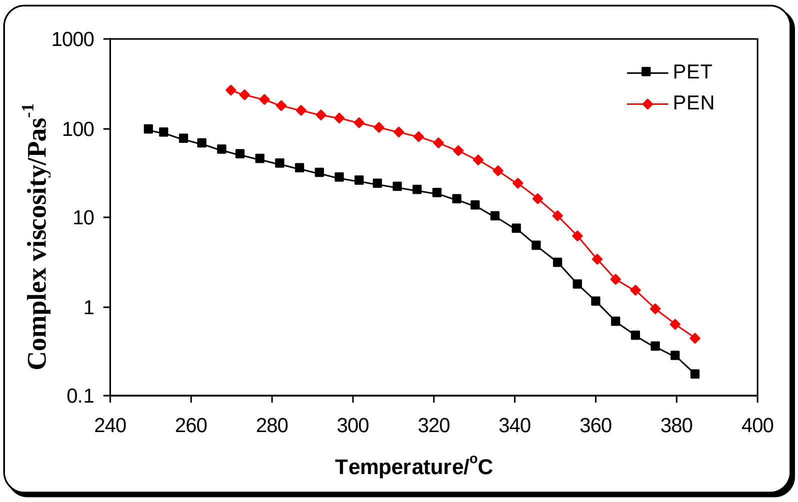


Figure 5.50 Complex viscosity measurements of PET and PEN as a function temperature, in dry nitrogen

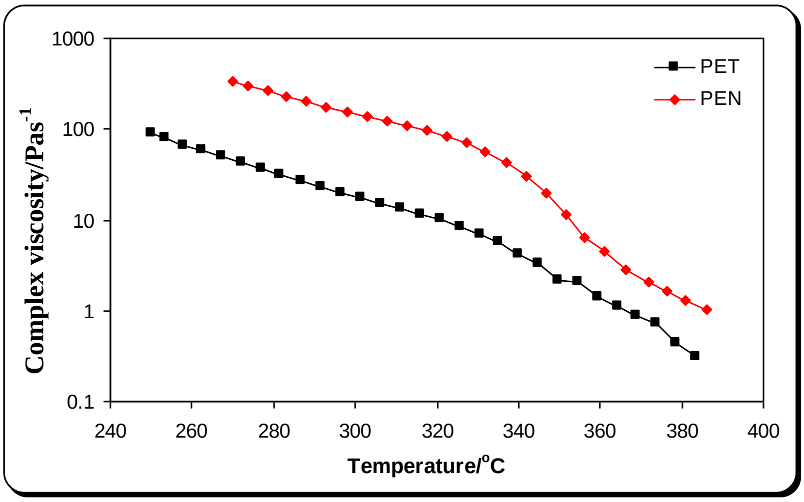


Figure 5.51 Complex viscosity measurements of PET and PEN as a function temperature, in dry air

5.3.6 ^{13}C Solid-State NMR Structural Analysis of Aged Samples of PET and PEN

All aged polyester samples were characterised using ^{13}C solid-state NMR. The spectra were all obtained using cross-polarisation methods, in an attempt to identify structural changes in PET and PEN as a result of ageing. It was hoped that some changes may be evident in the spectra to indicate the nature of degradation species responsible for both gel formation and discolouration in PET and PEN. *Figure 5.52* illustrates the ^{13}C solid-state NMR spectra obtained for virgin PET and PEN film samples. The C atoms responsible for producing ^{13}C NMR signals in each of the polymer structures are fully assigned on the spectra.

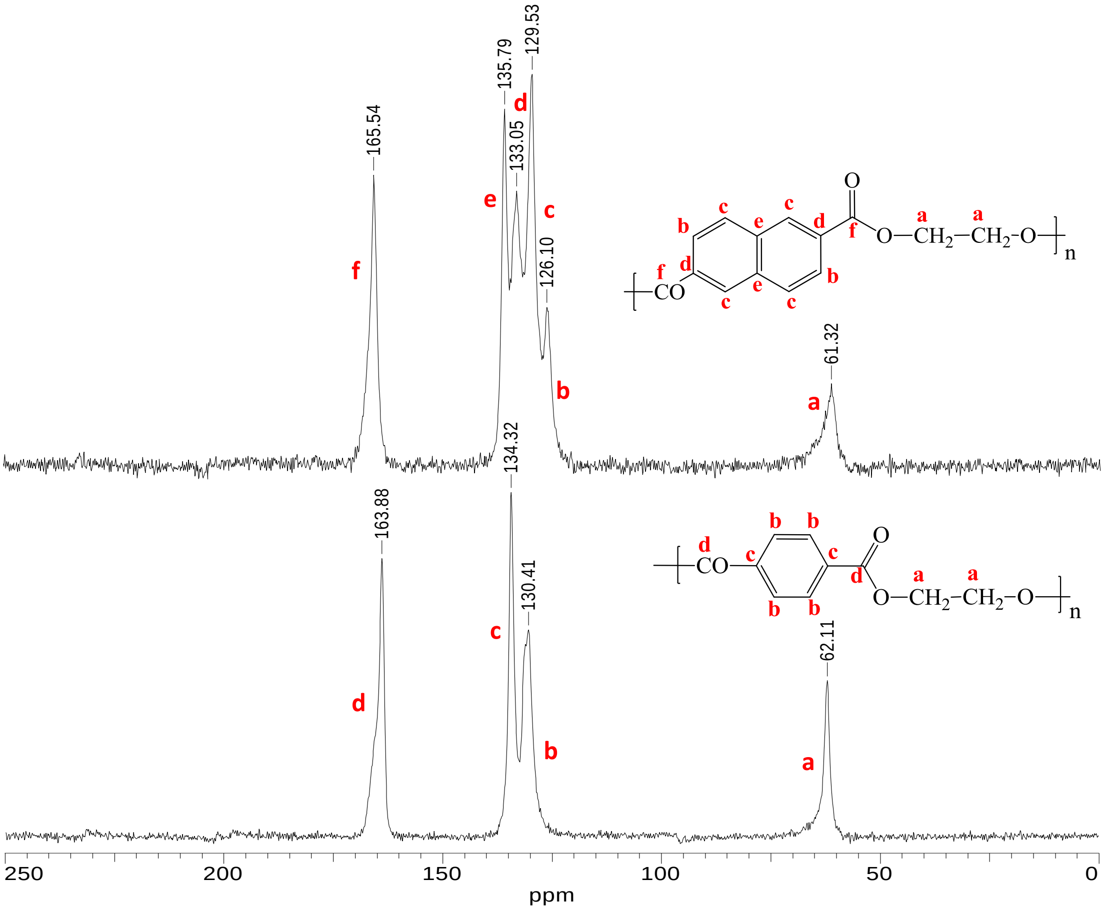


Figure 5.52 ^{13}C solid-state NMR spectra for virgin PET and PEN film samples

5.3.6.1 Residual Samples Aged Under Thermal and Thermal-Hydrolytic Conditions

Figure 5.53 illustrates the solid-state NMR spectra obtained for PET and PEN samples aged in dry nitrogen at temperatures of 288 - 320 °C. The chemical shifts of all ^{13}C NMR signals are identical between aged samples and the virgin materials. These results indicate that the bulk residual material does not differ significantly in structure from the original polyester starting materials, despite a small extent of degradation observed from volatilisation studies. It is thought that the polyester chains are simply shorter in length due to primary chain scission reactions. The only apparent difference in the NMR spectra of PET and PEN samples aged in dry nitrogen is the broadening of signals, particularly noticeable in PET aged at 320 °C and at all three temperatures of interest in PEN. Broadening of signals in ^{13}C solid-state NMR spectra is generally consistent with increased disorder or stiffening within the material, in contrast to narrow, resolved lines which indicate very high levels of molecular mobility.

Identical observations were noted for the ^{13}C NMR spectra derived from PET and PEN samples aged in wet, inert conditions. The chemical shifts of all ^{13}C NMR signals were identical between aged samples of PET and PEN and the virgin materials, once again indicating that the bulk residual material does not significantly differ in structure from the original polyester starting material, despite the increased extent of degradation observed in the presence of low levels of moisture. Once again, distinct broadening of the signals appeared to be the dominant feature in the ^{13}C NMR spectra of PEN samples aged in wet nitrogen, at all three temperatures of interest, consistent with increased disorder or the presence of rigid phases. The ^{13}C NMR spectra for PET and PEN samples aged in wet nitrogen can be found in *Chapter 8 Supplementary Material*. Therefore, despite the broadening observed on ageing, no differences are evident in the ^{13}C NMR spectra. Although some of the aromatic carbon signals cannot be observed due to broadening, the overall structure of the bulk material appears unchanged after ageing under thermal and thermal-hydrolytic conditions.

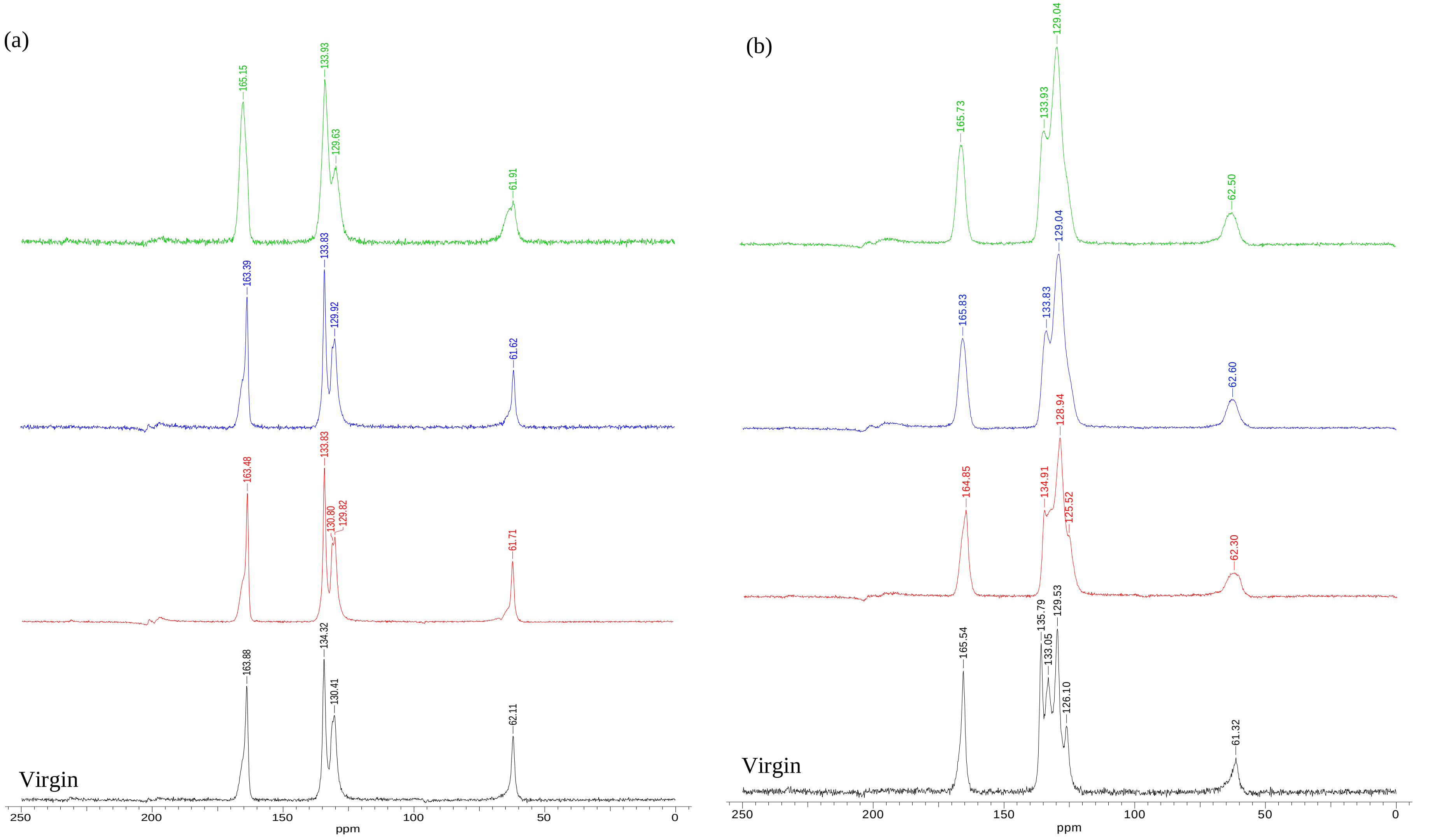


Figure 5.53^{13}C solid-state NMR spectra for (a) PET and (b) PEN samples aged in dry nitrogen at 288 °C, 300 °C and 320 °C for 4 hours

5.3.6.2 Residual Samples Aged Under Thermo-Oxidative Conditions

Figures 5.54 and *5.55* illustrate the ^{13}C solid-state NMR spectra obtained for PET samples aged in thermo-oxidative environments at temperatures of 288 - 320 °C. Due to resource constraints on the NMR spectrometer, only PET and PEN samples aged in the most extreme environments i.e. dry air and 42% oxygen were analysed.

The chemical shifts of the ^{13}C NMR signals for PET and PEN samples aged in dry air were found to be identical between all aged samples and the virgin material, as observed previously for samples aged in inert environments. These results, once again, indicate that the bulk residual materials does not differ significantly in structure from the original polyester starting materials, despite a significant degree of degradation observed from volatilisation studies, particularly for PET. The absence of new peaks in the NMR spectra indicates that any species responsible for discolouration and/or cross-linking in PET and PEN are not abundant enough to be detected.

Once again, the only difference evident in the NMR spectra of PET and PEN samples aged in dry air was broadening of signals, particularly noticeable as the ageing temperature increased. Due to the high extent of cross-linking present in these residual samples, this broadening was not unexpected due to the presence of very rigid phases. Therefore, despite strong evidence of cross-linking and discolouration from PET and PEN samples aged in dry air, no structural changes were detected from the NMR spectra.

In contrast to the NMR results for PET aged in dry air, one additional signal at 142 ppm was evident in the ^{13}C NMR spectrum for PET aged at 320 °C in dry 42% oxygen, illustrated in *Figure 5.55*. Unfortunately, after ageing PET at 288 °C under 42% dry oxygen, the residual material could not be removed from the aluminium surface. Therefore, NMR analysis could only be performed on PET samples aged at 300 °C and 320 °C.

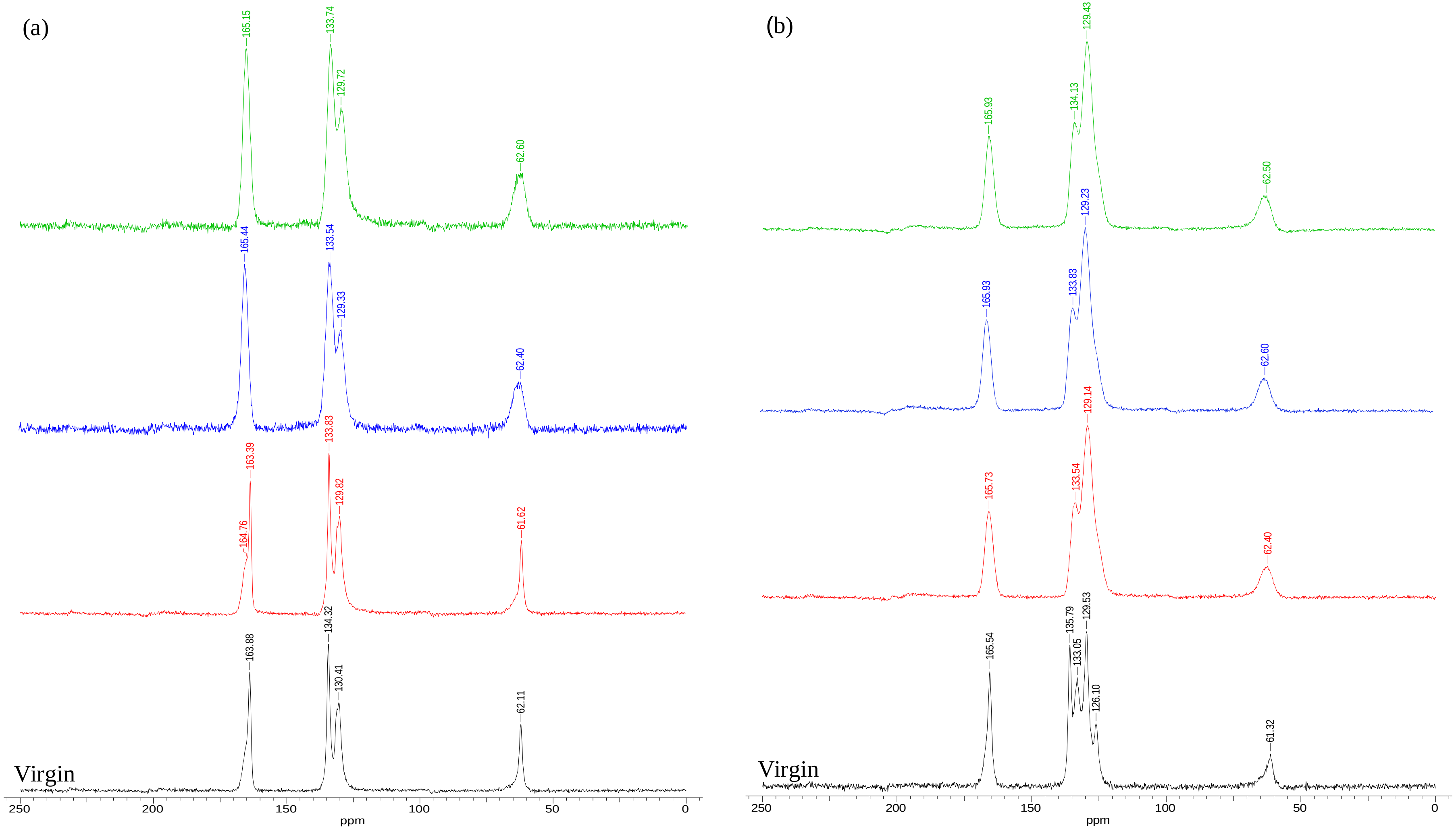


Figure 5.54 ^{13}C solid-state NMR spectra for (a) PET and (b) PEN samples aged in dry air at 288 °C, 300 °C and 320 °C for 4 hours

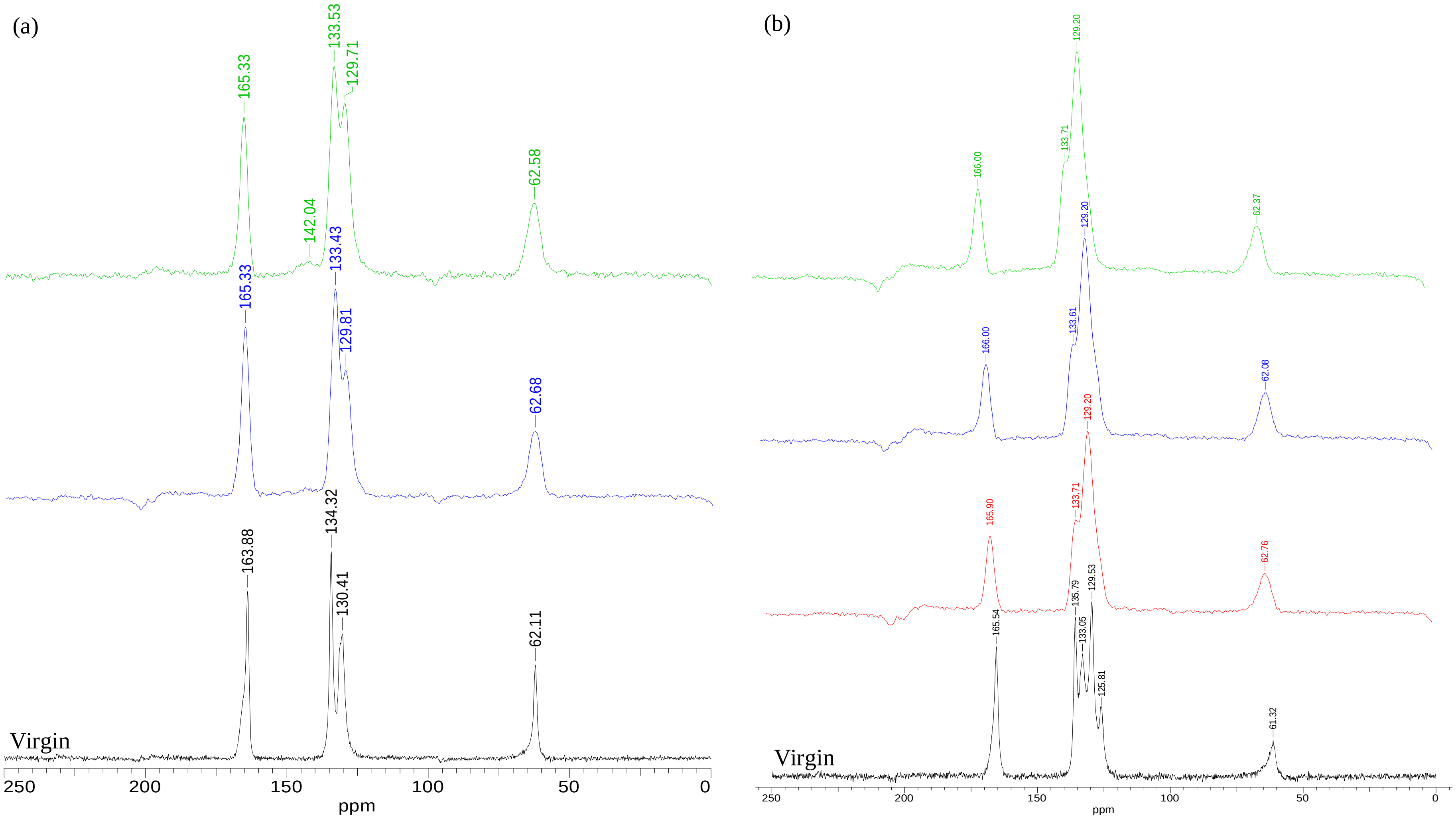


Figure 5.55 ^{13}C solid-state NMR spectra for (a) PET and (b) PEN samples aged in dry 42% oxygen at 288 °C, 300 °C and 320 °C for 4 hours

From *Figure 5.55*, identical spectral broadening effects can be observed in PET samples aged at all temperatures in dry 42% oxygen due to increased rigidity within the system. However, one small additional ^{13}C signal begins to emerge in PET samples aged at 320 °C in dry 42% oxygen. This new, broad ^{13}C signal is evident around 142 ppm and appears to be from quaternary carbon. Such structural information may well be evidence for cross-linking within aromatic rings in PET, as illustrated in *Figure 5.56*.

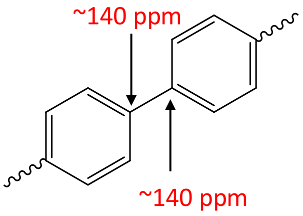


Figure 5.56 Cross – linking within aromatic rings in PET showing predicted chemical NMR shifts for quaternary carbons

In contrast to PET, no new signals were evident in the ^{13}C NMR spectra for PEN samples aged in 42% dry oxygen, as illustrated in *Figure 5.55*. However, these signals may just be very difficult to detect due to the increased spectral broadening observed in PEN, in comparison to PET. Due to the overall increase in the number of carbon atoms, present in different chemical environments in PEN, quaternary carbon signals from cross-linked species may simply be overlapping with other signals in the spectrum.

As the majority of ^{13}C NMR solid-state spectra shown so far have only exhibited spectral broadening, with no evidence of new ^{13}C signals that can be attributed to cross-linked sites, a small set of selected samples were submitted for ^{13}C solid-state NMR analysis, using an alternative pulse sequence, known as dipolar dephasing. Dipolar dephasing can simplify a high-resolution ^{13}C NMR spectrum by removing signals that originate from ^{13}C nuclei that are directly bonded to hydrogen. Therefore, the resulting spectrum contains only signals from species not attached to hydrogen (i.e. quaternary carbons). It was hoped that these studies would identify any additional ^{13}C quaternary carbons, not detected in cross-polarisation NMR spectra in aged PEN samples and confirm the presence of quaternary aromatic carbons in samples of PET aged in dry 42% oxygen. *Figure 5.57* illustrates the dipolar dephased ^{13}C solid-state NMR spectra obtained for virgin PET and PEN film samples. The quaternary carbon atoms responsible for producing each of the ^{13}C NMR signals, in both polymer structures, are fully assigned on the spectra.

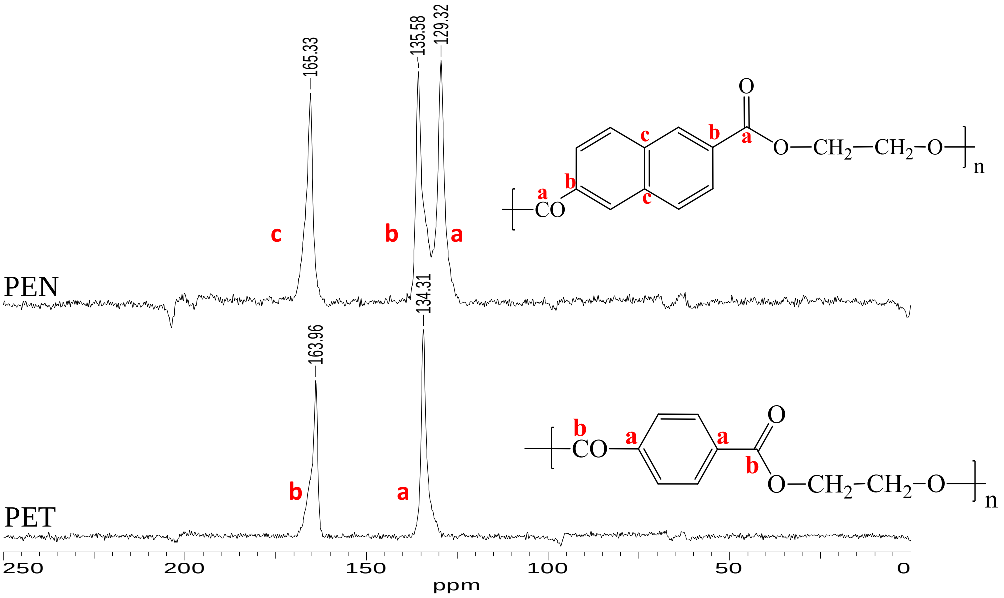


Figure 5.57 Dipolar dephased ^{13}C solid-state NMR spectra for virgin PET and PEN film samples

Two major ^{13}C NMR signals can be observed from the dipolar dephased spectra, illustrated in *Figure 5.58*, for PET samples aged in dry 42 % oxygen. These signals belong to quaternary aromatic and ester carbons, also present in the virgin material. After ageing, another small quaternary carbon signal can be observed in PET samples aged at 320 °C in dry 42% oxygen, identical to the observations discussed previously using cross-polarisation NMR. Again, this signal is supporting evidence of aromatic cross-linked species in PET, resulting in a broad quaternary carbon signal at 142 ppm.

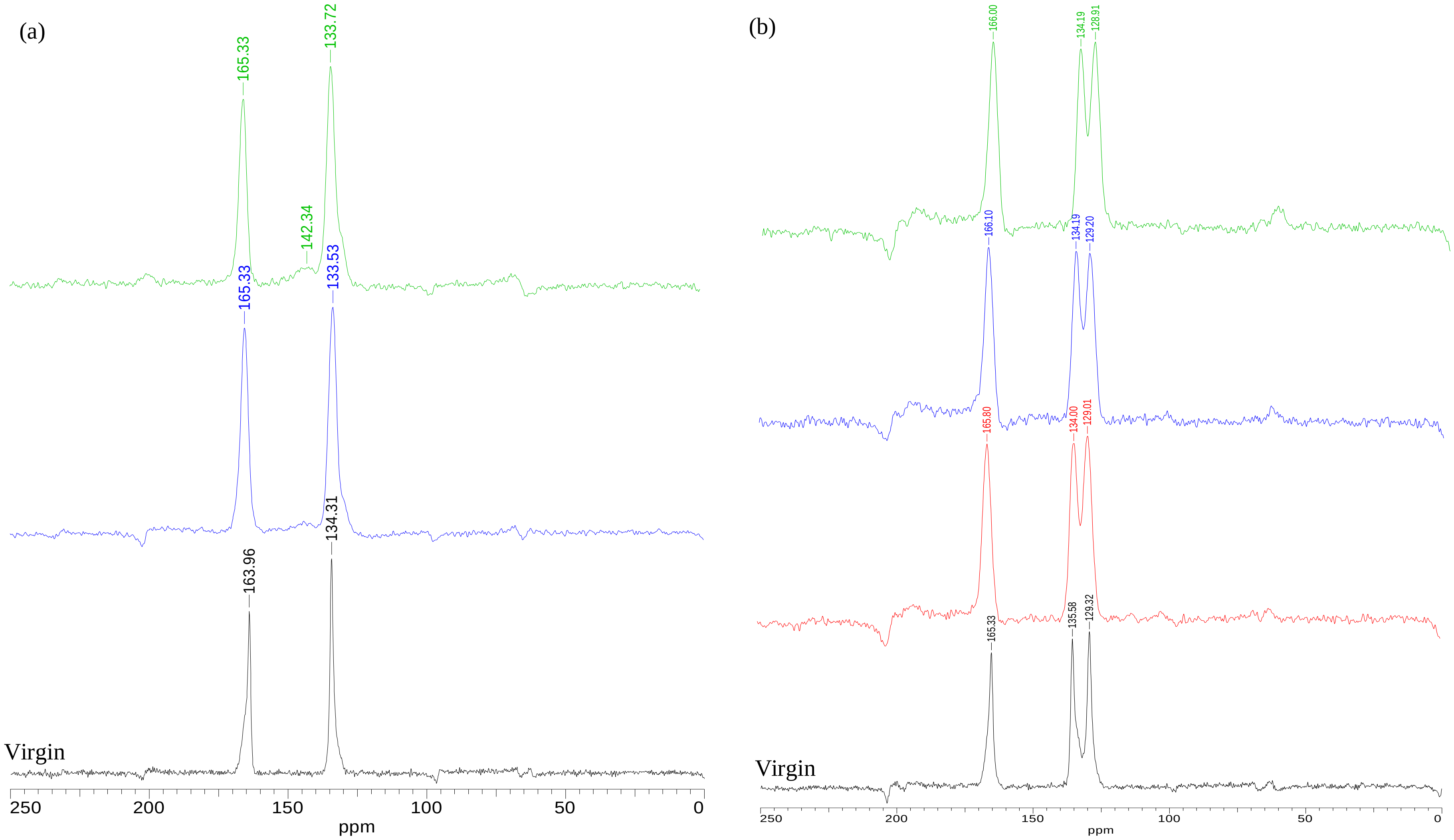


Figure 5.58 Dipolar dephased ^{13}C solid-state NMR spectra for (a) PET and (b) PEN samples aged in dry 42% oxygen at 288°C, 300 °C and 320 °C for 4 hours

Identical to the results reported previously for spectra obtained using cross-polarisation methods, no further structural evidence was found in dipolar dephased spectra of PEN samples aged in 42% dry oxygen, illustrated in *Figure 5.58*. Therefore, no further indication as to the type of cross-linked species formed in PEN was provided i.e. aromatic or aliphatic ^{13}C cross-linked sites on ageing under typical processing temperatures.

5.3.6.3 Residual Samples Aged Under Thermo-Oxidative-Hydrolytic Conditions

The chemical shifts of all ^{13}C NMR signals for PET and PEN samples aged in wet oxidative conditions were found to be identical to those observed previously for the samples aged in dry oxidative conditions and can be found in *Chapter 8 Supplementary Material*. Therefore, despite the subsequent increase and decrease observed in volatilisation and gel formation, respectively, on ageing in the presence of moisture, no significant structural differences were evident between PET and PEN samples aged in dry and wet 3% oxygen, air and 42% oxygen at temperatures between 288 °C and 320 °C. Both cross-polarisation and dipolar dephased spectra obtained for PET and PEN samples aged under wet air were found to exhibit only spectral broadening effects, known to arise due to reduced molecular mobility. One small additional ^{13}C signal emerged again at 142ppm in PET samples aged at 320 °C in wet 42% oxygen, thought to result from the presence of quaternary carbon. Both cross-polarised and dipolar dephased spectra were found to detect these additional quaternary carbon, providing further evidence of cross-linking within aromatic rings in PET. In agreement with the observations noted for PEN samples aged in dry 42% oxygen, no new signals were evident in the ^{13}C NMR spectra for PEN samples aged in 42% wet oxygen.

Therefore, no apparent differences could be observed between the ^{13}C NMR spectra of PET and PEN samples aged in dry and wet oxidative environments. The overall structure of the bulk PEN material appeared unchanged on ageing in dry and wet thermo-oxidative conditions, indicating that the species responsible for both discolouration and cross-linking are not abundant enough to be detected. Therefore, despite competing thermo-oxidative cross-linking and hydrolytic chain scission reactions in PET and PEN, resulting in increased volatilisation and a reduction in gel formation, no further evidence can be found to indicate that the species responsible for discolouration and cross-linking in thermo-oxidative-hydrolytic ageing differ from those formed during thermo-oxidative ageing. Therefore, it is presumed that the thermo-oxidative-hydrolytic degradation species, responsible for discolouration and cross-linking in PET and PEN, are identical in structure to those formed during thermo-oxidative degradation.

5.3.7 ATR-FTIR Analysis of Aged Samples of PET and PEN

In addition to solid-state NMR, FTIR analysis was also performed on the residual aged materials using an Agilent 5500a FTIR spectrometer containing a diamond ATR cell. However, all spectra of the PET and PEN aged materials appeared identical to the virgin, unaged samples, indicating once again that the species for cross-linking and discolouration are not abundant enough to be detected, as discussed previously. Therefore, all ATR data can therefore be found in *Chapter 8 Supplementary Material*.

5.3.8 FTIR Analysis of Aged Samples of Solvent Cast PET and PEN Films

5.3.8.1 Residual Samples Aged Under Thermal and Thermal-Hydrolytic Conditions

In addition to NMR and ATR spectroscopic analysis of residual ageing material, a small set of studies examined solvent cast thin films exposed to identical thermal ageing conditions to illustrate the changes in the IR absorption spectra before and after ageing. Similar to the UV-visible spectra discussed previously in Section 5.3.2, differences in the film thickness and sample size of starting material may result in minor differences from the residual ageing material, however, the IR spectra still enable the degradation of PET and PEN to be mapped as a function of ageing temperature and ageing environment. *Figures 5.59* and *5.60* illustrate the solvent cast virgin PET and PEN films prior to ageing with the structural assignments for each absorption band illustrated in Table *5.13*. Only minor differences exist in the spectra for virgin PET and PEN due to differences in their aromatic species.

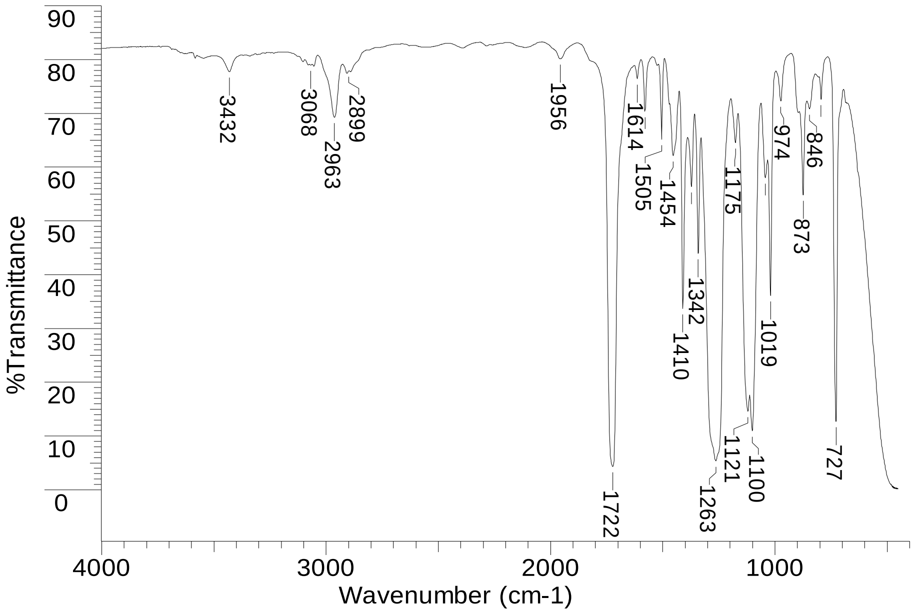


Figure 5.59 IR spectra of solvent cast PET film

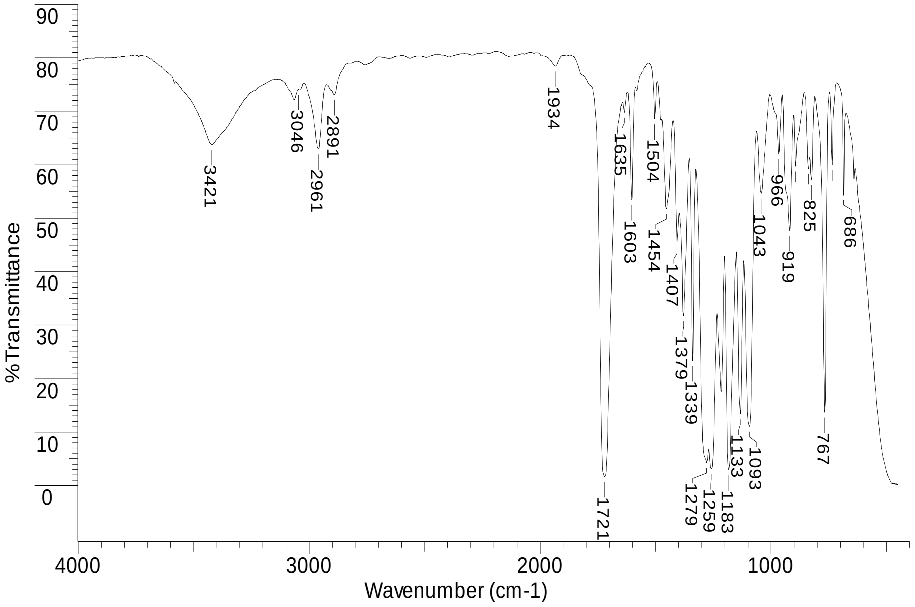


Figure 5.60 IR spectra of solvent cast PEN film

PET Wavenumber/cm^{-1}	**PEN Wavenumber/cm^{-1}**	**Absorption Modes**
3432	3421	O-H stretching of EG end group
3068	3046	Aromatic C-H stretching
2963, 2899	2961, 2891	Aliphatic C-H stretching
1956	1934	Aromatic summation band
1722	1721	Carbonyl C=O stretching bands
1614,1579,1505,1455	1635, 1603, 1504, 1454	Aromatic skeletal stretching bands
1410	1407	-CH_2- deformation band
1263,1121	1259,1133	C(O)-O stretching of ester group
1175,1042,1019	1183, 1093, 1043	Band in the skeletal ring region are indicative of aromatic substitution pattern and indicate 1,4-substitution
974	966	O-CH_2 stretching of EG segment
873	825	C-H deformation of two adjacent coupled hydrogens on aromatic ring(s)
727	767	Associated with the out of plane deformations of the two carbonyl substituents on the aromatic ring(s)

Table 5.13 IR peak assignments from solvent cast films of PET and PEN [15,17,18]

On ageing PET and PEN in dry nitrogen at 288 °C, only minor changes can be observed in the IR spectra illustrated in *Figure 5.61*. One additional IR signal develops at 1553 cm^{-1} on ageing PET in dry nitrogen. This signal can be attributed to aromatic skeletal stretching and indicates changes in the conjugated aromatic structure of the polymer residue in contrast to virgin PET. On ageing at higher temperatures, the intensity of this signal at 1553 cm^{-1} increases as observed in *Figure 5.62*, coinciding with increased volatilisation and thus degradation. Interestingly, although changes are observed in the vibrational region of the IR spectra at 1553 cm^{-1}, no changes are evident in the fingerprint region of the IR spectra at all ageing temperatures, indicating that the substitution pattern is not likely to be changing on degradation of PET under thermal conditions. Such minor changes discussed do not provide any evidence as to the structure of species responsible for discolouration or gel formation, instead they are likely to be the result of chain scission reactions of the polymer backbone resulting in 1, 4 disubstituted carbonyl species. Identical results were observed for PET samples aged under thermal-

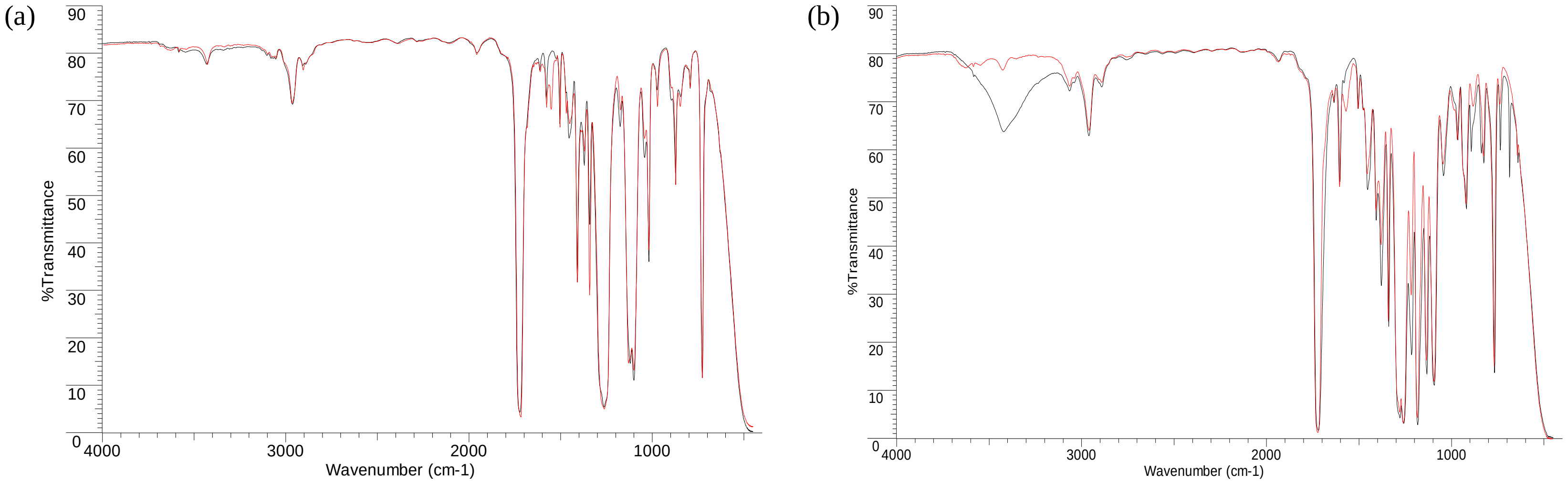


Figure 5.61 IR spectra of solvent cast (a) PET and (b) PEN film before and after ageing at 288 °C in dry nitrogen for 4 hours

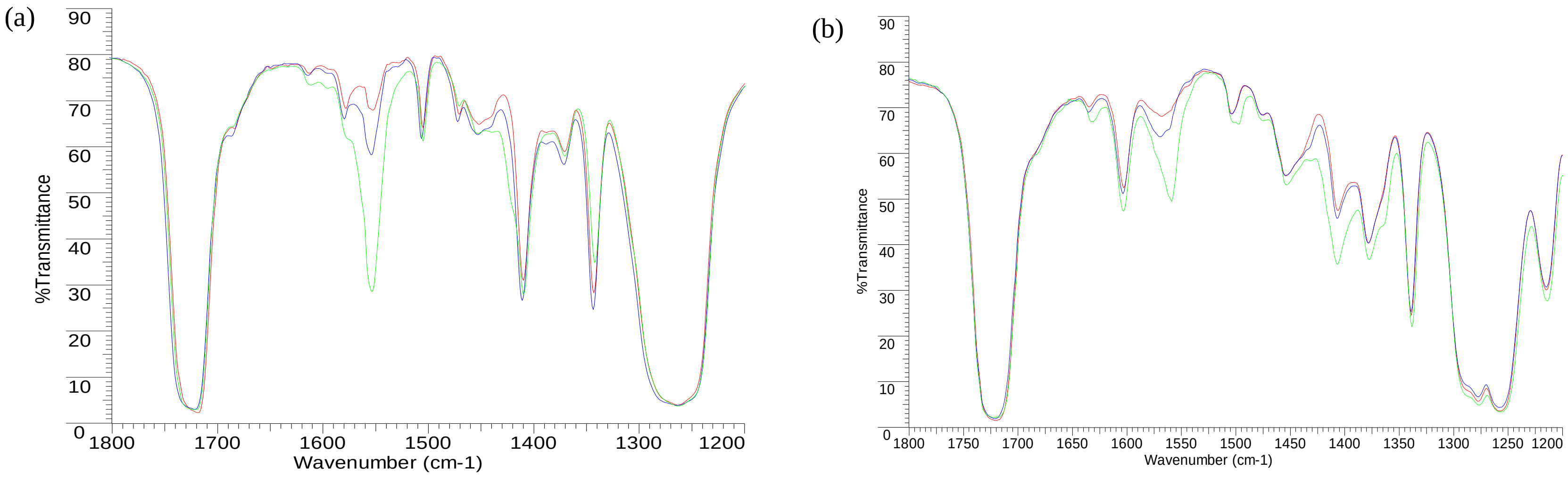


Figure 5.62 IR spectra for solvent cast (a) PET and (b) PEN samples aged in dry nitrogen at 288 °C, 300 °C and 320 °C for 4 hours

hydrolytic conditions at 288 – 320 ^{o}C, the IR spectra of which can be found in *Chapter 8 Supplementary Material.* On ageing in the presence of low moisture content, the intensity of the IR band formed at 1553 cm^{-1} is increased in comparison to PET samples aged in dry thermal conditions, as a result of increased degradation.

Although differences may appear evident in the IR spectra of PEN before and after ageing in dry nitrogen at 288 ^{o}C, the majority of these changes are a result of solvent evaporation upon ageing. Although both PET and PEN were dried above their T_g prior to analysing the IR spectra of the virgin material, solvent still remained trapped within the PEN matrix. This is not entirely surprising due to the reduced chain mobility of PEN making it increasingly difficult for solvent to volatilise at low temperatures. On ageing PEN, IR signals at 3421, 1215, 880, 736 and 686 cm^{-1} diminish due to evaporation of hexafluoroisopropanol trapped within the solvent cast PEN films. As observed for PET on ageing under thermal conditions, a new peak in the region of naphthalene skeleton stretching vibrations arises around 1568 cm^{-1} and progressively increases in intensity with increasing ageing temperature. This identical peak is present also on ageing PEN under thermal-hydrolytic conditions and once again signifies main chain scission and thus formation of degradation species with identical substitution patterns to that of virgin PEN. As the extent of degradation is lower in PEN than PET, the intensity of this signal at 1568 cm^{-1} is reduced in PEN in comparison to PET at all ageing temperatures under thermal and thermal-hydrolytic conditions.

5.3.8.2 Residual Samples Aged Under Thermo-Oxidative and Thermo-Oxidative-Hydrolytic Conditions

As expected, the complexity of the IR spectra for PET and PEN increases upon ageing in the presence of oxygen. Identical to samples aged under thermal and thermal-hydrolytic conditions, a large IR band evolved at 1550 – 1590 cm^{-1} on ageing PET in dry air, as illustrated in *Figure 5.63*. The appearance of this IR band increased with ageing temperature and also coincided with changes in the C-H region

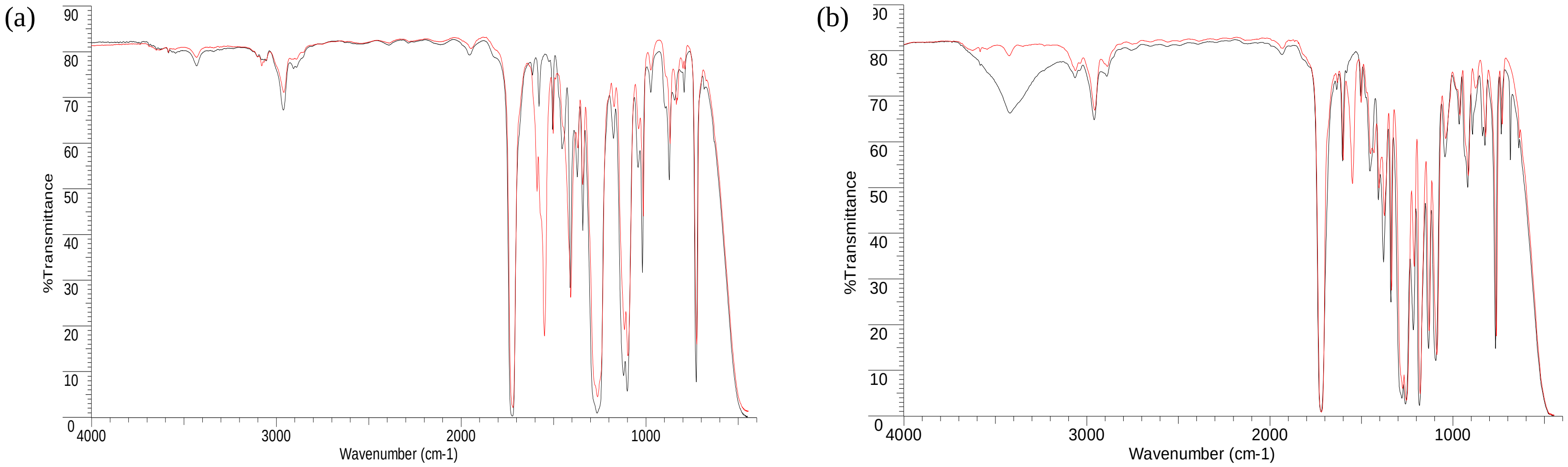


Figure 5.63 IR spectra of solvent cast (a) PET and (b) PEN film before and after ageing at 288 °C in dry air for 4 hours

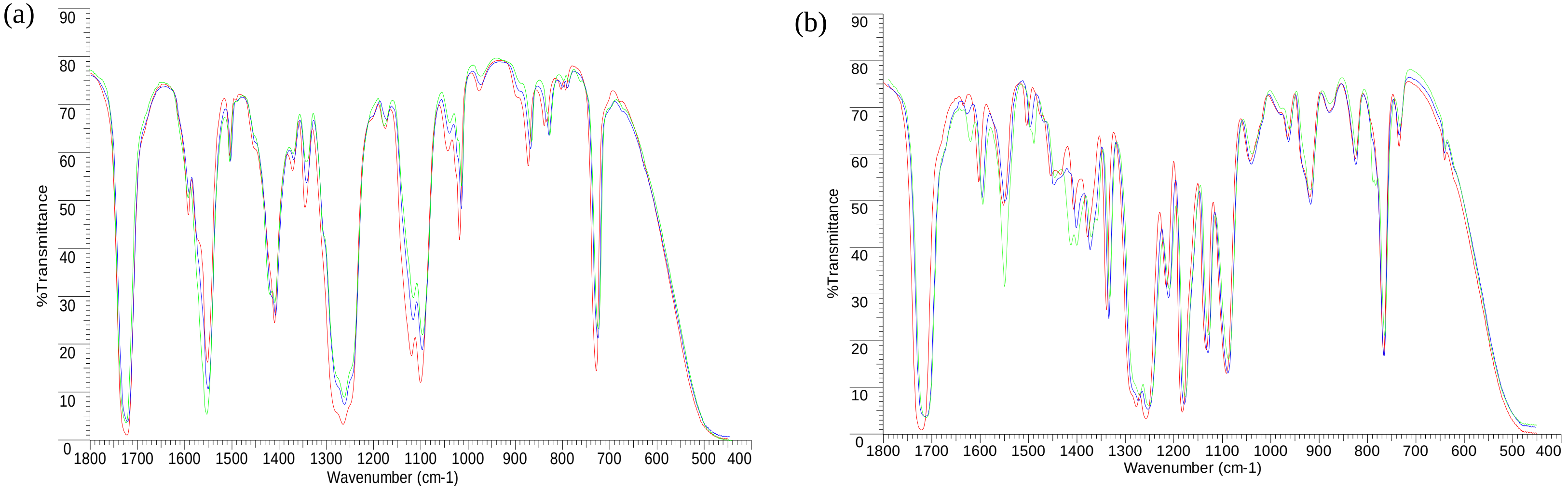


Figure 5.64 IR spectra for solvent cast (a) PET and (b) PEN samples aged in dry air at 288 °C, 300 °C and 320 °C for 4 hours

of the IR spectrum at wavelengths less than 1000 cm^{-1}. Such IR bands indicate build - up of conjugated aromatic species in the polymer residue, with the changes in the C- H deformation region symptomatic of changes in the substitution pattern of the aromatic rings. The IR bands around 870 cm^{-1}, associated with the C-H deformation of two adjacent hydrogen's and thus indicative of 1,4 substitution, appear to diminish with increased ageing temperature, whilst simultaneously, a band at 823 cm^{-1} evolves. This additional band at 823 cm^{-1} is most likely due to a change in the substitution pattern of the aromatic species.

In addition, to changes noticed in the substitution patterns, the intensity of the IR band around 1410 cm^{-1} significant increases in intensity on ageing PET in air at 288 ^{o}C as a result of O-H bending or C-O-H bending. This indicates significant formation of carbonyl species, most likely to be aldehydic species such as benzaldehyde or similar derivatives due to the absence of changes observed around 3000 cm^{-1} for O-H stretching of carboxylic acid species. On increasing the ageing temperature for PET aged in air, an increase in the intensity of the IR band at 1552 cm^{-1} can be observed in *Figure 5.64* along with a decrease in the intensity of all IR bands below 1500 cm^{-1}. This includes all IR bands representative of C-O stretching (1320 to 1210 cm^{-1}) and O-H bending (1440 to 1395 cm^{-1} and 950 to 910 cm^{-1}) and indicates a higher concentration of aromatic rings with further chain scission and thus volatilisation of side group substituents. Degradation of PET in the presence of low moisture content produced similar spectral trends to those samples aged under dry air illustrating that thermo-oxidative degradation is the dominant reaction over hydrolytic degradation. The IR spectra for PET samples aged in wet air can be found in *Chapter 8 Supplementary Material.*

In agreement with the volatilisation results already reported, the degradation of PEN on ageing in dry and wet air appears minimal in contrast to PET. The IR spectra of solvent cast films of PEN on ageing in oxidative conditions show only minimal changes in contrast to the virgin material. As observed for all PET samples, a minor increase in the peak at 1552 cm^{-1} can be observed on ageing PEN in dry air, in contrast to samples aged in an inert environment, with a further increase in intensity of this same peak observed on increasing ageing temperature and ageing in the presence of low moisture content. Besides this minor change, all other IR bands remain identical in wavenumber and intensity, highlighting the minimal impact ageing in oxygen has on the degradation of PEN at typical processing temperatures.

All of the above IR evidence therefore suggests that the degradation of PET and PEN is likely to result in a main chain structure consisting predominantly of highly absorbing and highly coloured aromatic ring species.

5.3.9 Discussion of Thermal Degradation of PET and PEN at Typical Processing Temperatures

The extent of degradation has been shown to differ quite significantly in both polyesters on ageing under purely thermal conditions. However, the mechanisms by which both polyesters thermally degrade are still thought to be similar.

At an ageing temperature of 288 °C, under thermal ageing conditions, experimental evidence suggests that very little degradation is ongoing in PEN, in comparison to PET. The extent of volatilisation observed in PEN was very low, even after an ageing period of 24 hours, suggesting that the increased thermal stability of PEN leads to a reduction in the extent of chain scission reactions occurring, in comparison to PET. This evidence is supported by melt rheology studies of PEN illustrating that the melt viscosity of PEN at 288 °C increases over a 60 minute period. This indicates that the main activity ongoing within the PEN polyester melt is chain extension i.e. further polymerisation of the polyester chain ends and not chain scission. Further polymerisation results in an increase in the overall length of the polymer chains and increase in molar mass. The absence of significant gel formation, discolouration and structural changes in PEN samples aged at 288 °C also suggest that PEN degradation is minimal at 288 °C. Similarly, no significant increase in the CEG concentration was observed for PEN samples aged at 288 °C, in comparison to the virgin material suggesting that the polyester chains are more likely to be polymerising instead of branching or degrading during ageing.

In contrast to the results observed for PEN, evidence suggests that more significant degradation of PET occurs on ageing at 288 °C under thermal conditions. This is evident from the increase in volatilisation and CEG concentration observed after ageing. Primary chain scission of ester linkages is therefore thought to be ongoing in PET at 288 °C, followed by some secondary degradation reactions, resulting in the formation of volatile degradation products. Melt-rheology studies can, once again, support the experimental observations discussed above. The melt viscosity of PET at 288 °C was seen to increase initially over the first 30 minutes, prior to decreasing for the remaining 30 minutes. This illustrates that chains composed of free acid end groups initially polymerise, prior to degrading after 30 minutes, resulting in a decrease in melt viscosity. The starting melt viscosity values for PET samples aged at 288 °C were also recognised to be lower in comparison to PEN, providing beneficial, increased flow of the polyester from the extrusion die.

Despite, an increase in the extent of degradation observed for PET, in comparison to PEN, the overall extent of degradation occurring in both PET and PEN under thermal conditions at 288 °C remains low. This is evident from the low extent of volatilisation, absence of discolouration and gels from the residual film samples recovered and lack of significant changes observed in the overall structure of the residual material analysed by ^{13}C NMR studies.

On increasing the ageing temperature to 300 °C, thermal volatilisation of both PET and PEN were found to increase, with the extent of volatilisation in PET remaining higher than that of PEN. This highlights a reduction in chain extension and an increase in chain scission in both polyesters. As the ageing time progressed, both PET and PEN exhibit an initial increase in melt viscosity as polymerisation takes place, prior to degradation resulting in a decrease in melt viscosity. This time period within which polymerisation occurs and the melt viscosity increases is extended in PEN, in comparison to PET. On increasing the ageing temperature to 300 °C, a lower melt viscosity was observed for both polyesters, indicating increased flow from the extrusion die. Once again, the starting melt viscosity was higher in PEN than PET.

The overall extent of degradation in both PET and PEN at 300 °C is therefore increased in comparison to ageing at 288 °C, but still appears to be reasonably low. Both PET and PEN exhibit low volatilisation levels, no discolouration or gel formation in the residual material and a lack of structural changes after ageing. Similar CEG concentrations were found in both polyesters at 300 °C, thought to be a result of the sharp increase in primary chain scissions reactions in PEN and increase in secondary degradation reactions in PET.

Volatilisation of both PET and PEN were found to increase, yet again, on increasing the ageing temperature to 320 °C under thermal conditions. This is not entirely surprising and is thought to be a result of increased chain scission reactions, leading to the formation of volatile secondary degradation products. On ageing at 320 ^{o}C, a constant decrease in melt viscosity of PET and PEN was observed with time illustrating that the dominant reaction is thermal degradation. This is supported by an increase in CEG concentration observed for PET and PEN residues, despite the lack of structural changes observed from ^{13}C NMR spectra. Thermal degradation is also thought to result in the discolouration observed in both PET and PEN residues aged at 320 °C. However, due to the lack of structural changes observed in the ^{13}C NMR spectra for these residual samples, it is very difficult to propose any degradation structures which may contribute to the discolouration observed. The degradation structures, responsible for the discolouration, are thought to be present in only very small quantities and exhibit similar chemical functional groups in both PET and PEN due to the similar extent of discolouration observed in both materials under thermal conditions. It is highly probable that the coloured species in PET and PEN result from extensive conjugation within the polymeric system and are unlikely to be highly branched or cross-linked as such species would result in the formation of gels.

Overall, the experimental evidence presented above leads us to believe that the degradation chemistry ongoing in PET and PEN under thermal conditions at temperatures of 288 - 320 °C is identical. However, the difference lies in the rate and extent to which the main degradation reactions occur in both polyesters. This is evident from both variations in the extent of volatilisation and the CEG concentrations observed from aged samples of PET and PEN.

From TVA studies, outlined in *Chapter 4*, on PET and PEN at a processing temperature of 300 °C, it has been proposed that PET and PEN form cyclic oligomers prior to undergoing chain scission at the ester linkages, as illustrated in *Figure 4.45*. PET was then shown to undergo further degradation reactions after prolonged exposure resulting in the formation of products such as CO, CO_2, acetaldehyde and ethylene glycol. However, the absence of secondary degradation products such as CO and CO_2 in PEN highlighted a reduction in the overall extent of degradation, in comparison to PET. Therefore, at temperatures of 288 °C under thermal ageing conditions, similar degradation mechanisms are thought to occur to those proposed previously from TVA studies. Both PET and PEN are proposed to form cyclic oligomers, via the ionic mechanism illustrated in *Figure 4.45,* prior to undergoing chain scission reactions. However, the rate at which these cyclic oligomers form and then decompose is thought to be very different for PET and PEN. At 288 °C, PET is thought to undergo rapid formation of cyclic oligomers, which degrade via chain scission reactions after prolonged exposure, resulting in an increase in the CEG concentration, in comparison to virgin PET. A small degree of secondary degradation is then thought to occur in PET forming small quantities of volatile degradation products, typically acetaldehyde, CO and CO_2. In contrast to this, the additional steric hindrance of naphthalene groups in PEN is thought to result in a rapid decrease in the rate of cyclic oligomer formation at 288 °C. Due to the increased thermal stability of PEN, the extent to which these cyclic oligomers degrade is also thought to be poor, resulting in low volatilisation levels and no significant increase in the CEG concentration, in comparison to the virgin material.

On increasing the ageing temperature to 300 °C and 320 °C, the extent of primary chain scission in PEN is thought to increase subsequently resulting in the formation of additional acid end groups. However, the extent of volatilisation observed is still lower in PEN, than PET. As discussed previously, it is feasible that secondary degradation reactions in PEN, which result in the formation of volatile degradation products, could simply be occurring at a much slower rate than those in PET. This would result in CEG’s in PEN being consumed at a slower rate than those in secondary degradation reactions of PET, leading to an overall higher concentration of CEG’s and decrease in volatilisation as observed. Alternatively, the increased melt viscosity of PEN, in comparison to PET, could simply be limiting the diffusion of volatile degradation products from the polyester melt, therefore limiting the overall extent of volatilisation. With increased ageing temperature, the melt viscosity obviously decreases in both polyesters. The overall melt viscosity of PEN is higher than that of PET at all temperatures. Therefore, as the nature and thus volatility of the degradation products in PEN differ due to the presence of bulky naphthalene groups, in comparison to phenyl groups in PET, this may limit their volatilisation from the polyester melt.

5.3.10 Discussion of Thermal-Hydrolytic Degradation of PET and PEN at Typical Processing Temperatures

Our attempt to promote degradation and volatilisation of PEN, beyond that observed during thermal ageing studies succeeded. A marginal increase in volatilisation of both polyesters was observed on introducing levels of low moisture (1.5 - 2% AH) into the ageing system, promoting hydrolytic degradation. As observed previously under dry, thermal conditions, the overall extent of volatilisation in PEN, after ageing in a moist environment, was found to be reduced in comparison to PET. This is thought to be due to identical reasons discussed previously for thermal ageing i.e. an overall reduction in degradation rate and thus secondary degradation reactions in PEN and/or slow diffusion of volatile degradation products from the PEN polyester melt.

At an ageing temperature of 288 °C, experimental evidence suggests that hydrolytic degradation is the dominant degradation process occurring in PEN. An increase in the CEG concentration was observed for samples of PEN aged at 288 °C, in comparison to virgin PEN and a marginal increase was observed in the extent of volatilisation, in comparison to thermally aged samples. Although volatilisation levels are still low, even after ageing periods of 24 hours in wet nitrogen, degradation activity appears to be increased, in comparison to thermal degradation of PEN. In contrast to PEN, increased degradation is evident in PET samples aged in wet nitrogen at 288 °C as the material undergoes rapid, thermal and hydrolytic degradation reactions. This results in an overall increase in the extent of volatilisation and a higher concentration of CEG's, in comparison to PET samples aged in thermal conditions. However, again the overall extent of volatilisation in PET remains low, even after long term ageing. Similar to thermal degradation of PET and PEN, no gels, discolouration or structural changes were detected from the residual PET and PEN materials analysed after ageing in thermal-hydrolytic conditions at 288 °C.

On increasing the ageing temperature to 300 °C under thermal-hydrolytic conditions, thermal degradation of PEN is thought to become significant in relation to hydrolytic degradation, leading to increased formation of CEG's and volatile degradation products, in comparison to PEN degraded in purely thermal conditions. Identical thermal and hydrolytic degradation reactions are also thought to be ongoing in PET, resulting in an overall increase in the extent of degradation and thus volatile product formation, in comparison to PEN. Similar CEG concentrations were found in both polyesters at 300 °C and were thought to be a result of the sharp increase in primary chain scissions reactions of PEN and increase in secondary degradation reactions of PET, as discussed previously for thermal ageing of PET and PEN. Nevertheless, both PET and PEN still exhibit relatively low levels of volatilisation with no discolouration, gel formation or structural changes observed on analysis of the residual material.

Finally, the extent of volatilisation in both PET and PEN were found to increase again, on increasing the ageing temperature to 320 °C under thermal-hydrolytic conditions. This illustrates further thermal and hydrolytic degradation reactions are occurring in PET and PEN on ageing, with thermal degradation thought to be the dominant degradation reaction at the highest ageing temperature. These conclusions are supported by the increase in CEG concentration observed for PET and PEN residues, despite a lack of structural changes observed from ^{13}C NMR spectra. No significant discolouration was evident in any samples of PET and PEN aged in thermal-hydrolytic conditions at 288 - 320 °C, indicating that similar degradation chemistry is ongoing in both polyesters.

Overall, the experimental evidence presented above leads us to believe that PET and PEN undergo similar thermal and hydrolytic degradation reactions leading to a marginal increase in volatilisation and overall CEG concentration, in comparison to samples aged in the absence of low moisture levels. These results are not entirely surprising as both thermal and hydrolytic degradation reactions can occur at such high processing temperatures, increasing the overall extent of degradation, leading to the formation of additional acid end groups. For each ester chain scission reaction in both PET and PEN, both hydrolytic and thermal degradation lead to the formation of one carboxylic acid end group, as illustrated for PEN in *Figure 5.65*. The difference between thermal and hydrolytic degradation therefore remains in the chemical nature of the second chain end formed; thermal degradation results in the formation of a vinyl ester group, while a hydroxyl chain end is formed in hydrolytic degradation of PET and PEN. Therefore, the overall end group distribution within PET and PEN will depend on the extent to which both polyesters undergo thermal and hydrolytic degradation.

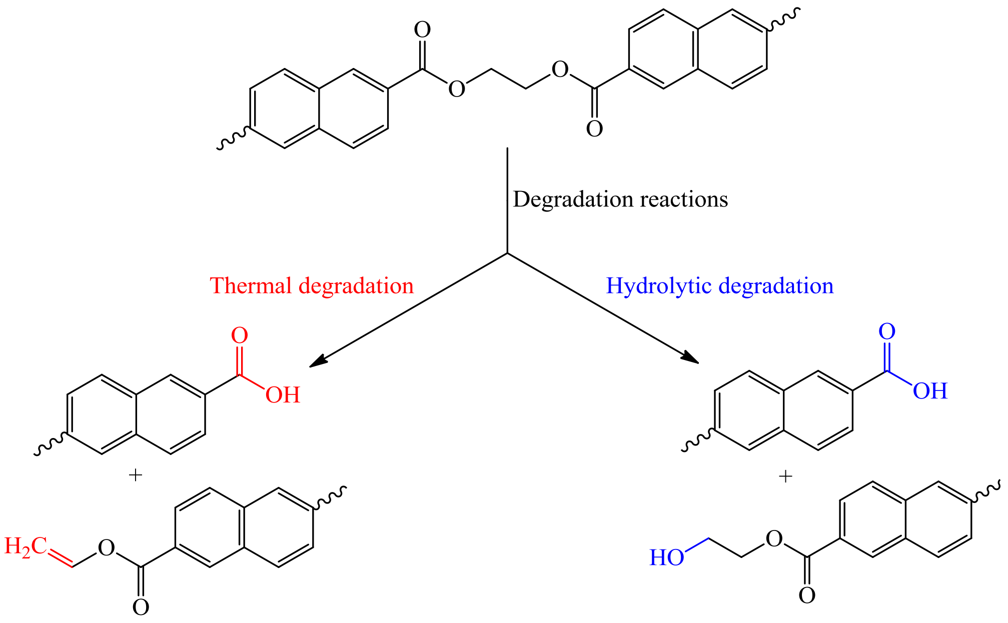


Figure 5.65 Competing thermal and hydrolytic degradation reactions in PEN

The differences in the distribution of chain ends in PET and PEN during thermal and hydrolytic degradation may therefore provide an explanation as to why discolouration of both PET and PEN was observed on ageing in thermal conditions at 320 °C, but not thermal-hydrolytic conditions. On ageing PET and PEN under thermal conditions, the formation of vinyl ester groups is inevitable. Therefore, it is possible that these vinyl end groups further polymerise with one another, leading to the formation of conjugated and thus coloured polyene species. One mechanism, resulting in the formation of coloured species of this nature has been illustrated previously in *Figure 1.39*.

In contrast to thermal ageing, hydrolytic degradation does not result in the formation of vinyl ester groups; instead hydroxyl chain ends are formed. Due to the increased reactivity of hydroxyl groups, these chain ends are more likely to undergo further degradation reactions elsewhere in the polymer chain as they do not have the ability to self polymerise. These secondary degradation reactions are likely to result in the formation of additional volatile degradation products such as acetaldehyde i.e. hydroxyl chain end groups can undergo scission to result in the formation of vinyl alcohol, which can rearrange instantaneously to form acetaldehyde. Therefore, on ageing PET and PEN under thermal-hydrolytic conditions, it is proposed that hydrolysis dominates over thermal degradation, resulting in a reduction in the overall formation of vinyl ester end groups and an increase in the formation of hydroxyl chain ends. This results in an increase in volatilisation and decrease in discolouration, as observed for both PET and PEN aged in thermal-hydrolytic conditions**.**

5.3.11 Discussion of the Thermo-Oxidative Degradation of PET and PEN at Typical Processing Temperatures

From the ageing studies completed on PET and PEN under thermo-oxidative conditions, the extent of degradation has once again been shown to differ between polyesters. Differences observed in the extent of volatilisation, gel formation and discolouration highlight that the thermo-oxidative degradation chemistry varies in

PET and PEN. Such variations are thought to have serious implications for the prevention of die streaks during processing of PEN.

Volatilisation of PET was found to significantly increase on ageing in the presence of oxygen, highlighting that PET is increasingly susceptible towards thermo-oxidative degradation at typical processing temperatures. With an increase in temperature and oxygen concentration, the extent of volatilisation in PET was found to increase further, due to extensive thermo-oxidative degradation. In contrast to PET, attempts to significantly increase volatilisation of PEN in the presence of oxygen failed. Even on ageing under highly oxidative environments i.e. 42% oxygen, and for long ageing periods at the highest ageing temperature, volatilisation levels of PEN were still particularly low, in comparison to PET. PEN is therefore thought to be increasingly less sensitive towards thermo-oxidative degradation.

Different chemical processes, which result in, or prevent volatilisation, are therefore thought to be ongoing in PET and PEN. Due to the poor extent of volatilisation observed in PEN under highly oxidative ageing environments, PEN is thought to be restricting the diffusion of bulky, volatile degradation products from the polyester melt due to its higher melt viscosity. With increased temperature, the melt viscosity decreases in both PET and PEN, with an overall higher melt viscosity observed in PEN than PET. Therefore, as the nature and thus volatility of the degradation products differ in PEN due to the presence of bulky naphthalene rings, their volatilisation from the polyester melt could be restricted.

The restricted melt flow of PEN was also evident from comparative examination of the residual PET and PEN samples recovered from thermo-oxidative ageing studies. The overall surface area of PEN was found to decrease after high temperature ageing, in contrast to an increase in surface area observed for PET samples. The decrease in melt viscosity and thus increased sample dispersion in PET can contribute towards degradation as an increase in surface area will obviously increase volatilisation by virtue of increased exposure area, resulting in an increase in the overall extent of volatilisation with increased ageing temperature. Although, degradation is generally considered to have a detrimental effect during polymer processing, such ageing conditions are advantageous to increase the flow of polymer from the die. However, with increased processing temperatures, the melt viscosity of PEN still remains high. Therefore, despite evidence of degradation from the formation of highly discoloured residual material after thermo-oxidative ageing, the PEN samples appear to shrink rather than exhibit surface spreading. This is thought to be due to the high extent of gel formation in PEN, in comparison to PET, influencing the overall volatilisation rates.

Under thermo-oxidative conditions, it is proposed that chain scission and cross-linking reactions compete, varying the proportion of volatile and cross-linked gel species formed as a result of ageing. Therefore, the overall extent of gel formation in PET and PEN was found to vary with the extent of volatilisation. On increasing the volatilisation of PET, by ageing at high temperatures in highly oxidative environments, the overall extent of gel formation was found to decrease. This is thought to be due to an overall reduction in the formation of oxidative cross-linked species due to a significant increase in the formation of volatile products. However, with such low levels of volatilisation observed in PEN, it can be proposed that the dominant degradation reaction in PEN under thermo-oxidative conditions is evidently cross - linking. The overall % gel content within PEN samples aged in the presence of oxygen was found to be very high, in comparison to PET. Therefore, oxygen must have the ability to diffuse into the highly viscous PEN melt, enabling extensive thermo-oxidative cross-linking reactions to occur. These reactions are thought to involve PEN degradation products with low volatility, which remain trapped within the highly viscous PEN melt.

Unfortunately the exact structural nature of the cross – linked species formed in PET and PEN cannot be positively identified. However, from ^{13}C solid state NMR analysis of the residual materials, results indicate that the cross-linked reactions in PET occur at aromatic sites, and not aliphatic sites due to the presence of a small, additional quaternary aromatic carbon signal. Cross-linking at aromatic carbon sites result in the formation of interconnected aromatic rings, with a high degree of conjugation. As conjugated species have very high extinction coefficients in the visible spectrum, from the presence of a number of chromophores, the formation of these interconnected aromatic ring species are therefore thought to contribute to the extensive discolouration observed in PET. One possible mechanism for the crosslinking of aromatic rings occurs due to the presence of acidic, thermally labile hydrogens adjacent to the aliphatic linkages. This mechanism was proposed by Holland *et al.* [15] and is illustrated in *Figure 5.66*. Alternatively, chain scission between the aromatic rings and ester functional groups would result in the formation of benzyl radicals which could undergo cross-linking reactions.

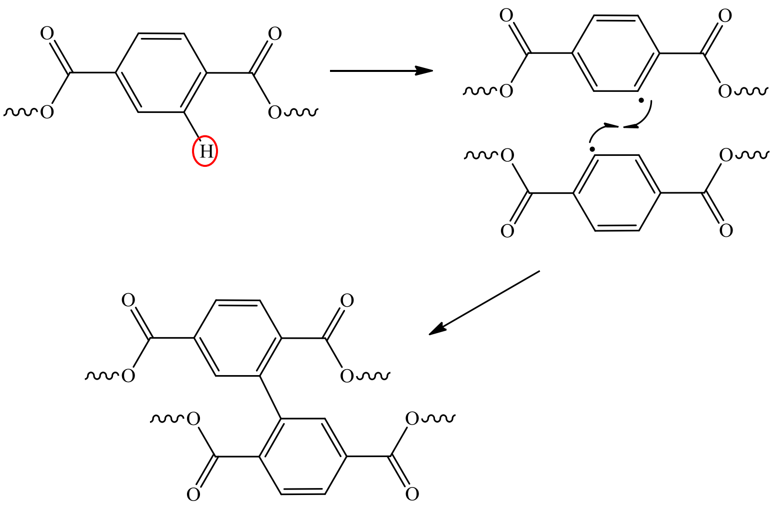


Figure 5.66 Mechanism for the formation of cross-linked structures in PET

The mechanisms discussed above and illustrated in *Figure 5.66* contradict reports of the formation of aliphatic network structures by Yoda *et al.* [16]. However, formation of such aliphatic network structures in PET, are thought to be unlikely due the extent of chain scission occurring during thermo-oxidative degradation resulting in the formation of additional volatile degradation products, the majority of which derive from the aliphatic, ester segments of the polyester chain. These cross-linked networks, illustrated in *Figure 5.67*, also exhibit less conjugation and are much less likely to result in the discolouration observed after thermo-oxidative ageing of PET.

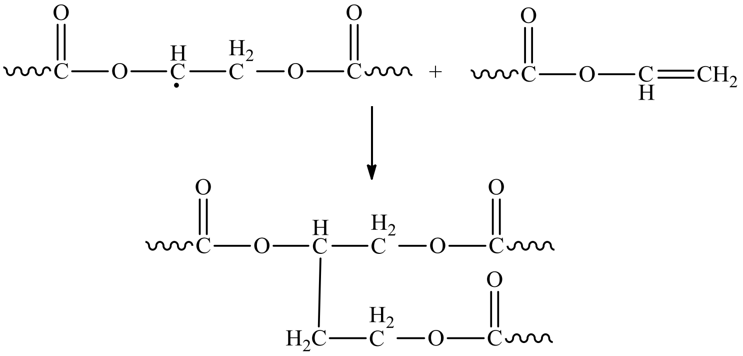


Figure 5.67 Formation of network structures in PET with aliphatic bridges

Although thermo-oxidative cross-linking reactions have been shown to be more dominant and aggressive in PEN than PET, the above mechanisms proposed for the cross-linking of PET are thought to be similar in PEN. Despite a lack of evidence for the presence of additional quaternary carbons, from the ^{13}C NMR spectra of residual PEN samples aged in oxidative environments, the cross-linking reactions are still thought to occur at aromatic sites, resulting in the formation of highly conjugated systems. Due to the presence of naphthalene groups in PEN, in contrast to phenyl groups in PET, greater conjugation will exist providing a possible explanation for the increased discolouration of PEN, in comparison to PET. One mechanism proposed by Botelho *et al.*[13] for the formation of highly conjugated bis-naphthalene cross-linked structures in PEN has been illustrated previously in *Figure 1.45*. Naphthalene radicals are formed in this mechanism by scission of the entire ester linkage from the aromatic ring, leaving an ester and naphthalene radical. Alternatively, the presence of acidic, thermally labile hydrogens adjacent to the aliphatic linkages may result in the formation of naphthalene radical species which undergo cross-linking to form bis-naphthalene type structures. This hydrogen abstraction reaction, shown previously for PET, can occur more easily in PEN than PET due to the increased reactivity of PEN in comparison to PET. Due to the presence of only single benzene rings in PET, with identical C-C bond lengths, the aromaticity and resonance energy is high. However, the presence of fused rings in PEN, with one pair of π electrons shared per naphthalene unit, results in uneven distribution of C-C bond lengths. This reduces the overall aromaticity and delocalisation energy, increasing the reactivity of aromatics in PEN, in comparison to PET.

Experimental evidence therefore suggests that the formation of cross-linked species, in both PET and PEN under thermo-oxidative degradation conditions, is directly related to the discolouration in both polyesters. Discolouration of PET and PEN was found to be most significant in samples aged in the presence of oxygen, indicating that thermo-oxidative conditions contribute more to the discolouration of PET and PEN than thermal conditions. With increased ageing temperature and oxygen concentration, the extent of gel formation was found to increase in both polyesters, accompanied by an increase in the extent of discolouration observed. The overall extent of discolouration and gel formation was most pronounced in PEN than PET, suggesting that the naphthalene ring is involved in the discolouration reactions.

On examination of all results obtained from the thermal and thermo-oxidative degradation of PET and PEN, it can be proposed that two mechanistic pathways contribute to the discolouration in both polyesters.

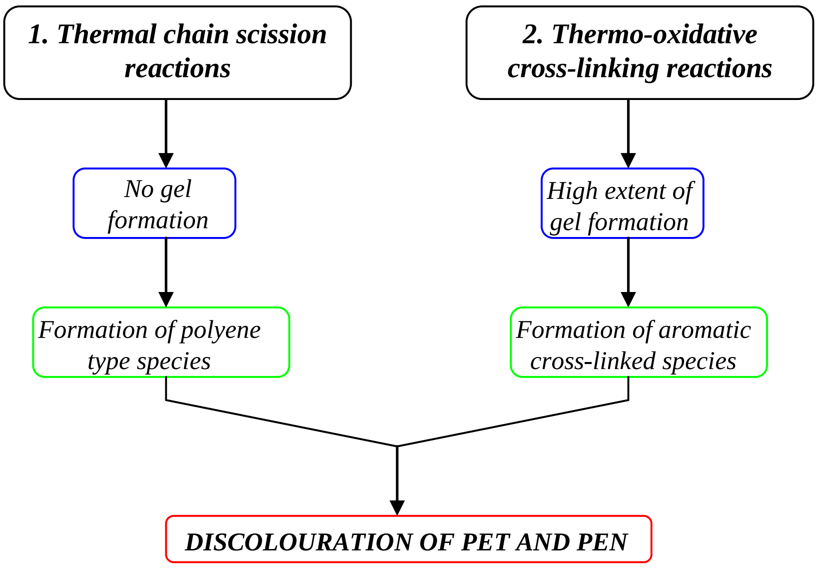


Figure 5.68 Discolouration degradation pathways in PET and PEN

The first mechanistic pathway is thought to originate from thermal degradation of PET and PEN. With an increase in ageing temperature under thermal conditions, vinyl ester groups formed from chain scission reactions are thought to undergo further polymerisation to result in the formation of conjugated and thus coloured polyene type species. As the extent of discolouration in PET and PEN samples was found to identical after thermal ageing, the benzene and naphthalene groups are not thought to be involved in this discolouration pathway. The second mechanistic pathway is believed to originate from thermo-oxidative degradation of PET and PEN. This pathway results in extensive cross-linking reactions, forming highly conjugated and highly absorbing benzene and naphthalene ring species in PET and PEN, respectively. Under thermo-oxidative conditions, the discolouration in PEN is thought to be more extensive than PET due to increased cross-linking reactions as a result of poor volatilisation. With increased cross-linking activity, involving highly absorbing naphthalene ring species, the extent of conjugation and presence of chromophoric species remains greater in comparison to PET, leading to more extensive discolouration in PEN than PET. Although, the first mechanistic pathway will also proceed under thermo-oxidative conditions, cross-linking reactions leading to the formation of network structures and thus discolouration will dominate.

5.3.12 Discussion of the Thermo-Oxidative Hydrolytic Degradation of PET and PEN at Typical Processing Temperatures

By combining moisture, high temperature and oxygen, it was hoped that significant degradation of PET and PEN would result due to competing thermal, thermo-oxidative and hydrolytic degradation reactions. However, the overall extent of volatilisation observed on ageing PEN in thermo-oxidative-hydrolytic conditions still remained poor.

A small increase in volatilisation of both polyesters was observed on introducing low moisture levels (1.5 - 2% AH) into the ageing system, promoting hydrolytic degradation. However, thermo-oxidative degradation remains as the dominant reaction occurring under thermo-oxidative-hydrolytic ageing conditions. Unlike the increased sensitivity of PET towards the presence of oxygen, neither PET nor PEN show increased sensitivity to ageing in the presence of low levels of moisture. Higher moisture levels therefore appear necessary in order to promote hydrolytic degradation of PET and PEN and increase the extent of volatilisation, particularly in PEN.

The discolouration, melt-flow characteristics and structural analysis of PET and PEN samples aged in wet oxidative environments were found to be identical to samples aged in dry oxidative conditions, indicating once again that hydrolytic degradation has little impact on the ongoing chemical processes during ageing. However, with a small increase in volatilisation observed on ageing in thermo-oxidative-hydrolytic conditions, a significant decrease was observed in the extent of gel formation in samples of both PET and PEN, in comparison to samples aged in dry oxidative environments.

Under thermo-oxidative-hydrolytic ageing conditions, it can therefore be proposed that hydrolytic degradation and cross-linking reactions compete, resulting in a decrease in the overall extent of gel formation and an increase in volatilisation. Such competing hydrolytic and thermo-oxidative degradation reactions are thought to be beneficial for eliminating die streaks. By reducing the extent of gel formation and marginally increasing the extent of volatilisation, the build-up of highly cross-linked residual material on the die should be reduced. However, as we appear unable to increase the levels of volatilisation in PEN beyond 15%, on ageing in high temperature and high oxygen concentration, the overall extent of gel formation remains very high, with a low proportion of soluble products.

On increasing the oxygen concentration and temperature during thermo-oxidative hydrolytic ageing of PEN, the overall extent of cross-linking appears to remain particularly high, in comparison to PET, even with the small decrease in gel content associated with hydrolytic degradation. Thermo-oxidative cross-linking therefore dominates over hydrolytic degradation in PEN at high processing temperatures and high oxygen concentration. The degradation species believed to be responsible for the formation of cross-linked and discoloured species in both PET and PEN are thought to be identical to the species formed during thermo-oxidative degradation of both polyesters, discussed previously. In addition to high gel formation in PEN, in comparison to PET, low volatilisation levels and poor melt flow observed in both dry and wet oxidative environments, will contribute to problematic removal of residual PEN material from the die. Other strategies, besides oxidative degradation in the presence of low moisture levels, are therefore required to exploit further degradation of PEN for the purpose of reducing die-streaks.

5.3.13 High Humidity Degradation Studies of PET and PEN

One final set of degradation studies were completed to investigate the role of temperature, water and oxygen on the degradation of PEN, in comparison to PET, at typical processing temperatures. Degradation of PET was found to be increasingly sensitive to the presence of oxygen, leading a significantly high extent of volatilisation on ageing under thermo-oxidative conditions. In contrast to PET, degradation and thus volatilisation of PEN was found to be particularly problematic. Degradation of PEN is not particularly sensitive to the presence of oxygen or low moisture levels leading to difficulties in promoting degradation for the purpose of preventing build up of degradation material on the die extrusion hardware.

Therefore, other strategies were employed in attempt to promote further degradation of PEN. The first of these to be explored included high temperature degradation studies of PEN, in comparison to PET. Although, not a favourable route for practical or economical purposes, ageing studies were completed on PET and PEN up to temperatures of 370 ^{o}C. The raw data for the high temperature studies of PET and PEN can be found in *Chapter 8 Supplementary Material*.

On increasing the ageing temperature of PET and PEN to 370 ^{o}C, increased thermal degradation and a subsequent increase in the formation of volatile degradation products was achieved. Volatilisation of PET was found to be most pronounced in the presence of air, with no significant changes in the extent of volatilisation observed on ageing PEN in an inert and oxidative environment. Discolouration of PET and PEN were found to be identical at high ageing temperatures with increased melt flow observed once again for PET aged in the presence of air. High temperature thermo-oxidative conditions are therefore ideal for promoting the degradation of PET. However, despite a higher extent of volatilisation observed for PEN, in comparison to all other ageing studies, the levels of volatilisation were still lower than observed in PET accompanied by poor melt flow. The additional formation of thermo-oxidative cross-linked species, particularly in PEN is thought to complicate and limit volatilisation, in comparison to PET. Ideally, the ageing conditions necessary for PEN will promote volatilisation, subsequently leading to reduction in the formation of oxidative-cross linked species and an overall reduction in the thickness of the residual deposit. Such conditions are thought to lead to enhanced operational improvements preventing die streaks during processing of PEN.

The second strategy adopted in an attempt to promote volatilisation of PEN, to similar levels observed in PET, was ageing under high humidity. As low moisture levels have previously been shown to increase volatilisation levels and reduce the extent of cross-linking in both PET and PEN, experimental conditions were modified in an attempt to increase levels of moisture within the ageing system. By increasing the levels of moisture present during ageing of PEN, it was hoped that hydrolytic degradation reactions would dominate over thermal and thermo-oxidative degradation reactions, leading to an increase in the volatilisation levels and a decrease in the extent of cross-linked species formed. DuPont Teijin films can create similar high humidity ageing environments, under processing conditions, by the use of a large humidity unit.

5.3.13.1 Volatilisation Studies

Figures 5.69 and *5.70* present the volatilisation data for PET and PEN samples aged at 288 ^{o}C to 320 ^{o}C at various humidity levels in both inert and oxidative environments. The raw data used to generate such plots can be found in *Chapter 8 Supplementary Material*. Volatilisation of PEN was found to increase significantly on increasing the moisture levels under both nitrogen and air. This is due to an increase in chain scission reactions as a result of hydrolytic degradation. On ageing PEN in high moisture content, the extent of volatilisation was not found to differ significantly between samples aged in nitrogen and air. A relatively linear relationship can be observed between the extent of volatilisation and moisture content for all PEN samples aged in nitrogen and air, with only a small increase in volatilisation observed, particularly at lower moisture levels, on changing the ageing environment from nitrogen to air. This once again highlights that PEN is not particularly susceptible to thermo-oxidative degradation, in direct contrast to PET. Instead, PEN has shown to be increasingly susceptible towards hydrolytic degradation. On introducing high moisture content, volatilisation levels up to 59% were achieved in air, in comparison to volatilisation levels of only 11% obtained under thermo-oxidative-hydrolytic conditions at low moisture levels.

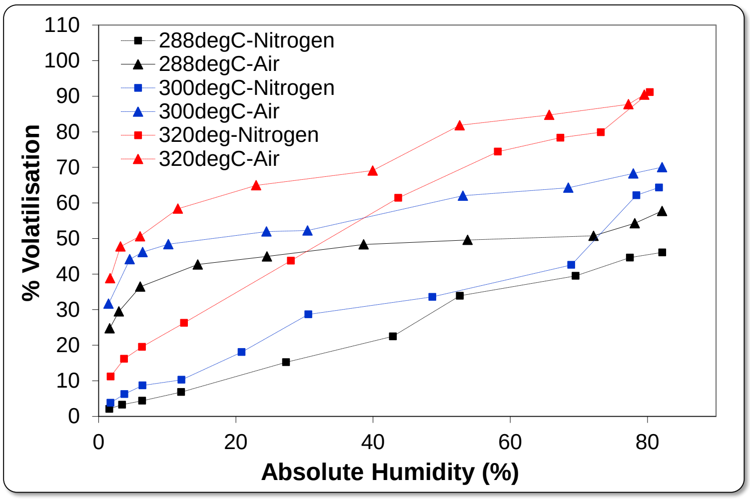


Figure 5.69 Volatilisation results for PET samples aged at various humidity levels in nitrogen and air at temperatures of 288 - 320 °C for 4 hours

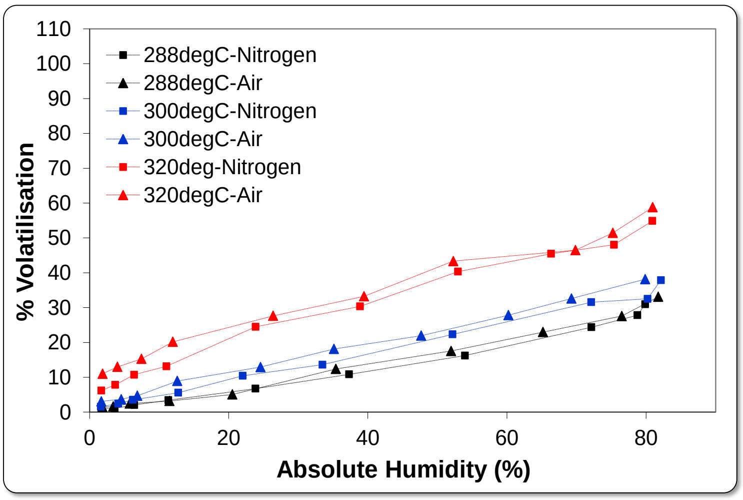
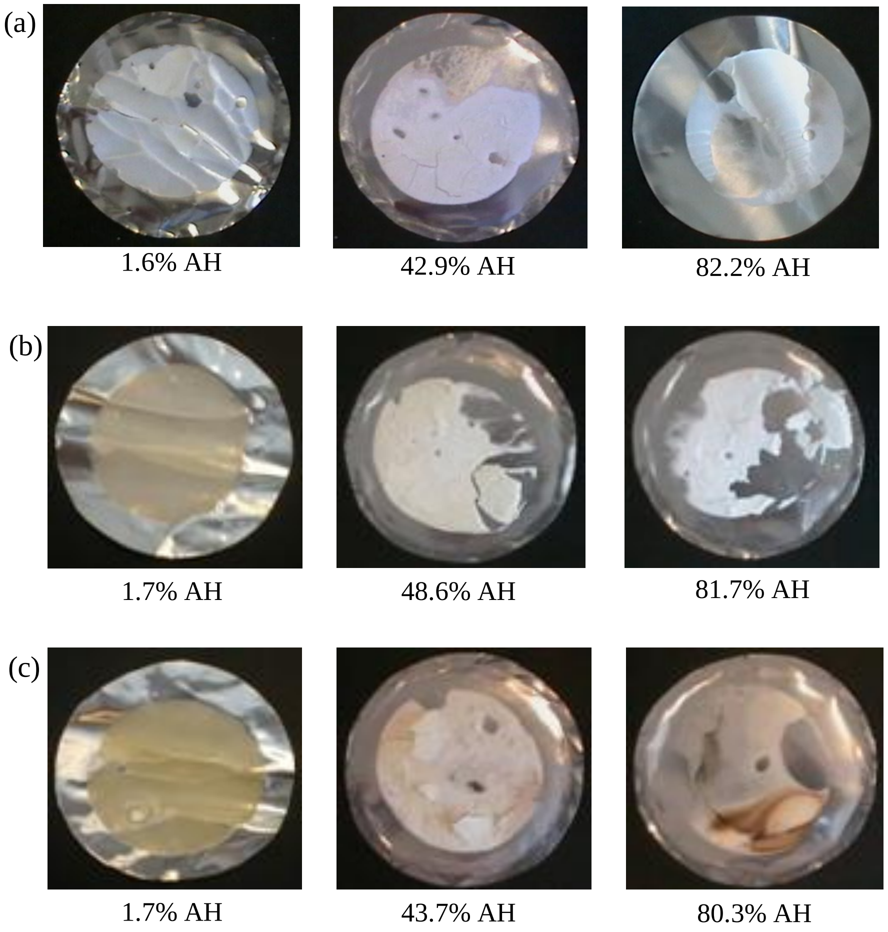


Figure 5.70 Volatilisation results for PEN samples aged at various humidity levels in nitrogen and air at temperatures of 288 - 320 °C for 4 hours

More complex volatilisation trends can be observed for PET from *Figure 5.69* with considerable overlap in trend lines for ageing of samples in inert and oxidative environments. On ageing PET at the lowest temperature of 288 ^{o}C in nitrogen, a considerable increase in the extent of volatilisation can be observed on increasing humidity levels. However, on introduction of oxygen into the ageing system, even at low moisture content, significant volatilisation can be observed indicating that oxidative degradation is the dominant reaction over hydrolysis. On increasing the ageing temperature to 300 ^{o}C, similar trends can be observed to those seen at 288 ^{o}C in both air and nitrogen, with only a marginal increase in volatilisation as a result of increased ageing temperature. On reaching the highest ageing temperature of 320 ^{o}C, high levels of volatilisation can be achieved with increasing moisture levels even under purely thermal conditions. Once again, volatilisation does increase on introduction of oxygen into the ageing system, however this difference is not as significant as observed at 288 ^{o}C. The PET curves, represented for samples aged at all three temperatures in nitrogen and air, show small volatilisation differences with increasing humidity levels. Such results, indicate that hydrolysis dominates on introduction high moisture levels into the ageing system, as expected.

5.3.13.2 Discolouration of Residual PET and PEN Film Samples

In an identical manner to previous studies, all residual PET and PEN film samples were examined for discolouration. *Figures 5.71 - 5.74* illustrate the residual film samples obtained from PET and PEN after ageing at three different humidity levels i.e. low, medium and high humidity levels in nitrogen and air for 4 hours at 320 °C. All other images can be found in *Chapter 8 Supplementary Material*. The overall extent of discolouration for PET and PEN samples aged at different moisture levels in an inert atmosphere were not found to differ greatly to those aged under dry inert conditions. As observed previously, increased discolouration can be observed on reaching the highest ageing temperature of 320 ^{o}C. Despite the lack of discolouration observed in all samples aged in nitrogen at different moisture levels, the mass of residual material remaining after degradation was seen to differ.

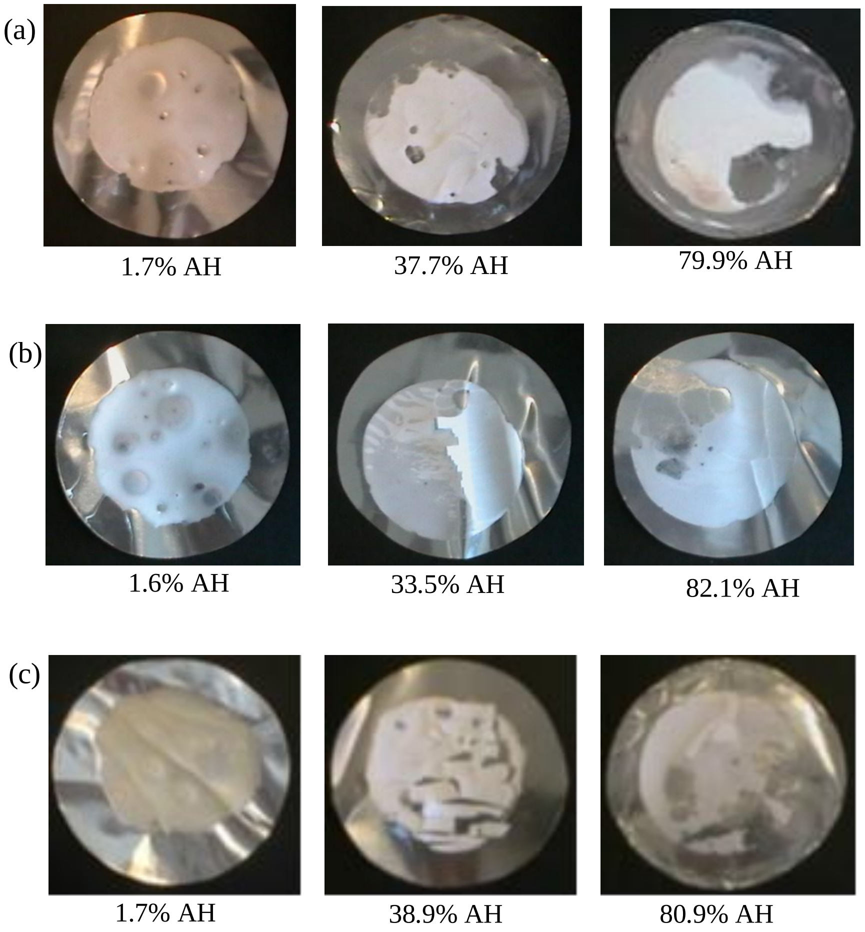


(a) 1.6% AH, 42.9% AH, 82.2% AH

(b) 1.7% AH, 48.6% AH, 81.7% AH

(c) 1.7% AH, 43.7% AH, 80.3% AH

Figure 5.71 Residual film samples from PET after high humidity ageing for 4 hours in nitrogen at (a) 288 °C (b) 300 °C and (c) 320 °C

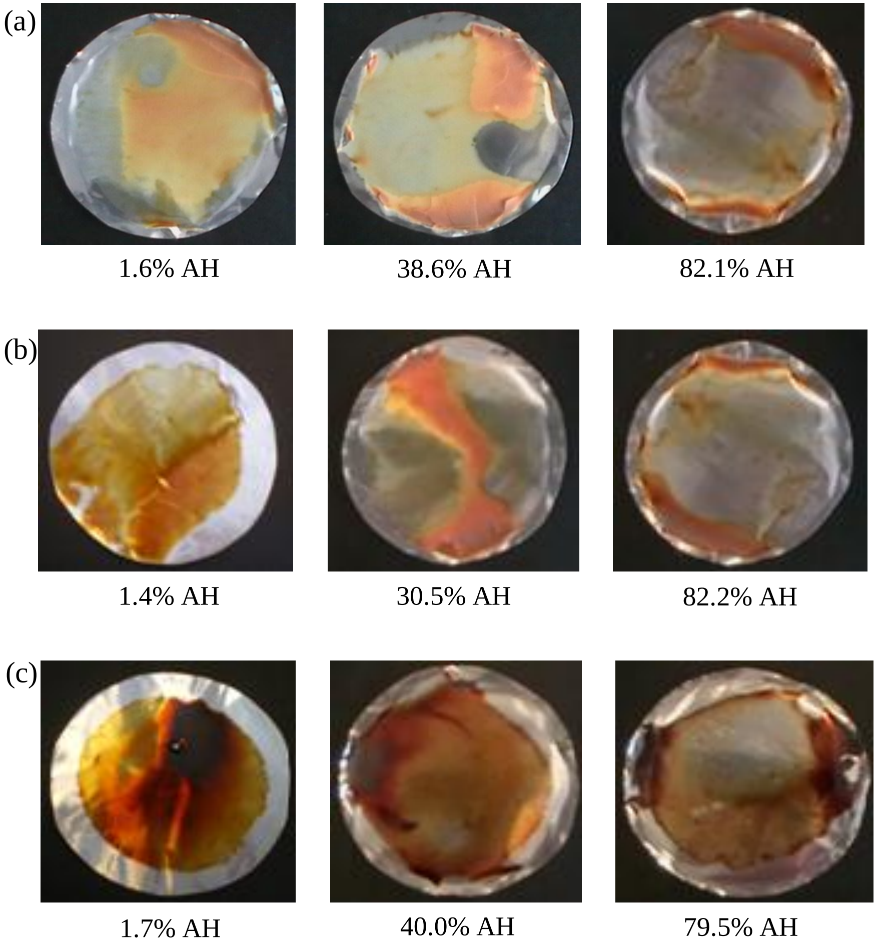


(a) 1.7% AH, 37.7% AH, 79.9% AH

(b) 1.6% AH, 33.5% AH, 82.1% AH

(c) 1.7% AH, 38.9% AH, 80.9% AH

Figure 5.72 Residual film samples from PEN after high humidity ageing for 4 hours in nitrogen at (a) 288 °C (b) 300 °C and (c) 320 °C

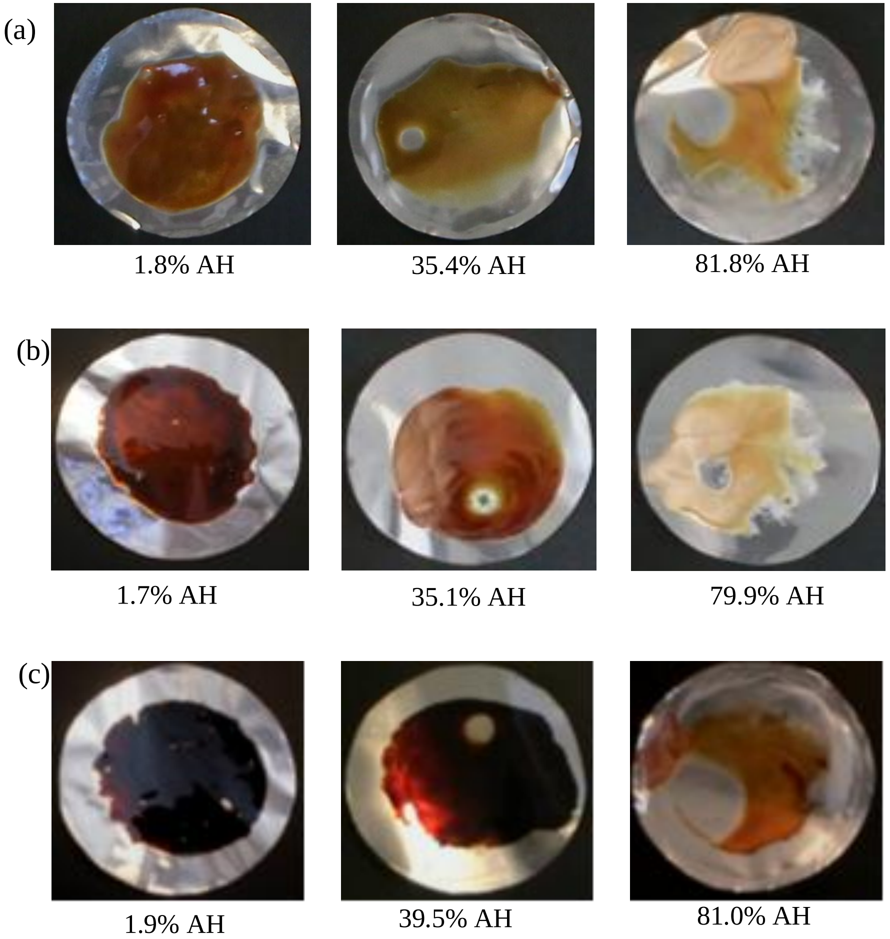


1.6% AH 38.6% AH 82.1% AH

1.4% AH 30.5% AH 82.2% AH

1.7% AH 40.0% AH 79.5% AH

Figure 5.73 Residual film samples from PET after high humidity ageing for 4 hours in air at (a) 288 °C (b) 300 °C and (c) 320 °C



1.8% AH 35.4% AH 81.8% AH

1.7% AH 35.1% AH 79.9% AH

1.9% AH 39.5% AH 81.0% AH

Figure 5.74 Residual film samples from PET after high humidity ageing for 4 hours in air at (a) 288 °C (b) 300 °C and (c) 320 °C

As expected, on increasing the absolute humidity, a reduction in the mass of residual material is visible from the images illustrated in *Figures 5.71 - 5.74*. This is simply due to increased levels of volatilisation and increased surface spread as a result of decreased intrinsic viscosity and thus melt viscosity.

On ageing samples in air, discolouration of PET and PEN was found to be more extensive than that observed in an inert ageing environment, due to thermo-oxidative degradation. As discussed previously for PET and PEN samples aged under thermo-oxidative conditions, such reactions lead to the formation of cross-linked, highly conjugated species, which are thought to contribute to discolouration. On ageing PEN samples under air at low moisture levels, the residual samples appear black in colour. However, on increasing the absolute humidity, the colour and appearance of the residual material can be seen to differ quite significantly. With increased moisture levels, the extent of discolouration can be seen to reduce in PEN aged under air. This is simply thought to be due to significant degradation of PEN in the presence of increased moisture levels, resulting in increased levels of volatilisation and a reduction in the overall thickness of the residual deposit. On ageing PEN in air at high moisture levels, the extent of surface spread can also be seen to differ. By increasing moisture levels, not only does the extent of volatilisation increase, but the surface coverage of PEN samples can be seen to increase. Such observations are in direct contrast to those noted previously for PEN samples aged under dry inert and oxidative environments where all samples were found to shrink at all three ageing temperatures. Therefore, by introducing high moisture levels into the ageing system, we can significantly increase the volatilisation and melt flow of PEN far beyond anything observed previously.

5.3.13.3 Gel Formation in Residual PET and PEN Film Samples

Introducing low moisture levels (1.5 - 2% AH) into the ageing system has previously been shown to promote volatilisation of PEN and reduce the overall extent of thermo-oxidative cross-linking due to competing hydrolytic and oxidative cross-linking reactions. Therefore, as high moisture levels appear to have significant impact on the overall levels of volatilisation, it was hoped that the extent of oxidative cross-linking and thus gel formation in PEN can also be reduced on ageing in high humidity environments. *Figures 5.75 and 5.76* illustrate the % gel content recovered from PET and PEN samples aged at 320 °C in air, at various moisture levels. In this instance, due to the higher levels of the volatilisation, the gel content is expressed as a % of the original sample mass. All raw gel data for PET and PEN samples aged under various moisture levels in nitrogen and air can be found in *Chapter 8 Supplementary Material*.

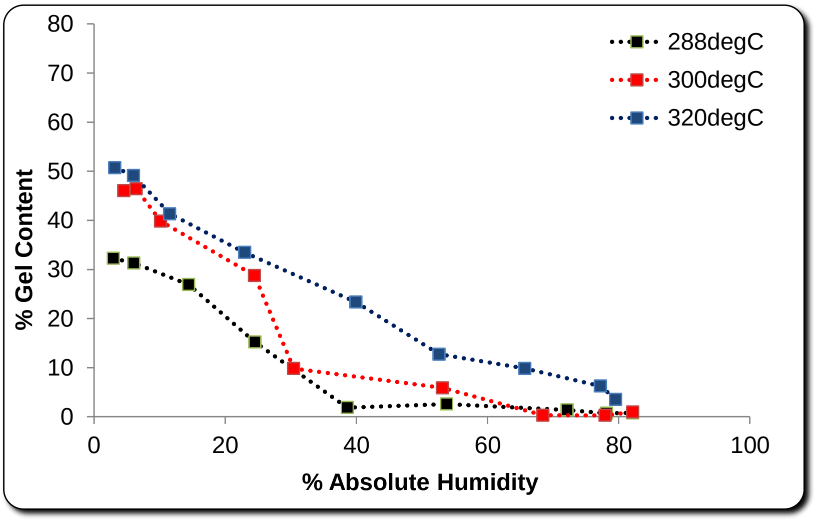


Figure 5.75 % Gel content in PET samples aged at 288 - 320 ^{o}C in air at various humidity levels for 4 hours - expressed as a % of original sample mass

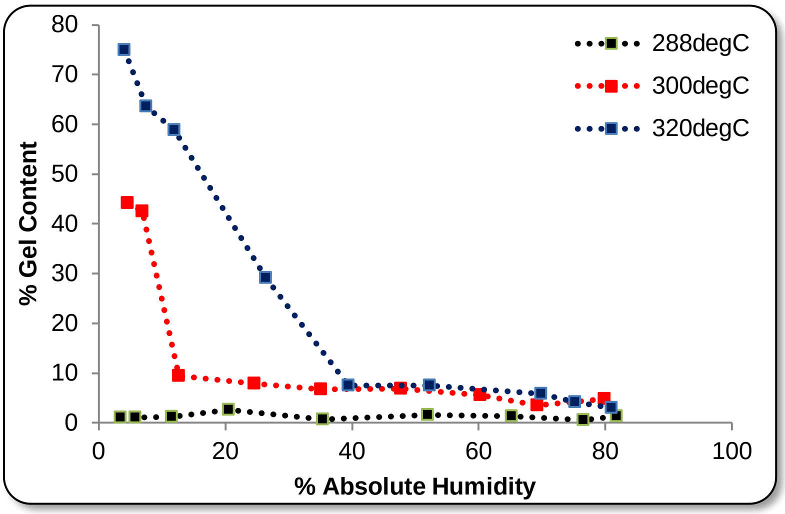


Figure 5.76 % Gel content in PEN samples aged at 288 - 320 ^{o}C in air at various humidity levels for 4 hours - expressed as a % of original sample mass

On examining the extent of gel formation in residual PEN samples aged in oxidative environments, the % gel content was found to vary quite considerably with moisture content. All samples of PEN, aged at 300 – 320 ^{o}C in moisture levels below 40% AH, were found to be insoluble in the selected solvent mixture, in contrast to the high degree of solubility observed for samples aged at higher moisture levels i.e. greater than 40% AH. The extent of gel formation in PEN was therefore found to significantly decrease on increasing humidity levels from 1 - 40% AH. At humidity levels ≥ 40%, the extent of gel formation was found to slowly decrease and then plateau towards gel content values similar to those observed for PEN samples aged under an inert atmosphere. Therefore, it can be confirmed that high moisture content (i.e. greater than 40% AH) reduces the overall extent of oxidative cross-linking and thus gel formation, as hypothesised previously. Hydrolysis is thought to dominate at high moisture levels, severely limiting competing oxidative cross-linking reactions in PEN.

Similar trends exist for PET, with a steady decrease in gel content with increasing moisture levels during ageing. As expected, gel content was found to be higher in samples aged at higher temperatures, however on reaching 80% AH gel species cannot form due to the high levels of moisture within the ageing system. It must finally be noted that the cross-linked species in PET and PEN cannot be destroyed once formed under processing conditions, the presence of high moisture levels will only prevent the formation of such species.

5.3.14 Discussion of the High Humidity Degradation of PEN at Typical Processing Temperatures

On increasing the moisture concentration on ageing PET and PEN at temperatures of 288 - 320 ^{o}C, increased hydrolytic degradation and a subsequent increase in the formation of volatile degradation products can be achieved. Volatilisation of both PET and PEN were found to be most pronounced on ageing at the highest moisture concentration in air. In addition to increased volatilisation on ageing under air, the extent of cross-linking was also seen to drastically decrease on increasing the absolute humidity above 40%, accompanied by increased melt flow of the polyester. Increased volatilisation, increased melt flow and a reduction in oxidative cross-linking all result from competing thermal/thermo-oxidative and hydrolytic degradation reactions and would lead to enhanced operational improvements particularly for the prevention of die streaks during processing of PEN.

Based on evidence presented in the literature and degradation results presented for PET and PEN, it is thought that the chain ends play an important role in determining the rate of hydrolytic degradation. Some researchers have proposed that the hydrolytic degradation mechanism of PET is an autocatalytic reaction and that the concentration of carboxyl end groups controls the hydrolytic degradation. [7,19,20,21] Therefore, on ageing PET and PEN in increasingly high moisture levels, an increase in the number of end groups will occur as a result of degradation. Any carboxyl end groups that are exposed on the polymer chains will be hydrophilic in nature due to the electronegativity of the oxygen groups, making the functional group polar. These polar functional groups will attract polar water molecules, subsequently resulting in penetration of more water into the system, providing conditions for an autocatalytic reaction, in contrast to random chain scission reactions.

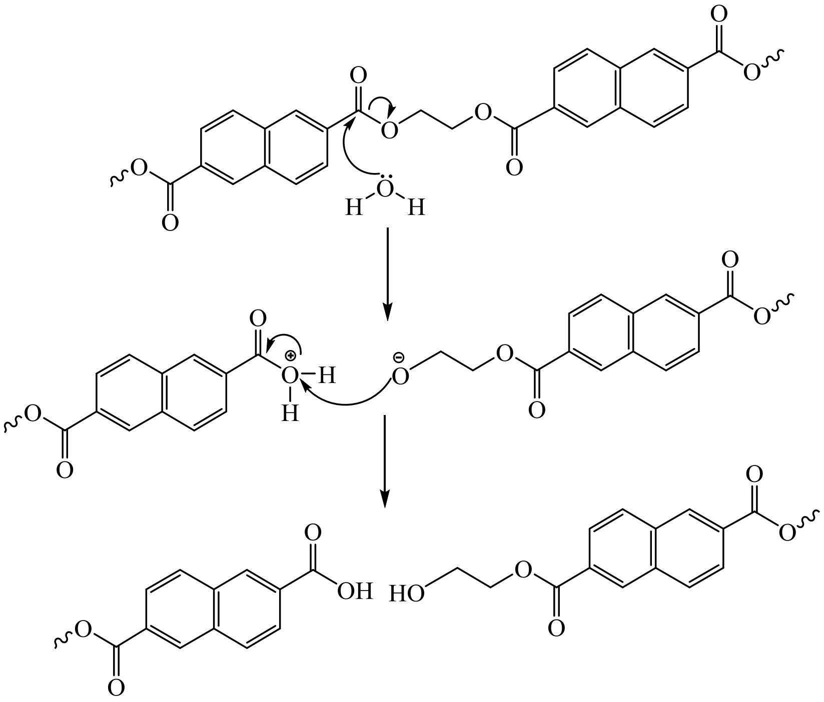


Figure 5.77 Chain scission mechanism for hydrolytic degradation of PEN

As all of the above results indicate that both high temperature and high humidity strongly influence the volatilisation of PEN, one final study was completed in an attempt to promote volatilisation of PEN, beyond that observed on ageing at 320 ^oC under high humidity. This involved combining the effects of high temperature and high humidity by ageing PEN in air for 4 hours at 80% AH and 350 ^oC. Increasingly high levels of volatilisation were achieved, precisely 95%, indicative that high temperature and high humidity have a pronounced impact on promoting degradation of PEN. By increasing the extent of volatilisation significantly, by combined high temperature and high humidity, the build-up of highly cross-linked residual material on the die will be substantially reduced.

5.4 Conclusions and Recommendations

From the thermal, thermal-hydrolytic, thermo-oxidative and thermo-oxidative-hydrolytic ageing studies completed on PET and PEN, the extent of degradation has been shown to differ between both polyesters. 3D surface plots have been generated to illustrate the interactions of temperature, oxygen and humidity levels on the volatilisation and gel formation in PET and PEN. Suitable die lip atmospheric conditions, which reduce the overall polymer viscosity by means of promoting volatilisation and reducing the extent of organic debris and gel formation, have been identified for both polyesters. It is deduced that these conditions will minimise die streaks when processing PET and PEN films.

On ageing PET in dry inert conditions, degradation and thus chain scission is minimal with an increase in melt viscosity suggestive of chain extension rather than chain scission. Inert atmospheres do preserve residue with little gel formation in contrast to air atmospheres, which promote cross-linking reactions. Both air and high oxygen atmospheres promote volatilisation of PET, increasing gel concentration but reducing absolute gel content due to increased volatilisation.

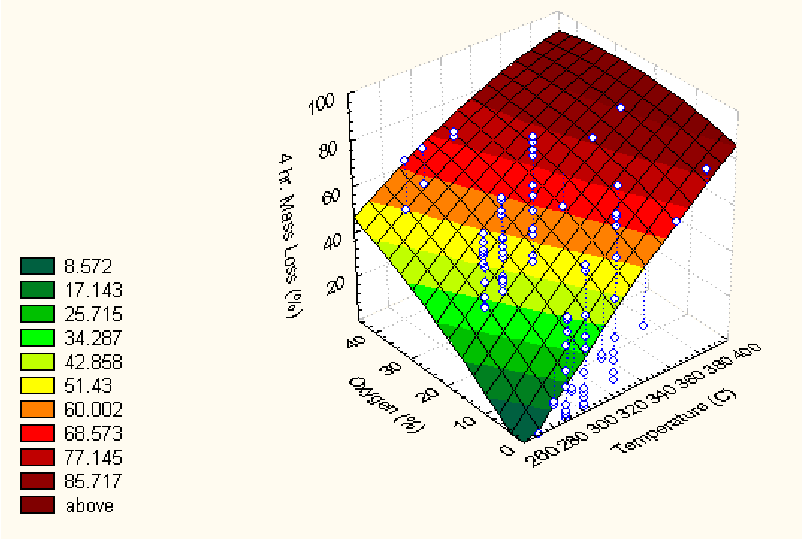


Figure 5.78 3D surface plot to illustrate impact of temperature and oxygen concentration on volatilisation of PET

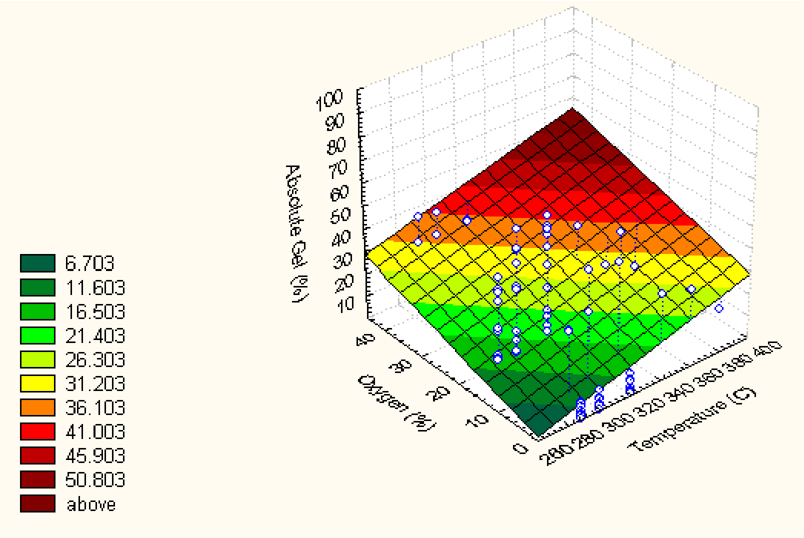


Figure 5.79 3D surface plot to illustrate impact of temperature and oxygen concentration on absolute gel formation in PET

Increasing temperature increases volatilisation of PET, however this coincides with an increase in both relative and absolute gel concentrations. This suggests that high lip temperatures may be detrimental to die streaks, even although volatilisation is increased. High oxygen concentrations and high temperature both volatilise PET lip residue, with a combination of both eliminating almost all lip residue. Increasing moisture rapidly results in increased volatilisation and a reduction in absolute and relative gel content in PET, particularly at high temperatures. Water interferes with cross-linking reactions in PET, thus preventing the formation of significant quantities of gel. Therefore, high temperature and high humidity is required to maintain high volatilisation levels and limit gel formation. Additional volatilisation of PET in air occurs above humidity levels of 60%, whereby hydrolytic degradation dominates as the exclusion of oxygen is likely. Both water and oxygen were found to improve deposit flow as a result of increased volatilisation and reduction in absolute gel content.

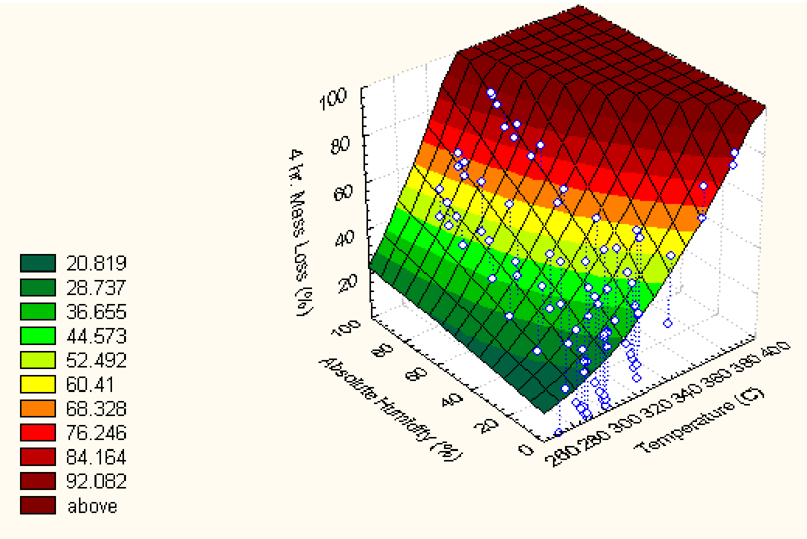


Figure 5.80 3D surface plot to illustrate impact of temperature and absolute humidity on volatilisation of PET

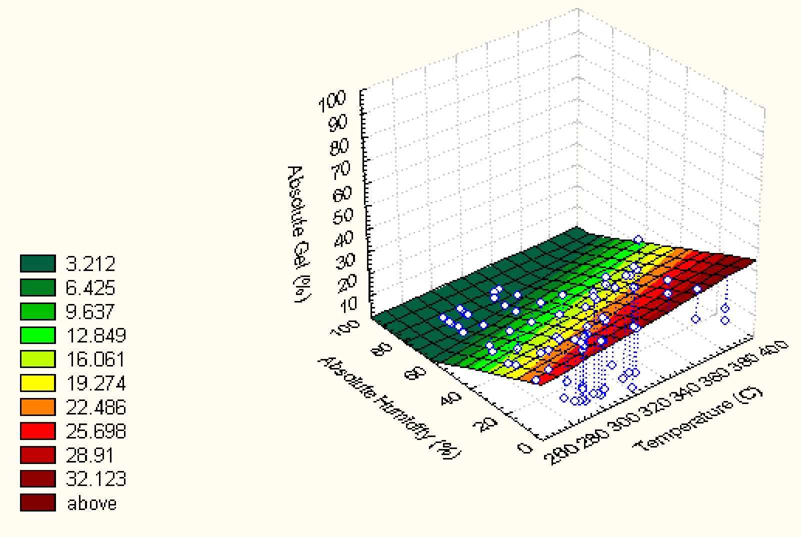


Figure 5.81 3D surface plot to illustrate impact of temperature and absolute humidity on absolute gel formation in PET

In contrast to PET, attempts to significantly increase volatilisation of PEN in the presence of oxygen proved more difficult. Degradation of PEN in an inert environment proved similar to PET, with low levels of volatilisation and gel formation, thus deeming inert conditions unfavourable for the prevention of die streaks.

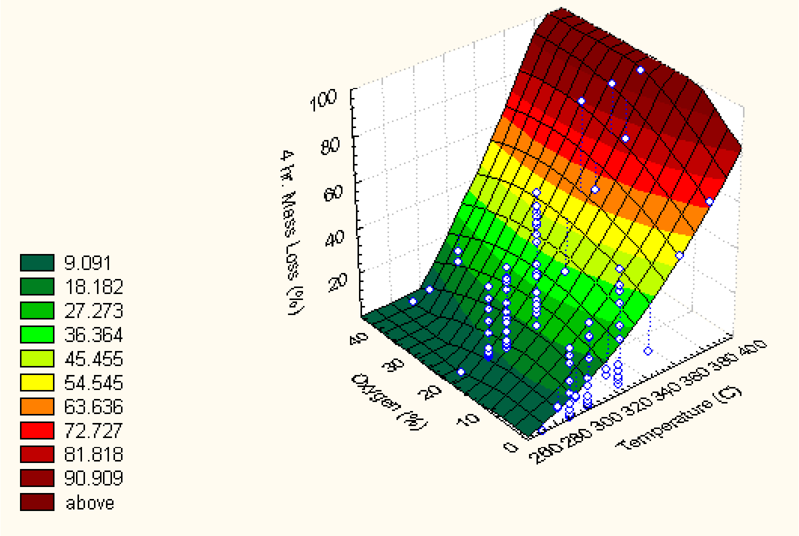


Figure 5.82 3D surface plot to illustrate impact of temperature and oxygen concentration on volatilisation of PEN

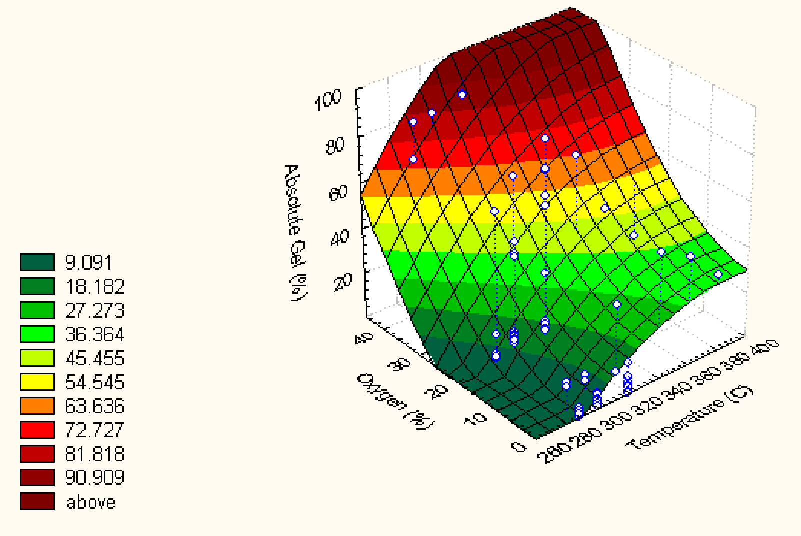


Figure 5.83 3D surface plot to illustrate impact of temperature and oxygen concentration on gel formation in PEN

On increasing oxygen concentration, only a marginal increase in volatilisation was observed in PEN, however unlike PET, this was accompanied by a significant increase in both relative and absolute gel formation with little apparent effect on deposit flow. As outlined previously, oxidative cross-linking reactions are thought to dominate in PEN, with the high melt viscosity of PEN thought to restrict the diffusion of bulky degradation products from the polyester melt, increasing the rate of secondary cross-linking reactions leading to a reduction in the overall extent of volatilisation. Both gel formation (absolute and residual) and volatilisation of PEN were also found to increase on raising the ageing temperature. High die lip temperatures are therefore likely to be detrimental to die streaks, and should be combined with moisture or reduced oxygen atmospheres to minimise gel formation and promote deposit flow.

High moisture levels significantly improve deposit flow, increase volatilisation of PEN and substantially reduce gel content in the presence of oxygen, indicative of competing hydrolysis and oxidative cross-linking reactions. Hydrolysis of PEN is thought to dominate and prevent the formation of oxidative cross-linked species or alternatively produce volatile species which are more resistant to cross-linking. Therefore, both high temperature and high humidity appear vital to promote volatilisation of PEN and minimise lip residue.

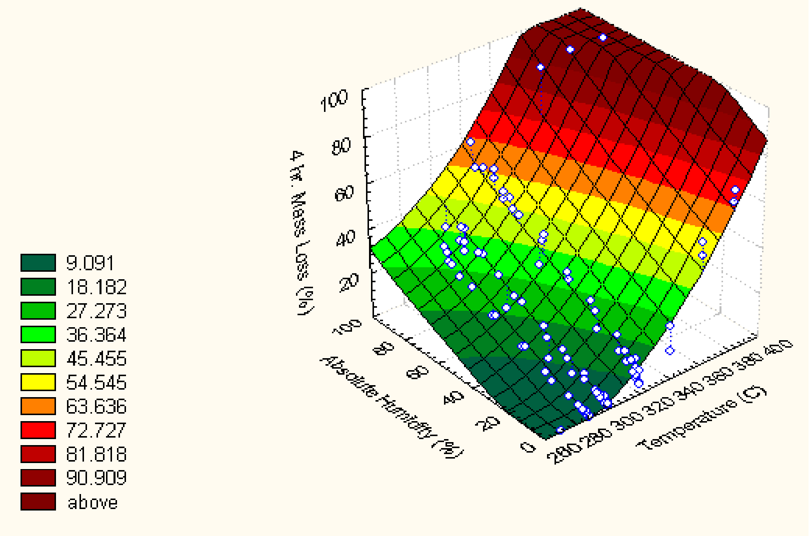


Figure 5.84 3D surface plot to illustrate impact of temperature and absolute humidity on volatilisation of PEN

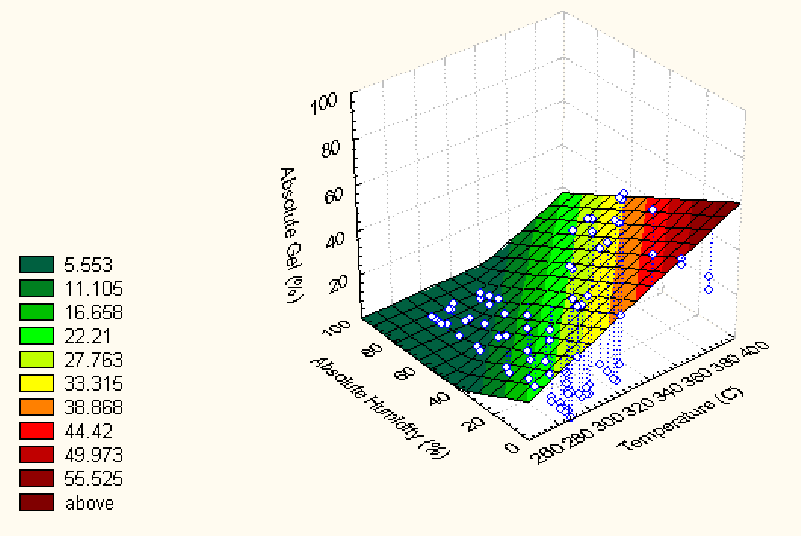


Figure 5.85 3D surface plot to illustrate impact of temperature and absolute humidity on gel formation in PEN

To promote degradation of PET and PEN for the purpose of preventing die streaks, conditions are required such that volatilisation and melt flow are maximised and the formation of oxidative cross-linked gel species is minimised. High humidity environments appear favourable for both PET and PEN processing, with recommendations to maximise oxygen concentration for PET but minimise for PEN. High temperatures can be used to reduce streak causing lip deposits, however, this must be accompanied by high humidity to avoid excess gel formation.

5.5 References

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6 AGEING OF PET AND PEN UNDER MODERATELY ACCELERATED CONDITIONS

6.1 Background to Research

As highlighted throughout this research, degradation of PET and PEN polyesters is inevitable during synthesis and processing as the polyesters are exposed to high temperatures, both under non-oxidative and oxidative conditions in the presence of moisture. These conditions can result in a combination of thermal, thermo-oxidative and hydrolytic degradation reactions leading to the evolution of volatile degradation products and significant loss of crucial polymer properties. Unfortunately, hydrolytic degradation of polyester chips is also particularly inevitable during post-polymerisation cooling processes and storage. The hydroxyl, carboxyl and ester groups within the polyester network are likely to retain water and therefore if the polyester chips were to be processed directly, their molar mass would significantly decrease as a result of hydrolytic degradation. For this reason, polyester chips are crystallised, to avoid sintering during drying, and then dried for several hours to reduce the moisture content prior to processing.

The effect of this pre-processing drying treatment on the thermal degradation of PET polyester chips has been investigated. Villain *et al.* [1] examined the overall mass loss behaviour of PET when dried under air and nitrogen at 160 °C for 800 minutes, prior to thermal degradation at processing temperatures of 280 °C and 310 °C. The most significant mass loss was reported when drying and degradation were performed under air, due to oxidative degradation leading to a reduction in the overall length of the polymer chains. PEN is reported to have increased thermal [2] and hydrolytic resistance [3] in comparison to PET, however due to a lack of research on PEN, few studies have been published and no research has been conducted on the effects of drying on the degradation of PEN.

In this research, the extent of degradation in PET and PEN is reported after ageing under different drying conditions. PET and PEN polyester chips were aged under dry nitrogen, dry air, wet nitrogen and wet air environments at temperatures of 140, 160, 170 and 190 ^{o}C. The ageing temperatures selected were based around the typical drying temperatures currently used during the pre-processing treatment of PET. With increasing temperature, the degradation mechanism during ageing is thought to differ. Hydrolysis is believed to dominate over extended periods of time at lower ageing temperatures (i.e. 140 - 160 ^{o}C) with oxidative degradation dominating at higher ageing temperatures (i.e. 190 ^{o}C). This contrasting set of ageing conditions, at which the polyester samples were exposed to, enables the effects of temperature, water and oxygen to be mapped onto the resultant property changes of PET and PEN.

6.2 Experimental Details

6.2.1 Materials

Commercial samples of PET and PEN were kindly supplied by DuPont Teijin Films. Both PET and PEN were supplied as transparent chips with a weight average molar mass (M_w) of 24900 ± 141 g mol $^{-1}$ and 20200 ± 71 g mol $^{-1}$, respectively. Prior to use, the polyester chips were stored for several hours in a vacuum desiccator at room temperature, to remove any surface water.

6.2.2 Ageing Apparatus

The purpose of the experimental apparatus was to age samples under contrasting environments; dry nitrogen, wet nitrogen, dry air and wet air at elevated temperatures, over a period of 24 hours. This enabled the effects of thermal, thermal-hydrolytic, thermo-oxidative and thermo–oxidative-hydrolytic degradation to be studied in both polyesters. A schematic representation of the ageing apparatus is illustrated in *Figure 6.1.*

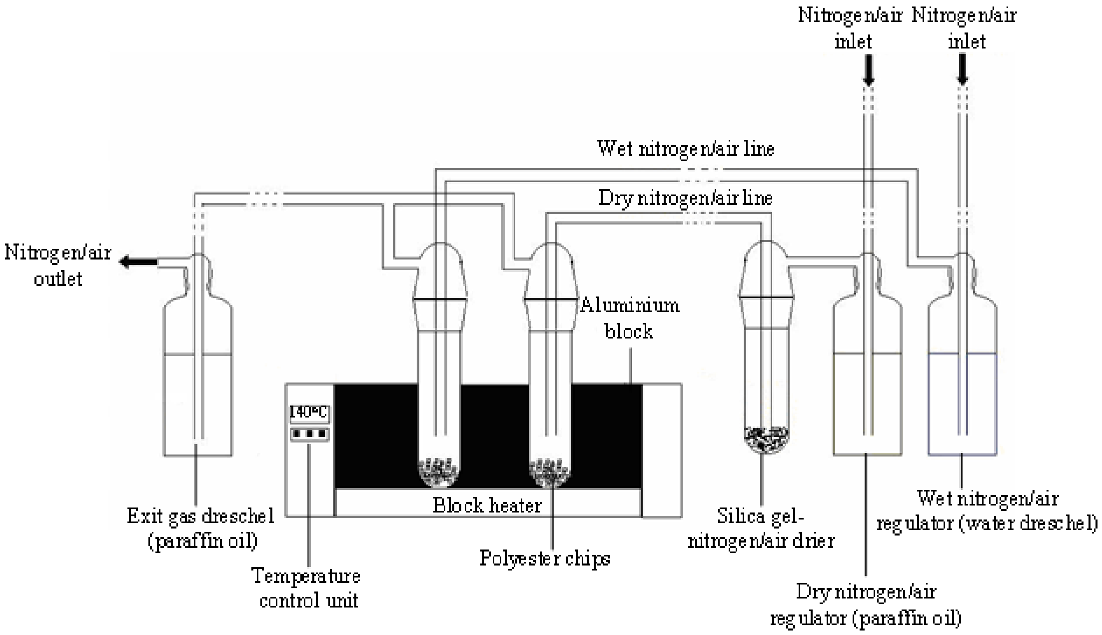

Figure 6.1 Apparatus for ageing PET and PEN

The apparatus consisted of a thermostatically controlled block heater capable of reaching temperatures of 200 ^{o}C ± 1.0 ^{o}C. 1 g of polymer chip sample was placed in each sample tube for ageing and dry/wet, nitrogen/air were fed individually into each sample chamber yielding dry non-oxidative, wet non-oxidative, dry oxidative and wet oxidative conditions. Flowing gas through a dreschel bottle containing water created a wet atmosphere (1.6% absolute humidity) and silica gel created a dry atmosphere. The temperatures studied were 140, 160, 170 and 190 ^{o}C and the gas flow was regulated using a flow meter, supplying 50 mL min^{-1} to each sample chamber. After the drying temperature was programmed on the block heater, the system was left to equilibrate for 30 minutes prior to starting the experiment time of 24 hours. After completion, all samples were dried in a vacuum oven at 60 ^{o}C for a period of 24 hours to remove any surface water prior to analysis.

A combination of analysis techniques were employed in order to characterise and track the physical and chemical changes in the aged polyester samples. Changes in the physical morphology of the samples as a result of ageing, such as crystalline content/behaviour, were characterised primarily using the heat-cool-reheat DSC programme outlined in *Section 3.1.3.2*. The high temperature stability of all samples was assessed using TGA, the method of which is outlined in Section *3.2.3.1*. TGA analysis was performed under an inert atmosphere in order to determine if the different ageing conditions had significant impact on the overall thermal stability of the material. The molar mass of the aged polyester samples was also expected to vary under the action of thermal, thermo-oxidative and hydrolytic conditions. Therefore changes in the molar mass of the polyester samples were characterised using GPC, the method of which is outlined in *Section 3.4*.

6.3 Results and Discussion

6.3.1 Physical Observations of PET and PEN after Ageing

Prior to reporting DSC, TGA and GPC results, it is important to consider the physical appearance of the polymers after ageing. In addition to a significant decrease in molar mass and subsequent loss in mechanical, physical and chemical properties expected as a result of ageing, discolouration is also likely to be evident. Yellowing of polyesters is a severe problem in synthesis and melt processing and is thought to be a result of both thermal and thermo-oxidative degradation.[2,4,5,6,7,8] The transparency of both PET and PEN renders both polyesters suitable for the production of blow moulded bottles and packaging materials, however discolouration can adversely affect the end use of the final product, making it suitable only for materials where colour is not an issue.

All PET samples aged under dry nitrogen and dry air were found to be crystalline (i.e. white, opaque) with no hint of discolouration at any ageing temperature. Similarly, PET samples aged under wet nitrogen and wet air were also found to be crystalline, however discolouration was evident in PET samples aged at 190 ^{o}C. Initially, on observation of the aged PEN samples, it was evident that all samples were not fully crystalline, in contrast to PET. Under all environments at 140 ^{o}C, the PEN samples were found to be only partially crystalline (i.e. partly opaque). However, this is not entirely surprising as significant crystallisation of PEN does not occur until 180 ^{o}C, with the rate of maximum crystallisation occurring around 210 ^{o}C. With increased ageing temperature, under all environments, the PEN samples were found to anneal from transparent, amorphous polyester chips to white, crystalline polyester chips. No discolouration of PEN was evident under all environments at ageing temperatures of 140 ^{o}C and 160 ^{o}C. However, in contrast to PET, discolouration was evident in the PEN samples aged at 170 ^{o}C under all environments. Of all PET and PEN samples aged, the most significant discolouration was evident in PEN samples aged under all environments at 190 ^{o}C. This increased discolouration of PEN is in agreement with the studies completed by Botelho *et al.* [9] and Scheirs *et al.* [10] Both studies report that PEN discolours more rapidly than PET, suggesting that the discolouration is due to the formation of highly conjugated and highly absorbing naphthalene structures formed as a result of degradation.

In addition to the discolouration of aged PET and PEN samples, a loss in mechanical strength was apparent. All PET samples aged at 190 ^{o}C had reduced mechanical strength, in comparison to all other samples. These polyester chips became brittle after ageing and crumbled readily when pressure was exerted upon them. The most significant loss of mechanical strength was noted in PET samples aged under dry and wet air at 190 ^{o}C. Similar to PET, a loss in mechanical strength was evident in PEN. All PEN samples aged at 190 ^{o}C were found to have reduced mechanical strength, to the extent that the polyester chips became brittle and crumbled when pressure was exerted upon them. In contrast to PET, the PEN samples aged under wet air at 170 ^{o}C were also found to be very brittle, indicating a more significant loss in mechanical strength in PEN than in PET aged under identical conditions. Of all PET and PEN samples aged, the most significant loss in mechanical properties was evident in PEN samples aged under wet air at 190 ^{o}C.

6.3.2 Thermal Stability of PET and PEN after Ageing

The thermal stability of all aged polyester samples was assessed using TGA to determine if there were any changes in the polyesters significant enough to impact on their degradation profile. Changes in the overall thermal stability of PET and PEN will be observed if significant degradation of the polyester chains (e.g. hydrolytic chain scission at the ester linkages or oxidative cross-linking) has occurred during ageing.

Figures 6.2 - 6.5 illustrate the thermal stability of PET and PEN samples aged under all environments at temperatures of 140 °C and 190 °C. Due to such minor changes observed in the overall thermal stability of all aged samples of PET and PEN, the TGA curves are only shown for the samples aged at the lowest and highest temperatures. All other TGA curves can be found in *Chapter 8 Supplementary Material*. *Tables 6.1* and *6.2* present the temperatures of degradation from the TGA curves illustrated in *Figures 6.2 - 6.5.* Comparison of the TGA results reveals no significant differences in the mass loss behaviour and therefore overall thermal stability between the virgin and aged samples of PET and PEN.

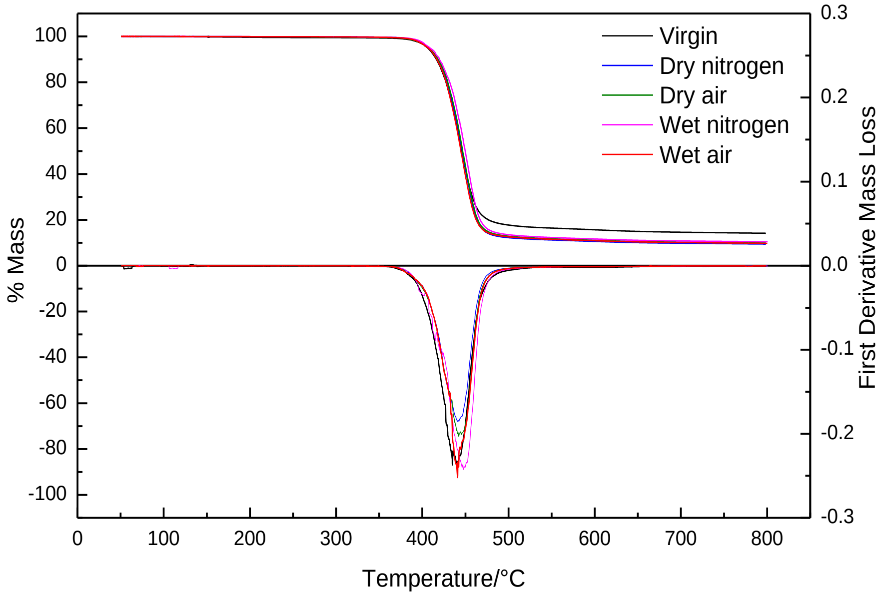

Figure 6.2 TG curves of PET samples aged under different environments at 140°C

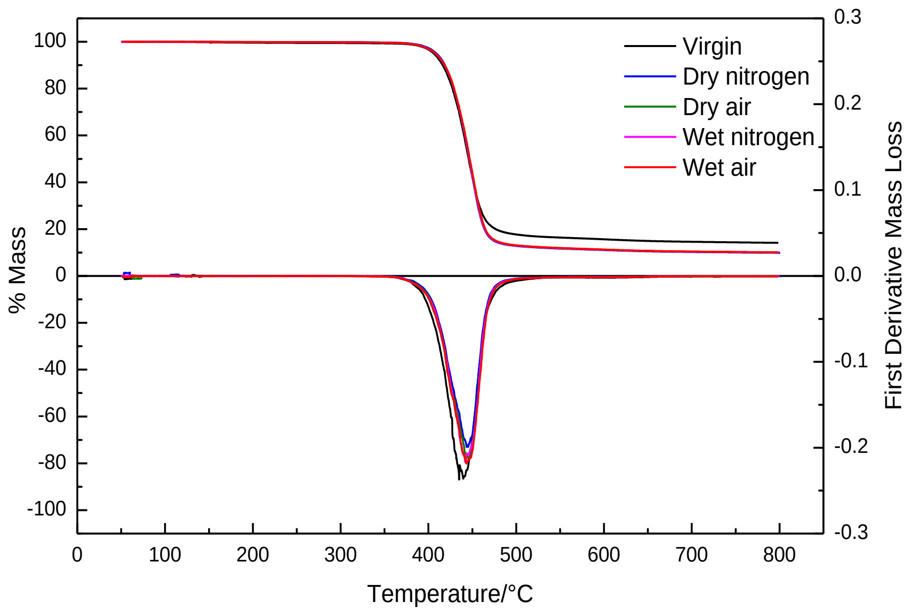

Figure 6.3 TG curves of PET samples aged under different environments at 190°C

Ageing environment	*Ageing temperature/°C*	*Onset of degradation/°C*	*Temperature of maximum mass loss/°C*	*Mass remaining at 800 °C/%*
Virgin	N/A	406	440	14
Dry nitrogen	140	406	441	10
Dry nitrogen	190	409	444	10
Dry air	140	407	446	9
Dry air	190	408	446	10
Wet nitrogen	140	409	448	10
Wet nitrogen	190	408	442	10
Wet air	140	408	441	10
Wet air	190	408	444	10

Table 6.1 Degradation temperatures from TG curves of PET samples aged at 140 °C and 190 °C

All samples of PET appear to undergo only one significant mass loss step, starting around 406 °C, due to thermal degradation of the polyester backbone i.e. chain scission at the ester bonds. Small differences are evident in the % mass of PET remaining after degradation. All PET samples aged under dry and wet, inert and oxidative environments have a marginally lower % residual mass after degradation, in comparison to the virgin material. This suggests that the extent of chain scission prior to analysis is more significant in aged PET than virgin PET. Shorter polymer chains, formed as a result of chain scission degradation reactions during ageing, will volatilise faster, resulting in a lower overall % mass of polyester remaining. However, despite these differences in residual mass, the extent of degradation in all aged PET samples is not sufficient enough to change the overall thermal stability of the material. Therefore, regardless of changes in the overall physical appearance and mechanical strength of aged PET samples, in comparison to virgin PET, the overall thermal stability of the materials remains unchanged.

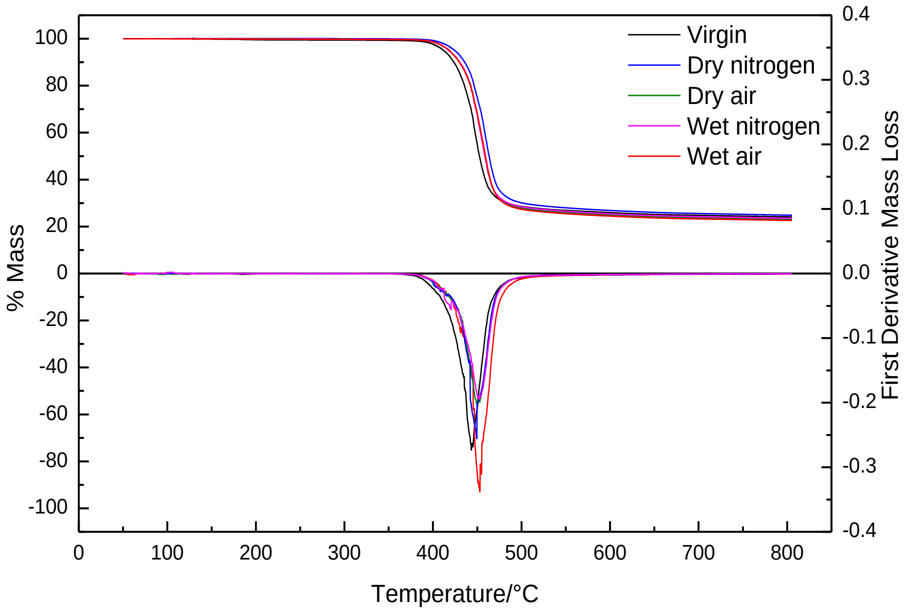

Figure 6.4 TG curves of PEN samples aged under different environments at 140^{o}C

From *Figures 6.4* and *6.5*, it can be observed that aged samples of PEN also appear to undergo only one significant mass loss step, starting above 412 ^{o}C. This is identical to PET and is again due to thermal degradation of the polymer backbone i.e. chain scission at the ester bonds. It is also apparent that no distinct differences exist between the thermal stability of PEN samples aged under different environments between temperatures of 140 °C and 190 °C. However, the onset temperatures of degradation and temperatures of maximum mass loss are marginally higher for virgin and aged samples of PEN, in comparison to PET. This is thought to be a result of the enhanced delocalisation of charge across the naphthalene ring units in PEN, increasing the stability of the ester linkages. Interestingly, no significant differences are evident in the % mass of original polymer remaining after the degradation of aged PEN samples, in comparison to virgin PEN. Degradation of PEN is therefore thought to be minimal under the ageing conditions studied.

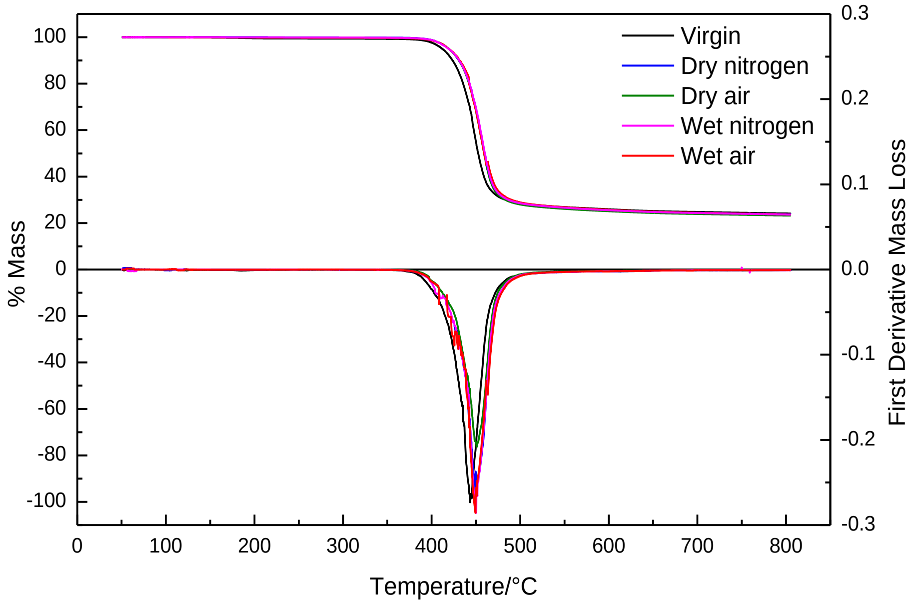

Figure 6.5 TG curves of PEN samples aged under different environments at 190^{o}C

Ageing environment	***Ageing temperature/^{o}C***	***Onset of degradation/^{o}C***	***Temperature of maximum mass loss/^{o}C***	***Mass remaining at 800^{o}C/%***
Virgin	N/A	412	443	24
Dry nitrogen	140	423	451	25
Dry nitrogen	190	418	449	24
Dry air	140	417	448	23
Dry air	190	418	450	23
Wet nitrogen	140	415	447	24
Wet nitrogen	190	417	447	24
Wet air	140	418	451	23
Wet air	190	417	450	24

Table 6.2 Degradation temperatures from TG curves of PEN samples aged at 140 ^{o}C and 190 ^{o}C

6.3.3 Changes in Molar Mass of PET and PEN after Ageing

Despite insignificant changes in the overall thermal stability of aged samples of PET and PEN, the molar mass is thought to vary under the action of thermal, thermo-oxidative and hydrolytic conditions. Therefore changes in the molar mass of virgin and aged samples of PET and PEN were characterised using GPC.

Table 6.3 presents the number average molar masses (M_n), weight average molar masses (M_w) and polydispersity values determined for all aged samples of PET by GPC. Comparison of the GPC data presented indicates that thermal degradation of PET is minimal up to ageing temperatures of 190 °C under dry nitrogen. A small decrease in M_w and M_n is noted only at 190 °C under dry air indicating that the presence of oxygen is promoting the degradation of PET at the highest ageing temperature. Oxidative degradation of PET is initiated by heat and oxygen leading to the formation of hydroperoxides at methylene sites within the polymer chains. [11] These hydroperoxides are unstable and therefore undergo a series of chain scission degradation reactions. Degradation is further accelerated when ageing is performed under moist thermal conditions, with a decrease in molar mass noticeable from 140 °C in wet nitrogen. This indicates that although significant degradation of PET does not occur under the influence of purely thermal conditions (i.e. dry nitrogen), the presence of water induces degradation of PET at lower ageing temperatures.

Ageing environment	*Ageing temperature/^{o}C*	*M_w/g mol^{-1}*	*M_n/g mol^{-1}*	*Polydispersity*
Virgin	N/A	24900 ± 141	8725 ± 64	2.9
Dry nitrogen	140	24350 ± 71	8480 ± 57	2.9
Dry nitrogen	160	24200	8600 ± 57	2.8
Dry nitrogen	170	24650 ± 212	8660 ± 99	2.8
Dry nitrogen	190	24950 ± 71	8865 ± 78	2.8
Dry air	140	23800 ± 141	9120 ± 14	2.6
Dry air	160	24150 ± 212	9030 ± 71	2.7
Dry air	170	24550 ± 71	8830	2.8
Dry air	190	21300	7610 ± 14	2.8
Wet nitrogen	140	22950 ± 212	8310 ± 14	2.8
Wet nitrogen	160	22650 ± 354	8145 ± 21	2.8
Wet nitrogen	170	21600	8050 ± 42	2.7
Wet nitrogen	190	19350 ± 71	8000 ± 113	2.4
Wet air	140	23250 ± 212	8520 ± 14	2.7
Wet air	160	21100	7745 ± 50	2.7
Wet air	170	18800 ± 141	7025 ± 149	2.7
Wet air	190	16800 ± 141	6510 ± 156	2.6

Table 6.3 GPC average molar mass results for PET samples aged under different environments at temperatures between 140 - 190^{o}C

Hydrolytic degradation of PET is reported to involve chain scission at the ester linkages. Each water molecule breaks down one ester bond, leading to the formation of one carboxyl and one hydroxyl group. During hydrolytic ageing of PET, it is believed that water diffuses into the amorphous regions of the polymer where hydrolysis occurs at a rate dependant on the sample shape, morphology and crystallinity, in addition to the temperature and relative humidity of the surrounding environment. [7,8,12,13,14,15] At temperatures below the glass transition temperature of PET, hydrolytic degradation is thought to be negligible. However, above the glass transition temperature, increased mobility of the polymer chains enables penetration of water into the amorphous regions, increasing the rate of hydrolytic degradation. Therefore as the ageing temperature increases from 140 ^{o}C to 190 ^{o}C under thermal-hydrolytic conditions, more extensive degradation occurs with the most significant decrease in molar mass observed at 190 °C. Similarly, the presence of water during the thermo-oxidative ageing of PET has significant impact on the molar mass distribution of PET. Samples aged under thermo-oxidative-hydrolytic conditions, at temperatures between 140 °C and 190 °C, all exhibit a pronounced decrease in the average molar mass with increased ageing temperature. A small decrease in the average molar mass values can be observed for PET samples aged under thermo-oxidative-hydrolytic conditions (i.e. wet air) at 140 °C. The extent of this degradation is only marginally higher than that observed for degradation of PET under purely thermo-oxidative conditions (i.e. dry air) at 140 °C. However, as the ageing temperature increases, the extent of degradation increases and a sharp decrease in the average molar mass can be observed for PET samples aged at 160, 170 and 190 °C. All GPC curves for PET samples aged under all ageing environments can be found in *Figure 6.6.*

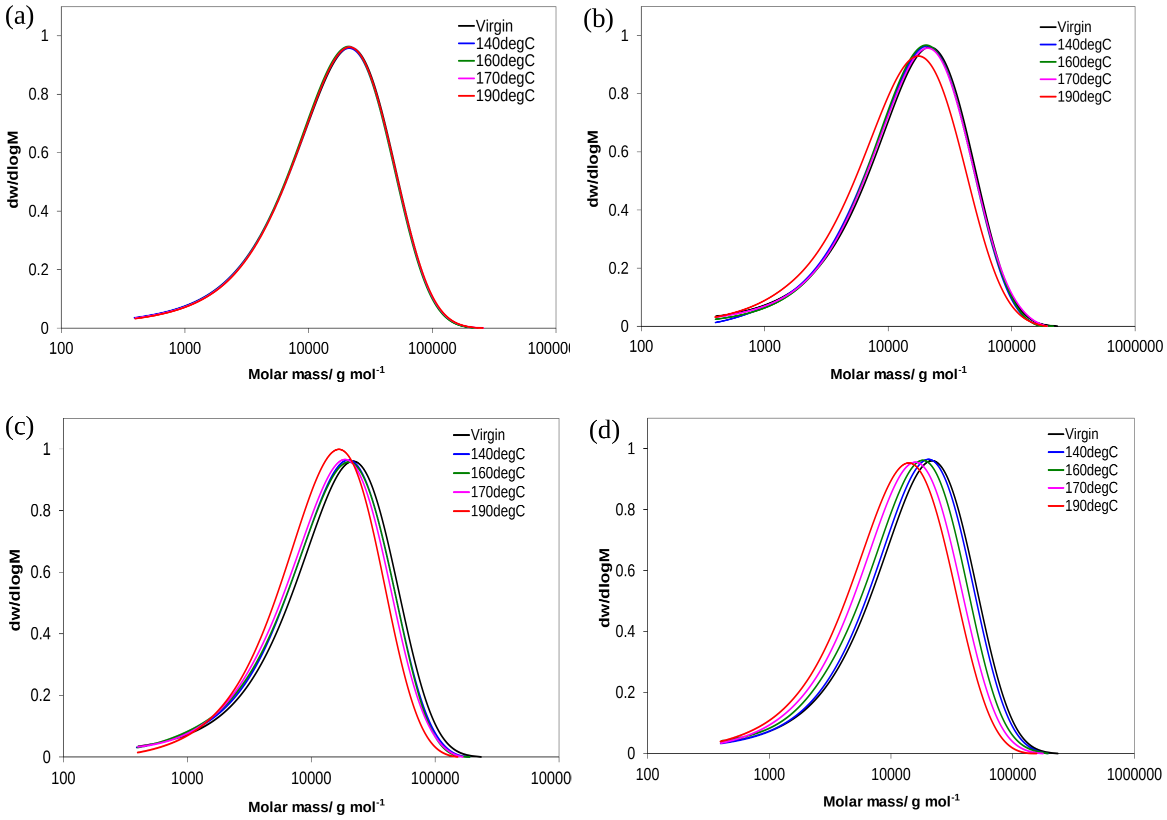

Figure 6.6 GPC molar mass distribution of PET aged under (a) dry nitrogen (b) dry air (c) wet nitrogen and (d) wet air

The GPC results therefore demonstrate that the dominant degradation reaction in PET differs with ageing temperature. At the lowest ageing temperature of 140 ^oC, no significant changes in M_w are evident with contrasting ageing conditions and therefore it is impossible to deduce which degradation process is dominant. In contrast, the GPC results for PET indicate that hydrolytic degradation is the dominant degradation reaction occurring between 160 ^oC and 170 ^oC. From *Table 6.3*, it can be seen that degradation of PET is minimal under purely thermal and thermo-oxidative ageing conditions, indicating that even the presence of air is not enough to result in significant degradation of PET at 160 ^oC and 170 ^oC. However, significant changes in M_w can be observed in both PET samples aged under thermal-hydrolytic and thermo-oxidative-hydrolytic conditions indicating that hydrolytic degradation is likely to be the dominant degradation reaction occurring at 160 ^oC and 170 ^oC. Obviously, the decrease in molar mass is larger in PET samples aged at 170 ^oC than 160 ^oC indicating that progressively more hydrolytic degradation is occurring at 170 ^oC due to increased mobility of the polymer chains.

GPC results for PET aged under contrasting environments at 190 ^oC illustrate that changes in M_w are not only influenced by the presence of water, but also oxygen. No significant changes in M_w can be observed under thermal conditions, indicating once again that thermal degradation of PET is minimal at temperatures up to 190 ^oC. However, a large decrease in the molar mass of the aged system can be seen on the introduction of oxygen (i.e. dry air) at 190 ^oC highlighting that the presence of oxygen, during ageing at increased temperatures, promotes the degradation of PET. The most significant decrease in M_w can be observed in PET samples aged under thermo-oxidative-hydrolytic conditions at 190 ^oC. Therefore, as the temperature is increased, it is thought that oxidative degradation begins to compete with hydrolytic degradation as the dominant degradation process, resulting in the largest changes in the molar mass of aged PET samples. The dominant degradation reaction in PET has therefore been shown to differ with ageing temperature. At lower temperatures i.e. 140 - 170 ^oC, it has been illustrated that hydrolysis is the dominant degradation reaction, with thermo-oxidative degradation competing with hydrolytic degradation as the temperature is increased to 190 ^oC.

Difficulties were experienced during the analysis of aged PEN samples by GPC due to the crystallinity that developed upon ageing - this was sufficient enough to render the polymer insoluble. As a consequence, all aged samples of PEN had to be rendered amorphous before dissolution was possible. This was performed simply by melting the samples at 320 ^{o}C in a DSC and quenching to the amorphous state. Whilst this involved imposing a new thermal history on all samples, it was hoped that the fact that all aged samples of PEN had the same thermal history superimposed, would still enable comparative use of the GPC data thus obtained.

Table 6.4 presents the M_n, M_w and polydispersity values determined by GPC for PEN samples aged under different environments at 190 °C. The molar mass distribution curves for PEN can be found in *Figure 6.7*. Due to such minor changes observed in the overall molar mass distribution of PEN samples aged under the harshest conditions i.e. 190 ^{o}C, it was deemed unnecessary to analyse all other PEN samples by GPC. Comparison of the GPC data obtained for aged PEN samples reveals no significant changes in the overall molar mass of the aged PEN samples, in comparison to virgin PEN. Degradation of PEN, under all ageing conditions, is therefore minimal up to temperatures of 190 ^{o}C. However, one question remains unanswered - why do the aged samples of PEN embrittle badly if the material has not degraded (i.e. no decrease in molar mass observed)?

Ageing environment	***Ageing temperature/^{o}C***	***M_w/g mol^{-1}***	***M_n/g mol^{-1}***	***Polydispersity***
Virgin	N/A	20200 ± 71	5455 ± 233	3.7
Dry nitrogen	190	20700 ± 283	5505 ± 276	3.8
Dry air	190	22950 ± 71	6490 ± 71	3.5
Wet nitrogen	190	19700 ± 141	4780 ± 0	4.1
Wet air	190	19650 ± 71	4760 ± 57	4.1

Table 6.4 GPC average molar mass results for PEN samples aged under different environments at 190^{o}C

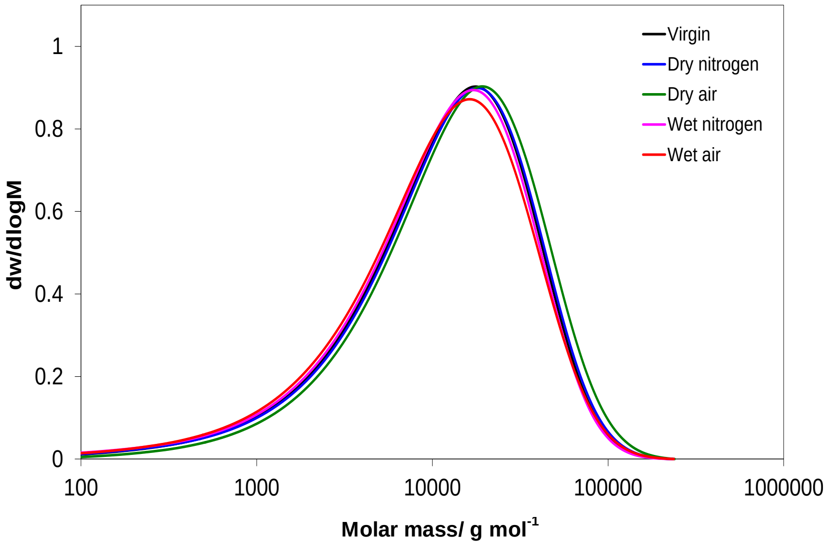

Figure 6.7 GPC molar mass distribution of PEN samples aged at 190 °C

6.3.4 Changes in Physical Morphology after Ageing

Although distinct trends were evident in the molar mass distribution curves for aged PET, the overall thermal stability of the aged PET/PEN samples assessed by TGA, was unchanged relative to the unaged samples. It was therefore of interest to determine if any significant changes in the physical morphology of PET and PEN could be observed as a result of ageing. Crystalline content and behaviour was monitored in all samples using DSC.

6.3.4.1 Initial DSC Heating Cycle (Cycle 1)

The initial DSC heating cycle was performed in order to destroy the thermal history of the samples prior to studying permanent morphological changes. However, it can also provide information on the extent of crystallinity in samples, formed as a result of ageing.

Figure 6.8 represents the initial DSC heating cycle obtained for PET samples aged under dry nitrogen between temperatures of 140 °C and 190 °C, in comparison to virgin PET. *Table 6.5* presents the temperatures of the DSC thermal transitions in all PET samples including the onset temperature of the crystalline melt (T_{onset}), the maximum temperature of the crystalline melt (T_{max}) and the enthalpy of the crystalline melt.

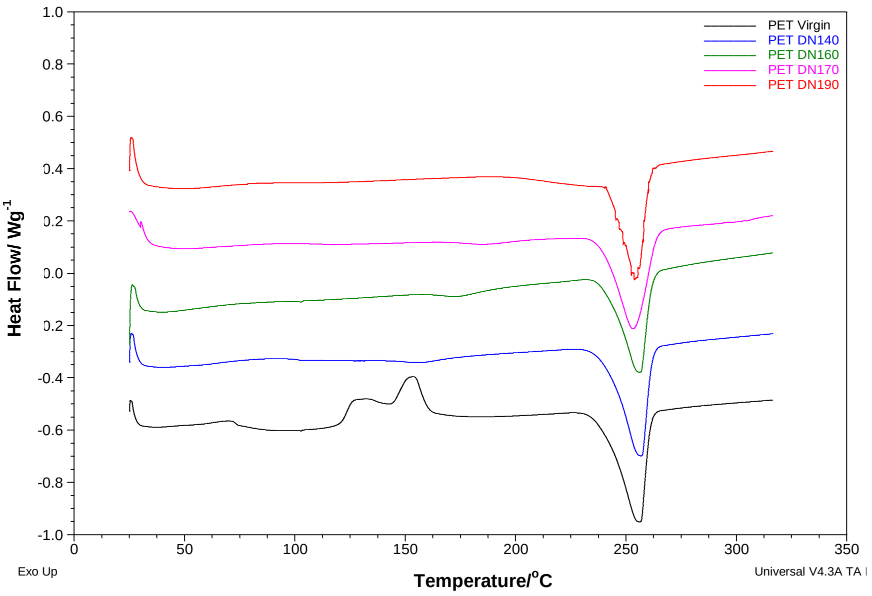

Figure 6.8 DSC curves of PET samples aged under dry nitrogen at temperature between 140 °C and 190 °C, cycle 1

From *Figure 6.8*, it can be observed that virgin PET exhibits a cold crystallisation peak around 150 °C, which is absent in the aged samples, indicating, as would be expected, that the virgin material had crystallised during the ageing process. Small, so-called, annealing peaks are evident some 10 - 20 °C above the ageing temperature in all aged samples of PET in addition to one crystalline melt peak. The T_{onset}, T_{max} and enthalpy of the crystalline melt peak were not found to differ significantly between samples of PET aged at 140, 160 and 170 °C under dry nitrogen, in comparison to unaged PET. An increase in the enthalpy of the crystalline melt can be observed for PET aged at 190 °C, however this is due to the annealing peak merging with the crystalline melt peak. The impact of thermo-oxidative, thermal-hydrolytic and thermo-oxidative-hydrolytic ageing on the crystalline content/behaviour of PET was found to be very similar to the results illustrated in *Figure 6.8* for thermal ageing and can therefore be found in *Chapter 8 Supplementary Material*.

Ageing environment	***Ageing temperature/°C***	***Enthalpy of crystalline melt/J g^{-1}***	***T_{onset} crystalline melt/°C***	***T_{max} crystalline melt/°C***
Virgin	N/A	35	241	256
Dry nitrogen	140	34	242	257
Dry nitrogen	160	30	242	256
Dry nitrogen	170	33	241	256
Dry nitrogen	190	42	244	254
Dry air	140	33	240	255
Dry air	160	36	241	255
Dry air	170	36	241	255
Dry air	190	43	240	255
Wet nitrogen	140	37	242	255
Wet nitrogen	160	38	241	255
Wet nitrogen	170	32	241	256
Wet nitrogen	190	41	244	258
Wet air	140	37	242	256
Wet air	160	36	241	256
Wet air	170	36	242	256
Wet air	190	34	242	256

Table 6.5 DSC thermal transitions in PET samples aged under different environments at temperatures between 140 °C and 190 °C, cycle 1

The impact of thermal, thermo-oxidative, thermal-hydrolytic and thermo-oxidative-hydrolytic ageing on the crystalline content/behaviour of PEN samples was also found to be similar in all samples. Therefore only one example has been illustrated. *Figure 6.9* represents the DSC curves obtained for PEN samples aged under dry nitrogen between temperatures of 140 °C and 190 °C, in comparison to unaged PEN.

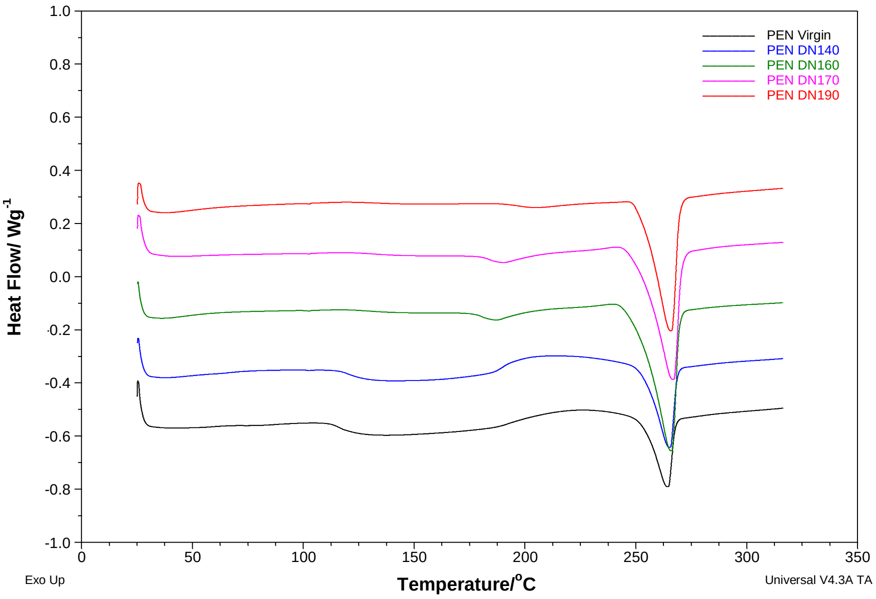

Figure 6.9 DSC curves of PEN samples aged under dry nitrogen at temperature between 140 ^{o}C and 190 ^{o}C, cycle 1

From *Figure 6.9*, a glass transition can be observed at 117 ^{o}C for unaged PEN and PEN aged at 140 °C, however as the glass transition phenomenon is purely an amorphous event, no glass transition temperatures can be observed in any PEN samples aged above 140 °C due to the increased levels of crystallinity formed during ageing. Similarly, due to the increased levels of crystallinity in PEN samples aged above 140 °C, no cold crystallisation event is evident on heating and small annealing peaks become visible, identical to those observed in PET. *Table 6.6* presents the temperatures of the DSC thermal transitions in all PEN samples including the T_{onset}, T_{max} and enthalpy of the crystalline melt. All DSC heating curves for PEN samples aged under dry air, wet nitrogen and wet air can be found in *Chapter 8 Supplementary Material*.

Ageing environment	***Ageing temperature/°C***	***Enthalpy of crystalline melt/J g^{-1}***	***T_{onset} crystalline melt/°C***	***T_{max} crystalline melt/°C***
Virgin	N/A	17	253	264
Dry nitrogen	140	18	254	265
Dry nitrogen	160	39	252	266
Dry nitrogen	170	36	252	267
Dry nitrogen	190	32	253	266
Dry air	140	37	252	265
Dry air	160	38	253	266
Dry air	170	38	252	265
Dry air	190	41	253	265
Wet nitrogen	140	35	253	267
Wet nitrogen	160	37	253	267
Wet nitrogen	170	37	252	265
Wet nitrogen	190	32	255	267
Wet air	140	39	252	266
Wet air	160	38	252	266
Wet air	170	34	253	267
Wet air	190	41	256	266

Table 6.6 DSC thermal transitions in PEN samples aged under different environments at temperatures between 140 °C and 190 °C, cycle 1

6.3.4.2 DSC Cooling Cycle (Cycle 2)

The DSC cooling cycle provides useful information on the crystallisation behaviour of the polyesters. *Table 6.7* presents the temperatures of the DSC transitions in all samples of PET including the T_{onset}, T_{max} and the enthalpy of crystallisation and *Figure 6.10* summarises the DSC cooling curves. As can be seen, the PET samples aged in dry nitrogen are little different from virgin PET. A small increase in the enthalpy of crystallisation can be observed for samples aged above 160 °C, however the T_{onset} and T_{max} values for crystallisation do not differ significantly. Interestingly, on observation of the DSC cooling cycles of PET samples aged under thermo-oxidative conditions (i.e. dry air), more significant variations in the crystalline behaviour were identified. A distinct trend exists between the ageing temperature and extent of crystallisation for PET samples aged above 140 ^{o}C. On increasing the ageing temperature above 140 ^{o}C, an increase in the enthalpy of crystallisation is evident, indicating that samples aged above 140 ^{o}C undergo crystallisation at an increased rate in comparison to samples aged at 140 ^{o}C and unaged PET. The onset temperature and temperature of maximum crystallisation are highest for PET aged at 190 ^{o}C, indicating that crystallisation is occurring most readily in this sample as it is cooled. Such differences in the enthalpy of crystallisation and thus rate of crystallisation are thought to be due to increased mobility of the polymer chains as a result of degradation. On increasing the ageing temperature above 140 ^{o}C, the extent of chain scission in amorphous regions progressively increases and thus results in formation of shorter chain fragments and free chain ends with increased conformational freedom. Subsequently, chain segments that were previously entangled can now readily crystallise, resulting in rapid crystallisation and thus an increase in the overall enthalpy of crystallisation. These results are in agreement with the decrease in molar mass observed from GPC as a result of thermo-oxidative degradation.

Under hydrolytic ageing conditions, degradation is also thought to occur rapidly, particularly at lower ageing temperatures. Therefore, it is expected that similar variations in the crystalline behaviour will be observed from PET samples aged under a hydrolytic environment. On interpretation of the DSC cooling data, a clear trend exists once again between the extent of crystallisation and ageing temperature of PET samples aged under hydrolytic conditions. On increasing the ageing temperature, an increase in the enthalpy of crystallisation is evident, indicating that crystallisation occurs at an increased rate, in comparison to unaged PET. The onset temperature and temperature maximum for crystallisation are highest for PET aged under moist thermo-oxidative conditions at 190 ^{o}C, indicating that crystallisation is occurring most readily in this sample (i.e. the lowest molar mass sample) as it is cooled.

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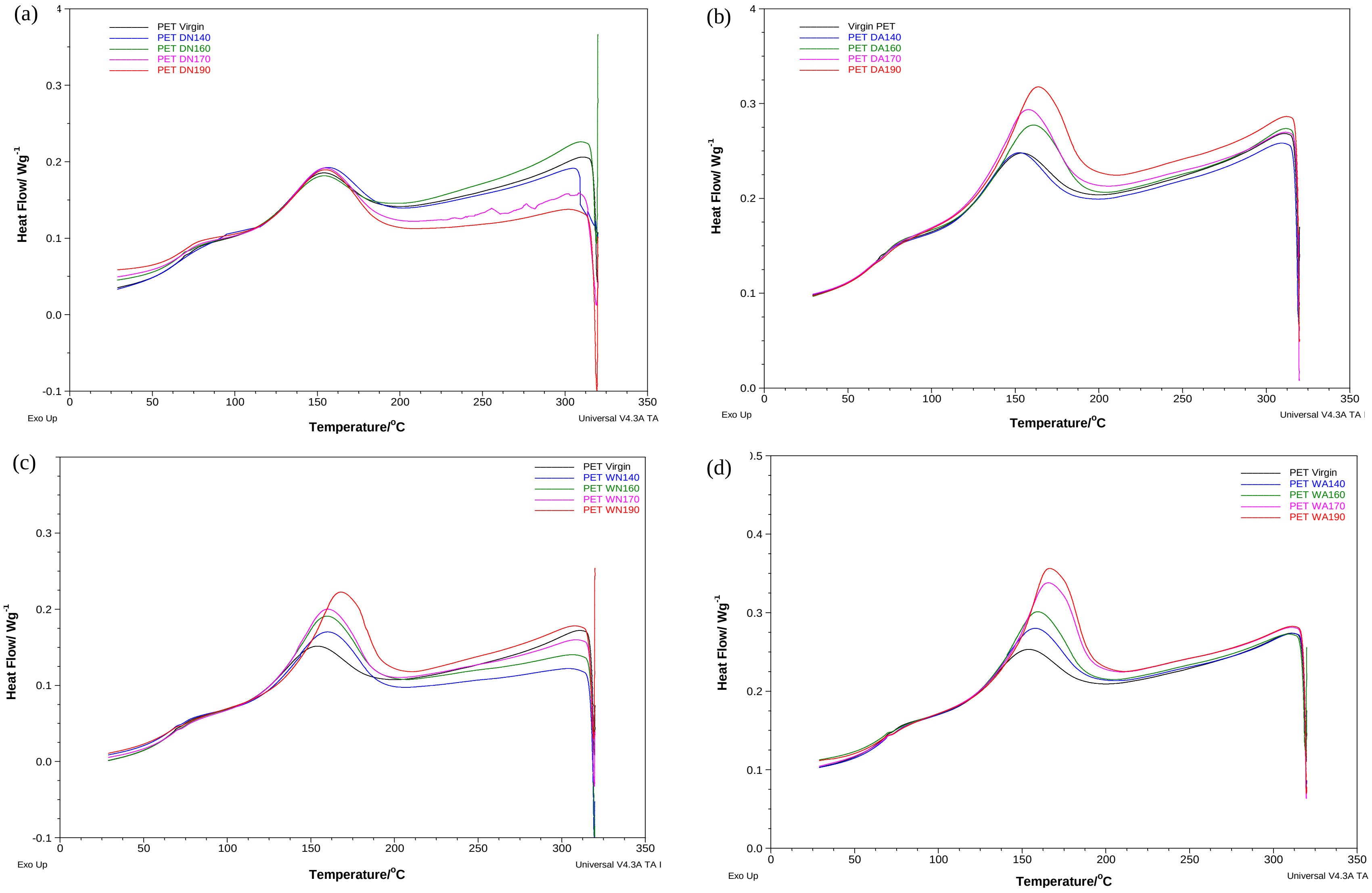

Figure 6.10 DSC of PET samples aged under (a) dry nitrogen (b) dry air (c) wet nitrogen and (d) wet air, cycle 2

Ageing environment	*Ageing temperature/^oC*	*Enthalpy of crystallisation/J g^{-1}*	*T_{onset} crystallisation/^oC*	*T_{max} crystallisation/^oC*
Virgin	N/A	16	186	152
Dry nitrogen	140	16	189	155
Dry nitrogen	160	15	186	152
Dry nitrogen	170	21	188	154
Dry nitrogen	190	22	188	155
Dry air	140	16	183	151
Dry air	160	22	190	159
Dry air	170	25	188	157
Dry air	190	29	192	163
Wet nitrogen	140	22	191	159
Wet nitrogen	160	26	191	159
Wet nitrogen	170	27	189	159
Wet nitrogen	190	29	191	167
Wet air	140	22	189	156
Wet air	160	33	192	165
Wet air	170	35	193	166
Wet air	190	36	193	168

Table 6.7 DSC thermal transitions in PET samples aged under different environments at temperatures between 140 ^oC and 190 ^oC, cycle 2

Therefore, this physical data illustrates that purely thermal degradation of PET is minimal up to temperatures of 190 ^oC. In the presence of oxygen, however, significant changes in the enthalpy of crystallisation were observed at ageing temperatures around 170 - 190 ^oC, indicating that the presence of oxygen does significantly influence the degradation of PET at the highest ageing temperatures. This provides further evidence that the dominant degradation reaction at the highest ageing temperatures is thermo-oxidative degradation as previously suggested. Ageing of PET under hydrolytic conditions was found to have the most significant impact on the overall enthalpy of crystallisation of PET at the lower ageing temperatures, indicating that hydrolysis is the dominant degradation reaction between 140 - 160 ^oC.

Degradation of PET was found to be most significant under combined thermo-oxidative-hydrolytic ageing conditions due to competing hydrolytic and oxidative degradation reactions within the polyester chains. These DSC results are thus in very good agreement with the GPC results reported previously.

In contrast to the results reported for aged samples of PET, no distinct changes in the crystallisation behaviour of PEN could be identified from the DSC cooling curves. All cooling curves were found to be identical, to the example illustrated in *Figure 6.11*, for all PEN samples aged under different environments.

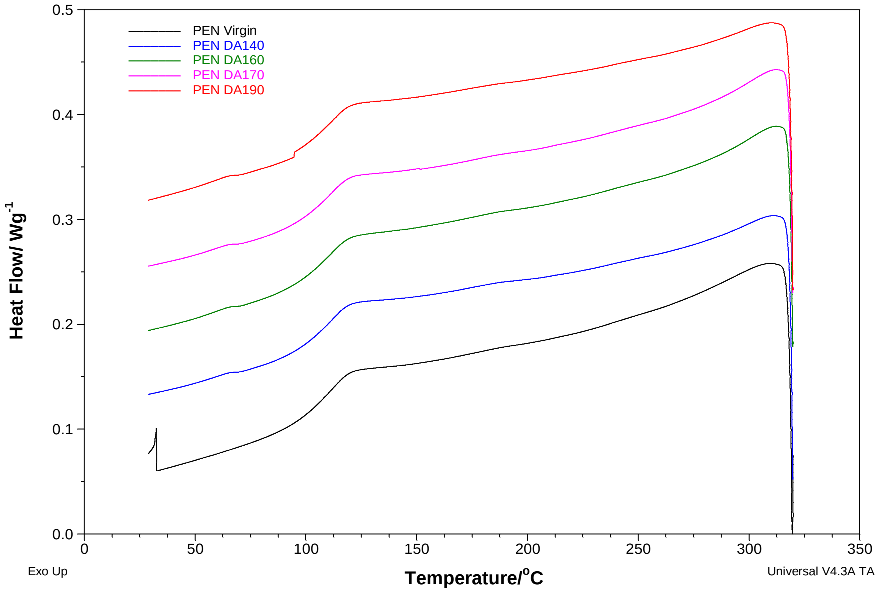

Figure 6.11 DSC thermal transitions in PEN samples aged under dry air, cycle 2

Aged samples of PEN did not undergo crystallisation on cooling, in contrast to the results reported previously for PET. Only a broad glass transition was observed in all PEN samples above 100 ^{o}C. Due to the presence of bulky naphthalene groups in PEN, the ease at which PEN can arrange its polymer chains into regular domains is reduced, in comparison to PET. Additionally, the non-linear 2,6-substitution pattern of aromatic rings in PEN, compared to a 1,4 linear substitution of the phenyl group in PET, reduces its tendency to crystallise. Therefore no crystallisation activity was observed from the DSC cooling curves of any aged samples of PEN. All DSC cooling curves and data for PEN samples aged under thermal, thermo-oxidative, thermal-hydrolytic and thermo-oxidative-hydrolytic environments can be found in *Chapter 8 Supplementary Material*.

6.3.4.3 DSC Second Heating Cycle (Cycle 3)

Any permanent changes in morphology, as a result of ageing, can be observed in the second DSC heating cycle. *Tables 6.8* and 6.*9* present the temperatures of the DSC thermal transitions in all aged samples of PET and PEN, respectively. *Figures 6.12* and *6.13* illustrate the DSC reheat curves collected for PET and PEN samples aged under dry nitrogen. All other curves for samples aged under dry air, wet nitrogen and wet air can be found in *Chapter 8 Supplementary Material*.

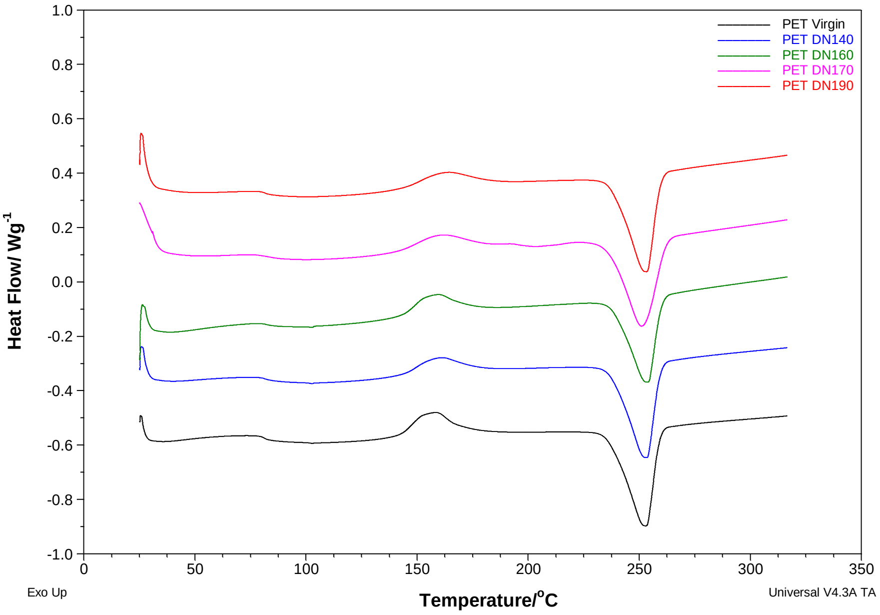

Figure 6.12 DSC of PET samples aged at temperatures between 140 – 190 °C under dry nitrogen, cycle 3

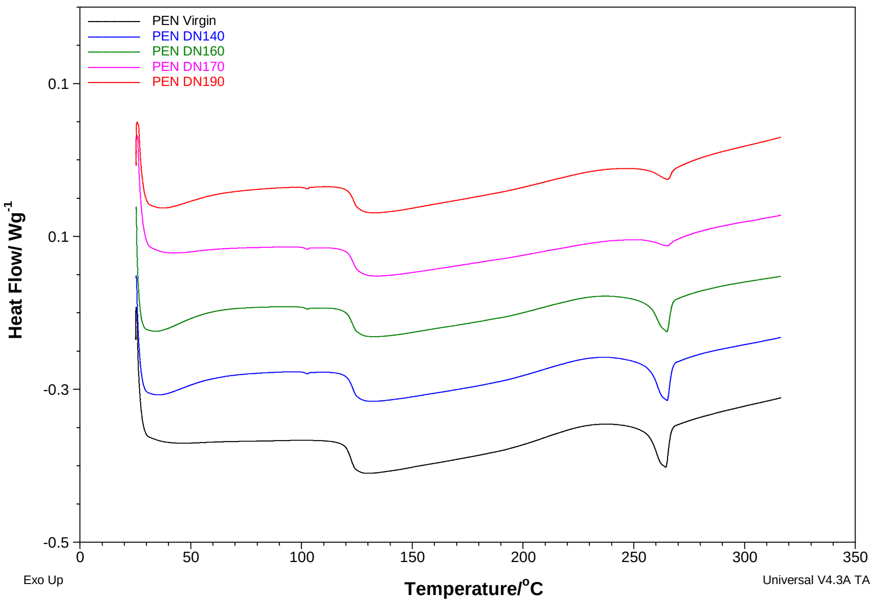

Figure 6.13 DSC of PEN samples aged at temperatures between 140 – 190 ^{o}C under dry nitrogen, cycle 3

The glass transition and cold crystallisation processes remain unaltered between samples of PET aged under dry nitrogen and unaged PET. However, trends for PET samples aged under dry air are evident, where the amount of cold crystallisation upon reheating decreases for samples aged under the most extreme conditions, as a simple consequence of the increased crystallisation activity during cooling. Generally, the melting process was found to be relatively constant between all aged samples of PET suggesting that no gross morphological changes occurred as a result of ageing. Similarly, the glass transition temperature of PEN remains unaltered with ageing and the crystallisation events all remain similar between aged and unaged samples of PEN. The enthalpy and maximum temperature for cold crystallisation of PEN are all difficult to determine due to low levels of crystallinity in all samples.

Ageing environment	***Ageing temperature /°C***	***T_g/°C***	***Enthalpy of crystallisation/ J g^{-1}***	***T_{onset} crystallisation/°C***	***T_{max} crystallisation/°C***	***Enthalpy of crystalline melt/J g^{-1}***	***T_{onset} crystalline melt/°C***	***T_{max} crystalline melt/°C***
Virgin	N/A	81	12	142	158	30	237	253
Dry nitrogen	140	81	8	143	160	29	238	253
Dry nitrogen	160	82	9	143	158	26	238	254
Dry nitrogen	170	82	9	140	161	32	236	251
Dry nitrogen	190	82	8	142	163	29	238	253
Dry air	140	82	10	142	158	29	237	253
Dry air	160	81	8	142	159	32	237	252
Dry air	170	81	7	141	157	33	238	253
Dry air	190	81	5	140	158	34	238	253
Wet nitrogen	140	81	9	141	160	32	237	253
Wet nitrogen	160	81	7	139	159	36	237	253
Wet nitrogen	170	82	5	138	160	32	238	253
Wet nitrogen	190	83	1	142	158	29	241	255
Wet air	140	81	8	141	159	32	238	253
Wet air	160	81	3	139	157	34	239	254
Wet air	170	82	2	137	155	35	239	254
Wet air	190	83	1	134	153	34	240	254

Table 6.8 DSC thermal transitions in PET samples aged under different environments at temperatures between 140 °C and 190 °C, cycle 3

Ageing environment	*Ageing temperature/^oC*	*$T_g/^oC$*	*Enthalpy of crystalline melt/J g^{-1}*	*T_{onset} crystalline melt/^oC*	*T_{max} crystalline melt/^oC*
Virgin	N/A	122	3	255	264
Dry nitrogen	140	123	3	256	265
Dry nitrogen	160	122	3	256	265
Dry nitrogen	170	123	1	256	265
Dry nitrogen	190	123	1	256	265
Dry air	140	122	5	256	264
Dry air	160	123	3	256	265
Dry air	170	123	3	256	265
Dry air	190	123	2	254	265
Wet nitrogen	140	124	3	257	266
Wet nitrogen	160	123	3	256	265
Wet nitrogen	170	123	3	256	265
Wet nitrogen	190	123	1	257	265
Wet air	140	123	5	256	265
Wet air	160	123	4	257	265
Wet air	170	124	3	257	266
Wet air	190	123	3	256	265

Table 6.9 DSC thermal transitions in PEN samples aged under different environments at temperatures between 140 ^oC and 190 ^oC, cycle 3

6.3.5 Relationship between Mechanical Properties and Ageing Conditions

From the ageing studies, completed on PET and PEN, the extent of degradation has been shown to differ between both polymers. Degradation of PET was largely influenced by the ageing environment and temperature. Although the overall thermal stability of PET remained unchanged after ageing, variations in the molar mass and crystalline content/behaviour were observed in aged PET samples, in addition to a loss in mechanical strength. The dominant degradation mechanism in PET was shown to differ with the ageing temperature. At lower ageing temperatures i.e. 140 - 170 ^{o}C, hydrolysis was revealed as the dominant degradation reaction, with thermo-oxidative degradation competing with hydrolytic degradation as the ageing temperature was increased to 190 ^{o}C.

In contrast to PET, all ageing environments and temperatures were found to have no detrimental effect on the overall thermal stability, molar mass or crystallisation content/behaviour of PEN. It is thought that this could be due to either one or a combination of the following factors: (1) Reduced chain mobility due to the significantly increased glass transition of PEN (122 ^{o}C) in comparison to PET (80 ^{o}C) (2) Increased crystallinity of PEN, in comparison to PET. This could contribute to the lack of chain scission reactions and thus overall extent of degradation as crystallites are impermeable to water and can act as barriers to oxygen and water (3) Hydrophobicity effects – the lack of degradation observed could simply be a result of increased hydrophobicity effects in PEN, in comparison to PET. The overall mass fraction of non-polar, aromatic sequences in PEN is greatly increased, due to the presence of additional phenyl rings. This results in a material with increasing hydrophobic character. However, none of above factors provides an explanation as to why aged samples of PEN embrittle badly when no decrease in molar mass is observed. This leads us onto believe that the embrittlement of both PET and PEN upon ageing seems to have a physical rather than a chemical origin. Although at the most extreme ageing conditions for PET, a decrease in molar mass is observed, this is too small to account for the severe embrittlement. Instead, we propose that the change in mechanical properties, in both PET and PEN, is due to crystallisation upon ageing, and secondary crystallisation in particular. Separate experiments not included here, illustrate that the primary crystallisation process of PET and PEN is complete within 25 minutes and 60 minutes, respectively, at 140 ^{o}C. Therefore, over the 24 hours of the ageing process, considerable secondary crystallisation can occur. Such crystallisation has been shown in the past to cause remarkable changes in mechanical properties. This is most notorious in the Biopol polyesters where secondary crystallisation upon room temperature storage embrittled mouldings and extrusions, even when plasticised, to the extent that it threatened the commercial development of the polymers. [16,17,18,19,20,21,22] The degree of secondary crystallisation, in the Biopol polyesters, was so small that it could not be readily detected by DSC, except through the presence of a low temperature so-called "annealing" melting peak as observed in the DSC curves of aged samples of PET and PEN.

6.4 Conclusions

The extent of degradation in PET and PEN has been examined after ageing under contrasting drying conditions, enabling the effects of temperature, water and oxygen to be mapped onto the resultant property changes. Degradation of PET was found to be largely influenced by the ageing environment and temperature and the dominant degradation mechanism was shown to differ with ageing temperature. In contrast to PET, the increased thermal and hydrolytic resistance of PEN has been illustrated with all ageing environments and temperatures having no detrimental effect on the overall thermal stability, molar mass or crystallisation content/behaviour of PEN. Embrittlement of both PET and PEN after ageing has been proposed to originate from secondary crystallisation developed upon ageing, causing remarkable changes to mechanical properties.

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7 FINAL CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER WORK

On examining the thermal, thermo-oxidative and hydrolytic degradation of PET and PEN throughout this thesis, it has been demonstrated that the degradation chemistry of both polyesters is not identical. A complex array of competing degradation reactions have been shown to occur in PET and PEN, particularly under thermo-oxidative conditions, yielding a variety of volatile degradation products and highly discoloured residual material. Although the impact of these degradation reactions is typically specific to the part of the film process where they occur, this research has presented an extensive variety of degradation studies, under a selection of processing environments and temperature regimes, to improve our fundamental understanding of the thermal, thermo-oxidative and hydrolytic degradation processes occurring in PEN, in comparison to PET. Information on the dominant degradation reactions occurring in PEN, in comparison to PET, is not only valuable to expand on the current literature knowledge, but will prove particularly useful for technical operators during film processing of PEN.

Although, degradation studies of PET and PEN under purely thermal conditions revealed differences in the onset temperatures and extent of degradation for PET and PEN, similar mechanisms of thermal degradation have been proposed to occur in both polyesters. From thermal analysis data presented, it has been demonstrated that PET and PEN only undergo one major thermal degradation process. This thermal degradation reaction is proposed to involve scission of the ester bonds in the polyester backbone resulting in the formation of vinyl ester and carboxylic acid end groups. This primary thermal degradation reaction is believed to be identical for both polymers; however it is still unclear whether this reaction proceeds via an ionic or radical mechanism.

Evolved gas analysis studies on the thermal degradation of PET up to temperatures of 550 ^{o}C revealed that degradation is likely to proceed via a radical based degradation mechanism. The action of homolytic bond scissions, occurring in the

PET backbone throughout the temperature region of 400 – 550 °C, not only accounts for the significant quantities of CO and CO_2 observed, but the variety of additional degradation products detected. CO and CO_2 are thought to continuously form by homolytic degradation reactions at the alkyl-oxygen or acyl-oxygen link respectively in PET. The resultant radicals then abstract hydrogen from elsewhere in the system or undergo disproportionation reactions with other radicals, formed as a result of homolytic scission, to result in a variety of products containing alkyl, acidic, aldehydic or vinyl groups at one or both ends of the PET chain. A mechanism for the thermal degradation of PET has been proposed to account for the generation of all degradation species and appears to correlate well with the TVA degradation mechanisms presented in the literature. [1]

Despite an observed increase in the overall thermal stability of PEN over its terephthalate counterpart, an essentially similar mechanism of thermal decomposition has been proposed from high temperature TVA studies of PEN. Identical homolytic chain scission reactions have been proposed for the thermal degradation of PEN, resulting in a similar range of degradation products observed in comparison to PET. Minor differences in the product distribution between volatile species of PET and PEN have been highlighted; however this is proposed to be a result of the distinct differences in volatility between benzene and naphthalene species.

In contrast with high temperature thermal degradation studies of PET and PEN, it has been demonstrated that ionic degradation reactions are dominant in both polyesters at processing temperatures due to the absence of significant quantities of CO and CO_2. CO and CO_2, formed as a result of homolytic chain scission reactions, were found to be absent in low temperature degradation studies of PEN, with only small traces detected in PET at temperatures of 300 °C and 320 °C. It is therefore very unlikely that the degradation mechanism of PET and PEN, at typical processing temperature, is predominately homolytic due to the negligible quantities of CO and CO_2 detected. Despite limited evolution of non-condensable and condensable volatile degradation species during degradation studies of PET and PEN at typical processing temperatures, the formation of cyclic oligomers has been proposed as the dominant degradation reaction. An identical reaction mechanism has been suggested for the formation of cyclic oligomers in PET and PEN; however the extent of cyclic oligomer formation is believed to be reduced in PEN, in comparison to PET, due to the presence of bulky naphthalene species reducing the ease at which such back-biting mechanisms can occur. Following formation of these cyclic oligomers via intramolecular cyclisation reactions, a series of further degradation reactions occur after prolonged exposure to generate acetaldehyde and ethylene glycol, with more extensive cyclic oligomer degradation thought to occur in PET than PEN due to the reduced thermal stability of PET in contrast to PEN.

It is plausible that the mechanism of thermal chain scission reactions, in both polyesters, varies as a function of temperature. The data presented in this thesis, suggests that an ionic based mechanism dominates at lower temperatures due to the absence of carbon oxides. On increasing the temperature, radical based degradation processes have been suggested as the dominant reaction due to significant generation of CO and CO_2. However, further evolved gas analysis would be required to confirm such hypotheses with the use of technology capable of detecting radical based chemistry such as electron spin resonance spectroscopy.

Although the extent of thermal degradation has been shown to differ between PET and PEN, the fundamental thermal degradation mechanisms appear identical. In contrast to these observations, variations in the thermo-oxidative chemistry have been highlighted for PEN on investigating the role of oxygen and water on the degradation of PET and PEN at typical processing temperatures. A combination of studies, including volatilisation, gel quantification and structural analyses revealed that different chemical processes, which result in, or prevent volatilisation are occurring in PET and PEN, respectively.

Following studies under thermo-oxidative conditions, it has been proposed that chain scission and cross-linking reactions compete, varying the proportion of volatile and cross-linked gel species formed as a result of ageing. The overall extent of gel formation in PET and PEN was therefore found to vary with the extent of volatilisation. On increasing the volatilisation of PET, by ageing at high temperatures in highly oxidative environments, the overall extent of gel formation was found to decrease. This is due to an overall reduction in the formation of oxidative cross-linked species due to a significant increase in the formation of volatile degradation products. However, with such low levels of volatilisation observed in PEN, it has been proposed that the dominant degradation reaction in PEN under thermo-oxidative conditions is evidently cross-linking. The overall % gel content, of PEN samples aged in the presence of oxygen, was found to be very high, in comparison to PET. These cross-linking reactions are proposed to involve PEN degradation products with low volatility, formed as a result of primary chain scission reactions. These degradation species remain trapped within the highly viscous PEN melt, undergoing secondary cross-linking reactions at an increased rate over their terephthalate equivalents.

Cross-linking reactions of PET and PEN, during thermo-oxidative degradation, have been proposed to occur predominately at the aromatic carbon sites, resulting in the formation of interconnected rings with a high degree of conjugation. Although their exact chemical nature cannot be positively identified, one possible mechanism for the crosslinking of aromatic rings has been proposed occurring from the presence of acidic, thermally labile hydrogens adjacent to the aliphatic linkages. This hydrogen abstraction reaction has been revealed to occur more readily in PEN than PET due to the increased reactivity of aromatics in PEN, in comparison to PET. Alternatively, chain scission between the aromatic rings and ester functional groups results in the formation of benzyl or naphthalene radicals which then undergo cross-linking reactions.

As aromatic cross-linked species have very high extinction coefficients in the visible spectrum, the formation of these interconnected aromatic ring species have been suggested to contribute to the extensive discolouration observed in both polyesters. Due to the presence of naphthalene groups in PEN, in contrast to phenyl groups in PET, greater conjugation exists providing an explanation for the increased discolouration observed in PEN, in comparison to PET. Although discolouration of PET and PEN does occur under thermal environments, discolouration appeared most significant in samples aged in the presence of oxygen. With increased ageing temperature and oxygen concentration, the extent of gel formation was found to increase in both polyesters, accompanied by an increase in the extent of discolouration observed. The overall extent of discolouration and gel formation was most pronounced in PEN than PET, suggesting that the naphthalene ring is involved in the discolouration reactions.

Two mechanistic pathways, which contribute to the discolouration in PET and PEN, have been proposed from thermal and thermo-oxidative degradation studies of both polyesters. The first mechanistic pathway is proposed to originate from thermal degradation of PET and PEN. With an increase in ageing temperature under thermal conditions, vinyl ester groups formed from chain scission reactions are believed to undergo further polymerisation to result in the formation of conjugated and thus coloured polyene type species. As the extent of discolouration in PET and PEN samples was found to identical after thermal ageing, the benzene and naphthalene groups are not thought to be involved in this discolouration pathway. However, the presence of low levels of moisture has been demonstrated to interrupt this discolouration pathway due to a change in the overall end group distribution within PET and PEN as the polymers undergo competing thermal and hydrolytic degradation reaction. With increasing hydrolytic degradation, the formation of vinyl ester end groups reduces, with an increase in hydroxyl chain ends formed. Due to the increased reactivity of hydroxyl groups, these chain ends undergo further degradation reactions elsewhere in the polymer chain as they do not have the ability to self polymerise. This results in an increase in the extent of volatilisation and reduction in discolouration, as observed for both PET and PEN aged in thermal-hydrolytic conditions.

A second mechanistic pathway for discolouration is proposed to originate from thermo-oxidative degradation of PET and PEN. This pathway results in extensive cross-linking reactions, forming highly conjugated and highly absorbing benzene and naphthalene ring species in PET and PEN, respectively. Oxidative degradation chemistry has been revealed as the dominant reaction over hydrolysis, with the impact of low moisture levels on the discolouration of PET and PEN found to be minimal. Although, the first mechanistic pathway is also proposed to proceed under thermo-oxidative conditions, cross-linking reactions leading to the formation of network structures and thus discolouration will dominate.

As the nature of the highly discoloured cross-linked species, proposed to form in PET and PEN under thermo-oxidative conditions, differ significantly from the vinyl ester species proposed to form during thermal degradation, further investigation into the species responsible for discolouration in PET and PEN could be explored. Although positive identification of the chemical species responsible for discolouration is unlikely to prevent such reactions occurring during processing of polyester film, identification of a technique suitable for generating detailed information on their chemical origin could enable processing conditions to be optimised such that the formation of species responsible for discolouration can be minimised. Techniques such as phosphorescence and fluorescence have been presented in the literature to monitor discolouration of polyesters, alongside model compounds, by detecting fluorescent aromatic side-groups in addition to excimers, produced as a result of intermolecular interactions between chromophores. [2,3,4] Validation of the nature of chromophores formed during degradation could be performed via studies examining a range of polyesters, with varied aromaticity, to understand the impact of aromaticity on colour formation. The uniformity of colour formation in PET and PEN could also be examined in addition to the changes in discolouration as a function of ageing time.

From the ageing studies completed under processing environment and temperature regimes, it has also been demonstrated that cross-linking reactions appear only to diminish when both polyesters are degraded in the presence of significant levels of moisture. On increasing the moisture concentration on ageing PET and PEN at processing temperatures, increased hydrolytic degradation and a subsequent increase in the formation of volatile degradation products was achieved. Volatilisation of both PET and PEN were found to be most pronounced on ageing at the highest moisture concentration in air. In addition to increased volatilisation on ageing under air, the extent of cross-linking was also seen to significantly decrease on increasing the absolute humidity above 40%, accompanied by increased melt flow of the polyester. Increased volatilisation, increased melt flow and a reduction in oxidative cross-linking, are all proposed to result from competing thermal/thermo-oxidative and hydrolytic degradation reactions ongoing in PET and PEN.

Suitable die lip atmospheric conditions have been identified for both polyesters, from the thermal, thermal-hydrolytic, thermo-oxidative and thermo-oxidative-hydrolytic ageing studies completed at typical processing conditions. It is proposed that these conditions will minimise die streaks during processing of PET and PEN films. High oxygen concentration and high temperature were found to volatilise PET lip residue, with a combination of both eliminating almost all lip residue. High moisture levels were also found to significantly increase volatilisation levels accompanied with a reduction in the absolute and relative gel content in PET, particularly at high temperatures. Both water and oxygen were found to improve deposit flow of PET as a result of increased volatilisation and reduction in absolute gel content. Therefore, a combination of high temperature, high oxygen concentration and high humidity have been recommended to maintain high volatilisation levels and limit gel formation in PET.

Degradation of PEN in an inert environment proved similar to PET, with low levels of volatilisation and gel formation. On increasing oxygen concentration, only a marginal increase in volatilisation was observed in PEN, however unlike PET, this was accompanied by a significant increase in both relative and absolute gel formation with little apparent effect on deposit flow. Oxidative cross-linking reactions have therefore proposed to dominate in PEN leading to a reduction in the overall extent of volatilisation. High moisture levels in PEN significantly improved deposit flow, increased volatilisation and substantially reduced gel content in the presence of oxygen, indicative of competing hydrolysis and oxidative cross-linking reactions. Similar to PET, hydrolysis is proposed to dominate and prevent the formation of oxidative cross-linked species or alternatively produce volatile species which are more resistant to cross-linking. Both gel formation and volatilisation of

PEN were found to increase on raising the ageing temperature. High die lip temperatures were therefore suggested to be detrimental to die streaks, and must be combined with moisture or reduced oxygen atmospheres to minimise gel formation and promote deposit flow.

Further attempts to promote volatilisation of PEN beyond that observed throughout this research may include examination of the volatilisation chemistry on modifying ageing surface. In contrast to the aluminum surface utilised for all degradation studies reported in this thesis, the extent of volatilisation in PET and PEN could be monitored on surfaces such as copper, brass, stainless steel, mild steel and glass. As copper, iron, cobalt ions and other transition metals are very active catalysts for hydroperoxide decomposition, this could lead to an increase in the decomposition rate of hydroperoxides and thus impact on the overall rate of oxidation.

Finally, the extent of degradation in PEN was found to differ quite significantly from that of PET during low temperature studies used to examine process drying conditions. Degradation of PET was largely influenced by the ageing environment and temperature with the dominant degradation reaction shown to differ with ageing temperature. Although the overall thermal stability of PET remained unchanged after ageing, variations in the molar mass and crystalline content/behaviour were observed in aged PET samples, in addition to a loss in mechanical strength. At low ageing temperatures of 140 - 170 ^{o}C, hydrolysis was revealed as the dominant degradation reaction, with thermo-oxidative degradation competing with hydrolytic degradation as the ageing temperature increased to 190 ^{o}C. In contrast to PET, all ageing environments and temperatures were found to have no detrimental effect on the overall thermal stability, molar mass or crystallisation content/behaviour of PEN. It has been suggested that this may be due to reduced chain mobility, increased crystallinity and/or hydrophobicity effects in PEN in contrast to PET. However, further studies could examine the crystallisation behaviour and thus molecular motion of PEN, in comparison to PET, via broadband dielectric spectroscopy. Embrittlement of both PET and PEN after ageing has been proposed to originate from secondary crystallisation developed upon ageing, causing remarkable changes to mechanical properties.

From the degradation studies of PET and PEN, described in this thesis, it has been demonstrated that the thermal degradation of PET and PEN is not dissimilar. However, differences in the dominant degradation reactions occurring in PEN, in comparison to PET, have been highlighted under thermo-oxidative conditions. By achieving a fundamental understanding of the dominant degradation reactions occurring in PEN, careful consideration of processing conditions can result in minimal or controlled degradation. This knowledge, required to enable the control of operating conditions during polyester processing, is particularly important for well ventilated environments whereby volatilisation of PEN is restricted as a result of extensive cross-linking.

7.1 References

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[2] Edge M.; Allen N.S.; Wiles R.; MacDonald W.A.; Mortlock S.V. *Polymer*, **1995**, *36 (2)*, 227.

[3] Allen N.; Edge M.; Daniels J.; Royall D. *Polym. Degrad. Stab.*, **1998**, *62*, 373.

[4] Edge M.; Allen N.S.; Wiles R.; MacDonald W.A.; Mortlock S.V. *Polym. Degrad. Stab.*, **1996**, *53*, 141.

8 SUPPLEMENTARY MATERIAL

8.1 Fundamental Degradation Studies of PET and PEN

8.1.1 Thermal Properties of PET and PEN

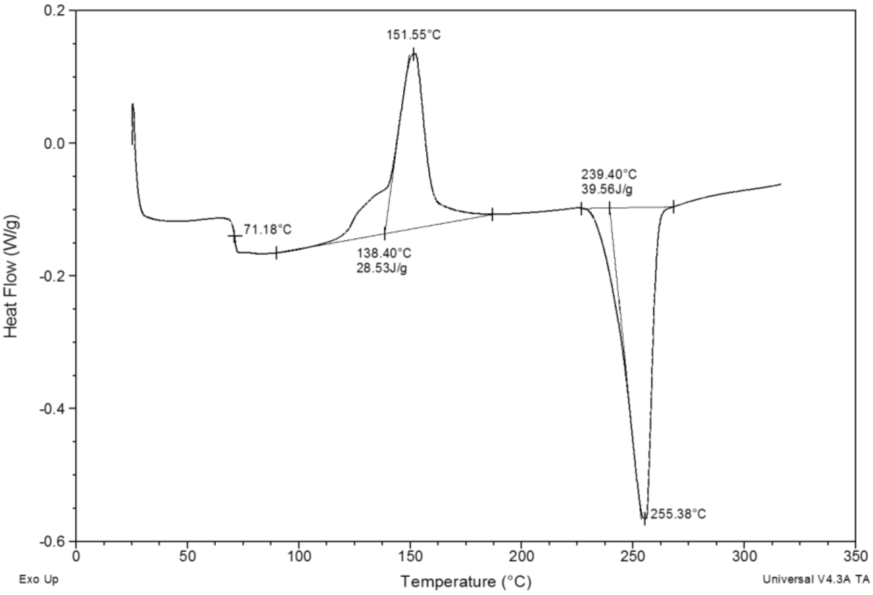


Figure 8.1 DSC of PET in N_2, heat-cool-reheat programme, cycle 1

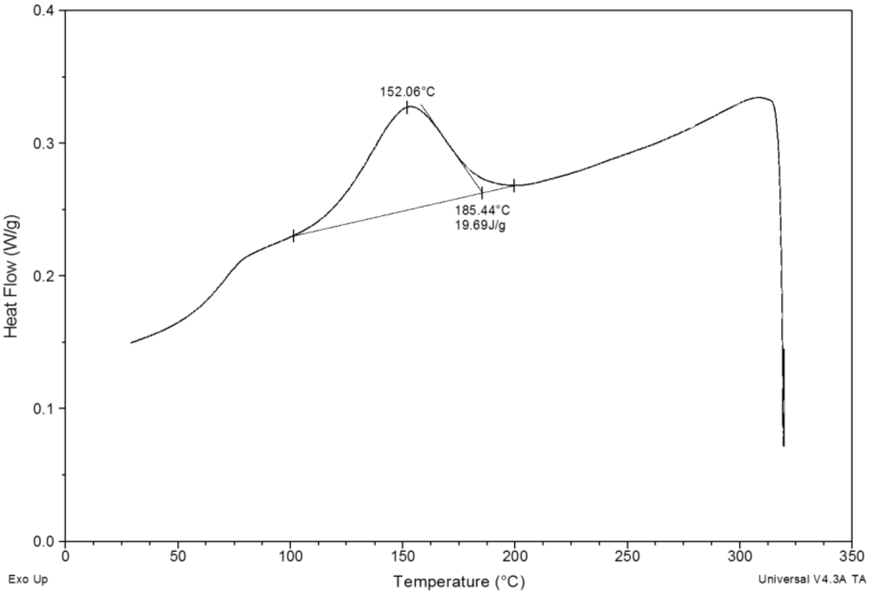


Figure 8.2 DSC of PET in N_2, heat-cool-reheat programme, cycle 2

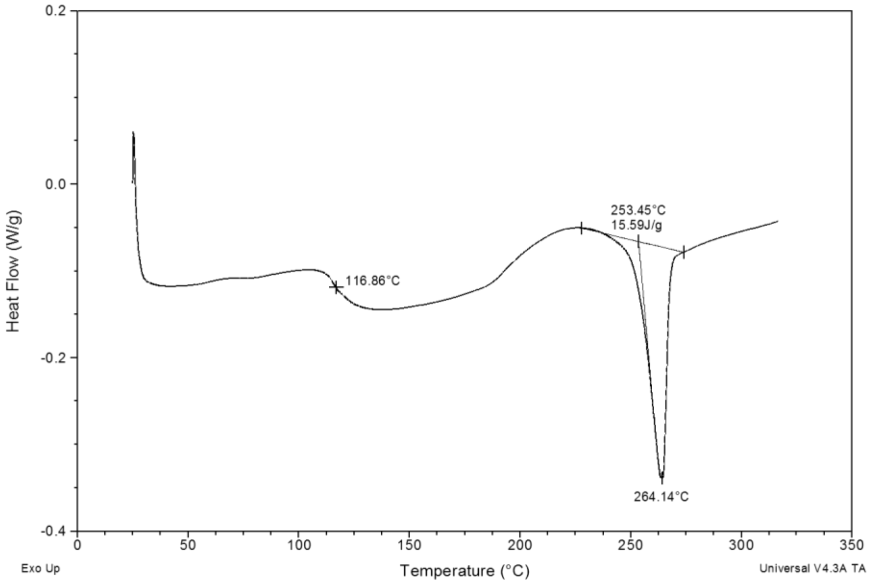


Figure 8.3 DSC of PEN in N_2, heat-cool-reheat programme, cycle 1

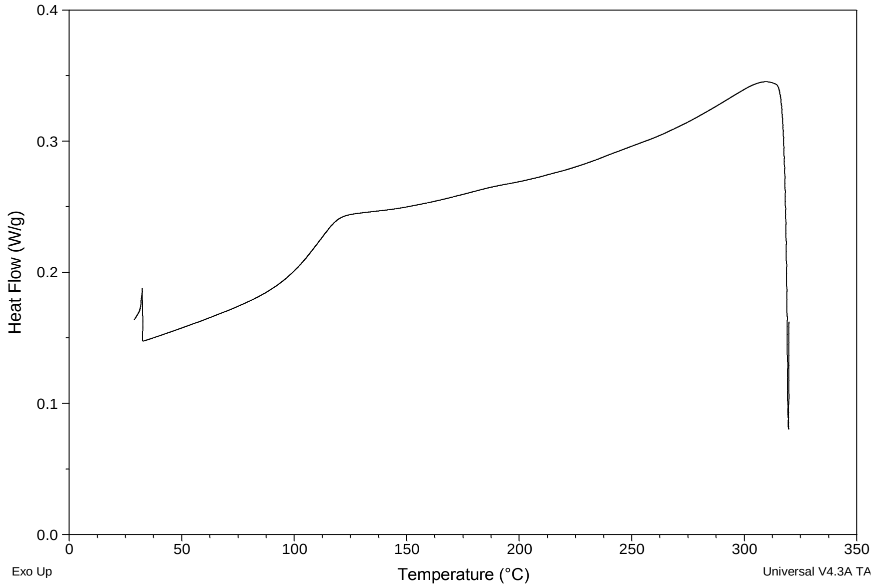


Figure 8.4 DSC of PEN in N_2, heat-cool-reheat programme, cycle 2

8.1.2 Thermal Volatilisation Studies of PET and PEN

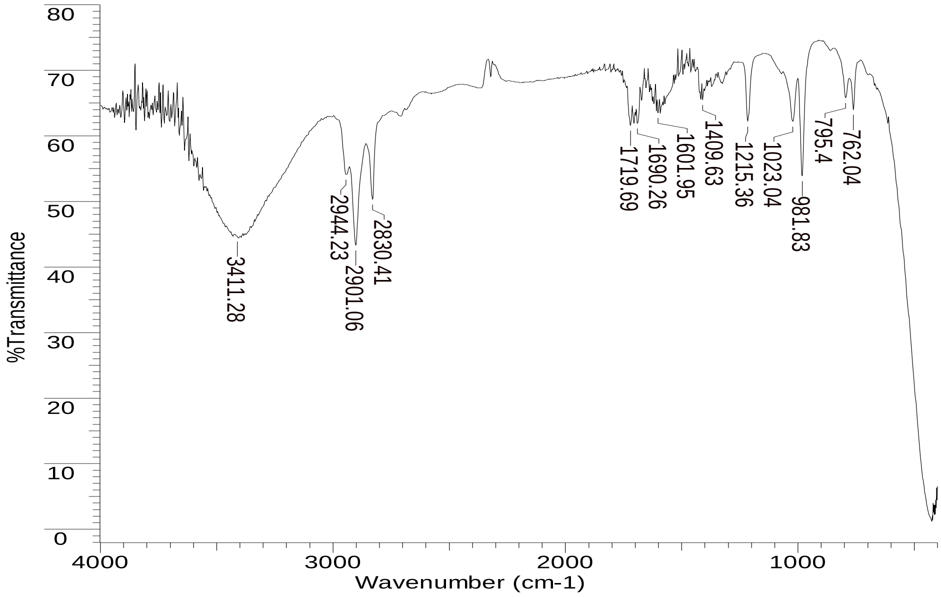


Figure 8.5 IR spectrum of water - PEN fraction 3

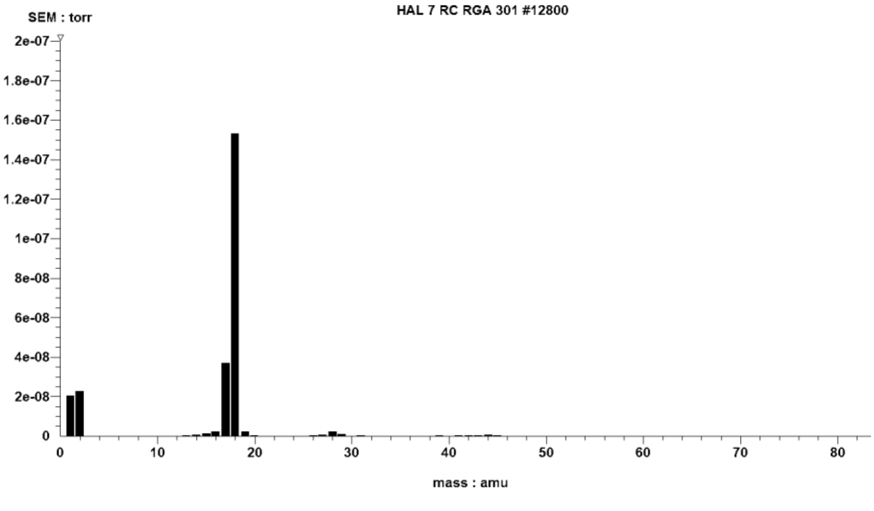


Figure 8.6 Mass spectrum of water - PEN fraction 3

8.1.3 TVA of PET and PEN at Processing Temperature

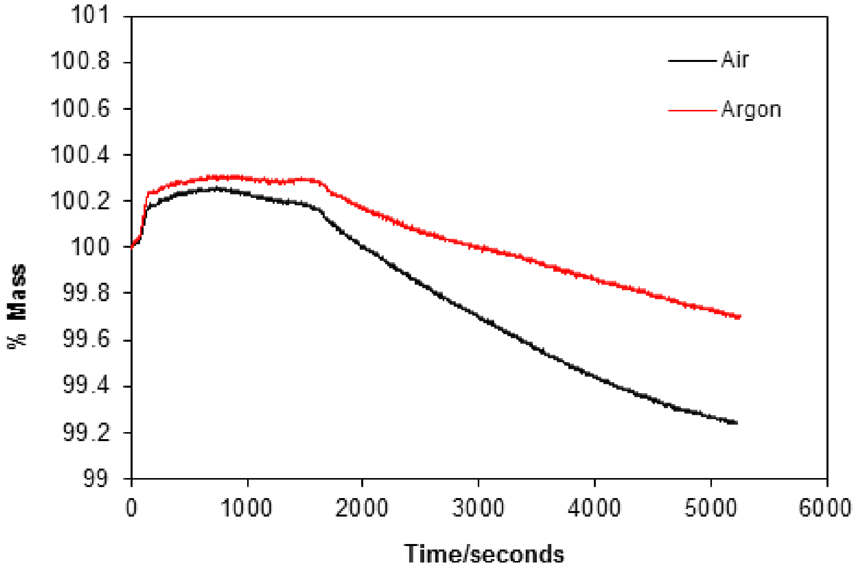


Figure 8.7 Isothermal TGA studies on PET at 290 °C under air and argon – 60 minute isothermal hold

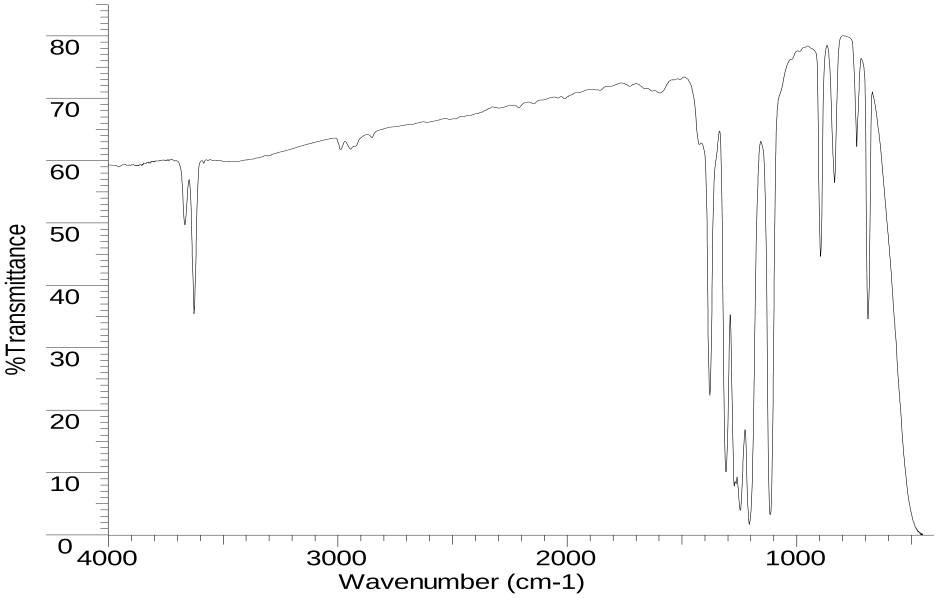


Figure 8.8 IR spectrum - PET fraction 1, 288 °C

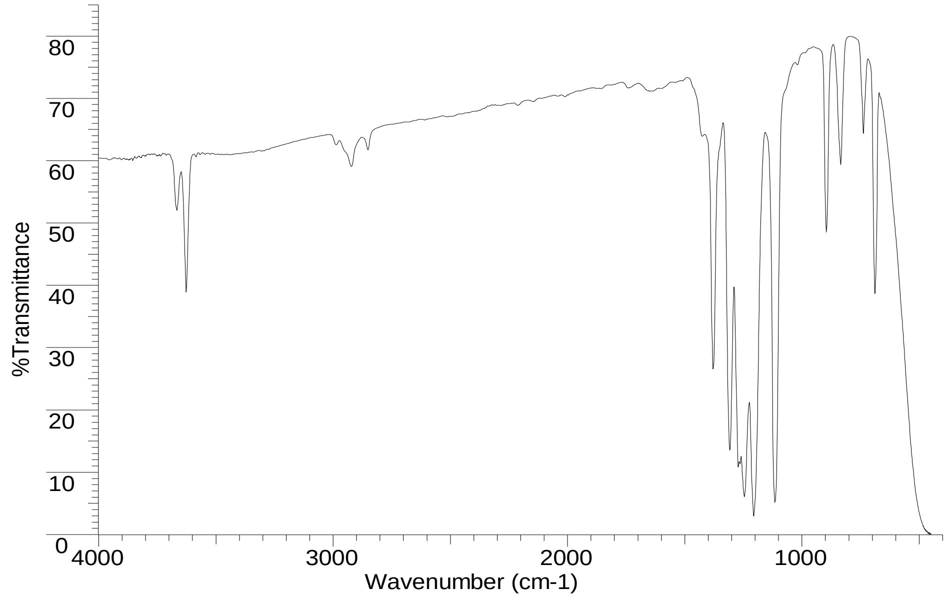


Figure 8.9 IR spectrum - PET fraction 1, 300 °C

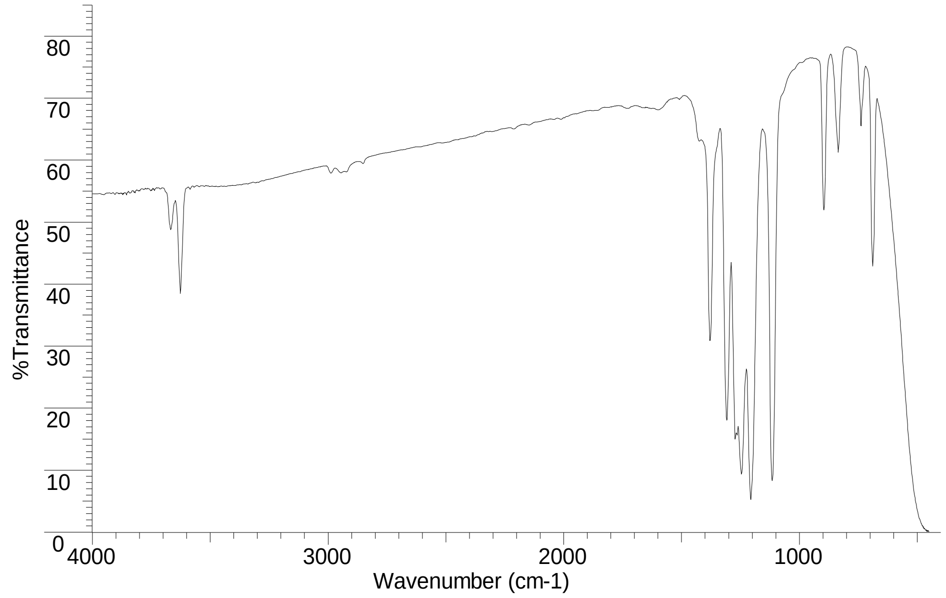


Figure 8.10 IR spectrum - PET fraction 1, 320 °C

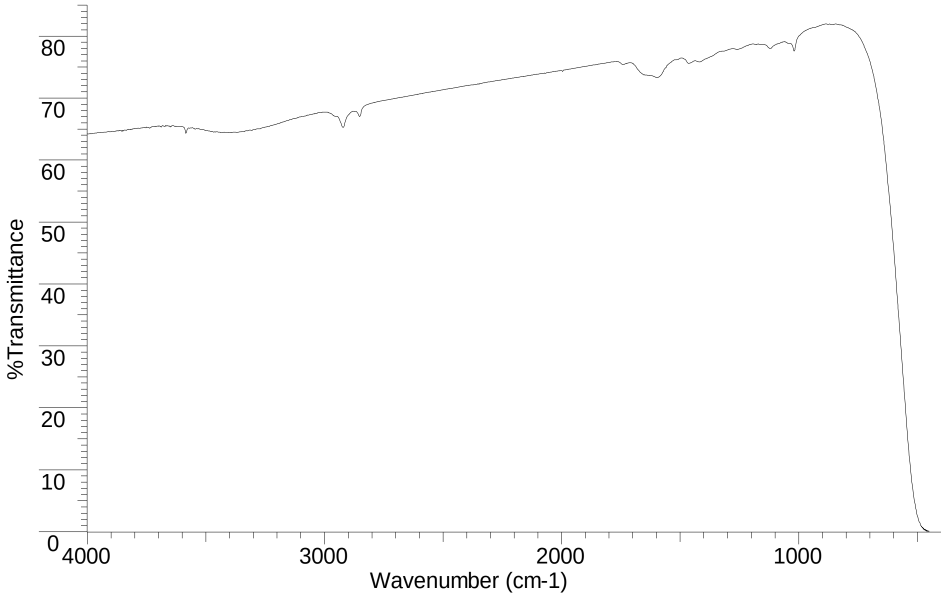


Figure 8.11 IR spectrum - PET fraction 2, 288 °C

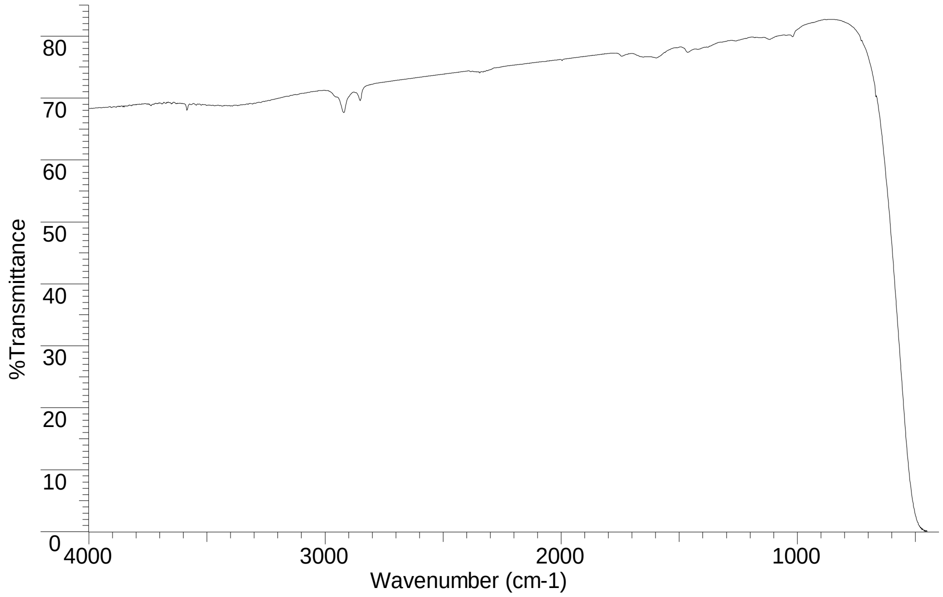


Figure 8.12 IR spectrum - PET fraction 2, 300 °C

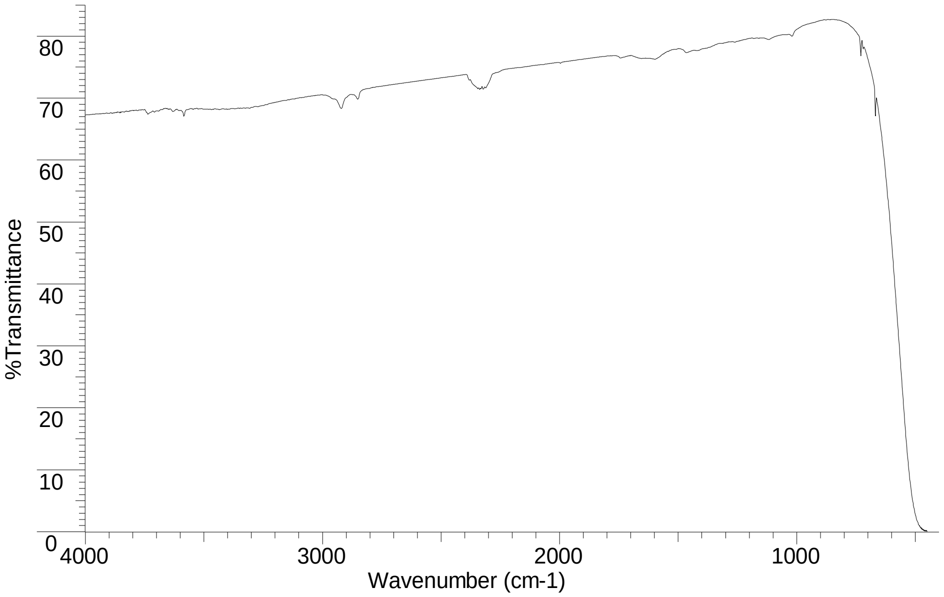


Figure 8.13 IR spectrum - PET fraction 2, 320 °C

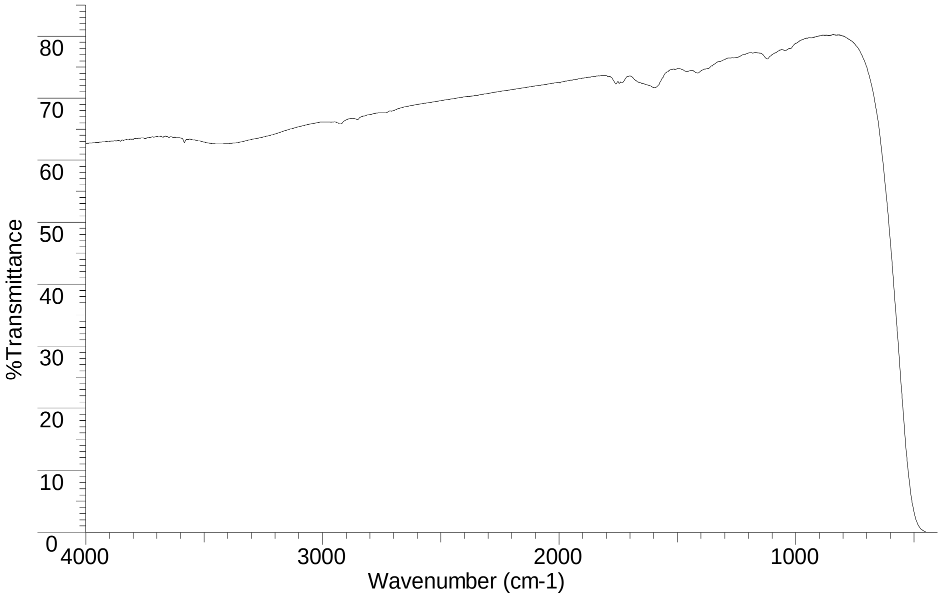


Figure 8.14 IR spectrum - PET fraction 3, 288 °C

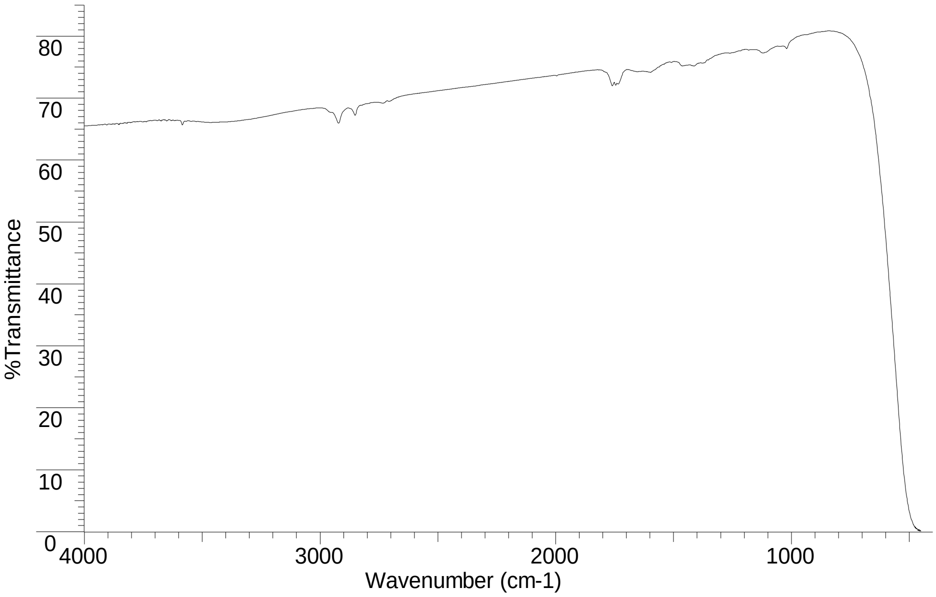


Figure 8.15 IR spectrum - PET fraction 3, 300 ^{o}C

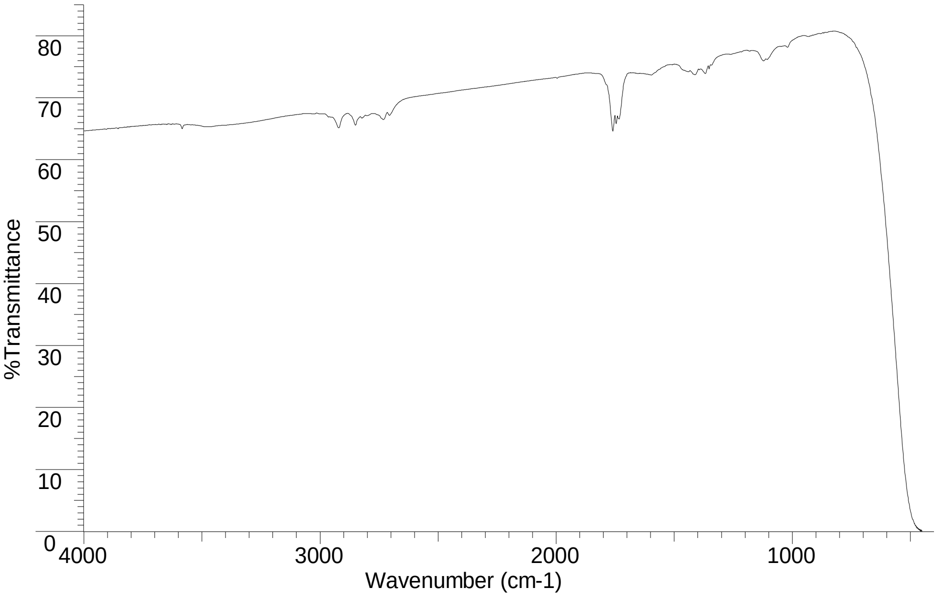


Figure 8.16 IR spectrum - PET fraction 3, 320 ^{o}C

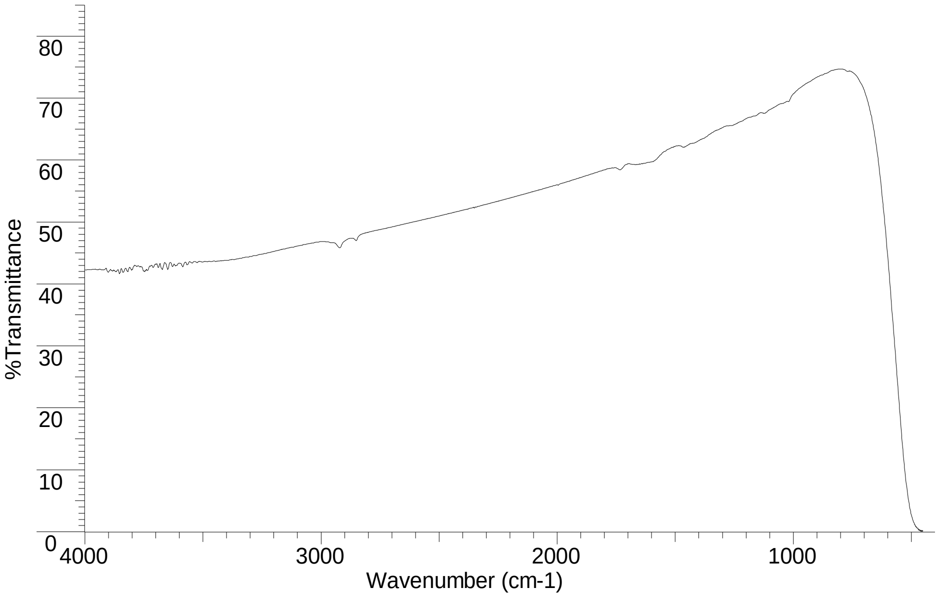


Figure 8.17 IR spectrum - PET fraction 4, 288 ^{o}C

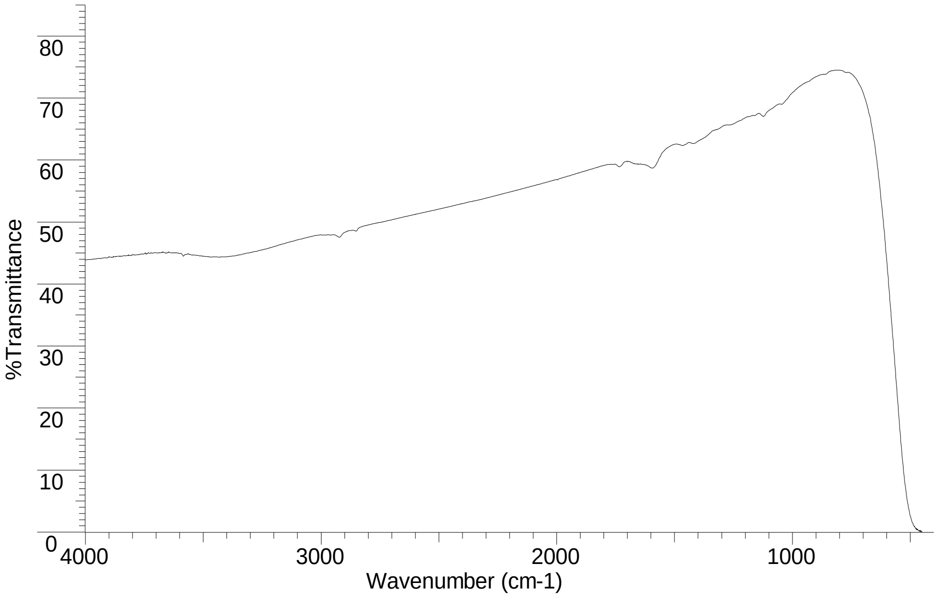


Figure 8.18 IR spectrum - PET fraction 4, 300 ^{o}C

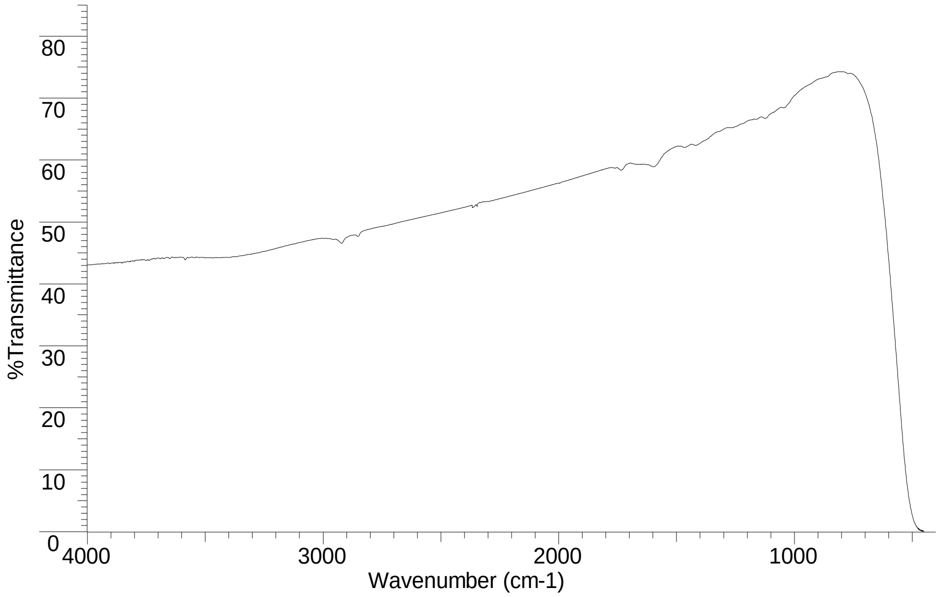


Figure 8.19 IR spectrum - PET fraction 4, 320 °C

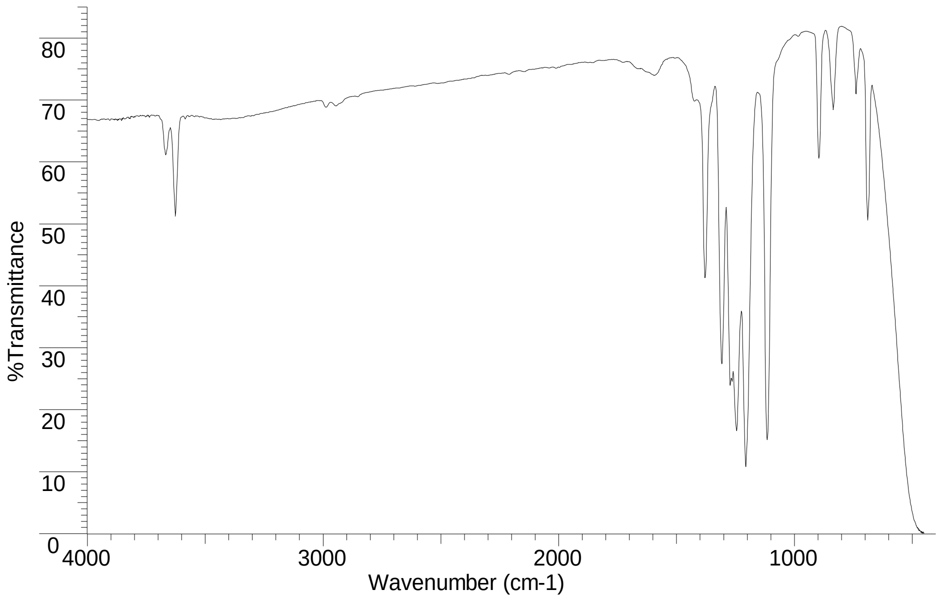


Figure 8.20 IR spectrum - PEN fraction 1, 288 °C

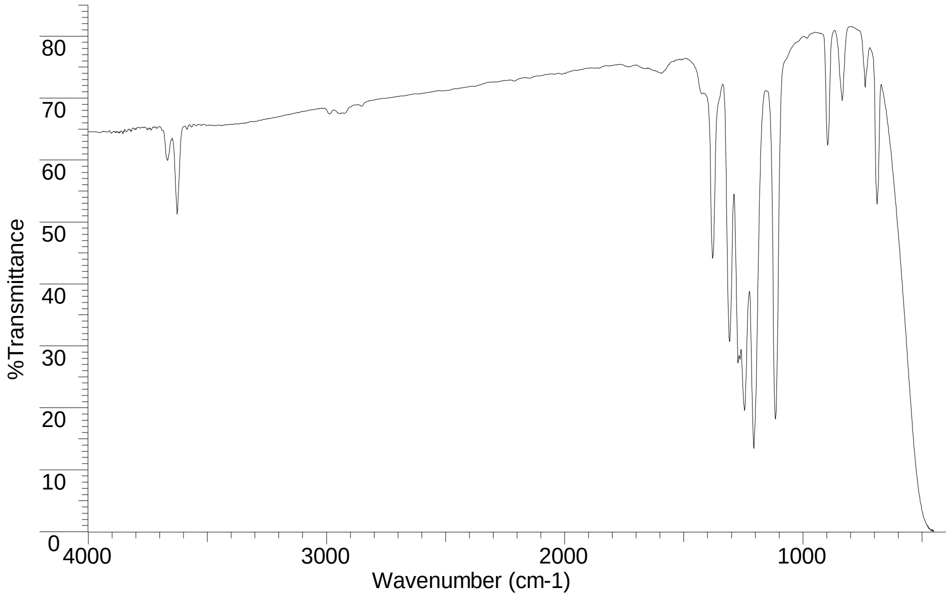


Figure 8.21 IR spectrum - PEN fraction 1, 300 ^{o}C

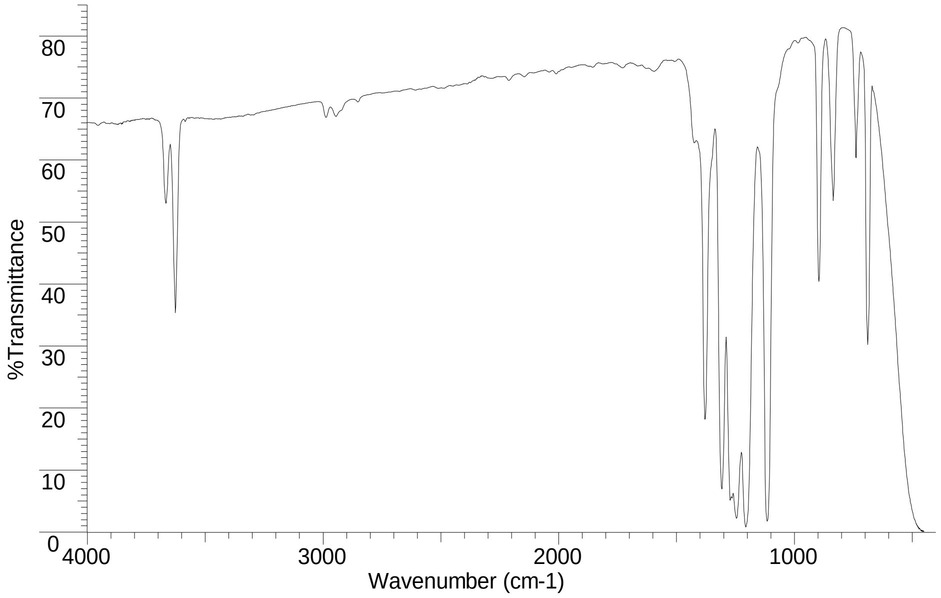


Figure 8.22 IR spectrum - PEN fraction 1, 320 ^{o}C

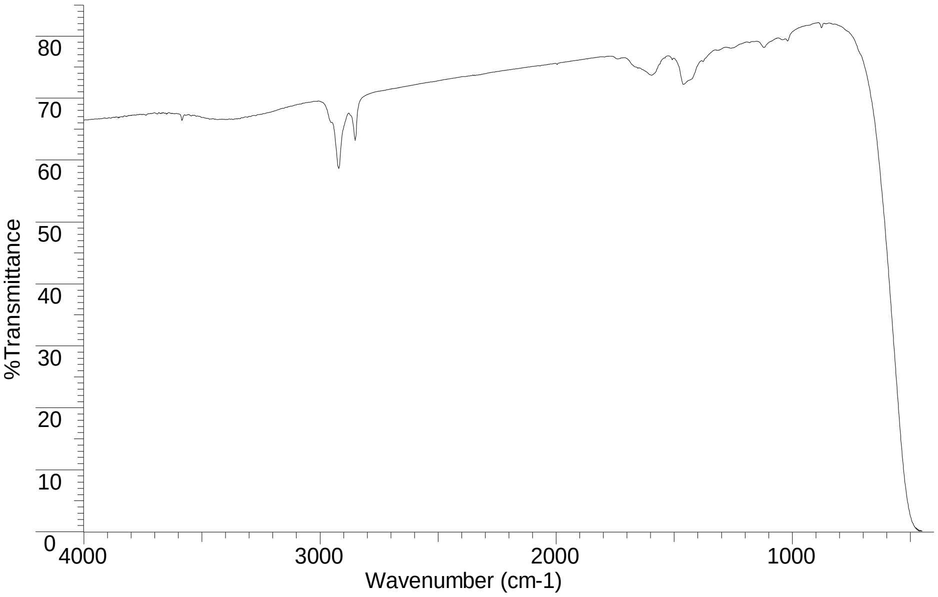


Figure 8.23 IR spectrum - PEN fraction 2, 288 ^{o}C

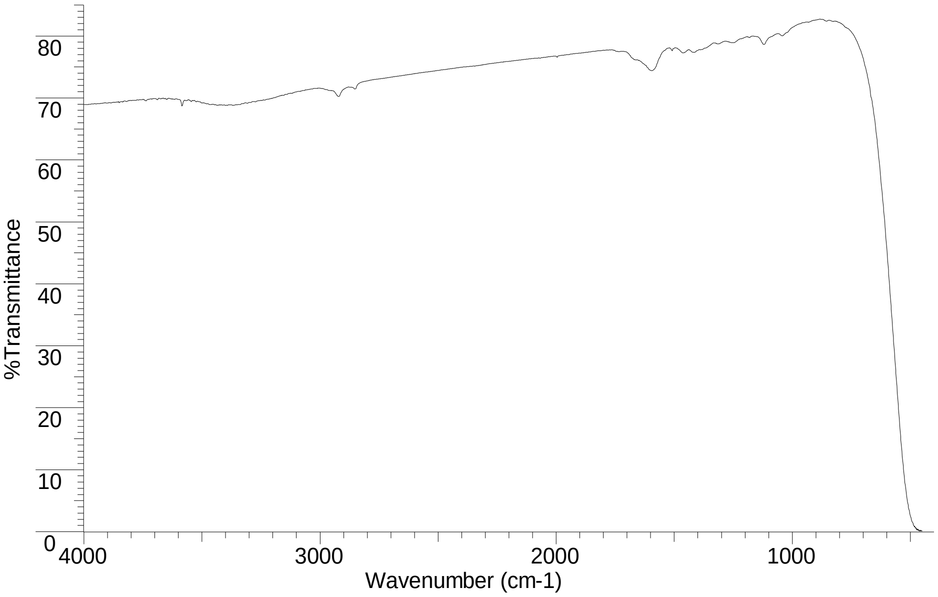


Figure 8.24 IR spectrum - PEN fraction 2, 300 ^{o}C

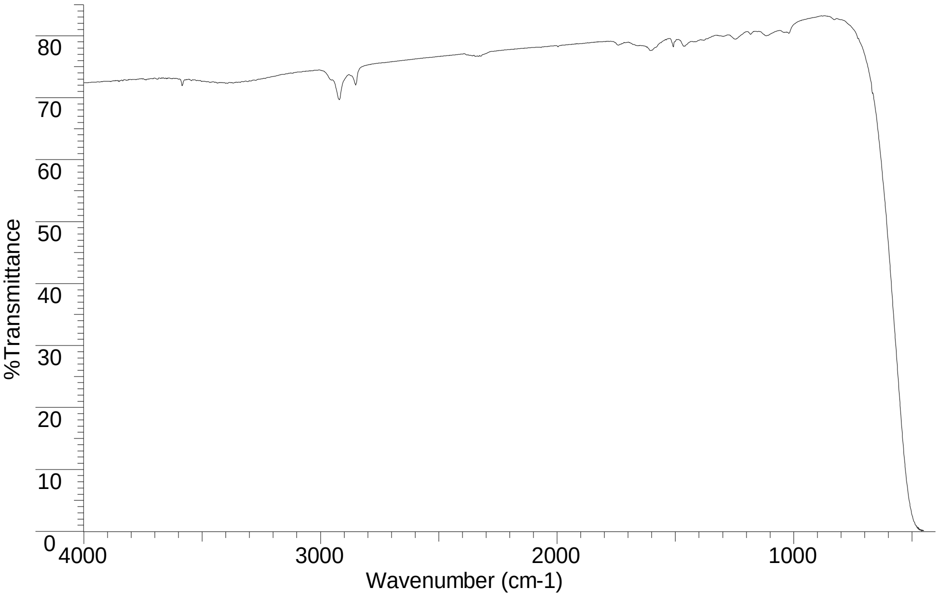


Figure 8.25 IR spectrum - PEN fraction 2, 320 °C

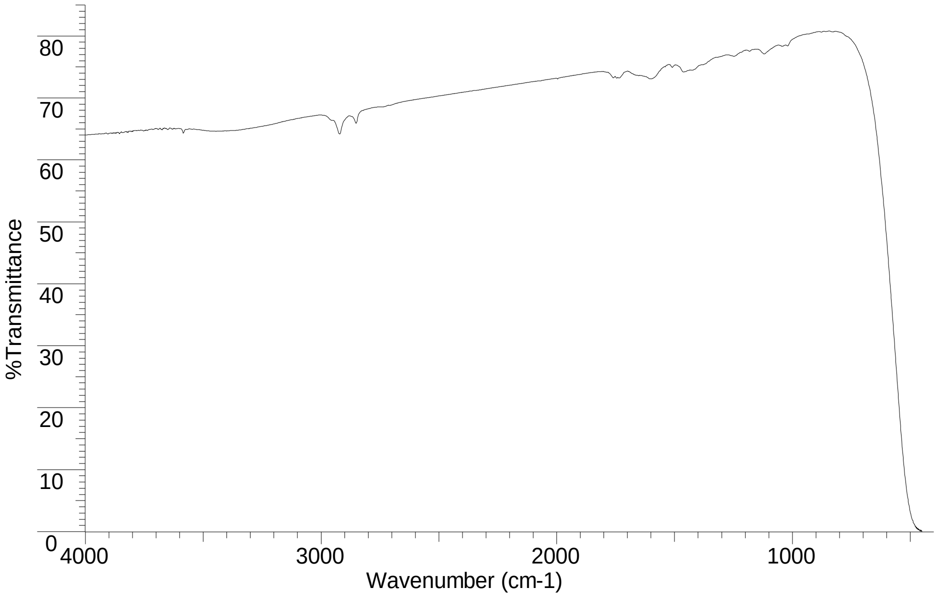


Figure 8.26 IR spectrum - PEN fraction 3, 288 °C

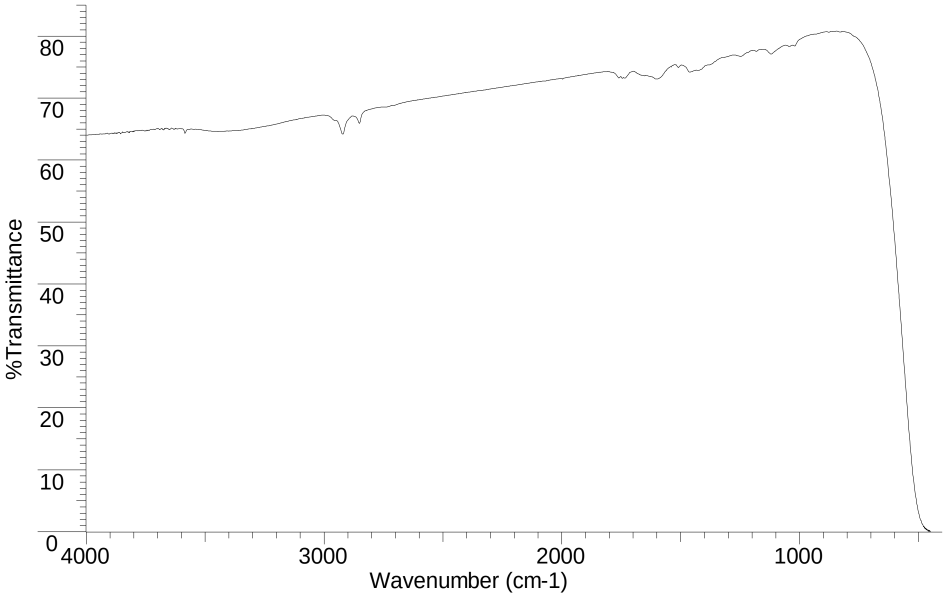


Figure 8.27 IR spectrum - PEN fraction 3, 300 ^{o}C

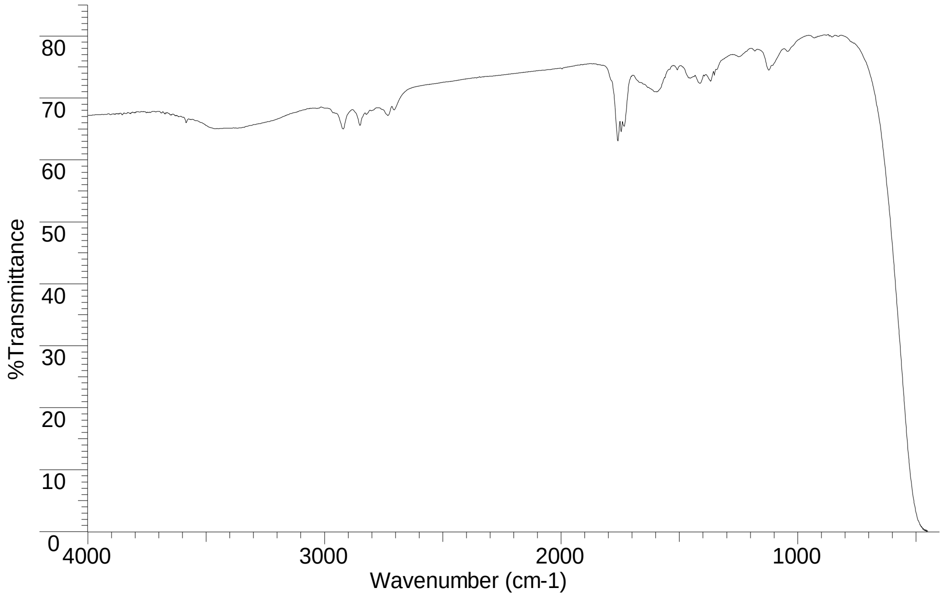


Figure 8.28 IR spectrum - PEN fraction 3, 320 ^{o}C

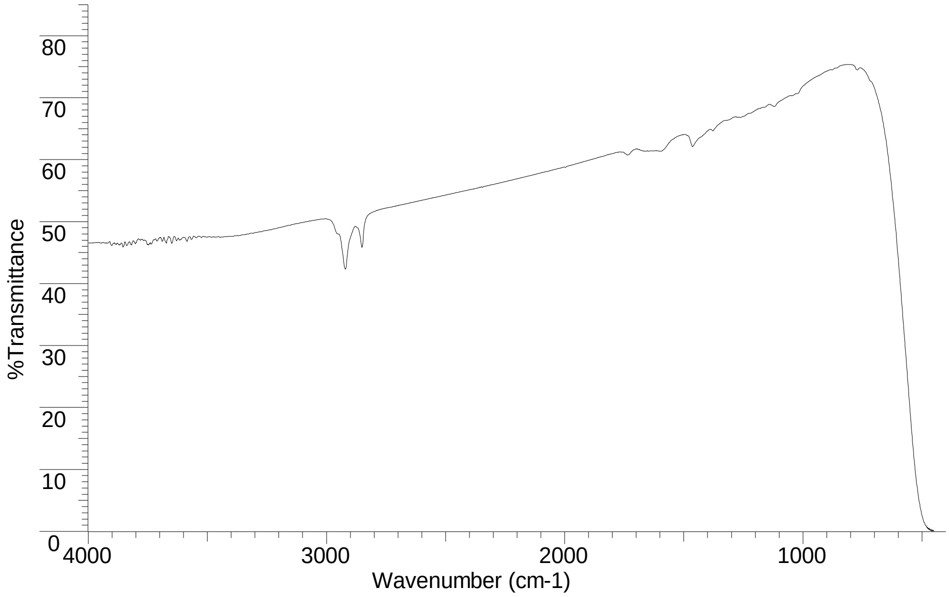


Figure 8.29 IR spectrum - PEN fraction 4, 288 ^{o}C

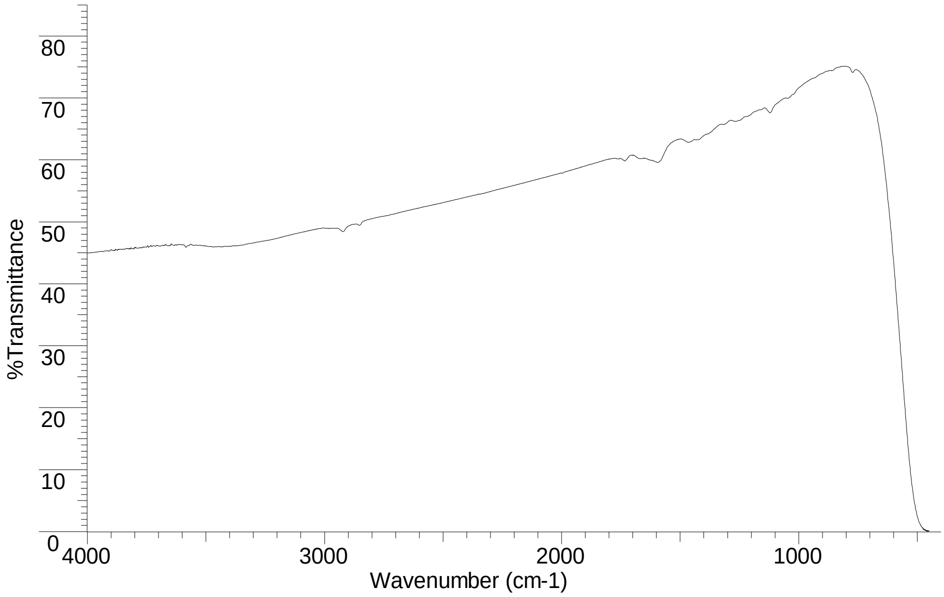


Figure 8.30 IR spectrum - PEN fraction 4, 300 ^{o}C

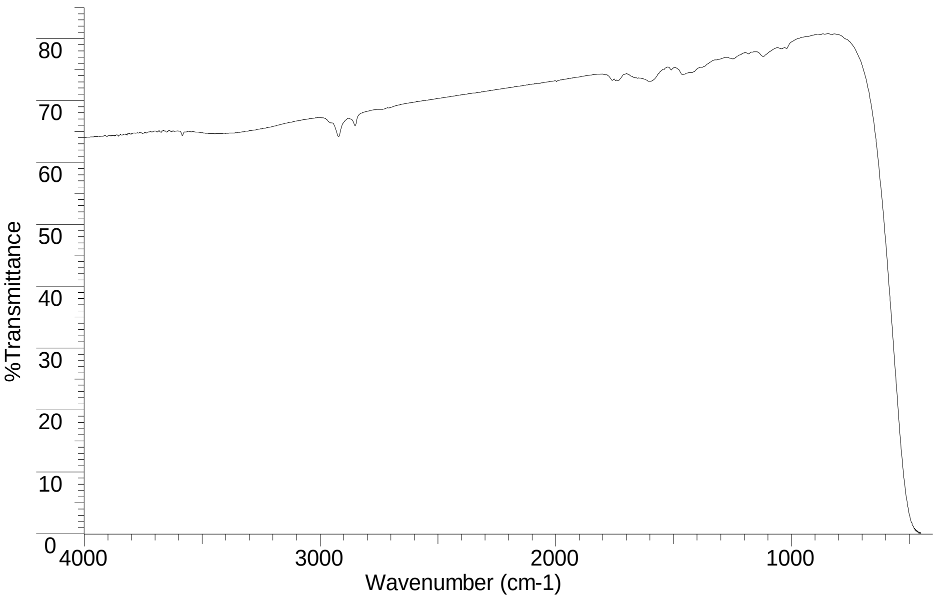


Figure 8.31 IR spectrum - PEN fraction 4, 320 ^{o}C

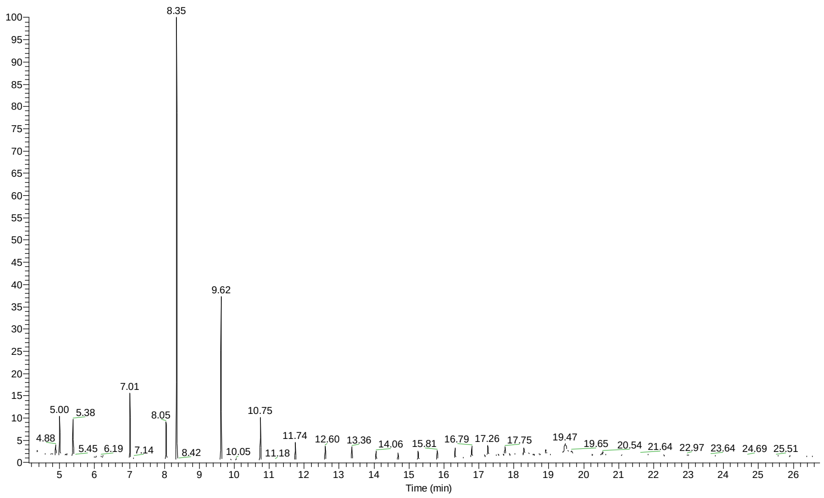


Figure 8.32 GC-MS total ion chromatogram (TIC) - PET fraction 4, 288 ^{o}C

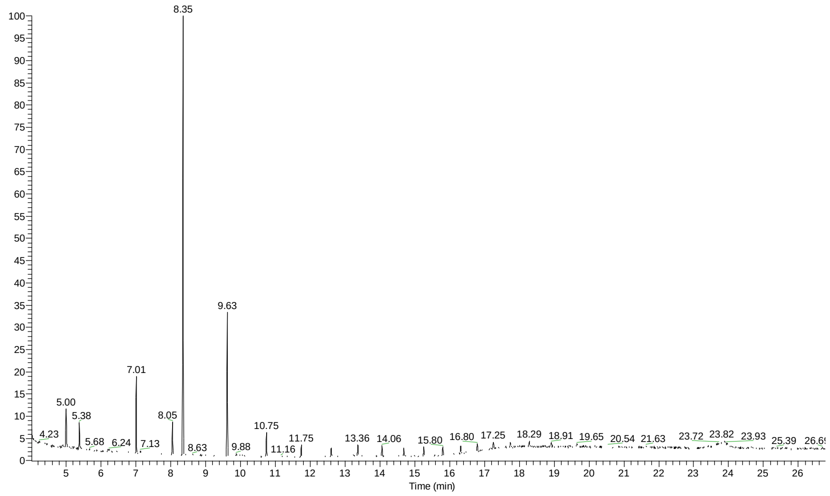


Figure 8.33 GC-MS total ion chromatogram (TIC) - PET fraction 4, 300 ^{o}C

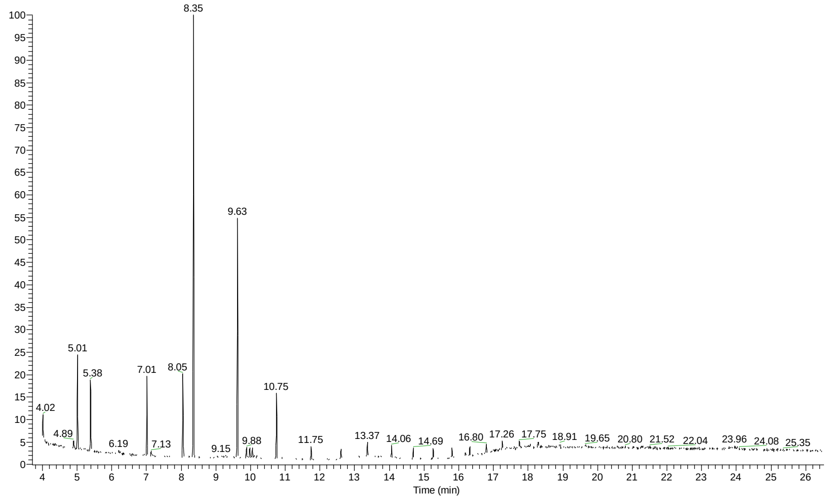


Figure 8.34 GC-MS total ion chromatogram (TIC) - PET fraction 4, 320 ^{o}C

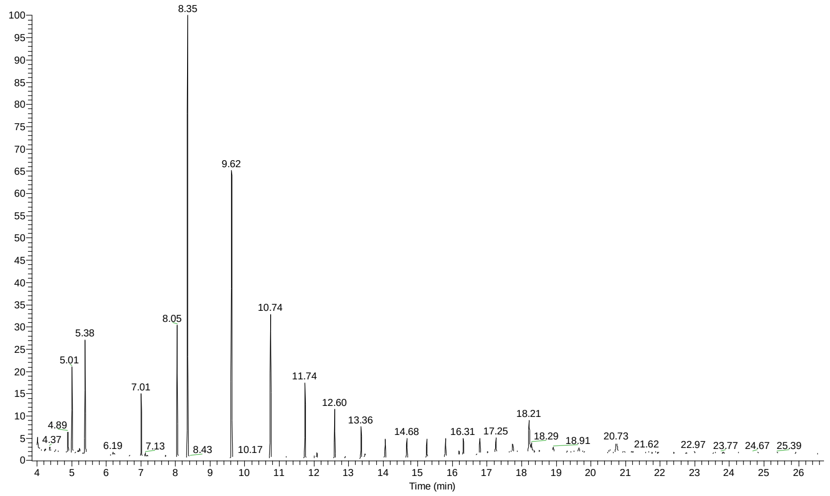


Figure 8.35 GC-MS total ion chromatogram (TIC) - PET cold ring fraction, 288 ^{o}C

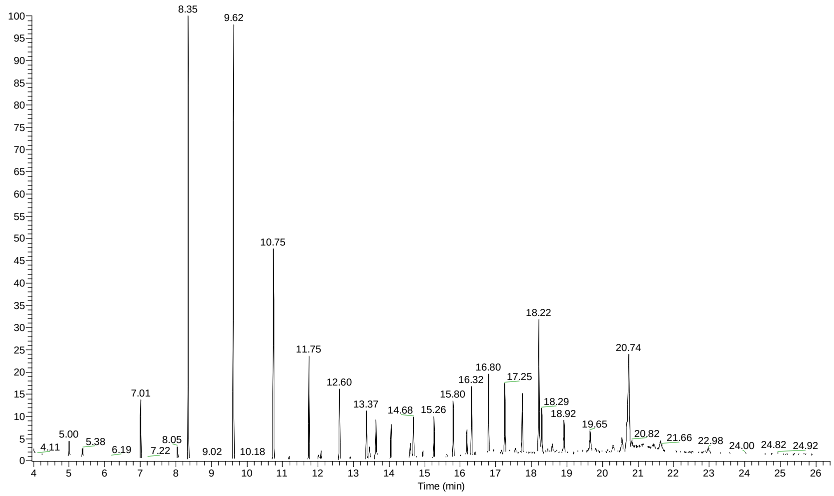


Figure 8.36 GC-MS total ion chromatogram (TIC) - PET cold ring fraction, 300 ^{o}C

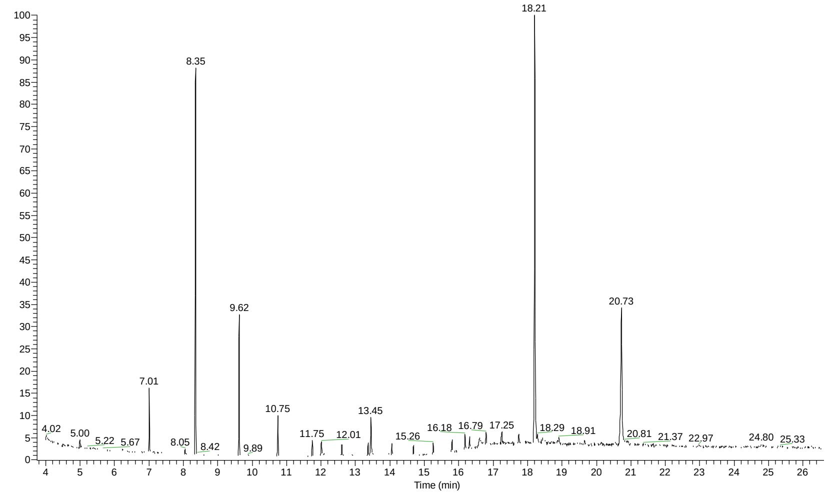


Figure 8.37 GC-MS total ion chromatogram (TIC) - PET cold ring fraction, 320 ^{o}C

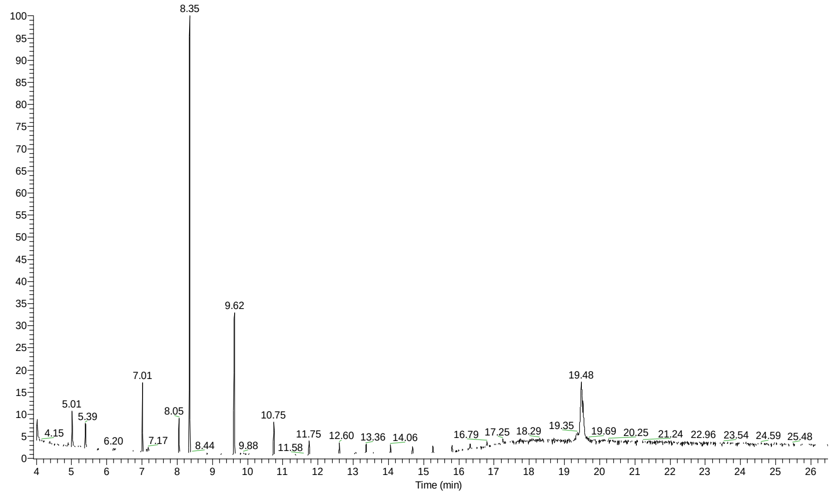


Figure 8.38 GC-MS total ion chromatogram (TIC) - PEN fraction 4, 288 ^{o}C

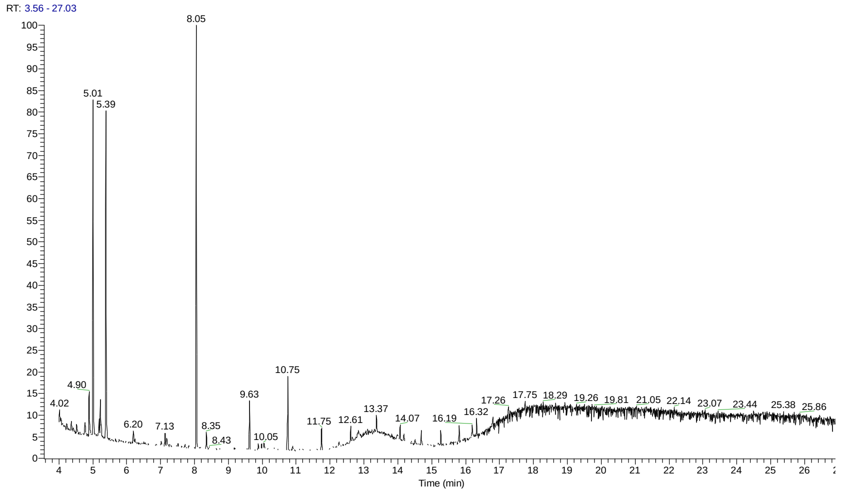


Figure 8.39 GC-MS total ion chromatogram (TIC) - PEN fraction 4, 300 °C

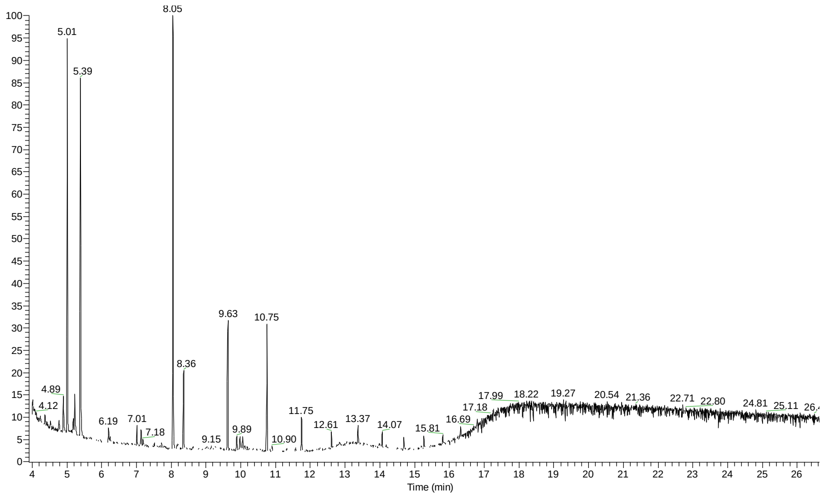


Figure 8.40 GC-MS total ion chromatogram (TIC) - PEN fraction 4, 320 °C

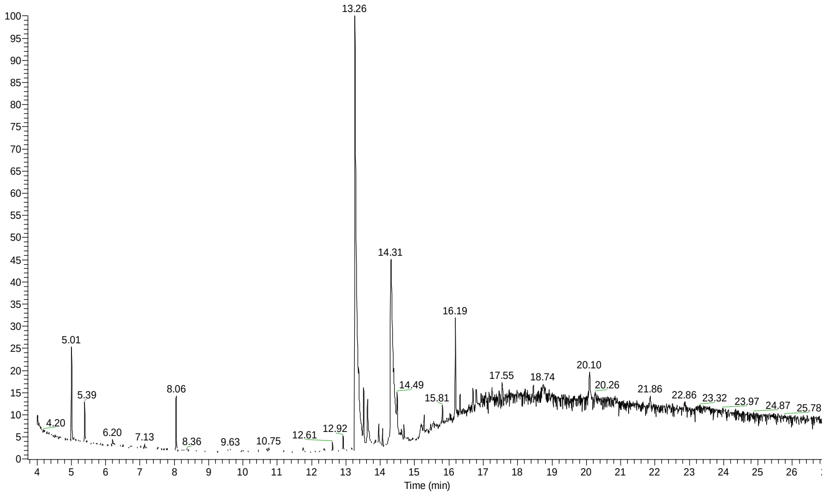


Figure 8.41 GC-MS total ion chromatogram (TIC) - PEN cold ring fraction, 288 °C

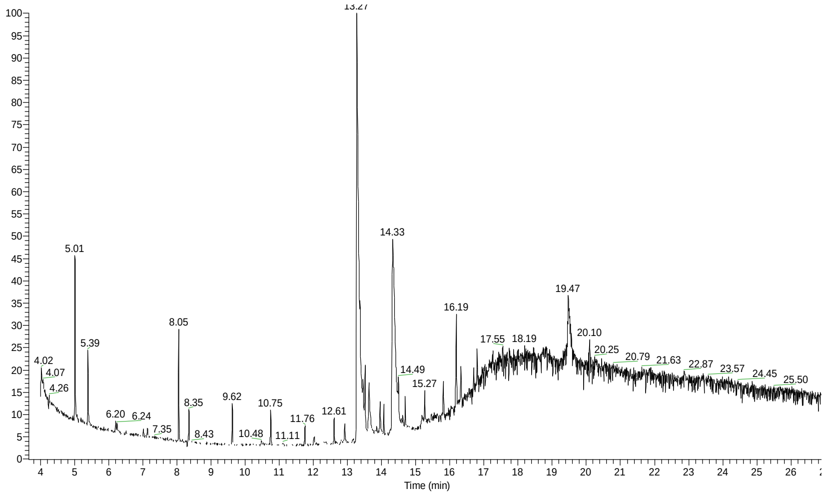


Figure 8.42 GC-MS total ion chromatogram (TIC) - PEN cold ring fraction, 300 ^{o}C

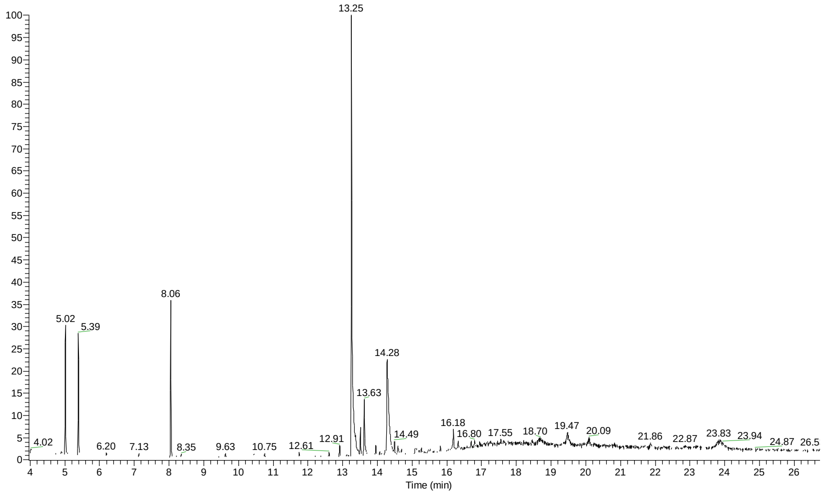


Figure 8.43 GC-MS total ion chromatogram (TIC) - PEN cold ring fraction, 320 ^{o}C

8.2 Ageing of PET and PEN under Controlled Processing Conditions

8.2.1 Introduction to PET and PEN Polyester Films

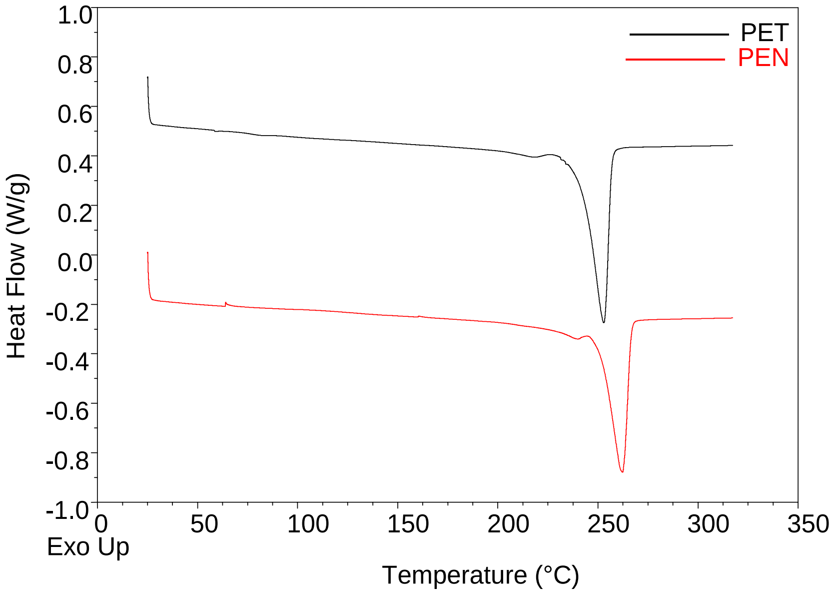


Figure 8.44 Thermal transitions in PET and PEN film determined by DSC, heat-cool-reheat programme under N_2, cycle 1

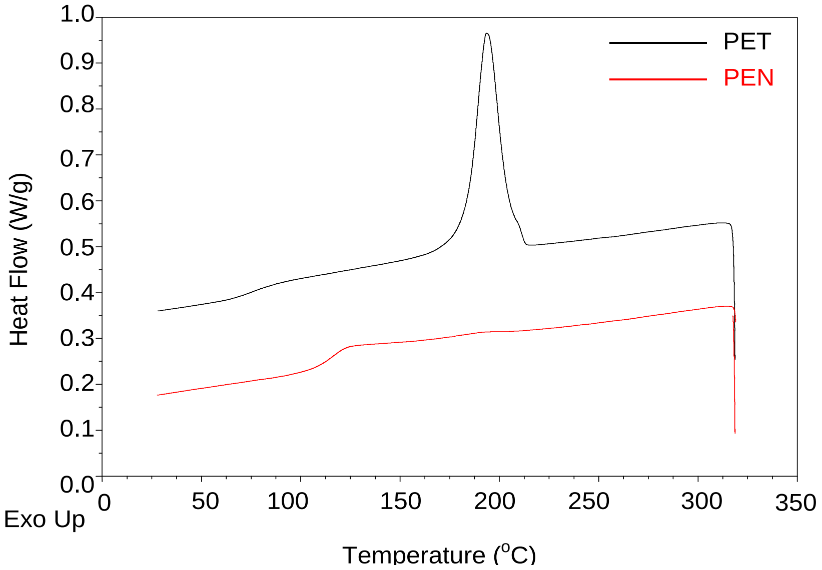


Figure 8.45 Thermal transitions in PET and PEN film determined by DSC, heat-cool-reheat programme under N_2, cycle 2

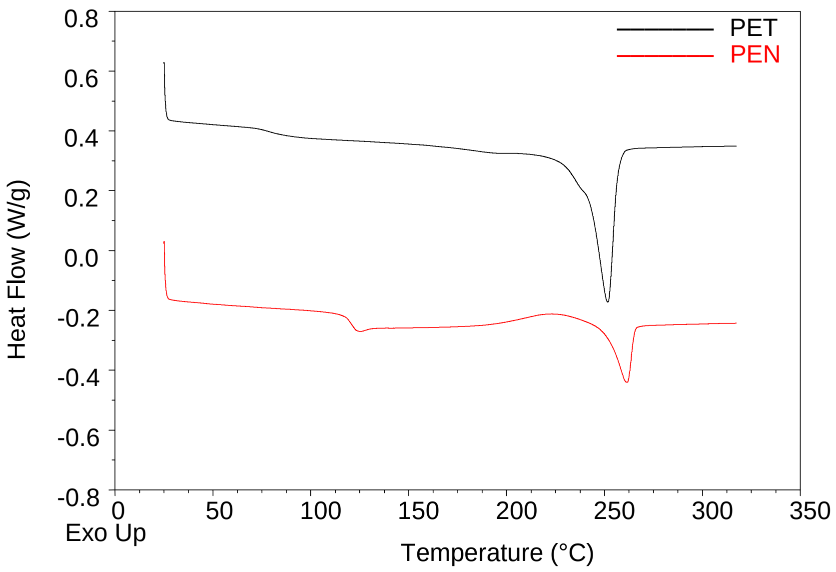


Figure 8.46 Thermal transitions in PET and PEN determined by DSC, heat-cool-reheat programme under N_2, cycle 3

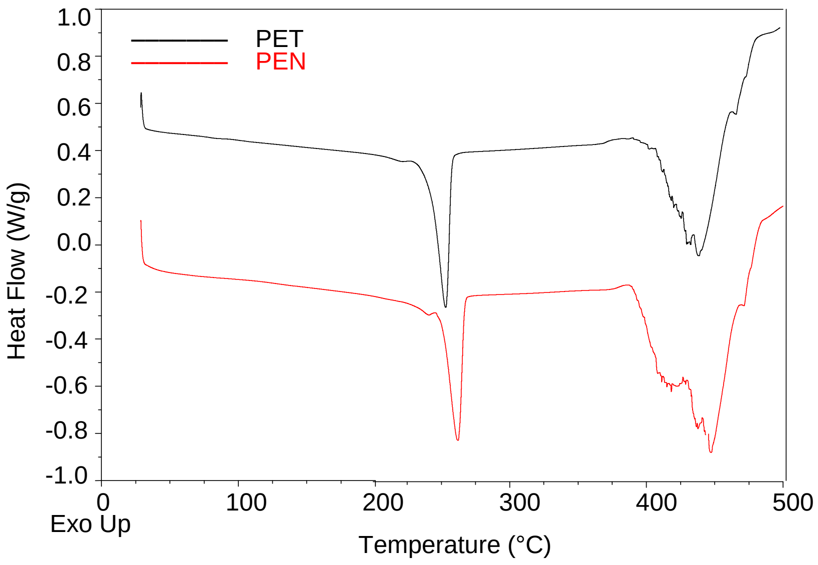


Figure 8.47 DSC degradation curves of PET and PEN in nitrogen, 30 - 500 °C, 10 °C min^{-1}

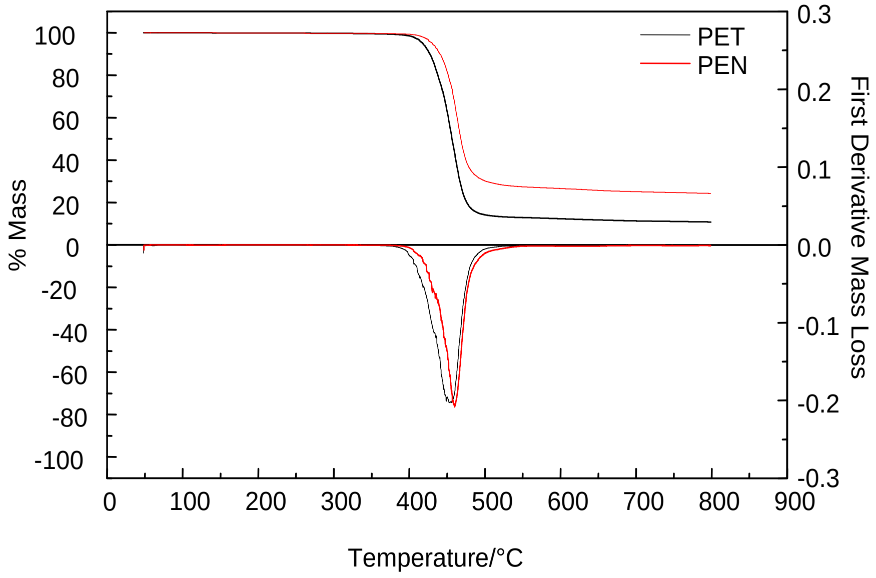


Figure 8.48 Thermogravimetry and differential thermogravimetry curves of PET and PEN in helium, 50 - 800 °C, 10 °C min^{-1}

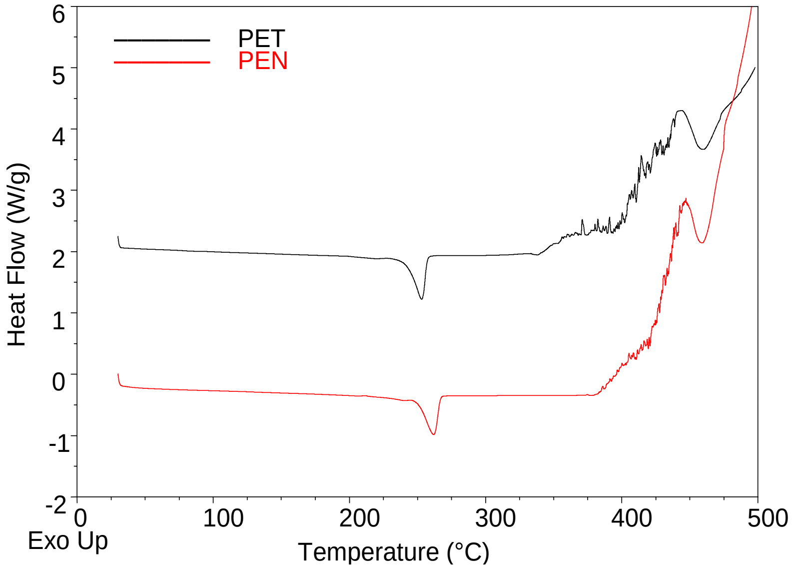


Figure 8.49 DSC degradation curves of PET and PEN in air, 30 - 500 °C, 10 °C min^{-1}

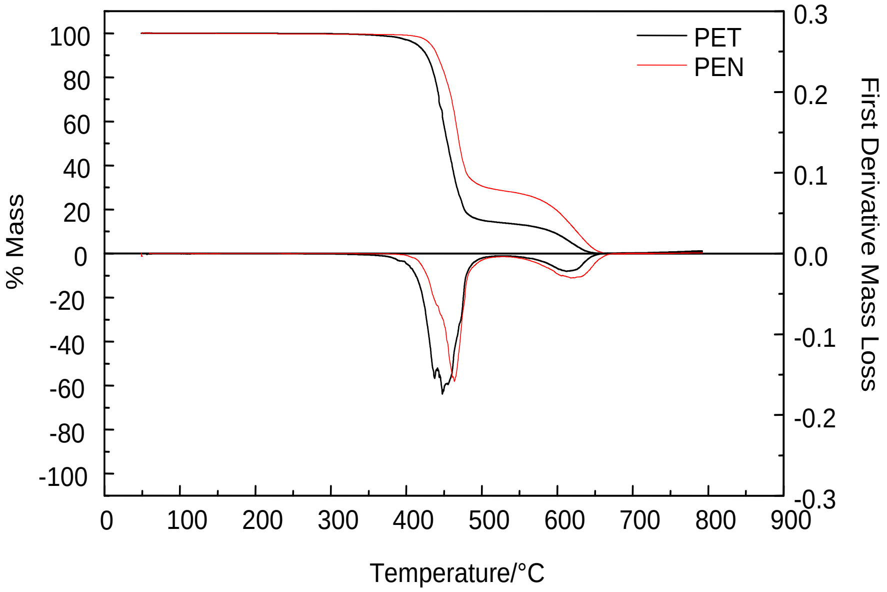


Figure 8.50 Thermogravimetry and differential thermogravimetry curves of PET and PEN in air, 50 - 800 °C, 10 °C min^{-1}

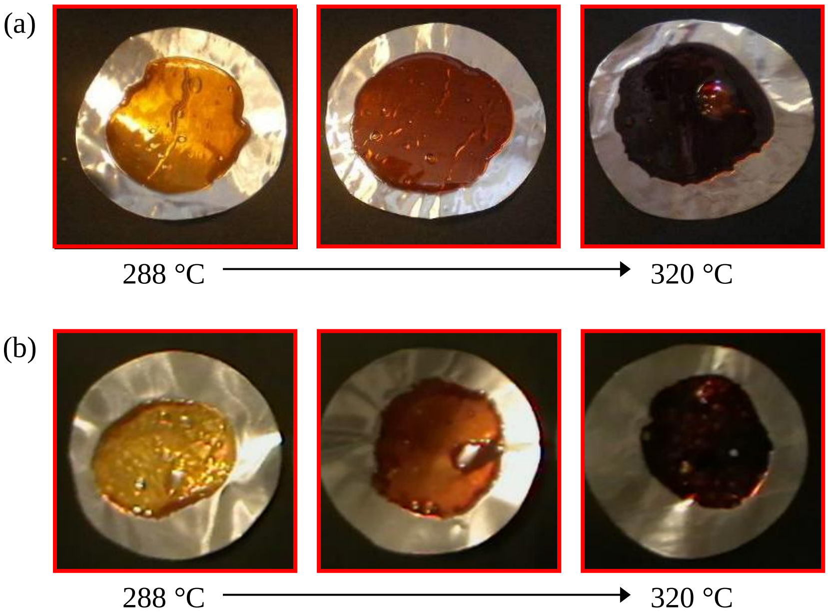


Figure 8.51 Residual film samples from (a) 125µm Q65FA coated PEN as supplied and (b) 125µm melt pressed Q71 uncoated PEN, aged in dry air for 4 hours

8.2.2 Volatilisation Studies of PET and PEN

8.2.2.1 Thermal and Thermal-Hydrolytic Volatilisation Studies

Polymer	*Ageing Temperature/^{o}C*	*Ageing Time/hours*	*% Volatilisation*
PET	288	1	0.4
PEN	288	1	0.3
PET	288	2	0.9
PEN	288	2	0.3
PET	288	4	1.2
PEN	288	4	0.6
PET	288	8	1.7
PEN	288	8	0.9
PET	288	24	5.8
PEN	288	24	2.4
PET	300	1	0.7
PEN	300	1	0.4
PET	300	2	1.2
PEN	300	2	0.5
PET	300	4	2.7
PEN	300	4	1.0
PET	300	8	3.6
PEN	300	8	1.6
PET	300	24	11.5
PEN	300	24	5.3
PET	320	1	2.5
PEN	320	1	1.2
PET	320	2	4.0
PEN	320	2	1.8
PET	320	4	8.1
PEN	320	4	4.2
PET	320	8	14.4
PEN	320	8	7.4
PET	320	24	38.4
PEN	320	24	20.4

Table 8.1 Volatilisation results for PET and PEN samples aged in dry nitrogen for 1 - 24 hours

Polymer	*Ageing Temperature/°C*	*Ageing Time/hours*	*% Volatilisation*
PET	288	1	0.5
PEN	288	1	0.4
PET	288	2	1.5
PEN	288	2	0.4
PET	288	4	2.1
PEN	288	4	1.1
PET	288	8	3.0
PEN	288	8	1.6
PET	288	24	13.6
PEN	288	24	5.1
PET	300	1	1.8
PEN	300	1	0.8
PET	300	2	2.7
PEN	300	2	0.7
PET	300	4	3.8
PEN	300	4	1.5
PET	300	8	4.3
PEN	300	8	3.5
PET	300	24	22.4
PEN	300	24	11.7
PET	320	1	1.3
PEN	320	1	1.9
PET	320	2	10.4
PEN	320	2	3.3
PET	320	4	11.2
PEN	320	4	6.2
PET	320	8	24.7
PEN	320	8	12.7
PET	320	24	50.4
PEN	320	24	36.1

Table 8.2 Volatilisation results for PET and PEN samples aged in wet (1.5 – 2% AH) nitrogen for 1 - 24 hours

8.2.2.2 Thermo-Oxidative and Thermo-Oxidative-Hydrolytic Volatilisation Studies

Polymer	*Ageing Temperature/°C*	*Ageing Time/hours*	*% Volatilisation*
PET	288	1	6.0
PEN	288	1	0.6
PET	288	2	13.9
PEN	288	2	0.7
PET	288	4	26.1
PEN	288	4	1.0
PET	288	8	36.0
PEN	288	8	1.7
PET	288	24	58.5
PEN	288	24	9.9
PET	300	1	18.4
PEN	300	1	0.6
PET	300	2	25.8
PEN	300	2	1.0
PET	300	4	28.5
PEN	300	4	2.4
PET	300	8	44.7
PEN	300	8	4.6
PET	300	24	62.4
PEN	300	24	18.7
PET	320	1	16.1
PEN	320	1	1.9
PET	320	2	25.4
PEN	320	2	2.9
PET	320	4	35.7
PEN	320	4	5.1
PET	320	8	43.5
PEN	320	8	15.6
PET	320	24	74.4
PEN	320	24	38.3

Table 8.3 Volatilisation results for PET and PEN samples aged in dry air for 1 - 24 hours

Polymer	*Ageing Temperature/^{o}C*	*Ageing Time/hours*	*% Volatilisation*
PET	288	1	6.7
PEN	288	1	0.6
PET	288	2	16.2
PEN	288	2	0.8
PET	288	4	24.8
PEN	288	4	1.4
PET	288	8	33.1
PEN	288	8	2.9
PET	288	24	60.5
PEN	288	24	10.9
PET	300	1	18.9
PEN	300	1	0.7
PET	300	2	24.9
PEN	300	2	1.1
PET	300	4	31.7
PEN	300	4	3.1
PET	300	8	49.2
PEN	300	8	6.0
PET	300	24	67.5
PEN	300	24	21.2
PET	320	1	22.9
PEN	320	1	3.5
PET	320	2	28.9
PEN	320	2	5.0
PET	320	4	38.8
PEN	320	4	11.0
PET	320	8	48.6
PEN	320	8	20.6
PET	320	24	85.9
PEN	320	24	40.0

Table 8.4 Volatilisation results for PET and PEN samples aged in wet (1.5 – 2% AH) air for 1 - 24 hours

8.2.3 ATR-FTIR Analysis of Gel Samples of PET and PEN

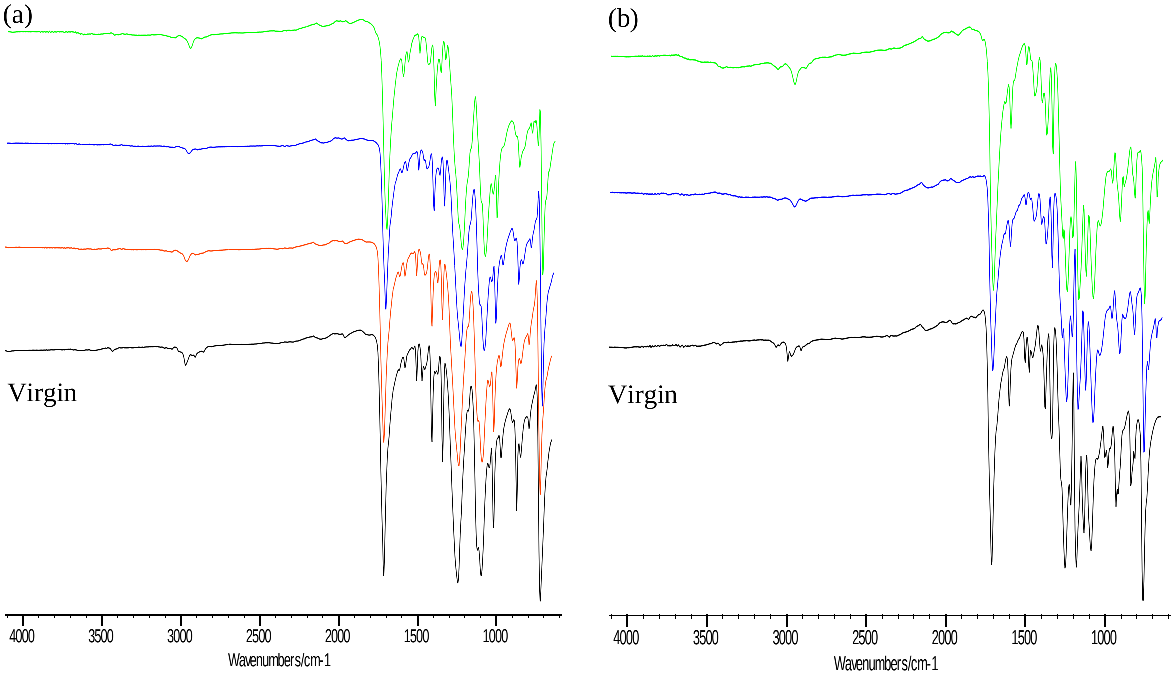


Figure 8.52 ATR spectra for (a) PET and (b) PEN gels aged at 320 °C in dry 3% oxygen, dry air and dry 42% oxygen for 4 hours

1

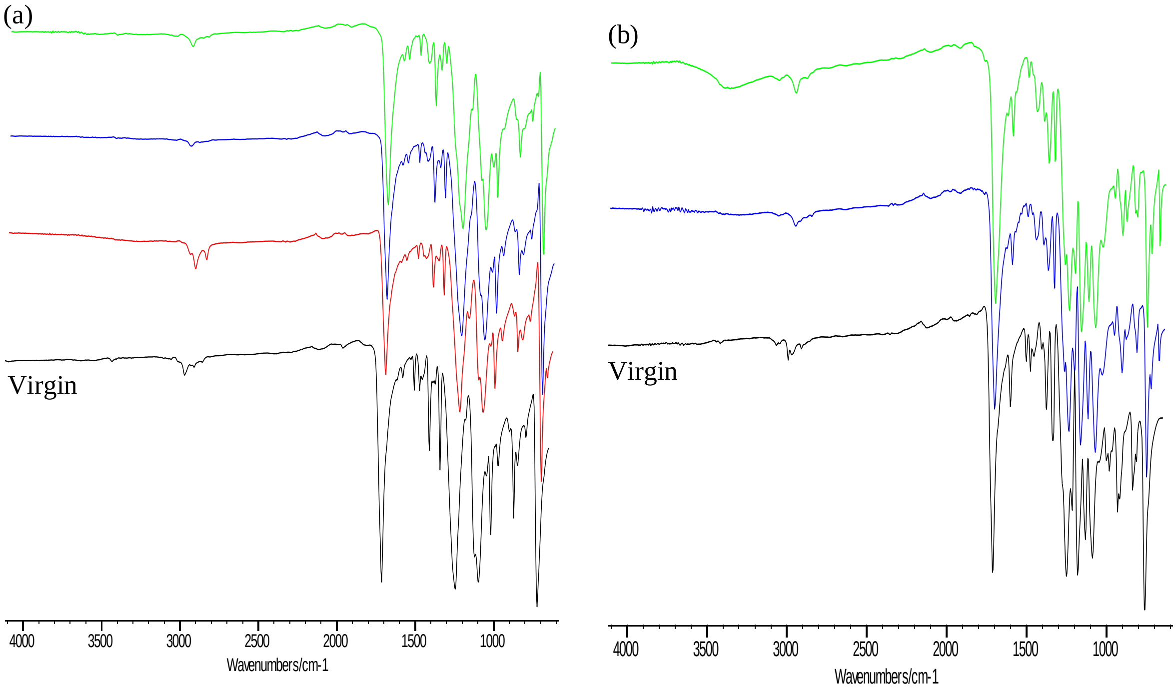


Figure 8.53 ATR spectra for (a) PET and (b) PEN gels aged at 320 °C in wet 3% oxygen, wet air and wet 42% oxygen for 4 hours

Ageing Environment	*Ageing Temperature/°C*	*% Volatile Products*	*% Gel Products*	*% Soluble Products*
Dry 3% oxygen	288	3.2	36.1	60.7
Dry air	288	26.1	37.7	36.2
Dry 42% oxygen	288	45.1	40.5	14.4
Dry 3% oxygen	300	5.3	57.8	36.9
Dry air	300	28.5	55.0	16.5
Dry 42% oxygen	300	53.0	39.4	7.6
Dry 3% oxygen	320	13.6	67.8	18.6
Dry air	320	35.7	55.0	9.3
Dry 42% oxygen	320	68.7	30.1	1.2

Table 8.5 Overall summary of degradation products in PET aged in dry oxidative environments for 4 hours

Ageing Environment	*Ageing Temperature/°C*	*% Volatile Products*	*% Gel Products*	*% Soluble Products*
Dry 3% oxygen	288	0.8	11.8	87.4
Dry air	288	1.0	65.4	33.6
Dry 42% oxygen	288	1.2	81.7	17.1
Dry 3% oxygen	300	1.4	11.0	87.6
Dry air	300	2.4	77.4	20.2
Dry 42% oxygen	300	3.2	82.9	13.9
Dry 3% oxygen	320	4.7	35.8	59.5
Dry air	320	5.1	87.9	7.0
Dry 42% oxygen	320	10.3	85.3	4.4

Table 8.6 Overall summary of degradation products in PEN aged in dry oxidative environments for 4 hours

Ageing Environment	*Ageing Temperature/°C*	*% Volatile Products*	*% Gel Products*	*% Soluble Products*
Wet 3% oxygen	288	4.7	35.3	60.0
Wet air	288	24.8	13.3	61.9
Wet 42% oxygen	288	66.9	29.4	3.7
Wet 3% oxygen	300	6.6	39.9	53.5
Wet air	300	31.7	29.7	38.6
Wet 42% oxygen	300	68.7	29.3	2.0
Wet 3% oxygen	320	15.3	55.1	29.6
Wet air	320	38.8	46.4	14.8
Wet 42% oxygen	320	70.4	29.5	0.1

Table 8.7 Overall summary of degradation products in PET aged in wet (1.5 – 2% AH) oxidative environments for 4 hours

Ageing Environment	*Ageing Temperature/°C*	*% Volatile Products*	*% Gel Products*	*% Soluble Products*
Wet 3% oxygen	288	0.9	9.9	89.2
Wet air	288	1.4	11.2	87.4
Wet 42% oxygen	288	1.8	66.0	32.2
Wet 3% oxygen	300	1.7	8.5	89.8
Wet air	300	3.1	49.5	47.4
Wet 42% oxygen	300	3.6	82.3	14.1
Wet 3% oxygen	320	7.3	5.7	87.0
Wet air	320	11.0	74.3	14.7
Wet 42% oxygen	320	15.1	84.8	0.1

Table 8.8 Overall summary of degradation products in PEN aged in wet (1.5 – 2% AH) oxidative environments for 4 hours

8.2.4 Carboxyl End Group Determination of Aged Samples of PET and PEN

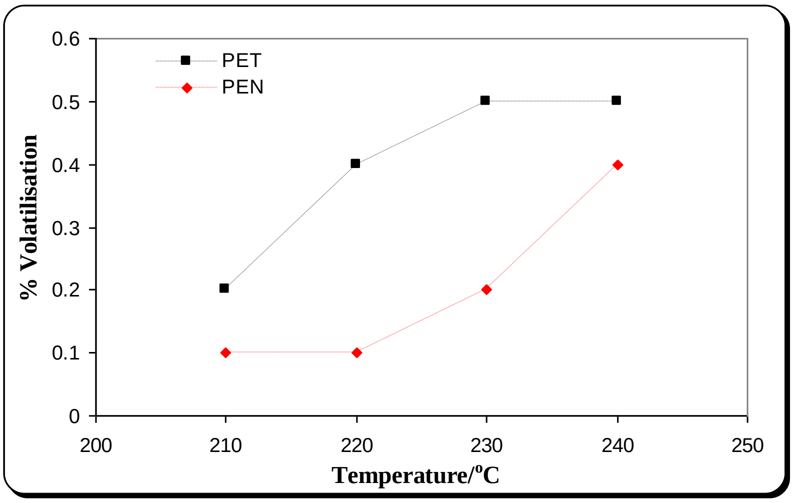


Figure 8.54 Volatilisation results for PET and PEN samples aged at solid-state polymerisation temperatures between 210 °C and 240 °C in dry nitrogen for 4 hours

Polymer	*Ageing Temperature (°C)*	*% Volatilisation*	*[COOH] (equiv. per 10^6 grams)*
PET	Virgin	N/A	42.8 ± 1.9
PEN	Virgin	N/A	34.7 ± 3.1
PET	210	0.2	42.2 ± 2.2
PEN	210	0.1	29.7 ± 2.1
PET	220	0.4	39.9 ± 3.5
PEN	220	0.1	28.1 ± 3.4
PET	230	0.5	34.9 ± 2.6
PEN	230	0.2	22.8 ± 1.9
PET	240	0.5	31.7 ± 2.9
PEN	240	0.4	22.9 ± 2.4

Table 8.9 Summary of volatilisation results and carboxyl end group concentration for PET and PEN samples aged at solid-state polymerisation temperatures between 210 °C and 240 °C in dry nitrogen for 4 hours

8.2.5 ^{13}C Solid-State NMR Structural Analysis of Aged Samples of PET and PEN

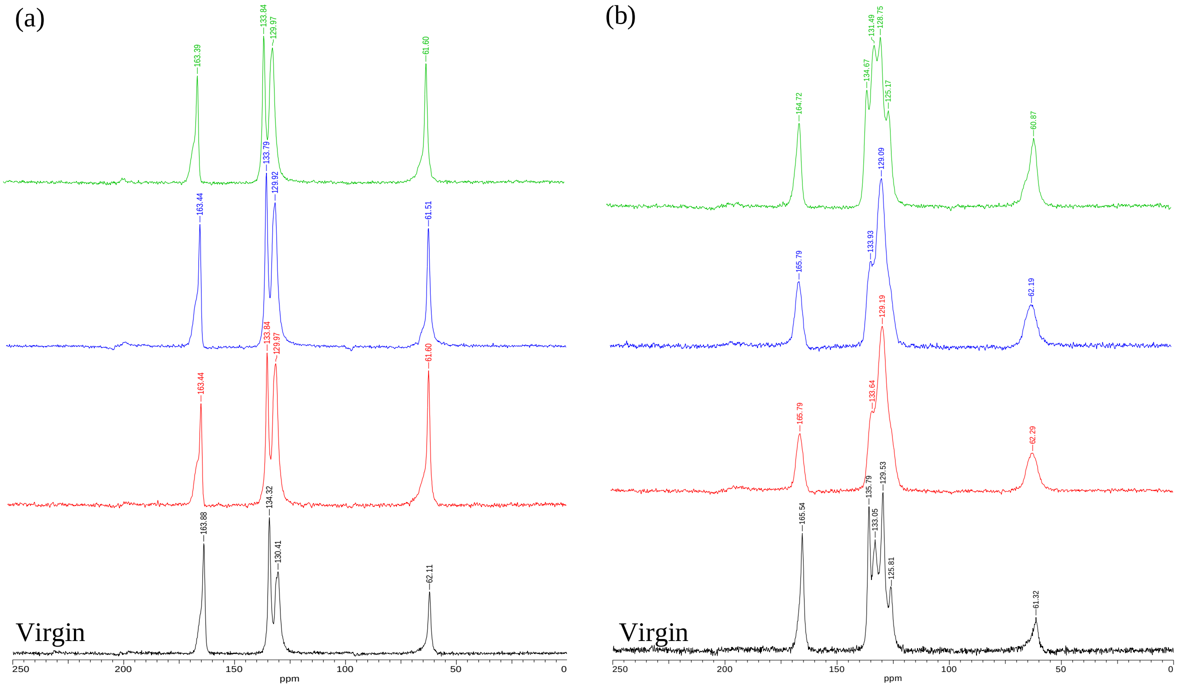


Figure 8.55 ^{13}C solid-state NMR spectra for (a) PET and (b) PEN samples aged in wet (1.5 - 2% AH) nitrogen at 288 °C, 300 °C and 320 °C for 4 hours

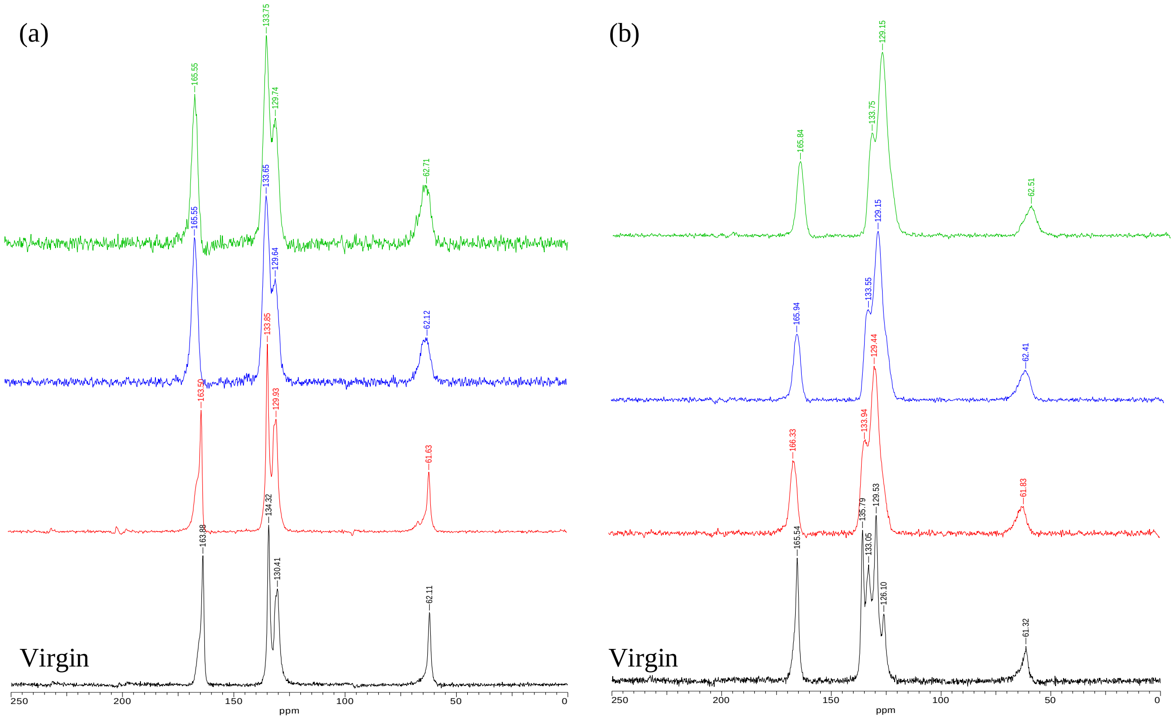


Figure 8.56 ^{13}C solid – state NMR spectra for (a) PET and (b) PEN samples aged in wet (1.5 - 2% AH) air at 288 °C, 300 °C and 320 °C for 4 hours

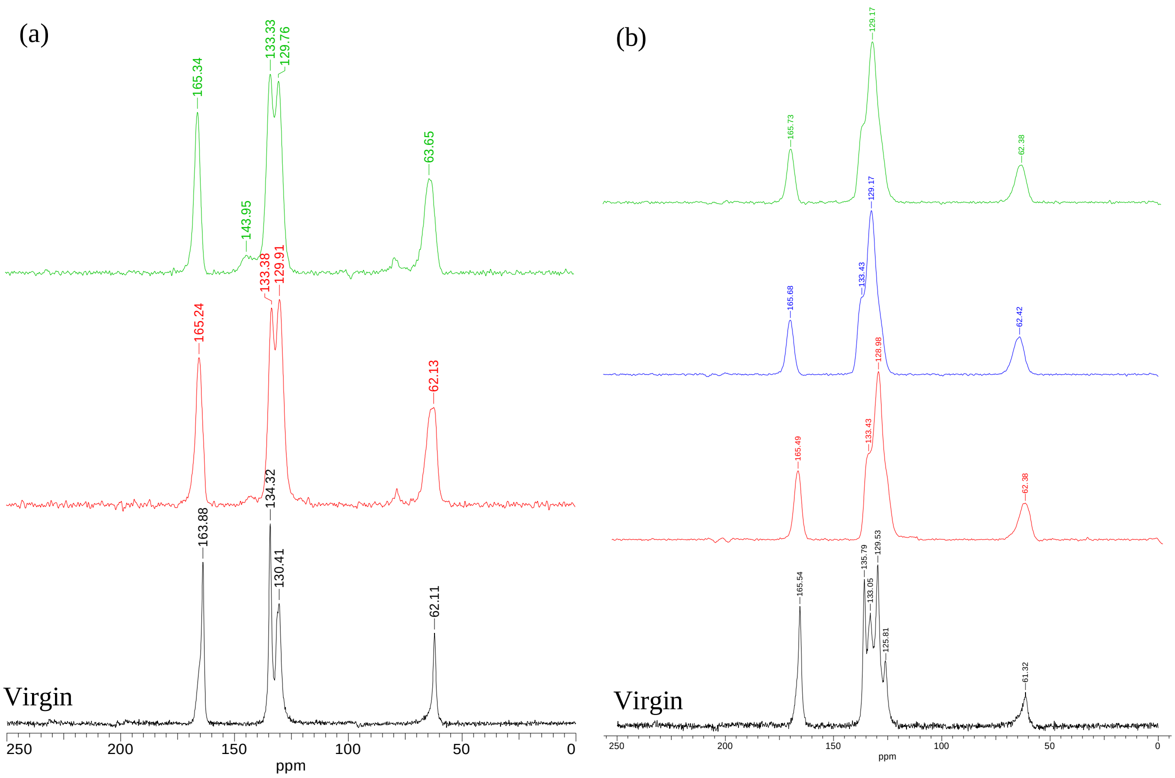


Figure 8.57 ^{13}C solid-state NMR spectra for (a) PET and (b) PEN samples aged in wet (1.5 – 2% AH) 42% oxygen for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

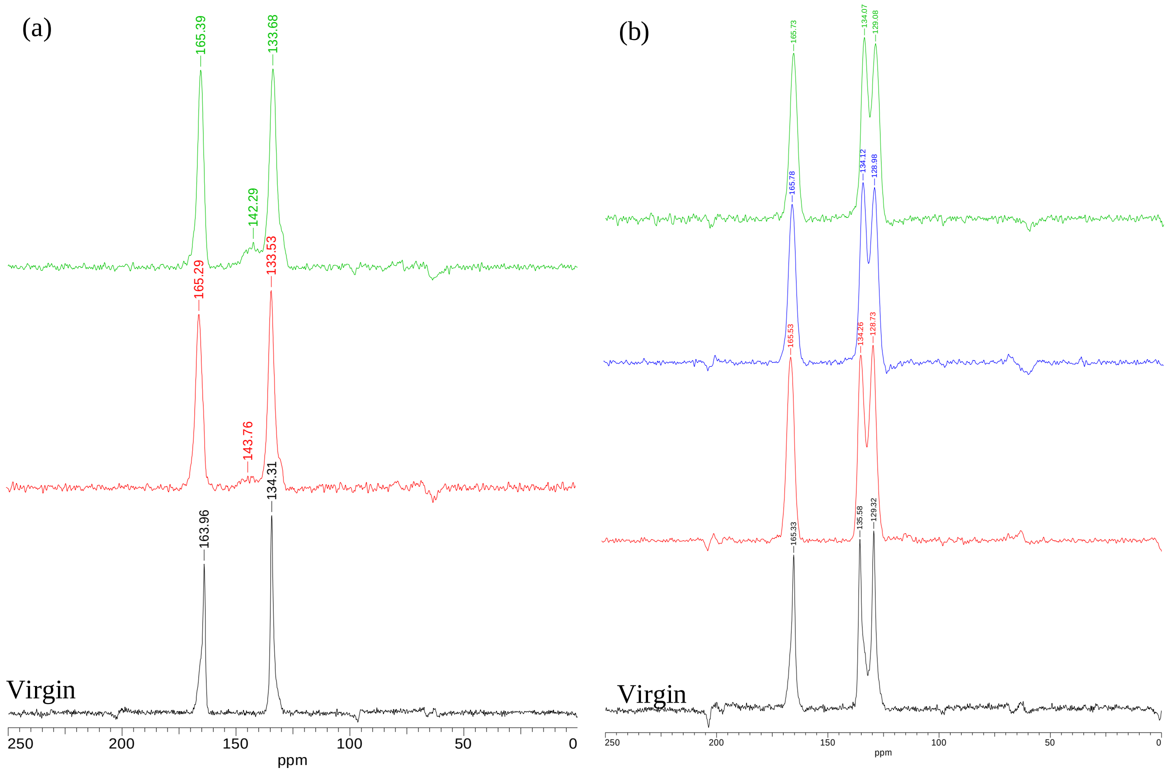


Figure 8.58 Dipolar dephased ^{13}C solid-state NMR spectra for (a) PET and (b) PEN samples aged in wet (1.5 – 2% AH) 42% oxygen for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

8.2.6 ATR-FTIR Analysis of Aged Samples of PET and PEN

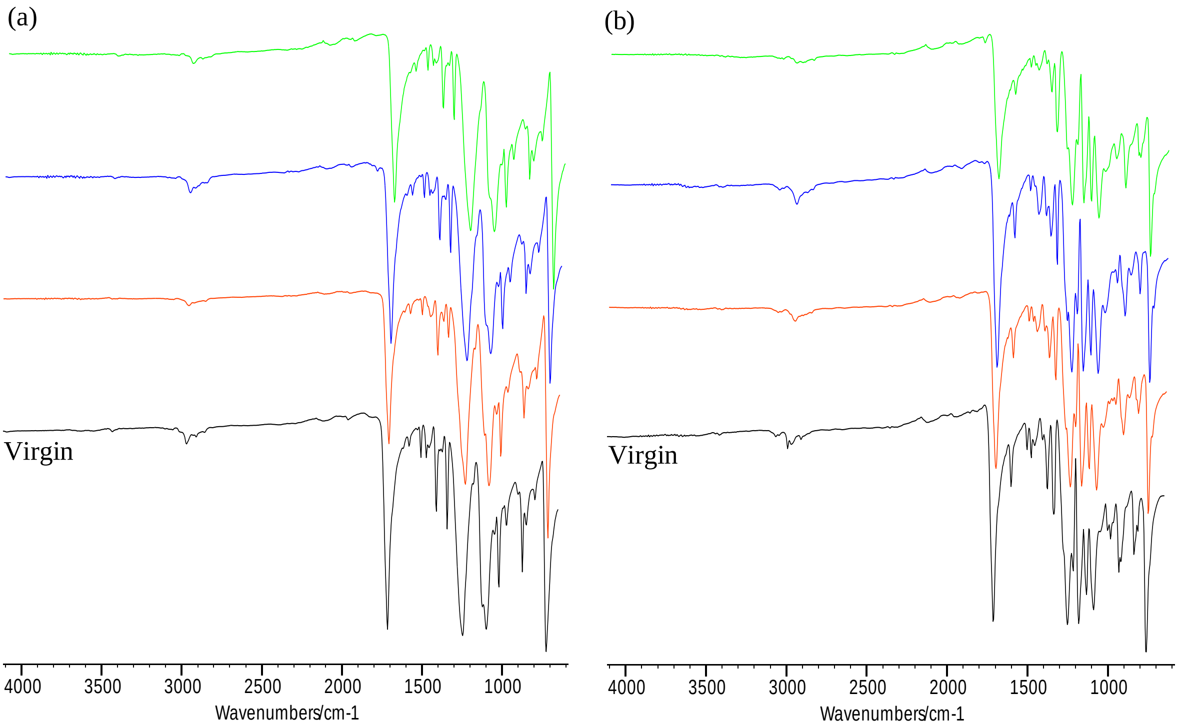


Figure 8.59 ATR spectra for (a) PET and (b) PEN samples aged in dry nitrogen for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

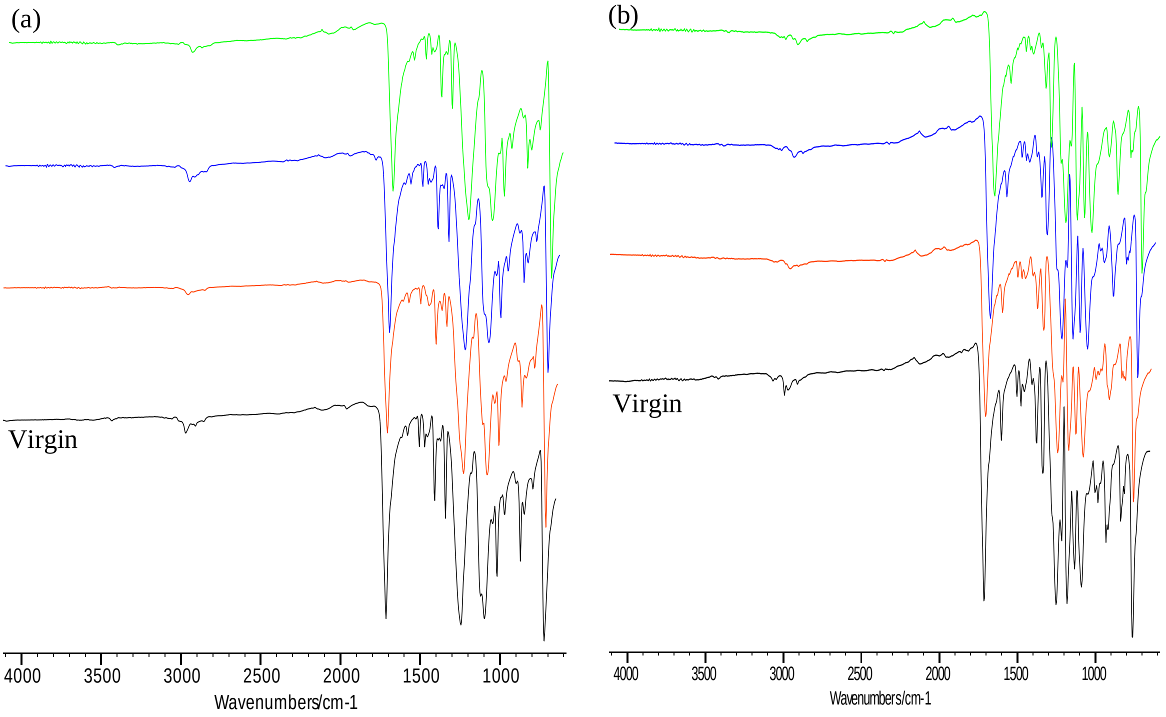


Figure 8.60 ATR spectra for (a) PET and (b) PEN samples aged in wet (1.5 – 2% AH) nitrogen for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

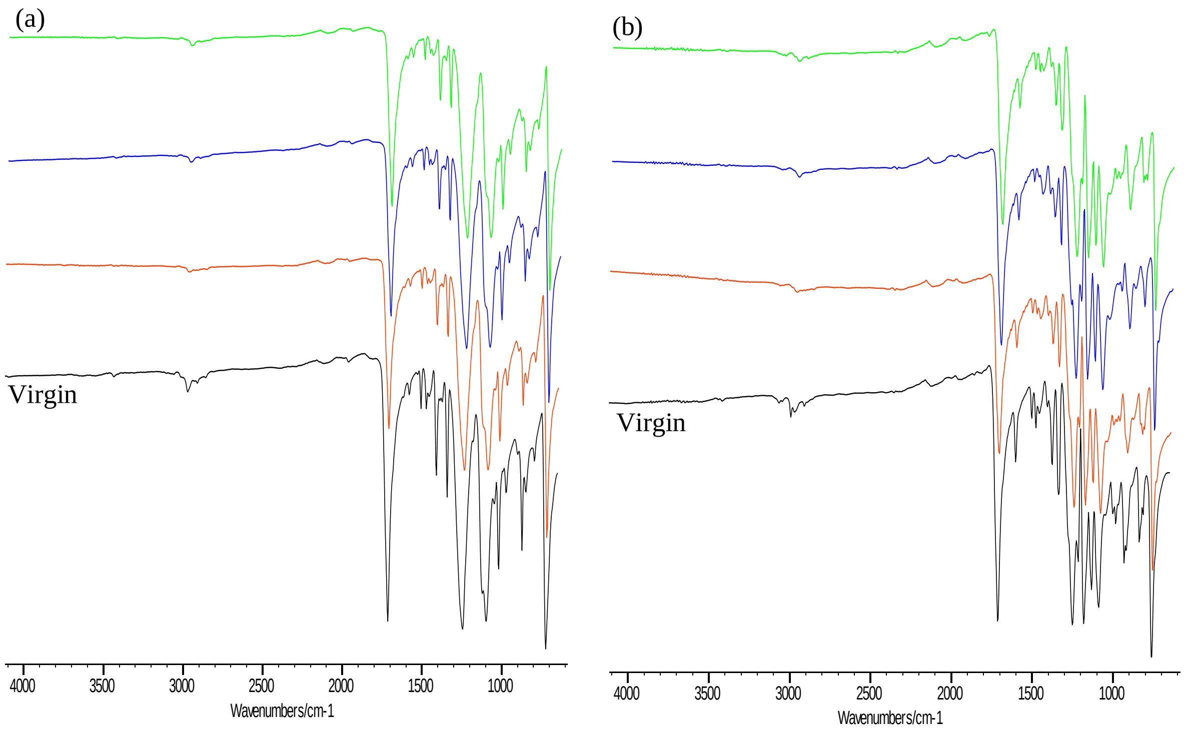


Figure 8.61 ATR spectra for (a) PET and (b) PEN samples aged in dry 3% oxygen for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

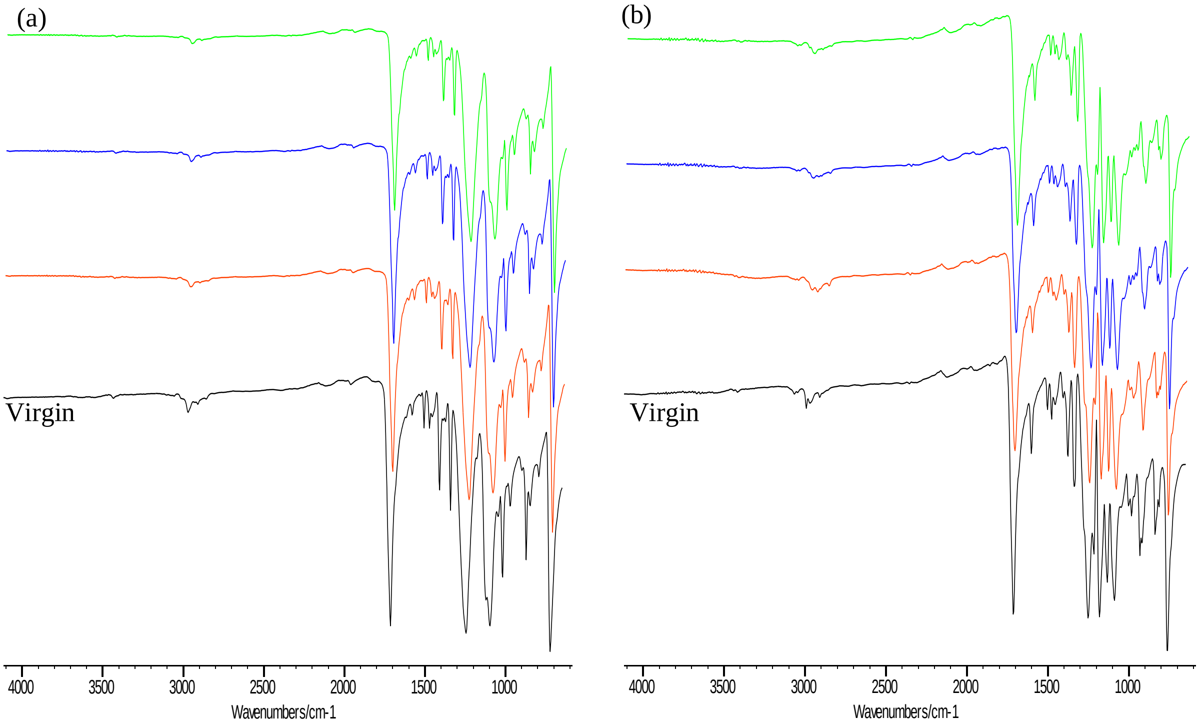


Figure 8.62 ATR spectra for (a) PET and (b) PEN samples aged in wet (1.5 – 2% AH) 3% oxygen for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

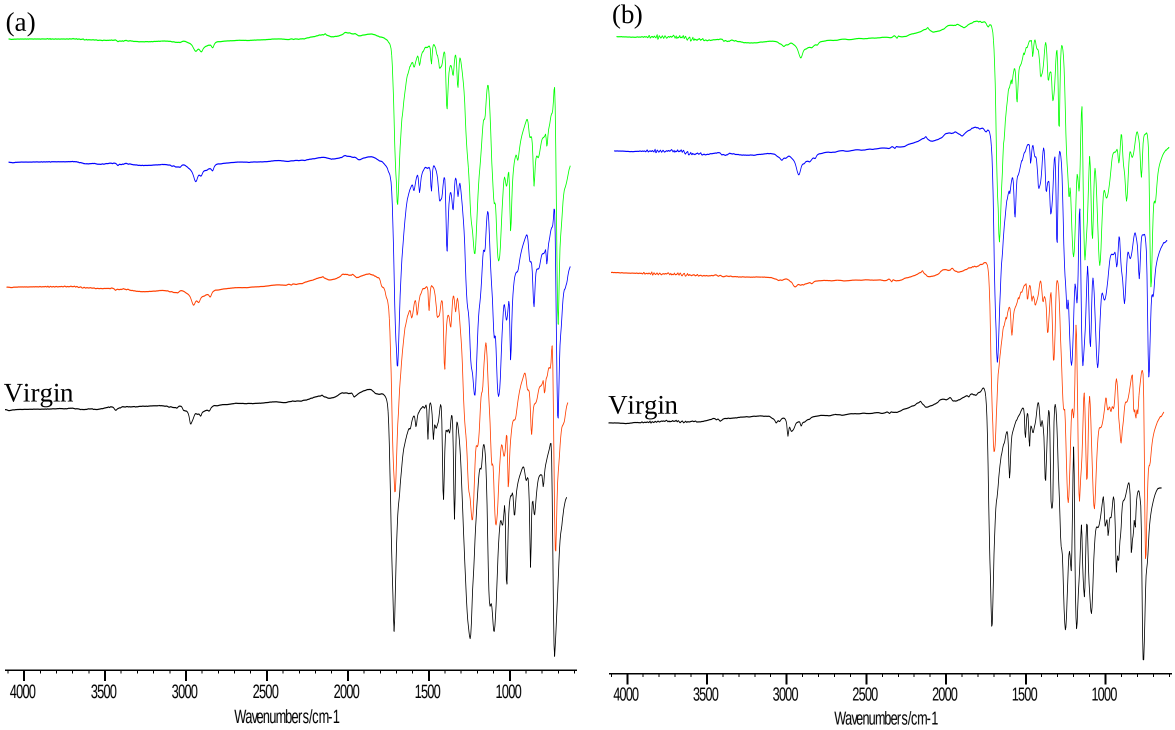


Figure 8.63 ATR spectra for (a) PET and (b) PEN samples aged in dry air for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

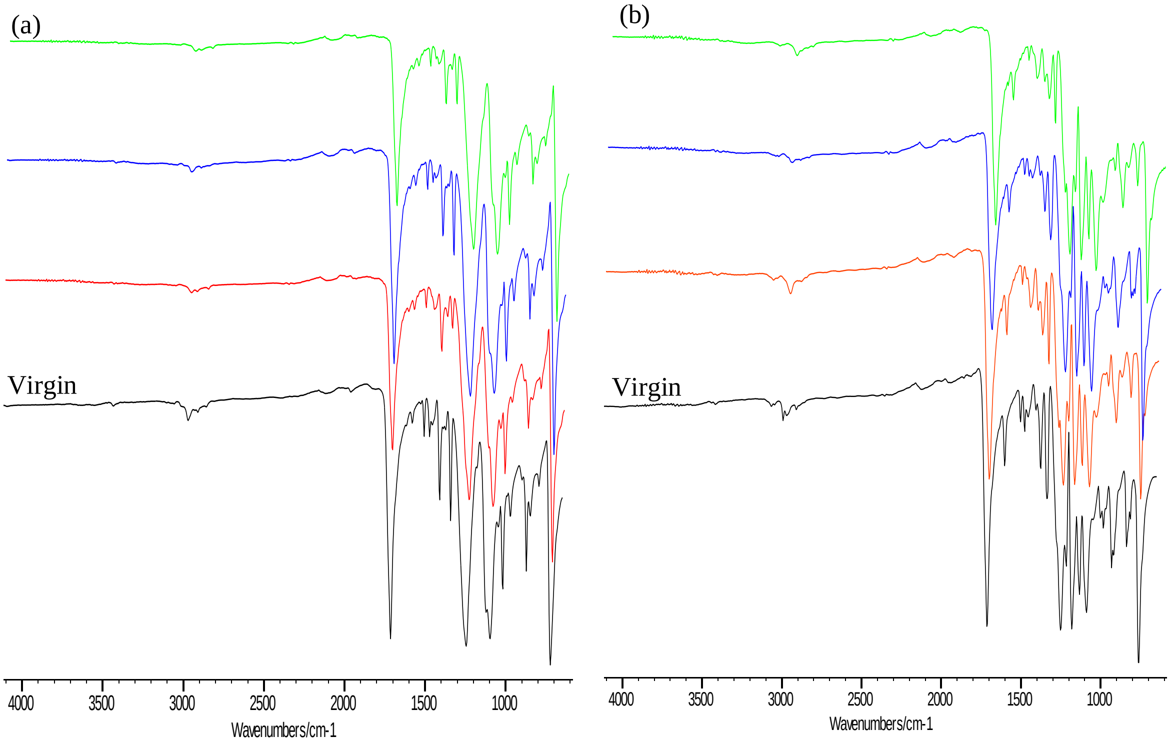


Figure 8.64 ATR spectra for (a) PET and (b) PEN samples aged in wet (1.5 – 2% AH) air for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

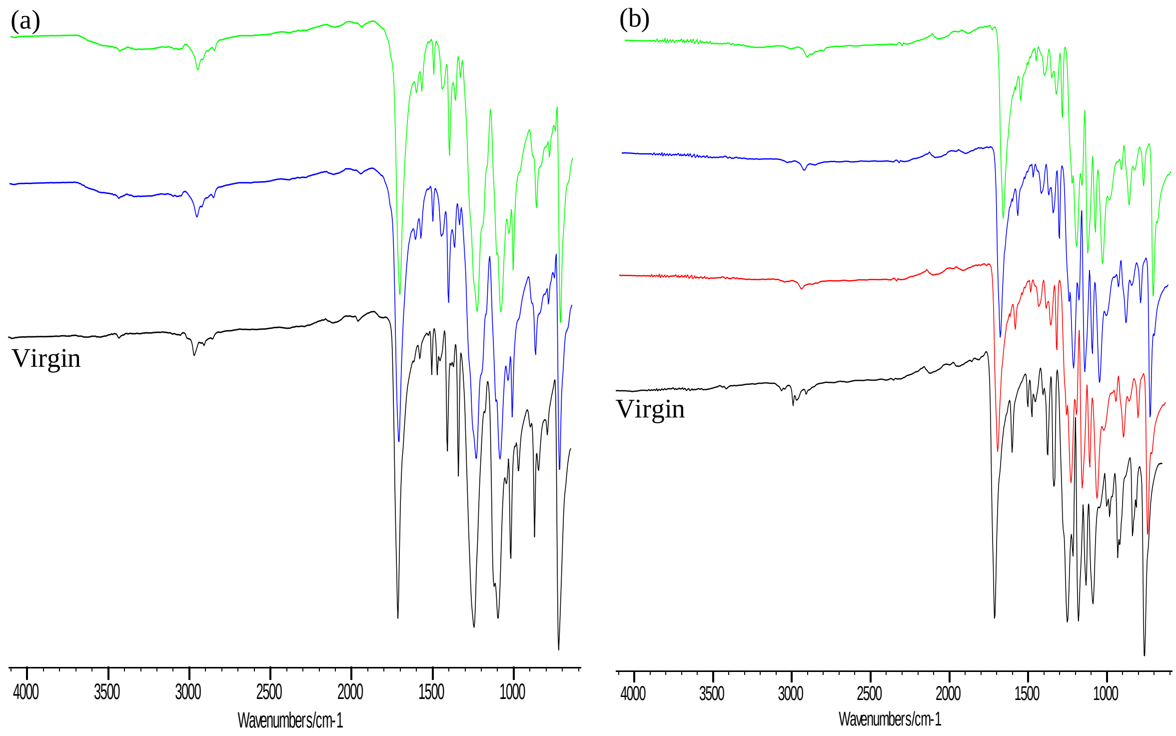


Figure 8.65 ATR spectra for (a) PET and (b) PEN samples aged in dry 42% oxygen for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

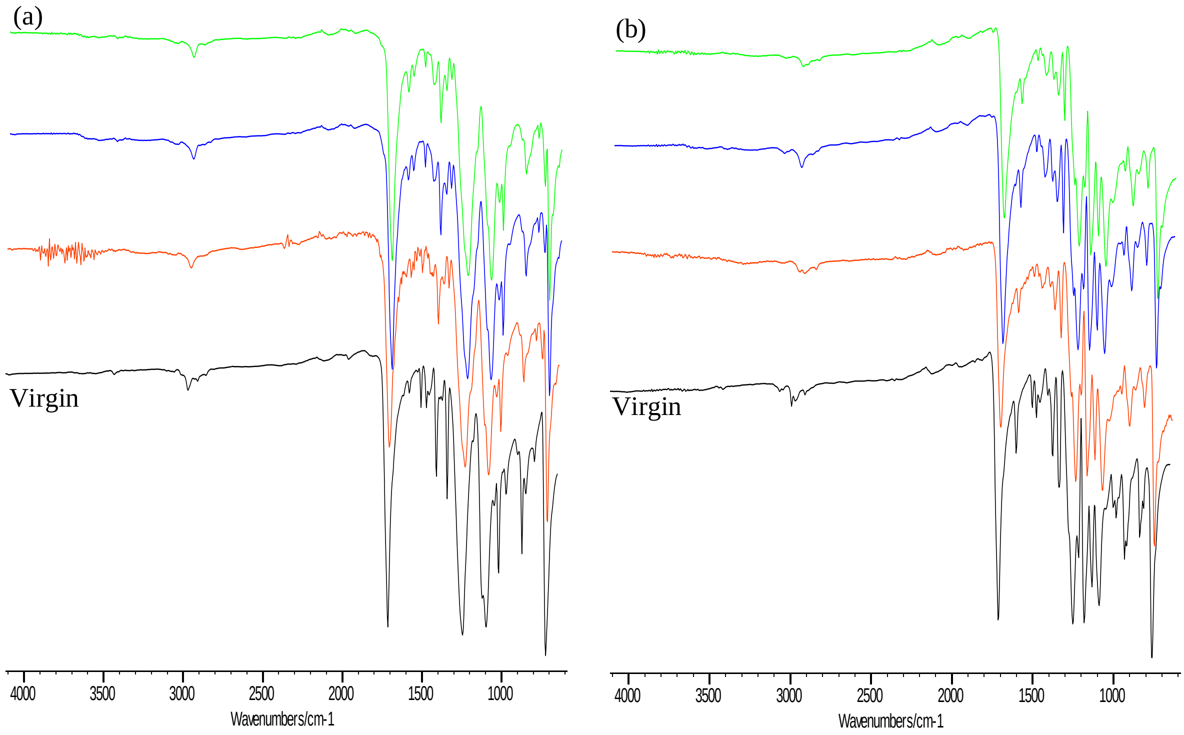


Figure 8.66 ATR spectra for (a) PET and (b) PEN samples aged in wet (1.5 – 2% AH) 42% oxygen for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

8.2.7 FTIR Analysis of Aged Samples of Solvent Cast PET and PEN Films

8.2.7.1 Residual Samples Aged Under Thermal Conditions

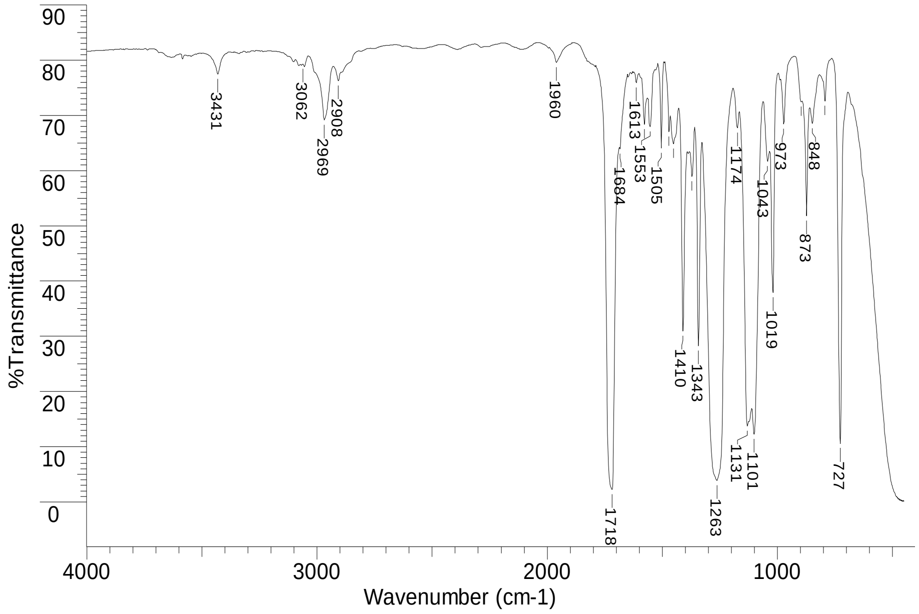


Figure 8.67 IR spectra for solvent cast PET samples aged in dry nitrogen for 4 hours at 288 °C for 4 hours

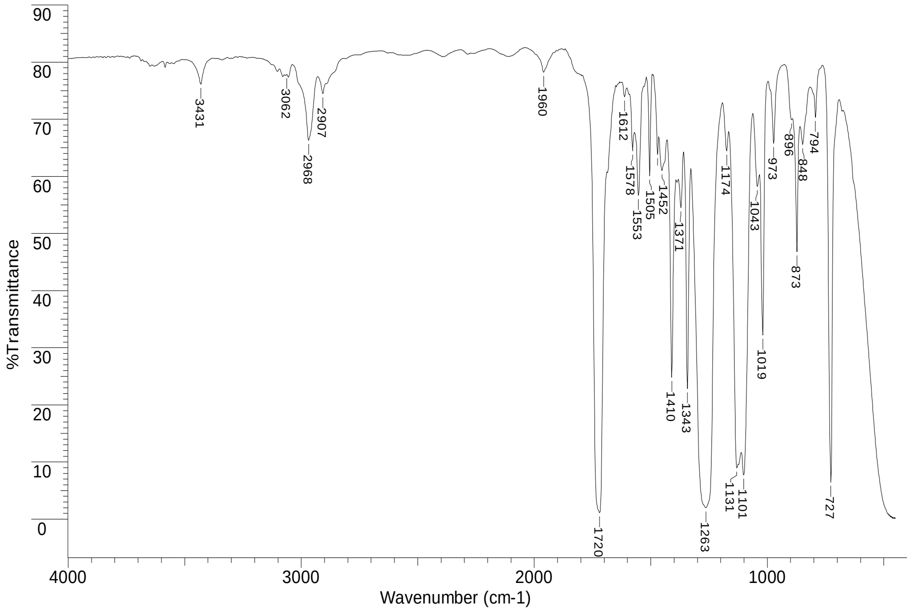


Figure 8.68 IR spectra for solvent cast PET samples aged in dry nitrogen for 4 hours at 300 °C for 4 hours

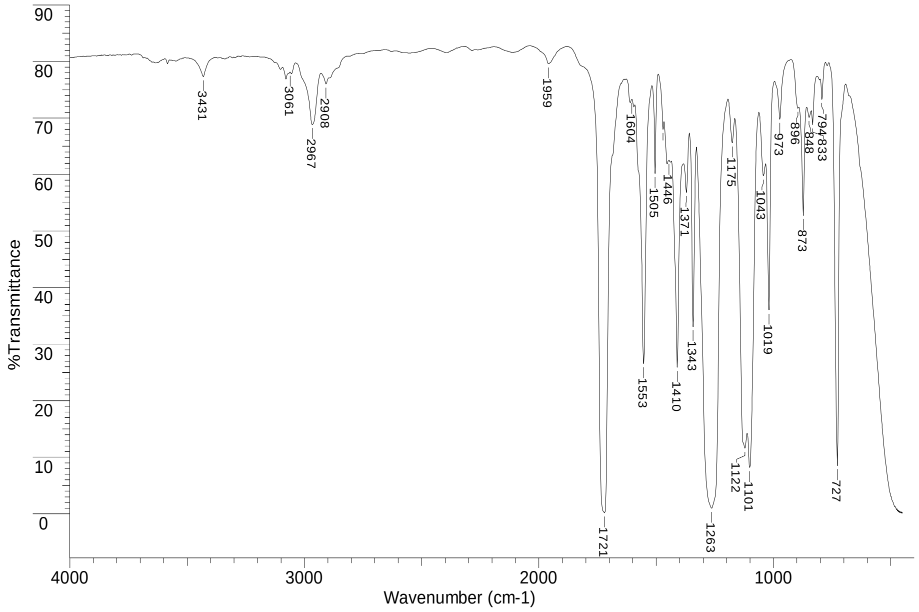


Figure 8.69 IR spectra for solvent cast PET samples aged in dry nitrogen for 4 hours at 320 °C for 4 hours

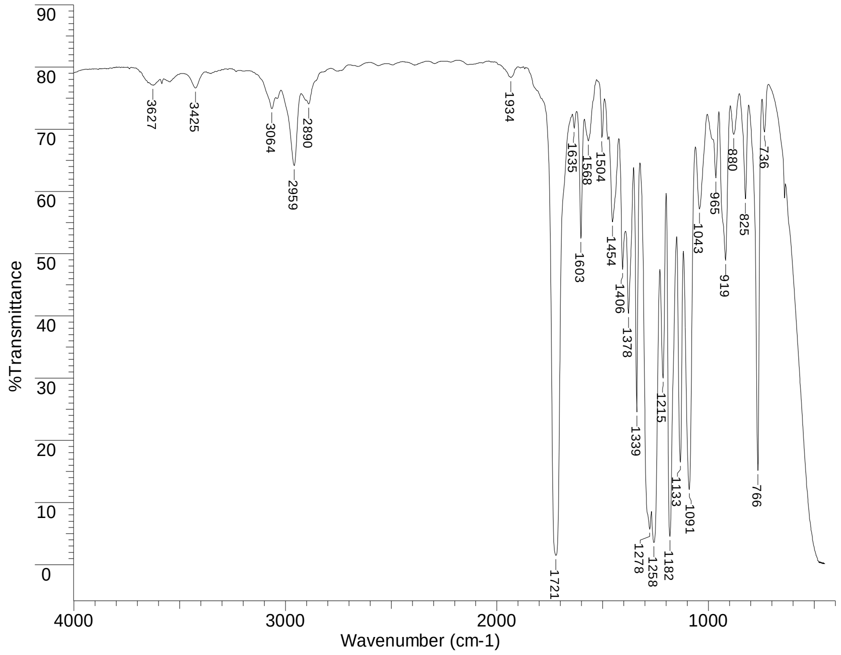


Figure 8.70 IR spectra for solvent cast PEN samples aged in dry nitrogen for 4 hours at 288 °C for 4 hours

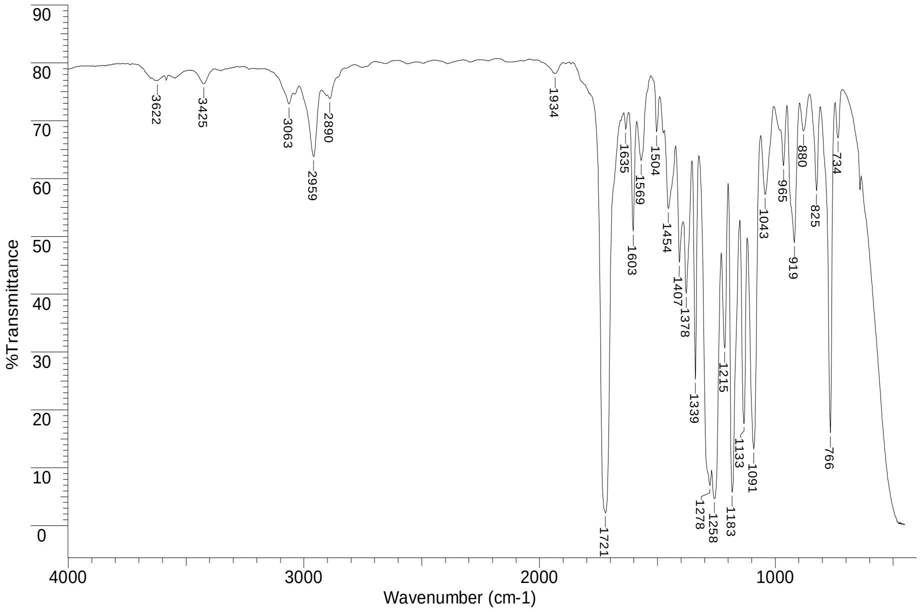


Figure 8.71 IR spectra for solvent cast PEN samples aged in dry nitrogen for 4 hours at 300 °C for 4 hours

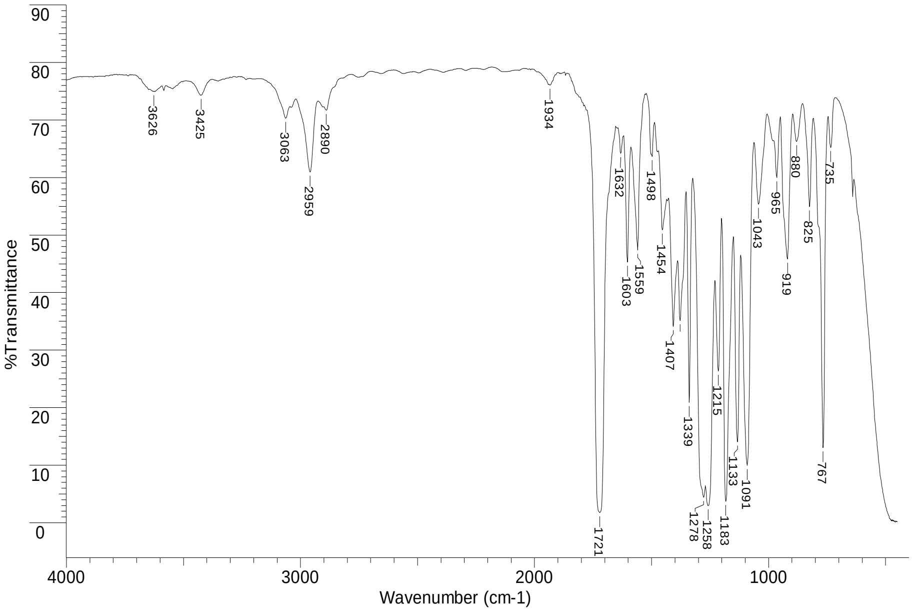


Figure 8.72 IR spectra for solvent cast PEN samples aged in dry nitrogen for 4 hours at 320 °C for 4 hours

8.2.7.2 Residual Samples Aged Under Thermal-Hydrolytic Conditions

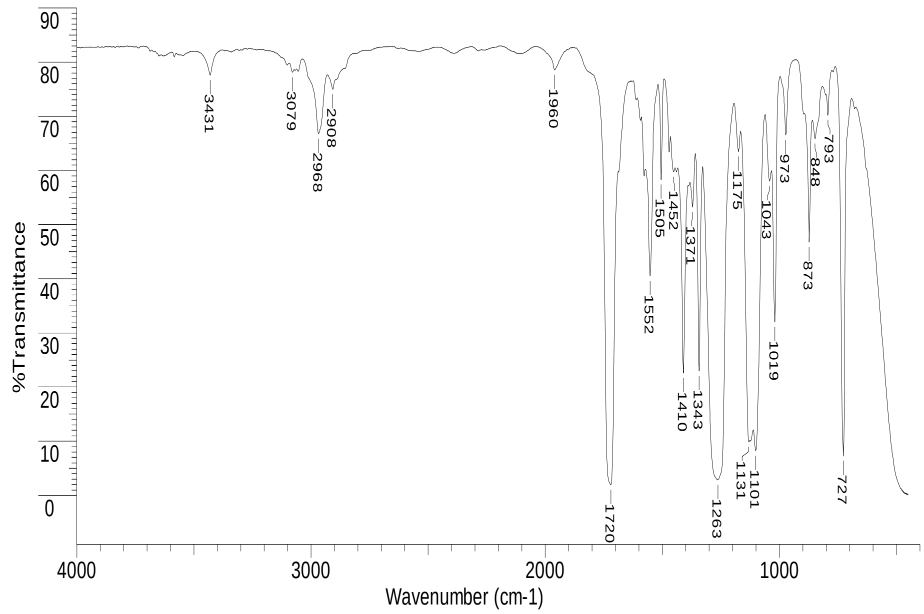


Figure 8.73 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) nitrogen for 4 hours at 288 °C for 4 hours

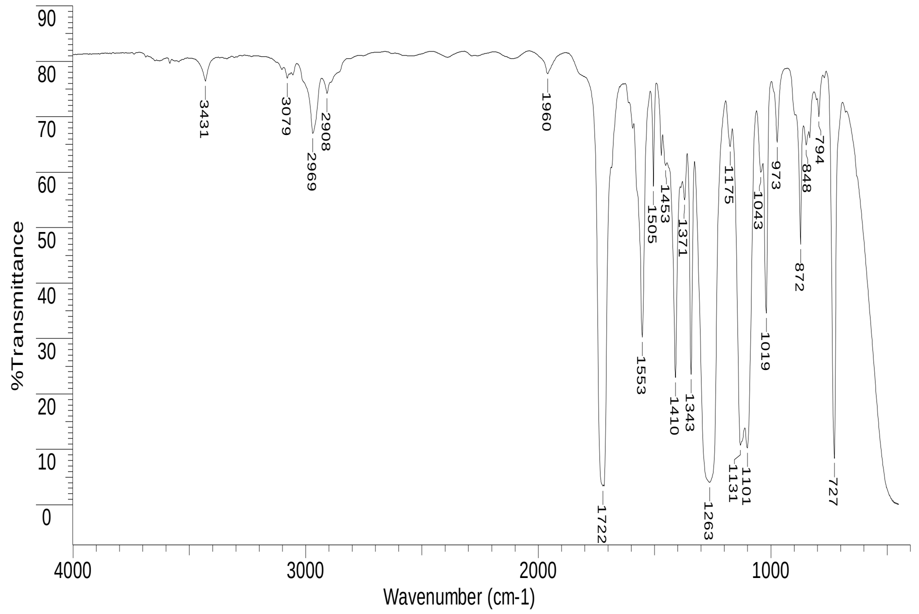


Figure 8.74 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) nitrogen for 4 hours at 300 °C for 4 hours

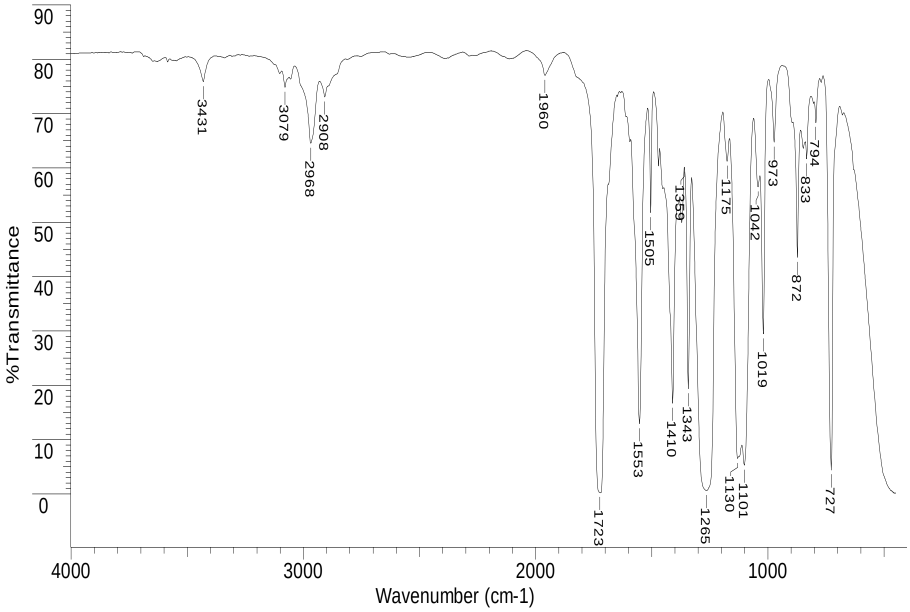


Figure 8.75 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) nitrogen for 4 hours at 320 °C for 4 hours

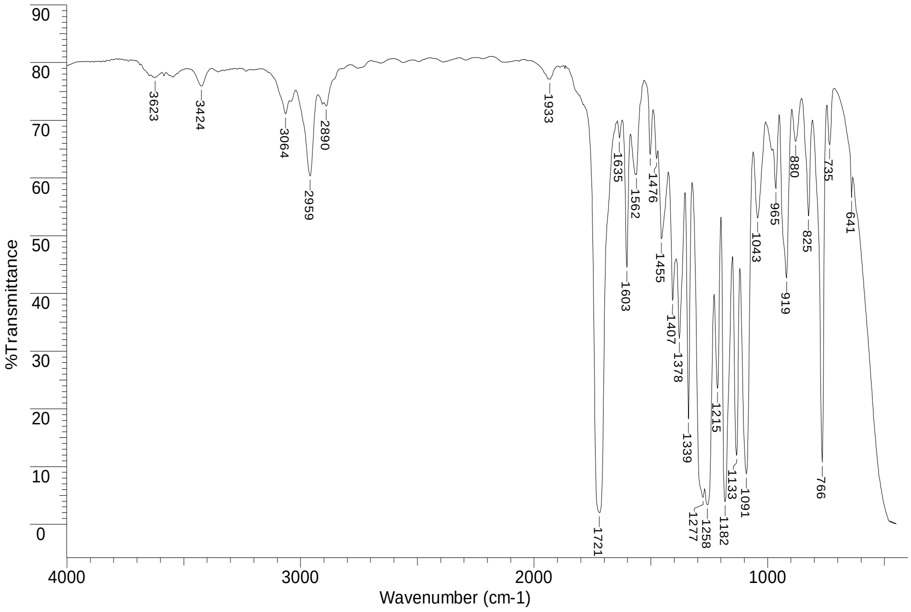


Figure 8.76 IR spectra for solvent cast PEN samples aged in wet (1.5 – 2% AH) nitrogen for 4 hours at 288 °C for 4 hours

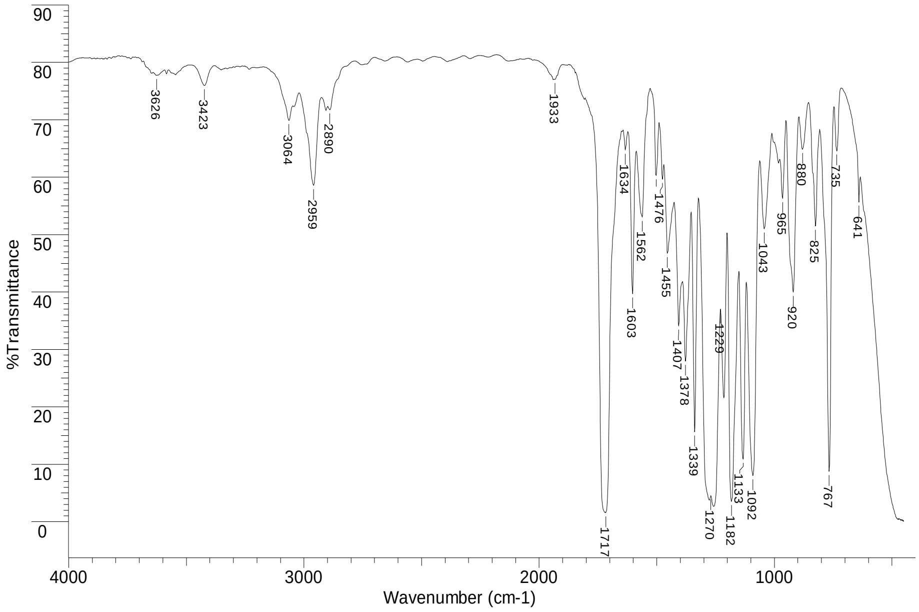


Figure 8.77 IR spectra for solvent cast PEN samples aged in wet (1.5 – 2% AH) nitrogen for 4 hours at 300 °C for 4 hours

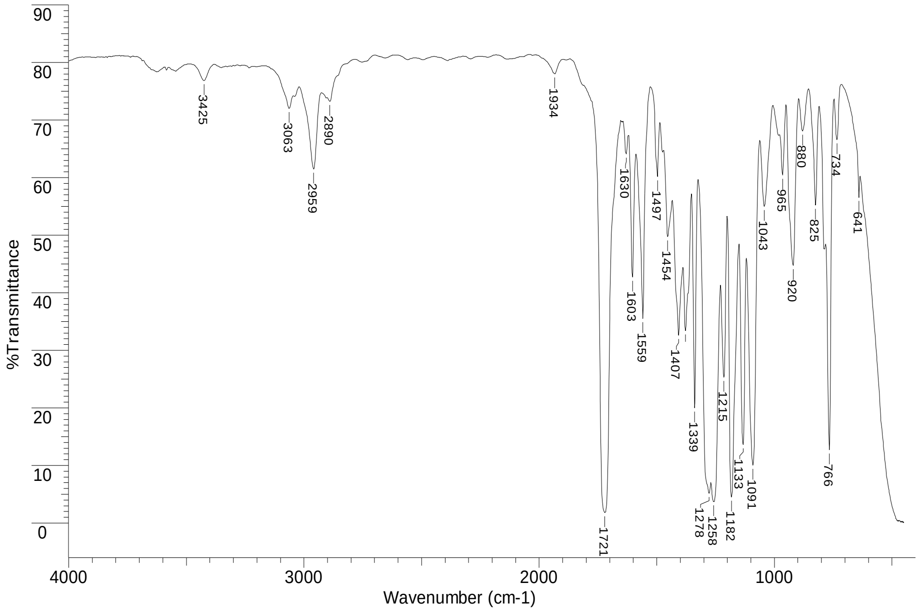


Figure 8.78 IR spectra for solvent cast PEN samples aged in wet (1.5 – 2% AH) nitrogen for 4 hours at 320 °C for 4 hours

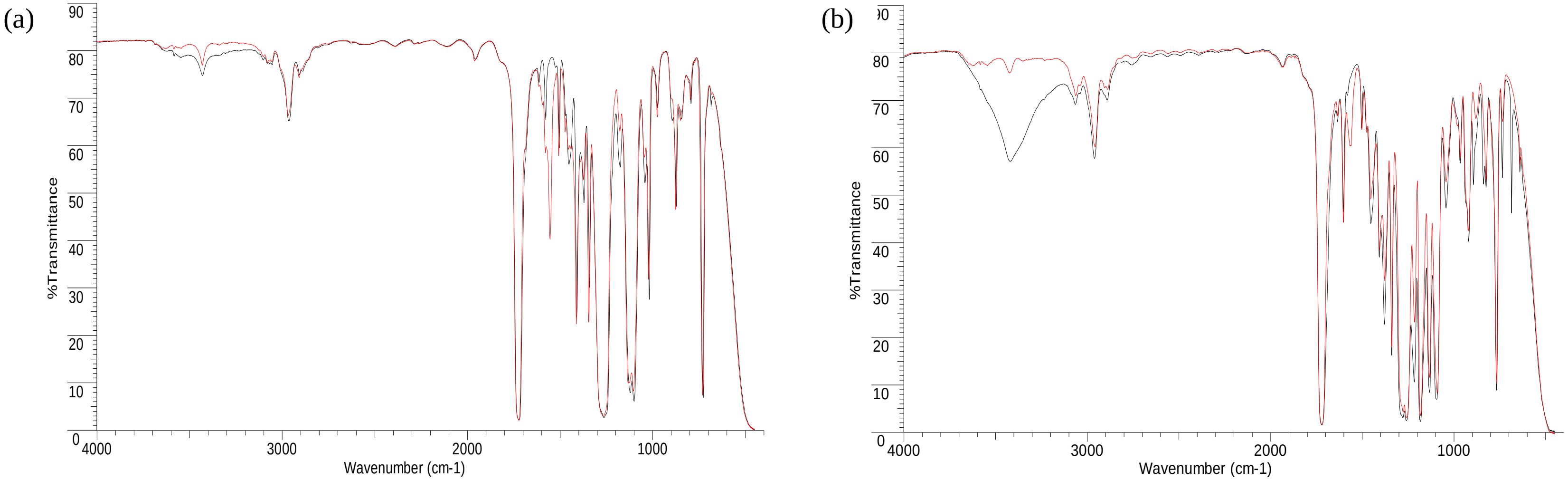


Figure 8.79 IR spectra of solvent cast (a) PET and (b) PEN film before and after ageing at 288 °C in wet (1.5 – 2% AH) nitrogen for 4 hours

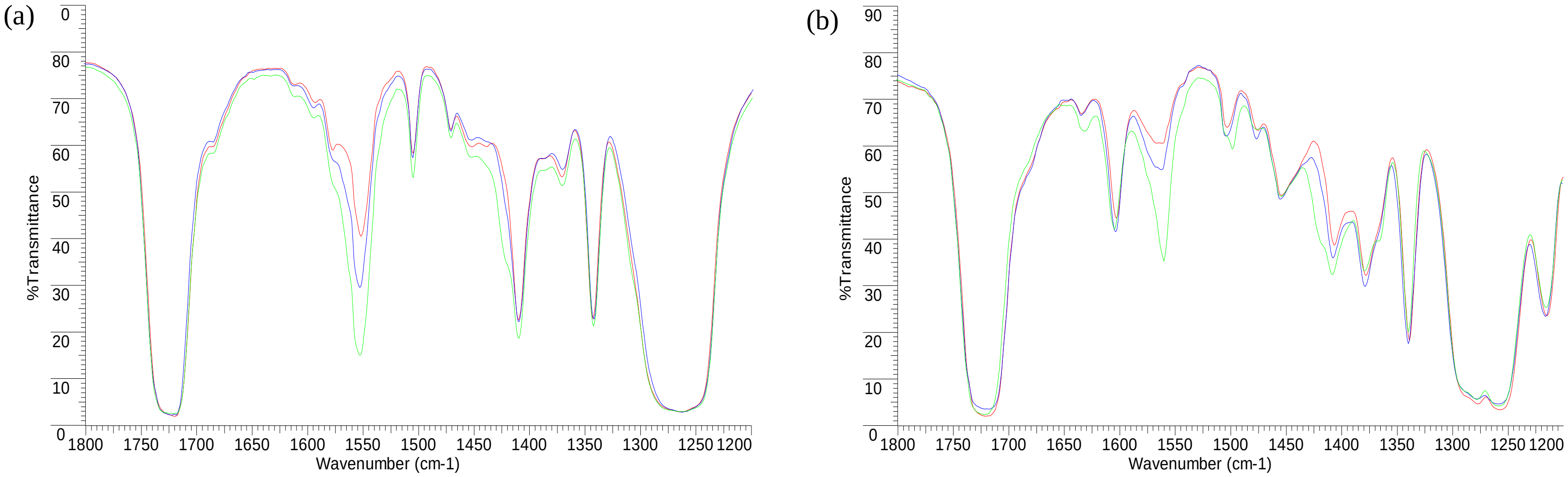


Figure 8.80 IR spectra for solvent cast (a) PET and (b) PEN samples aged in wet (1.5 – 2% AH) nitrogen at 288 °C, 300 °C and 320 °C for 4 hours

8.2.7.3 Residual Samples Aged Under Thermo-Oxidative Conditions

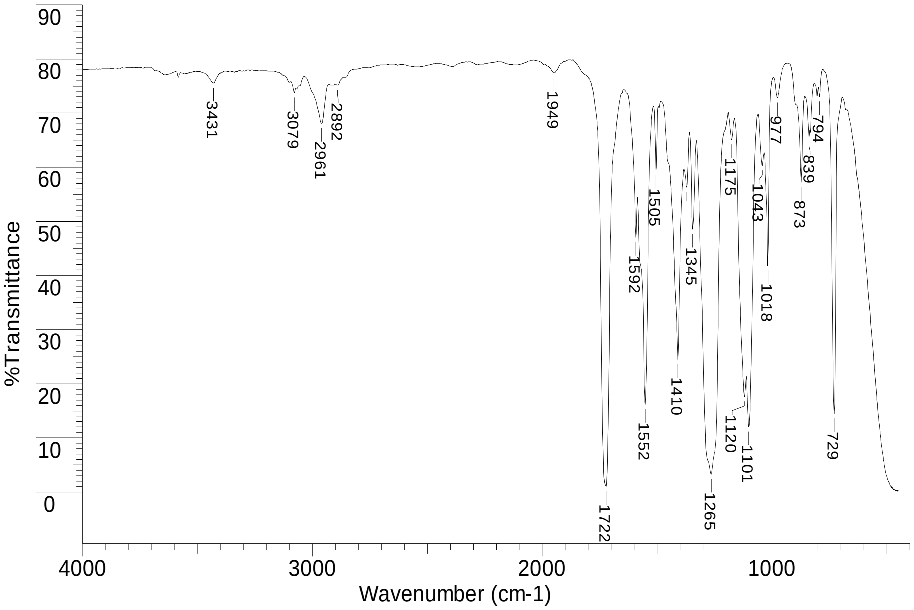


Figure 8.81 IR spectra for solvent cast PET samples aged in dry air for 4 hours at 288 °C for 4 hours

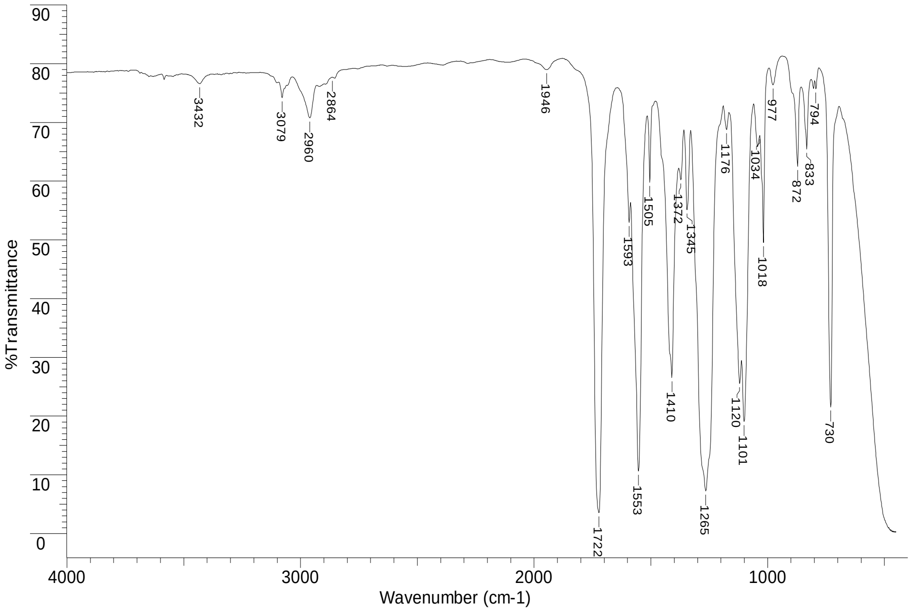


Figure 8.82 IR spectra for solvent cast PET samples aged in dry air for 4 hours at 300 °C for 4 hours

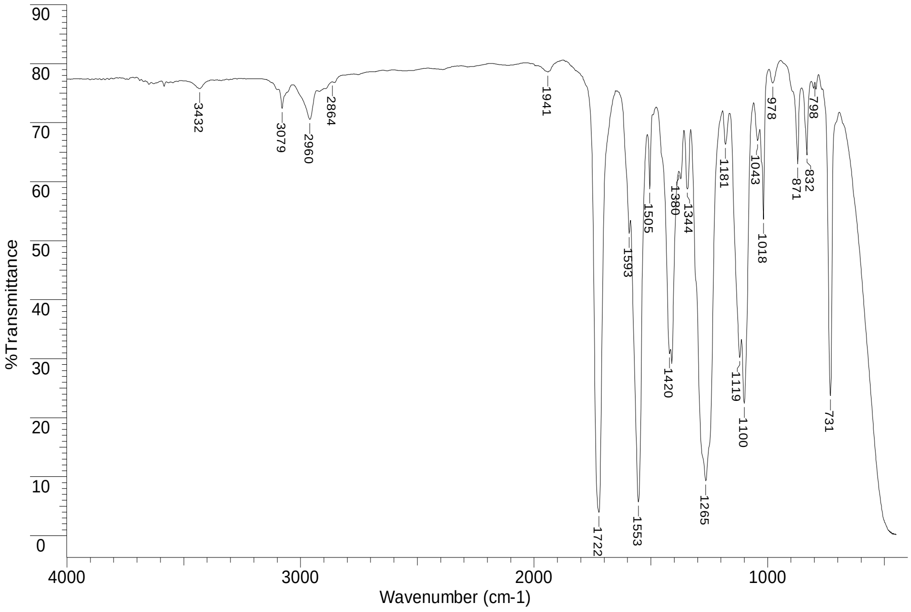


Figure 8.83 IR spectra for solvent cast PET samples aged in dry air for 4 hours at 320 °C for 4 hours

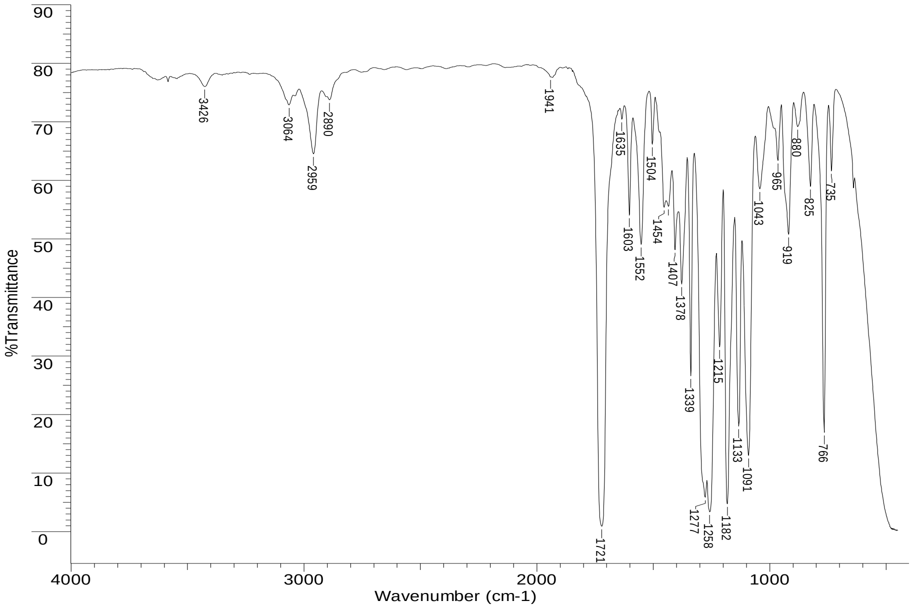


Figure 8.84 IR spectra for solvent cast PEN samples aged in dry air for 4 hours at 288 °C for 4 hours

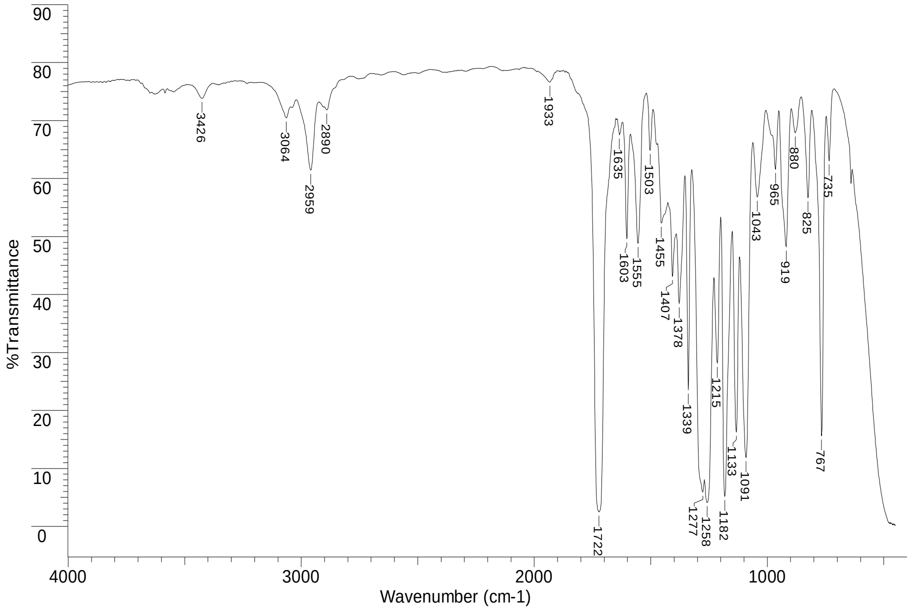


Figure 8.85 IR spectra for solvent cast PEN samples aged in dry air for 4 hours at 300 °C for 4 hours

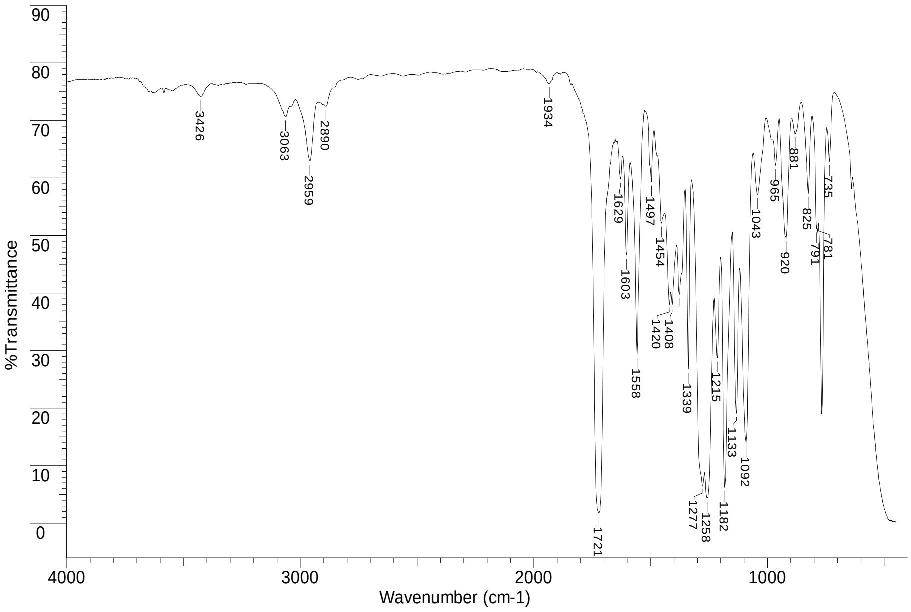


Figure 8.86 IR spectra for solvent cast PEN samples aged in dry air for 4 hours at 320 °C for 4 hours

8.2.7.4 Residual Samples Aged Under Thermo-Oxidative-Hydrolytic

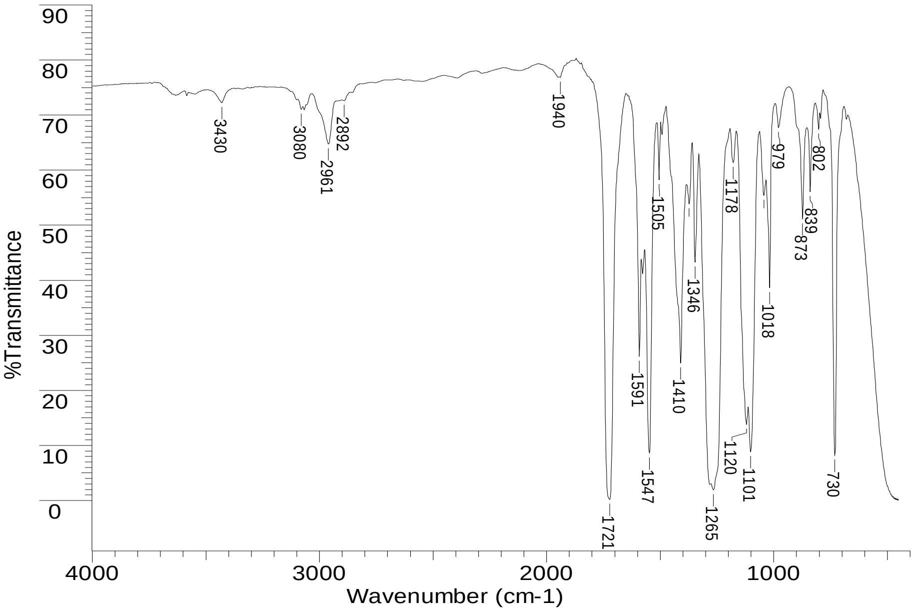


Figure 8.87 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) air for 4 hours at 288 °C for 4 hours

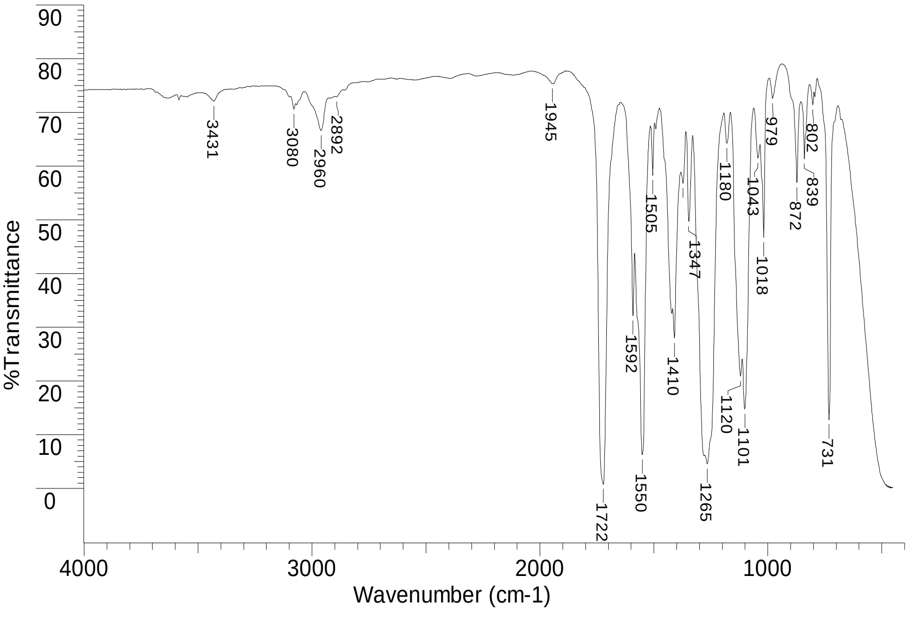


Figure 8.88 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) air for 4 hours at 300 °C for 4 hours

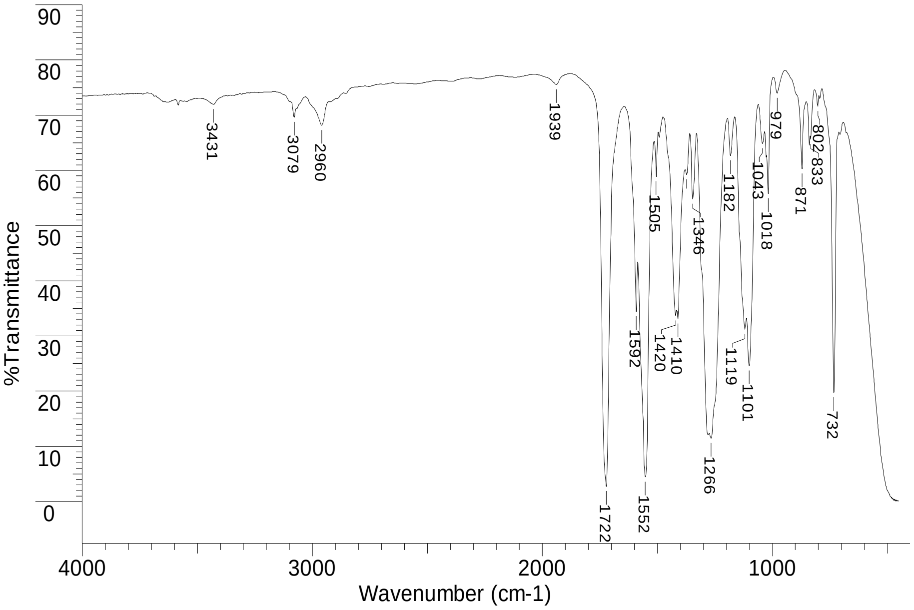


Figure 8.89 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) air for 4 hours at 320 °C for 4 hours

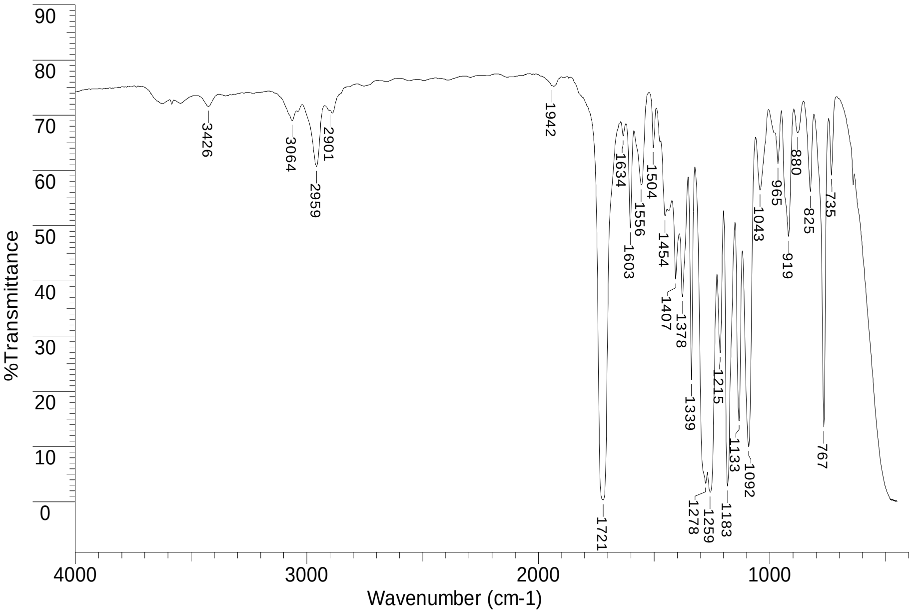


Figure 8.90 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) air for 4 hours at 288 °C for 4 hours

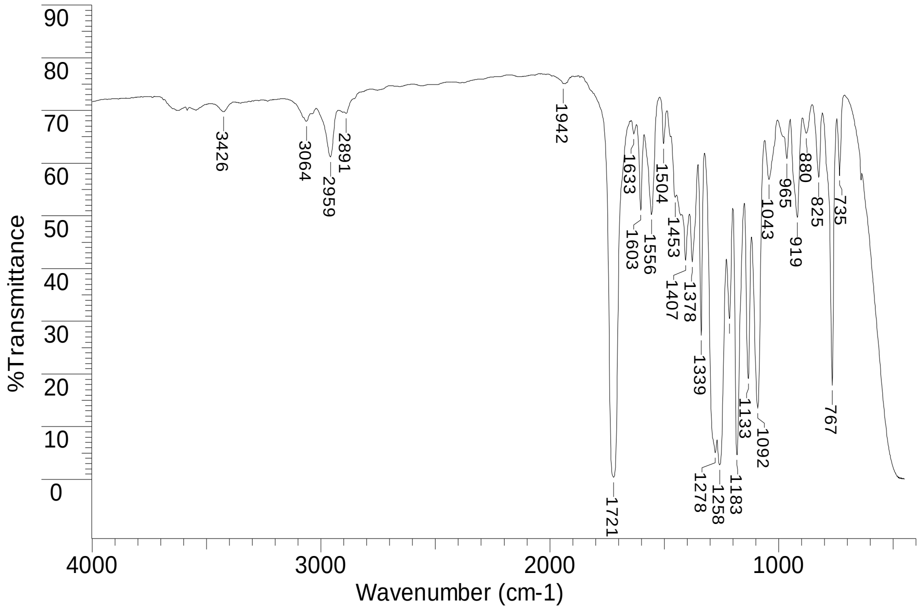


Figure 8.91 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) air for 4 hours at 300 °C for 4 hours

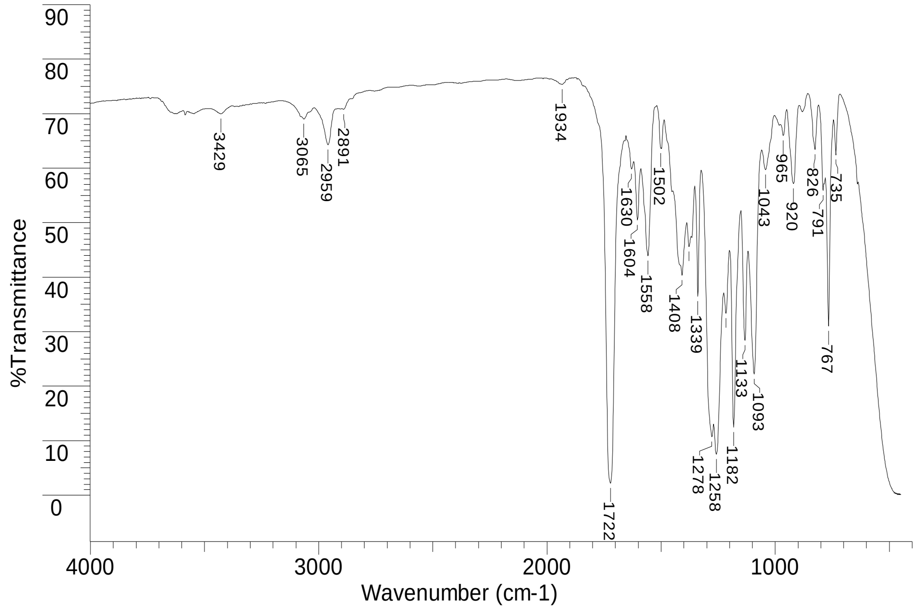


Figure 8.92 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) air for 4 hours at 320 °C for 4 hours

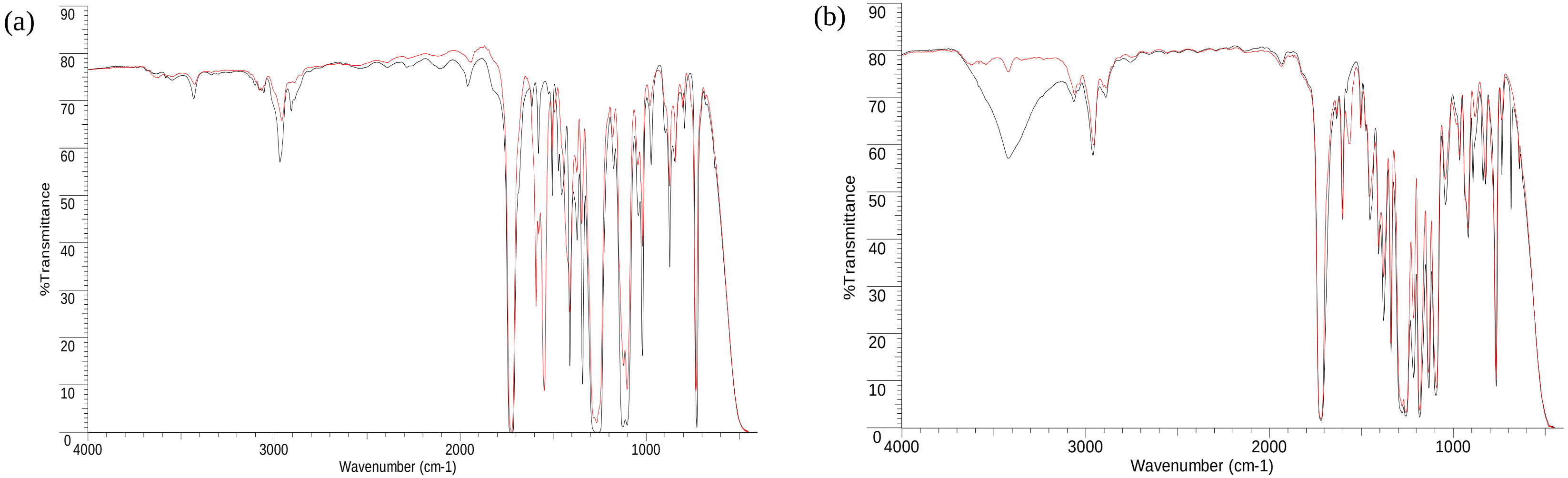


Figure 8.93 IR spectra of solvent cast (a) PET and (b) PEN film before and after ageing at 288 °C in wet (1.5 – 2% AH) air for 4 hours

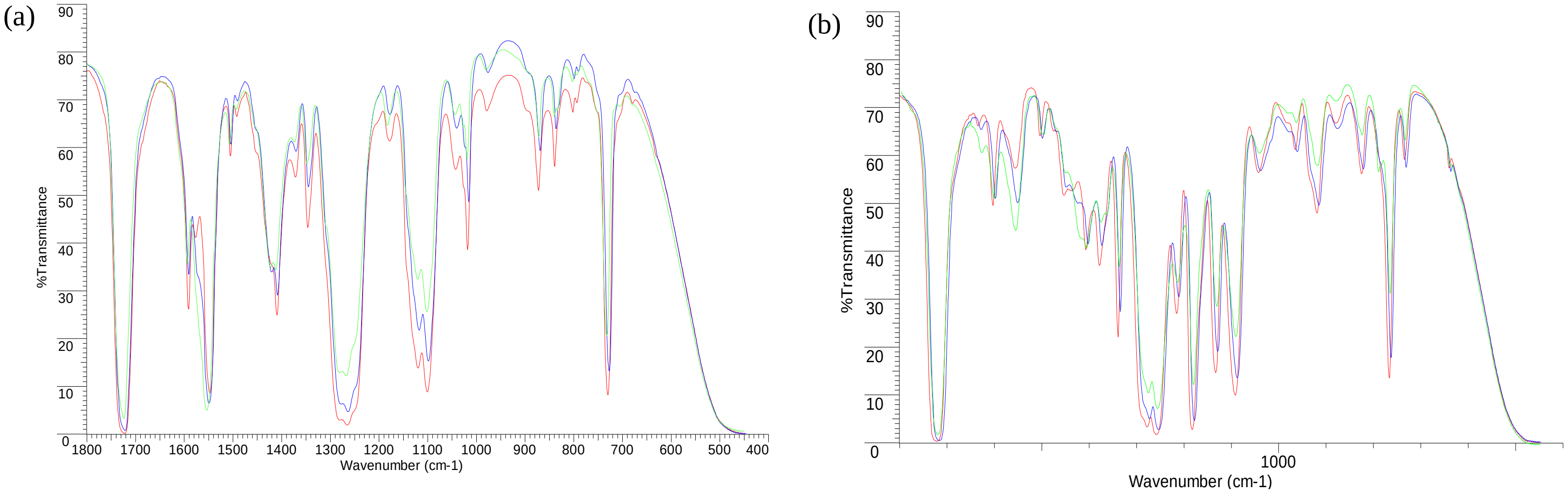


Figure 8.94 IR spectra for solvent cast (a) PET and (b) PEN samples aged in wet (1.5 – 2% AH) air at 288 °C, 300 °C and 320 °C for 4 hours

8.2.8 High Temperature Degradation Studies of PET and PEN

8.2.8.1 Volatilisation Studies

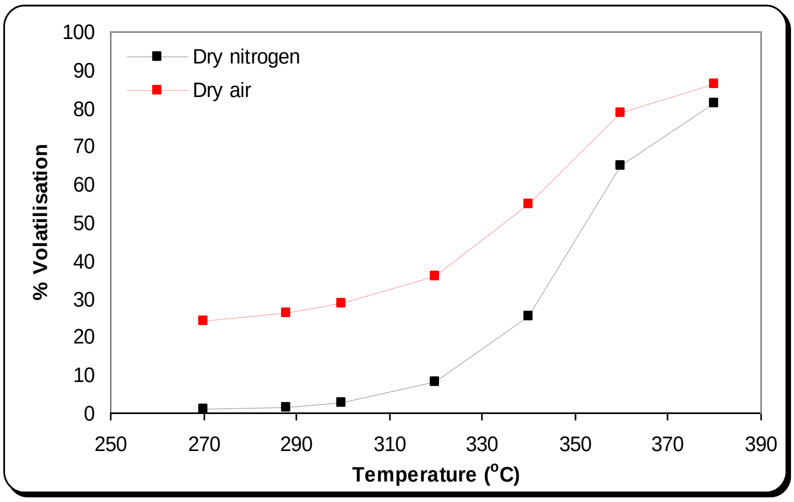


Figure 8.95 Volatilisation results for PET samples aged in dry nitrogen and dry air for 4 hours at temperatures between 270 °C and 380 °C

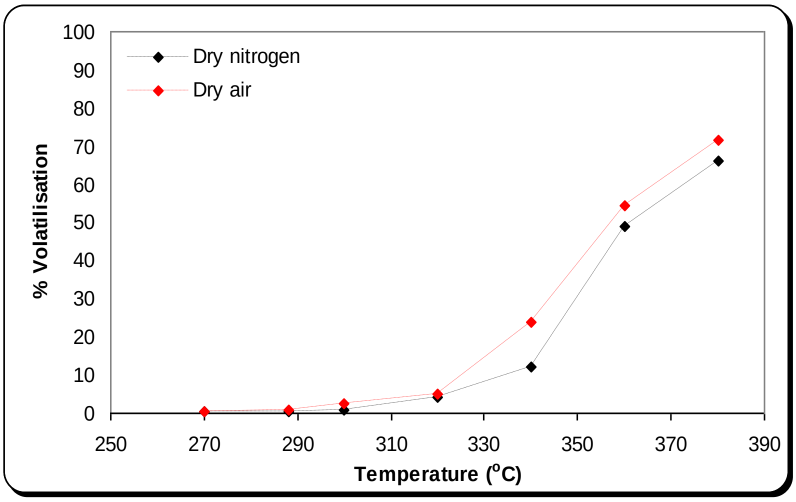


Figure 8.96 Volatilisation results for PEN samples aged in dry nitrogen and dry air for 4 hours at temperatures between 270 °C and 380 °C

Polymer	***Ageing Environment***	***Ageing Temperature (^{o}C)***	***% Volatilisation***
PET	Dry nitrogen	270	0.8
PEN	Dry nitrogen	270	0.4
PET	Dry air	270	24.1
PEN	Dry air	270	0.5
PET	Dry nitrogen	288	1.2
PEN	Dry nitrogen	288	0.6
PET	Dry air	288	26.1
PEN	Dry air	288	1.0
PET	Dry nitrogen	300	2.7
PEN	Dry nitrogen	300	1.0
PET	Dry air	300	28.5
PEN	Dry air	300	2.4
PET	Dry nitrogen	320	8.1
PEN	Dry nitrogen	320	4.2
PET	Dry air	320	35.7
PEN	Dry air	320	5.1
PET	Dry nitrogen	340	25.0
PEN	Dry nitrogen	340	12.3
PET	Dry air	340	54.5
PEN	Dry air	340	23.8
PET	Dry nitrogen	360	64.8
PEN	Dry nitrogen	360	48.8
PET	Dry air	360	78.5
PEN	Dry air	360	54.3
PET	Dry nitrogen	380	81.0
PEN	Dry nitrogen	380	66.1
PET	Dry air	380	86.1
PEN	Dry air	380	71.4

Table 8.10 Volatilisation results for PET and PEN samples aged in dry nitrogen and dry air for 4 hours between temperatures of 270 °C and 380 °C

8.2.8.2 Discolouration of Residual PET and PEN Film Samples

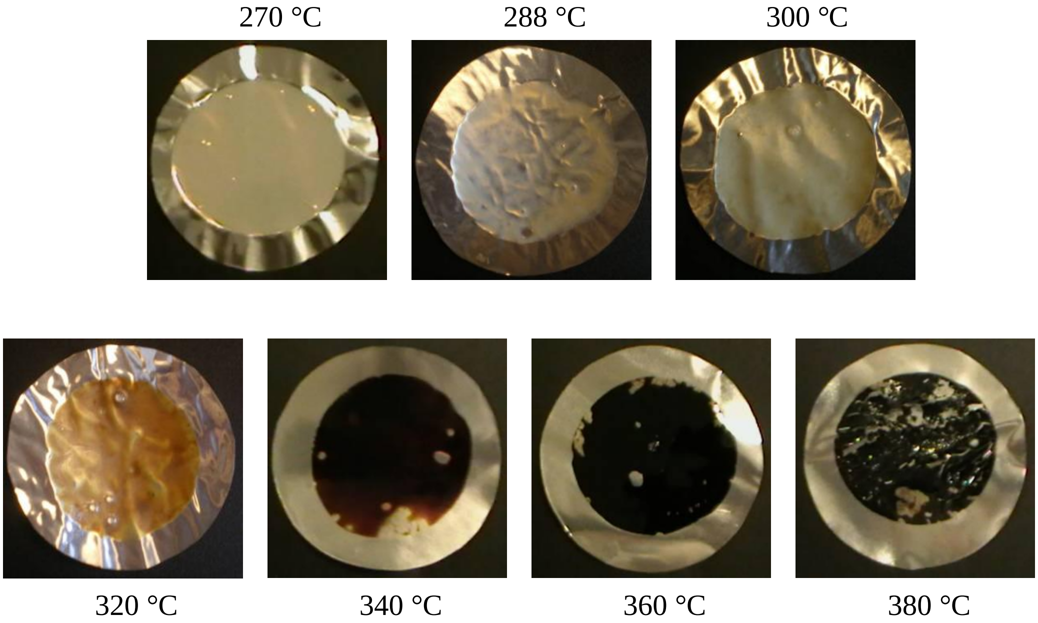


Figure 8.97 Residual film samples from PET aged in dry nitrogen for 4 hours at temperatures between 270 °C and 380 °C

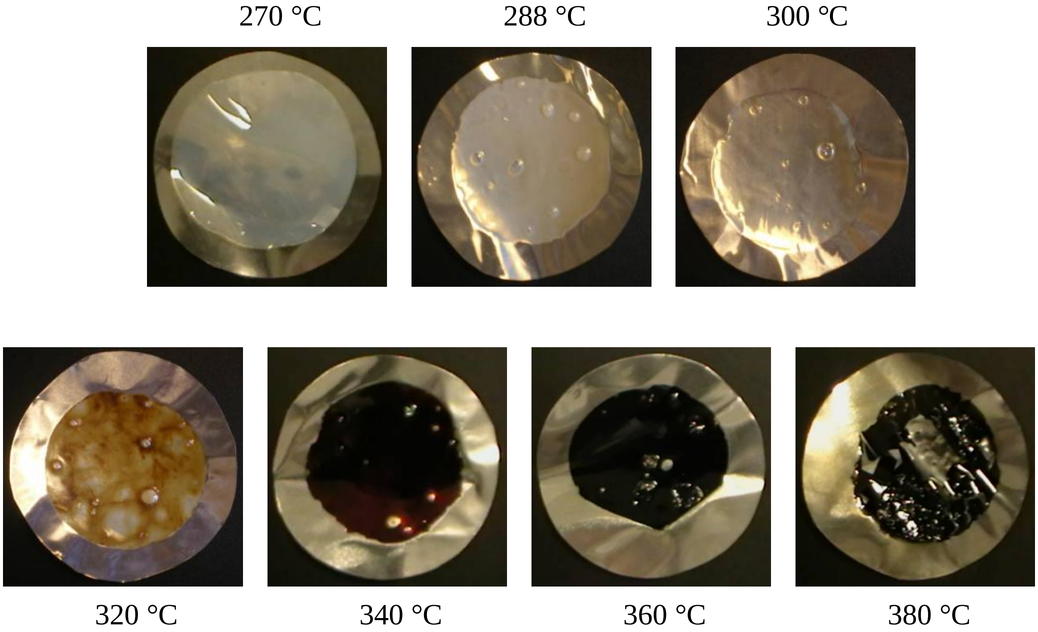


Figure 8.98 Residual film samples from PEN aged in dry nitrogen for 4 hours at temperatures between 270 °C and 380 °C

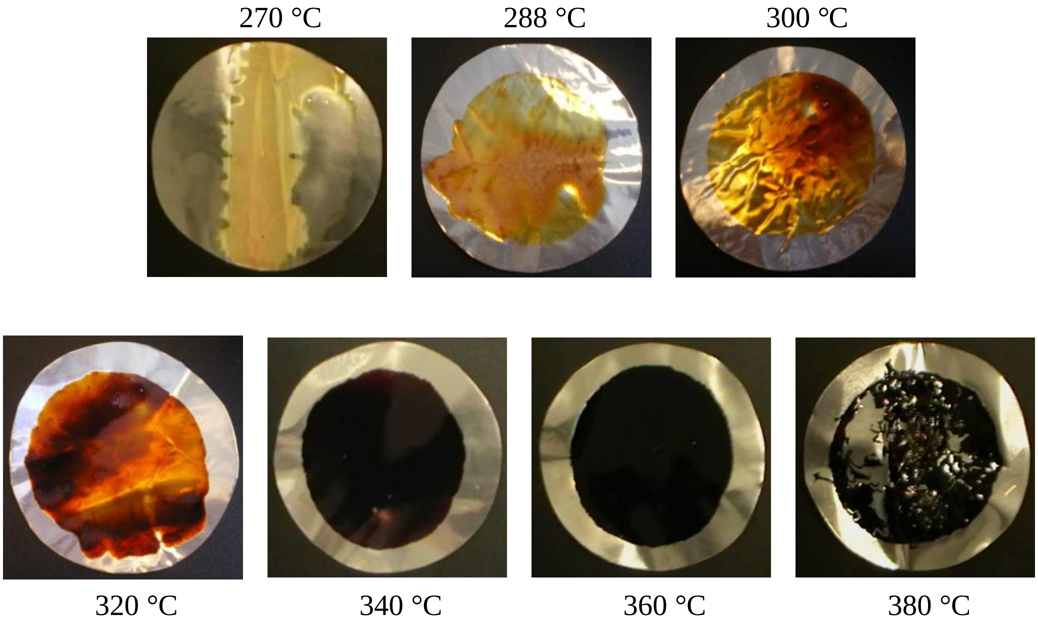


Figure 8.99 Residual film samples from PET aged in dry air for 4 hours at temperatures between 270 °C and 380 °C

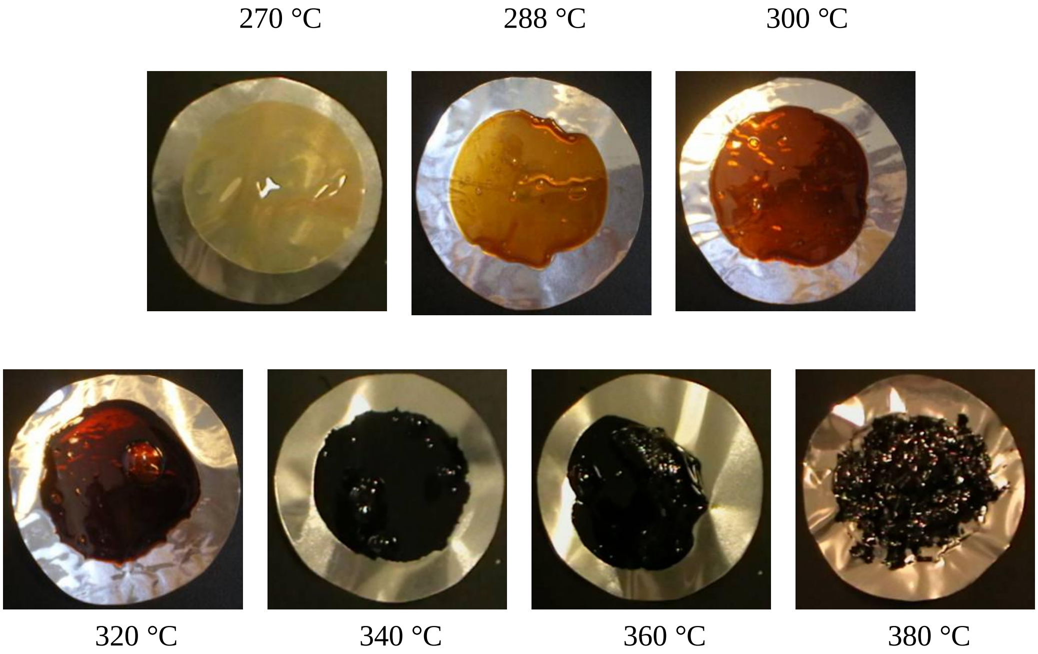


Figure 8.100 Residual film samples from PEN aged in dry air for 4 hours at temperatures between 270 °C and 380 °C

8.2.9 High Humidity Degradation Studies of PET and PEN

8.2.9.1 Volatilisation Studies

Ageing Temperature/ ^{o}C	Absolute Humidity/%	% Volatilisation	% Gels	% Soluble Products
288	1.6	2.1	7.4	90.5
288	3.4	3.3	5.5	91.2
288	6.4	4.4	4.1	91.5
288	12.0	6.8	2.3	90.9
288	27.3	15.2	1.5	83.2
288	42.9	22.5	0.3	77.2
288	52.7	33.9	0.6	65.5
288	69.5	39.5	0.2	60.3
288	77.5	44.7	0.4	54.9
288	82.2	46.1	0.3	53.6
300	1.7	3.8	5.4	90.8
300	3.8	6.3	4.9	88.8
300	6.4	8.7	3.2	88.1
300	12.1	10.3	2.4	87.3
300	20.9	18.1	0.3	81.6
300	30.6	28.7	0.5	70.8
300	48.6	33.6	0.3	66.1
300	68.9	42.6	0.4	57.0
300	78.4	62.2	0.3	37.5
300	81.7	64.3	0.3	35.3
320	1.7	11.2	2.1	86.7
320	3.7	16.2	7.4	76.5
320	6.3	19.5	3.5	77.0
320	12.4	26.3	6.5	67.3
320	28.0	43.8	6.2	50.0
320	43.7	61.4	2.2	36.4
320	58.2	74.4	1.3	24.3
320	67.3	78.4	1.4	20.3
320	73.2	79.9	1.1	19.0
320	80.4	91.1	0.7	8.2

Table 8.11 Volatilisation results for PET samples aged at various humidity levels in nitrogen at temperatures of 288 - 320 °C for 4 hours

Ageing Temperature/ °C	Absolute Humidity/%	Volatilisation/%	% Gels	% Soluble Products
288	1.6	24.8	13.3	61.9
288	3.0	29.5	32.3	38.2
288	6.1	36.5	31.3	32.2
288	14.5	42.7	26.9	30.4
288	24.5	45.0	15.2	39.8
288	38.6	48.3	1.9	49.8
288	53.8	49.6	2.6	47.8
288	72.2	50.8	1.4	47.9
288	78.2	54.3	0.7	45.0
288	82.1	57.7	0.8	41.5
300	1.4	31.7	29.7	38.6
300	4.5	44.2	46.0	9.8
300	6.4	46.2	46.4	7.4
300	10.2	48.4	39.8	11.8
300	24.5	52.0	28.8	19.3
300	30.5	52.3	9.8	37.9
300	53.1	62.0	5.9	32.1
300	68.5	64.3	0.3	35.4
300	77.9	68.3	0.3	31.5
300	82.2	70.1	1.0	29.0
320	1.7	38.8	46.4	14.8
320	3.2	47.7	50.7	1.5
320	6.0	50.6	49.1	0.2
320	11.6	58.4	41.3	0.3
320	23.0	65.0	33.5	1.6
320	40.0	69.1	23.3	7.6
320	52.6	81.8	12.7	5.5
320	65.7	84.8	9.8	5.4
320	77.3	87.7	6.2	6.0
320	79.5	90.4	3.5	6.0

Table 8.12 Volatilisation results for PET samples aged at various humidity levels in air at temperatures of 288 - 320 °C for 4 hours

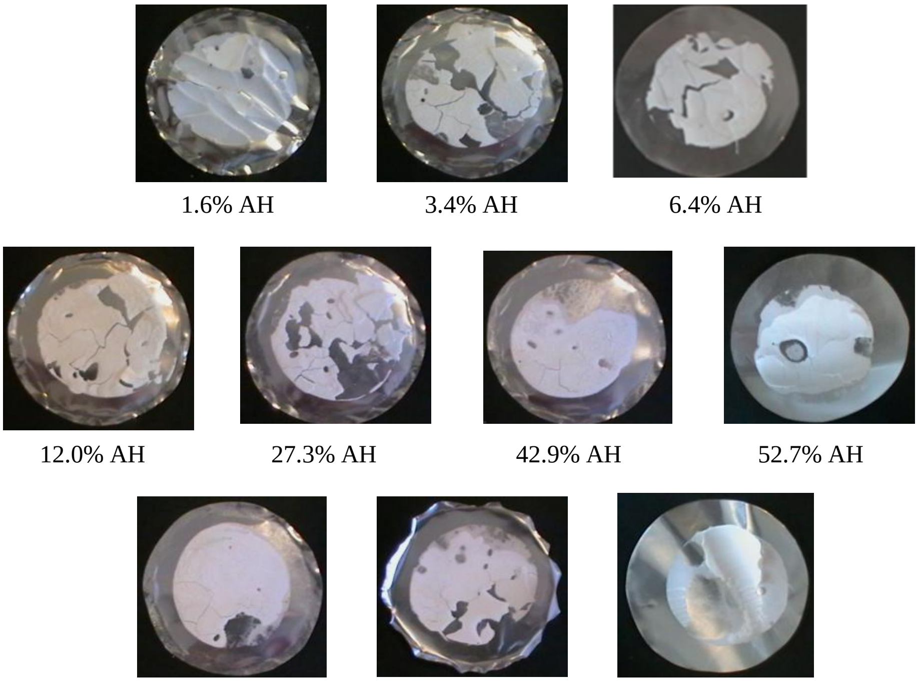
Ageing Temperature/ ^{o}C	**Absolute Humidity/%**	**Volatilisation/%**	**% Gels**	**% Soluble Products**
288	1.7	1.1	2.8	96.1
288	3.6	1.1	2.5	96.5
288	6.4	2.1	3.4	94.5
288	11.3	3.4	3.2	93.4
288	23.8	6.7	4.4	88.8
288	37.7	10.9	2.0	87.2
288	54.0	16.2	2.4	81.3
288	72.1	24.4	2.8	72.8
288	78.8	27.8	1.7	70.5
288	79.9	31.0	1.4	67.6
300	1.6	1.5	6.1	92.4
300	4.1	2.4	3.6	94.0
300	6.2	3.5	3.2	93.3
300	12.7	5.6	4.6	89.8
300	22.0	10.4	3.4	86.2
300	33.5	13.6	3.8	82.6
300	52.2	22.3	3.6	74.1
300	72.1	31.6	0.8	67.6
300	80.2	32.5	2.0	65.5
300	82.1	37.9	1.1	61.1
320	1.7	6.2	5.2	88.6
320	3.7	7.8	4.8	87.4
320	6.4	10.7	6.9	82.4
320	11.1	13.2	7.5	79.4
320	23.9	24.5	4.0	71.5
320	38.9	30.3	3.0	66.7
320	53.0	40.3	0.9	58.8
320	66.3	45.5	0.8	53.8
320	75.4	48.0	0.5	51.4
320	80.9	54.9	0.1	45.0

Table 8.13 Volatilisation results for PEN samples aged at various humidity levels in nitrogen at temperatures of 288 - 320 °C for 4 hours

Ageing Temperature/ ^{o}C	Absolute Humidity/%	Volatilisation/%	% Gels	% Soluble Products
288	1.8	1.4	11.2	87.4
288	3.4	1.6	1.1	97.3
288	5.8	2.5	1.1	96.5
288	11.5	3.2	1.2	95.6
288	20.5	5.1	2.6	92.3
288	35.4	12.4	0.7	86.9
288	52.0	17.6	1.6	80.9
288	65.2	23.0	1.3	75.7
288	76.5	27.6	0.6	71.9
288	81.8	33.1	1.3	65.6
300	1.7	3.1	49.5	47.4
300	4.6	3.7	44.2	52.1
300	6.9	4.7	42.5	52.8
300	12.6	8.9	9.4	82.7
300	24.6	12.9	7.9	79.1
300	35.1	18.1	6.8	75.1
300	47.7	21.9	6.9	71.2
300	60.2	27.8	5.6	66.6
300	69.3	32.6	3.5	63.9
300	79.9	38.2	4.8	57.1
320	1.9	11.0	74.3	14.7
320	4.0	13.0	74.9	12.2
320	7.5	15.3	63.6	21.2
320	12.0	20.2	58.9	20.9
320	26.4	27.6	29.2	43.2
320	39.5	33.2	7.5	59.3
320	52.3	43.3	7.5	49.2
320	69.9	46.5	5.9	47.6
320	75.2	51.5	4.2	44.3
320	81.0	58.8	3.1	38.1

Table 8.14 Volatilisation results for PEN samples aged at various humidity levels in air at temperatures of 288 - 320 °C for 4 hours

8.2.9.2 Discolouration of Residual PET and PEN Film Samples

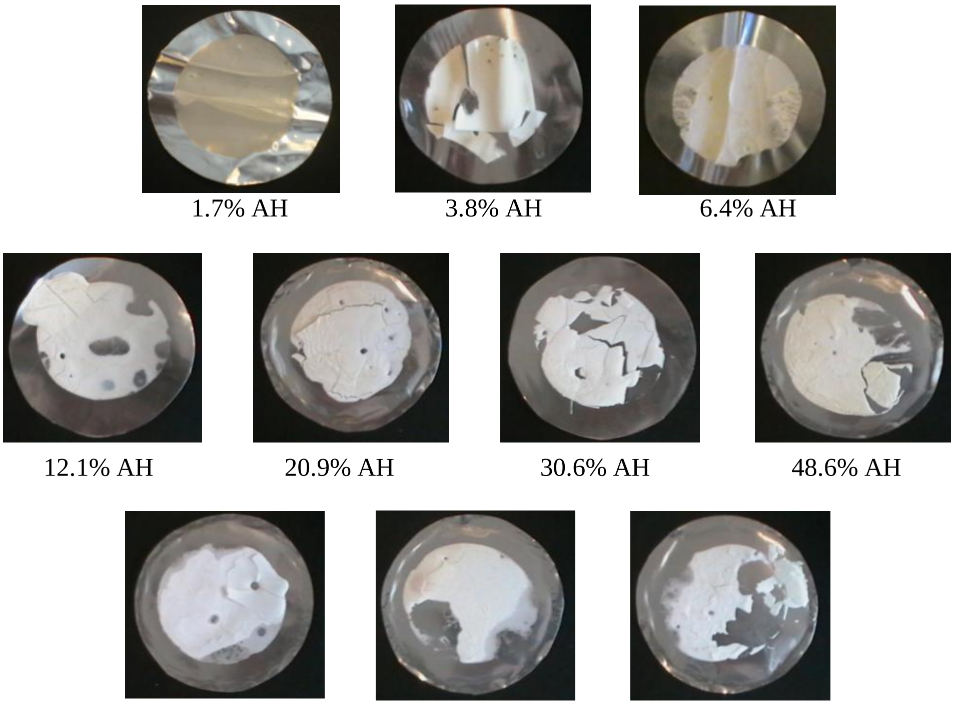


1.6% AH 3.4% AH 6.4% AH

12.0% AH 27.3% AH 42.9% AH 52.7% AH

69.5% AH 77.5% AH 82.2% AH

Figure 8.101 Residual film samples from PET after high humidity ageing in nitrogen, 288°C, 4 hours

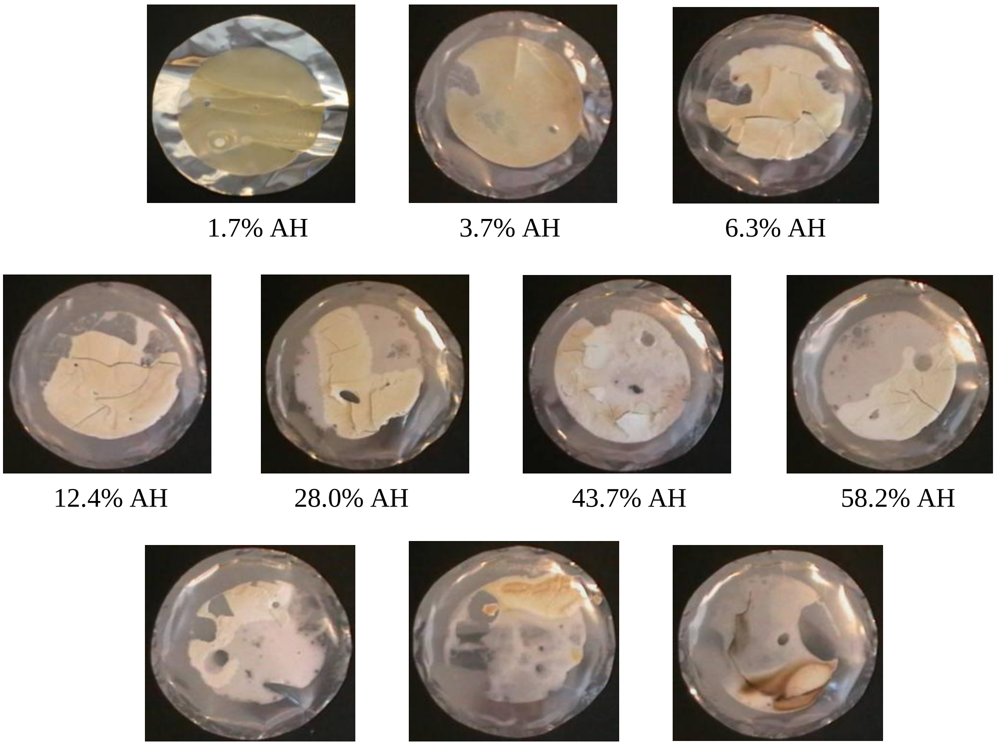


1.7% AH 3.8% AH 6.4% AH

12.1% AH 20.9% AH 30.6% AH 48.6% AH

68.9% AH 78.4% AH 81.7% AH

Figure 8.102 Residual film samples from PET after high humidity ageing in nitrogen, 300°C, 4 hours

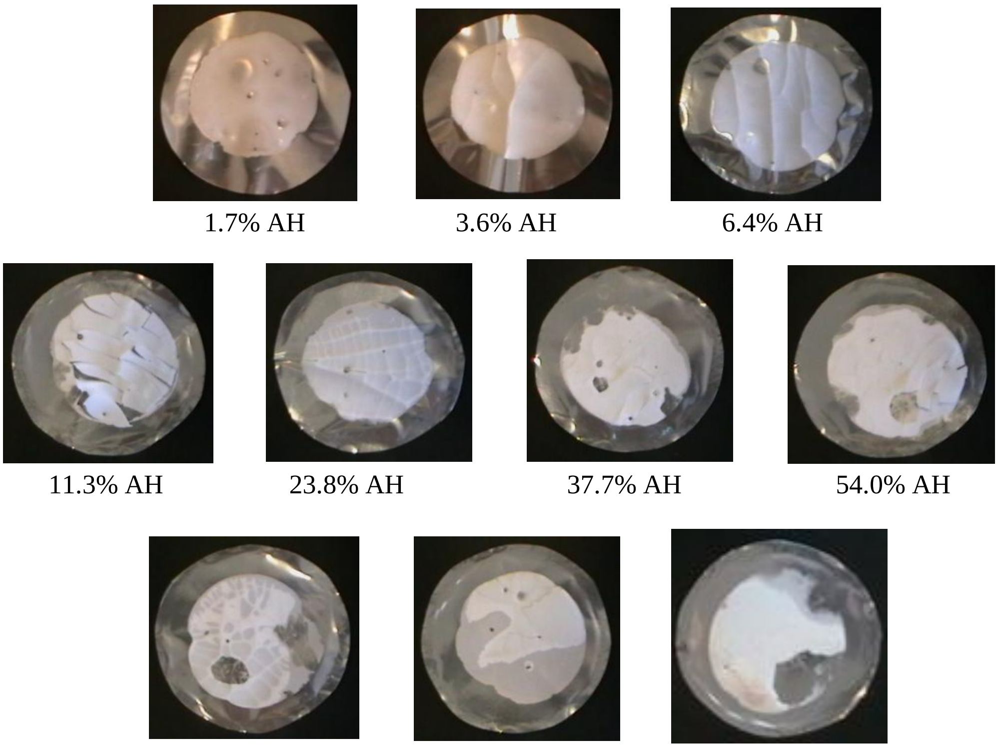


1.7% AH 3.7% AH 6.3% AH

12.4% AH 28.0% AH 43.7% AH 58.2% AH

67.3% AH 73.2% AH 80.3% AH

Figure 8.103 Residual film samples from PET after high humidity ageing in nitrogen, 320 °C, 4 hours

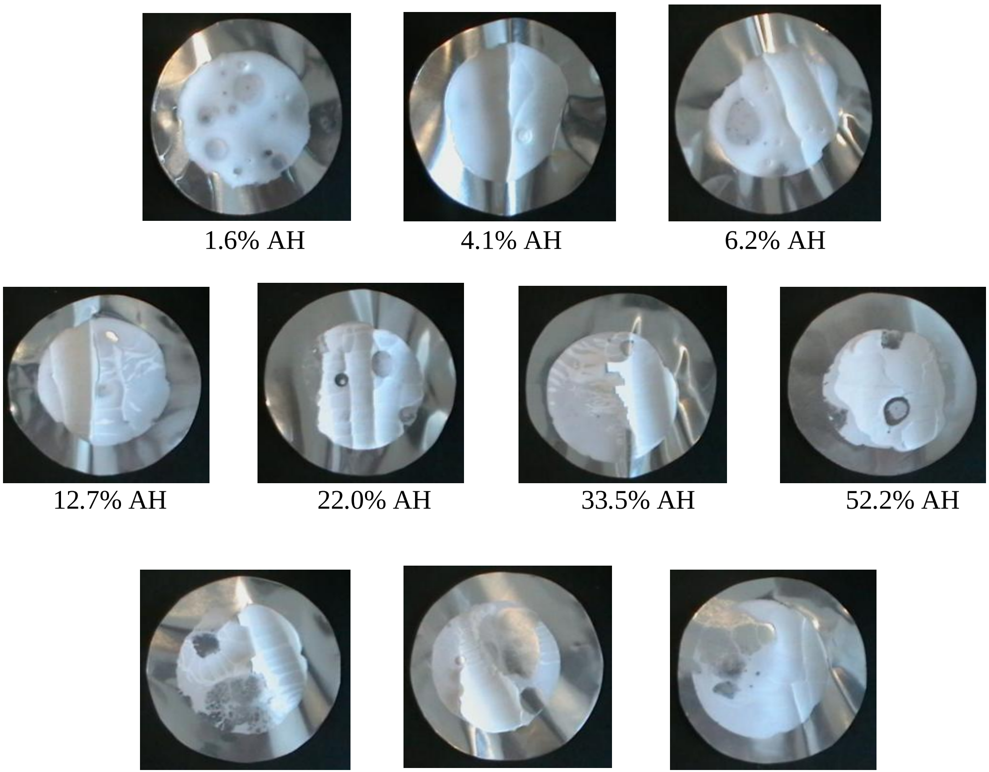


1.7% AH 3.6% AH 6.4% AH

11.3% AH 23.8% AH 37.7% AH 54.0% AH

72.1% AH 78.8% AH 79.9% AH

Figure 8.104 Residual film samples from PEN after high humidity ageing in nitrogen, 288 °C, 4 hours

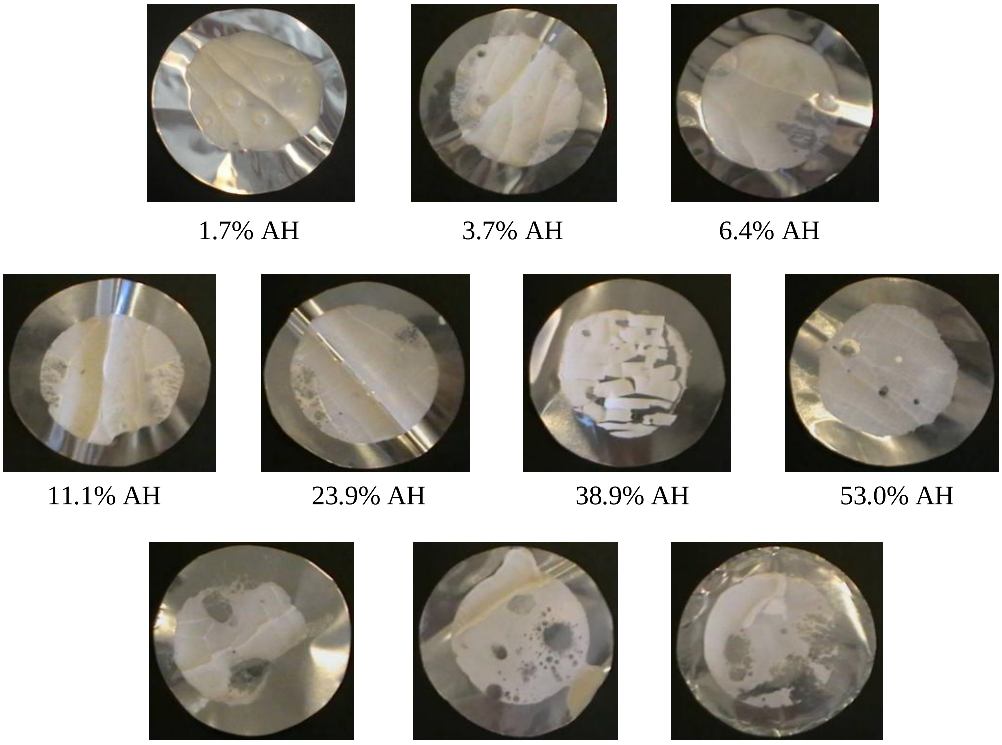


1.6% AH 4.1% AH 6.2% AH

12.7% AH 22.0% AH 33.5% AH 52.2% AH

72.1% AH 80.2% AH 82.1% AH

Figure 8.105 Residual film samples from PEN after high humidity ageing in nitrogen, 300°C, 4 hours

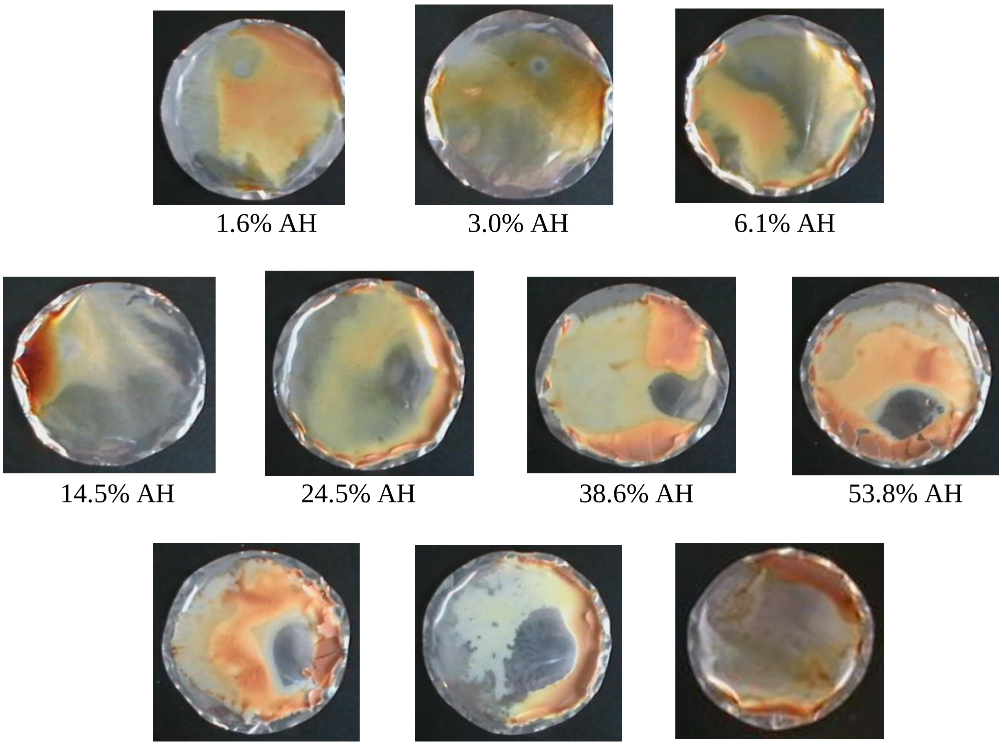


1.7% AH 3.7% AH 6.4% AH

11.1% AH 23.9% AH 38.9% AH 53.0% AH

66.3% AH 75.4% AH 80.9% AH

Figure 8.106 Residual film samples from PEN after high humidity ageing in nitrogen, 320°C, 4 hours

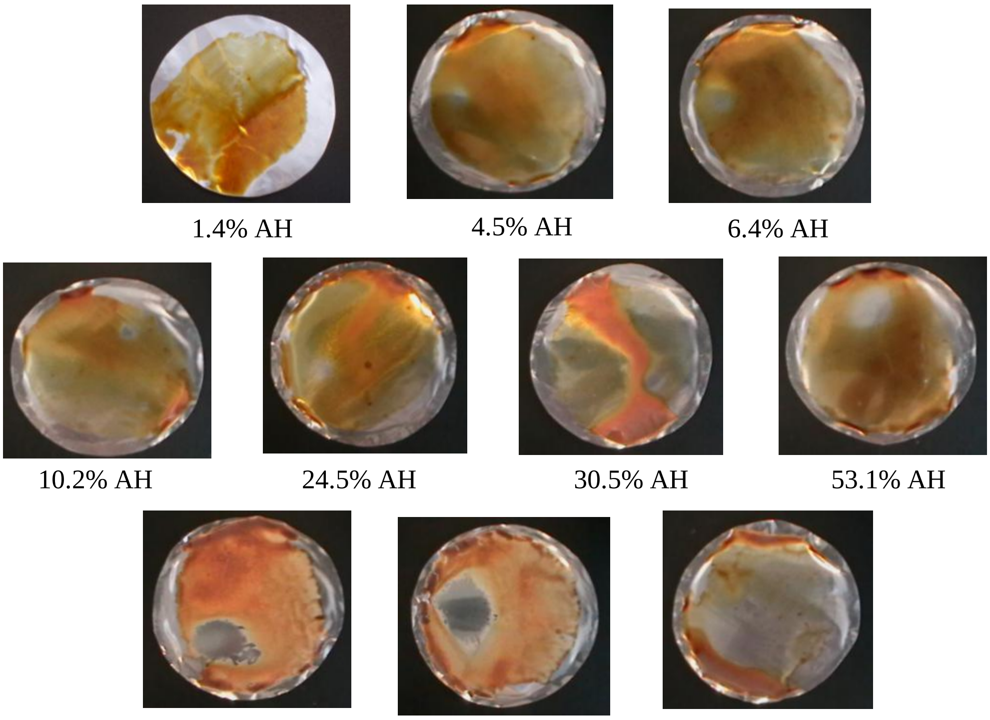


1.6% AH 3.0% AH 6.1% AH

14.5% AH 24.5% AH 38.6% AH 53.8% AH

72.2% AH 78.2% AH 82.1% AH

Figure 8.107 Residual film samples from PET after high humidity ageing in air, 288°C, 4 hours

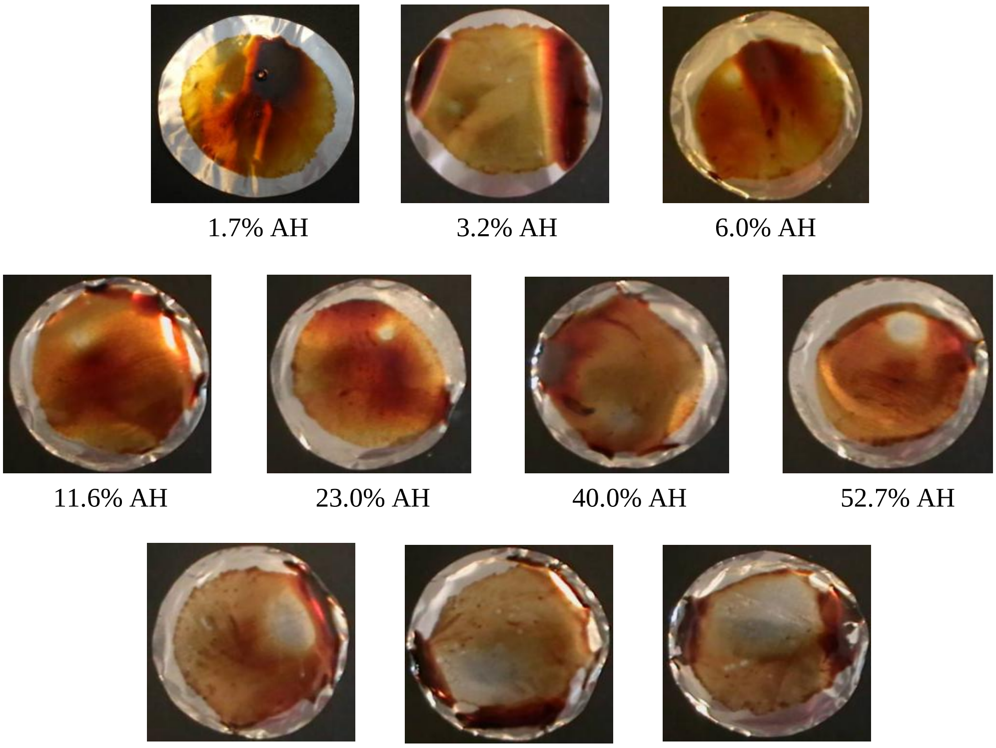


1.4% AH 4.5% AH 6.4% AH

10.2% AH 24.5% AH 30.5% AH 53.1% AH

68.5% AH 77.9% AH 82.2% AH

Figure 8.108 Residual film samples from PET after high humidity ageing in air, 300°C, 4 hours

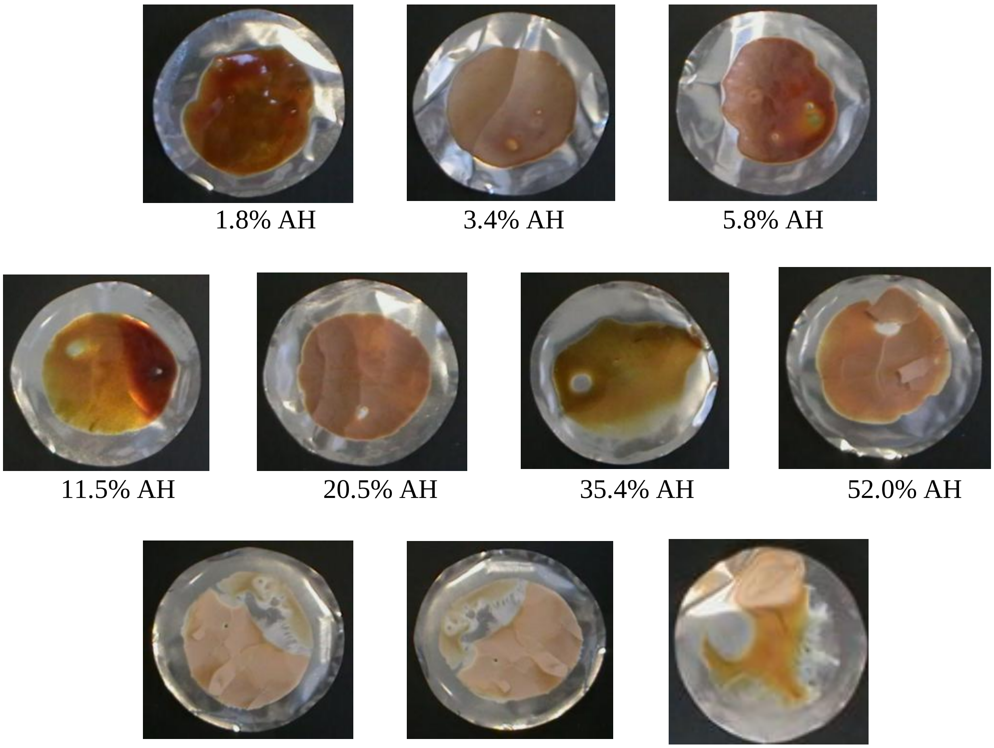


1.7% AH 3.2% AH 6.0% AH

11.6% AH 23.0% AH 40.0% AH 52.7% AH

65.7% AH 77.2% AH 79.5% AH

Figure 8.109 Residual film samples from PET after high humidity ageing in air, 320°C, 4 hours

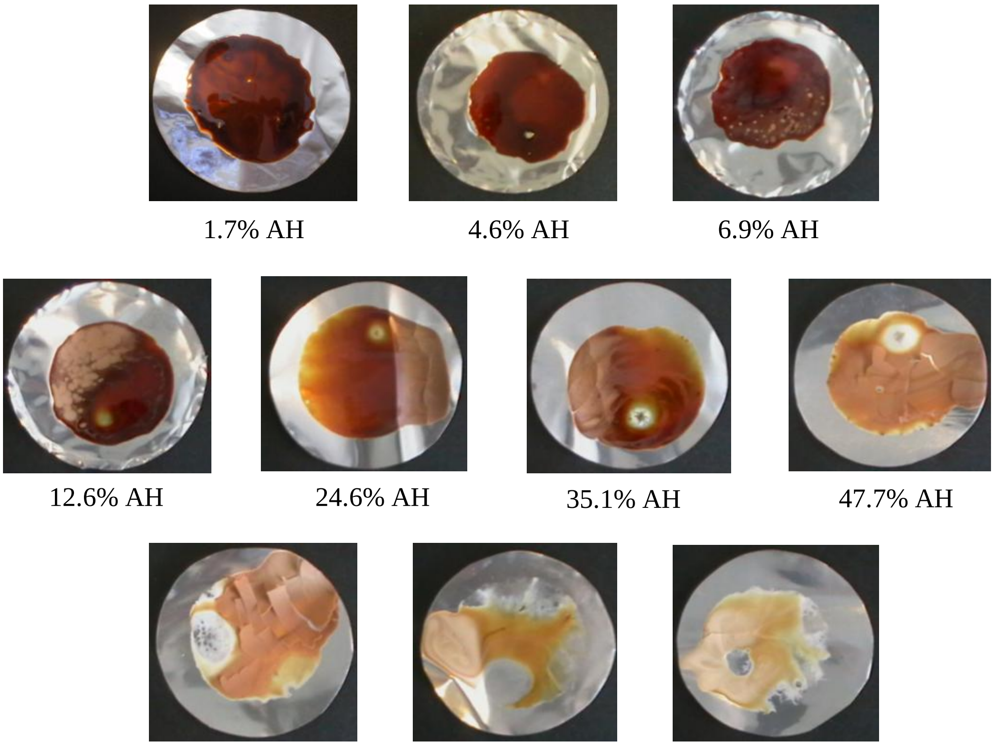


1.8% AH 3.4% AH 5.8% AH

11.5% AH 20.5% AH 35.4% AH 52.0% AH

65.2% AH 76.5% AH 81.8% AH

Figure 8.110 Residual film samples from PEN after high humidity ageing in air, 288°C, 4 hours

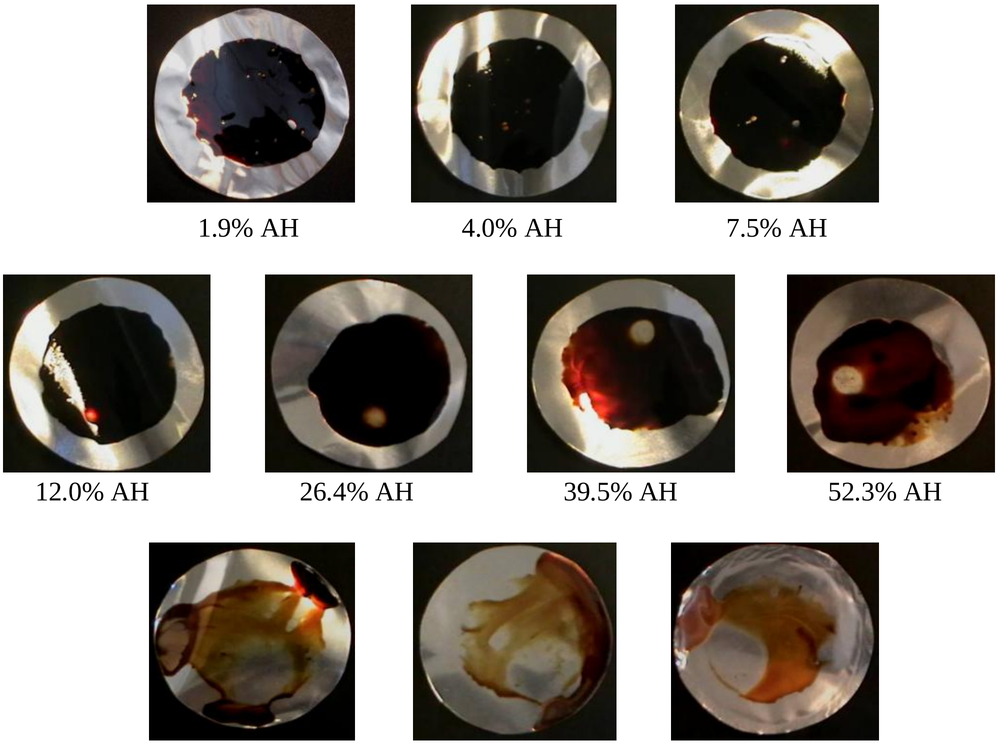


1.7% AH 4.6% AH 6.9% AH

12.6% AH 24.6% AH 35.1% AH 47.7% AH

60.2% AH 69.3% AH 79.9% AH

Figure 8.111 Residual film samples from PEN after high humidity ageing in air, 300 °C, 4 hours



1.9% AH 4.0% AH 7.5% AH

12.0% AH 26.4% AH 39.5% AH 52.3% AH

69.9% AH 75.2% AH 81.0% AH

Figure 8.112 Residual film samples from PEN after high humidity ageing in air, 320 °C, 4 hours

8.3 Ageing Studies of PET and PEN under Moderately Accelerated Conditions

8.3.1 Thermal Stability of PET and PEN after Ageing

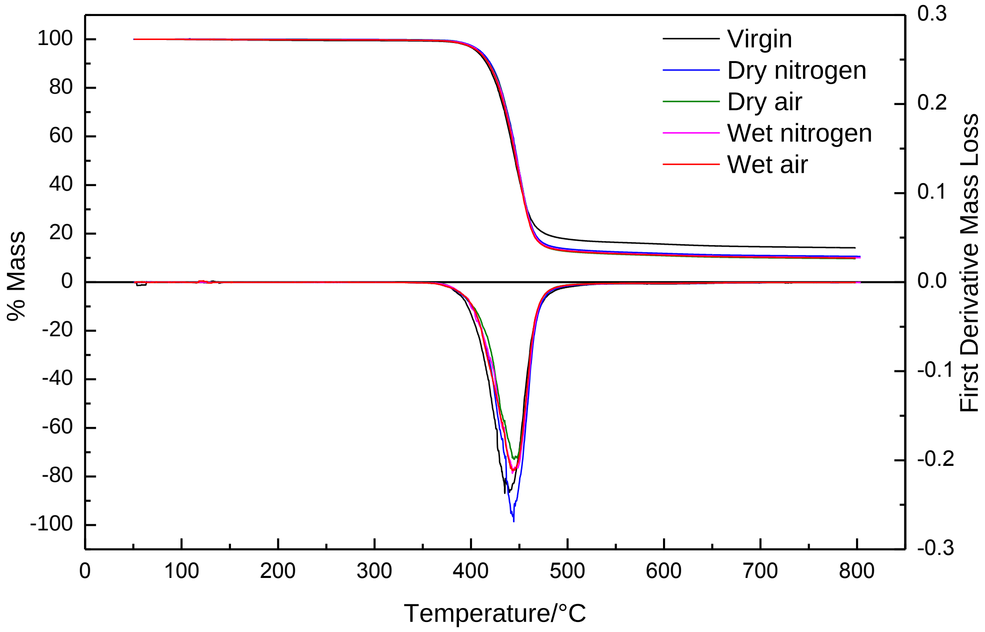


Figure 8.113 TG curves of PET samples aged under different environments at 160°C

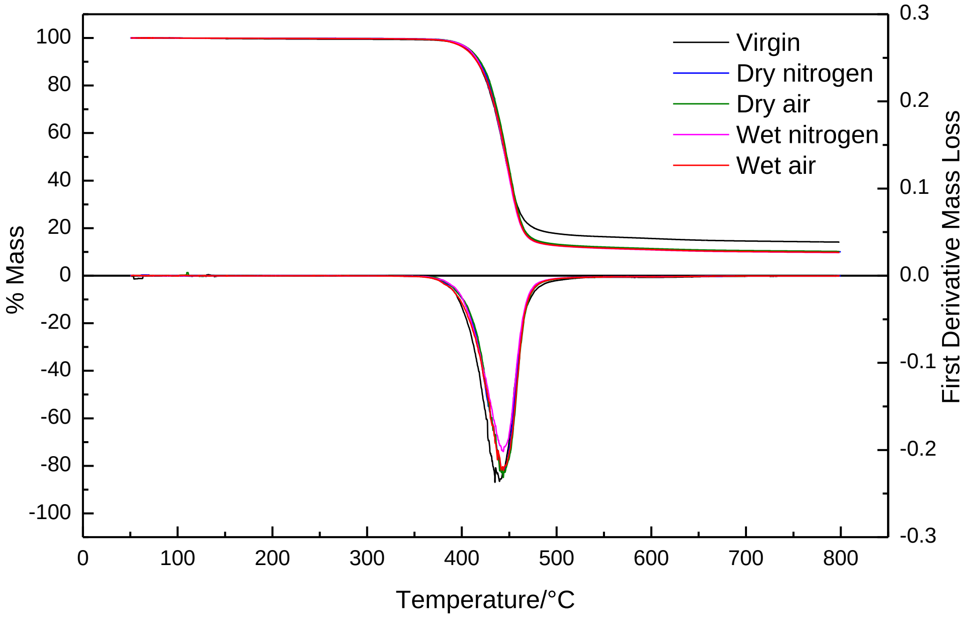


Figure 8.114 TG curves of PET samples aged under different environments at 170°C

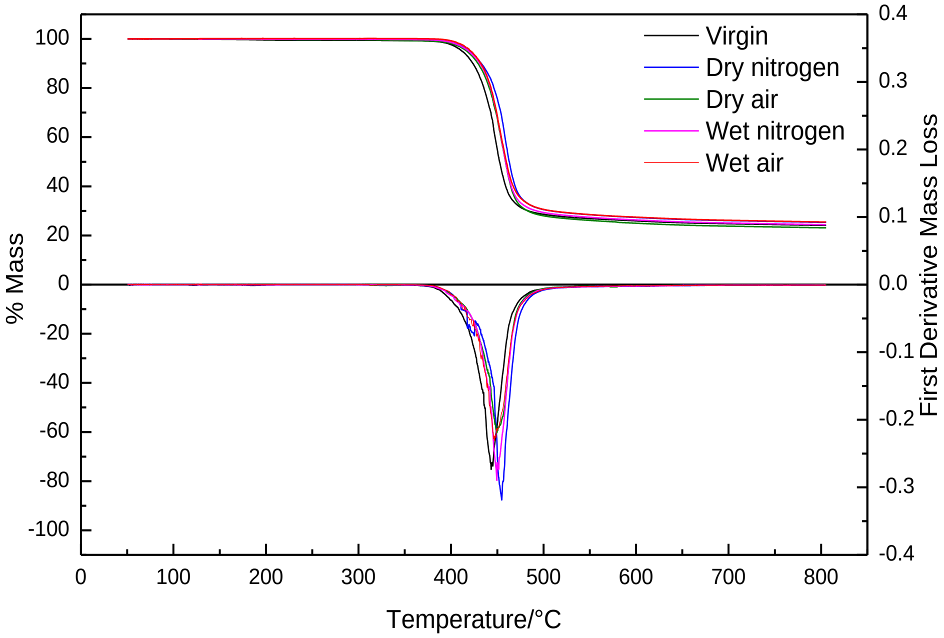


Figure 8.115 TG curves of PEN samples aged under different environments at 160^{o}C

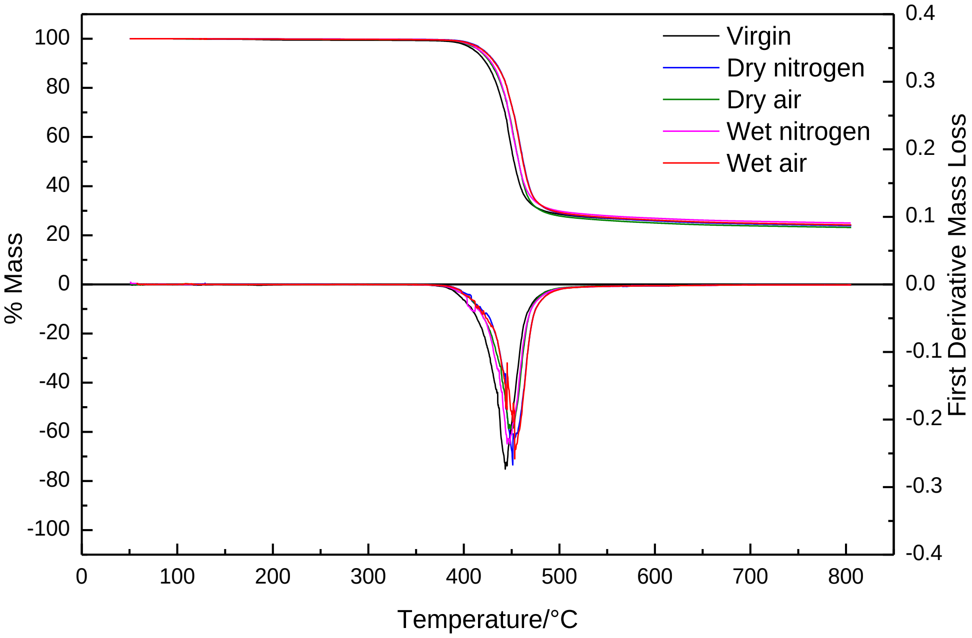


Figure 8.116 TG curves of PEN samples aged under different environments at 170^{o}C

8.3.2 Changes in Physical Morphology after Ageing

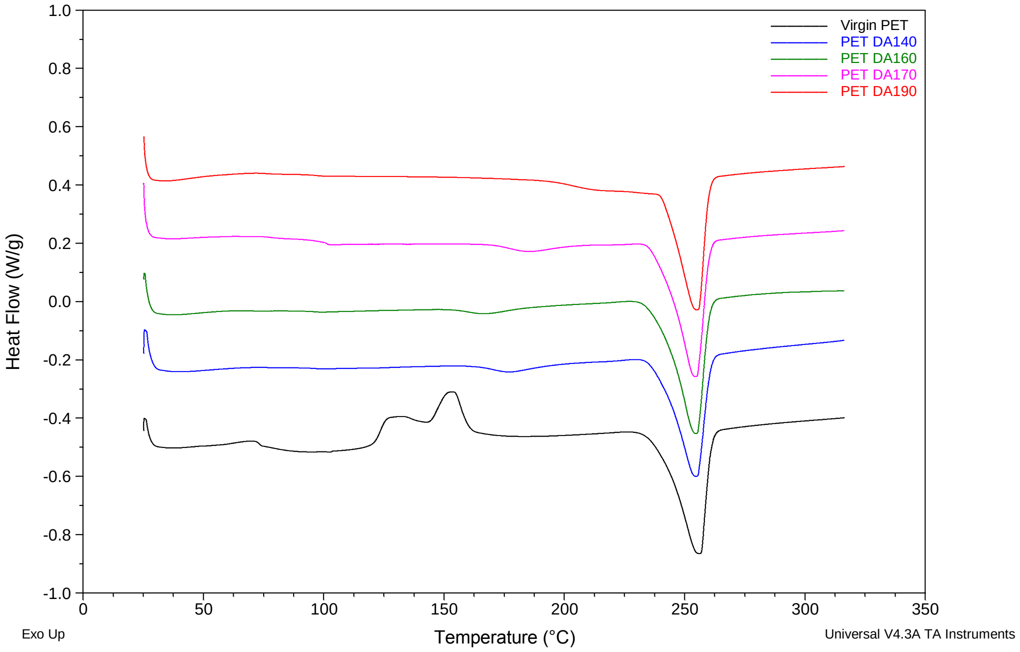


Figure 8.117 DSC of PET samples aged under dry air, cycle 1

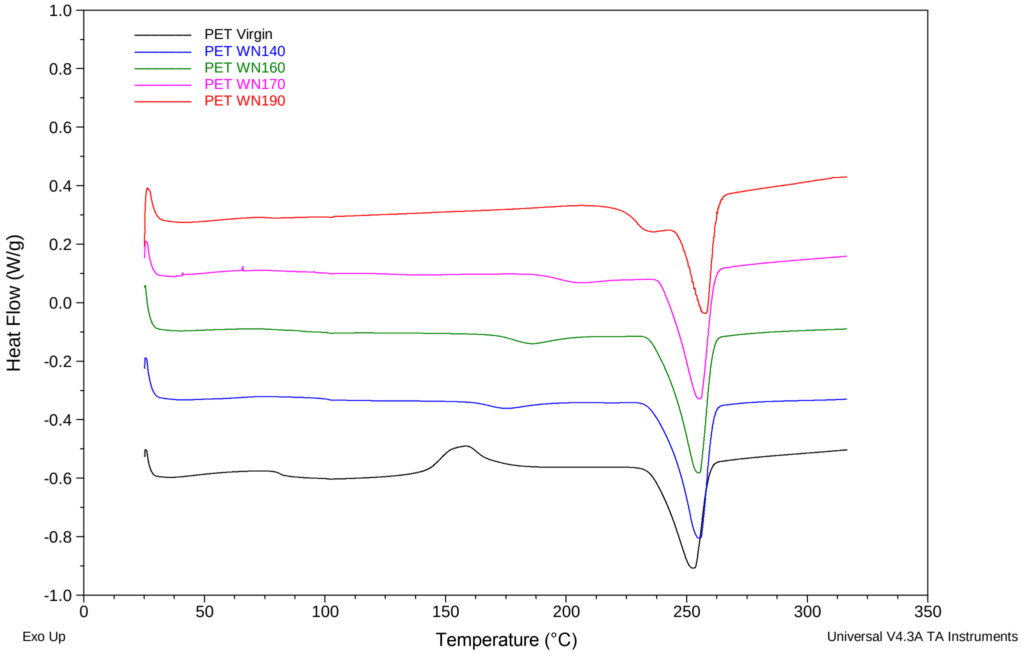


Figure 8.118 DSC of PET samples aged under wet (1.6% AH) nitrogen, cycle 1

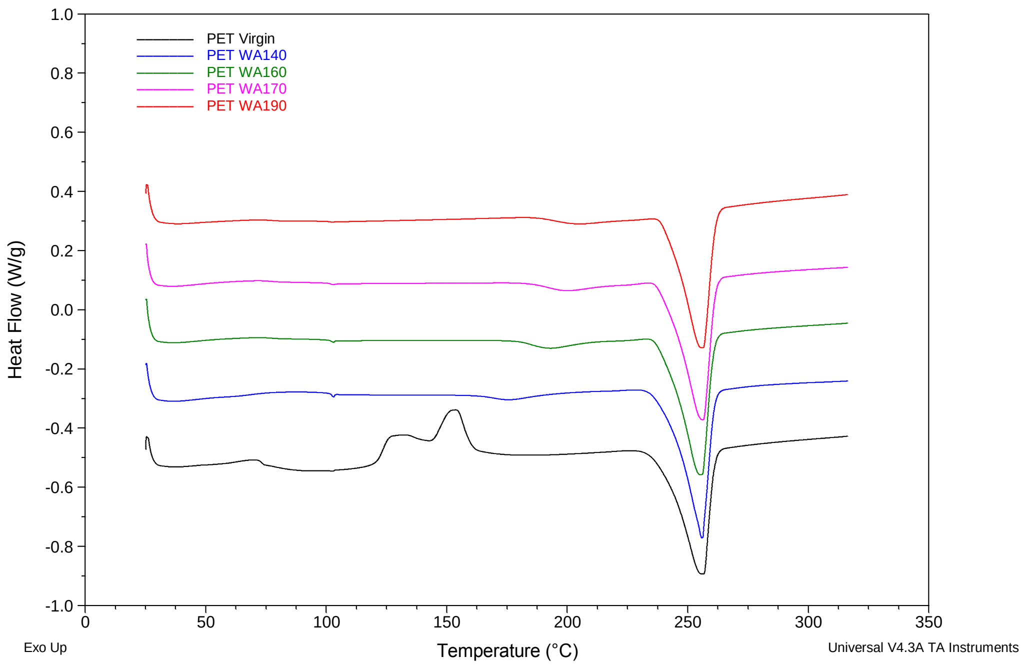


Figure 8.119 DSC of PET samples aged under wet (1.6% AH) air, cycle 1

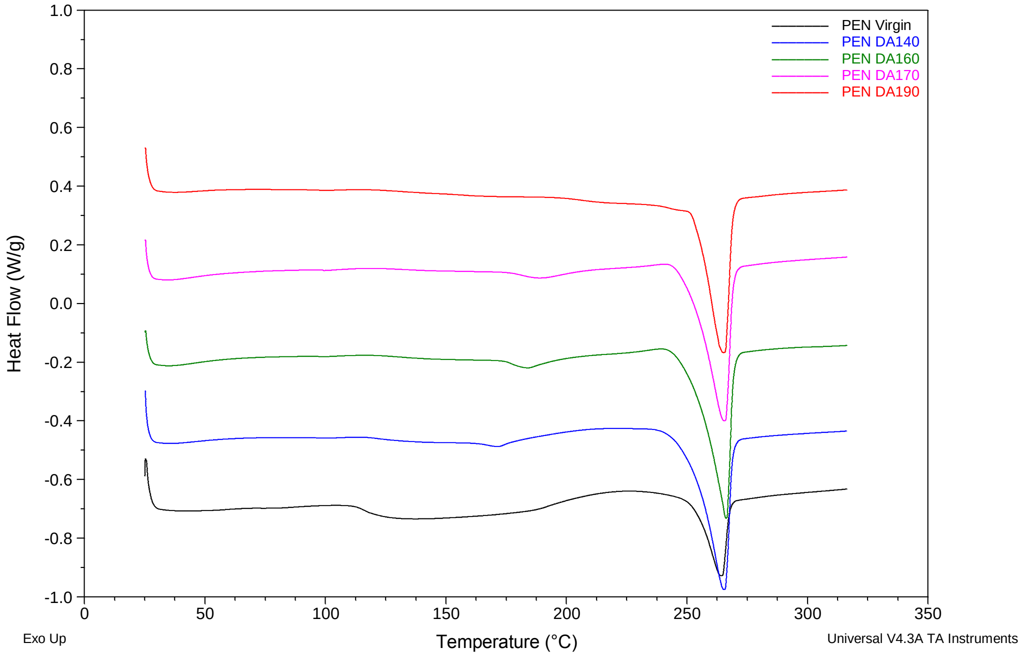


Figure 8.120 DSC of PEN samples aged under dry air, cycle 1

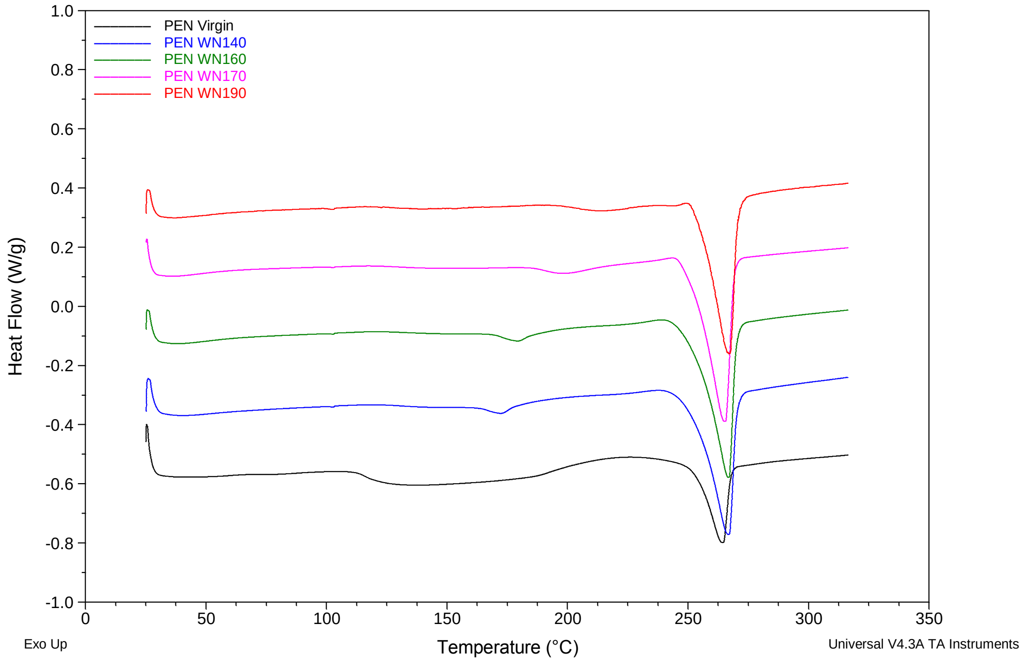


Figure 8.121 DSC of PEN samples aged under wet (1.6% AH) nitrogen, cycle 1

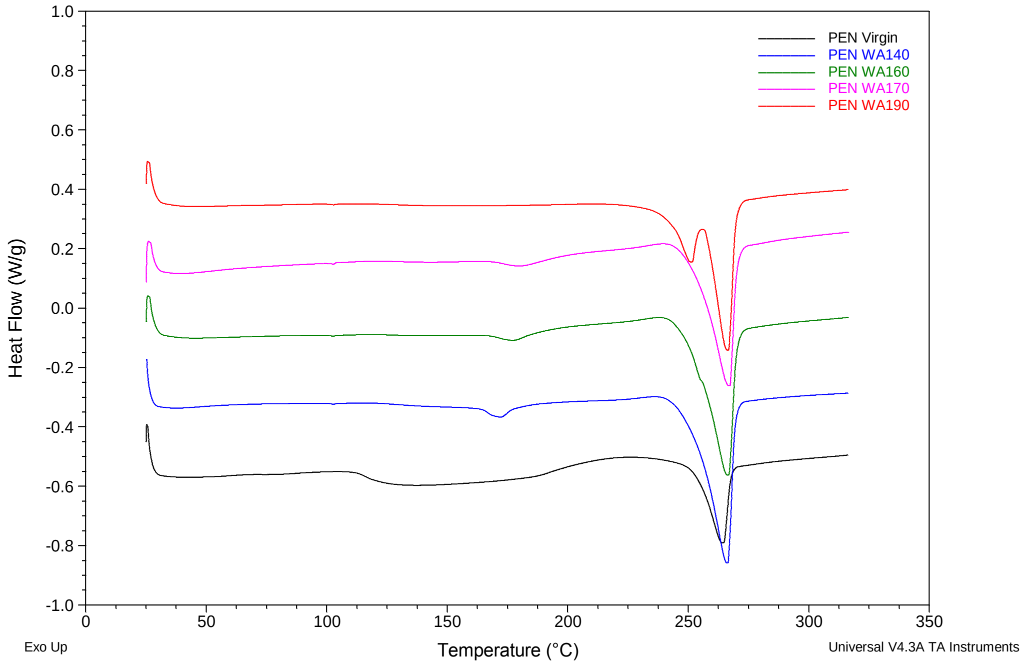


Figure 8.122 DSC of PEN samples aged under wet (1.6% AH) air, cycle 1

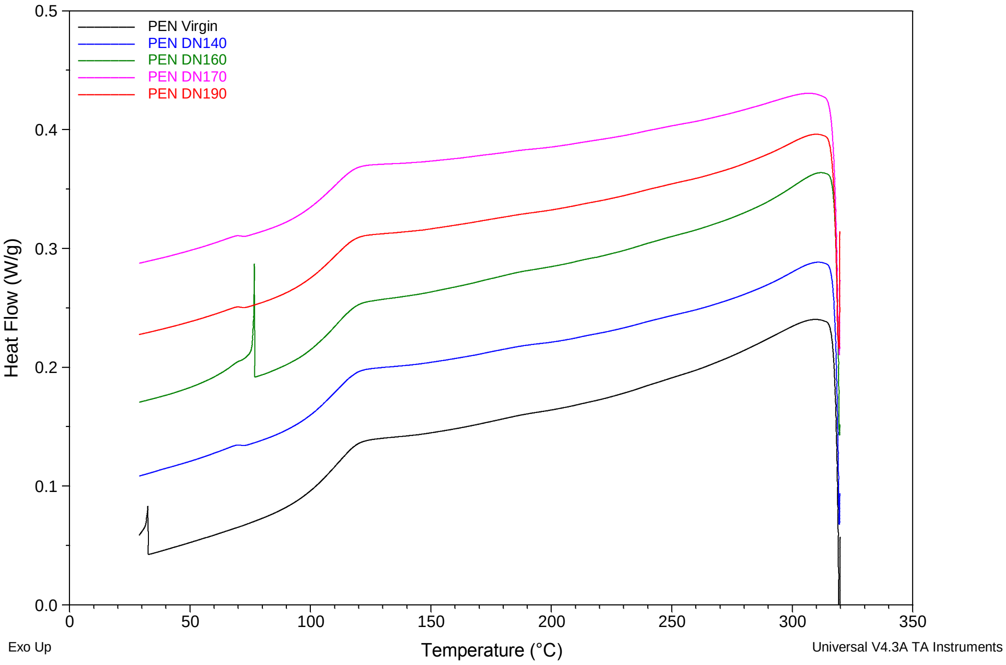


Figure 8.123 DSC of PEN samples aged under dry nitrogen, cycle 2

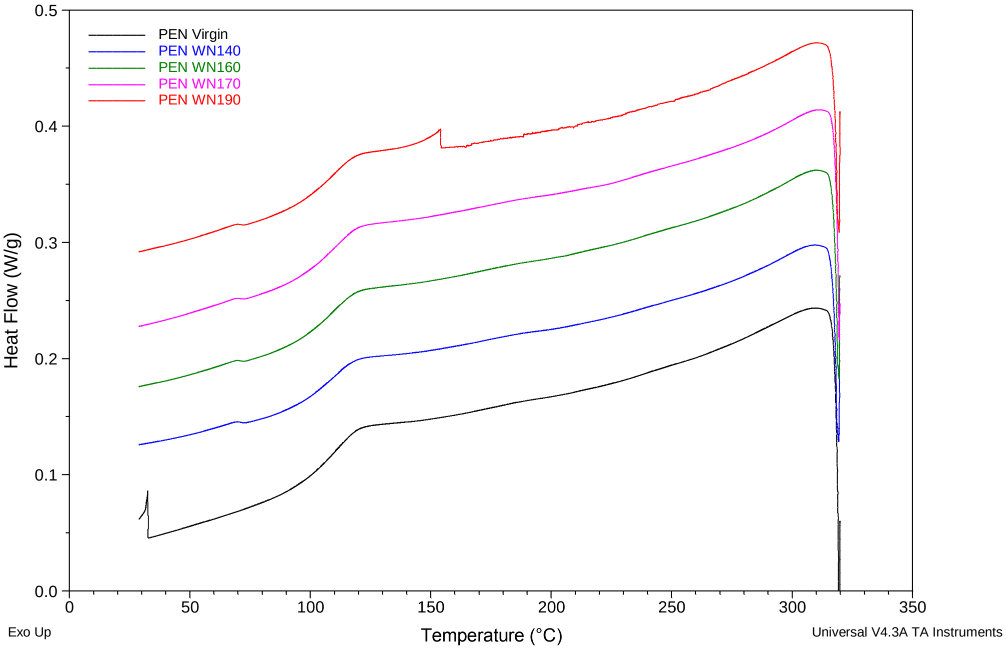


Figure 8.124 DSC of PEN samples aged under wet (1.6% AH) nitrogen, cycle 2

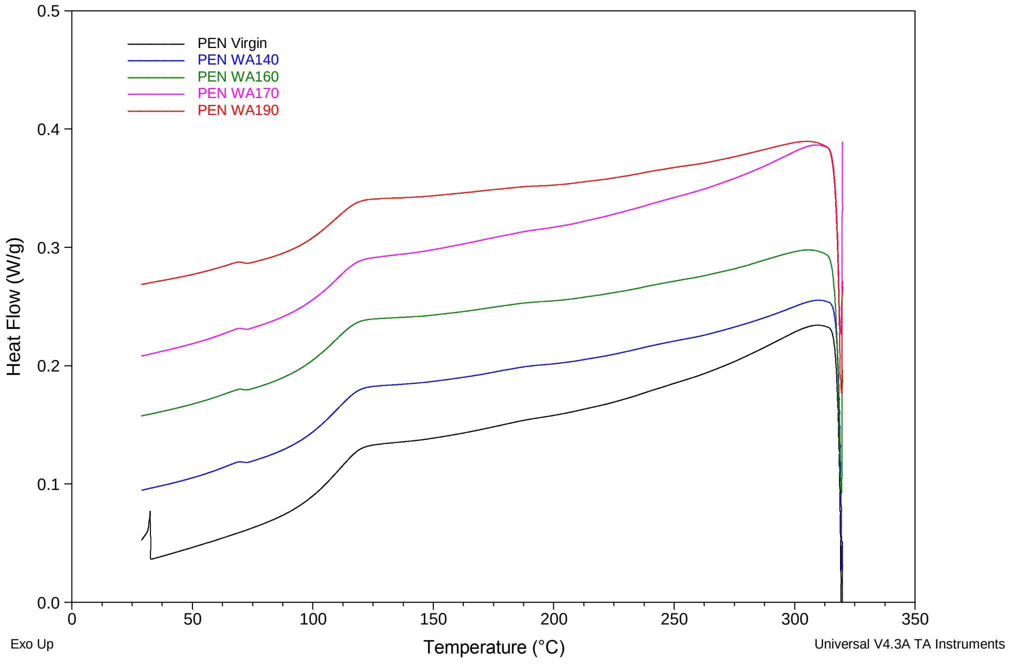


Figure 8.125 DSC of PEN samples aged under wet (1.6% AH) air, cycle 2

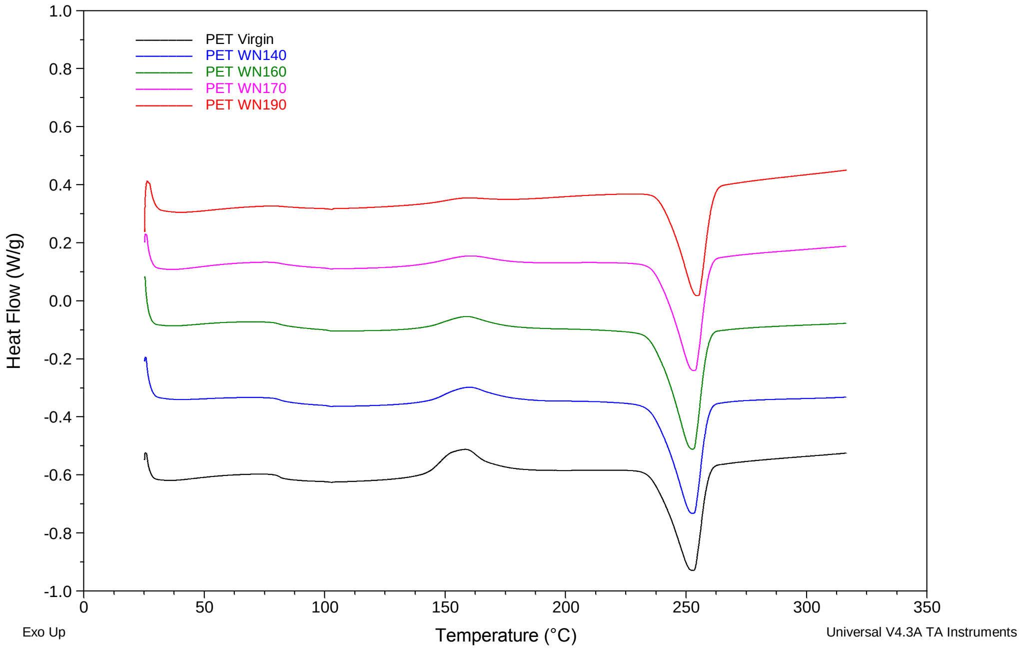


Figure 8.126 DSC of PET samples aged under wet (1.6% AH) nitrogen, cycle 3

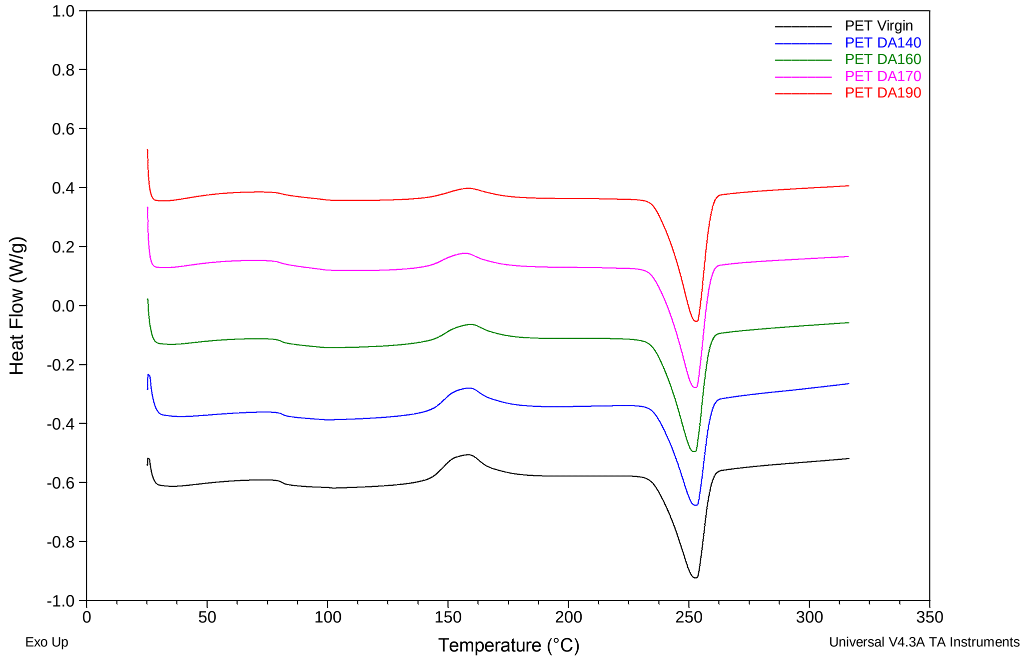


Figure 8.127 DSC of PET samples aged under dry air, cycle 3

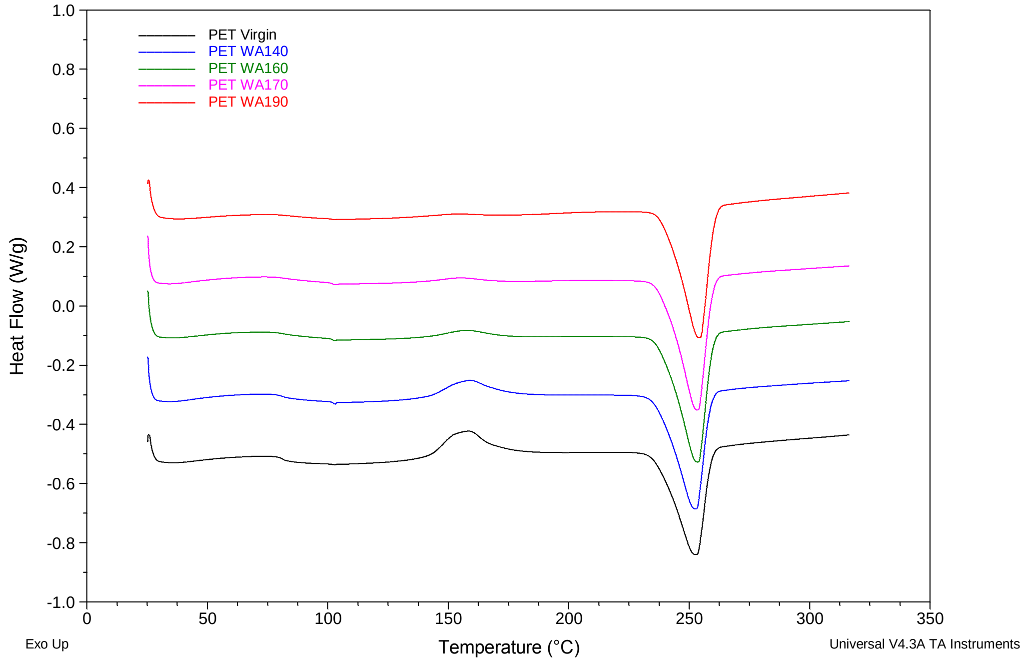


Figure 8.128 DSC of PET samples aged under wet (1.6% AH) air, cycle 3

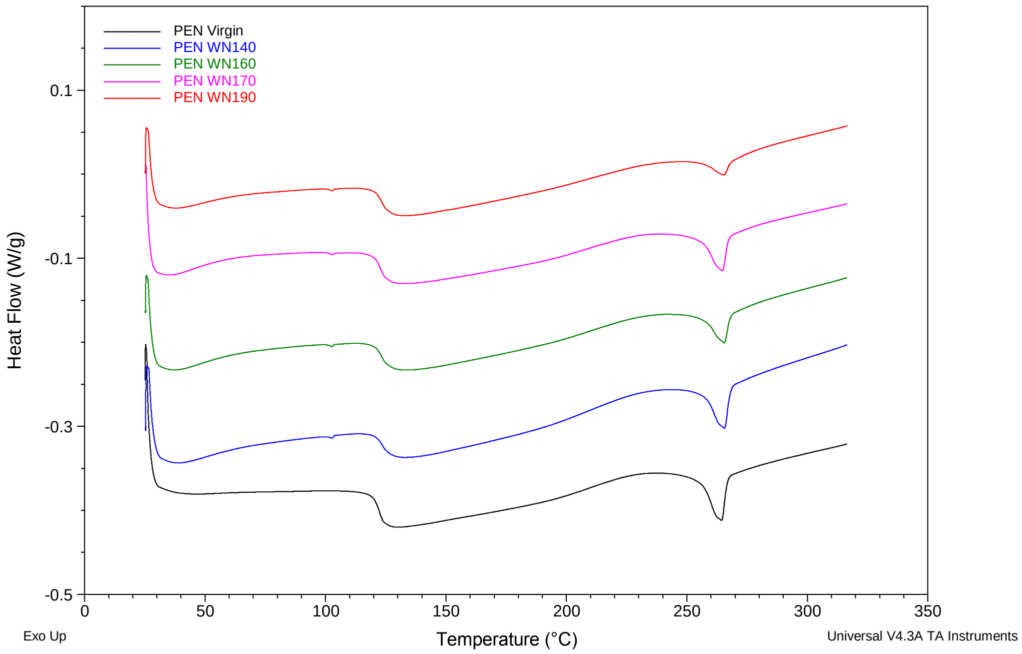


Figure 8.129 DSC of PEN samples aged under wet (1.6% AH) nitrogen, cycle 3

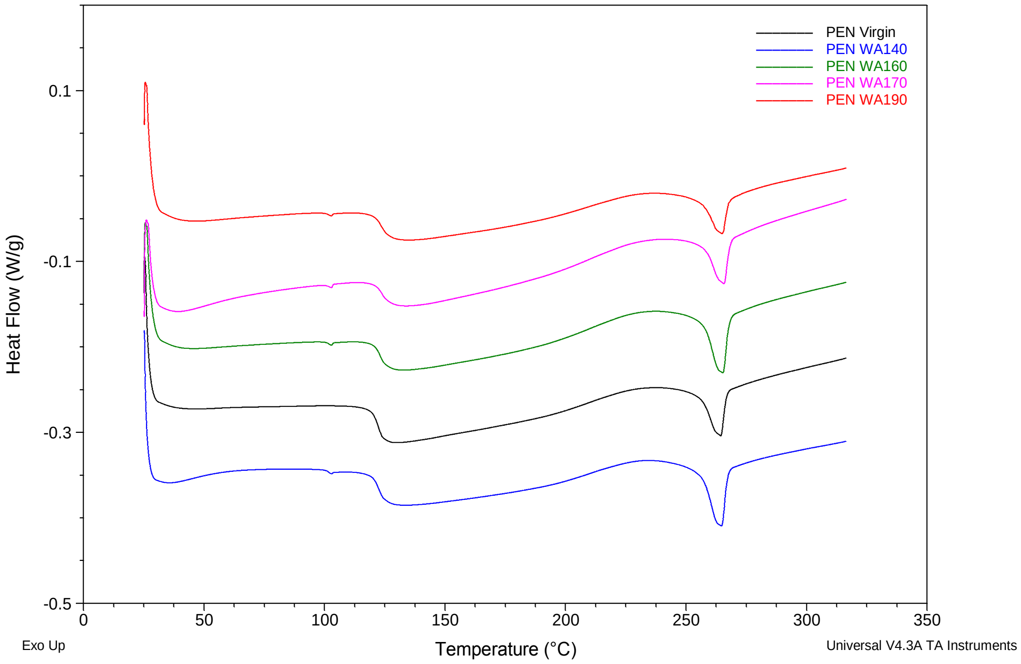


Figure 8.130 DSC of PEN samples aged under wet (1.6% AH) air, cycle 3

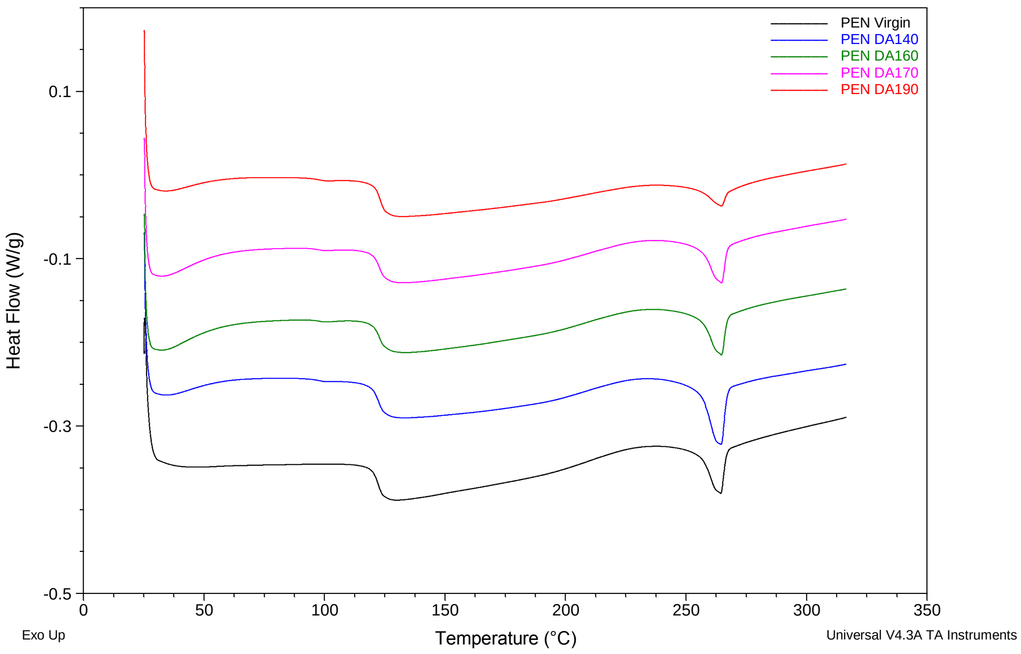


Figure 8.131 DSC thermal transitions in PEN samples aged under dry air, cycle 3

Ageing of Poly(ethylene terephthalate) and Poly(ethylene naphthalate) Under Moderately Accelerated Conditions

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ABSTRACT: PEN is thought to have increased thermal and hydrolytic resistance in comparison to PET. However, due to a lack of research, few studies have been published on the degradation of PEN. In our research, we report on the extent of degradation in PET and PEN after ageing under contrasting environments (dry nitrogen, dry air, wet nitrogen, and wet air) at temperatures between 140°C and 190°C. A combination of analysis techniques were employed in order to characterize and track the physical and chemical changes in the aged polyester samples, enabling the effects of temperature, water, and oxygen to be mapped onto the resultant property changes of PET and PEN. The extent of degradation has been shown to differ between both polymers and the dominant degradation mechanism in PET was shown to differ with ageing temperature. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4517–4529, 2012

Key words: degradation; polyesters; molecular weight distribution; thermal properties

INTRODUCTION

Introduction to polyesters

Synthetic polymers continue to play a significant role in society today due to their extensive applications. Modern lifestyles would be impossible without synthetic polymers used to produce valuable products such as protective packaging, insulation materials in buildings, medical devices, and key components for diverse applications such as renewable energy production. Polyesters, in particular, are currently one of the most important classes of synthetic thermoplastic polymers in use today, with applications ranging from bottles for carbonated soft drinks to fibers for clothing and polyester based film for use within the packaging and electronic industries.

The first synthesis of linear aliphatic polyesters began in the 1930s by Carothers at DuPont, USA; however these aliphatic polyesters did not succeed commercially due to their low melting points and poor hydrolytic stability.[1] This research did, however, inspire other scientists to attempt the synthesis of polyesters from ethylene glycol and terephthalic acid monomers, leading to the synthesis of the first linear aromatic polyester, poly(ethylene terephthalate) (PET), by Whinfield and Dickson in 1941.[2,3] Whinfield and Dickson identified PET as an excellent fiber forming polymer due to its low cost and thermal/mechanical properties, resulting in rapid expansion in the production of PET fibers. The development of polyester based films from PET followed thereafter. PET is now one of the leading commercial polymers, accounting for 8% of the total world plastic demand in 2009.[4] Its major commercial uses remain as a textile fiber, material for blow molded bottles and biaxially oriented film used for packaging, advanced photo systems, electrical and electronic applications.

Although the demand for PET remains very strong, applications exist which often require improved properties that PET cannot provide. These include increased mechanical strength for motor substrates, high temperature resistance for electronics and improved gaseous barrier properties for food packaging applications. One polymer that can provide such properties is poly(ethylene naphthalate) (PEN). PEN incorporates naphthalene rings into the polymer backbone as opposed to phenyl rings in PET. The naphthalene units stiffen the polymer backbone resulting in a higher glass transition temperature and improved thermal, mechanical, electrical, and barrier properties, in comparison to PET.[5,6] Although PEN was first produced in 1948, it is now only beginning to make a major appearance into the market place due to the lack of availability of the

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Additional Supporting Information may be found in the online version of this article.

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starting monomer, dimethyl-2,6-naphthalenedicarboxylate (NDC). Large-scale production of NDC was only introduced in the early 1990s leading to a significant increase in the raw material feed stocks for the production of PEN, reducing the overall cost of PEN resin.[1] This led to a substantial increase in the production and applications of PEN, with PEN now competing with PET in certain performance-driven markets based on its superior strength, heat stability, and barrier properties.

Degradation of polyesters

Degradation of polyesters, such as PET and PEN, is generally inevitable during synthesis and processing as the polyesters are exposed to high temperatures, both under non-oxidative and oxidative conditions in the presence of moisture. These conditions can result in a combination of thermal, thermo-oxidative, and hydrolytic degradation reactions leading to the evolution of volatile degradation products and significant loss of crucial polymer properties. Unfortunately, water uptake by polyester chips is particularly inevitable during post-polymerisation cooling processes and storage. The hydroxyl, carboxyl, and ester groups within the polyester network are likely to retain water and therefore if the polyester chips were to be processed directly, their molar mass would significantly decrease as a result of hydrolytic degradation. For this reason, polyester chips are crystallized, to avoid sintering during drying, and then dried for several hours to reduce the moisture content prior to processing.

The effect of this pre-processing drying treatment on the thermal degradation of PET polyester chips has been investigated. Villain et al.[7] examined the overall mass loss behavior of PET when dried under air and nitrogen at 160°C for 800 minutes, prior to thermal degradation at processing temperatures of 280°C and 310°C. The most significant mass loss was reported when drying and degradation were performed under air, due to oxidative degradation leading to a reduction in the overall length of the polymer chain. PEN is reported to have increased thermal[1] and hydrolytic[8] resistance in comparison to PET; however due to a lack of research on PEN, few studies have been published and no research has been conducted on the effects of drying on the degradation of PEN.

In our research, we report on the extent of degradation in PET and PEN after ageing under different drying conditions. PET and PEN polyester chips were aged under dry nitrogen, dry air, wet nitrogen and wet air environments at temperatures of 140, 160, 170, and 190°C. The ageing temperatures selected were based around the typical drying temperatures currently used during the pre-processing treatment of PET. With increasing temperature, the degradation mechanism during ageing is thought to differ. Hydrolysis is believed to dominate over extended periods of time at lower ageing temperatures (i.e., 140–160°C) with oxidative degradation dominating at higher ageing temperatures (i.e., 190°C). This contrasting set of ageing conditions, at which the polyester samples were exposed to, enables the effects of temperature, water and oxygen to be mapped onto the resultant property changes of PET and PEN.

EXPERIMENTAL

Materials

Commercial samples of PET and PEN were kindly supplied by DuPont Teijin Films. Both PET and PEN were supplied as transparent chips with a weight average molar mass (M_w) of 24900 ± 141 g mol^{-1} and 20,200 ± 71 g mol^{-1}, respectively. Prior to use, the polyester chips were stored for several hours in a vacuum desiccator at room temperature, to remove any surface water.

Ageing apparatus

The purpose of the experimental apparatus was to age samples under contrasting environments; dry nitrogen, wet nitrogen, dry air, and wet air at elevated temperatures, over a period of 24 h. This enabled the effects of thermal, thermal-hydrolytic, thermo-oxidative, and thermo-oxidative-hydrolytic degradation to be studied in both polyesters. A schematic representation of the ageing apparatus is illustrated in Figure 1.

The apparatus consisted of a thermostatically controlled block heater capable of reaching temperatures of 200°C ± 1.0°C. 1 g of polymer chip sample was placed in each sample tube for ageing and dry/wet, nitrogen/air were fed individually into each sample chamber yielding dry non-oxidative, wet non-oxidative, dry oxidative, and wet oxidative conditions. Flowing gas through a dreschel bottle containing water created a wet atmosphere (1.6% absolute humidity) and silica gel created a dry atmosphere. The temperatures studied were 140, 160, 170, and 190°C and the gas flow was regulated using a flow meter, supplying 50 mL min^{-1} to each sample chamber. After the drying temperature was programmed on the block heater, the system was left to equilibrate for 30 minutes prior to starting the experiment time of 24 h. After completion, all samples were dried in a vacuum oven at 60°C for a period of 24 h to remove any surface water prior to analysis.

A combination of analysis techniques were employed in order to characterize and track the

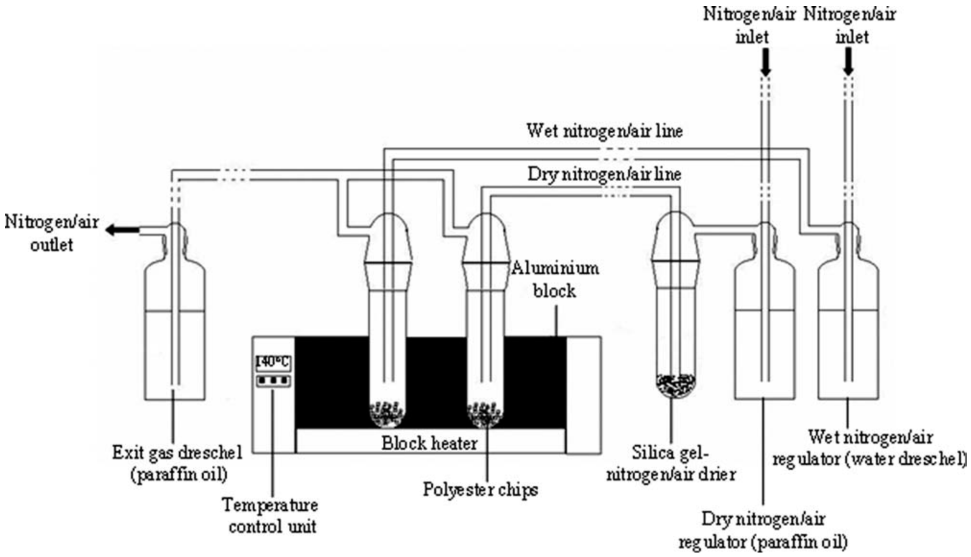

Figure 1 Apparatus for ageing PET and PEN.

physical and chemical changes in the aged polyester samples. Changes in the physical morphology of the samples as a result of ageing, such as crystalline content/behavior, were characterized primarily using differential scanning calorimetry (DSC). The high temperature stability of all samples was assessed using thermogravimetric analysis (TGA) to determine if the different ageing conditions had significant impact on the overall thermal stability of the material. The molar mass of the aged polyester samples was also expected to vary under the action of thermal, thermo-oxidative, and hydrolytic conditions. Therefore changes in the molar mass of the polyester samples were characterized using gel permeation chromatography (GPC).

Differential scanning calorimetry (DSC)

All samples were analyzed using a TA Q1000 DSC equipped with a RC90 refrigerated cooling system. The instrument was calibrated with a standard of indium and all samples were prepared in aluminum hermetic DSC pans. A heat-cool-reheat method was adopted, firstly heating the samples from 25°C to 320°C, at a rate of 10°C min^{-1}, to destroy their thermal history. Secondly, the samples were cooled from 320°C to 25°C, at a rate of 10°C min^{-1}, to impose a known thermal history on all samples. A second heating cycle was finally performed ramping from 25°C to 320°C, at a rate of 10°C min^{-1}. The heat-cool-reheat DSC method was conducted under a flow of dry nitrogen (20 mL min^{-1}) on 6 mg samples and all DSC data was processed using TA software. All temperature values quoted from the DSC curves are rounded to the nearest integral value, with an error of ±1°C.

Thermogravimetric analysis (TGA)

TGA studies were carried out using a Perkin Elmer TGA (TGA7), controlled using Windows based software on a bench-top PC. All experiments were carried out using 10 mg of sample under an inert atmosphere of helium. A heating profile of 50°C to 800°C was performed at a heating rate of 10°C min^{-1} and all data was processed using Origin software. From the data obtained, the % mass loss was recorded as a function of temperature and the onset temperatures of degradation were determined at 5% mass loss. The temperature values quoted from the TGA curves are rounded to the nearest integral value, with an error of ±1°C.

Gel permeation chromatography (GPC)

All practical GPC work was kindly undertaken by Smithers Rapra based in Shrewsbury, UK. The molar mass and molar mass distribution of the aged polyester samples were determined on a Viscotek TDA model 301 GPC, equipped with PL hexafluoroisopropanol (HFIP) gel guard columns and a refractive index detector. Measurements were carried out at 40°C, using HFIP with 25 m*M* sodium trifluoroacetate (NaTFAc) as the eluent, at a rate of 0.8 mL min^{-1}. Duplicate solutions of each sample were prepared by adding 10 mL of solvent to 20 mg of polymer and leaving overnight to dissolve. The solutions were thoroughly mixed and filtered through a 0.45 μm polytetrafluoroethylene (PTFE) filter prior to analysis. The GPC system was calibrated using polymethylmethacrylate (PMMA); therefore results are expressed as "PMMA equivalent" molar masses. Data was collected and analyzed using Polymer Laboratories 'Cirrus' software. For all samples, integration limits were selected to exclude any material with a PMMA equivalent molar mass of less than 400 g mol^{-1}. The results are summarized as the calculated molar mass averages and polydispersities (M_w/M_n) and the graphs are all plotted to the same area, the y-axis being a function of mass fraction.

RESULTS AND DISCUSSION

Physical observations of PET and PEN after ageing

Prior to reporting DSC, TGA, and GPC results, it is important to consider the physical appearance of the polymers after ageing. In addition to a significant decrease in molar mass and subsequent loss in mechanical, physical, and chemical properties expected as a result of ageing, discoloration is also likely to be evident. Yellowing of polyesters is a severe problem in synthesis and melt processing and is thought to be a result of both thermal and thermo-oxidative degradation.[1,9,10–13] The transparency of both PET and PEN renders both polyesters suitable for the production of blow molded bottles and packaging materials; however discoloration can adversely affect the end use of the final product, making it suitable only for materials where color is not an issue.

All PET samples aged under dry nitrogen and dry air were found to be crystalline (i.e., white, opaque), with no hint of discoloration at any ageing temperature. Similarly, PET samples aged under wet nitrogen and wet air were also found to be crystalline; however discoloration (yellowing) was evident in PET samples aged at 190°C. Initially, on observation of the aged PEN samples, it was evident that all samples were not fully crystalline, in contrast to PET. Under all environments at 140°C, the PEN samples were found to be only partially crystalline (i.e., partly opaque). However, this is not entirely surprising as significant crystallization of PEN does not occur until 180°C, with the rate of maximum crystallization occurring around 210°C. With increased ageing temperature, under all environments, the PEN samples were found to anneal from transparent, amorphous polyester chips to white, crystalline polyester chips. No discoloration of PEN was evident under all environments at ageing temperatures of 140°C and 160°C. However, in contrast to PET, discoloration was evident in the PEN samples aged at 170°C under all environments. Of all PET and PEN samples aged, the most significant discoloration was evident in PEN samples aged under all environments at 190°C. This increased discoloration of PEN is in agreement with the studies completed by Botelho et al.[14] and Scheirs et al.[15] Both studies report that PEN discolors more rapidly than PET, suggesting that the discoloration is due to the formation of highly conjugated and highly absorbing naphthalene structures formed as a result of degradation.

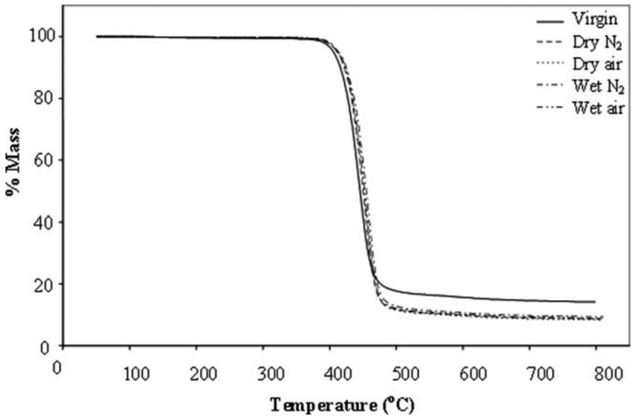

Figure 2 TG curves of PET samples aged under different environments at 140°C.

In addition to the discoloration of aged PET and PEN samples, a loss in mechanical strength was apparent. All PET samples aged at 190°C had reduced mechanical strength, in comparison to all other samples. These polyester chips became brittle after ageing and crumbled readily when pressure was exerted upon them. The most significant loss of mechanical strength was noted in PET samples aged under dry and wet air at 190°C. Similar to PET, a loss in mechanical strength was evident in PEN. All PEN samples aged at 190°C were found to have reduced mechanical strength, to the extent that the polyester chips became brittle and crumbled when pressure was exerted upon them. In contrast to PET, the PEN samples aged under wet air at 170°C were also found to be very brittle, indicating a more significant loss in mechanical strength in PEN than in PET aged under identical conditions. Of all PET and PEN samples aged, the most significant loss in mechanical properties was evident in PEN samples aged under wet air at 190°C.

Thermal stability of PET and PEN after ageing

The thermal stability of all aged polyester samples was assessed using TGA to determine if there were any changes in the polyesters significant enough to impact on their degradation profile. Changes in the overall thermal stability of PET and PEN will be observed if significant degradation of the polyester chains (e.g., hydrolytic chain scission at the ester linkages or oxidative cross-linking) has occurred during ageing.

Figures 2–5 illustrate the thermal stability of PET and PEN samples aged under all environments at temperatures of 140°C and 190°C. Due to such minor changes observed in the overall thermal stability of all aged samples of PET and PEN, the TGA curves

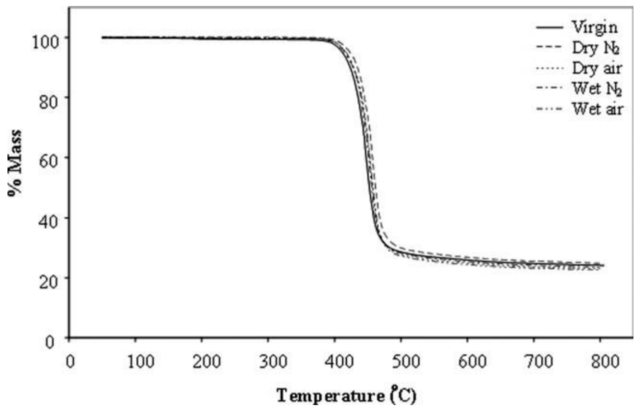

Figure 3 TG curves of PEN samples aged under different environments at 140°C.

are only shown for the samples aged at the lowest and highest temperatures. All other TGA curves can be found in the Supporting Information. Table I presents the temperatures of degradation from the TGA curves illustrated in Figures 2–5. Comparison of the TGA results reveals no significant differences in the mass loss behavior and therefore overall thermal stability between the virgin and aged samples of PET and PEN.

All samples of PET appear to undergo only one significant mass loss step, starting around 406°C, due to thermal degradation of the polyester backbone, i.e., chain scission at the ester bonds. Small differences are evident in the % mass of PET remaining after degradation. All PET samples aged under dry and wet, inert and oxidative environments have a marginally lower % residual mass after degradation, in comparison to the virgin material. This suggests that the extent of chain scission prior to analysis is more significant in aged PET than virgin PET. Shorter polymer chains, formed as a result of chain scission degradation reactions during ageing, will volatilize faster, resulting in a lower overall % mass of polyester remaining. However, despite these differences in residual mass, the extent of degradation in all aged PET samples is not sufficient enough to change the overall thermal stability of the material. Therefore, regardless of changes in the overall physical appearance and mechanical strength of aged PET samples, in comparison to virgin PET, the overall thermal stability of the materials remains unchanged.

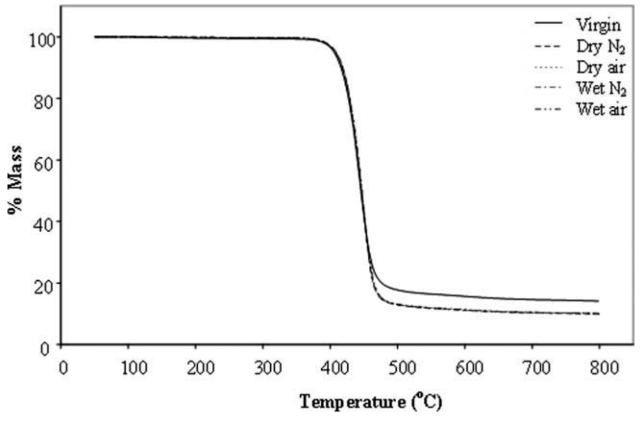

Figure 4 TG curves of PET samples aged under different environments at 190°C.

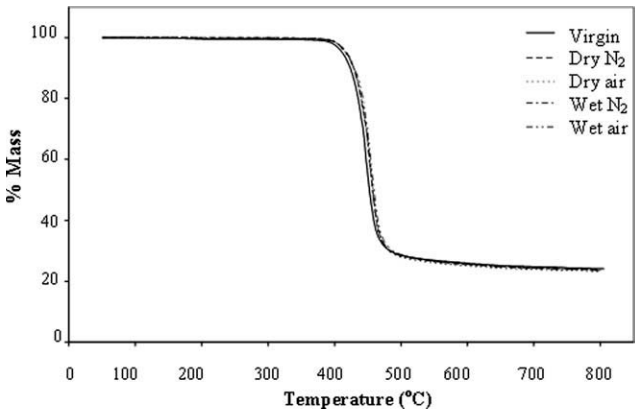

Figure 5 TG curves of PEN samples aged under different environments at 190°C.

From Figures 3 and 5, it can be observed that aged samples of PEN also appear to undergo only one significant mass loss step, starting above 412°C. This is identical to PET and is again due to thermal degradation of the polymer backbone, i.e., chain scission at the ester bonds. It is also apparent that no distinct differences exist between the thermal stability of PEN samples aged under different environments between temperatures of 140°C and 190°C. However, the onset temperatures of degradation and temperatures of maximum mass loss are marginally higher for virgin and aged samples of PEN, in comparison to PET. This is thought to be a result of the enhanced delocalization of charge across the naphthalene ring units in PEN, increasing the stability of the ester linkages. Interestingly, no significant differences are evident in the % mass of original polymer remaining after the degradation of aged PEN samples, in comparison to virgin PEN. Degradation of PEN is therefore thought to be minimal under the ageing conditions studied.

Changes in molar mass of PET and PEN after ageing

Despite insignificant changes in the overall thermal stability of aged samples of PET and PEN, the molar mass is thought to vary under the action of thermal, thermo-oxidative, and hydrolytic conditions. Therefore, changes in the molar mass of virgin and aged samples of PET and PEN were characterized using GPC.

TABLE I
Degradation Temperatures from TG Curves of PET and PEN Samples Aged at 140°C and 190°C

Polymer	Ageing environment	Ageing temperature, °C	Onset of degradation, °C	Temperature of maximum mass loss, °C	Mass remaining at 800°C, %
PET	Virgin	N/A	406	440	14
PET	Dry nitrogen	140	406	441	10
PET	Dry nitrogen	190	409	444	10
PET	Dry air	140	407	446	9
PET	Dry air	190	408	446	10
PET	Wet nitrogen	140	409	448	10
PET	Wet nitrogen	190	408	442	10
PET	Wet air	140	408	441	10
PET	Wet air	190	408	444	10
PEN	Virgin	N/A	412	443	24
PEN	Dry nitrogen	140	423	451	25
PEN	Dry nitrogen	190	418	449	24
PEN	Dry air	140	417	448	23
PEN	Dry air	190	418	450	23
PEN	Wet nitrogen	140	415	447	24
PEN	Wet nitrogen	190	417	447	24
PEN	Wet air	140	418	451	23
PEN	Wet air	190	417	450	24

Table II presents the number-average molar masses (M_n), weight-average molar masses (M_w), and polydispersity values determined for all aged samples of PET by GPC. Comparison of the GPC data presented indicates that thermal degradation of PET is minimal up to ageing temperatures of 190°C under dry nitrogen. A small decrease in M_w and M_n is noted only at 190°C under dry air indicating that the presence of oxygen is promoting the degradation of PET at the highest ageing temperature. Oxidative degradation of PET is initiated by heat and oxygen leading to the formation of hydroperoxides at methylene sites within the polymer chains.[16] These hydroperoxides are unstable and therefore undergo a series of chain scission degradation reactions. Degradation is further accelerated when ageing is performed under moist thermal conditions, with a decrease in molar mass noticeable from 140°C in wet nitrogen. This indicates that although significant degradation of PET does not occur under the influence of purely thermal conditions (i.e., dry nitrogen), the presence of water induces degradation of PET at lower ageing temperatures. Hydrolytic degradation of PET is reported to involve chain scission at the ester linkages. Each water molecule breaks down one ester bond, leading to the formation of one carboxyl and one hydroxyl group. During hydrolytic ageing of PET, it is believed that water diffuses into the amorphous regions of the polymer where hydrolysis occurs at a rate dependant on the sample shape, crystalline morphology of the sample, the relative humidity and temperature.[12,13,17–20] At temperatures below the glass transition temperature of PET, hydrolytic degradation is thought to be negligible. However, above the glass transition temperature, increased mobility of the polymer chains enables penetration of water into the amorphous regions, increasing the rate of hydrolytic degradation. Therefore, as the ageing temperature increases from 140°C to 190°C under thermal-hydrolytic conditions, more extensive degradation occurs with the most significant decrease in molar mass observed at 190°C. Similarly, the presence of water during the thermo-oxidative ageing of PET has significant impact on the molar mass distribution of PET. Samples aged under thermo-oxidative-hydrolytic conditions, at temperatures between 140°C and 190°C, all exhibit a pronounced decrease in the average molar mass with increased ageing temperature. A small decrease in the average molar mass values can be observed for PET samples aged under thermo-oxidative-hydrolytic conditions (i.e., wet air) at 140°C. The extent of this degradation is only marginally higher than that observed for degradation of PET under purely thermo-oxidative conditions (i.e., dry air) at 140°C. However, as the ageing temperature increases, the extent of degradation increases and a sharp decrease in the average molar mass can be observed for PET samples aged at 160, 170, and 190°C. All GPC curves for PET samples aged under all ageing environments can be found in the Supporting Information.

The GPC results therefore demonstrate that the dominant degradation reaction in PET differs with ageing temperature. At the lowest ageing temperature of 140°C, no significant changes in M_w are evident with contrasting ageing conditions and therefore it is impossible to deduce which degradation process is dominant. In contrast, the GPC results for PET indicate that hydrolytic degradation is the

TABLE II
GPC Average Molar Mass Results for PET Samples Aged Under Different Environments at Temperatures Between 140 and 190°C

Ageing environment	Ageing temperature, °C	M_w (g mol^{-1})	M_n (g mol^{-1})	Polydispersity
Virgin	N/A	24900 ± 141	8725 ± 64	2.9
Dry nitrogen	140	24350 ± 71	8480 ± 57	2.9
Dry nitrogen	160	24200	8600 ± 57	2.8
Dry nitrogen	170	24650 ± 212	8660 ± 99	2.8
Dry nitrogen	190	24950 ± 71	8865 ± 78	2.8
Dry air	140	23800 ± 141	9120 ± 14	2.6
Dry air	160	24150 ± 212	9030 ± 71	2.7
Dry air	170	24550 ± 71	8830	2.8
Dry air	190	21300	7610 ± 14	2.8
Wet nitrogen	140	22950 ± 212	8310 ± 14	2.8
Wet nitrogen	160	22650 ± 354	8145 ± 21	2.8
Wet nitrogen	170	21600	8050 ± 42	2.7
Wet nitrogen	190	19350 ± 71	8000 ± 113	2.4
Wet air	140	23250 ± 212	8520 ± 14	2.7
Wet air	160	21100	7745 ± 50	2.7
Wet air	170	18800 ± 141	7025 ± 149	2.7
Wet air	190	16800 ± 141	6510 ± 156	2.6

dominant degradation reaction occurring between 160°C and 170°C. From Table II, it can be seen that degradation of PET is minimal under purely thermal and thermo-oxidative ageing conditions, indicating that even the presence of air is not enough to result in significant degradation of PET at 160°C and 170°C. However, significant changes in M_w can be observed in both PET samples aged under thermal-hydrolytic and thermo-oxidative-hydrolytic conditions indicating that hydrolytic degradation is likely to be the dominant degradation reaction occurring at 160°C and 170°C. Obviously, the decrease in molar mass is larger in PET samples aged at 170°C than 160°C indicating that progressively more hydrolytic degradation is occurring at 170°C due to increased mobility of the polymer chains. GPC results for PET aged under contrasting environments at 190°C illustrate that changes in M_w are not only influenced by the presence of water, but also oxygen. No significant changes in M_w can be observed under thermal conditions, indicating once again that thermal degradation of PET is minimal at temperatures up to 190°C. However, a large decrease in the molar mass of the aged system can be seen on the introduction of oxygen (i.e., dry air) at 190°C highlighting that the presence of oxygen, during ageing at increased temperatures, promotes the degradation of PET. The most significant decrease in M_w can be observed in PET samples aged under thermo-oxidative-hydrolytic conditions at 190°C. Therefore, as the temperature is increased, it is thought that oxidative degradation becomes the dominant degradation process, resulting in the largest changes in the molar mass of aged PET samples. The dominant degradation reaction in PET has therefore been shown to differ with ageing temperature. At lower temperatures, i.e., 140–170°C, it has been illustrated that hydrolysis is the dominant degradation reaction, with thermo-oxidative degradation dominating at the highest ageing temperature of 190°C.

Difficulties were experienced during the analysis of aged PEN samples by GPC due to the crystallinity that developed upon ageing. This was sufficient enough to render the polymer insoluble. As a consequence, all aged samples of PEN had to be rendered amorphous before dissolution was possible. This was performed simply by melting the samples at 320°C in a DSC and quenching to the amorphous state. While this involved imposing a new thermal history on all samples, it was hoped that the fact that all aged samples of PEN had the same thermal history superimposed, would still enable comparative use of the GPC data thus obtained.

Table III presents the M_n, M_w, and polydispersity values determined by GPC for PEN samples aged under different environments at 190°C. The molar mass distribution curves for PEN can be found in the Supporting Information. Due to such minor changes observed in the overall molar mass distribution of PEN samples aged under the harshest conditions, i.e., 190°C, it was deemed unnecessary to analyze all other PEN samples by GPC. Comparison of the GPC data obtained for aged PEN samples reveals no significant changes in the overall molar mass of the aged PEN samples, in comparison to virgin PEN. Degradation of PEN, under all ageing conditions, is therefore minimal up to temperatures of 190°C. However, one question remains unanswered—why do the aged samples of PEN embrittle badly if the material has not degraded (i.e., no decrease in molar mass observed)?

TABLE III
GPC Average Molar Mass Results for PEN Samples Aged Under Different Environments at 190°C

Ageing environment	Ageing temperature, °C	M_w (g mol^{-1})	M_n (g mol^{-1})	Polydispersity
Virgin	N/A	20200 ± 71	5455 ± 233	3.7
Dry nitrogen	190	20700 ± 283	5505 ± 276	3.8
Dry air	190	22950 ± 71	6490 ± 71	3.5
Wet nitrogen	190	19700 ± 141	4780 ± 0	4.1
Wet air	190	19650 ± 71	4760 ± 57	4.1

Changes in physical morphology after ageing

Although distinct trends were evident in the molar mass distribution curves for aged PET, the overall thermal stability of the aged PET/PEN samples, assessed using TGA, was unchanged relative to the unaged samples. It was therefore of interest to determine if any significant changes in the physical morphology of PET and PEN could be observed as a result of ageing. Crystalline content and behavior was monitored in all samples using DSC.

Initial DSC heating cycle (cycle 1)

The initial DSC heating cycle was performed in order to destroy the thermal history of the samples prior to studying permanent morphological changes. However, it can also provide information on the extent of crystallinity in samples, formed as a result of ageing.

Figure 6 represents the initial DSC heating cycle obtained for PET samples aged under dry nitrogen between temperatures of 140°C and 190°C, in comparison to virgin PET. Table IV presents the temperatures of the DSC thermal transitions in all PET samples including the onset temperature of the crystalline melt (T_{onset}), the maximum temperature of the crystalline melt ($T_{\max}$), and the enthalpy of the crystalline melt. Virgin PET shows a cold crystallization peak around 150°C, which is absent for the aged samples, indicating, as would be expected, that they had crystallized during the ageing process. Small, so-called, annealing peaks are evident some 10–20°C above the ageing temperature in all aged samples of PET in addition to one crystalline melt peak. The T_{onset}, $T_{\max}$, and enthalpy of the crystalline melt peak were not found to differ significantly between samples of PET aged at 140, 160, and 170°C under dry nitrogen, in comparison to unaged PET. An increase in the enthalpy of the crystalline melt can be observed for PET aged at 190°C; however this is due to the annealing peak merging with the crystalline melt peak. The impact of thermo-oxidative, thermal-hydrolytic, and thermo-oxidative-hydrolytic ageing on the crystalline content/behavior of PET was found to be very similar to the results illustrated in Figure 6 for thermal ageing and can therefore be found in the Supporting Information.

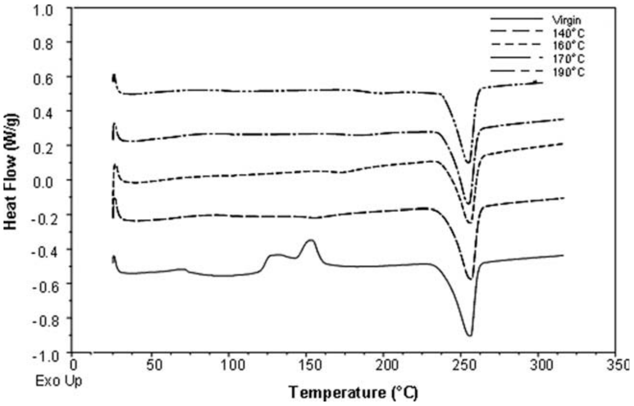

Figure 6 DSC curves of PET samples aged under dry nitrogen at temperatures between 140°C and 190°C, cycle 1.

The impact of thermal, thermo-oxidative, thermal-hydrolytic, and thermo-oxidative-hydrolytic ageing on the crystalline content/behavior of PEN samples was also found to be similar in all samples. Therefore only one example has been illustrated. Figure 7 represents the DSC curves obtained for PEN samples aged under dry nitrogen between temperatures of 140°C and 190°C, in comparison to unaged PEN. A glass transition can be observed at 117°C for unaged PEN and PEN aged at 140 °C; however as the glass transition phenomenon is purely an amorphous event, no glass transition temperatures can be observed in any PEN samples aged above 140°C due to the increased levels of crystallinity formed during ageing. Similarly, due to the increased levels of crystallinity in PEN samples aged above 140°C, no cold crystallization event is evident on heating and small annealing peaks become visible, identical to those observed in PET. Table V presents the temperatures of the DSC thermal transitions in all PEN samples including the T_{onset}, $T_{\max}$, and enthalpy of the crystalline melt. All DSC heating curves for PEN samples aged under dry air, wet nitrogen, and wet air can be found in the Supporting Information.

DSC cooling cycle (cycle 2)

The DSC cooling cycle provides useful information on the crystallization behavior of the polyesters.

TABLE IV
DSC Thermal Transitions in PET Samples Aged Under Different Environments at Temperatures Between 140°C and 190°C, Cycle 1

Ageing environment	Ageing temperature, °C	Enthalpy of crystalline melt, J g^{-1}	T_{onset} crystalline melt, °C	T_{max} crystalline melt, °C
Virgin	N/A	35	241	256
Dry nitrogen	140	34	242	257
Dry nitrogen	160	30	242	256
Dry nitrogen	170	33	241	256
Dry nitrogen	190	42	244	254
Dry air	140	33	240	255
Dry air	160	36	241	255
Dry air	170	36	241	255
Dry air	190	43	240	255
Wet nitrogen	140	37	242	255
Wet nitrogen	160	38	241	255
Wet nitrogen	170	32	241	256
Wet nitrogen	190	41	244	258
Wet air	140	37	242	256
Wet air	160	36	241	256
Wet air	170	36	242	256
Wet air	190	34	242	256

Table VI presents the temperatures of the DSC transitions in all samples of PET including the T_{onset}, T_{max}, and the enthalpy of crystallization. As can be seen, the PET samples aged in dry nitrogen are little different from virgin PET. A small increase in the enthalpy of crystallization can be observed for samples aged above 160°C; however the T_{onset} and T_{max} values for crystallization do not differ significantly. Interestingly, on observation of the DSC cooling cycles of PET samples aged under thermo-oxidative conditions (i.e., dry air), more significant variations in the crystalline behavior were identified. A distinct trend exists between the ageing temperature and extent of crystallization for PET samples aged above 140°C. On increasing the ageing temperature above 140°C, an increase in the enthalpy of crystallization is evident, indicating that samples aged above 140°C undergo crystallization at an increased rate in comparison to samples aged at 140°C and unaged PET. The onset temperature and temperature of maximum crystallization are highest for PET aged at 190°C, indicating that crystallization is occurring most readily in this sample as it is cooled. Such differences in the enthalpy of crystallization and thus rate of crystallization are thought to be due to increased mobility of the polymer chains as a result of degradation. On increasing the ageing temperature above 140°C, the extent of chain scission in amorphous regions progressively increases and thus results in formation of shorter chain fragments and free chain ends with increased conformational freedom. Subsequently, chain segments that were previously entangled can now readily crystallize, resulting in rapid crystallization and thus an increase in the overall enthalpy of crystallization. These results are in agreement with the decrease in molar mass observed from GPC as a result of thermo-oxidative degradation.

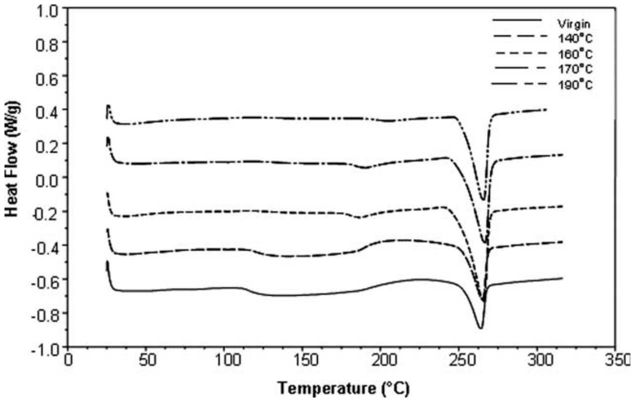

Figure 7 DSC curves of PEN samples aged under dry nitrogen at temperatures between 140°C and 190°C, cycle 1.

Under hydrolytic ageing conditions, degradation is also thought to occur rapidly, particularly at lower ageing temperatures. Therefore, it is expected that similar variations in the crystalline behavior will be observed from PET samples aged under a hydrolytic environment. On interpretation of the DSC cooling data, a clear trend exists once again between the extent of crystallization and ageing temperature of PET samples aged under hydrolytic conditions. On increasing the ageing temperature, an increase in the enthalpy of crystallization is evident, indicating that crystallization occurs at an increased rate, in comparison to unaged PET. The onset temperature and temperature maximum for crystallization are highest for PET aged under moist thermo-oxidative conditions at 190°C, indicating that crystallization is occurring most readily in this sample (i.e., the lowest molar mass sample) as it is cooled.

TABLE V
DSC Thermal Transitions in PEN Samples Aged Under Different Environments at Temperatures Between 140°C and 190°C, Cycle 1

Ageing environment	Ageing temperature, °C	Enthalpy of crystalline melt, J g^{-1}	T_{onset} crystalline melt, °C	T_{max} crystalline melt, °C
Virgin	N/A	17	253	264
Dry nitrogen	140	18	254	265
Dry nitrogen	160	39	252	266
Dry nitrogen	170	36	252	267
Dry nitrogen	190	32	253	266
Dry air	140	37	252	265
Dry air	160	38	253	266
Dry air	170	38	252	265
Dry air	190	41	253	265
Wet nitrogen	140	35	253	267
Wet nitrogen	160	37	253	267
Wet nitrogen	170	37	252	265
Wet nitrogen	190	32	255	267
Wet air	140	39	252	266
Wet air	160	38	252	266
Wet air	170	34	253	267
Wet air	190	41	256	266

Therefore, this physical data illustrates that purely thermal degradation of PET is minimal up to temperatures of 190°C. In the presence of oxygen, however, significant changes in the enthalpy of crystallization were observed at ageing temperatures around 170–190°C, indicating that the presence of oxygen does significantly influence the degradation of PET at the highest ageing temperatures. This provides further evidence that the dominant degradation reaction at the highest ageing temperatures is thermo-oxidative degradation as previously suggested. Ageing of PET under hydrolytic conditions was found to have the most significant impact on the overall enthalpy of crystallization of PET at the lower ageing temperatures, indicating that hydrolysis is the dominant degradation reaction between 140°C and 160°C. Degradation was found to be most significant under thermo-oxidative-hydrolytic ageing conditions due to the combined effect of hydrolytic and oxidative reactions. These DSC results are thus in very good agreement with the GPC results reported previously.

In contrast to the results reported for aged samples of PET, no distinct changes in the crystallization behavior of PEN could be identified from the DSC cooling curves. All cooling curves were found to be identical for all PEN samples aged under different environments. Aged samples of PEN did not

TABLE VI
DSC Thermal Transitions in PET Samples Aged Under Different Environments at Temperatures Between 140°C and 190°C, Cycle 2

Ageing environment	Ageing temperature, °C	Enthalpy of crystallization, J g^{-1}	T_{onset} crystallization, °C	T_{max} crystallization, °C
Virgin	N/A	16	186	152
Dry nitrogen	140	16	189	155
Dry nitrogen	160	15	186	152
Dry nitrogen	170	21	188	154
Dry nitrogen	190	22	188	155
Dry air	140	16	183	151
Dry air	160	22	190	159
Dry air	170	25	188	157
Dry air	190	29	192	163
Wet nitrogen	140	22	191	159
Wet nitrogen	160	26	191	159
Wet nitrogen	170	27	189	159
Wet nitrogen	190	29	191	167
Wet air	140	22	189	156
Wet air	160	33	192	165
Wet air	170	35	193	166
Wet air	190	36	193	168

TABLE VII
DSC Thermal Transitions in PET Samples Aged Under Different Environments at Temperatures Between 140°C and 190°C, Cycle 3

Ageing environment	Ageing temperature, °C	T_g (°C)	Enthalpy of crystallization, J g^{-1}	T_{onset} crystallization, °C	$T_{\max}$ crystallization, °C	Enthalpy of crystalline melt, J g^{-1}	T_{onset} crystalline melt, °C	$T_{\max}$ crystalline melt, °C
Virgin	N/A	81	12	142	158	30	237	253
Dry nitrogen	140	81	8	143	160	29	238	253
Dry nitrogen	160	82	9	143	158	26	238	254
Dry nitrogen	170	82	9	140	161	32	236	251
Dry nitrogen	190	82	8	142	163	29	238	253
Dry air	140	82	10	142	158	29	237	253
Dry air	160	81	8	142	159	32	237	252
Dry air	170	81	7	141	157	33	238	253
Dry air	190	81	5	140	158	34	238	253
Wet nitrogen	140	81	9	141	160	32	237	253
Wet nitrogen	160	81	7	139	159	36	237	253
Wet nitrogen	170	82	5	138	160	32	238	253
Wet nitrogen	190	83	1	142	158	29	241	255
Wet air	140	81	8	141	159	32	238	253
Wet air	160	81	3	139	157	34	239	254
Wet air	170	82	2	137	155	35	239	254
Wet air	190	83	1	134	153	34	240	254

undergo crystallization on cooling, in contrast to the results reported previously for PET. Only a broad glass transition was observed in all PEN samples above 100°C. Due to the presence of bulky naphthalene groups in PEN, the ease at which PEN can arrange its polymer chains into regular domains is reduced, in comparison to PET. Additionally, the non-linear 2,6-substitution pattern of aromatic rings in PEN, compared to a 1,4 linear substitution of the phenyl group in PET, reduces its tendency to crystallize. Therefore no crystallization activity was observed from the DSC cooling curves of any aged samples of PEN. All DSC cooling curves for PET and PEN samples aged under thermal, thermo-oxidative, thermal-hydrolytic, and thermo-oxidative-hydrolytic environments can be found in the Supporting Information.

DSC second heating cycle (cycle 3)

Any permanent changes in morphology, as a result of ageing, can be observed in the second DSC heating cycle. Tables VII and VIII present the temperatures of the DSC thermal transitions in all aged samples of PET and PEN, respectively. All DSC reheat curves for PET and PEN samples aged under dry nitrogen, dry air, wet nitrogen, and wet air can be found in the Supporting Information.

The glass transition and cold crystallization processes remain unaltered between samples of PET aged under dry nitrogen and unaged PET. However, trends for PET samples aged under dry air are evident, where the amount of cold crystallization upon reheating decreases for samples aged under the most extreme conditions, as a simple consequence of increased crystallisation during the cooling cycle. Generally, the melting process was found to be relatively constant between all aged samples of PET, suggesting that no gross morphological changes occurred as a result of ageing. Similarly, the glass transition temperature of PEN remains unaltered with ageing and the crystallization events all remain similar between aged and unaged samples of PEN. The enthalpy and maximum temperature for cold crystallization of PEN are all difficult to determine due to low levels of crystallinity in all samples.

Relationship between mechanical properties and ageing conditions

From the ageing studies, completed on PET and PEN, the extent of degradation has been shown to differ between both polymers. Degradation of PET was largely influenced by the ageing environment and temperature. Although the overall thermal stability of PET remained unchanged after ageing, variations in the molar mass and crystalline content/behavior were observed in aged PET samples, in addition to a loss in mechanical strength. The dominant degradation mechanism in PET was shown to differ with the ageing temperature. At lower ageing temperatures, i.e., 140–170°C, hydrolysis was revealed as the dominant degradation reaction, with thermo-oxidative degradation dominating at the highest ageing temperature of 190°C.

In contrast to PET, all ageing environments and temperatures were found to have no detrimental effect on the overall thermal stability, molar mass, or crystallization content/behavior of PEN. It is thought that this could be due to either one or a

TABLE VIII
DSC Thermal Transitions in PEN Samples Aged Under Different Environments at Temperatures Between 140°C and 190°C, Cycle 3

Ageing environment	Ageing temperature, °C	T_g (°C)	Enthalpy of crystalline melt, J g^{-1}	T_{onset} crystalline melt, °C	T_{max} crystalline melt, °C
Virgin	N/A	122	3	255	264
Dry nitrogen	140	123	3	256	265
Dry nitrogen	160	122	3	256	265
Dry nitrogen	170	123	1	256	265
Dry nitrogen	190	123	1	256	265
Dry air	140	122	5	256	264
Dry air	160	123	3	256	265
Dry air	170	123	3	256	265
Dry air	190	123	2	254	265
Wet nitrogen	140	124	3	257	266
Wet nitrogen	160	123	3	256	265
Wet nitrogen	170	123	3	256	265
Wet nitrogen	190	123	1	257	265
Wet air	140	123	5	256	265
Wet air	160	123	4	257	265
Wet air	170	124	3	257	266
Wet air	190	123	3	256	265

combination of the following factors: (1) reduced chain mobility due to the significantly increased glass transition of PEN (122°C) in comparison to PET (80°C); (2) increased crystallinity of PEN, in comparison to PET. This could contribute to the lack of chain scission reactions and thus overall extent of degradation as crystallites are impermeable to water and can act as barriers to oxygen and water; (3) hydrophobicity effects—the lack of degradation observed could simply be a result of increased hydrophobicity effects in PEN, in comparison to PET. The overall mass fraction of non-polar, aromatic sequences in PEN is greatly increased, due to the presence of additional phenyl rings. This results in a material with increasing hydrophobic character. However, none of above factors provides an explanation as to why aged samples of PEN embrittle badly when no decrease in molar mass is observed.

This leads us onto believe that the embrittlement of both PET and PEN upon ageing seems to have a physical rather than a chemical origin. Although at the most extreme ageing conditions for PET, a drop in molar mass is observed, this is too small to account for the severe embrittlement. Instead, we propose that the change in mechanical properties, in both PET and PEN, is due to crystallization upon ageing, and secondary crystallization in particular. Separate experiments not included here, illustrate that the primary crystallization process of PET and PEN is complete within 25 minutes and 60 minutes, respectively, at 140°C. Therefore, over the 24 h of the ageing process, considerable secondary crystallization can occur. Such crystallization has been shown in the past to cause remarkable changes in mechanical properties. This is most notorious in the Biopol polyesters where secondary crystallization upon room temperature storage embrittled moldings and extrusions, even when plasticized, to the extent that it threatened the commercial development of the polymers.[21–27] The degree of secondary crystallization, in the Biopol polyesters, was so small that it could not be readily detected by DSC, except through the presence of a low temperature so-called annealing melting peak as observed in the DSC curves of aged samples of PET and PEN.

CONCLUSIONS

The extent of degradation in PET and PEN has been examined after ageing under contrasting drying conditions, enabling the effects of temperature, water, and oxygen to be mapped onto the resultant property changes. Degradation of PET was found to be largely influenced by the ageing environment and temperature and the dominant degradation mechanism was shown to differ with ageing temperature. In contrast to PET, the increased thermal and hydrolytic resistance of PEN has been illustrated with all ageing environments and temperatures having no detrimental effect on the overall thermal stability, molar mass, or crystallization content/behavior of PEN. Embrittlement of both PET and PEN after ageing has been proposed to originate from secondary crystallization developed upon ageing, causing remarkable changes to mechanical properties.

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