1 INTRODUCTION

The work presented in this thesis has focused on studies of the cure of epoxy resins that can be used to form the resin matrix of composite materials used in many industrial applications, e.g. strengthening bridges and masonry, repairing pipes, in the production of technology for renewable energy sources, in the aerospace industry and for producing marine vessels. This chapter provides an overview of the project and an introduction to composites, epoxy resins, epoxy resin cure and characterisation, and also water ingress into epoxy systems.

1.1 OVERVIEW

The project has been complementary to the DTI ACLAIM (Advanced Composite Life Assessment and Integrity Management) project led by ESR Technology Ltd., the National Physical Laboratory, Doosan Babcock Energy Limited and Deepsea Engineering and Management. The project was also in collaboration with a range of other industrial partners including: Powergen, Highways Agency, NetworkRail, Vestas Wind Systems, Insensys, HSE, DML, Parsons Birnkerhoff, Inoes Chlor, Eurocomposites, Insys and Birmingham University. The main aim of the ACLAIM project was to develop techniques and protocols to provide an integrated approach to assess the integrity of Advanced Composite Structures. The project aimed to produce information on the possible approaches that might be used for monitoring the integrity of composite structures. The academic input was to explore the possible techniques available for monitoring the cure of the resins within the composites and also to consider the factors which would influence the durability of the structure. The industrial partners were involved in assessment of possible methods of non-destructive examination of composites, design of assessment procedures and creation of guidance documentation. The overall aim of the project was to create a greater understanding of the fabrication process and durability, leading to a greater confidence in the use of composite materials. The ideal output from the project would be to identify how composites might be used as lower maintenance cost materials (through remote monitoring and multi-functional sensors) and minimize structural/component failures. Composites are being increasingly used in environments where structural monitoring is desirable, such as wind turbines and off-shore applications.

The work carried out in this part of the project (at Strathclyde University) has been in collaboration with the Sensors and Composites group at Birmingham University. The long-term objective of the university work was to develop a sensor that could be used for the in situ monitoring of a composite used in an industrial application, e.g. as a patch for a fault in an oil pipe or used to strengthen a bridge. It was hoped that the sensor could include optical fibres and the possible use of Near Infra-red (NIR) spectroscopy (Birmingham) as well as dielectric spectroscopy (Strathclyde).

The main objectives of the work presented in this thesis were to:

- Characterise the cure process of two model systems and four commercial systems using dielectric spectroscopy, differential scanning calorimetry (DSC), Fourier transform infra-red (FT-IR) spectroscopy, and rheology measurements.
- Carry out a moisture ingress study for several of the systems, using gravimetric measurements and dielectric spectroscopy.

Techniques such as FT-IR would allow the cure process and water ingress monitoring to be studied at a molecular level. Rheological, DSC and dielectric measurements would allow observations of the changes occurring in the bulk of the material.

1.2 COMPOSITES

A composite is a material that is formed from two (or sometimes more) materials with different properties. The two materials do not blend or dissolve into each other but just coexist, and the composite material has unique properties. The connectivity between the two or more phases that are present in a composite material is critical to the material achieving its performance characteristics. The main advantage of composites is that they can combine strength with stiffness of the two phases that are present and high performance can be achieved in light-weight materials [1]. Some well-known building materials are composites such as wood, mud bricks and concrete. Wood is made of long fibres of cellulose (also found in cotton and linen) that are held together by lignin. The resultant composite material is therefore strong but reasonably light-weight. In mud bricks, adding straw to the mud before it dries imparts good tensile strength as well as good compressive strength, and in concrete small stones/gravel are bound by cement to give a strong composite that can then be strengthened even more with addition of metal rods, wires, mesh or cables [1].

The properties of the material can be tailored to suit the specific role that the composite will fulfill, e.g. it may be resistant to chemicals, heat or weathering, be tough but flexible, or be clear (optically) but rigid and strong. As the production of an object from a composite material usually involves a mould of some type, composites can be moulded into complex shapes, and so be utilised for a variety of applications and industries, e.g. biomedical, aerospace, automotive, sporting goods and the architecture/infrastructure industries. The overall properties of the composite are determined by the properties of the reinforcing material (fibre), the properties of the matrix (e.g. resin), the ratio of reinforcing material to the matrix, and the geometry and orientation of the fibres in the composite [1]. Abraham and McIlhagger [2] report that as well as these factors the overall properties are also reliant on the degree of cure of the resin matrix and the void content. Chehura *et al.* [3] agree with this and state that the residual cure in the end product, as well as the development of internal stresses during cure, have a significant effect on the properties of the composite.

Most composites are made from the matrix or binder material surrounding and binding together the reinforcement material (e.g. fragments or a cluster of fibres of a stronger material). The most common commercial composite material is fiberglass. It was developed in the late 1940s and is still used nowadays for boat hulls, surfboards, sporting goods, swimming pool linings, building panels and car bodies. It is produced from fibres of glass woven into a mat and impregnated with a thermoset plastic. It is also possible to create composites using injection moulding of thermoplastic matrices. However this will not be considered within this thesis.

Composites can be divided into three main classes [1]:

1. Polymer Matrix Composites- the most common and also known as Fibre Reinforced Polymers (FRPs). They use a resin as the matrix and a variety of fibres (e.g. glass, carbon, aramid/Kevlar, high strength polyethylene) as the reinforcement. This thesis will only consider thermoset materials as these are the most commonly used in engineering structural applications.
2. Metal Matrix Composites- found mainly in the automotive industry, and use a metal (e.g. aluminium) as the matrix with e.g. silicon carbide fibres.
3. Ceramic Matrix Composites- used for composites that are required to withstand very high temperatures and use a ceramic as the matrix with short fibres of e.g. silicon carbide or boron nitride.

In many modern polymer matrix composites the plastic used will be a thermosetting resin, e.g. polyester, epoxy resins and vinylester. These are usually made of two liquid components (a resin and a curing agent or catalyst) that cure over time (and sometimes require the application of heat) to become hard and rigid. The process is irreversible making the material heat resistant, and other properties of the final product will be dependent on the resin system used as well as the reinforcing material. Jones [4] states that the matrix should have: a low viscosity (for fibre impregnation); high reactivity on curing; good mechanical properties (of the cured system); and should cure without the formation of volatiles. The resin system chosen will depend upon the application. For example, for repairs to, or lining of, a crude oil storage tank (made of steel) located in the desert in the Middle East an epoxide resin would be most suitable due to its excellent shelf-life at high temperatures, and its lack of volatile components. However, for a concrete structure in the United Kingdom, an epoxy resin and a polyester would both be equally fit for the purpose [5]. Thermoplastics (e.g. nylon and polypropylene) may also be used, and these are hard at low temperatures and soften upon heating. They can sometimes be advantageous though as they have greater fracture toughness, a long shelf life (for the raw material), lend themselves to recycling and generally do not involve any organic solvents in the curing process so are less of a health hazard to those curing them. However, thermoplastics will require the resin to be heated to a high temperature and may only be used where hot processing methods are appropriate.

Glass fibres are the most common type of reinforcement material, as although carbon fibres are much stronger than glass ones, they are more expensive to produce. They are light and strong and so are used in the aerospace industry as well as in the sports goods industry, e.g. to manufacture lightweight golf clubs [4]. They can also be used in place of metal for the repair or replacement of damaged bones. Some polymers can also be used as the actual reinforcing material, e.g. Kevlar which is a strong polymeric fibre used in the production of structural body parts of aircraft and bulletproof vests and helmets.

Li *et al.* [6] report that the main disadvantage of composites is the instability of the end-product quality. They state this is due in the main to the production process and that it is necessary to implement quality control with a monitoring system that is able to recognise features of the progress of the process, i.e. in situ cure monitoring. Pethrick [7] also states that it is necessary to be able to follow the cure process and identify key events, e.g. gelation, phase separation and vitrification. Gopal *et al.* [8] report that residual stresses caused by the cure cycle (temperature and duration) can lead to matrix cracking within the matrix which in turn affects the strength of the material and can also expose the fibres to degradation. Therefore, it is necessary to find the optimal cure cycle to minimise defects in the final composite material.

Other areas in which work has been done to improve the properties of the finished composite include water absorption, ageing and flammability. Boinard *et al.* [9] and Kim *et al.* [10] state that composites made with epoxy resins as the matrix can be prone to water absorption and hence the functional, structural and mechanical properties of the composite are degraded, particularly for epoxy/metallic or epoxy/ceramic composites. Kim *et al.* [10] have researched polymer-nanoclay composites and claim that they have excellent barrier properties. In another paper, Boinard *et al.* [11] looked at ageing as well as moisture ingress in glass-fibre reinforced plastics (GRPs) and report that the fabrication method influences the ageing behaviour. Brown et al. [12] report that using 2-5% of organically modified mica type silicate, e.g. montmorillonite clay, can reduce the flammability of a composite material.

1.3 EPOXY RESINS

1.3.1 Introduction

Epoxies are used widely throughout industry as coatings, adhesives, insulators, and in composites as they exhibit low shrinkage, good electrical properties, adhesion and resistivity to impact and are also relatively moisture resistant. Their ability to bond to many different substrates makes them ideal adhesives and sealants. There are many commercially available epoxy resins and curing agents, with each individual system having different properties. This allows epoxy resins to be used in a wide range of applications and industries, e.g. from adhesives for DIY to producing the composite panels used in the aerospace industry. The term ‘epoxy resin’ refers to both the uncured (monomer) resin and the cross-linked end product. Epoxy resins were first synthesised commercially in the 1930s and 1940s by Pierre Castan (Switzerland) and Sylvan Greenlee (US) [13, 14], and have two or more epoxide groups (oxirane). These epoxy (end) groups react with a curing agent (or hardener) to form a three dimensional, thermosetting polymer by the formation of covalent bonds. The process is exothermic and can occur at various temperatures depending on the resin-hardener system. There are also many different additives and modifiers that are used in the commercially available systems to impart specific properties or characteristics.

See Table 1 for examples of applications of various commercial systems (applications for Sikadur®31 supplied with material).

Table 1. Applications of various commercially available epoxy resin systems.

Trade Name	**Manufacturer/ Supplier**	**Application(s)**
Sikadur®-31 Normal	Sika Ltd.	Structural adhesive for e.g. bridge strengthening.
Prime 20/ SPX3260	SP Systems Ltd.	Infusion resin in e.g. manufacture of wind turbine blades [15].
Araldite® PY306	Huntsman	Filament winding, pultrusion, casting, RTM and as a general adhesive [16].
Tactix® 123	Huntsman	Filament winding [16].
EPON™ RESIN 164	Resolution Performance Products	For use in printed wiring boards and as an adhesive [17].
PR55-ST	DML Devonport	Used in wet lay-up of pipe repairs [18].

1.3.2 Epoxy Resins (monomer)

Epoxy resins can be classified according to their epoxide equivalent weight (EEW), also known as Epoxy Molar Mass (EMM), which is the equivalent weight of resin (in grams) containing one epoxide group. The higher the EMM the higher the viscosity, e.g. Lee [13] states that low molecular weight resins, with relatively low viscosities, have an EMM of 175-200. He goes on to state that the EMM is (generally) half the average molecular weight of the resin, since it can be assumed that the linear chain has no side branching and that an epoxy group terminates each end as in Figure 1 below which shows the generalised structure of a diglycidyl ether of bisphenol A (DGEBA). It should however be noted that in commercial systems trifunctional or higher epoxy monomers can sometimes be used to achieve specific physical properties and therefore it is important to establish the EMM for an unknown material.

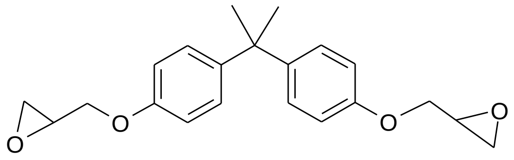
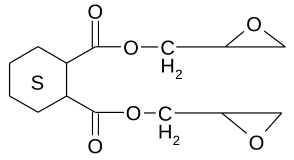
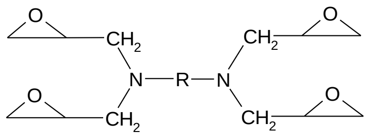
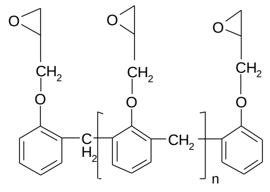
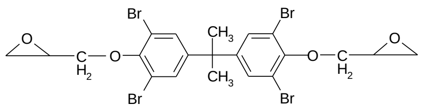
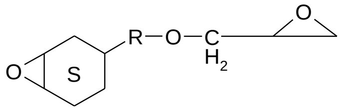


Figure 1. Generalised structure of (pure) DGEBA with terminating epoxy groups.

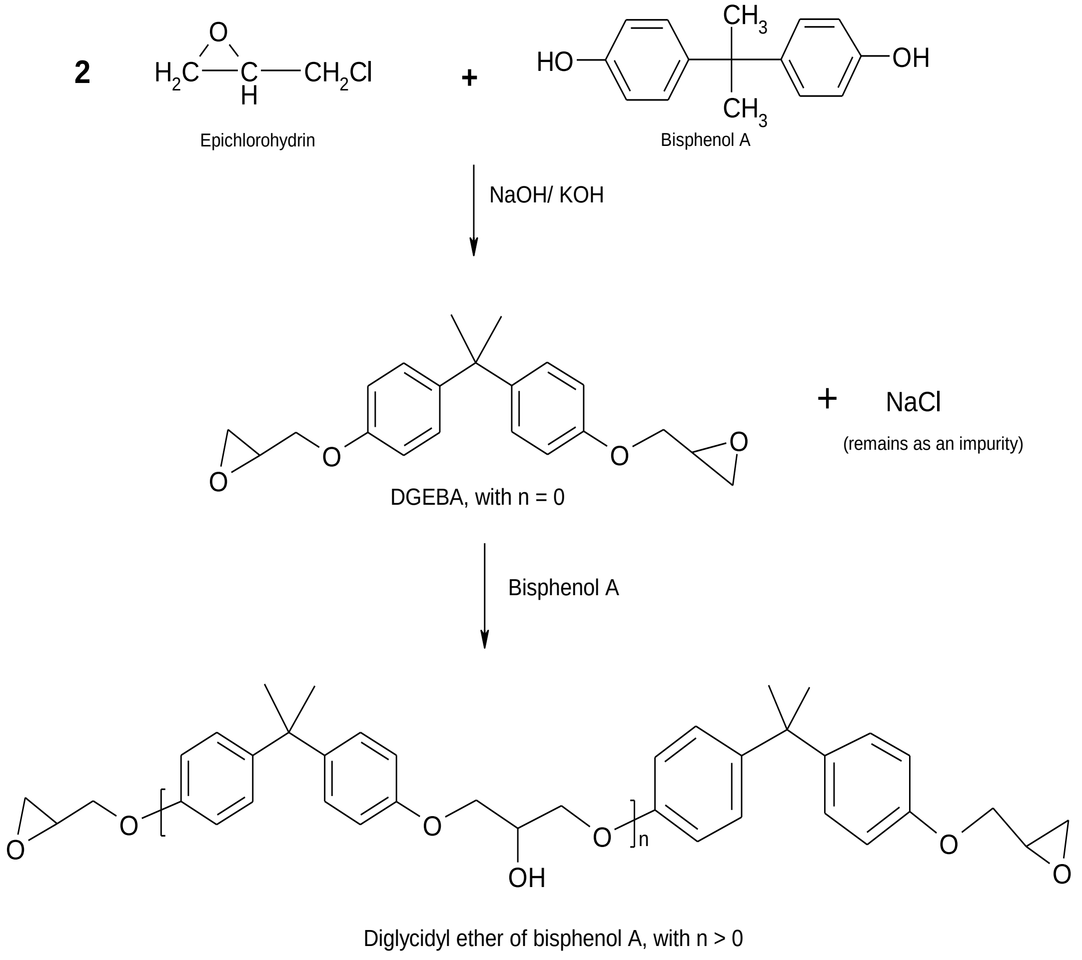
Resins can be divided into six classes according to Weatherhead [5]: bisphenol-A-based; glycidyl esters; glycidyl amines; novolacs (based on bisphenol F); brominated resins; cycloaliphatic and other resins. Resins based primarily on bisphenol A are used in this study, and therefore the other classes will not be discussed in as much detail. See Table 2 for the general structure and applications of the other classes.

Table 2. Classes of epoxy resin other than bisphenol-A-based [5].

Resin Class	**General/ Example structure**	**Applications**
Glycidyl Esters		High voltage electrical insulators and heat cured laminates. Used with anhydride hardeners to give systems with viscosities and reactivities suitable for vacuum impregnation, laminating and casting applications.
Glycidyl Amines		Mostly cured with anhydrides to give products with good high temperature strength retention and good resistance to nuclear radiation. Used for wet lay-up lamination and filament winding.
Novolacs		High temperature stability and good chemical resistance. However with certain curing agents they have a low strain at break (1-1.5%).
Brominated Resins		Give flame retardancy to composites so used for, e.g. printed circuit boards.
Other resins	e.g. cycloaliphatic ring containing epoxide group. 	Designed by government/ military for high performance composites for aerospace industry.

where ‘S’ denotes a saturated ring structure; and ‘R’ is usually an aliphatic chain or carbonyl g.

Bisphenol-A-based resins were the first to be produced commercially and are the most widely available epoxy resins because of the relatively low cost of manufacture (the components can be derived from natural gas or coking by-products [13]). They are formed by the reaction between bisphenol A and epichlorohydrin, in the presence of sodium hydroxide, to give a diglycidyl ether of bisphenol A (DGEBA). See Figure 2 for the structures. Resins produced in this way consist of a mixture of different molecular weight species (the distribution is what affects the viscosity/ melting point), and the more epichlorohydrin available for reacting, the lower the molecular weight.



n = 0,1,2,3 etc.
n = 0 represents the pure diglycidyl ether of bisphenol A

Figure 2. Reaction of epichlorohydrin with bisphenol A to produce DGEBA.

Weatherhead [5] and Ellis [14] state that the commercially available liquid resins, EMM range 180-196, have a tendency to crystallise during storage due to their relatively high purity. This is because most contain greater than 90% of pure DGEBA (where n=0) - a colourless crystalline material with a melting point of 43-46°C and an EMM of 170. Weatherhead [5] goes on to say that the condition tends to occur when the resins are stored under fluctuating temperatures at approximately 0-10°C, and that the addition of a small amount of higher molecular weight resin or a filler/diluent can prevent the problem. Another solution suggested is to blend a bisphenol F (see Figure 3 below for the structure) with the bisphenol A in the ratio of about 70/30 A/F. The resultant epoxy has a lower viscosity and tends not to crystallise, and the end-product properties remain similar to when just bisphenol A is used. However, it is more expensive to make bisphenol F and so the cost of the system is driven up. Weatherhead [5] reports heating a resin that has crystallised to above 50°C followed by thorough stirring will return it to its liquid state.

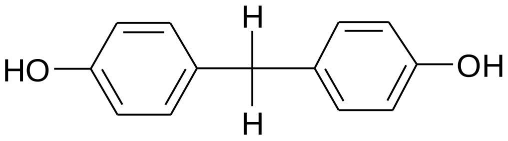


Figure 3. Structure of bisphenol F.

1.3.3 Curing Agents

Curing agents are also known as hardeners, catalysts or activators. They are di- or poly-functional, and typically include primary and secondary amines, polyamides and organic anhydrides. Most curing agents open the epoxide ring on the epoxy and become chemically bound in the network. Catalytic curing agents, such as boron trifluoride, can also be used and cause self-polymerisation of the resin [5]. This thesis will focus on the study of amine cured epoxy resins and will not consider cationic cure of the monomer.

Amine curing agents can be primary or secondary amines, aliphatic, alicyclic or aromatic. The commercially available amines are generally polyamines and can contain primary and secondary amine groups, e.g. the aliphatic amine triethylenetetramine (TETA). See Figure 4 for the structure of TETA. The reactivity of the secondary amine is slower than that of the primary amine and this will have an effect on the way in which the three-dimensional resin structure develops during the cure process.

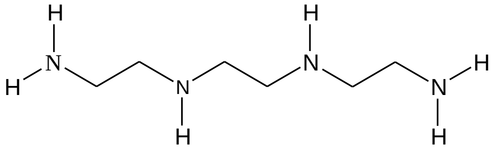


Figure 4. Structure of TETA showing 2 primary and 2 secondary amine groups.

Alicyclic amines can contain tertiary as well as primary and secondary amines, but may require an accelerator (e.g. salicylic acid or phenol) to cure at room temperature. An example of an alicyclic amine (without tertiary amines) is isophoronediamine (IPD), as shown in Figure 5.

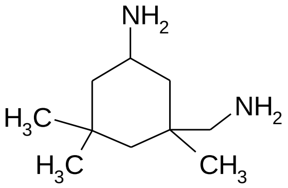


Figure 5. Structure of isophoronediamine (IPD).

Aromatic amines, such as diaminodiphenylsulphone (DDS), are generally solid and used for systems that cure above room temperature. They can be dissolved into the resin with a little heating (just above the melt temperature of the amine) before being heated to the curing temperature. See Figure 6 for structure of DDS.

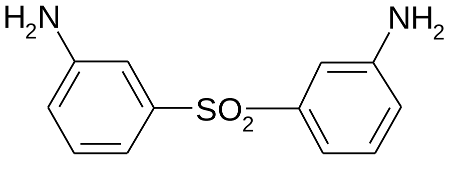


Figure 6. Structure of 3,3'- diaminodiphenylsulphone (DDS).

Weatherhead [5] reports that organic anhydrides will not react directly with an epoxy and so an accelerator such as a tertiary amine is required. He also states that the cured systems are generally more thermally stable and have better resistance to radiation than amine cured systems. Many of the organic anhydrides available are based on the methylated and hydrogenated derivatives of phthalic anhydride (EPA). See Figure 7 for structure of EPA.

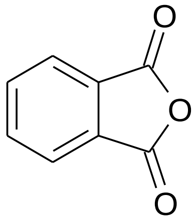


Figure 7. Structure of phthalic anhydride (EPA).

Polyamide curing agents can also be used and are mostly used in coating systems [5]. They include aminopolyamides, amidopolyamides and imidazolines. Other curing agents used with epoxies include the boron trifluoride complexes (can be used as the sole curing agent or as an accelerant in a system), substituted imidazoles (again on their own or as accelerants) and dicyandiamide (Dicy). Dicy is used with solid DGEBA and is a solid itself. The system is dissolved in a suitable solvent (e.g. dimethylformamide) to form a prepreg solution, and then heated to approximately 150-170°C to allow the cure to take place- an accelerator (e.g. benzyldimethylamine (BDMA)) is sometimes required to give necessary cure schedule.

1.3.4 Diluents and Fillers

Diluents can be added to epoxy resins to lower the viscosity, improve the handling properties, allow better incorporation of other additives (e.g. fillers), improve the characteristics (e.g. wetting) of the cured product and can also improve how the resin is incorporated into fibrous reinforcement materials [19, 20]. Weatherhead [5] states that the higher the proportion of diluent added, the lower the viscosity, mechanical properties and chemical resistance of the cured system. Shaw [19] agrees with this saying that although viscosity is reduced, reactive diluents also decrease the functionality of the system leading to a decrease in cross-linking density which affects the physical and mechanical properties of the cured system. It should also be noted that most diluents can cause the gel time for the system to be slightly longer than for the unmodified system [5]. Diluents can be termed as either non-reactive or reactive.

Non-reactive diluents do not become chemically bound in the cross-linked network leading to poorer chemical resistance in the end product. They can also lead to voids in the cured system if used in too high concentrations [19, 20]. Examples include aromatic hydrocarbons (e.g. toluene and xylene), dibutyl phthalate, styrene and various phenolic compounds [5, 19, 20]. Potter [20] reports that molar quantities of phenol accelerate the cure reaction, but molar quantities of acetone and benzene have a retarding effect, and goes on to state that it is thought to occur because the non-phenolic solvents reduce the concentration of reactants leading to the decrease in rate. Ashcroft [21] reports that benzyl alcohol is used as a plasticising diluent with the cycloaliphatic polyamine curing agent isophoronediamine. It reduces brittleness and can provide a weak accelerating effect.

Reactive diluents can either contain an epoxy group that allows the compound to get chemically bound in the network, or they can provide reactivity from another functional group. The epoxy-based ones that contain only one epoxide group per molecule can be considered as chain stoppers as they reduce the functionality of the system, and hence reduce the cross-linking [20]. They can also alter the EMM of the blend so the mixing ratio of epoxy to curing agent may have to be adjusted [5]. Poly-functional epoxy diluents can also be used, and these help to alleviate the problem of the decrease in cross-link density as the functionality of the system as a whole is not greatly affected by the incorporation of them. Examples include butadiene dioxide, diglycidyl ether and diethylene glycol diglycidyl ether [5, 19]. Examples of reactive diluents include: glycidyl ethers, e.g. phenyl glycidyl ether (PEG), glycidyl methacrylate and dibromophenyl glycidyl ether (D.E.R. 599); octylene and styrene oxide; and glycidyl ester of *tert*-carboxylic acid. See Figure 8 for structures of a range of diluents. Weatherhead [5] reports that if added to a DGEBA system that tends to crystallise, some reactive diluents can aggravate the problem. As mentioned previously, warming the resin and stirring thoroughly will correct the problem.

Reactive diluents that are not based on the epoxy ring are not as common, as although they have been shown to decrease the viscosity, they do not provide the same level of thermal resistance that the epoxy-based ones do. Examples include triphenyl phosphate and lactone compounds (e.g. butyrolactone) [19, 20].

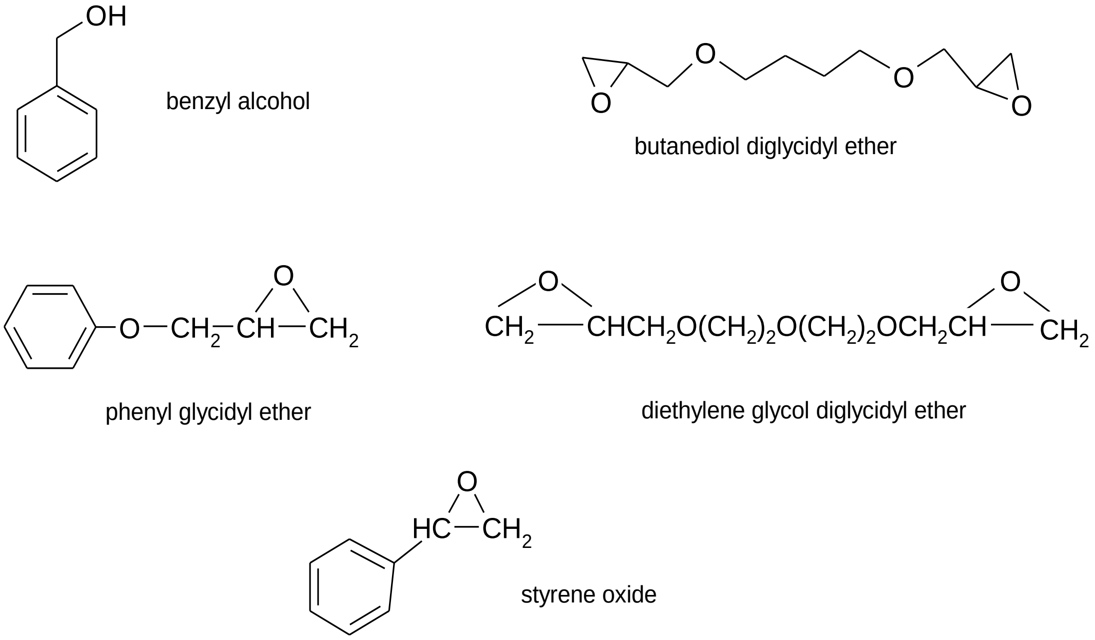


Figure 8. Structures of example diluents used in epoxy resins.

Fillers are added to epoxy resin systems to modify the properties and characteristics of the cured product. There are many fillers that are commonly used and each type will impart different properties, but the general advantages to using them include: reduced formulation cost, shrinkage, water absorption and thermal expansion coefficient; improved heat-ageing properties, toughness and abrasion resistance; increased thermal conductivity and heat deflection temperature; and decreased exotherm. Disadvantages include: increased viscosity and density (hence weight); increased dielectric constant and handling difficulties (i.e. more difficult to machine); a tendency to trap air; decreased impact and tensile strengths (with certain fillers); and a loss of transparency [19, 20].

Potter [20] reports that filled systems are essential for large castings because the fillers absorb part of the heat evolved during the cure reaction, and hence the filler reduces temperature 'high spots'. Shaw [19] also reports that fillers can reduce the exotherm, and goes on to say that this occurs because the addition of filler into a mixture reduces the quantity of resin in the mass being mixed, and the filler increases the thermal conductivity, so the heat is removed from the centre of the curing mass. In a similar manner, fillers reduce shrinkage upon curing by 'bulk replacement' of the resin with the filler that does not take part in the reaction (and hence the cross-linking process) [19]. The filler type and particle size will affect the increase in viscosity caused by the filler, i.e. fibrous fillers have more effect than particulate ones, and small particles increase viscosity more than larger ones due to surface area effects [19]. See Table 3 [19] below for examples of fillers that are commonly used in epoxy resin systems and the properties they modify.

Table 3. Filler types and potential modification to property of cured system [19].

Filler	**Modification to properties of unfilled cured resin system**
Aluminium	Machinability, impact resistance, thermal conductivity, dimensional stability
Aluminium silicate	Extender, pigmentation, dimensional stability, chemical resistance
Al trioxide	Flame retardation
Arsenic pentoxide	Thermal resistance
Calcium silicate	Mechanical properties
Carbon black	Reinforcement, pigmentation, thermal & electrical conductivity, thermal resistance
Copper	Electrical & thermal conductivity, mechanical properties
Colloidal silica	Thixotropy
Fibrous glass	Impact strength
Graphite	Lubricity, pigmentation, thermal & electrical conductivity, abrasion resistance
Glass microballoons	Density reduction
Kaolin clay	Extender
Mica	Electrical & moisture resistance, dielectric properties, extender, thermal conductivity
Sand	Abrasion, thermal conductivity
Titanium dioxide	Pigmentation, dielectric properties, extender
Talc	Extender
Zirconium silicate	Arc resistance

As well as diluents and fillers, epoxy resin systems can also be modified with resinous, elastomeric and thermoplastic modifiers, and flexibilising/plasticising additives [19, 20]. Resinous modifiers are typically 'alloyed' with the epoxy to enhance the toughness, and fluorinated epoxy resins provide better moisture resistance. Examples include polyurethanes, styrene-butadiene co-polymers, silicons and fluorinated polymers, with coal tar pitch being a resinous modifier that was commonly used in the 1960s. Flexibilising and plasticising agents are typically used to help alleviate brittleness. Flexibilisers (e.g. polyamides, polysulphides, carboxyl-terminated polymers) are long chain molecules that become covalently linked to the network during cure (internal plasticisation), and plasticisers (e.g. dibutyl phthalate) are long chain molecules that do not become incorporated into the network. The addition of flexibilisers, as well as alleviating brittleness, can also: reduce the exotherm and the shrinkage; result in a more 'strain tolerant' system; reduce mechanical strength and electrical properties; and reduce the chemical and solvent resistance [20].

The use of elastomeric modifiers has been reported [19] to be a more successful way of reducing brittleness in epoxy resin systems, and examples include reactive butadiene-acrylonitrile rubbers, polysiloxanes, fluoroelastomers and acrylate elastomers. Thermoplastics can also be used to enhance the toughness, but these are mostly only considered for relatively high cross-linked density epoxies that will be used for high temperature applications. Miscellaneous additives include halogens and antimony trioxide to impart flame retardancy, coupling agents (e.g. organosilanes) to improve moisture resistance, and solvents (e.g. toluene and xylene) that are added to systems for surface coating applications.

1.4 EPOXY RESIN CURE

As an epoxy and a hardener react together during the curing process, the system extends linearly and the viscosity builds up. The system will begin to branch after a time and the three- dimensional network will begin to form, leading to gelation. Elias [22] defines a gel as a chemically or physically cross-linked polymer that is highly swollen by a solvent. Epoxies form chemical gels that are generally strong and irreversible due to the dense cross-linking bonding, as opposed to physical gels (e.g. hair gel) that have weaker (and reversible) hydrogen bonding, ionic and/or dipolar interactions [22, 23]. Pethrick [24] describes gelation as the theoretical point at which the viscosity tends to infinity, and Wisanrakkit *et al.* [25] describes it as corresponding to ‘the incipient formation of an infinite network’. The cure may then continue and a three dimensional network will be built up until vitrification is reached, i.e. when the glass transition temperature equals or exceeds the cure temperature. Reactions can continue to occur after vitrification as there are still unreacted sites. This process, known as post-curing, occurs over a long timeframe but is quickened by heating. Post-curing increases the density, glass transition temperature and the mechanical modulus of the material [26].

Gillham [25, 27] introduced a Time-Temperature-Transformation (TTT) diagram to characterise the cure processes of epoxy resins by showing the time it takes to reach a certain event (on a plot of isothermal cure temperature against the cure time). Figure 9 shows an adaptation of one of Gillham’s TTT diagrams. The diagram shows the states that the system moves through throughout cure, e.g. unreacted monomers, gelation, vitrification, complete cure and degradation. The terms in the diagram can be defined as follows [25]: T_{g0} is the glass transition temperature of the uncured (unreacted) system; ${}_{gel}T_g$ is the temperature at which gelation and vitrification meet on the plot; and $T_{g\infty}$ is the (maximum) glass transition temperature of the fully cured system. Below T_{g0} the reaction is very slow as it occurs in the glassy state; between T_{g0} and ${}_{gel}T_g$, the resin will be a liquid but the reaction will continue without reaching gelation until the glass transition temperature of the system reaches the cure temperature, and then vitrification can occur when T_g equals T_{cure}. If T_{cure} becomes greater than T_g, devitrification can occur, and the reaction would proceed until T_g equals $T_{g\infty}$, i.e. the material would be in the rubbery state [25].

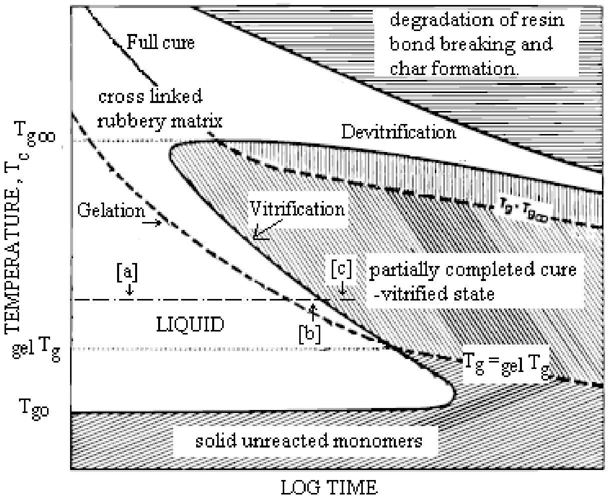


Figure 9. Time-Temperature-Transformation (TTT) Diagram (adapted from Gillham[27]).

Due to the way in which the network builds up, there may be unreacted epoxy and amine groups locked into positions making it impossible for them to react [13, 20]. Therefore, the system is unlikely to reach the theoretical degree of cure expected if the epoxy and hardener were mixed in stoichiometric proportions. Jones [4] states that complete reaction of the epoxy groups is unlikely to be achieved unless the system is cured for long times at high temperatures, i.e. post-curing. This results in higher heat-distortion temperatures and better chemical resistance.

Curing usually occurs by chain extension and, to a lesser extent, etherification (Figure 10) [13, 28]. In an epoxy-amine reaction, the lone pair of electrons on the nitrogen of the reactive group acts as a nucleophile and attacks the CH_2 on the epoxy ring (this is the unhindered carbon). This results in the ring opening and the formation of a hydroxyl group on the other carbon of the ring (Figure 10 (a)). In the case of a primary amine, this reaction produces a secondary amine that can react in the same way and form a second chain on the nitrogen (Figure 10 (b)). The system continues to build up linearly until gelation is reached and then the three dimensional network begins to form. Etherification may occur between the epoxide ring and the alcohol group, resulting in a very long chain system (Figure 10 (c)). However, Lee [13] states that this reaction is unlikely to occur in the presence of primary and secondary amines. He goes on to state that although some tertiary amines can promote the alcohol-epoxy reaction, the tertiary amine produced in Figure 10 (b) is generally too immobile or sterically hindered to allow the reaction to proceed. Potter [20] agrees that reaction (c) is unlikely and also that the tertiary amine can be too immobile to catalyse the reaction. Kamon and Furukawa [28] add to this by reporting that reaction (c) is unlikely to occur in a system that has stoichiometric equivalents of epoxy and amine, or where there is an excess of amine.

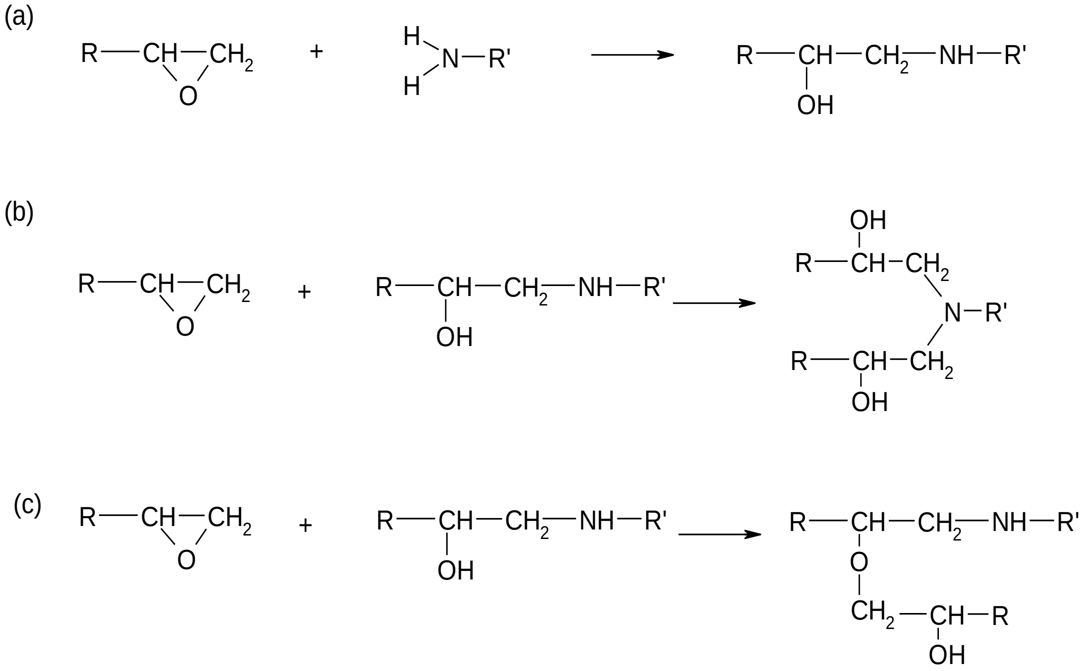


Figure 10. Reaction mechanisms of an epoxy resin with a primary amine (a) and a secondary amine (b), and the etherification reaction between the epoxy resin and an aliphatic hydroxyl (c).

For the epoxy-anhydride cure reaction, Park and Jin [29] state that the anhydride reacts with the secondary hydroxyl group on the resin to form a phthalic monoester, and the carboxyl group that is formed can then react with the epoxy ring and form a diester. A third reaction between the monoester from step (a) and a secondary alcohol is also possible. Figure 11 shows these reactions. Lee [13] agrees with steps (a) and (b) but then states that four other reactions are possible: etherification of the epoxy rings with hydroxyl groups; reaction of the monoester with a hydroxyl to give a di-ester and water; hydrolysis of the anhydride by water to give the corresponding acid; and the hydrolysis of the monoester with water to give an acid and an alcohol.

He goes on to state that only the first of these is as common as steps (a) and (b) from Figure 11.

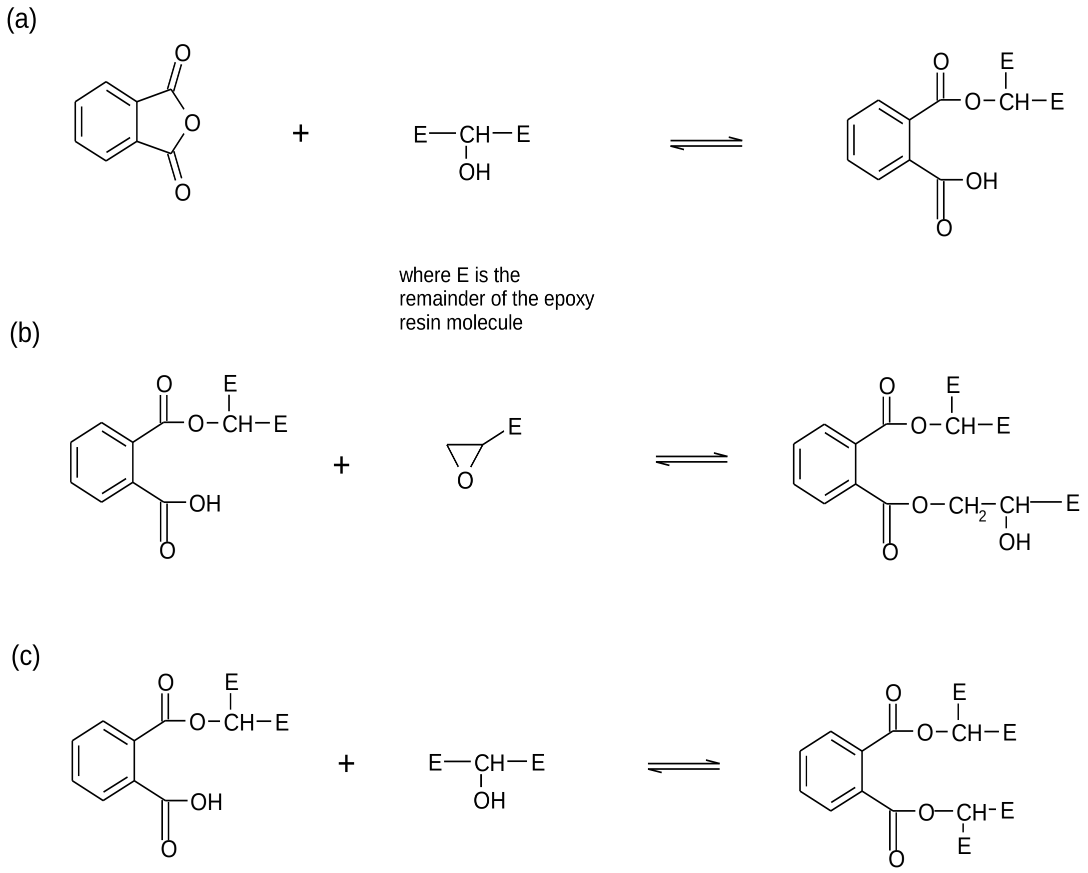


Figure 11. Reaction mechanism of an epoxy resin cured with an anhydride (uncatalysed reaction).

Alternatively, Kamon and Furukawa [28] report that, in the presence of a tertiary amine, the anhydride is activated with the amine, and so the amine acts as a catalyst (Figure 12). They go on to report that when the epoxy and anhydride are in the presence of a tertiary amine the reaction is initiated at a lower temperature than if the amine was absent. Lee [13] reports that adding small amounts of alcoholic or phenolic hydroxyl, or using amines that contain them, will speed up the epoxy-amine reaction as hydrogen bonding effects assist in opening the epoxy ring, and phenol is mentioned as being particularly good at this. He also reports that solvents that do not contain this grouping (e.g. acetone and benzene) slow the reaction down by diluting the reactants.

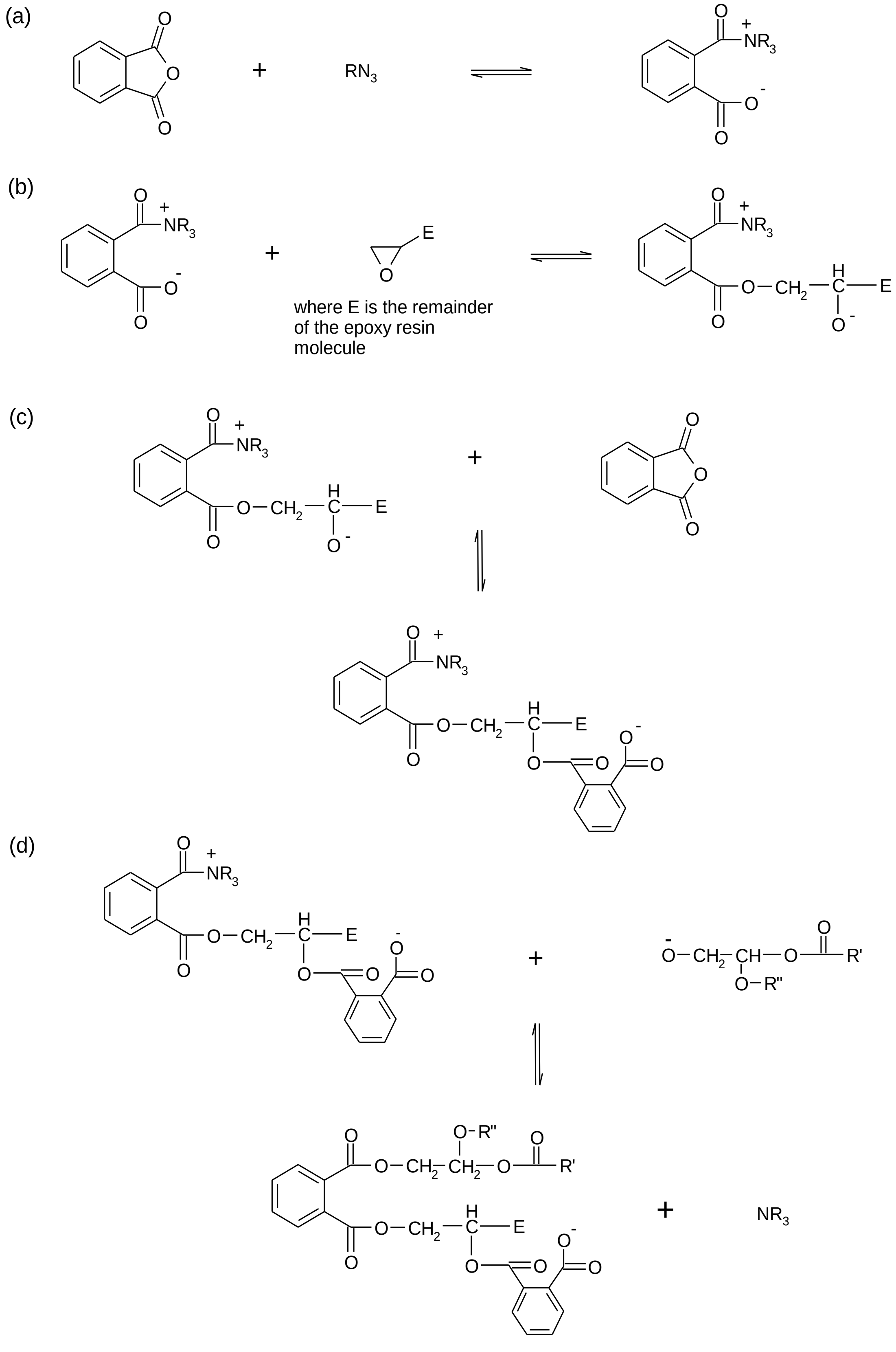


Figure 12. Reaction mechanism of an epoxy resin cured with an anhydride (in combination with a tertiary amine catalyst).

1.4.1 Cure Characterisation

Cure monitoring can be done by various methods including infra-red (IR) spectroscopy, refractive index changes, differential scanning calorimetry (DSC), dielectric spectroscopy, rheology and dynamic mechanical thermal analysis (DMTA). Ellis [30] reports that cure can be monitored as functions of the cure temperature (T_c) as well as the cure time (t_c) by the: direct assay of the concentration of the reactive groups; indirect estimation of the extent of the chemical reaction; and/ or by the measurement of changes in the physical and mechanical properties.

The activation energy can be calculated from the cure monitoring data and Potter [31] reports that the activation energy of amine cured reactions is generally in the range of 8 to 14 kcal per mole (33.5 to 58.6 kJ mol^{-1}), depending on the particular system used and the method of measurement.

The direct assay usually applies to the epoxy content but can also be used for the hydroxyl group or the chlorine content, and is usually done by ‘wet’ analysis (e.g. titration) or chromatographic methods (e.g. gel permeation chromatography (GPC) and nuclear magnetic resonance spectroscopy (NMR)). Ellis [30] states that both methods have limitations, e.g. ‘wet’ analysis can only be done prior to gelation and more than one type of analysis is generally required, and the chromatographic methods can lack in sensitivity. Potter [20] reports that the ‘swollen particle’ method can be used to determine the concentration of epoxide groups in a cured polymer. It involves suspending the cured resin (in very fine particle size) in a solvent that swells it. A titration is then done on the swollen particles and the reagents diffusing into and out of the particles. The results are reported to be comparable with those obtained from IR spectroscopy. In IR, the (integrated) intensity of the peak being followed can be directly related to the concentration of the corresponding reactive group [13, 32-38]. Fourier transform infra-red (FT-IR) spectroscopy can combat the problems of sensitivity that traditional IR suffers from (due to the overlapping of bands). The spectra taken at various times throughout the cure can show the loss of the epoxy ring concentration and the increase of the hydroxyl concentration [20].

The band chosen for monitoring is usually at *ca.* 915cm^{-1} and attributed to the epoxy ring (there is also an associated band at 4535cm^{-1} in the overtone region), but bands corresponding to other functional groups can also be used. Near infra-red (NIR) can also be used and has been reported [30] to be more advantageous due to the spectra being less complicated (with less overlapping) and the fact that only strong bands have significant absorption in the overtone region. Potter [20] states that care must be taken when interpreting IR data as the loss of an epoxy group (and hence the decrease in peak intensity) does not necessarily imply that a cross-linking bond has been formed.

The glass transition temperature (T_g) can be used to provide information about the extent of cure and the nature of the cross-linking within a system, and hence its thermal stability [20] as it plays a role in the ability of chain segments to move as was described above. One of the most rapid and convenient methods of determining the T_g is by DSC [39-43]. Georjon *et al.* [39] reports that there is a one-to-one relationship between the T_g and the degree of cure, and state that the T_g can therefore be used to follow/ measure the extent of cure. They go on to say that DiBenedetto's equation (that was re-worked by Pascault and Williams) is used to convert the T_g measured by DSC into the degree of conversion. DSC works by measuring the difference in rates of heat absorption of a sample (compared to an inert reference heated at the same time) when it is heated at a constant rate. The theory of this method will be covered in Chapter 2. It is also possible to infer the T_g by measuring the dynamic mechanical properties, i.e. by DMTA [2, 12, 28, 44-46]. As the rigid solid sample is heated the modulus will change as the sample will move into the rubbery state (see TTT diagram above) above the T_g [20].

Rheology has also been used to measure the cure of epoxy resins both as a method on its own and in conjunction with other methods [24, 47-52]. It can be difficult to make rheological measurements using conventional methods (e.g. capillary, rotational and vibrational (oscillatory) rheometers) due to epoxy resins curing to form a solid mass that can damage the instrument, but this can be overcome by using disposable plates or by the vibrating paddle technique [48].

Dielectric analysis (DEA) and DSC have been used together to monitor the cure of epoxy systems [40-42]. Koike [40] reports that dielectric analysis is a very effective nondestructive method for investigating the cure process. In a plot of the dielectric loss, ε”, against the logarithm of the frequency for a particular isothermal temperature, the maximum frequency value, f_{max} can be used to calculate the dielectric relaxation time, τ. The relaxation occurs as the system changes from the liquid state to an ungelled glassy state, due to an increase in the molecular weight. Koike goes on to state that it is possible to plot the relaxation time against the cure time, and the resultant lines are similar to viscosity plots (as produced from rheology studies) indicating that relaxation time is proportional to viscosity. The paper also states that there is a relationship between the relaxation time and the T_g, and so the T_g can be predicted by dielectrics, i.e. nondestructively compared to DSC. The data shown in a graph of T_g versus cure time shows good correlation between the DSC data and the predicted T_g from the dielectric analysis. Eloundou [41] also reports good correlation between T_g values obtained from DSC and predicted from dielectrics. Preu and Mengel [42] studied cure using dielectric analysis and DSC, and reported that dielectric analysis is an effective method for following the reaction in fast curing systems. Bidstrup and Simpson [43, 53] reported that by analysing epoxy-amine samples by DSC, dielectrics and rheology, a relationship between the viscosity and the conductivity of the system can be developed that allows in situ dielectric cure monitoring. However, they point out that this relationship only holds up to the gelation stage of cure and further work is needed.

1.5 WATER INGRESS

1.5.1 Introduction

When water is absorbed into a cured epoxy resin it behaves like a plasticiser and causes the glass transition temperature and the modulus to be reduced [4], which can lead to the structural integrity of the material failing. Jones [4] states that the T_g can be reduced by *ca.* 20K per 1% moisture. Absorbed water can be ‘bound’ or ‘free’. Barrie [54] states that since water molecules are relatively small and strongly associated through hydrogen bonding, in polar polymers strong localised interactions can form between the polymer and the water molecules. He also states that in non-polar polymers the water molecules tend to cluster in the voids - 'free' water. Simple resin systems initially obey Fickian diffusion kinetics and as such are reversible under absorption/desorption conditions. However, compounded materials are more likely to show irreversible conditions such as leaching, blistering or crazing.

1.5.2 Measurement of Water Ingress

Water ingress into a polymer can be monitored most easily by gravimetric analysis of submerged blocks, of known dimensions and weight, which are removed from the water at set time intervals, weighed and replaced in the water. Fickian Diffusion theory can then be used to calculate the diffusion coefficient, D. Accelerated ageing can be done to show the effects of moisture ingress as the diffusion coefficient increases with increasing ageing temperature [4].

Crank and Park [55] state that gravimetric analysis is the simplest method, but that if only very small quantities of solvent are absorbed the error in the calculation of D is increased. Other methods they mention to look at diffusion include refractive index measurements, radiation absorption methods and nuclear magnetic resonance (NMR).

As stated above, the T_g and modulus are affected by the uptake of water into a cured epoxy resin, therefore dielectric spectroscopy and DSC can both be used to track changes in the T_g, while DMTA can be used to follow changes in the modulus.

1.6 AIMS OF PROJECT

The first aim of this project was to characterise the cure of several epoxy resin systems using dielectric spectroscopy, DSC, FT-IR spectroscopy and rheology measurements. It was hoped to build up an understanding of the cure process and correlate the results produced by the different methods to establish whether dielectric spectroscopy can be used to monitor the cure of epoxy resins in the field without specialist training in interpretation of the results. The second aim was to quantify moisture ingress through gravimetric measurements and dielectric spectroscopy.

1.7 REFERENCES

1. Pethrick, R.A., *Polymer Science and Technology for Engineers and Scientists*. 2010: Whittles Caithness.

2. Abraham, D. and R. McIlhagger, *Glass fibre epoxy composite cure monitoring using parallel plate dielectic analysis in comparison with thermal and mechanical testing techniques.* Composites Part A, 1998. **29A**: p. 811-819.

3. Chehura, E., A.A. Skordos, C.-C. Ye, S.W. James, I.K. Partridge, and R.P. Tatam, *Strain development in curing epoxy resin and glass fibre/epoxy composites monitored by fibre Bragg grating sensors in birefringent optical fibre.* Smart Mater. Struct., 2005. **14**: p. 354-362.

4. Jones, F.R., *Chapter 8: Composite materials*, in *Chemistry and Technology of Epoxy Resins*, B. Ellis, Editor. 1993, Blackie Academic & Professional: Glasgow.

5. Weatherhead, R.G., *FRP Technology: Fibre Reinforced Resin Systems*. 1980: Applied Science Publishers Ltd., London.

6. Li, C., M. Cao, R. Wang, Z. Wang, Y. Qiao, L. Wan, Q. Tian, H. Liu, D. Zhang, T. Liang, and C. Tang, *Fibre-optic composite cure sensor: monitoring the curing process of composite material based on intensity modulation.* Composites Science and Technology, 2003. **63**: p. 1749-1758.

7. Pethrick, R.A., *Overview of fundamental aspects of dielectric monitoring of cure of some resins used in composite manufacture.* Plastics, Rubber and Composites Processing and Applications, 1998. **27**(6): p. 257-265.

8. Gopal, A.K., S. Adali, and V.E. Verijenko, *Optimal temperature profiles for minimum residual stress in the cure process of polymer composites.* Composite Structures, 2000. **48**: p. 99-106.

9. Boinard, P., W.M. Banks, and R.A. Pethrick, *Changes in the dielectric relaxations of water in epoxy resin as a function of the extent of water ingress in carbon fibre composites.* Polymer, 2005. **46**: p. 2218-2229.

10. Kim, J.-K., C. Hu, R.S.C. Woo, and M.-L. Sham, *Moisture barrier characteristics of organoclay-epoxy nanocomposites.* Composites Science and Technology, 2005. **65**: p. 805-813.

11. Boinard, E., R.A. Pethrick, J. Dalzel-Job, and C.J. MacFarlane, *Influence of resin chemistry on water uptake and environmental ageing in glass fibre reinforced composites-polyester and vinyl ester laminates.* Journal of Materials Science, 2000. **35**: p. 1931-1937.

12. Brown, J., I. Rhoney, and R.A. Pethrick, *Epoxy resin based nanocomposites: 1. Diglycidylether of bisphenol A (DGEBA) with triethylenetetramine (TETA).* Polym Int, 2004. **53**: p. 2130-2137.

13. Lee, H.N., *Epoxy Resins: Their Applications and Technology*. 1957: McGraw-Hill.

14. Ellis, B., *Chapter 1: Introduction to the chemistry, synthesis, manufacture and characterisation of epoxy resins*, in *Chemistry and Technology of Epoxy Resins*, B. Ellis, Editor. 1993, Blackie Academic & Professional: Glasgow.

15. http://www.spsystems.com/.

16. http://www.huntsman.com/.

17. http://www.resins.com/resins/.

18. http://www.devonport.co.uk/.

19. Shaw, S.J., *Chapter 4: Additives and modifiers for epoxy resins*, in *Chemistry and Technology of Epoxy Resins*, B. Ellis, Editor. 1993, Blackie Academic & Professional: Glasgow.

20. Potter, W.G., *Epoxide Resins*. 1970, London: Butterworth & Co.

21. Ashcroft, W.R., *Chapter 2: Curing agents for epoxy resins*, in *Chemistry and Technology of Epoxy Resins*, B. Ellis, Editor. 1993, Blackie Academic & Professional: Glasgow.

22. Elias, H.-G., *An Introduction to Polymer Science*. 1997, Weinheim & New York: VCH.

23. Bordi, F., G. Paradossi, C. Rinaldi, and B. Ruzicka, *Chemical and physical hydrogels: two case systems studied by quasi elastic light scattering.* Physica A: Statistical Mechanics and its Applications, 2002. **304**(1-2): p. 119.

24. Pethrick, R.A., *Chapter 3: Rheological Studies Using a Vibrating Probe*, in *Rheological Measurement*, A.A. Collyer and D.W. Clegg, Editors. 1998, Chapman & Hall: London.

25. Wisankrakkit, G., J.K. Gillham, and J.B. Enns, *The Glass Transition Temperature (Tg) as a Parameter for Monitoring the Cure of an Amine/Epoxy System at Constant Heating Rates.* Journal of Applied Polymer Science, 1990. **41**(7-8): p. 1895-1912.

26. Johari, G.P., *Chapter 6: Electrical properties of epoxy resins*, in *Chemistry and Technology of Epoxy Resins*, B. Ellis, Editor. 1993, Blackie Academic & Professional: Glasgow.

27. Gillham, J.K., *The TBA Torsion Pendulum: a Technique for Characterising the Cure and Properties of Thermosetting Systems.* Poly Int, 1997. **44**: p. 262-276.

28. Kamon, T. and H. Furukawa, *Curing Mechanisms and Mechanical Properties of Cured Epoxy Resins.* Advances in Polymer Science, 1986. **80**: p. 173-202.

29. Park, S.-J. and F.-L. Jin, *Thermal stabilities and dynamic mechanical properties of sulfone-containing epoxy resin cured with anyhdride.* Polymer Degradation and Stability, 2004. **86**: p. 515-520.

30. Ellis, B., *Chapter 3: The kinetics of cure and network formation*, in *Chemistry and Technology of Epoxy Resins*, B. Ellis, Editor. 1993, Blackie Academic & Professional: Glasgow.

31. Potter, K., *Chapter 7: Matrix Resins, in An Introduction to Composite Products*. 1997, London: Chapman & Hall. 74-88.

32. Hayward, D., E. Hollins, P. Johncock, I. McEwan, R.A. Pethrick, and E.A. Pollock, *The cure and diffusion of water in halogen containing epoxy/amine thermosets.* Polymer, 1997. **38**(5): p. 1151-1168.

33. Kortaberria, G., P. Arruti, N. Gabilondo, and I. Mondragon, *Curing of an epoxy resin modified with poly(methylmethacrylate) monitored by simultaneous dielectric/ near infrared spectroscopies.* European Polymer Journal, 2004. **40**: p. 129-136.

34. Lin, R.-H. and J.-H. H, *In situ FT-IR and DSC investigation on the cure reaction of the dicyanate/diepoxide/diamine system.* Poly Int, 2001. **50**: p. 1073-1081.

35. Fouchal, F., J.A.G. Knight, and P.M. Dickens, *Monitoring the polymerization of a diglycidyl ether bisphenol-A/2,2'-dimethyl-4,4'-methlenebis (cyclohexlamine) matrix with a fourier transofrm infrared optical fibre sensor.* Proc Instn Mech Engrs: Part L: J. Materials: Design and Applications, 2004. **218**(L4): p. 331-342.

36. Garrido, M., M.S. Larrechi, and F.X. Rius, *Modeling of Complex Viscosity Changes in the Curing of Epoxy Resins from Near- Infrared Spectroscopy and Multivariate Regression Analysis.* Applied Spectroscopy, 2004. **58**(12): p. 1424-1430.

37. Abdelkader, A.F. and J.R. White, *Curing characteristics and internal stresses in epoxy coatings: Effect of crosslinking agent.* Journal of Materials Science, 2005. **40**: p. 1843-1854.

38. Tadros, R. and D.C. Timm, *Fourier-Transform Infrared Analysis of a Linear, Anhydride-Cured Epoxy.* Macromolecules, 1995. **28**: p. 7441-7446.

39. Georjon, O., J. Galy, and J.P. Pascault, *Isothermal Curing Of An Uncatalyzed Dicyanate Ester Monomer - Kinetics And Modeling.* Journal Of Applied Polymer Science, 1993. **49**(8): p. 1441-1452.

40. Koike, T., *Dielectric Relaxation During Isothermal Curing of Epoxy Resin with an Aromatic Amine.* Journal of Applied Polymer Science, 1992. **44**(4): p. 679-690.

41. Eloundou, J.P., J.F. Gerard, J.P. Pascault, and D. Kranbuehl, *Modeling complex permittivity of an epoxy-amine system using simultaneous kinetic and microdielectric studies.* Macromolecular Chemistry And Physics, 2002. **203**(13): p. 1974-1982.

42. Preu, H. and M. Mengel, *Experimental and theoretical study of a fast curing adhesive.* International Journal of Adhesion and Adhesives, 2007. **27**: p. 330-337.

43. Bidstrup, S.A. and J.O. Simpson, *The Effect of Stoichiometry on Chain Segment and Ion Mobility in Partially Polymerized Epoxy Systems.* Journal Of Polymer Science Part B-Polymer Physics, 1995. **33**: p. 43-54.

44. Ivanova, K.I., R.A. Pethrick, and S. Affrossman, *Investigation of hydrothermal ageing of a filled rubber toughened epoxy resin using dynamic mechanical thermal analysis and dielectric spectroscopy.* Polymer, 2000. **41**: p. 6787-3796.

45. Francis, B., V.L. Rao, G.V. Poel, F. Posada, G. Groeninchx, R. Ramaswamy, and S. Thomas, *Cure kinetics, morphological and dynamic mechanical analysis of diglycidyl ether of bisphenol-A epoxy resin modified with hydroxyl terminated poly(ether ether ketone) containing pendent tertiary butyl groups.* Polymer, 2006. **47**: p. 5411-5419.

46. Pethrick, R.A., E.A. Hollins, I. McEwan, A.J. MacKinnon, D. Hayward, and L.A. Cannon, *Dielectric, Mechanical and Structural, and Water Absorption Properties of a Thermoplastic-Modified Epoxy Resin: Poly (ether sulfone)-Amine Cured Epoxy Resin.* Macromolecules, 1996. **29**: p. 5208-5214.

47. Hayward, D., R.A. Pethrick, B. Eling, and E. Colbourn, *Prediction of the Rheological Properties of Reactive Polymer Systems.* Poly Int, 1997. **44**: p. 248-254.

48. Affrossman, S., A. Collins, D. Hayward, E. Trottier, and R.A. Pethrick, *A versatile method of characterising cure in filled reactive polymer systems.* Journal of the Oil & Colour Chemists Association, 1989. **72**(11): p. 452-454.

49. Khan, A.S., O. Lopez-Pamies, and R. Kazmi, *Thermo-mechanical large deformation response and constitutive modeling of viscoelastic polymers over a wide range of strain rates and temperatures.* International Journal of Plasticity, 2006. **22**: p. 581-601.

50. Hudson, N.E., R.A. Pethrick, H.A. Barnes, and G.E. Eccelston, *Postgraduate Course: Process Rheology*. 2006, Strathclyde University.

51. Peng, W. and B. Reidl, *The Chemorheology of phenol-formaldehyde thermoset resin and mixtures of the resin with lignin fillers.* Polymer, 1994. **35**(6): p. 1280-1286.

52. Nunez-Regueira, L., C.A. Gracia-Fernandez, and S. Gomez-Barreiro, *Use of rheology, dielectric analysis and differentail scanning calorimetry for gel time determination of a thermoset.* Polymer, 2005. **46**: p. 5979-5985.

53. Simpson, J.O. and S.A. Bidstrup, *Rheological and Dielectric Changes During Isothermal Epoxy-Amine Cure.* Journal Of Polymer Science Part B-Polymer Physics, 1995. **33**: p. 55-62.

54. Barrie, J.A., *Chapter 8. Water in Polymers*, in *Diffusion in Polymers*, J. Crank and G.S. Park, Editors. 1968, Academic Press Inc. Ltd.: London.

55. Crank, J. and G.S. Park, *Chapter 1. Methods of Measurement*, in *Diffusion in Polymers*, J. Crank and G.S. Park, Editors. 1968, Academic Press Inc. Ltd.: London.