8 SUPPLEMENTARY MATERIAL

8.1 Fundamental Degradation Studies of PET and PEN

8.1.1 Thermal Properties of PET and PEN

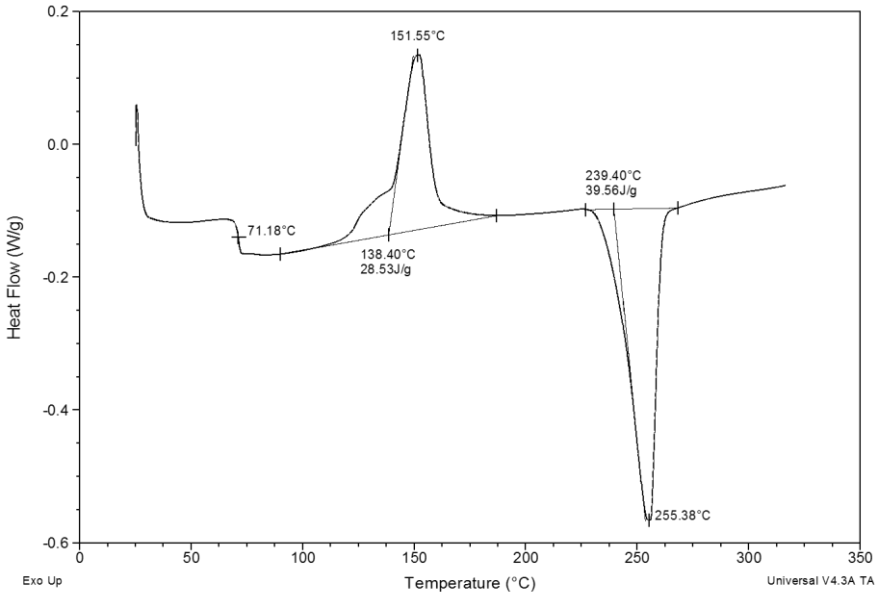

Figure 8.1 DSC of PET in N_2, heat-cool-reheat programme, cycle 1

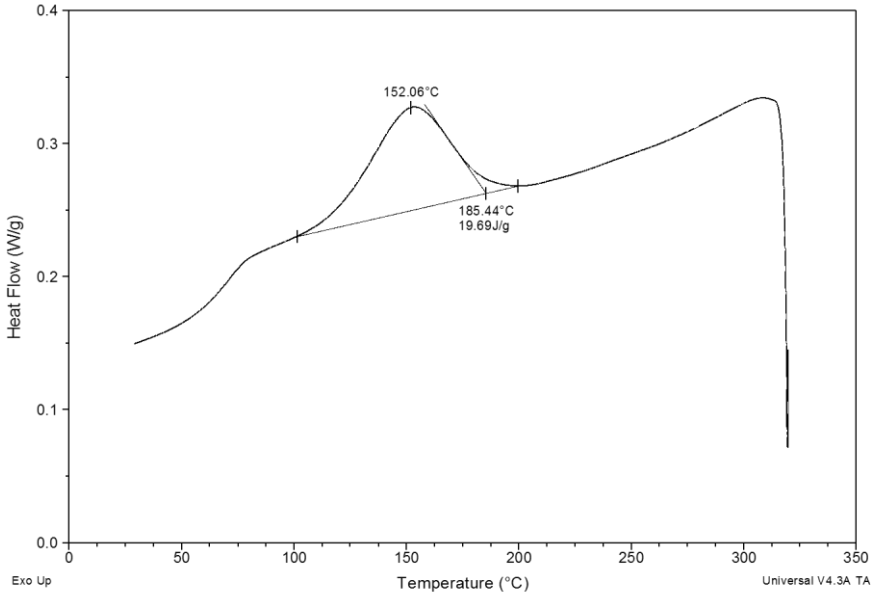

Figure 8.2 DSC of PET in N_2, heat-cool-reheat programme, cycle 2

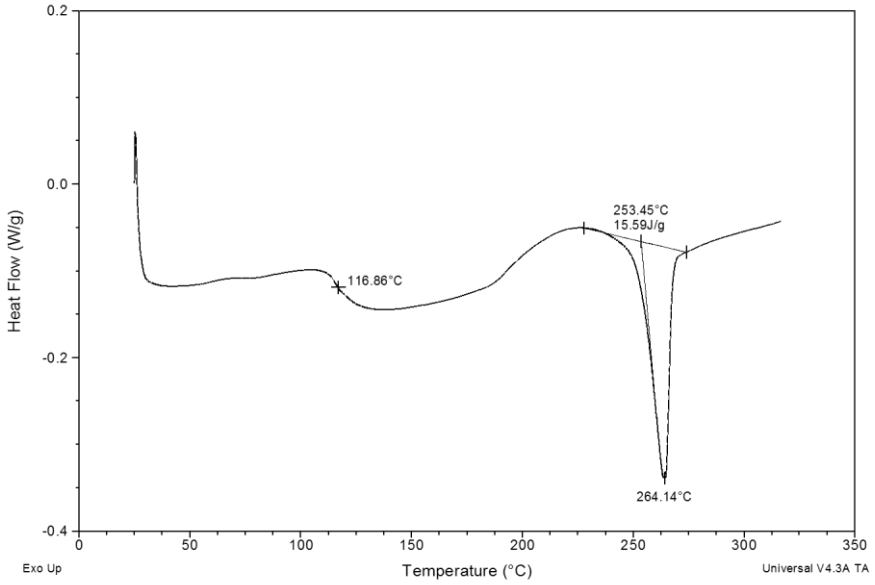

Figure 8.3 DSC of PEN in N_2, heat-cool-reheat programme, cycle 1

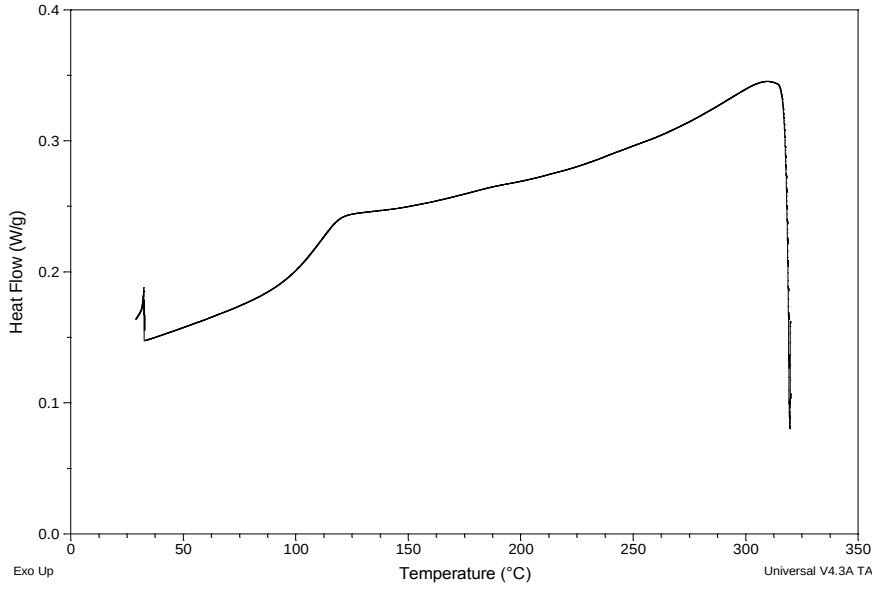

Figure 8.4 DSC of PEN in N_2, heat-cool-reheat programme, cycle 2

8.1.2 Thermal Volatilisation Studies of PET and PEN

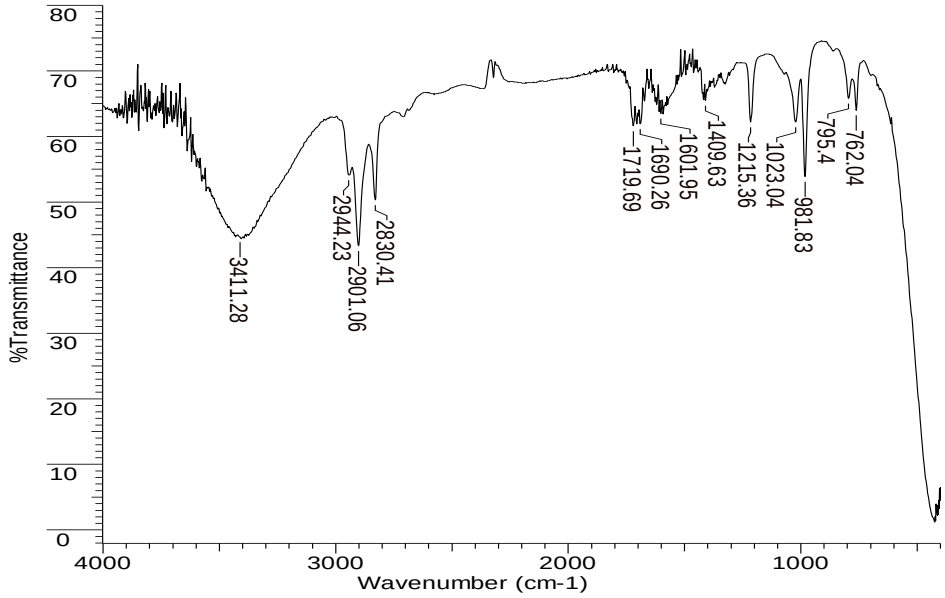

Figure 8.5 IR spectrum of water - PEN fraction 3

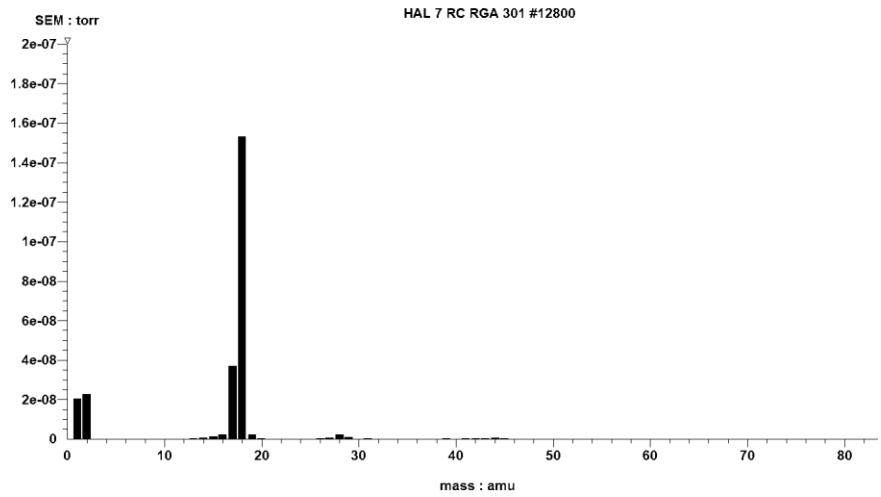

Figure 8.6 Mass spectrum of water - PEN fraction 3

8.1.3 TVA of PET and PEN at Processing Temperature

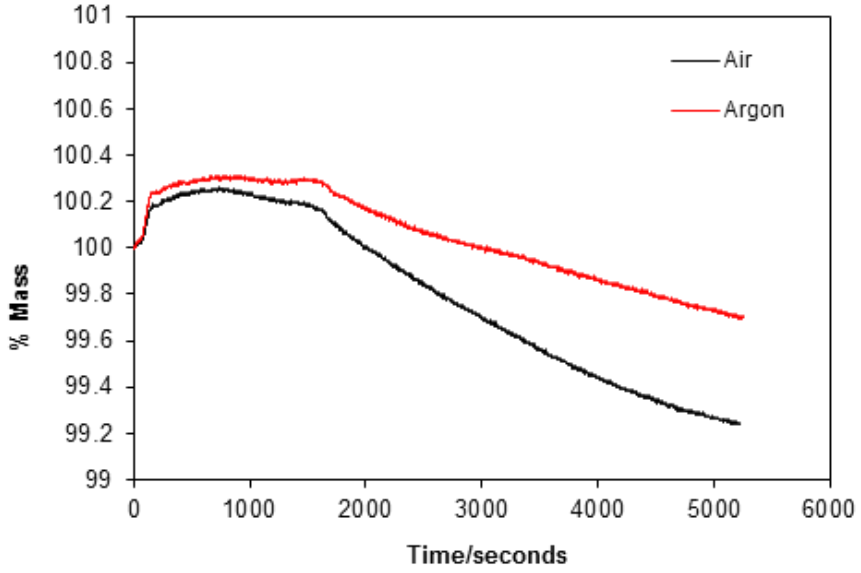

Figure 8.7 Isothermal TGA studies on PET at 290 °C under air and argon – 60 minute isothermal hold

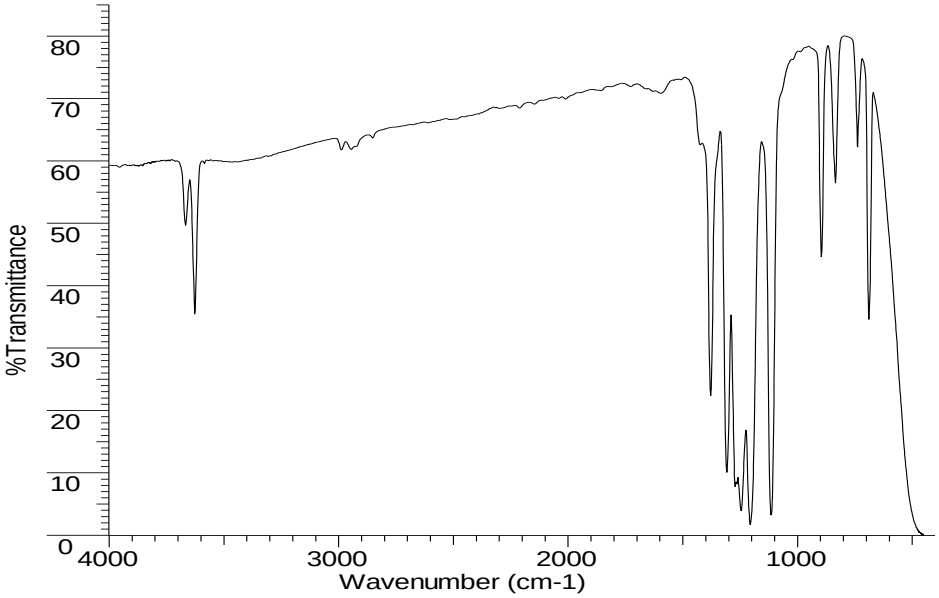

Figure 8.8 IR spectrum - PET fraction 1, 288 °C

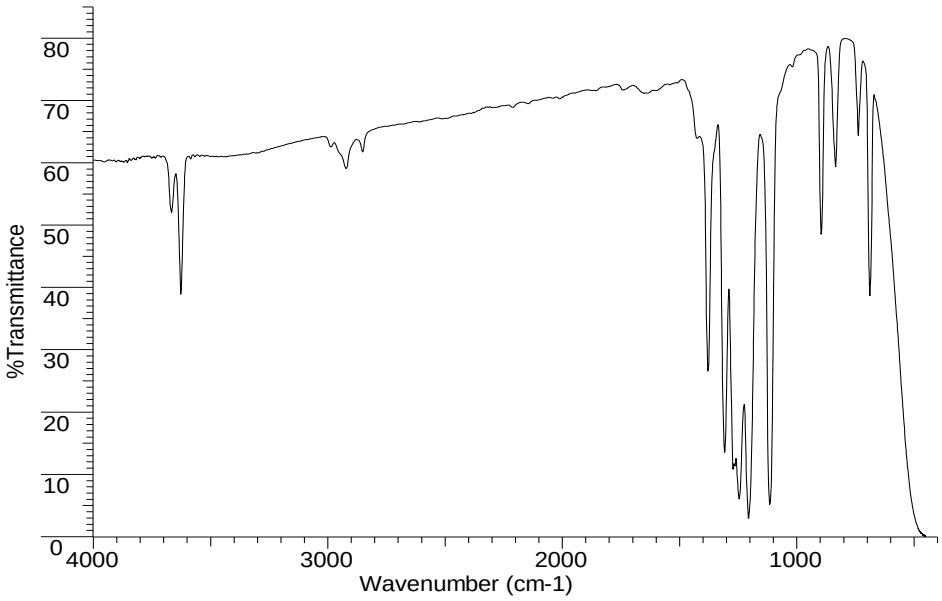

Figure 8.9 IR spectrum - PET fraction 1, 300 ^{o}C

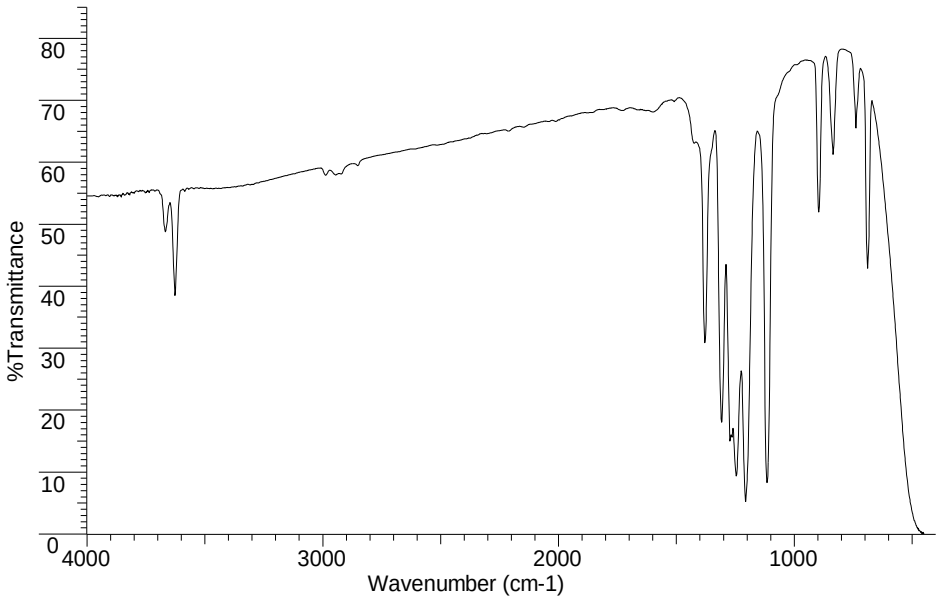

Figure 8.10 IR spectrum - PET fraction 1, 320 ^{o}C

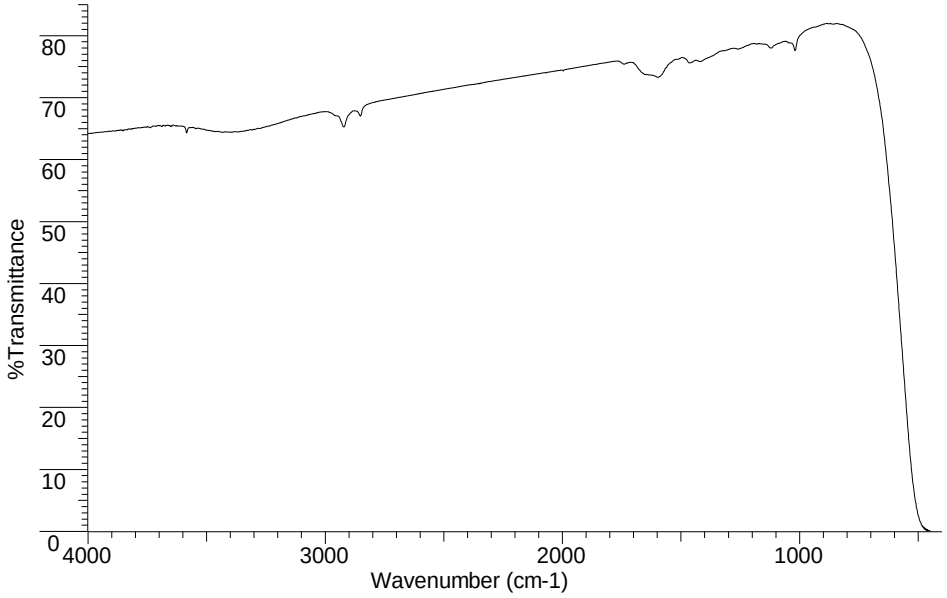

Figure 8.11 IR spectrum - PET fraction 2, 288 ^{o}C

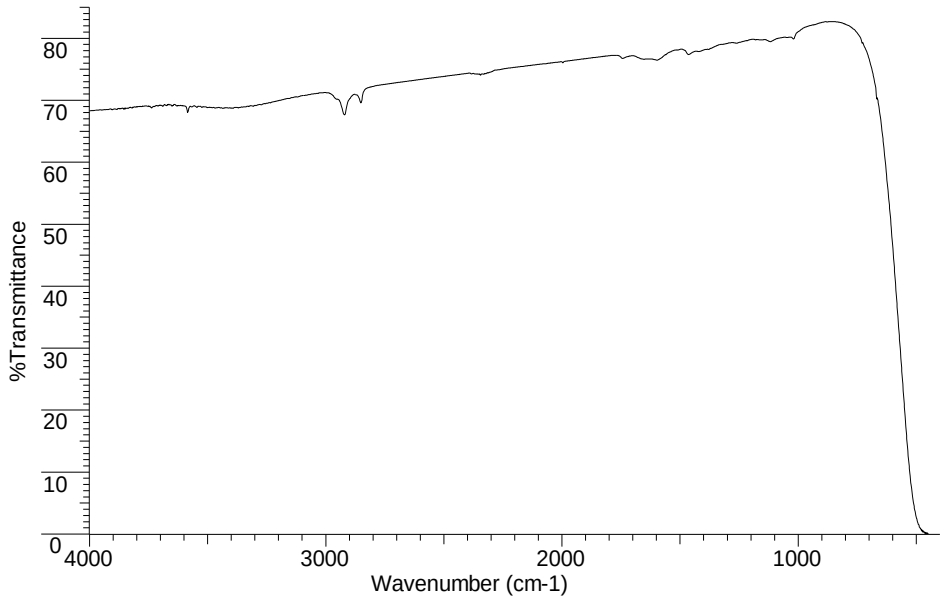

Figure 8.12 IR spectrum - PET fraction 2, 300 ^{o}C

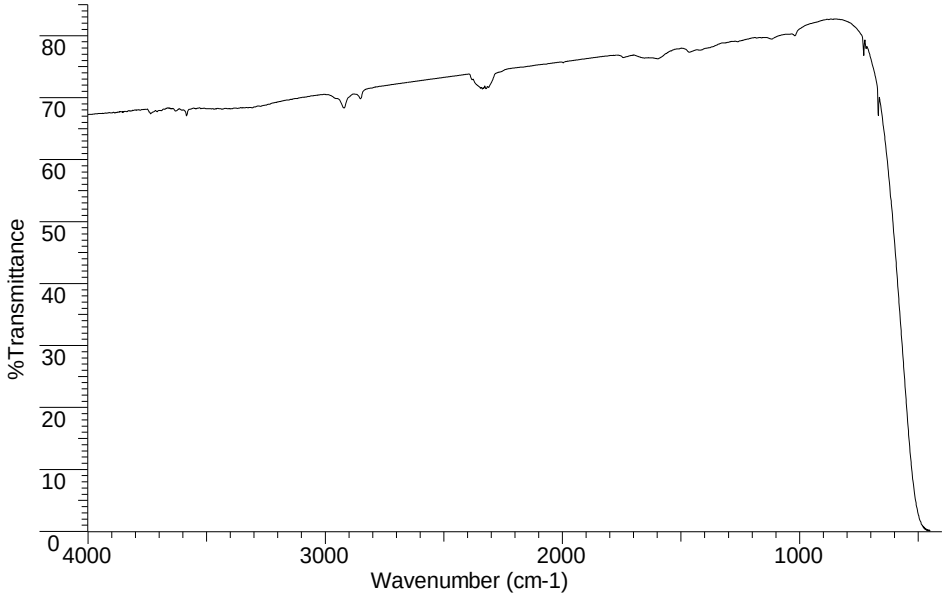

Figure 8.13 IR spectrum - PET fraction 2, 320 ^{o}C

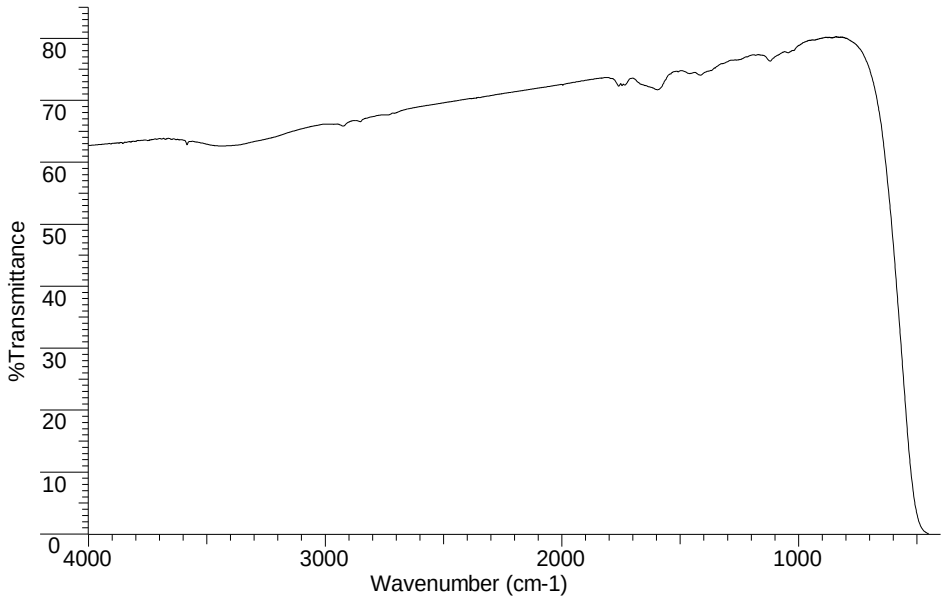

Figure 8.14 IR spectrum - PET fraction 3, 288 ^{o}C

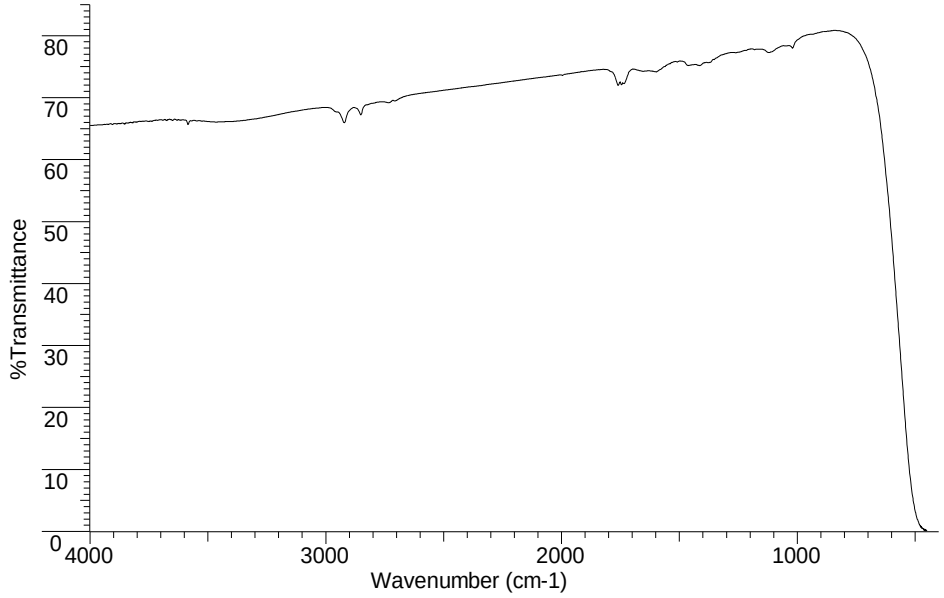

Figure 8.15 IR spectrum - PET fraction 3, 300 ^{o}C

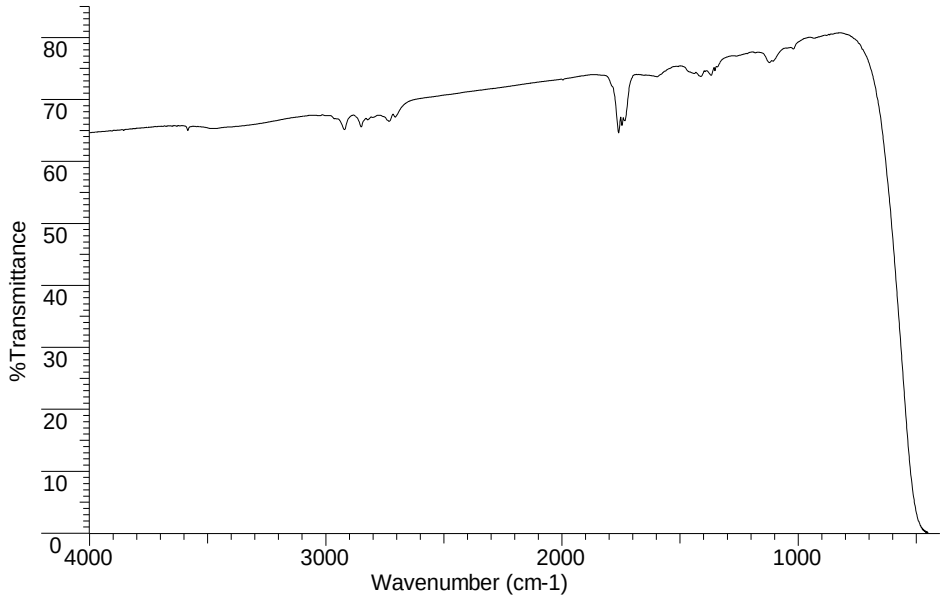

Figure 8.16 IR spectrum - PET fraction 3, 320 ^{o}C

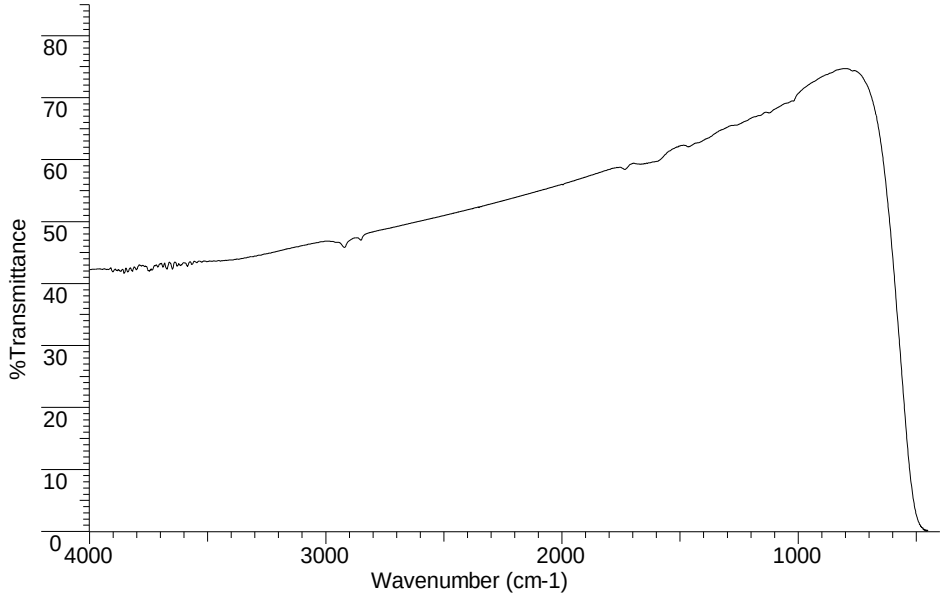

Figure 8.17 IR spectrum - PET fraction 4, 288 ^{o}C

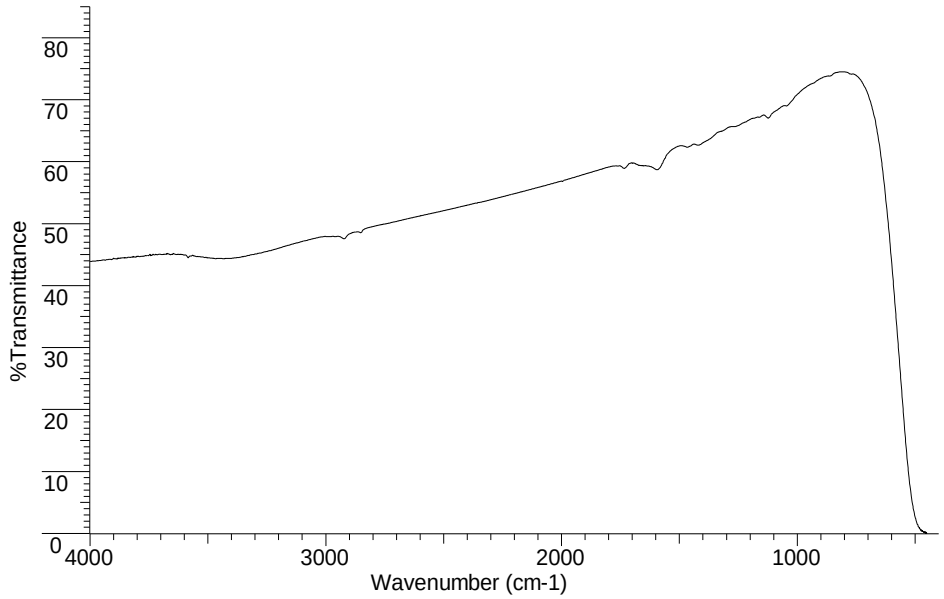

Figure 8.18 IR spectrum - PET fraction 4, 300 ^{o}C

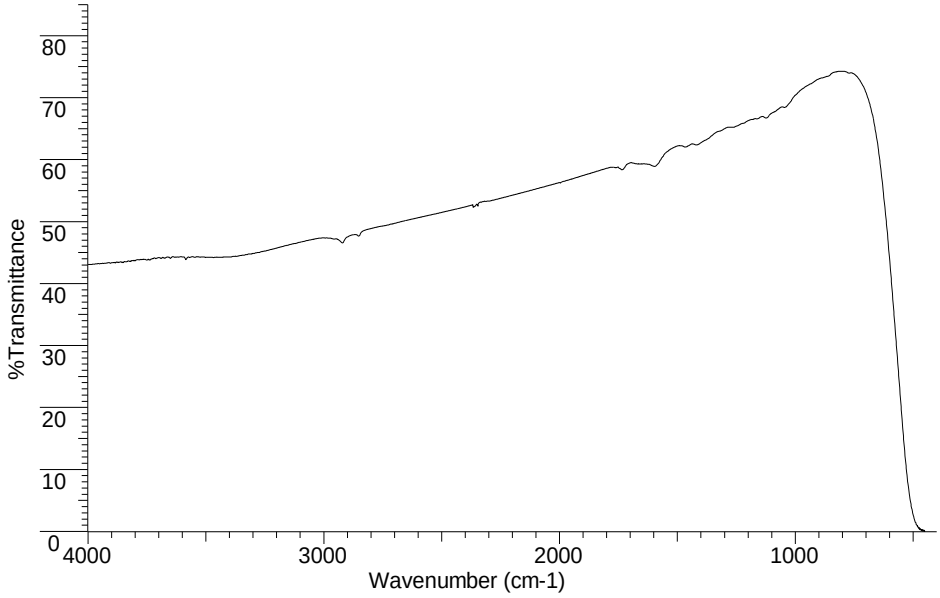

Figure 8.19 IR spectrum - PET fraction 4, 320 °C

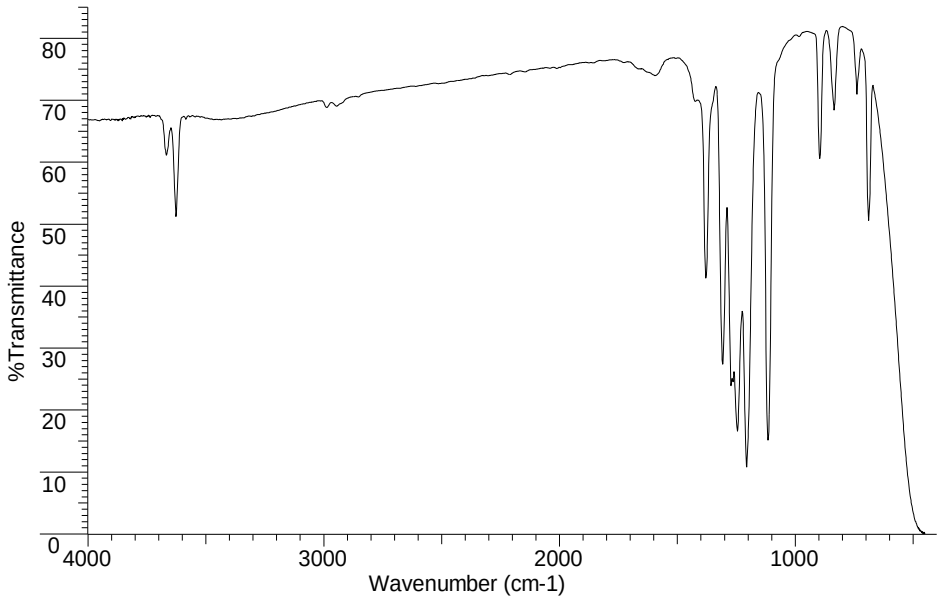

Figure 8.20 IR spectrum - PEN fraction 1, 288 °C

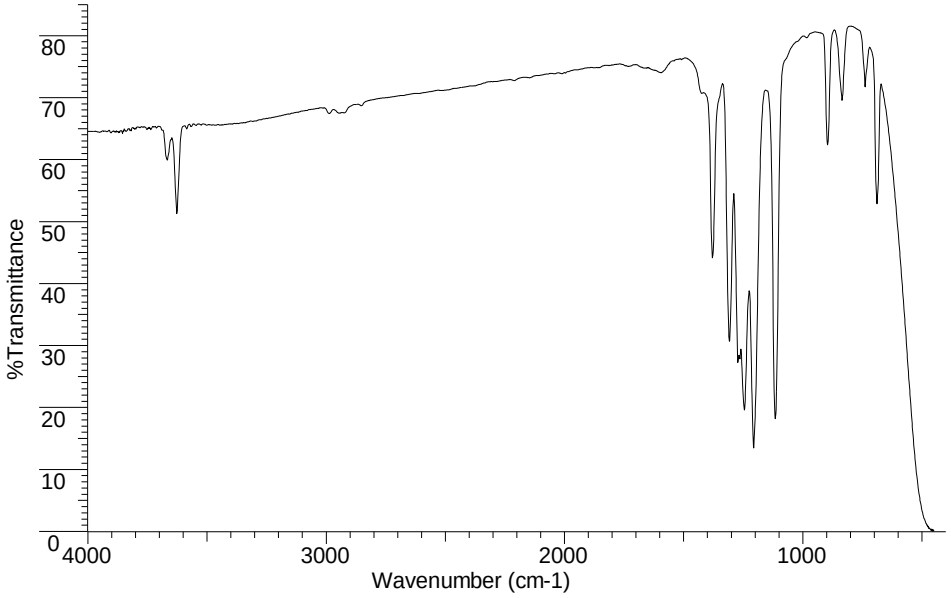

Figure 8.21 IR spectrum - PEN fraction 1, 300 °C

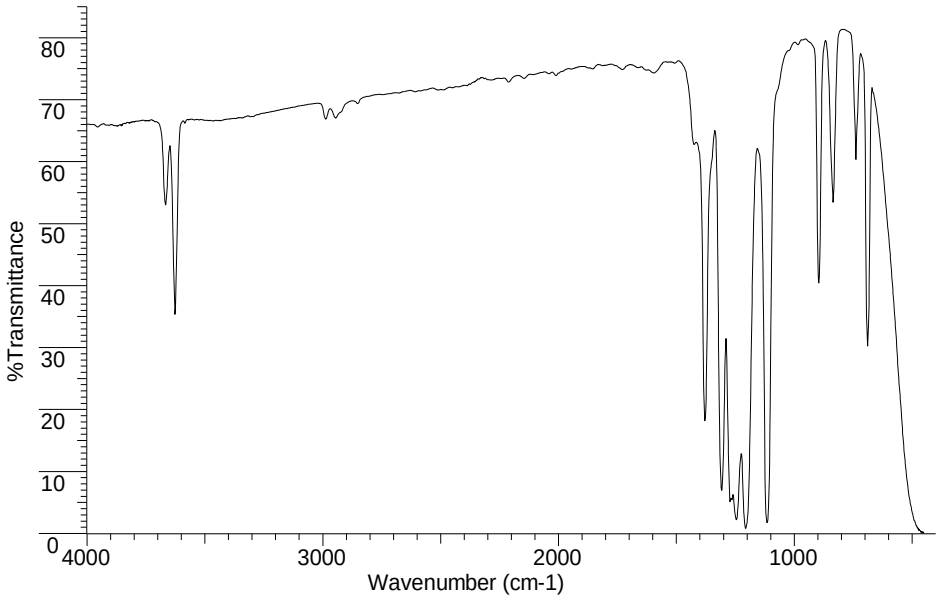

Figure 8.22 IR spectrum - PEN fraction 1, 320 °C

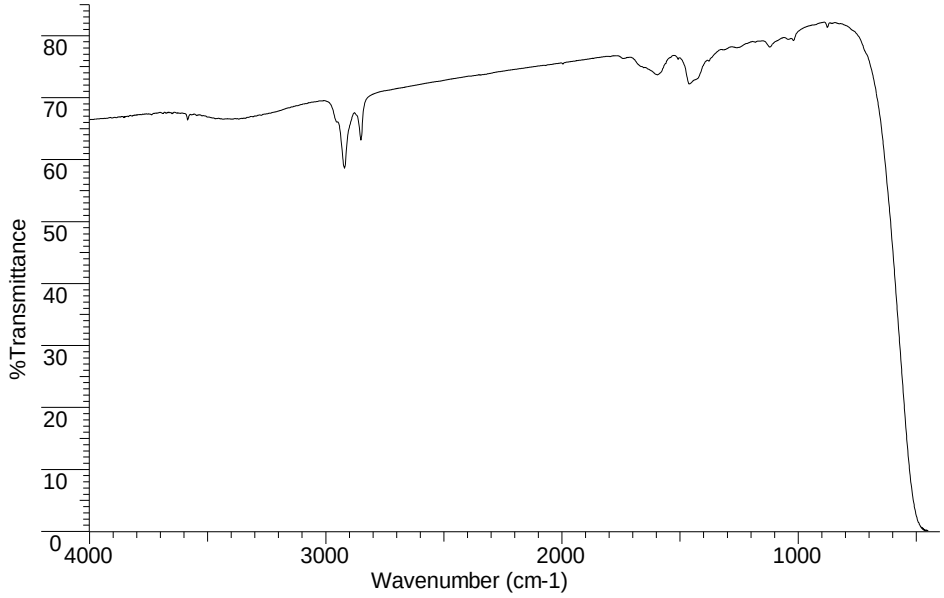

Figure 8.23 IR spectrum - PEN fraction 2, 288 °C

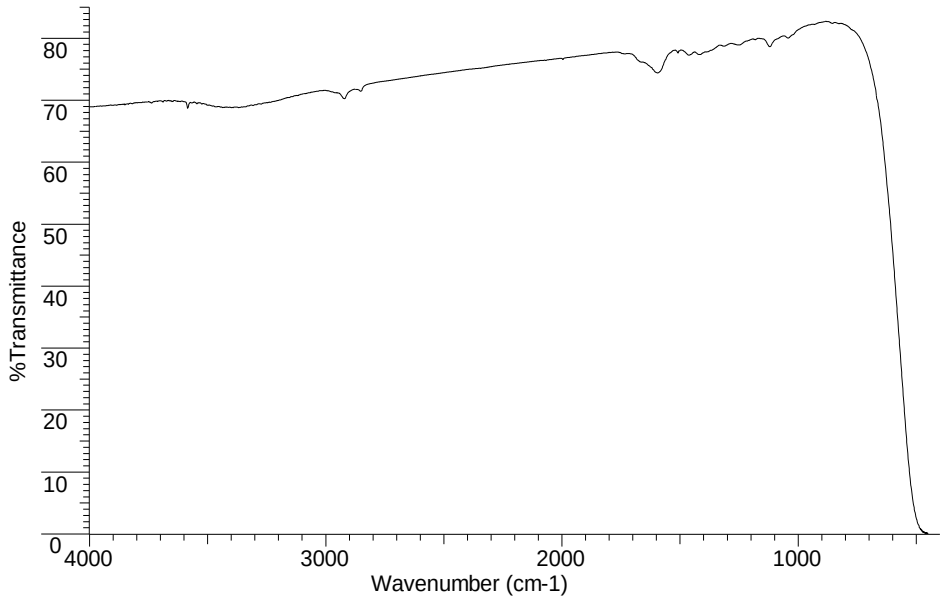

Figure 8.24 IR spectrum - PEN fraction 2, 300 °C

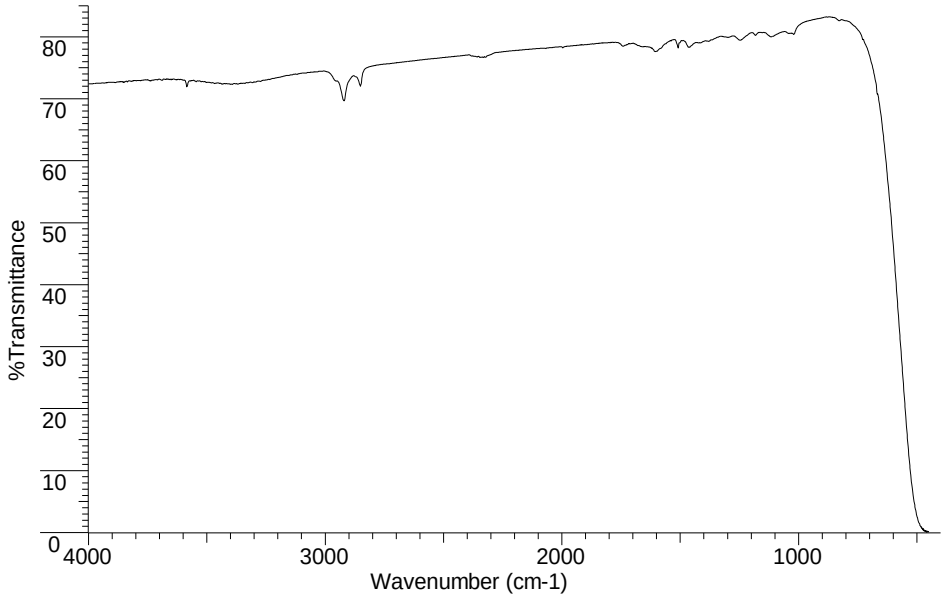

Figure 8.25 IR spectrum - PEN fraction 2, 320 ^{o}C

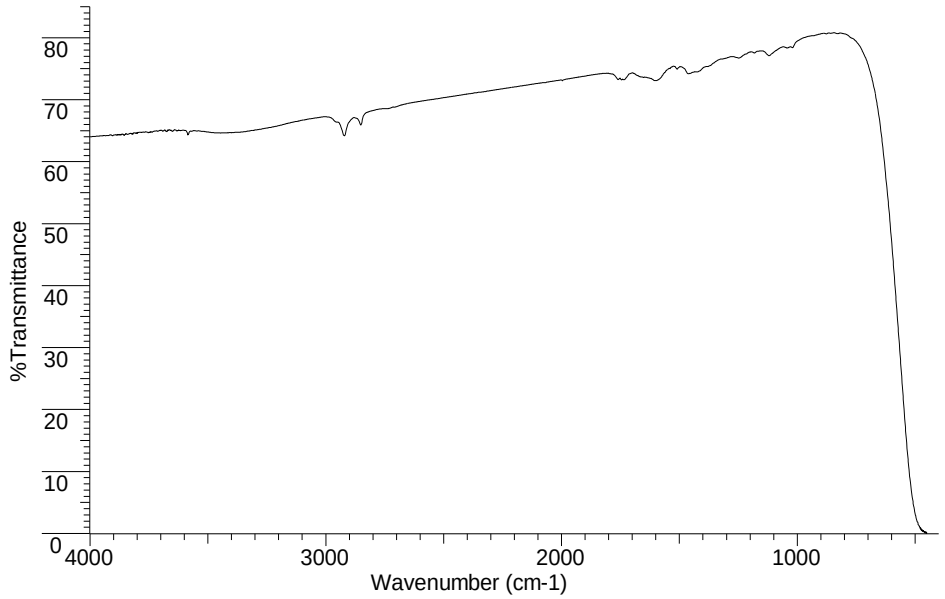

Figure 8.26 IR spectrum - PEN fraction 3, 288 ^{o}C

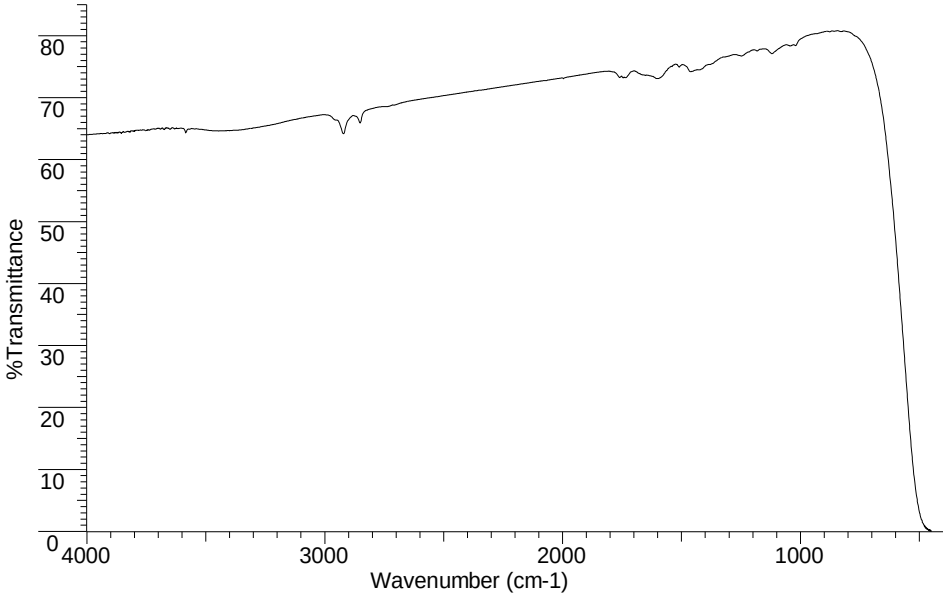

Figure 8.27 IR spectrum - PEN fraction 3, 300 ^{o}C

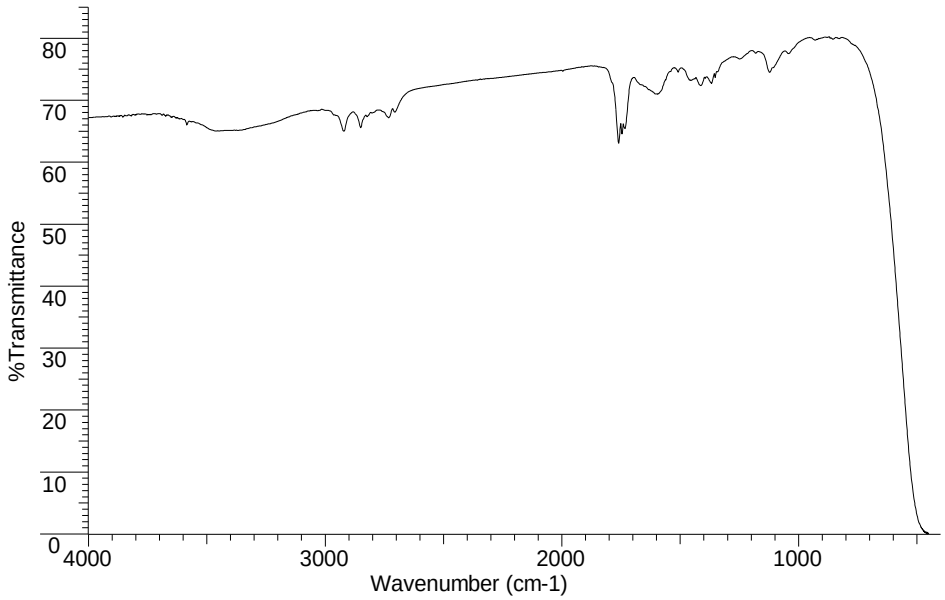

Figure 8.28 IR spectrum - PEN fraction 3, 320 ^{o}C

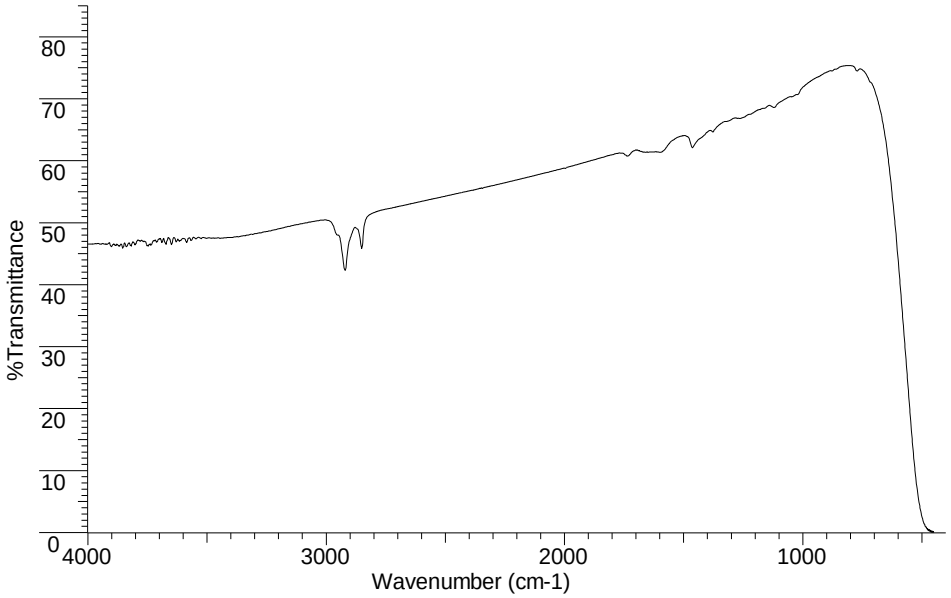

Figure 8.29 IR spectrum - PEN fraction 4, 288 °C

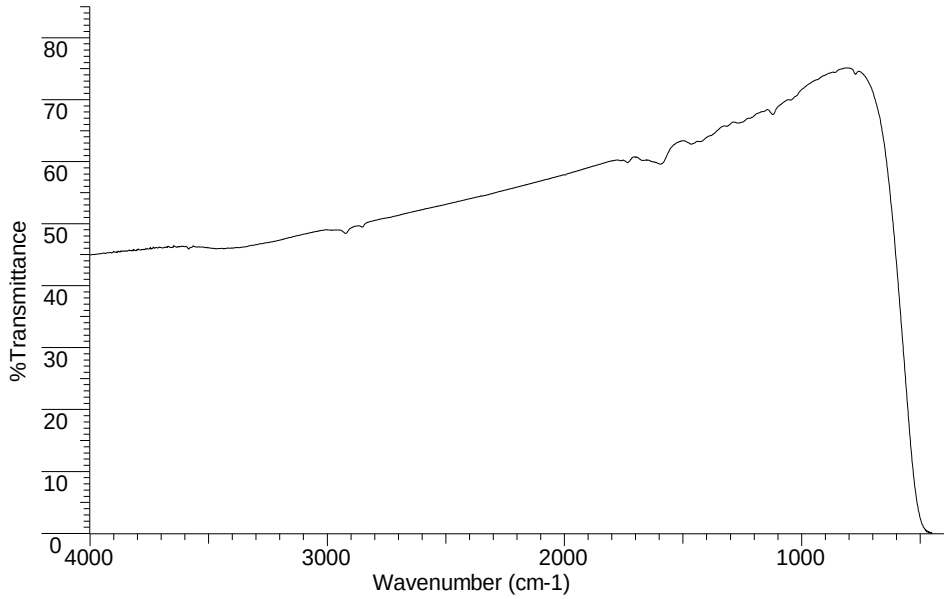

Figure 8.30 IR spectrum - PEN fraction 4, 300 °C

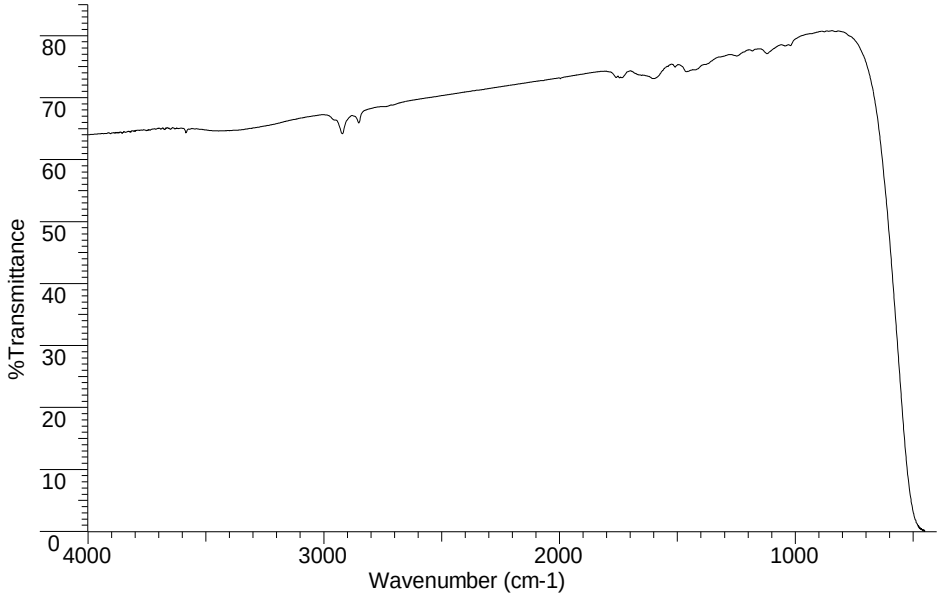

Figure 8.31 IR spectrum - PEN fraction 4, 320 ^{o}C

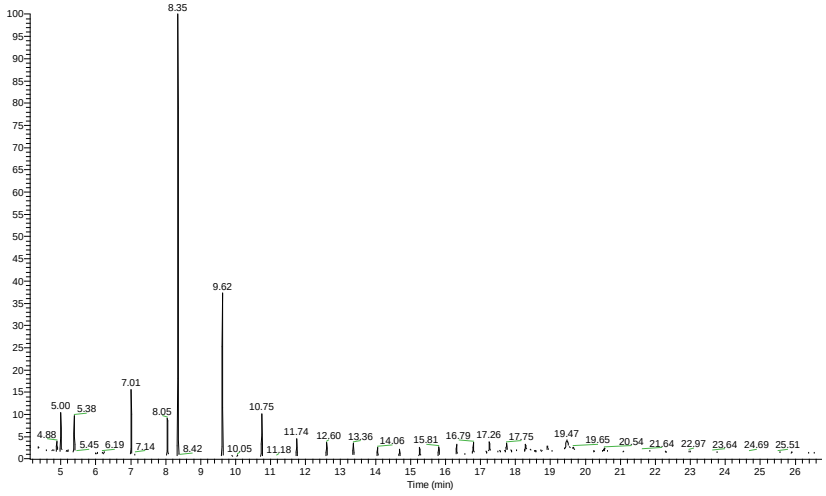

Figure 8.32 GC-MS total ion chromatogram (TIC) - PET fraction 4, 288 ^{o}C

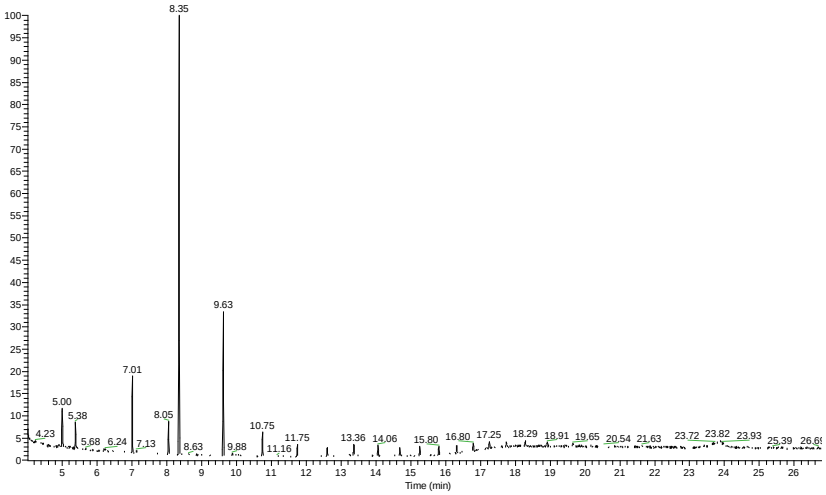

Figure 8.33 GC-MS total ion chromatogram (TIC) - PET fraction 4, 300 ^{o}C

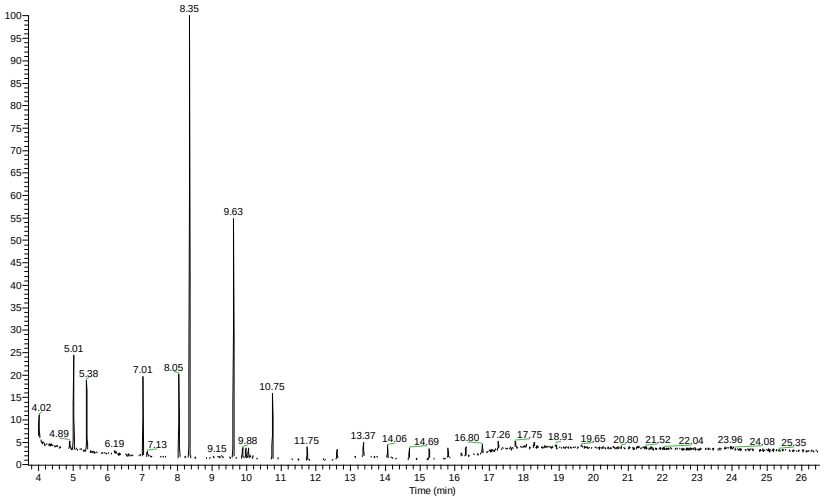

Figure 8.34 GC-MS total ion chromatogram (TIC) - PET fraction 4, 320 ^{o}C

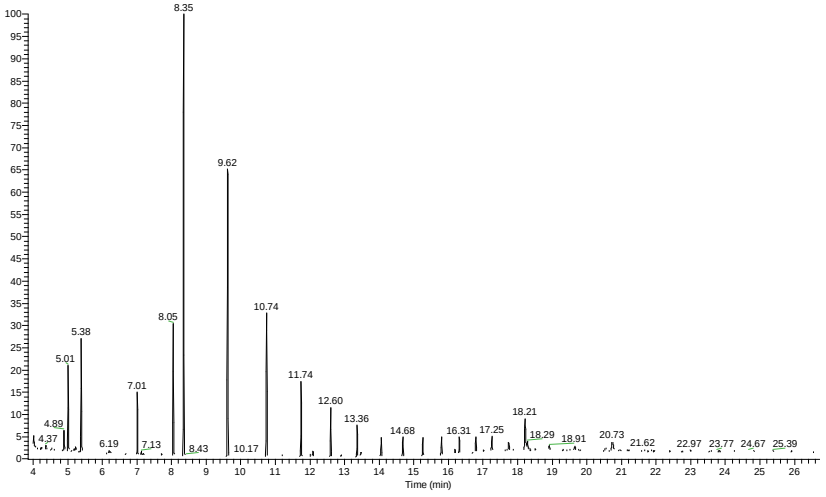

Figure 8.35 GC-MS total ion chromatogram (TIC) - PET cold ring fraction, 288 ^{o}C

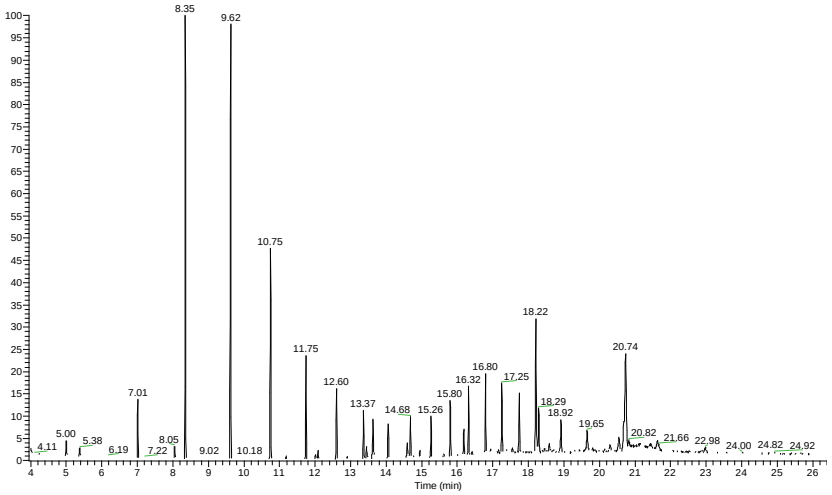

Figure 8.36 GC-MS total ion chromatogram (TIC) - PET cold ring fraction, 300 ^{o}C

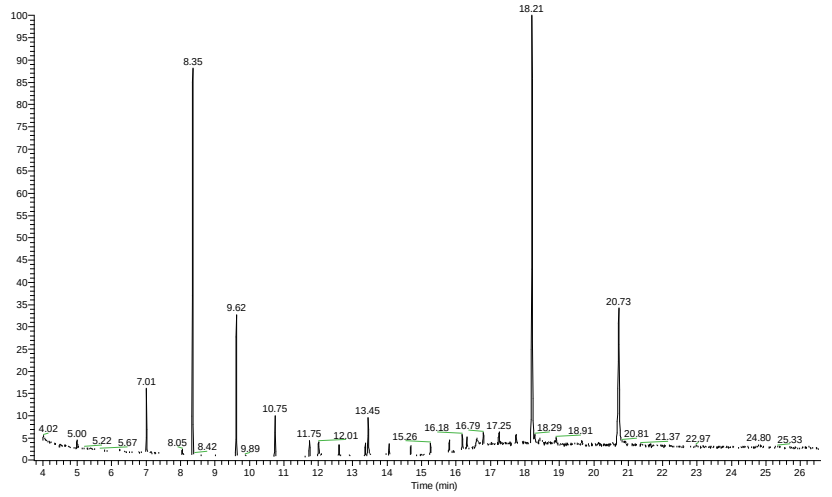

Figure 8.37 GC-MS total ion chromatogram (TIC) - PET cold ring fraction, 320 ^{o}C

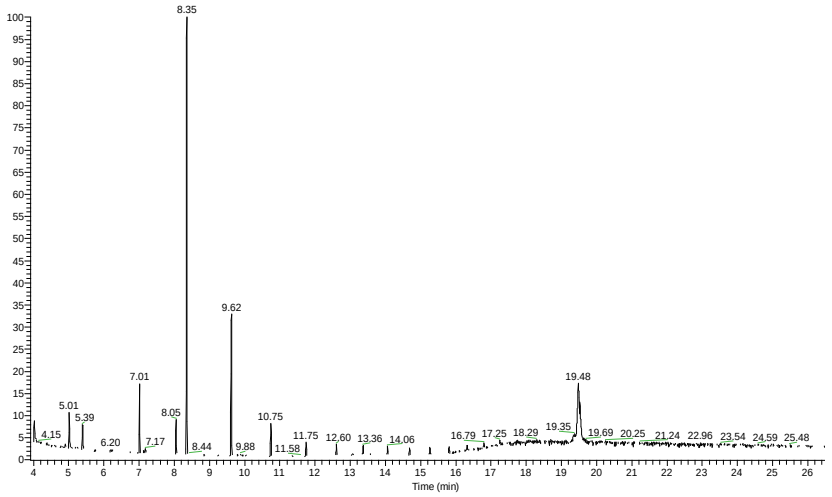

Figure 8.38 GC-MS total ion chromatogram (TIC) - PEN fraction 4, 288 ^{o}C

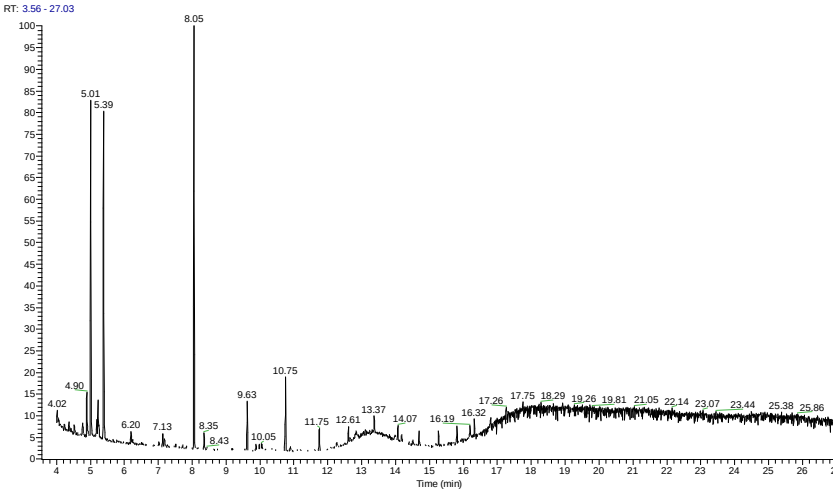

Figure 8.39 GC-MS total ion chromatogram (TIC) - PEN fraction 4, 300 °C

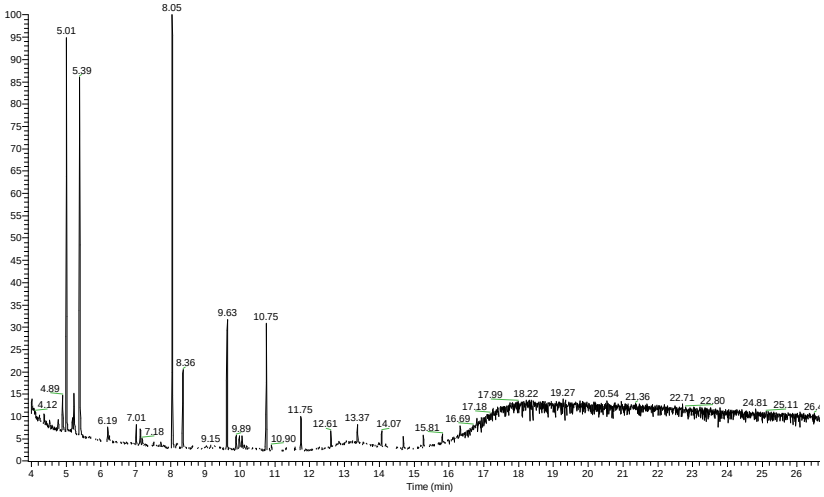

Figure 8.40 GC-MS total ion chromatogram (TIC) - PEN fraction 4, 320 °C

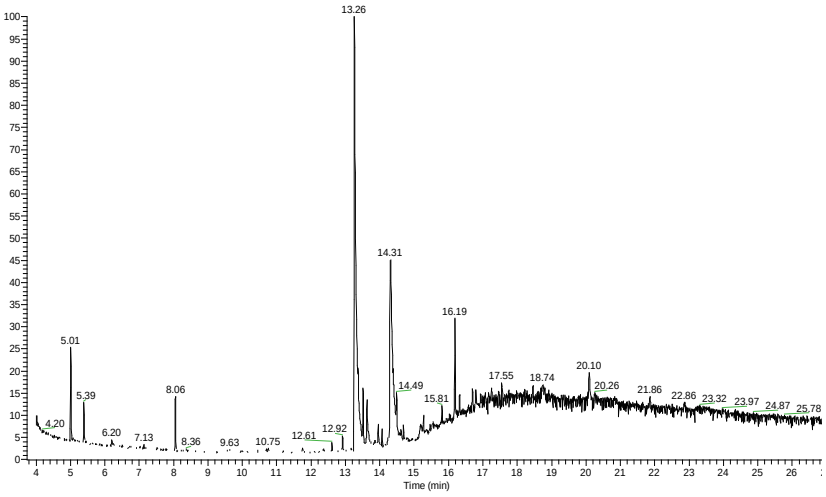

Figure 8.41 GC-MS total ion chromatogram (TIC) - PEN cold ring fraction, 288 °C

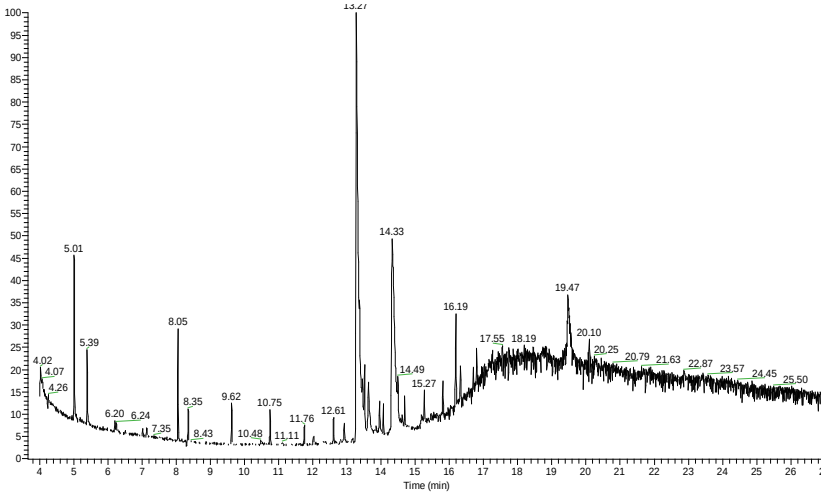

Figure 8.42 GC-MS total ion chromatogram (TIC) - PEN cold ring fraction, 300 °C

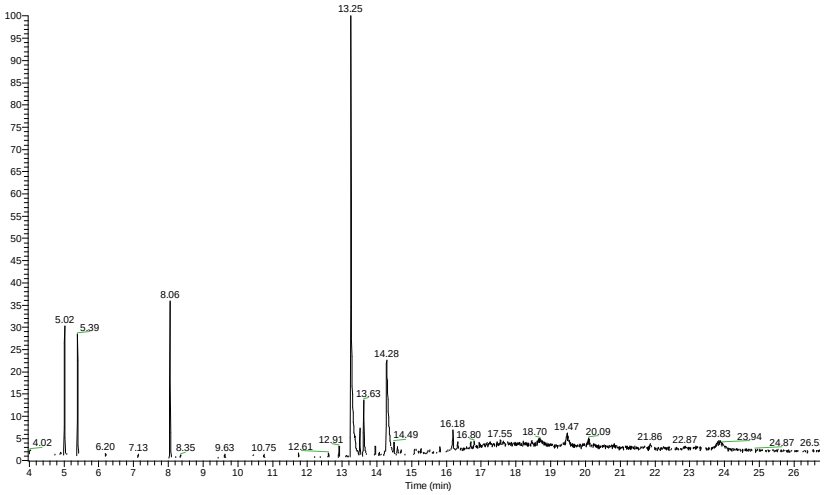

Figure 8.43 GC-MS total ion chromatogram (TIC) - PEN cold ring fraction, 320 °C

8.2 Ageing of PET and PEN under Controlled Processing Conditions

8.2.1 Introduction to PET and PEN Polyester Films

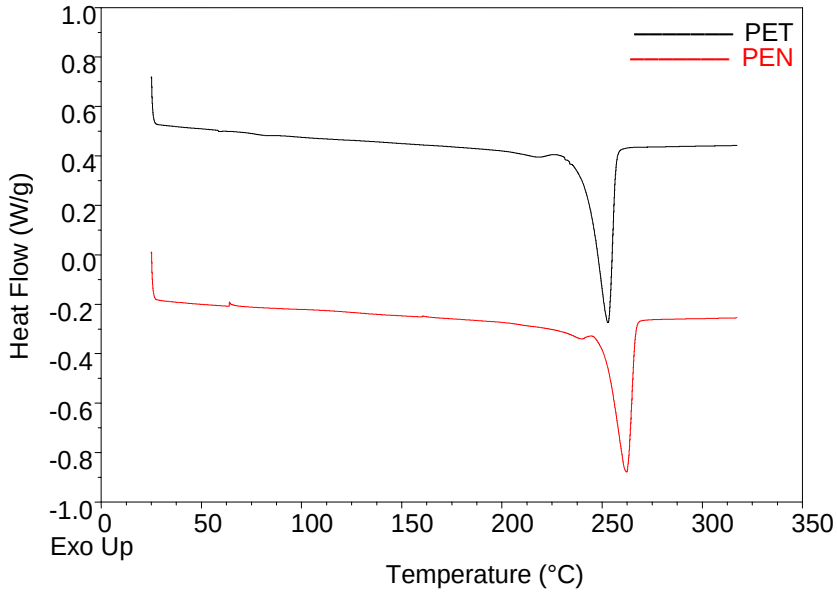

Figure 8.44 Thermal transitions in PET and PEN film determined by DSC, heat-cool-reheat programme under N_2, cycle 1

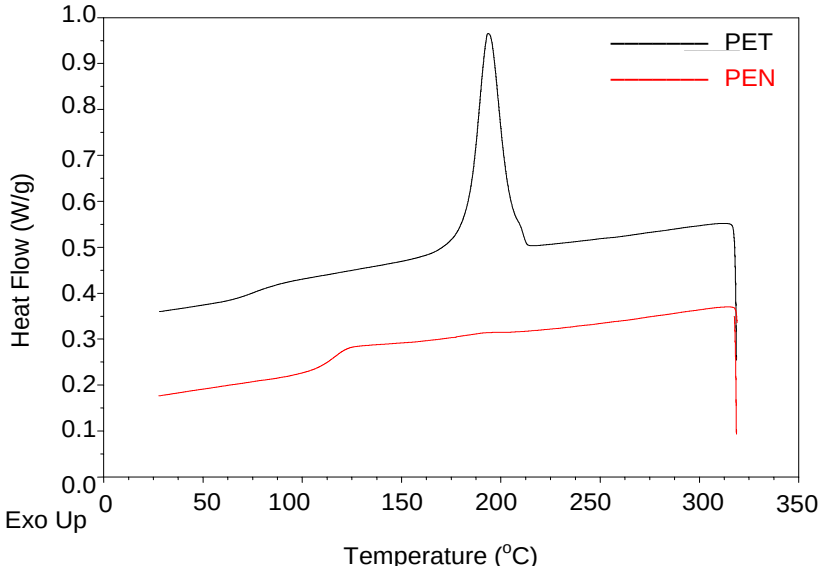

Figure 8.45 Thermal transitions in PET and PEN film determined by DSC, heat-cool-reheat programme under N_2, cycle 2

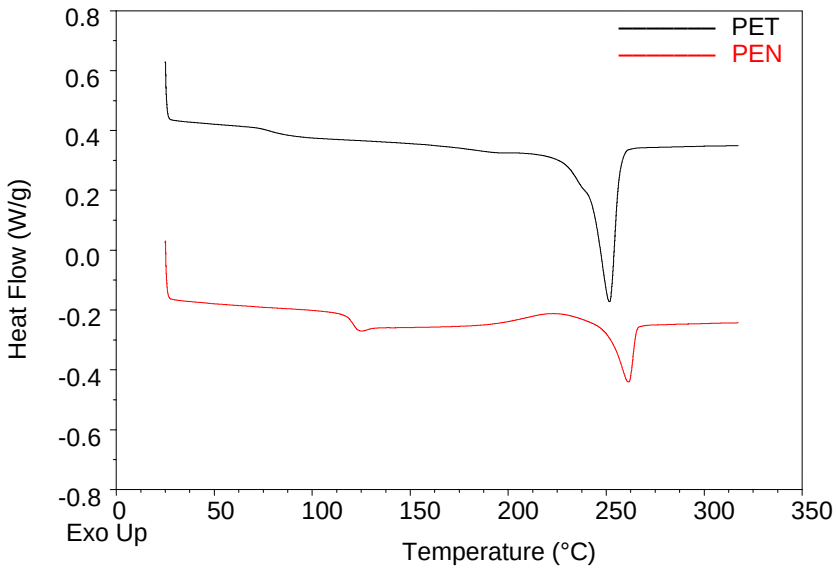

Figure 8.46 Thermal transitions in PET and PEN determined by DSC, heat-cool-reheat programme under N_2, cycle 3

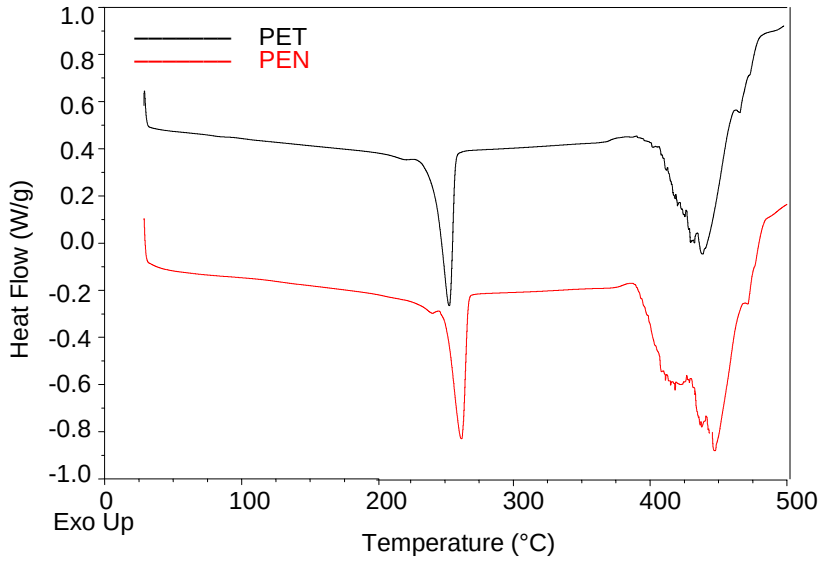

Figure 8.47 DSC degradation curves of PET and PEN in nitrogen, 30 - 500 ^{o}C, 10 ^{o}C min^{-1}

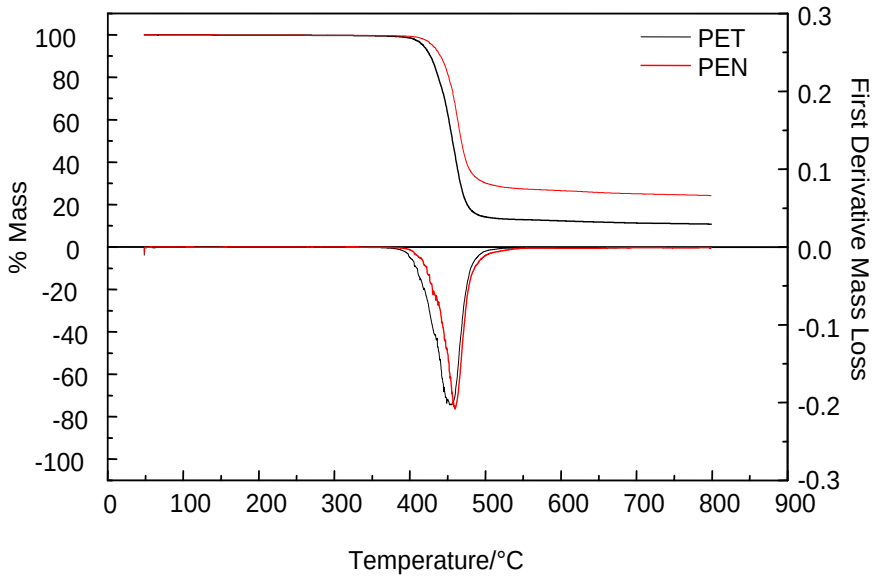

Figure 8.48 Thermogravimetry and differential thermogravimetry curves of PET and PEN in helium, 50 - 800 °C, 10 °C min^{-1}

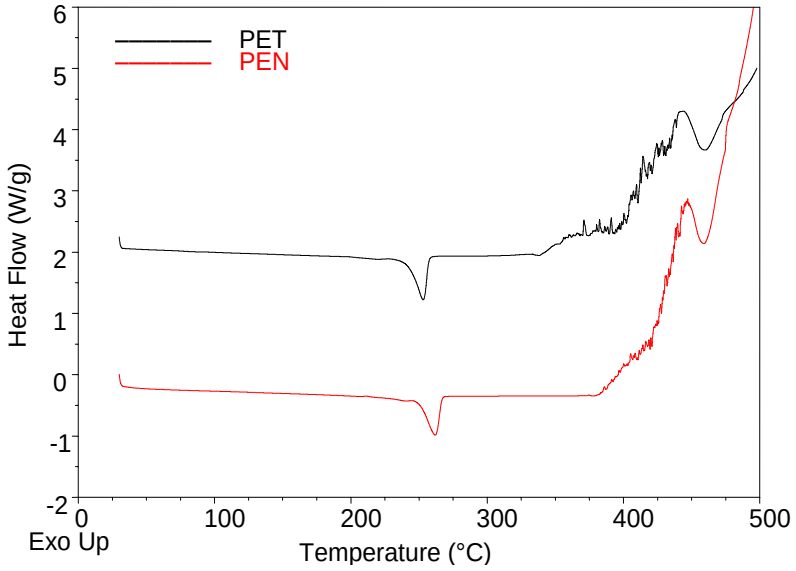

Figure 8.49 DSC degradation curves of PET and PEN in air, 30 - 500 °C, 10 °C min^{-1}

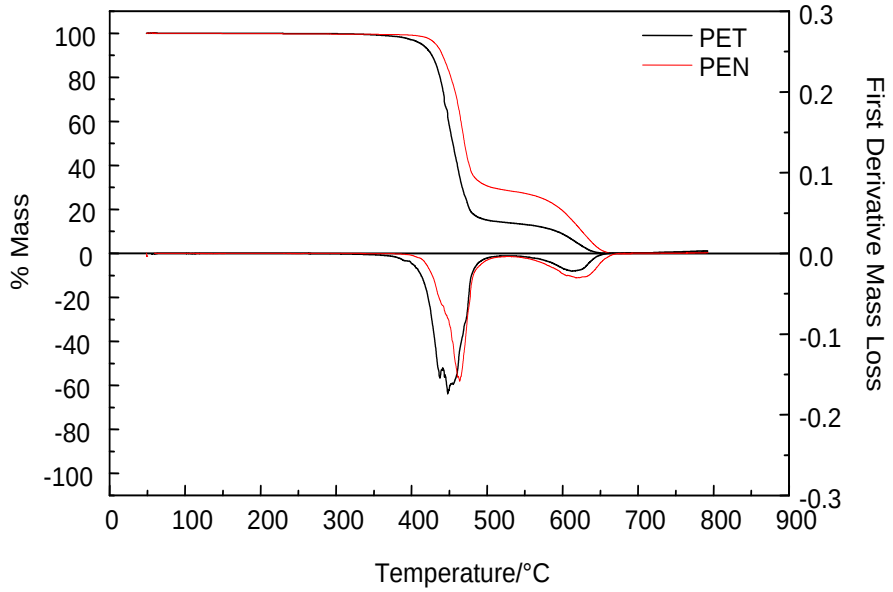

Figure 8.50 Thermogravimetry and differential thermogravimetry curves of PET and PEN in air, 50 - 800 °C, 10 °C min^{-1}

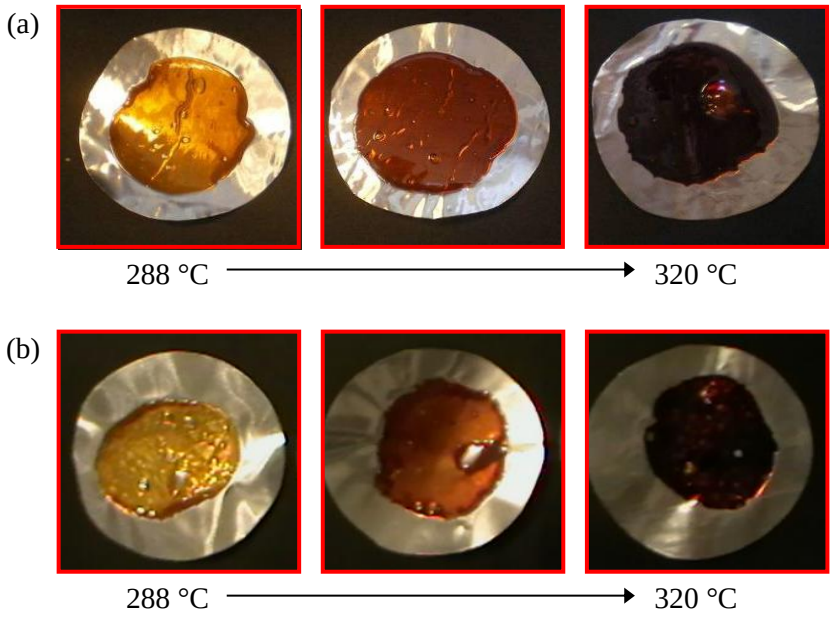

Figure 8.51 Residual film samples from (a) 125µm Q65FA coated PEN as supplied and (b) 125µm melt pressed Q71 uncoated PEN, aged in dry air for 4 hours

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/^{o}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

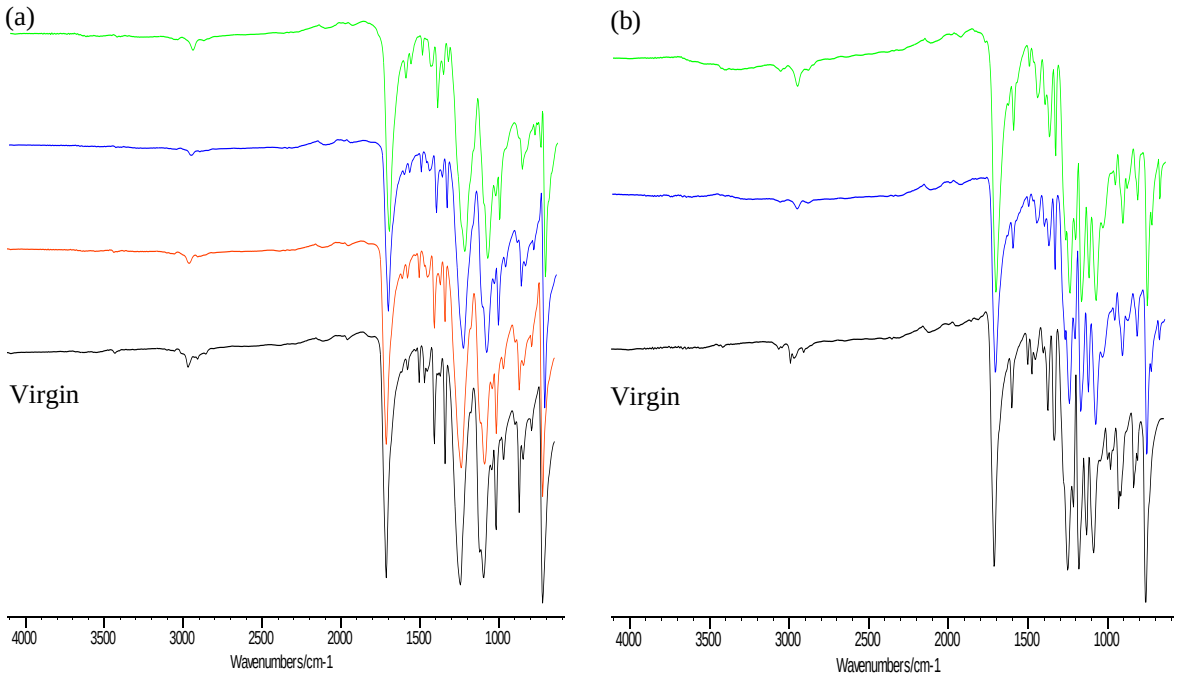

Figure 8.52 ATR spectra for (a) PET and (b) PEN gels aged at 320 ˚C in dry 3% oxygen, dry air and dry 42% oxygen for 4 hours

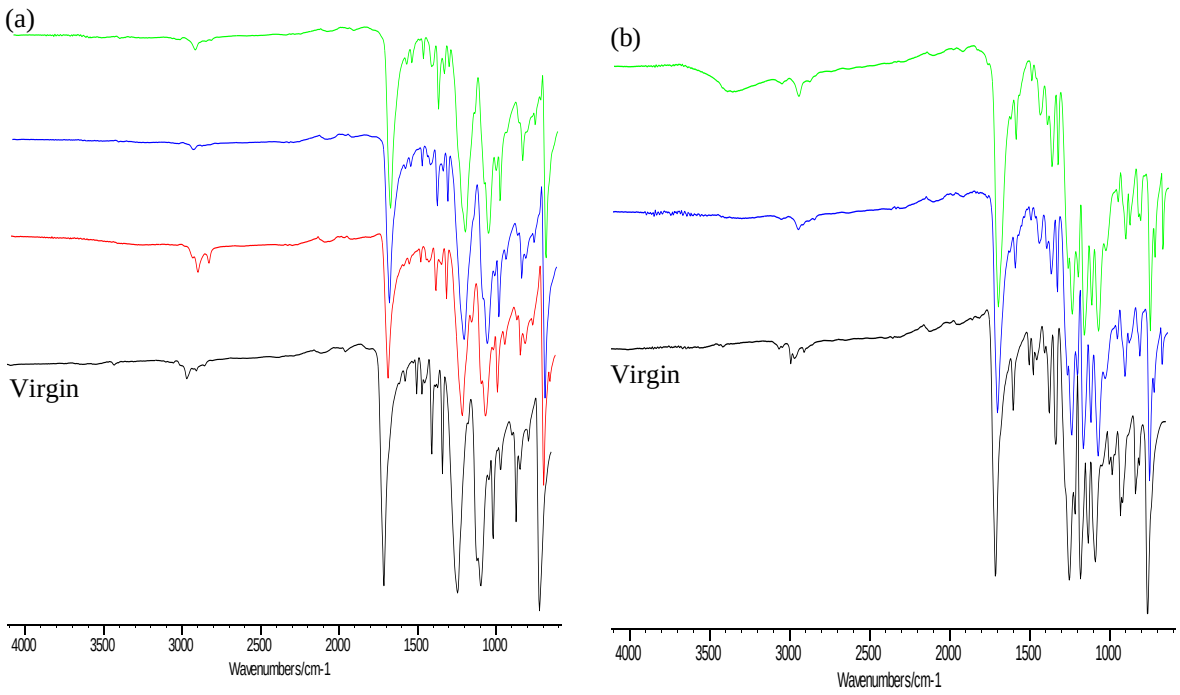

Figure 8.53 ATR spectra for (a) PET and (b) PEN gels aged at 320 °C in wet 3% oxygen, wet air and wet 42% oxygen for 4 hours

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

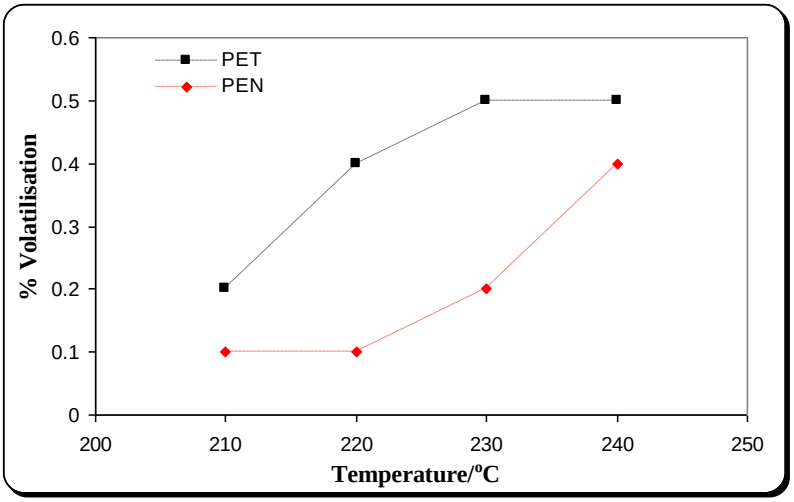

Figure 8.54 Volatilisation results for PET and PEN samples aged at solid-state polymerisation temperatures between 210 °C and 240 °C in dry nitrogen for 4 hours

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

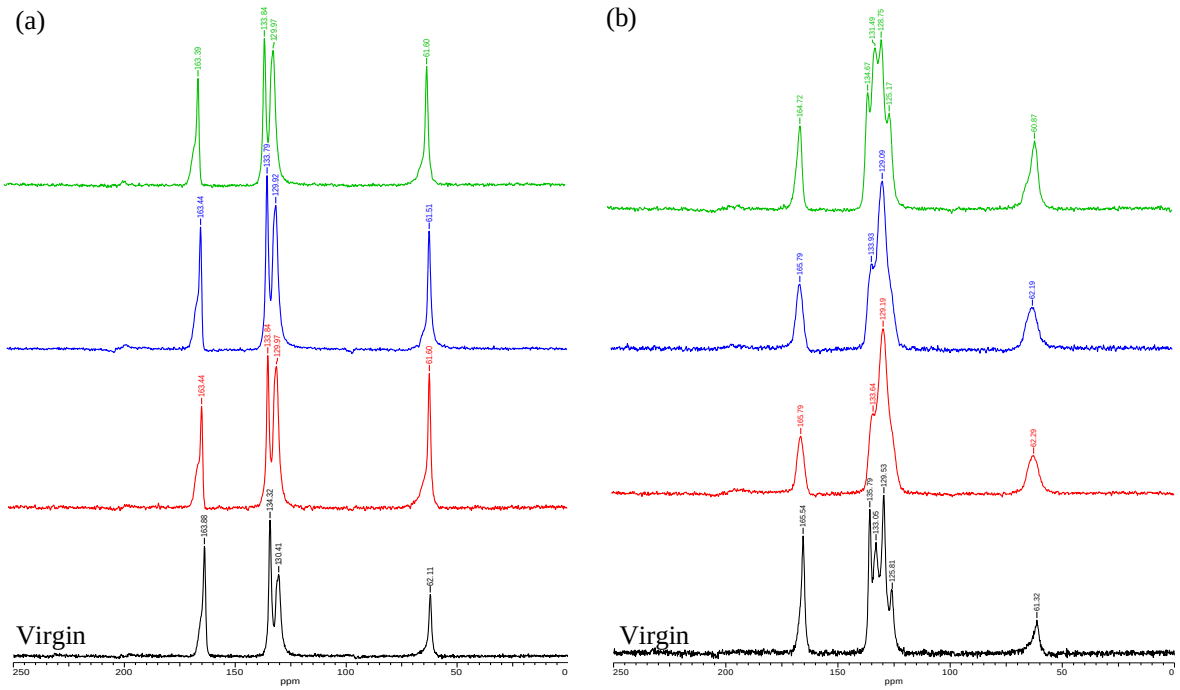

Figure 8.55 ^{13}C solid-state NMR spectra for (a) PET and (b) PEN samples aged in wet (1.5 - 2% AH) nitrogen at 288 °C, 300 °C and 320 °C for 4 hours

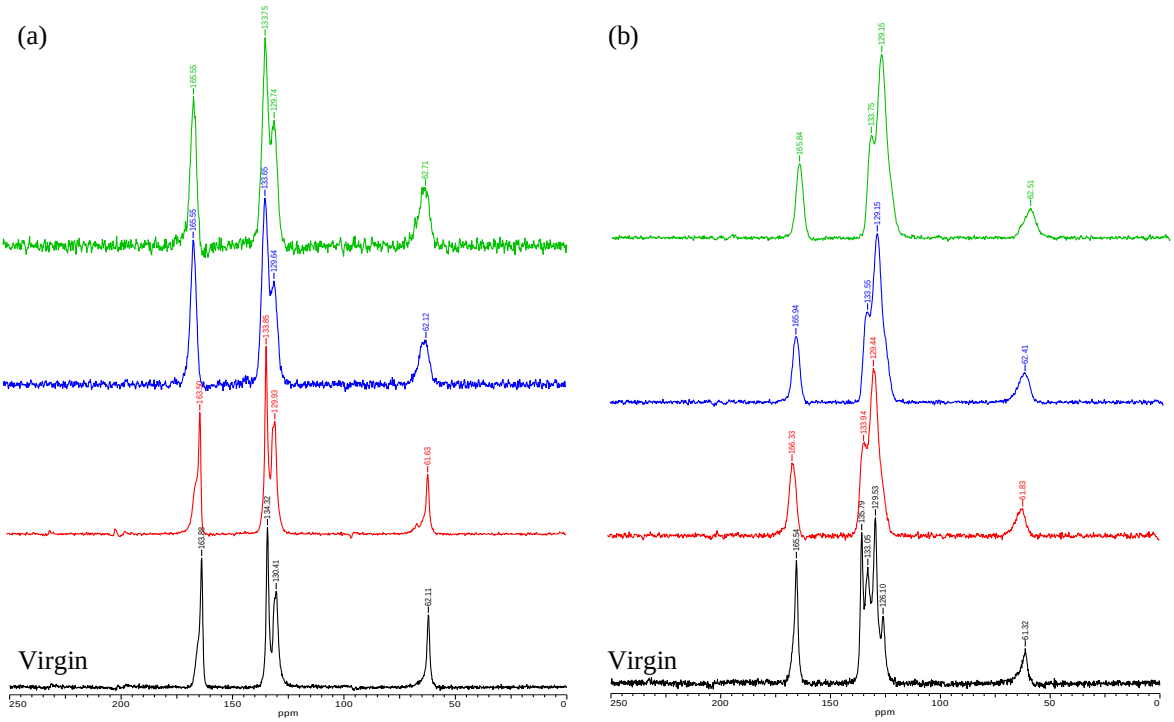

Figure 8.56 ^{13}C solid – state NMR spectra for (a) PET and (b) PEN samples aged in wet (1.5 - 2% AH) air at 288 °C, 300 °C and 320 °C for 4 hours

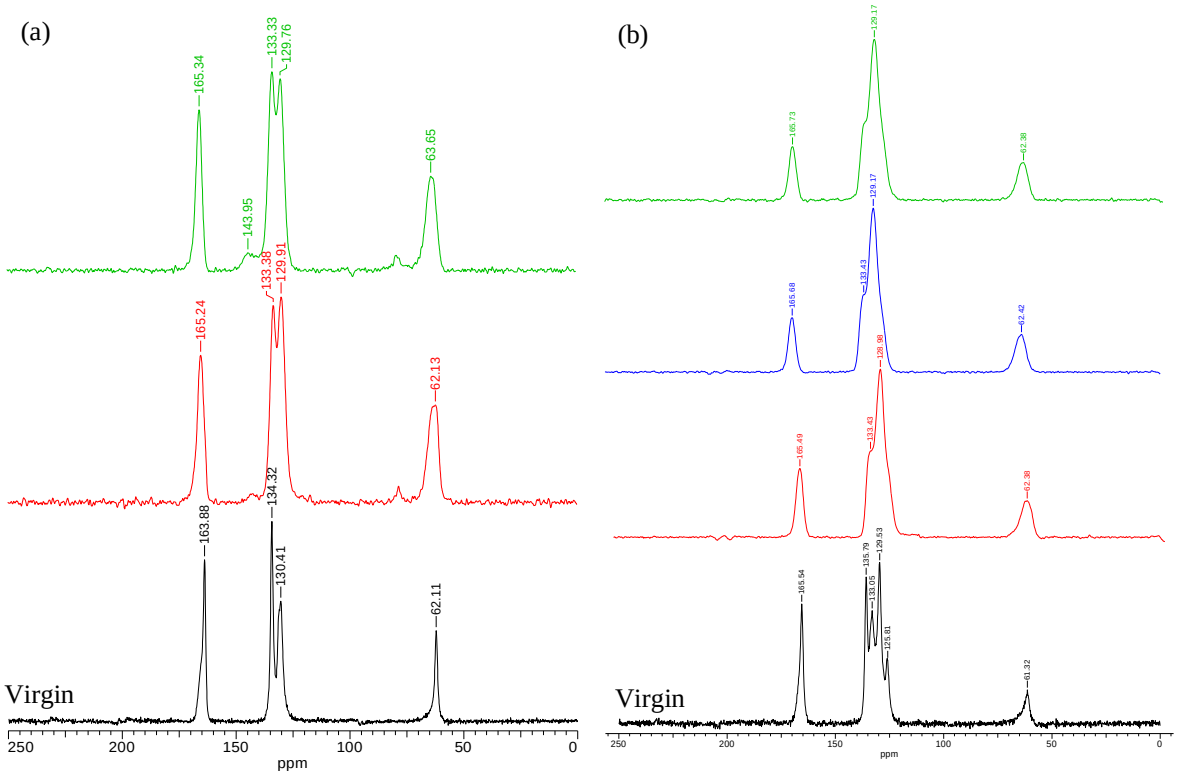

Figure 8.57 ^{13}C solid-state NMR spectra for (a) PET and (b) PEN samples aged in wet (1.5 – 2% AH) 42% oxygen for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

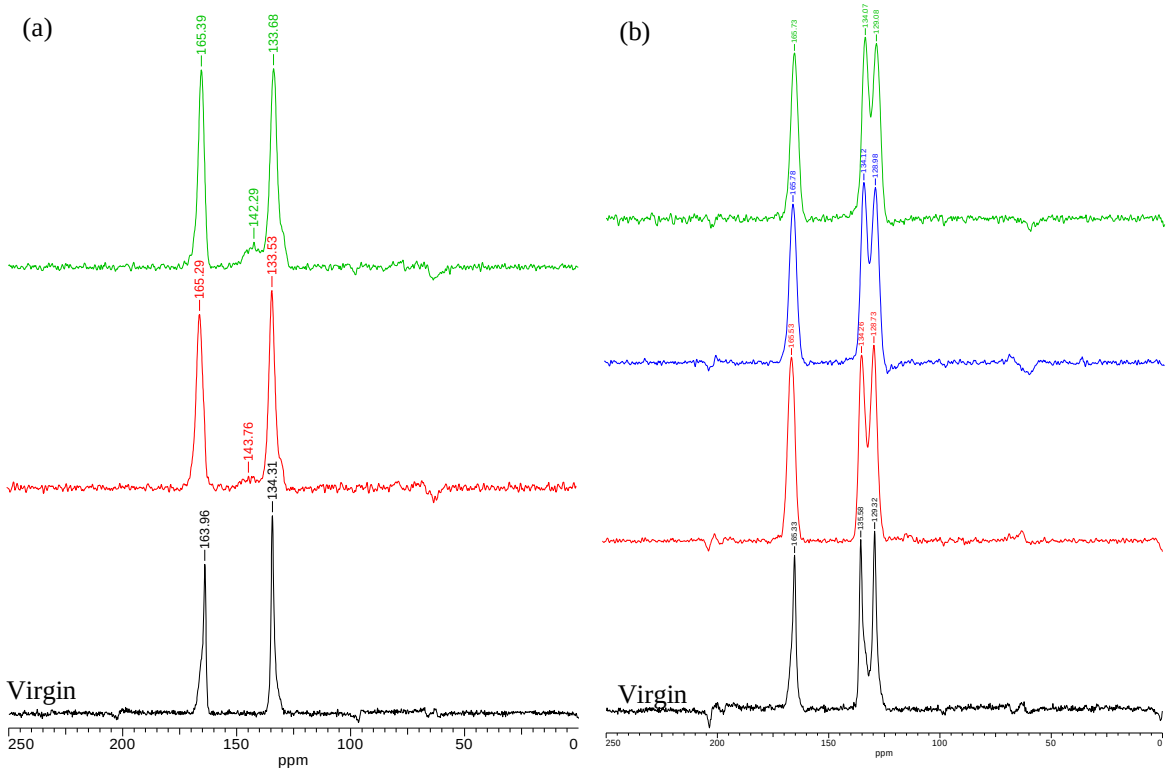

Figure 8.58 Dipolar dephased ^{13}C solid-state NMR spectra for (a) PET and (b) PEN samples aged in wet (1.5 – 2% AH) 42% oxygen for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

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

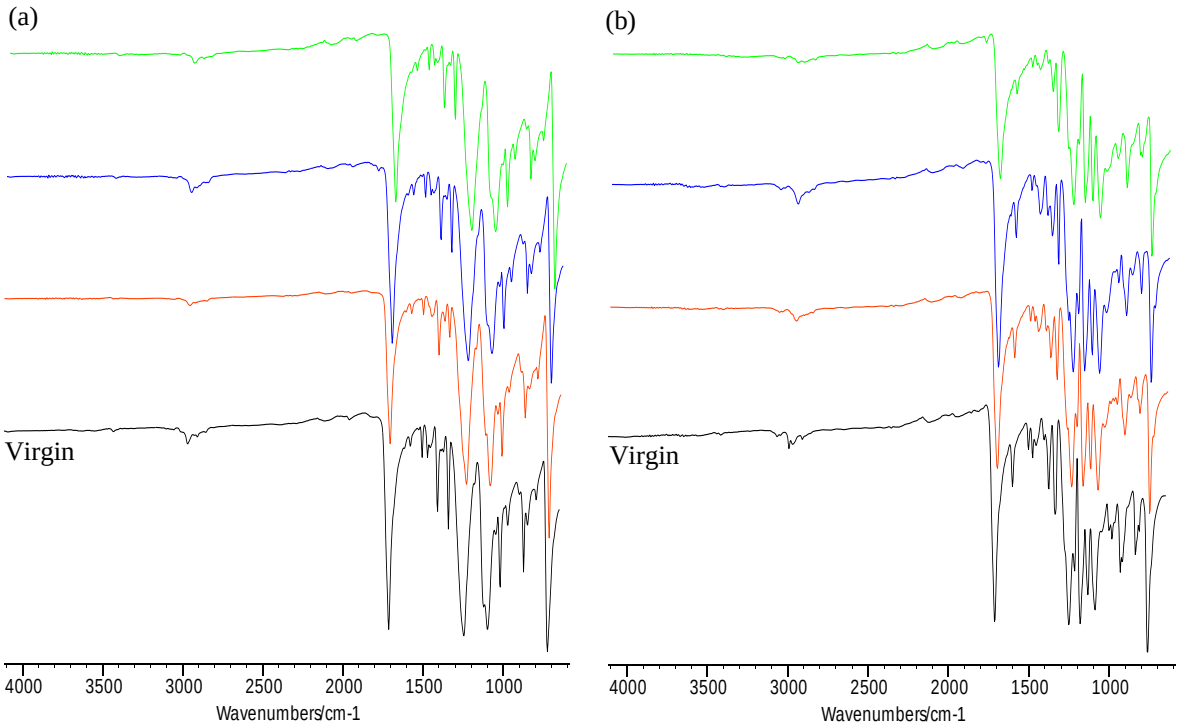

Figure 8.59 ATR spectra for (a) PET and (b) PEN samples aged in dry nitrogen for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

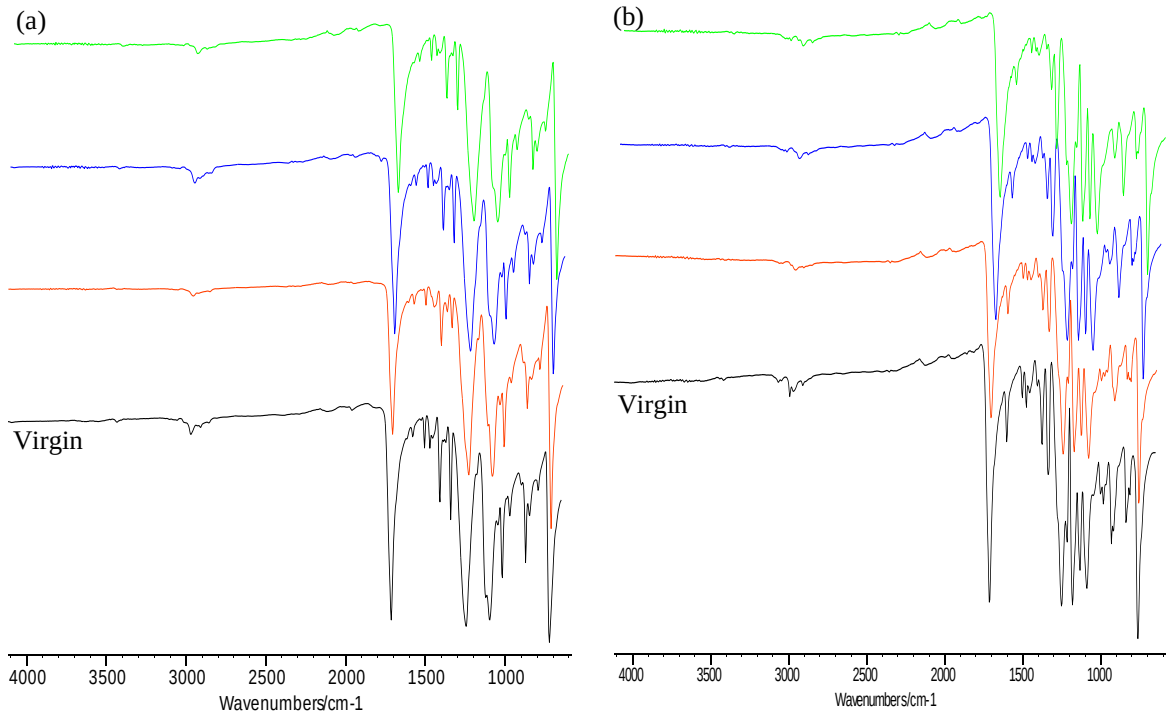

Figure 8.60 ATR spectra for (a) PET and (b) PEN samples aged in wet (1.5 – 2% AH) nitrogen for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

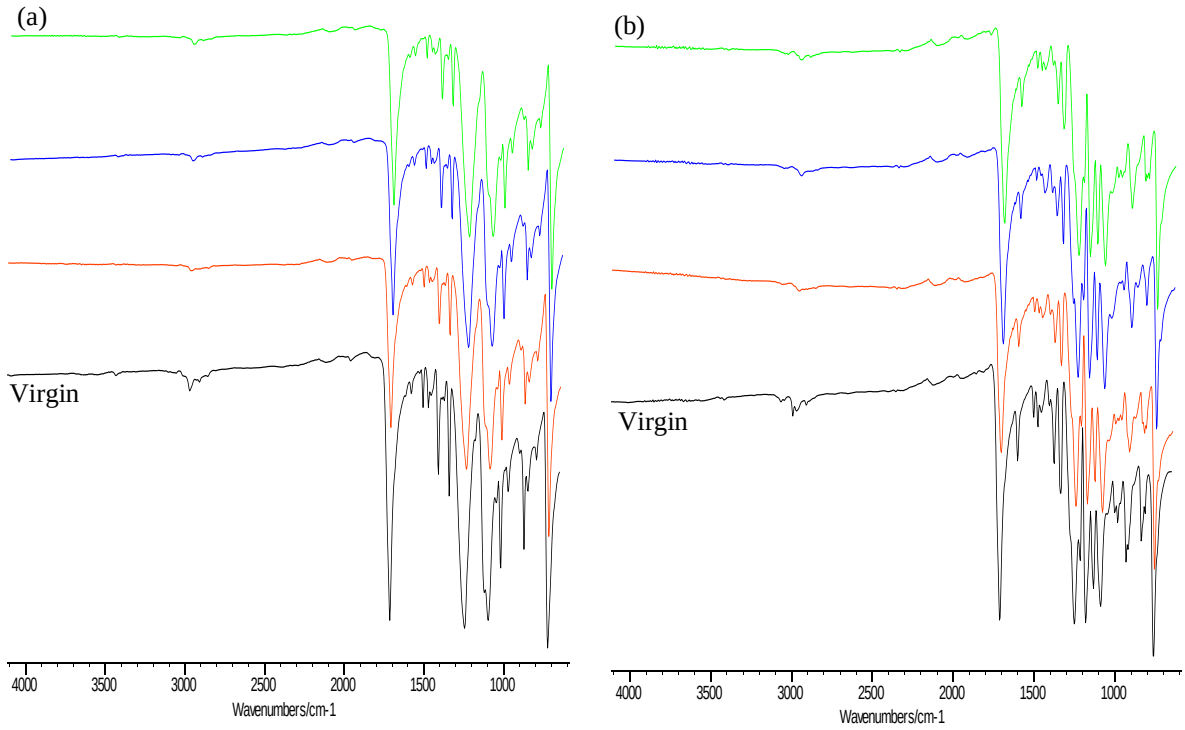

Figure 8.61 ATR spectra for (a) PET and (b) PEN samples aged in dry 3% oxygen for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

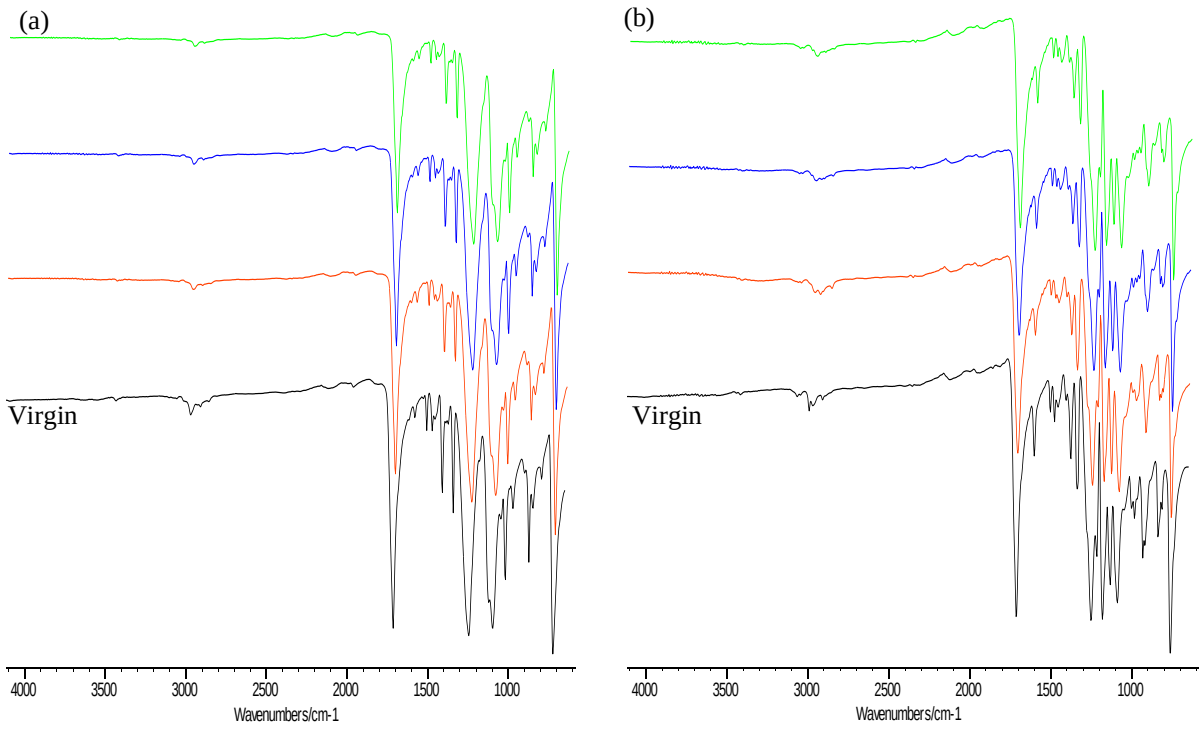

Figure 8.62 ATR spectra for (a) PET and (b) PEN samples aged in wet (1.5 – 2% AH) 3% oxygen for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

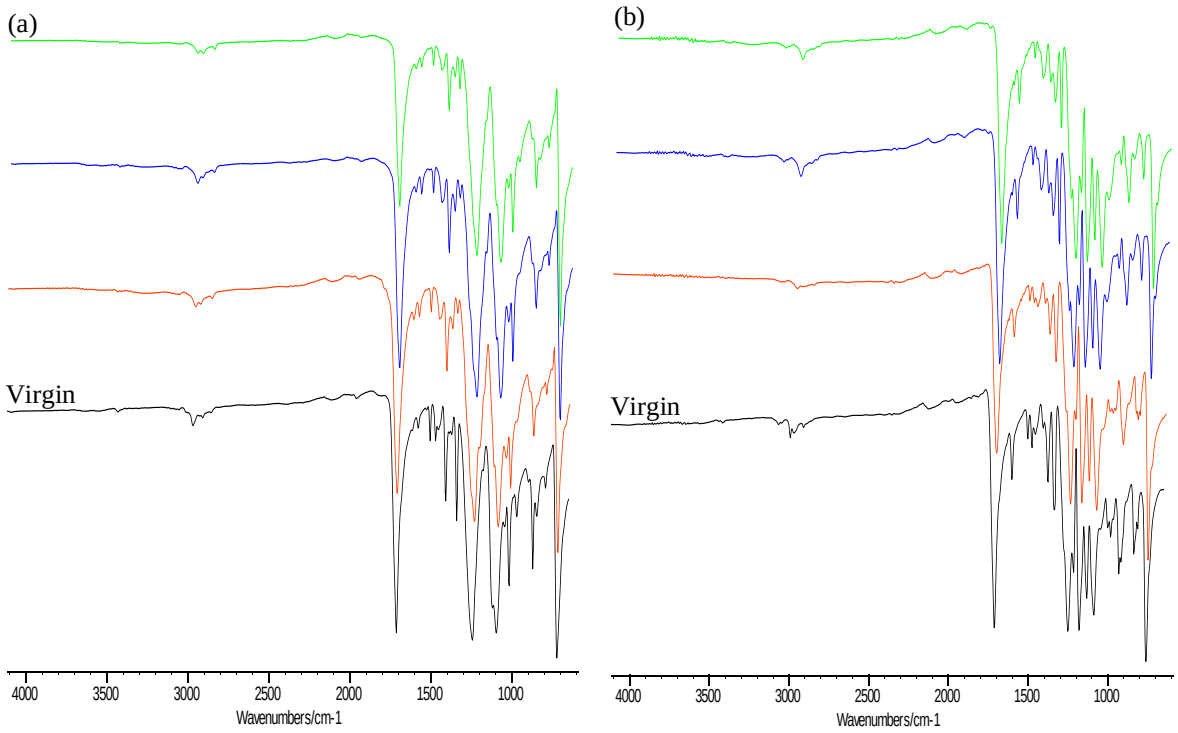

Figure 8.63 ATR spectra for (a) PET and (b) PEN samples aged in dry air for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

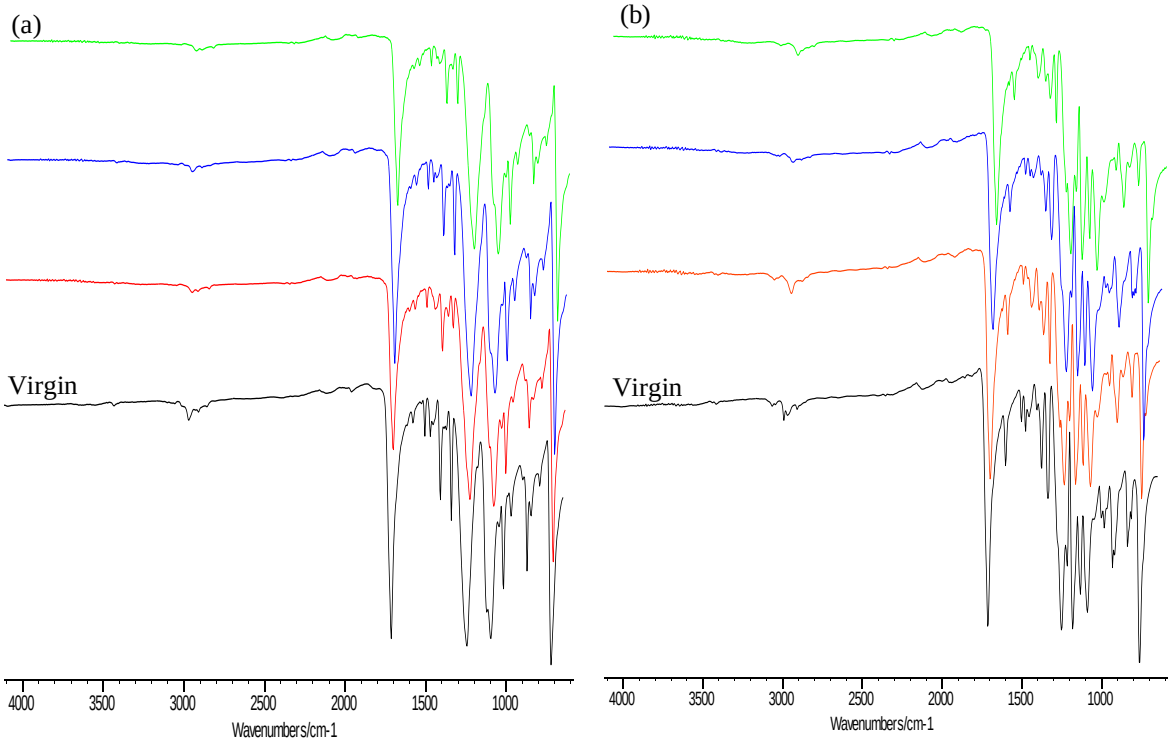

Figure 8.64 ATR spectra for (a) PET and (b) PEN samples aged in wet (1.5 – 2% AH) air for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

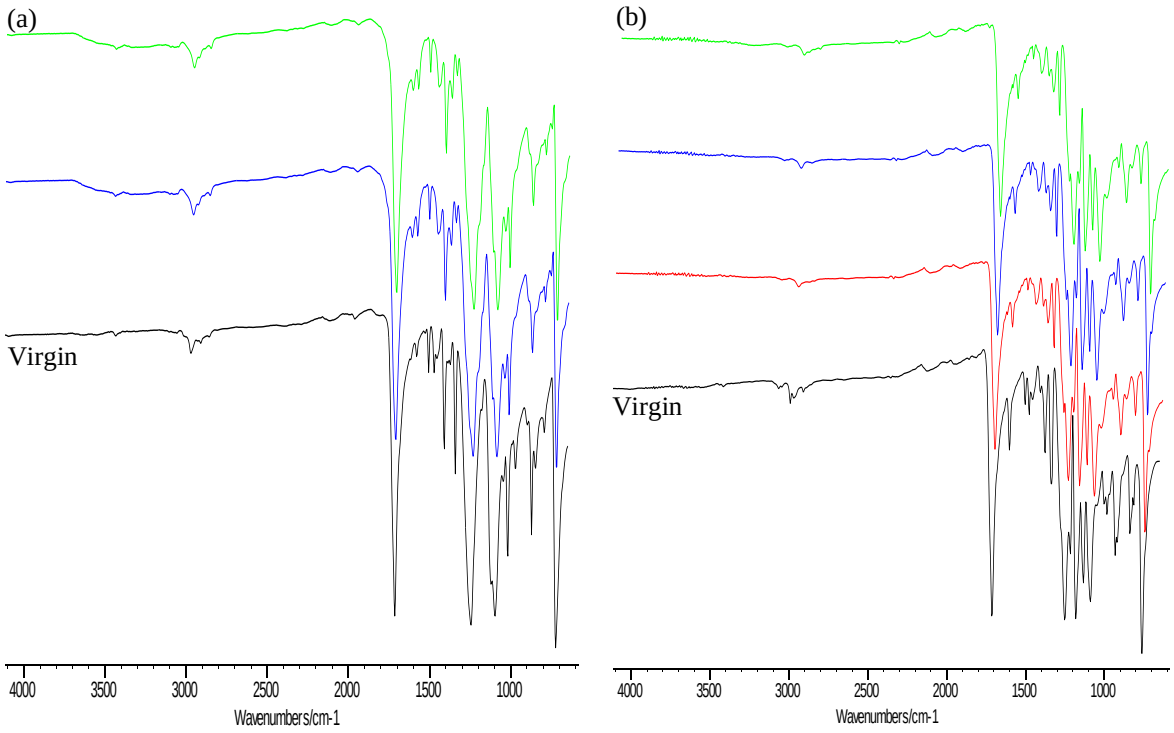

Figure 8.65 ATR spectra for (a) PET and (b) PEN samples aged in dry 42% oxygen for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

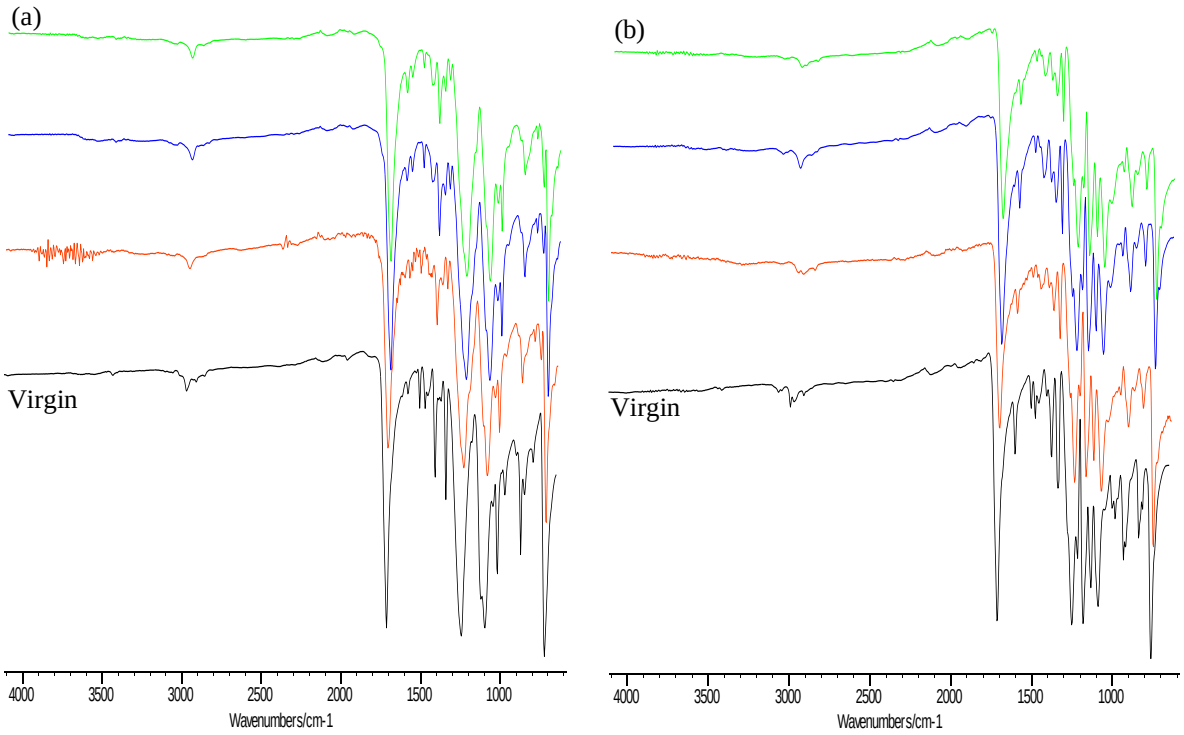

Figure 8.66 ATR spectra for (a) PET and (b) PEN samples aged in wet (1.5 – 2% AH) 42% oxygen for 4 hours at 288 °C, 300 °C and 320 °C for 4 hours

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

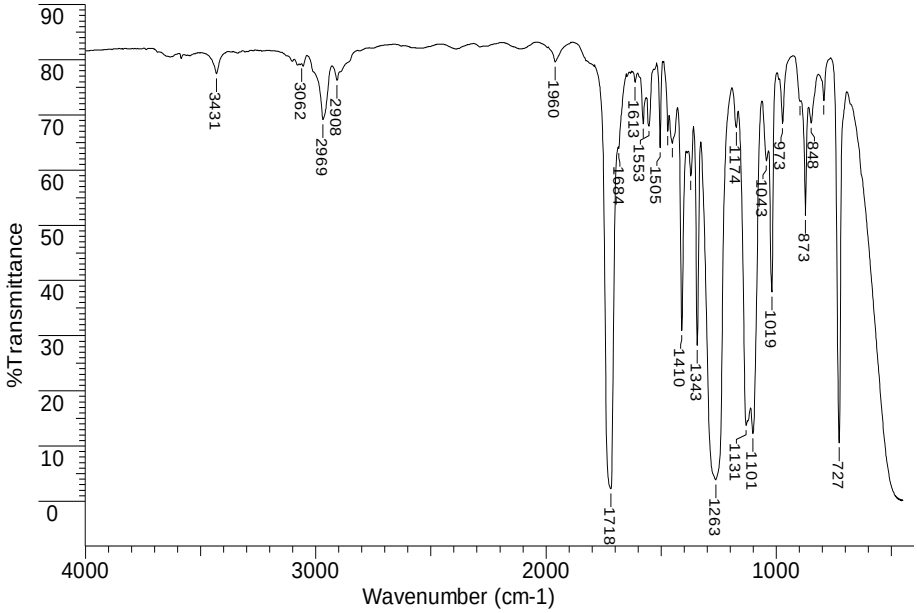

Figure 8.67 IR spectra for solvent cast PET samples aged in dry nitrogen for 4 hours at 288 °C for 4 hours

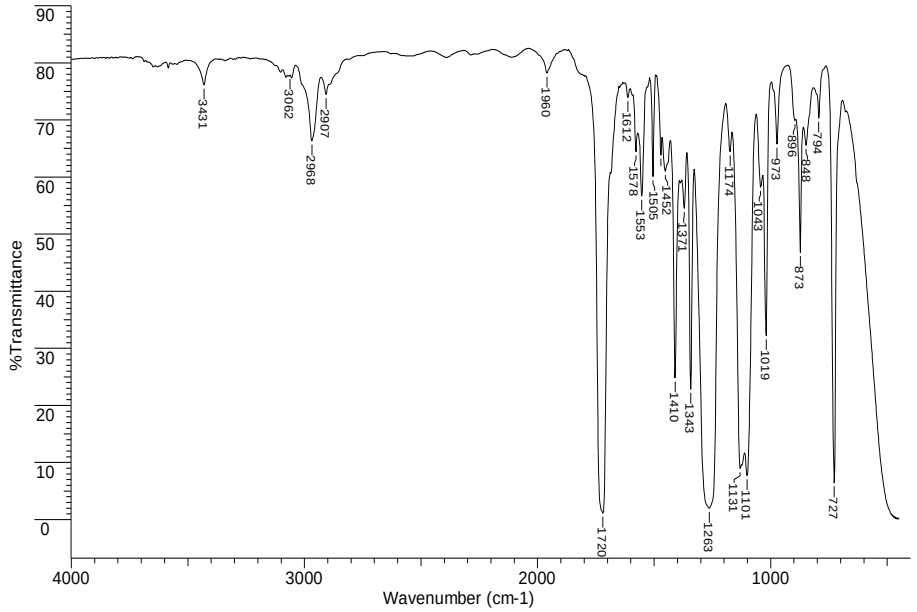

Figure 8.68 IR spectra for solvent cast PET samples aged in dry nitrogen for 4 hours at 300 °C for 4 hours

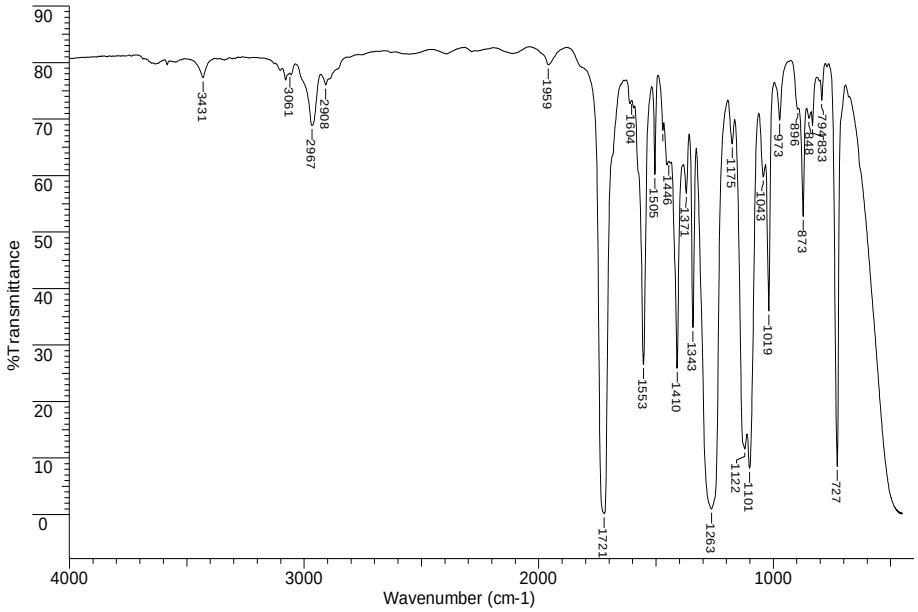

Figure 8.69 IR spectra for solvent cast PET samples aged in dry nitrogen for 4 hours at 320 °C for 4 hours

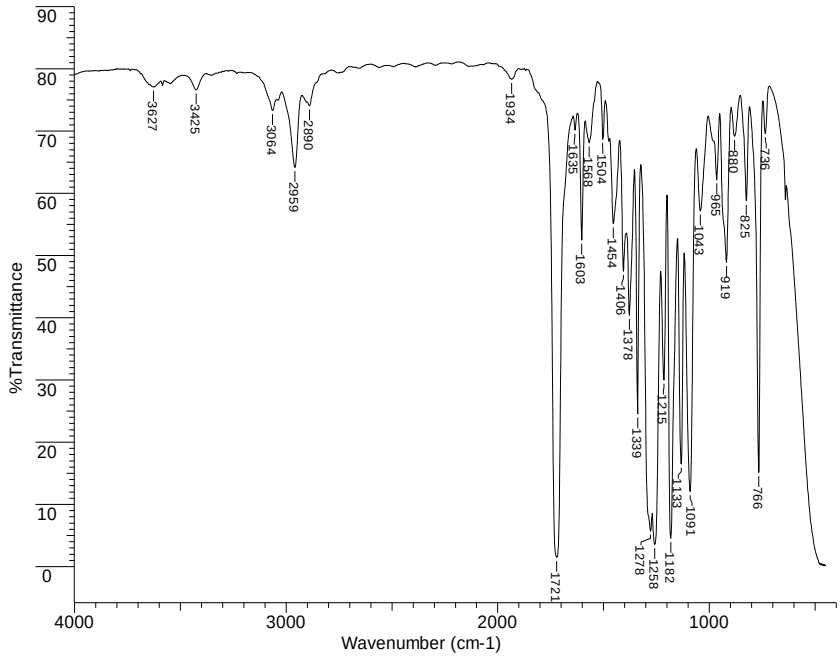

Figure 8.70 IR spectra for solvent cast PEN samples aged in dry nitrogen for 4 hours at 288 °C for 4 hours

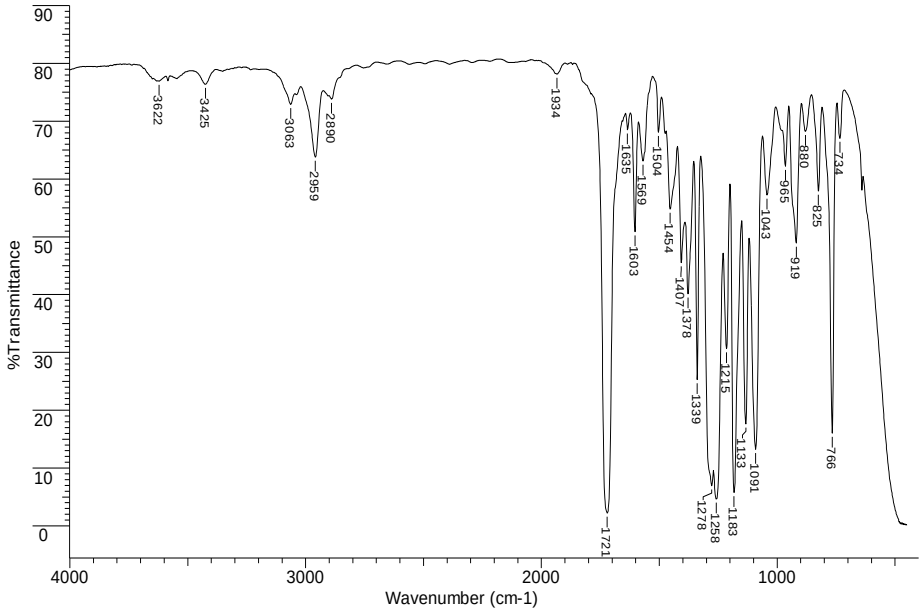

Figure 8.71 IR spectra for solvent cast PEN samples aged in dry nitrogen for 4 hours at 300 °C for 4 hours

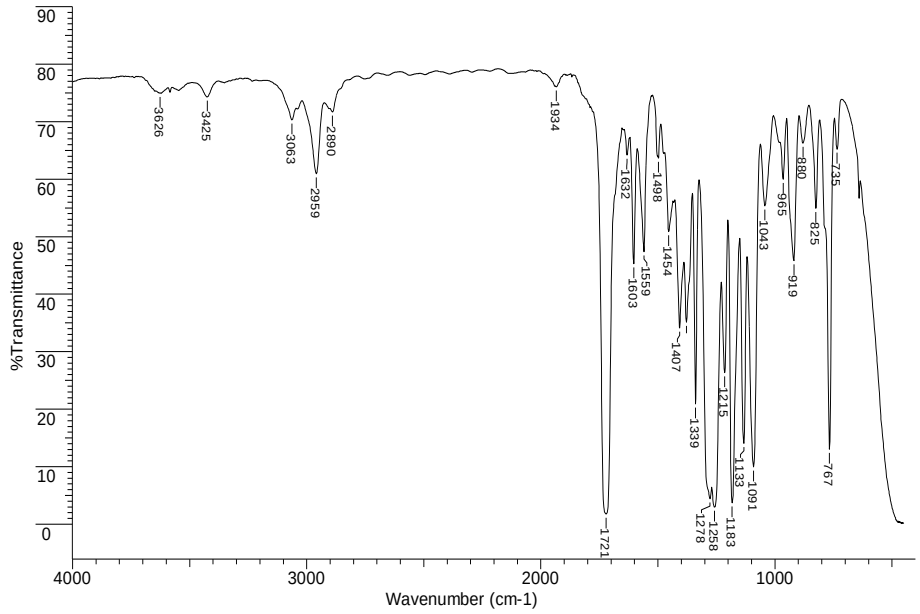

Figure 8.72 IR spectra for solvent cast PEN samples aged in dry nitrogen for 4 hours at 320 °C for 4 hours

8.2.7.2 Residual Samples Aged Under Thermal-Hydrolytic Conditions

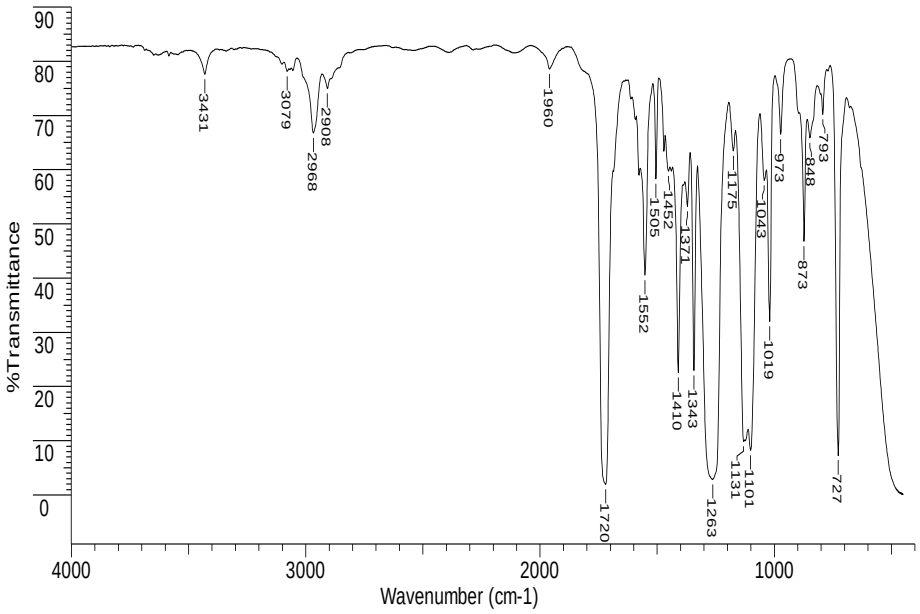

Figure 8.73 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) nitrogen for 4 hours at 288 °C for 4 hours

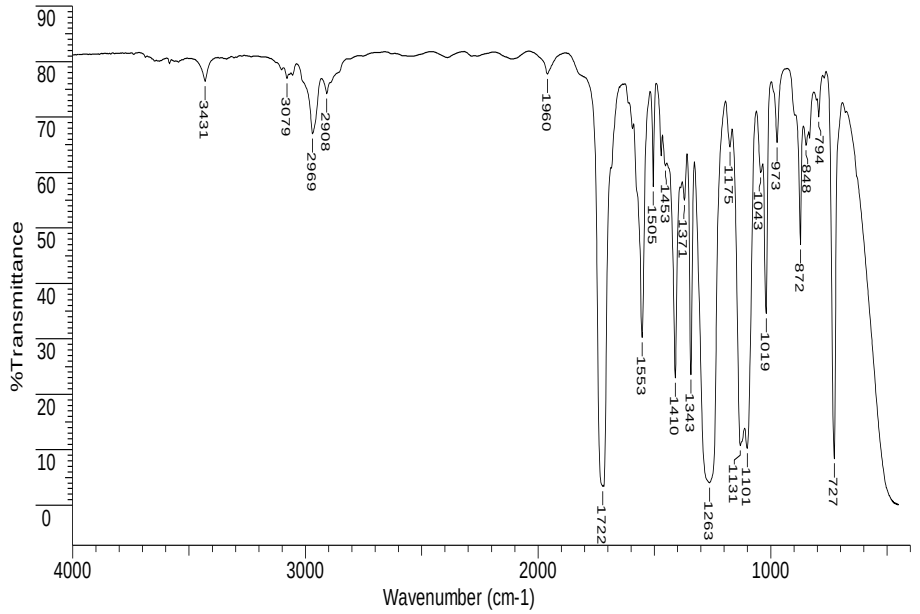

Figure 8.74 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) nitrogen for 4 hours at 300 °C for 4 hours

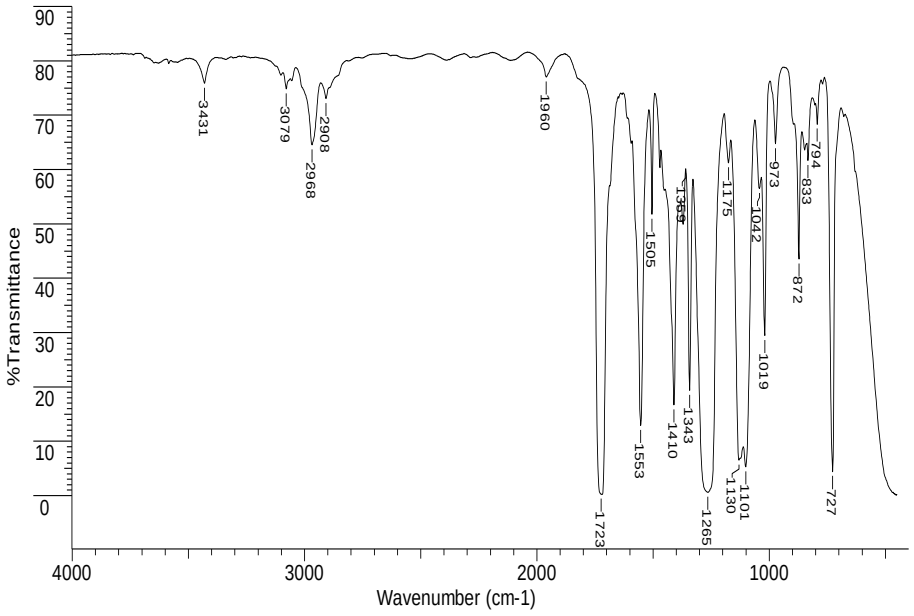

Figure 8.75 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) nitrogen for 4 hours at 320 °C for 4 hours

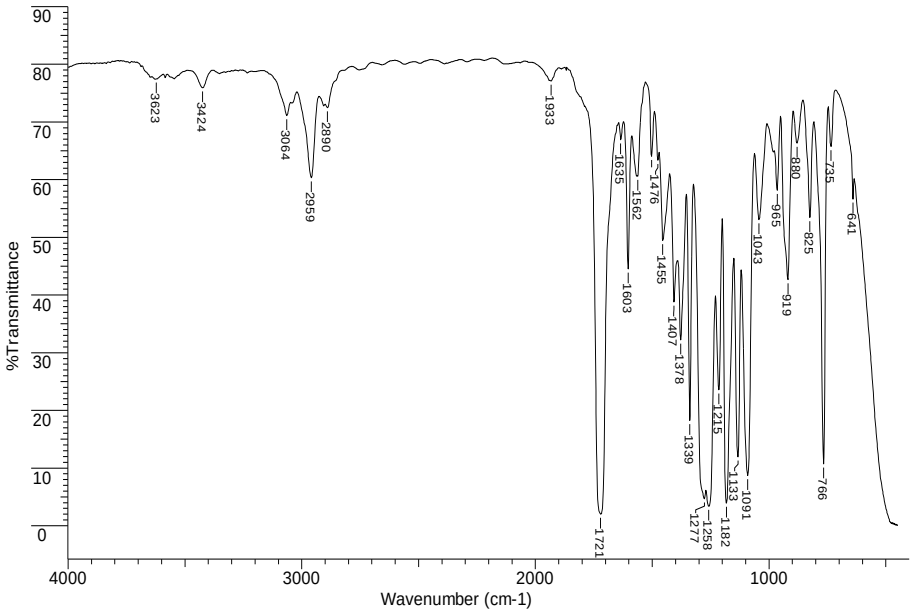

Figure 8.76 IR spectra for solvent cast PEN samples aged in wet (1.5 – 2% AH) nitrogen for 4 hours at 288 °C for 4 hours

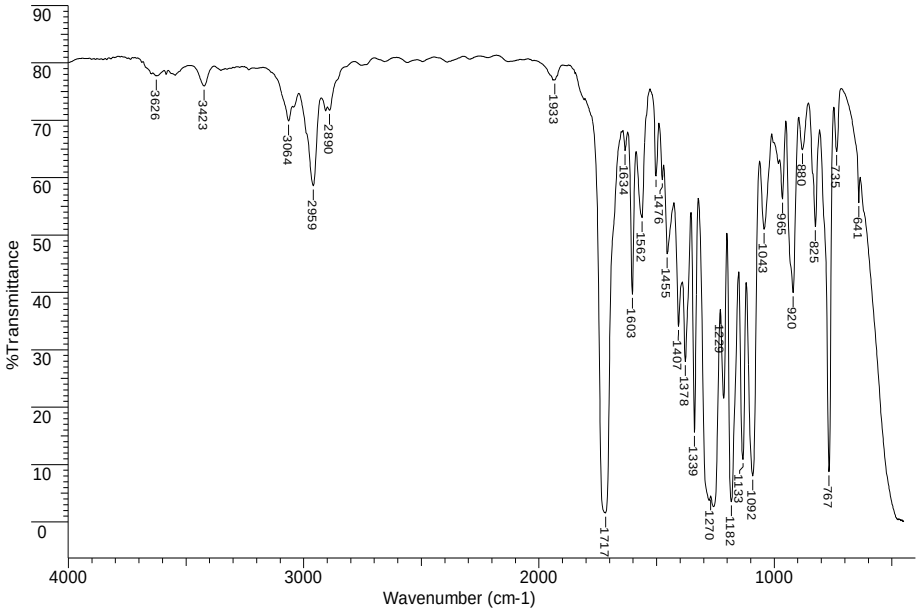

Figure 8.77 IR spectra for solvent cast PEN samples aged in wet (1.5 – 2% AH) nitrogen for 4 hours at 300 °C for 4 hours

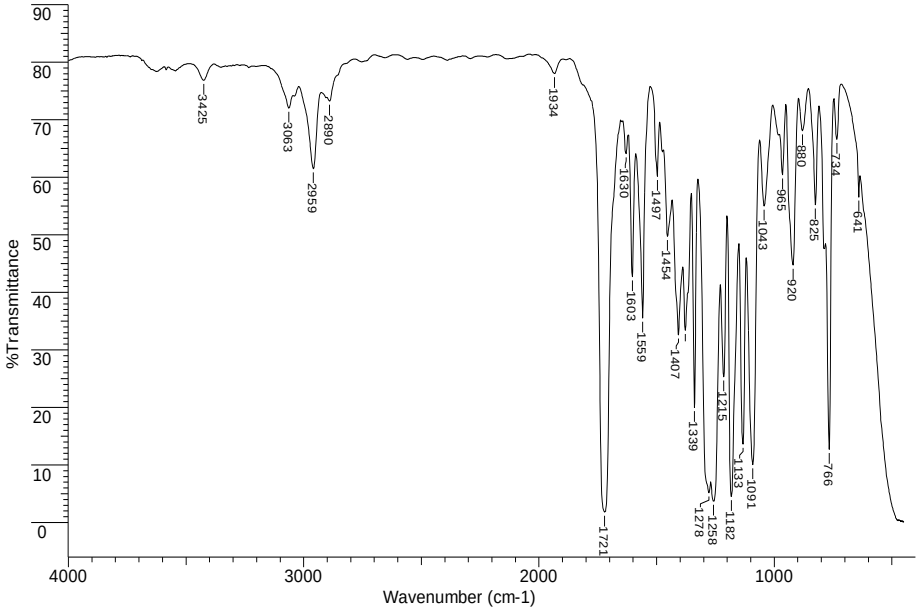

Figure 8.78 IR spectra for solvent cast PEN samples aged in wet (1.5 – 2% AH) nitrogen for 4 hours at 320 °C for 4 hours

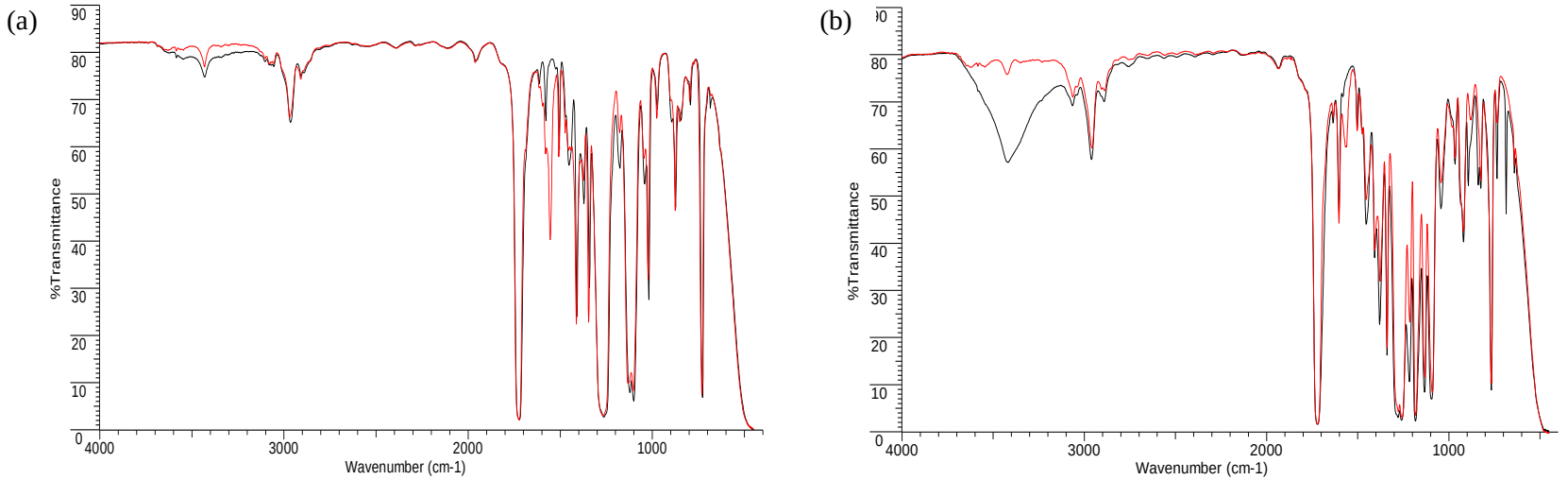

Figure 8.79 IR spectra of solvent cast (a) PET and (b) PEN film before and after ageing at 288 °C in wet (1.5 – 2% AH) nitrogen for 4 hours

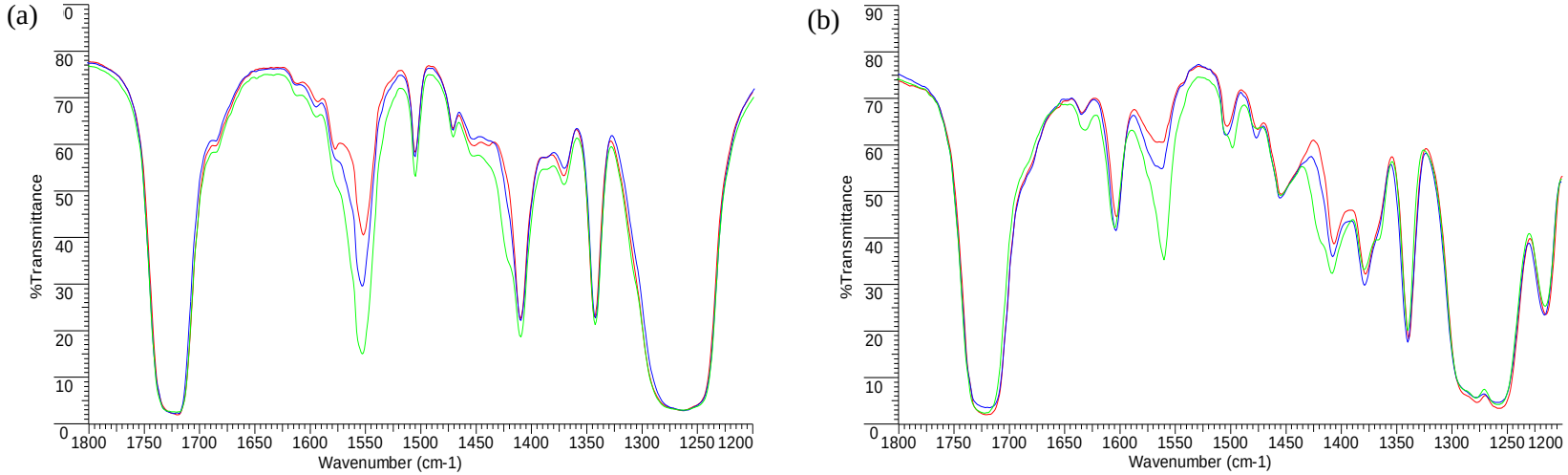

Figure 8.80 IR spectra for solvent cast (a) PET and (b) PEN samples aged in wet (1.5 – 2% AH) nitrogen at 288 °C, 300 °C and 320 °C for 4 hours

8.2.7.3 Residual Samples Aged Under Thermo-Oxidative Conditions

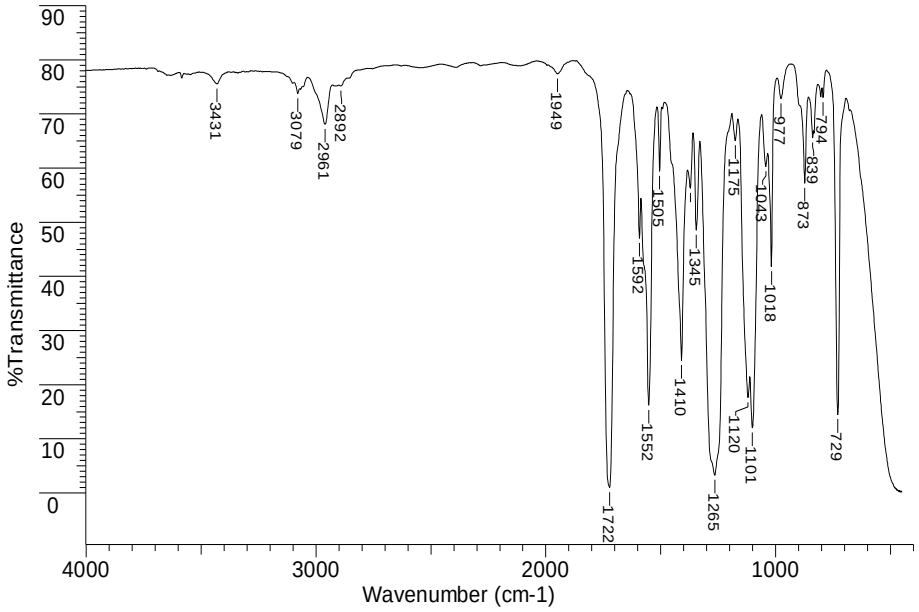

Figure 8.81 IR spectra for solvent cast PET samples aged in dry air for 4 hours at 288 °C for 4 hours

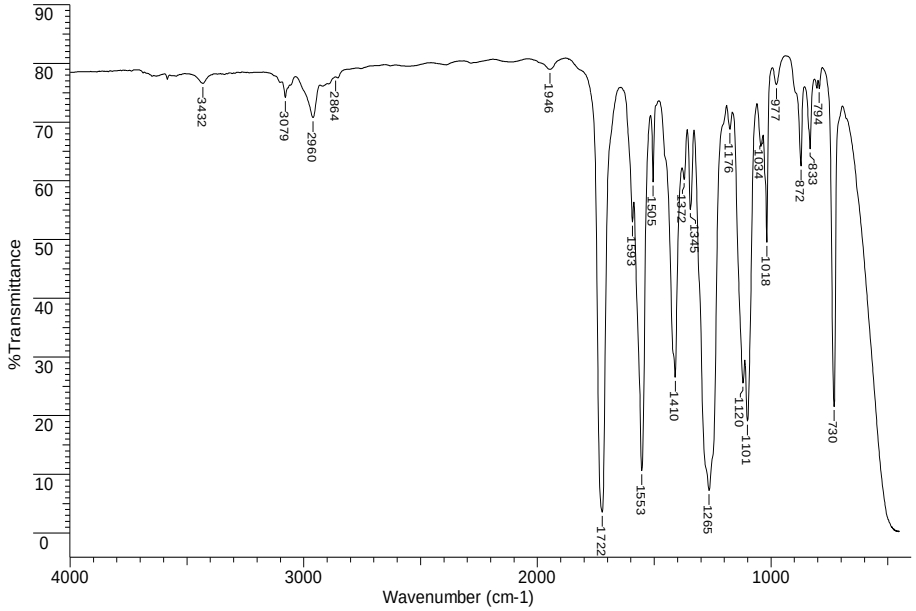

Figure 8.82 IR spectra for solvent cast PET samples aged in dry air for 4 hours at 300 °C for 4 hours

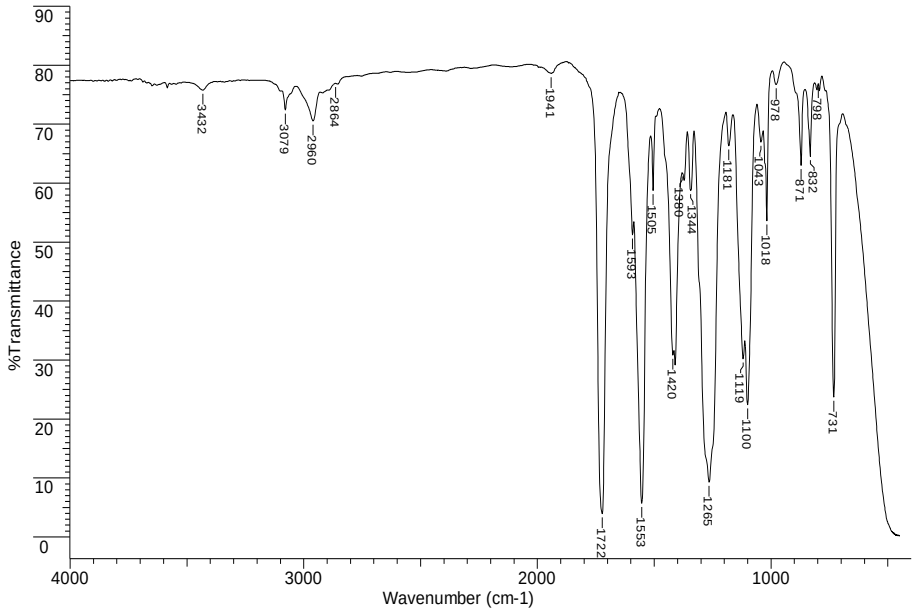

Figure 8.83 IR spectra for solvent cast PET samples aged in dry air for 4 hours at 320 °C for 4 hours

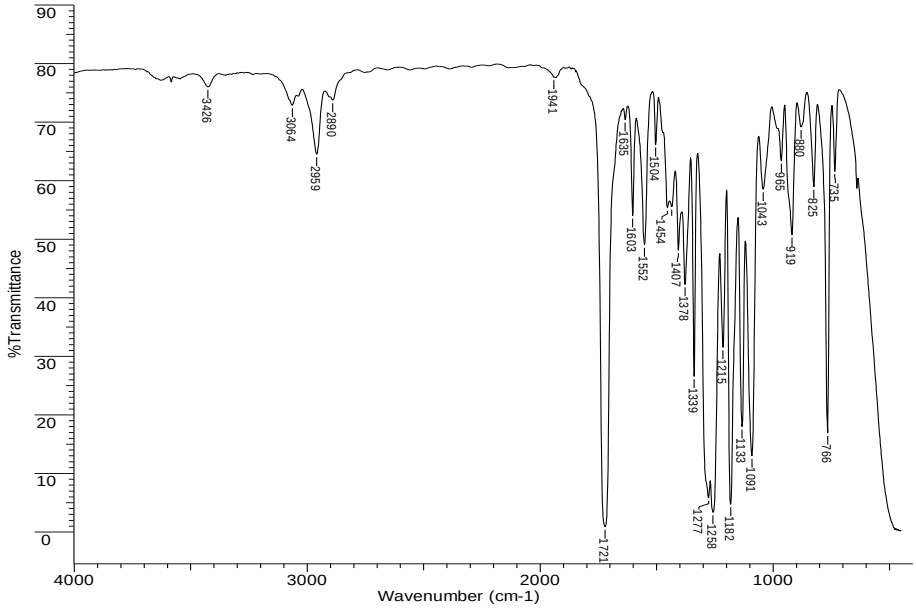

Figure 8.84 IR spectra for solvent cast PEN samples aged in dry air for 4 hours at 288 °C for 4 hours

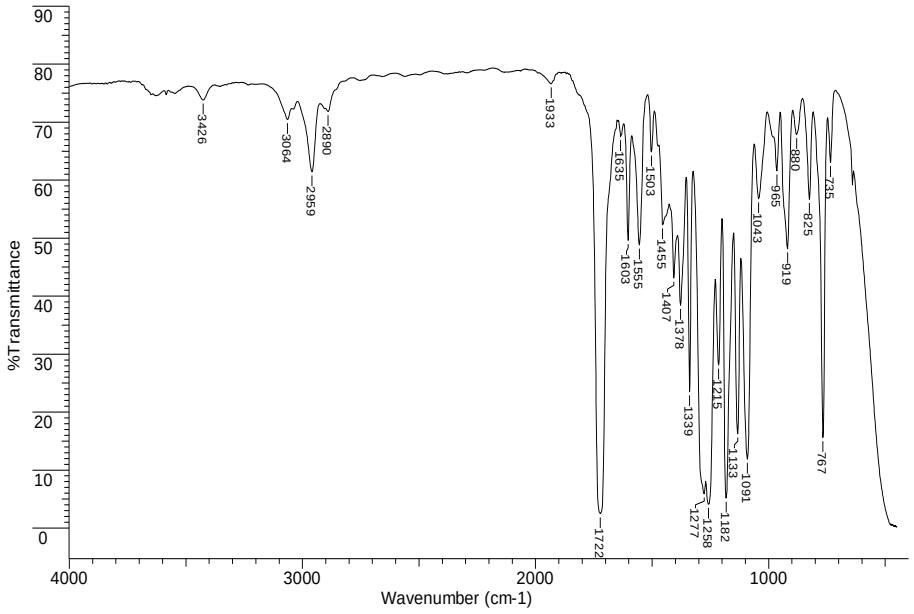

Figure 8.85 IR spectra for solvent cast PEN samples aged in dry air for 4 hours at 300 °C for 4 hours

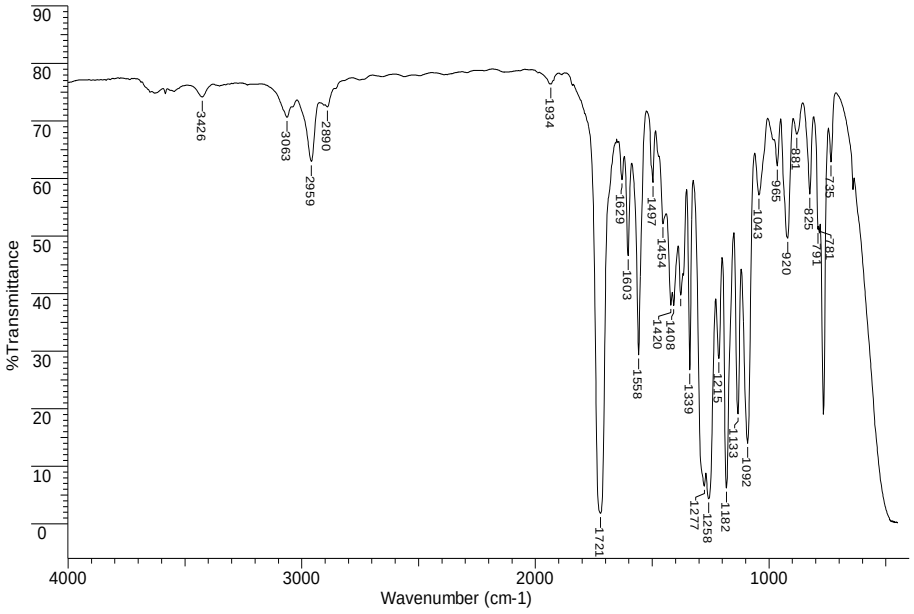

Figure 8.86 IR spectra for solvent cast PEN samples aged in dry air for 4 hours at 320 °C for 4 hours

8.2.7.4 Residual Samples Aged Under Thermo-Oxidative-Hydrolytic

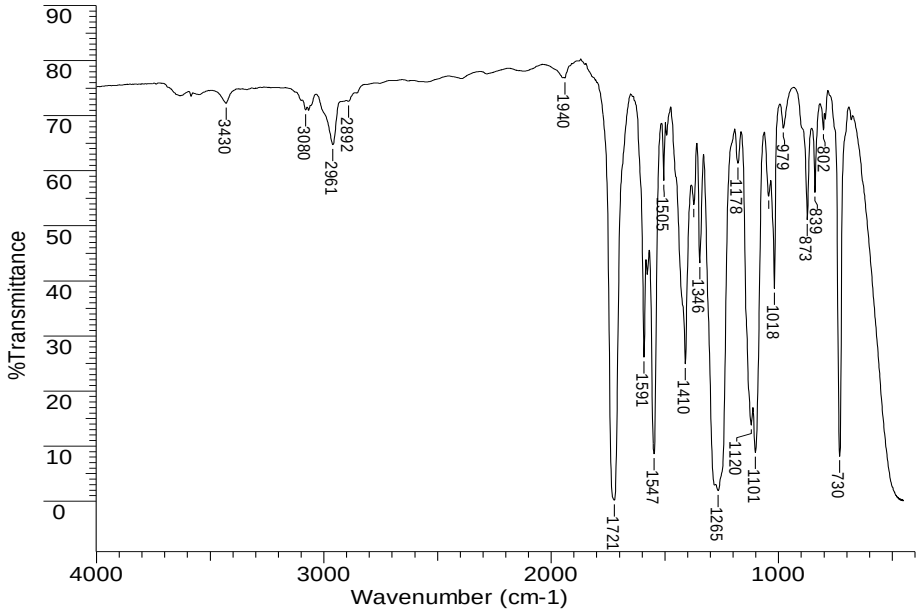

Figure 8.87 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) air for 4 hours at 288 °C for 4 hours

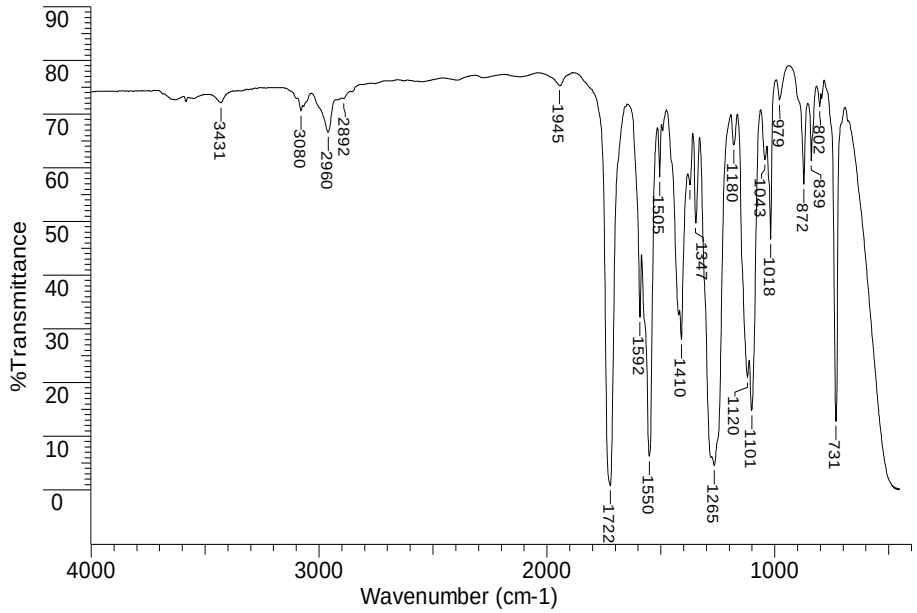

Figure 8.88 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) air for 4 hours at 300 °C for 4 hours

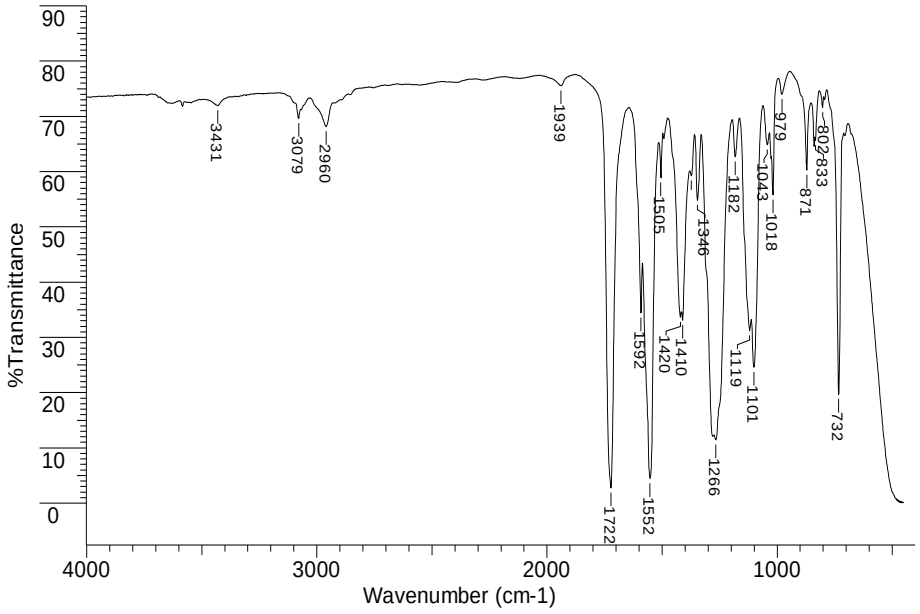

Figure 8.89 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) air for 4 hours at 320 °C for 4 hours

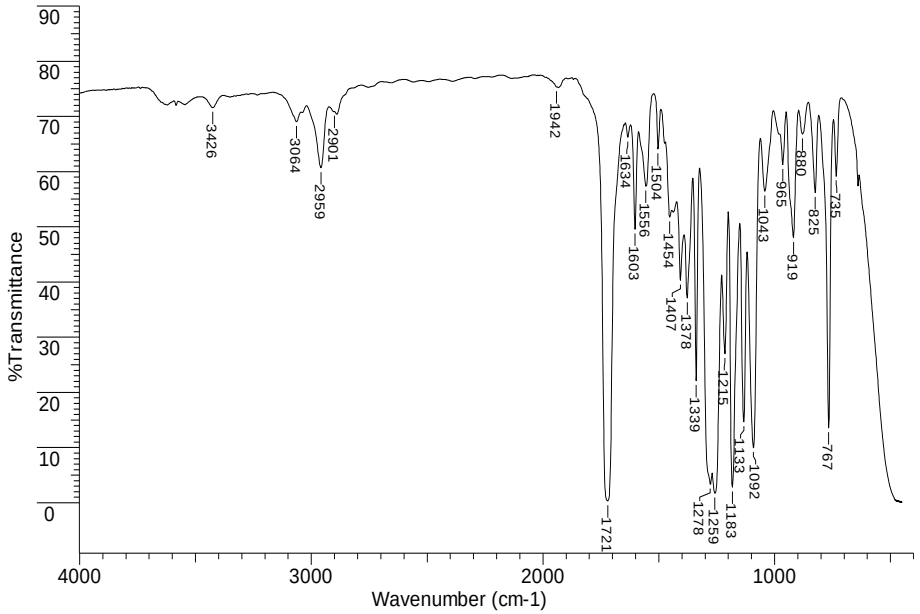

Figure 8.90 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) air for 4 hours at 288 °C for 4 hours

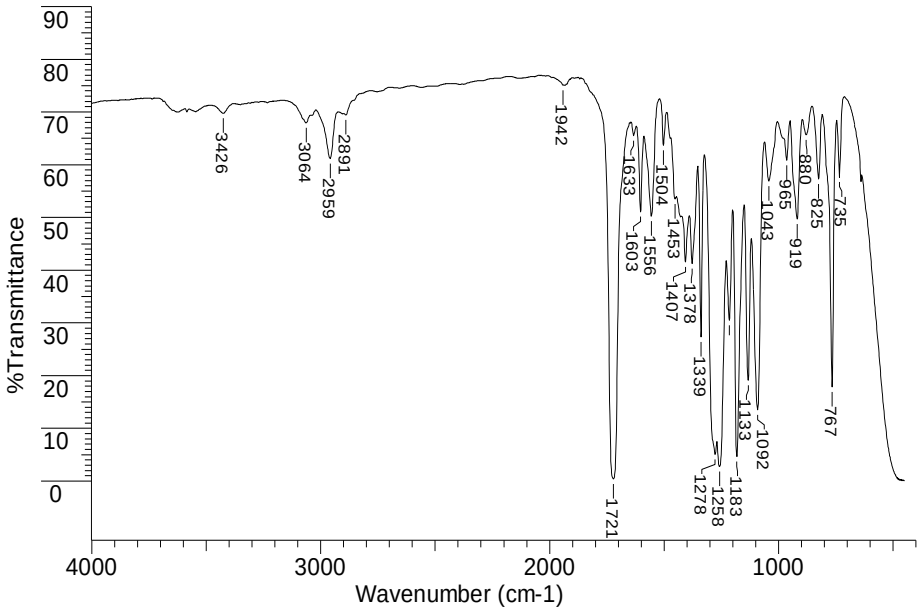

Figure 8.91 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) air for 4 hours at 300 °C for 4 hours

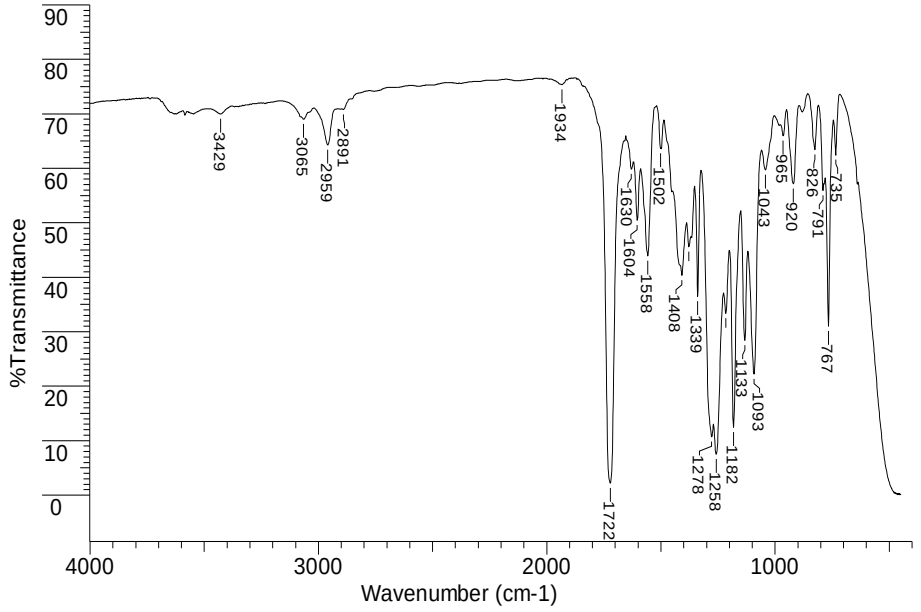

Figure 8.92 IR spectra for solvent cast PET samples aged in wet (1.5 – 2% AH) air for 4 hours at 320 °C for 4 hours

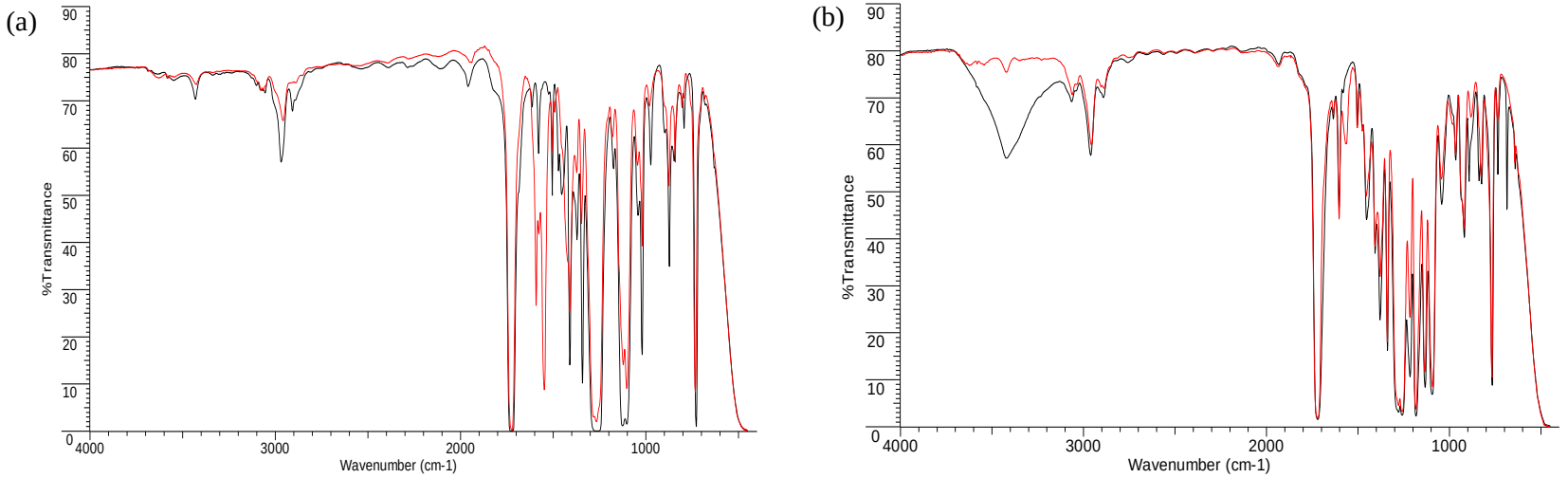

Figure 8.93 IR spectra of solvent cast (a) PET and (b) PEN film before and after ageing at 288 °C in wet (1.5 – 2% AH) air for 4 hours

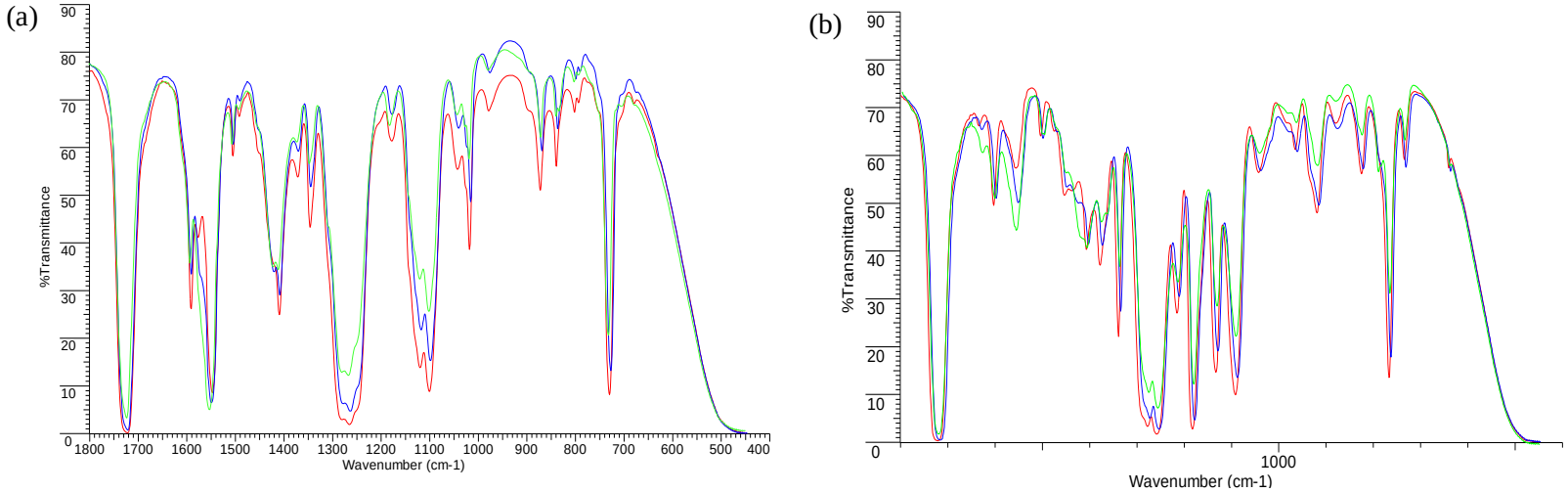

Figure 8.94 IR spectra for solvent cast (a) PET and (b) PEN samples aged in wet (1.5 – 2% AH) air at 288 °C, 300 °C and 320 °C for 4 hours

8.2.8 High Temperature Degradation Studies of PET and PEN

8.2.8.1 Volatilisation Studies

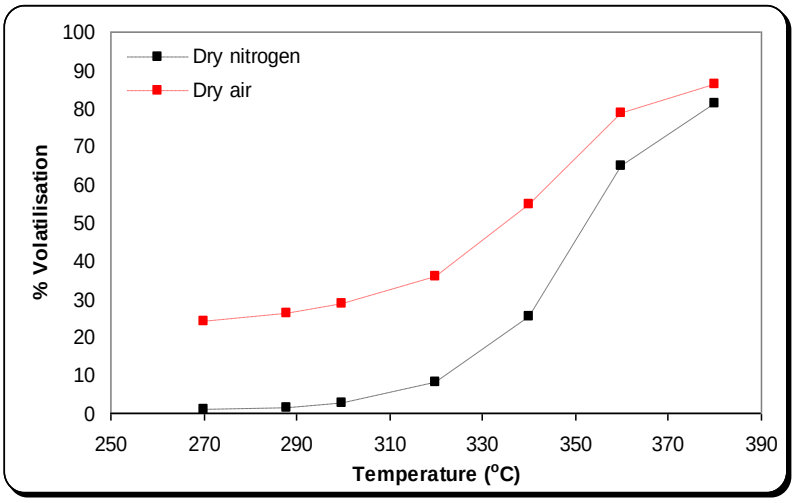

Figure 8.95 Volatilisation results for PET samples aged in dry nitrogen and dry air for 4 hours at temperatures between 270 °C and 380 °C

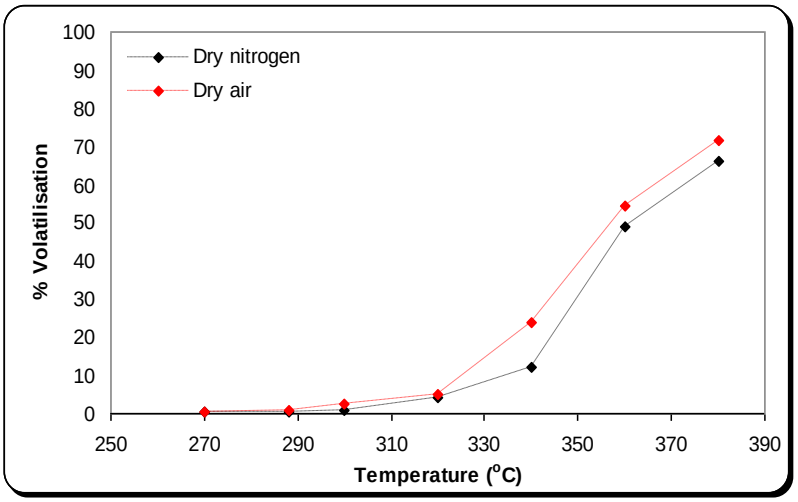

Figure 8.96 Volatilisation results for PEN samples aged in dry nitrogen and dry air for 4 hours at temperatures between 270 °C and 380 °C

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

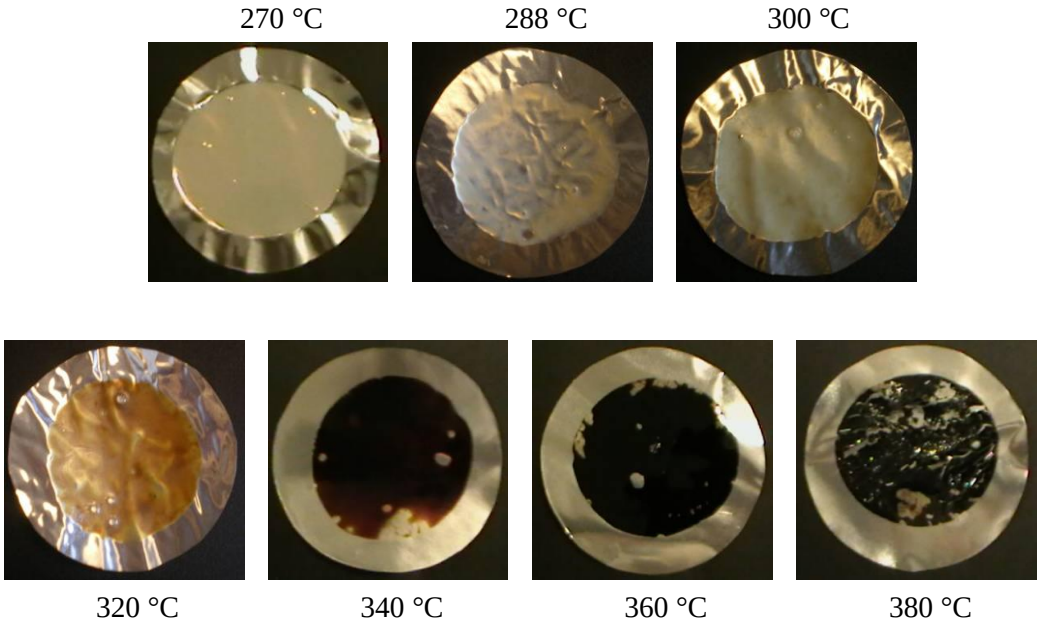

Figure 8.97 Residual film samples from PET aged in dry nitrogen for 4 hours at temperatures between 270 °C and 380 °C

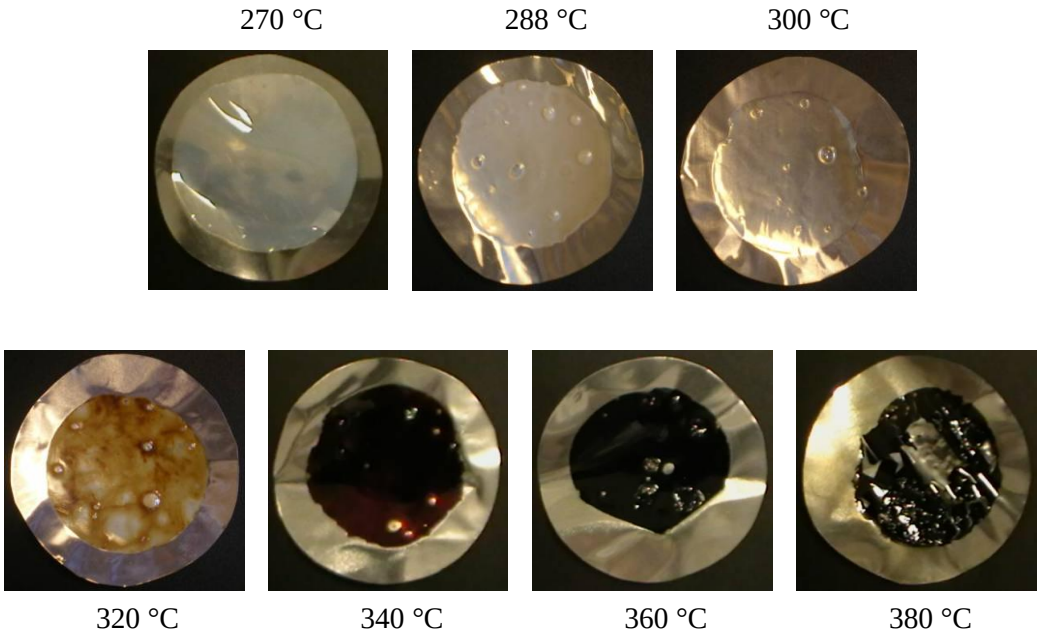

Figure 8.98 Residual film samples from PEN aged in dry nitrogen for 4 hours at temperatures between 270 °C and 380 °C

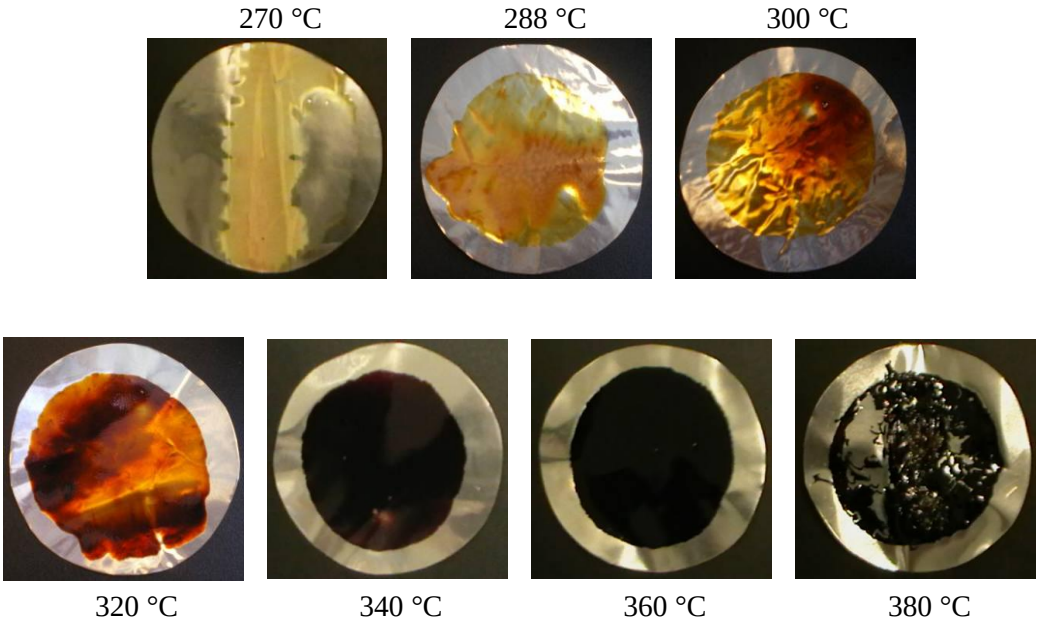

Figure 8.99 Residual film samples from PET aged in dry air for 4 hours at temperatures between 270 °C and 380 °C

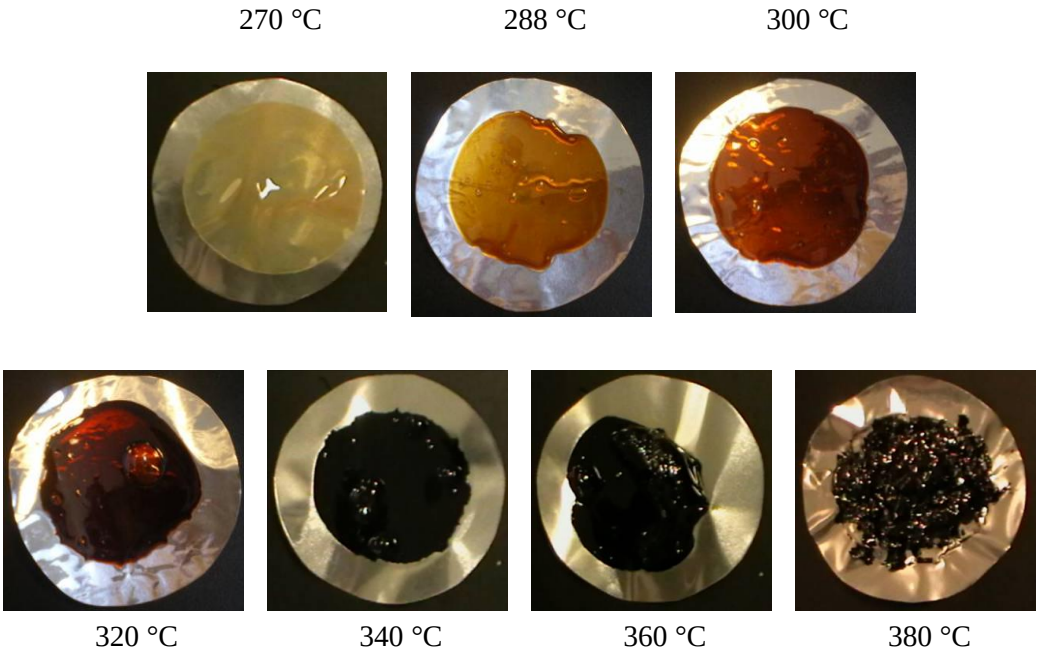

Figure 8.100 Residual film samples from PEN aged in dry air for 4 hours at temperatures between 270 °C and 380 °C

8.2.9 High Humidity Degradation Studies of PET and PEN

8.2.9.1 Volatilisation Studies

Ageing Temperature/ °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/ ^{o}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/ °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/ °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

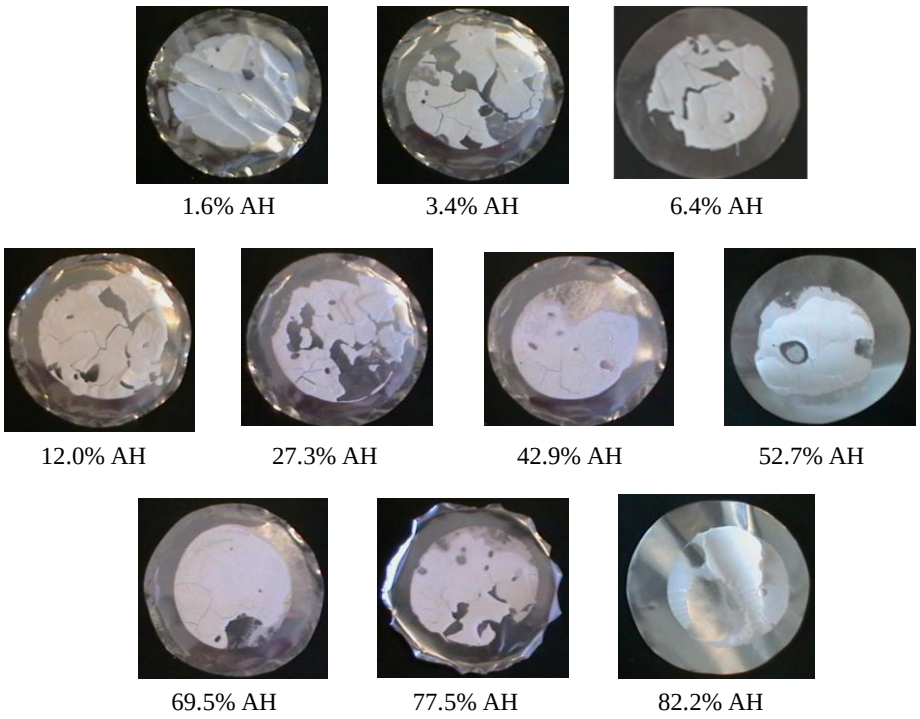

Figure 8.101 Residual film samples from PET after high humidity ageing in nitrogen, 288°C, 4 hours

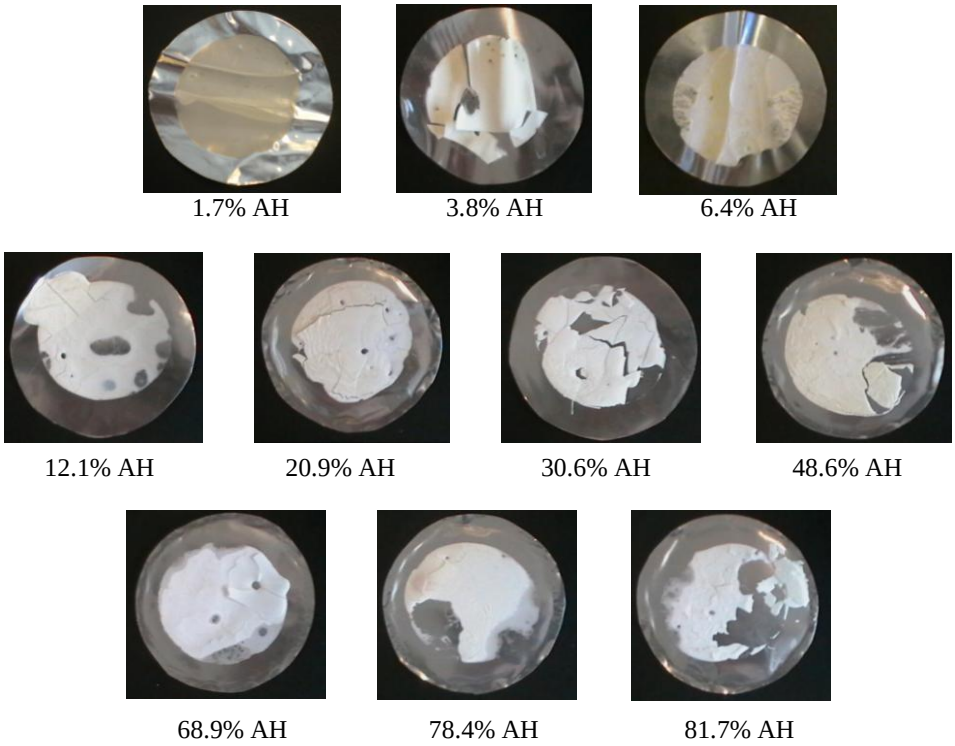

Figure 8.102 Residual film samples from PET after high humidity ageing in nitrogen, 300°C, 4 hours

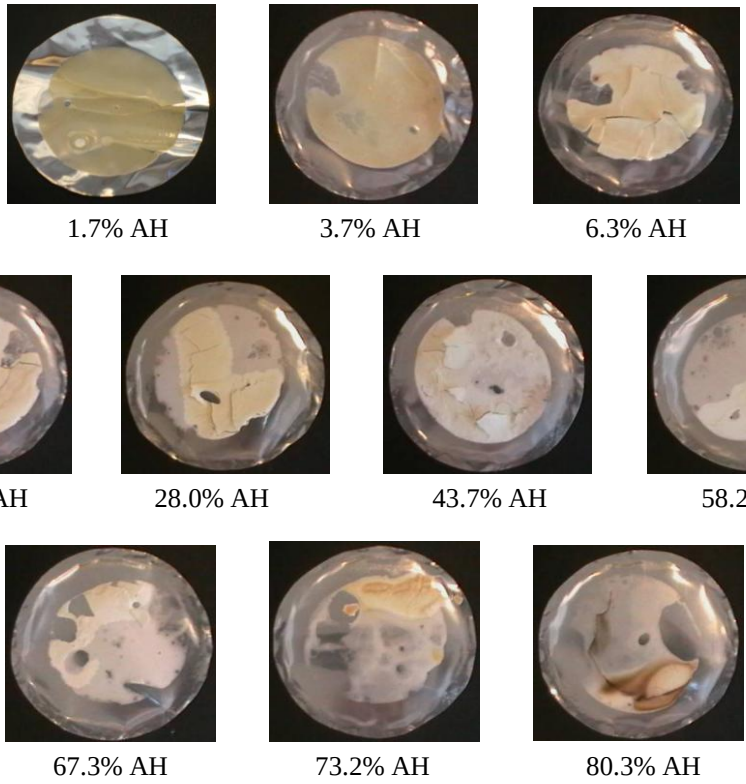

Figure 8.103 Residual film samples from PET after high humidity ageing in nitrogen, 320°C, 4 hours

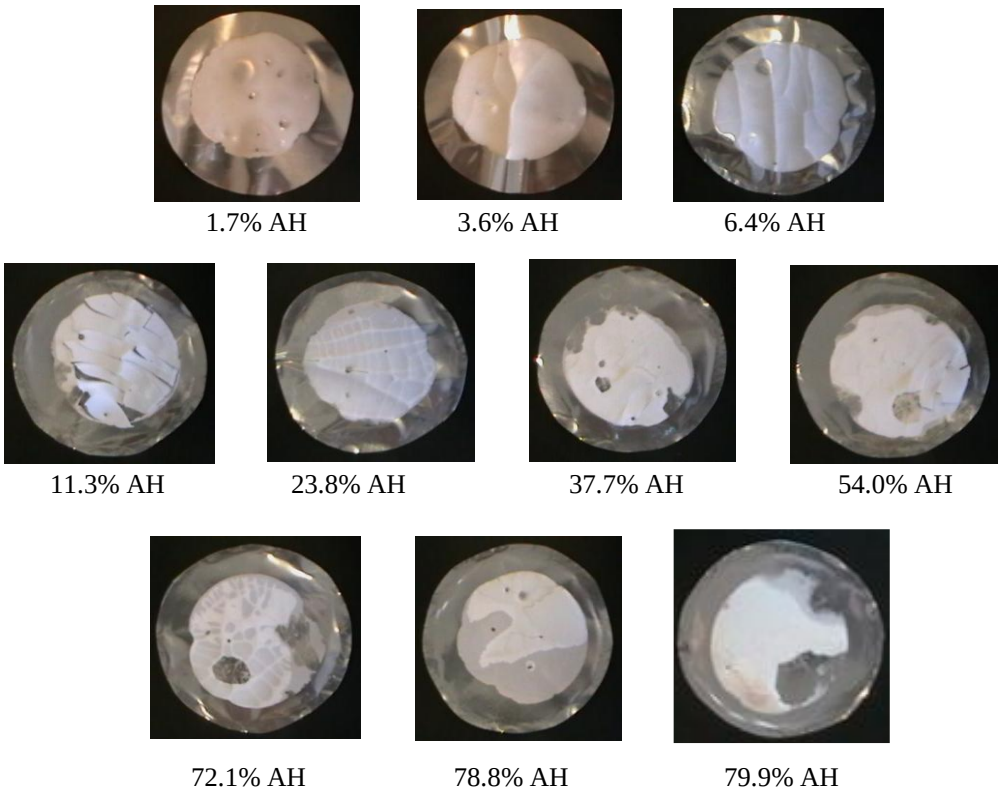

Figure 8.104 Residual film samples from PEN after high humidity ageing in nitrogen, 288°C, 4 hours

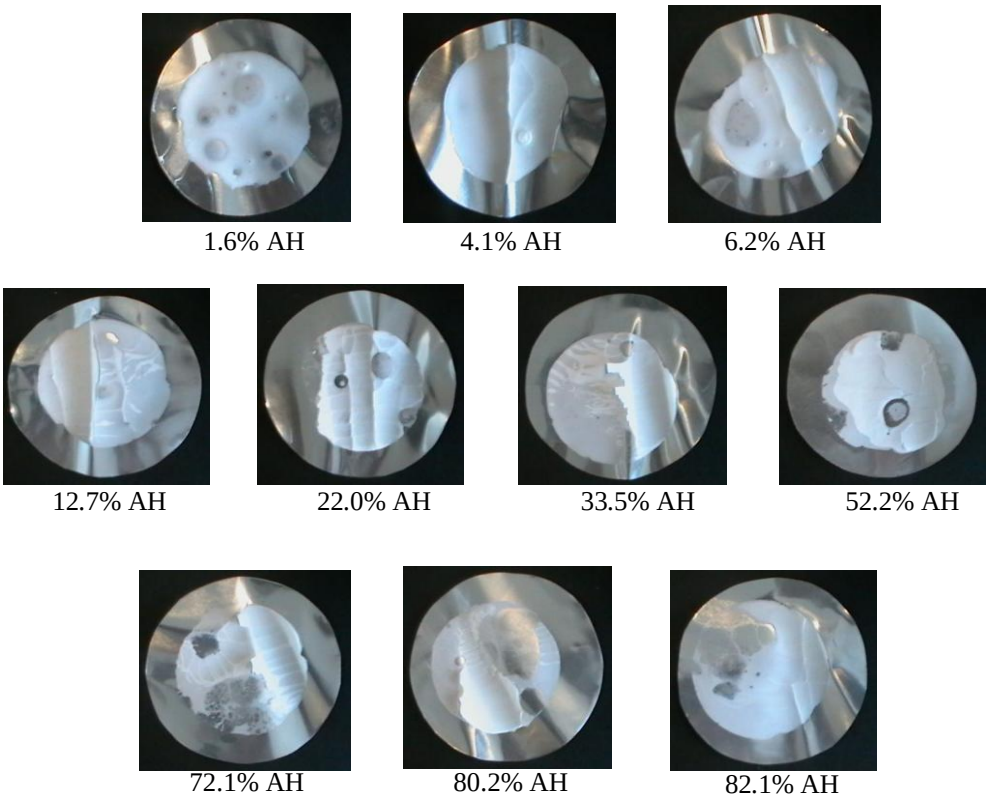

Figure 8.105 Residual film samples from PEN after high humidity ageing in nitrogen, 300 ^{o}C, 4 hours

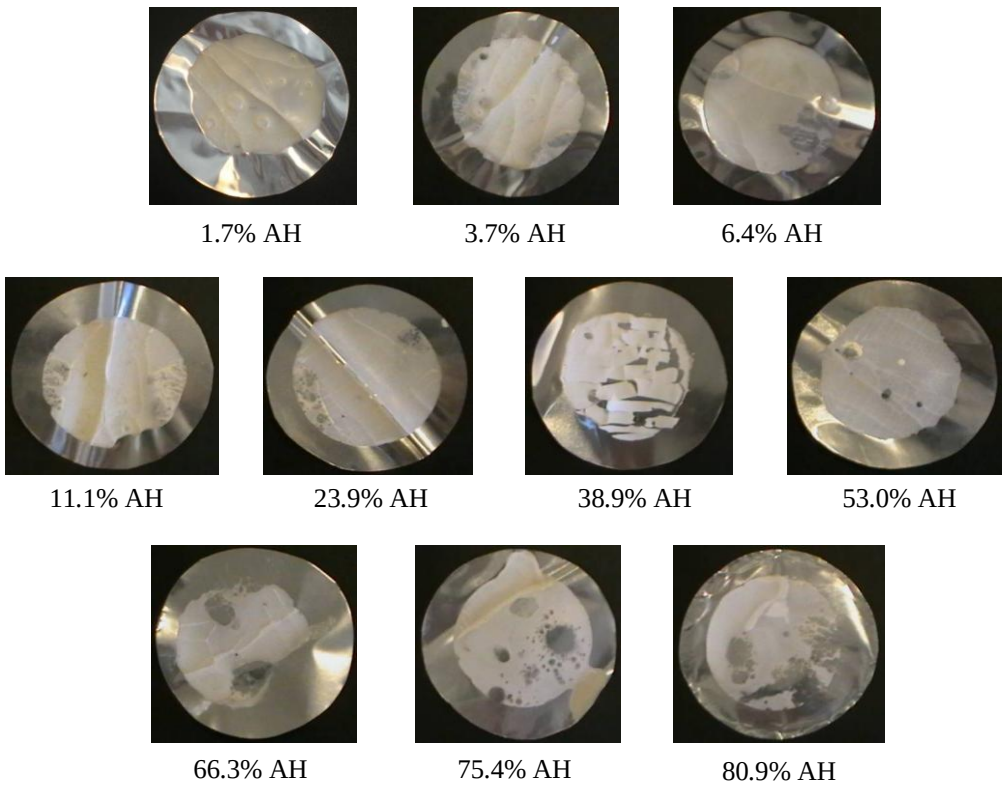

Figure 8.106 Residual film samples from PEN after high humidity ageing in nitrogen, 320 ^{o}C, 4 hours

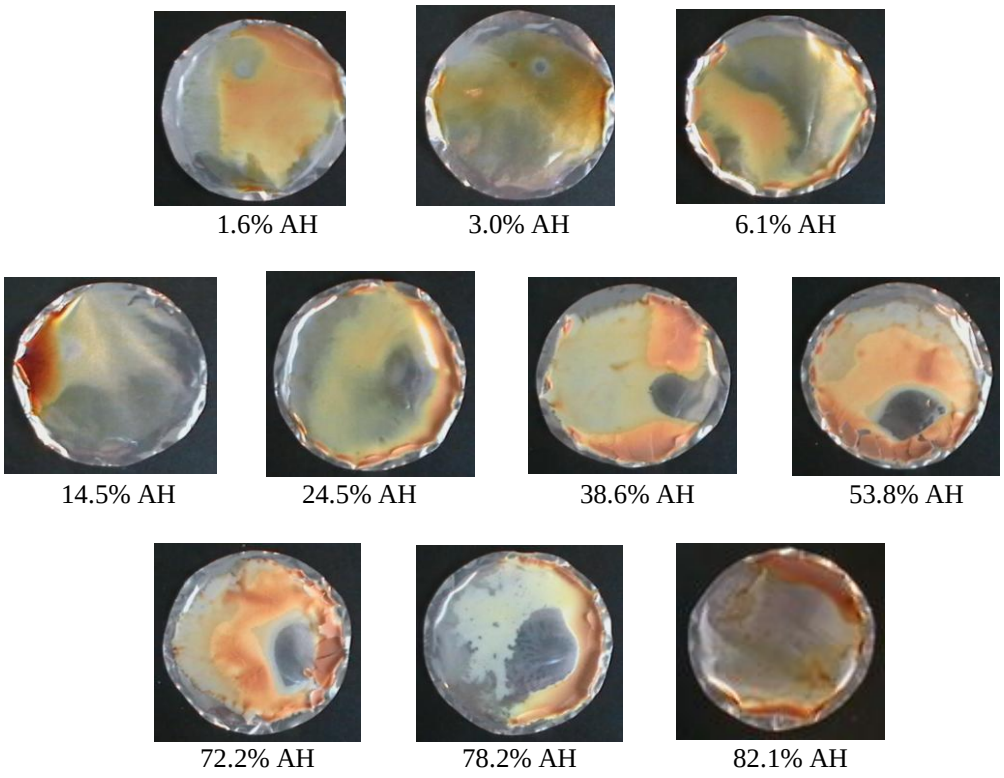

Figure 8.107 Residual film samples from PET after high humidity ageing in air, 288 °C, 4 hours

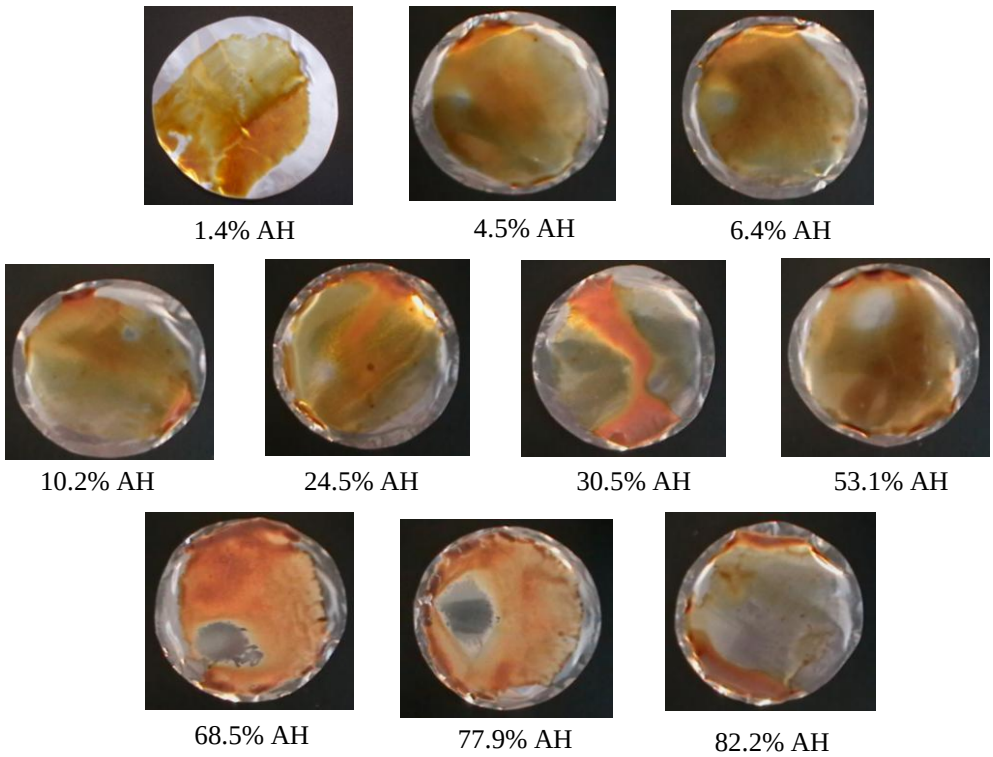

Figure 8.108 Residual film samples from PET after high humidity ageing in air, 300 °C, 4 hours

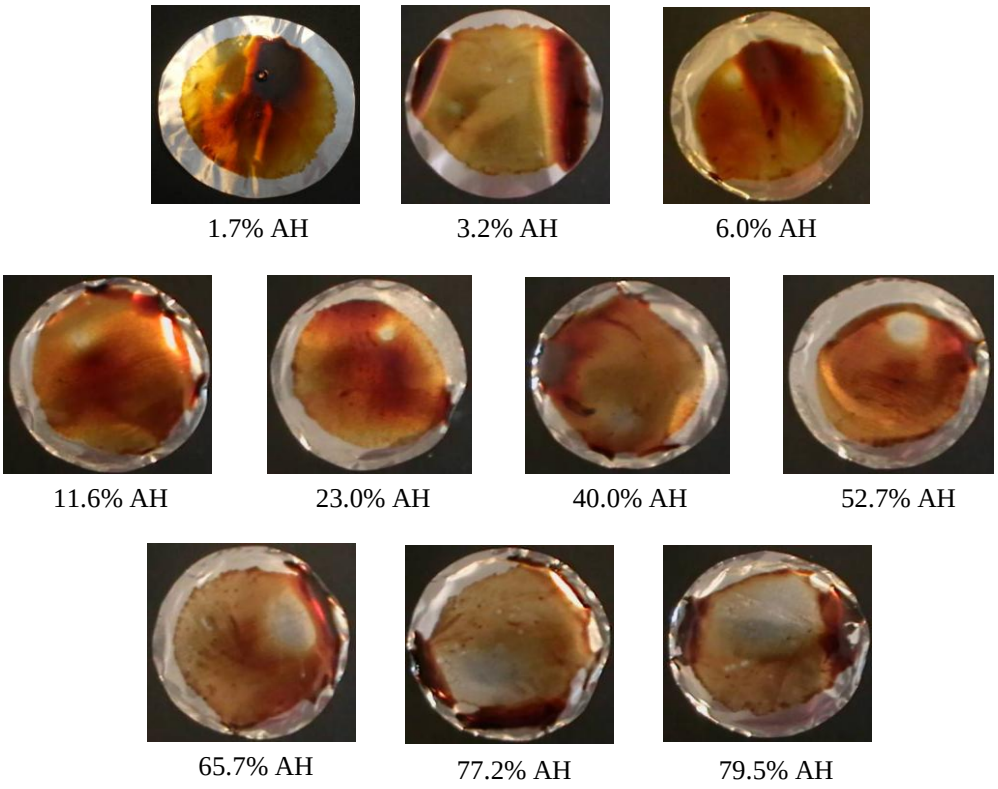

Figure 8.109 Residual film samples from PET after high humidity ageing in air, 320 °C, 4 hours

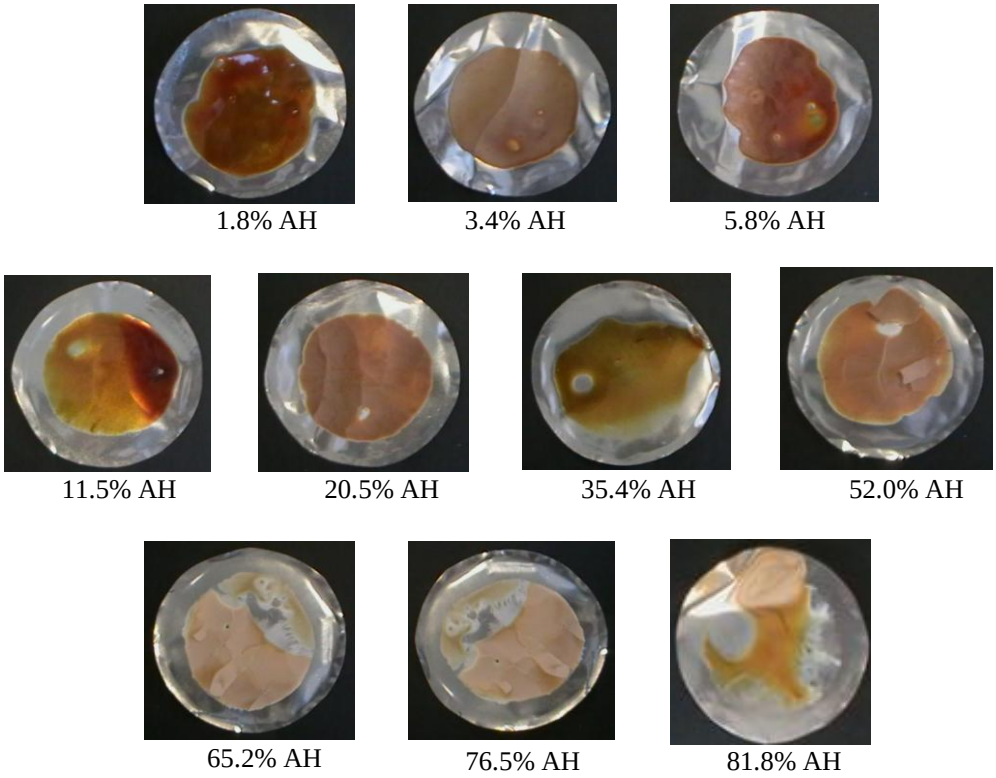

Figure 8.110 Residual film samples from PEN after high humidity ageing in air, 288 °C, 4 hours

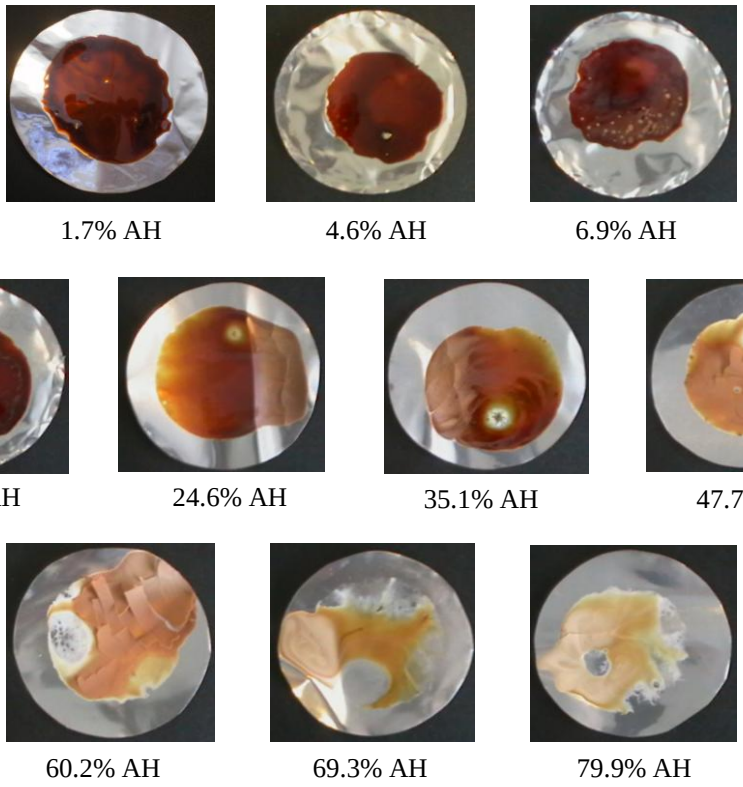

Figure 8.111 Residual film samples from PEN after high humidity ageing in air, 300 °C, 4 hours

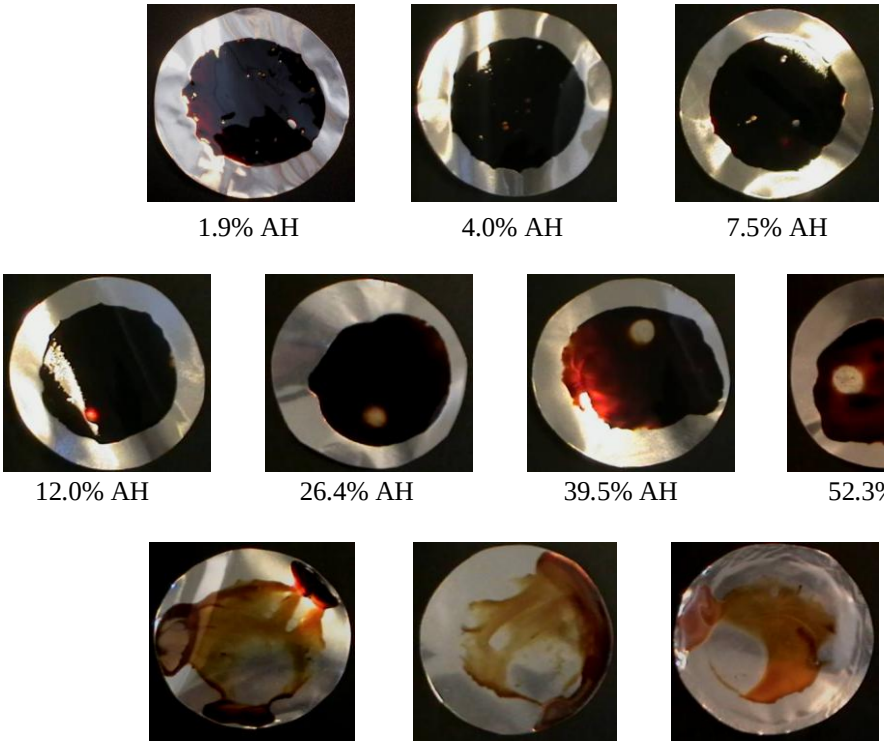

Figure 8.112 Residual film samples from PEN after high humidity ageing in air, 320 °C, 4 hours

8.3 Ageing Studies of PET and PEN under Moderately Accelerated Conditions

8.3.1 Thermal Stability of PET and PEN after Ageing

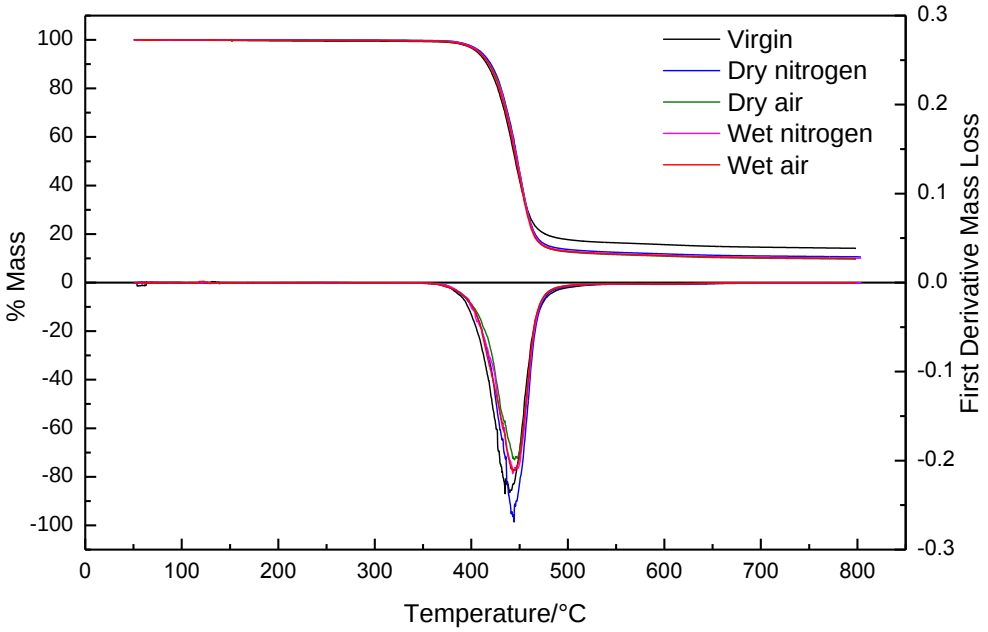

Figure 8.113 TG curves of PET samples aged under different environments at 160°C

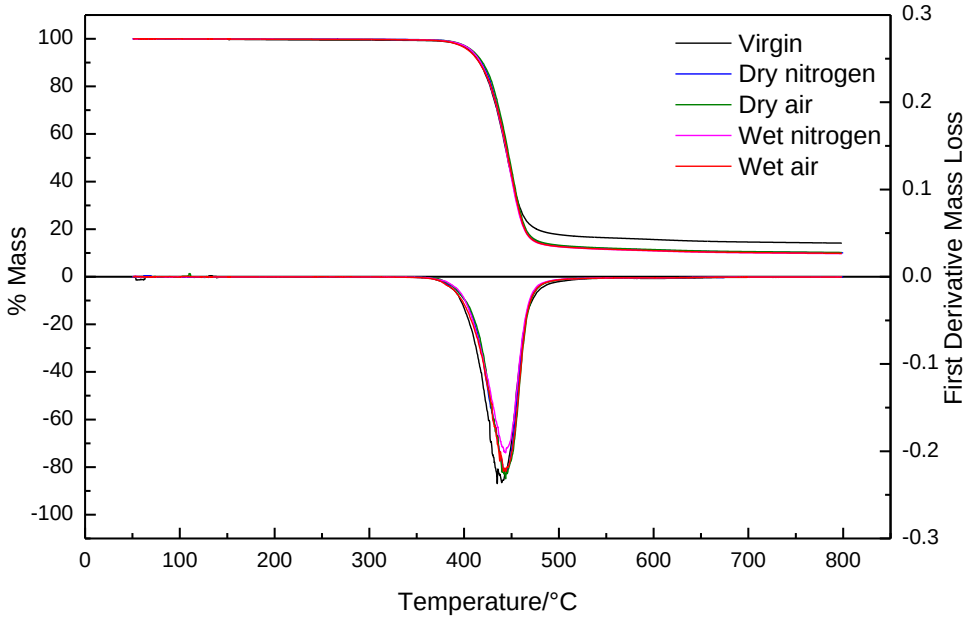

Figure 8.114 TG curves of PET samples aged under different environments at 170°C

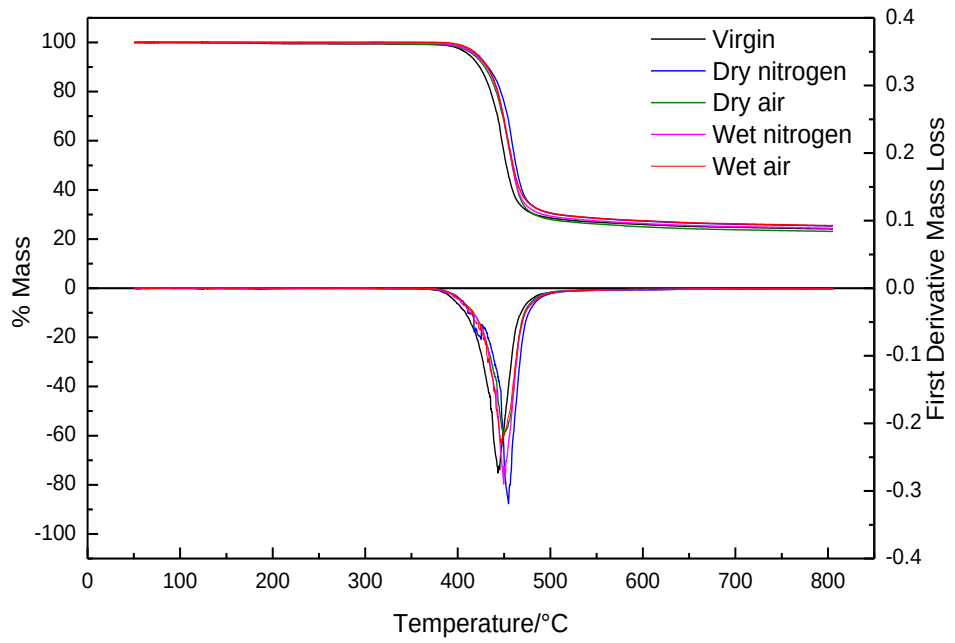

Figure 8.115 TG curves of PEN samples aged under different environments at 160°C

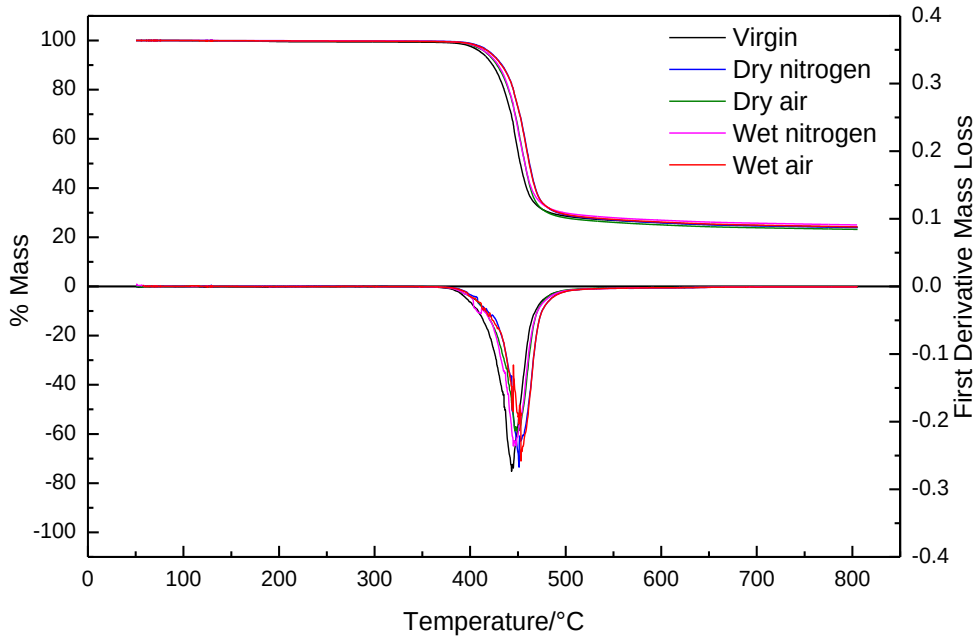

Figure 8.116 TG curves of PEN samples aged under different environments at 170°C

8.3.2 Changes in Physical Morphology after Ageing

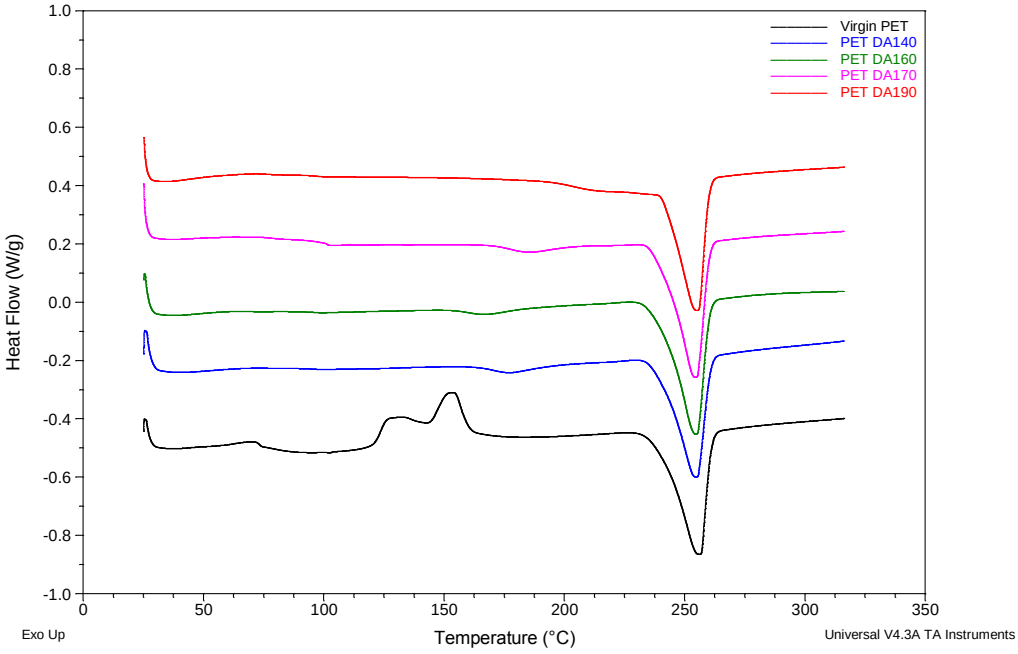

Figure 8.117 DSC of PET samples aged under dry air, cycle 1

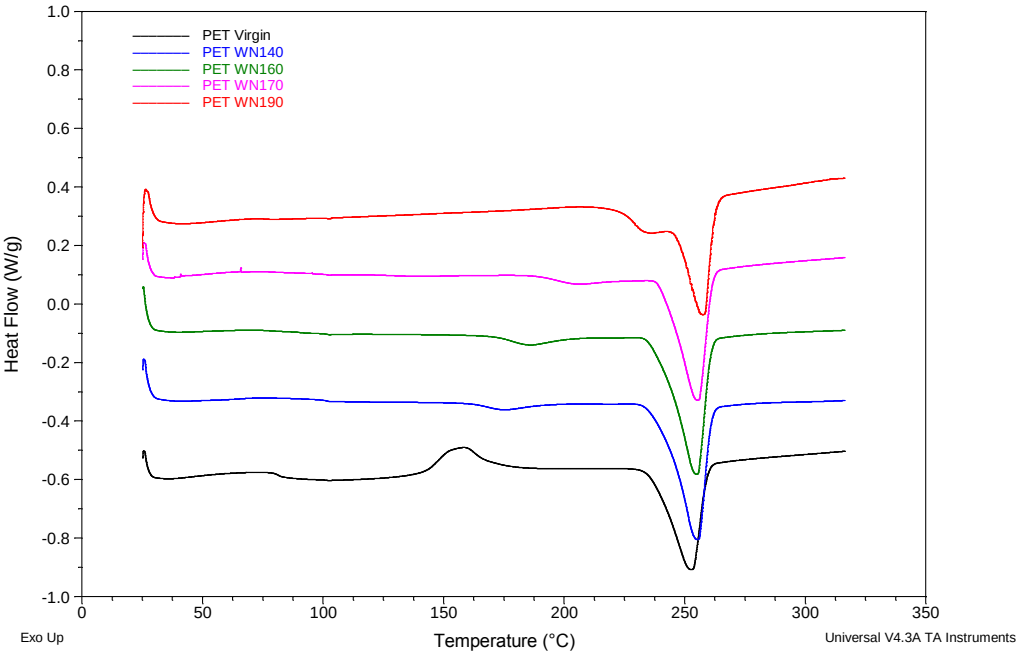

Figure 8.118 DSC of PET samples aged under wet (1.6% AH) nitrogen, cycle 1

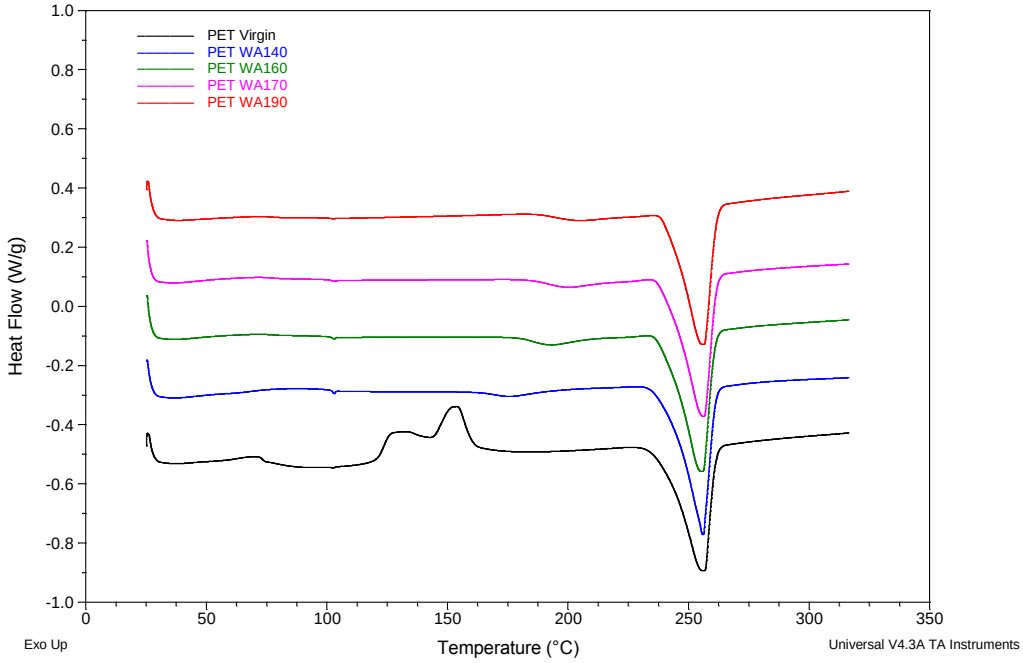

Figure 8.119 DSC of PET samples aged under wet (1.6% AH) air, cycle 1

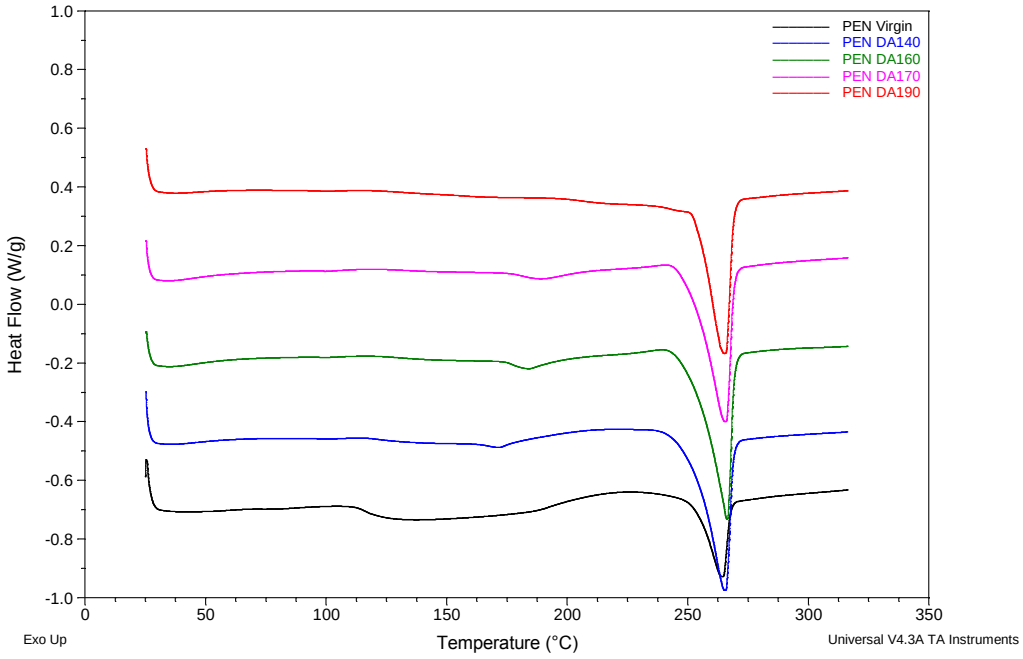

Figure 8.120 DSC of PEN samples aged under dry air, cycle 1

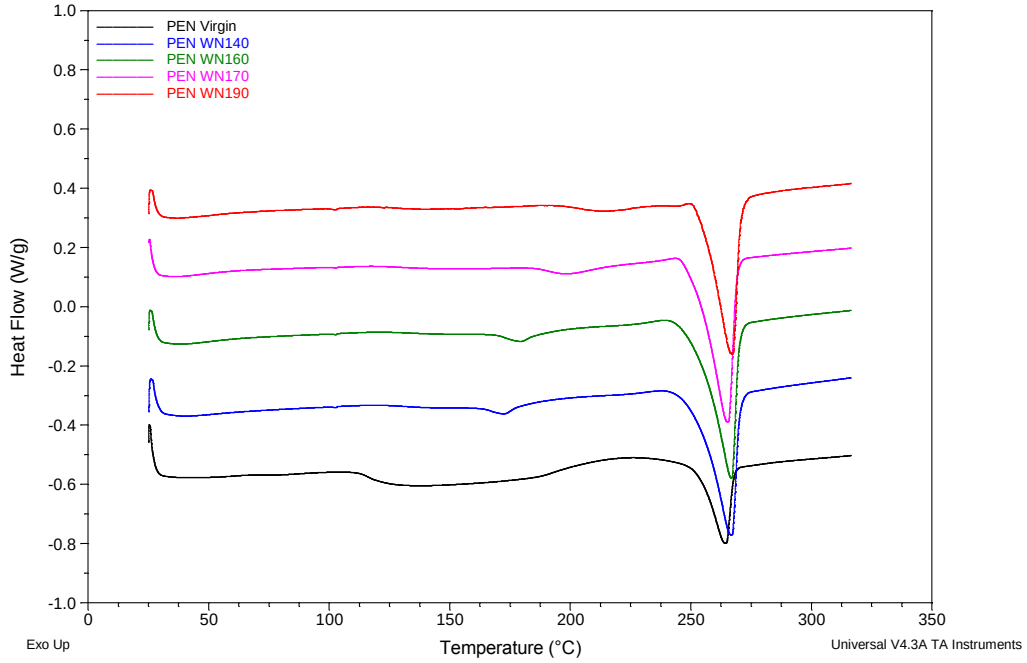

Figure 8.121 DSC of PEN samples aged under wet (1.6% AH) nitrogen, cycle 1

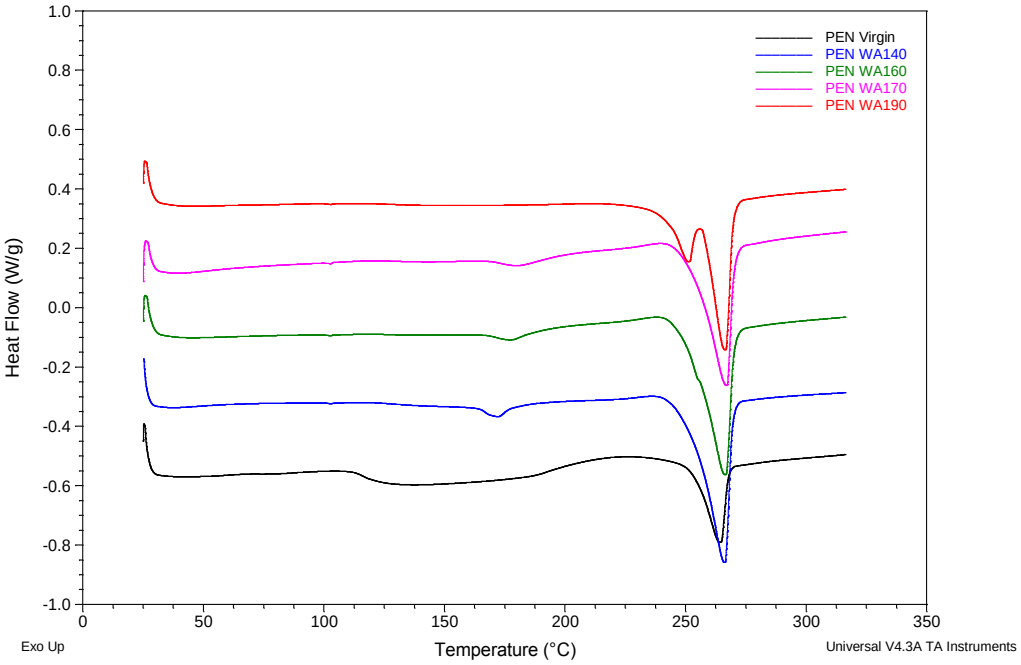

Figure 8.122 DSC of PEN samples aged under wet (1.6% AH) air, cycle 1

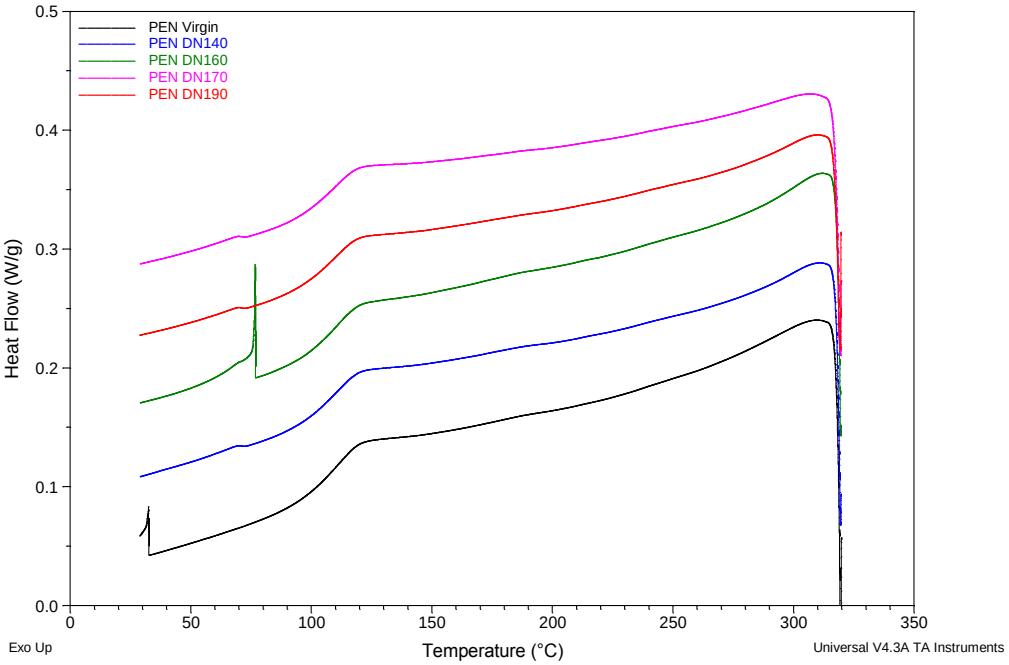

Figure 8.123 DSC of PEN samples aged under dry nitrogen, cycle 2

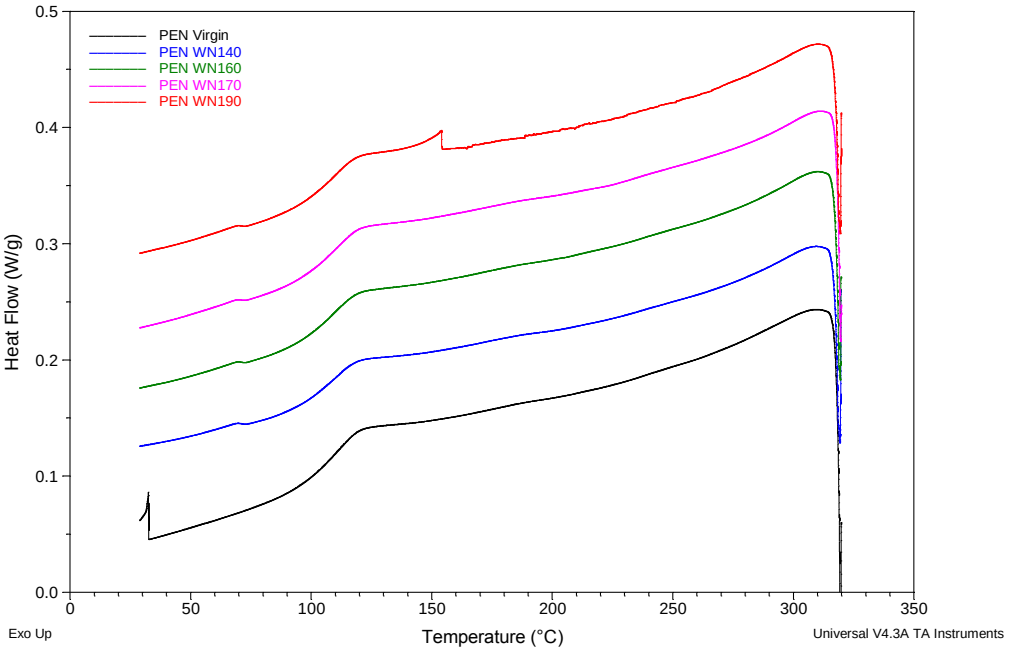

Figure 8.124 DSC of PEN samples aged under wet (1.6% AH) nitrogen, cycle 2

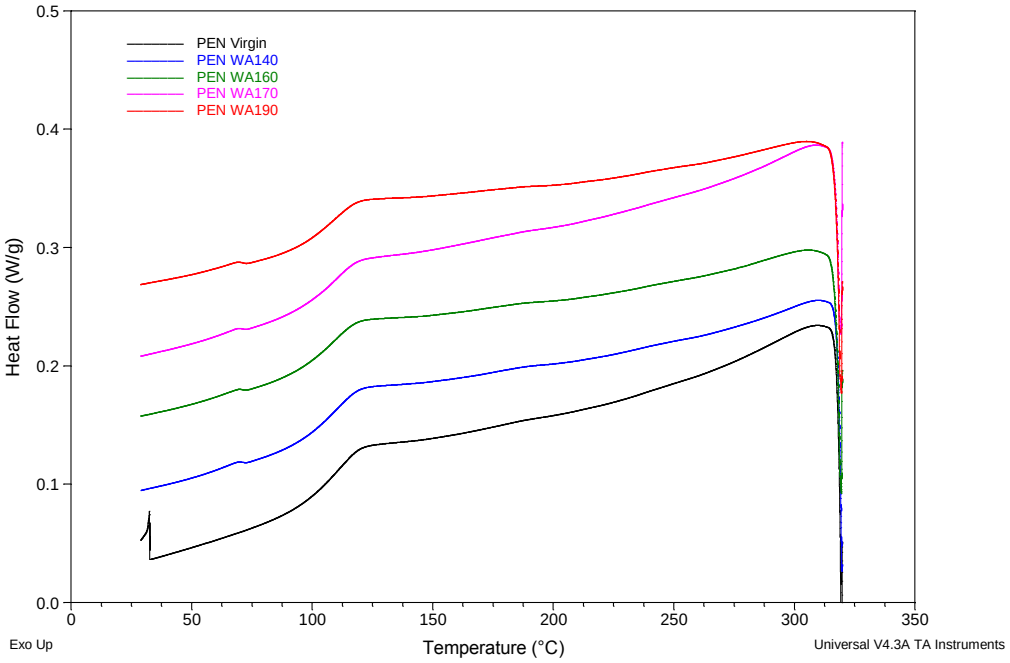

Figure 8.125 DSC of PEN samples aged under wet (1.6% AH) air, cycle 2

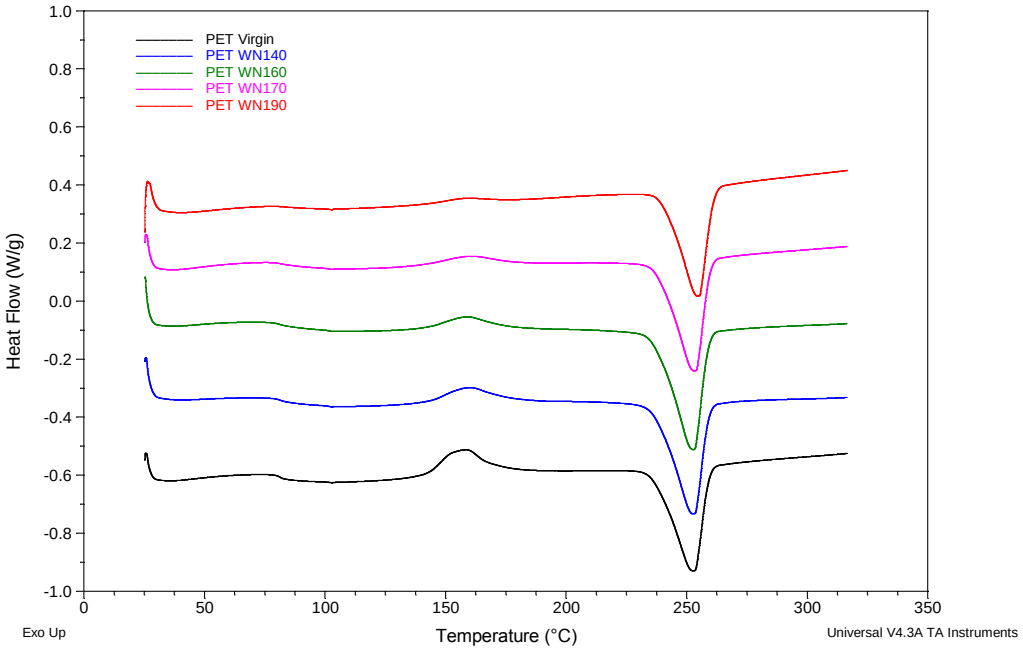

Figure 8.126 DSC of PET samples aged under wet (1.6% AH) nitrogen, cycle 3

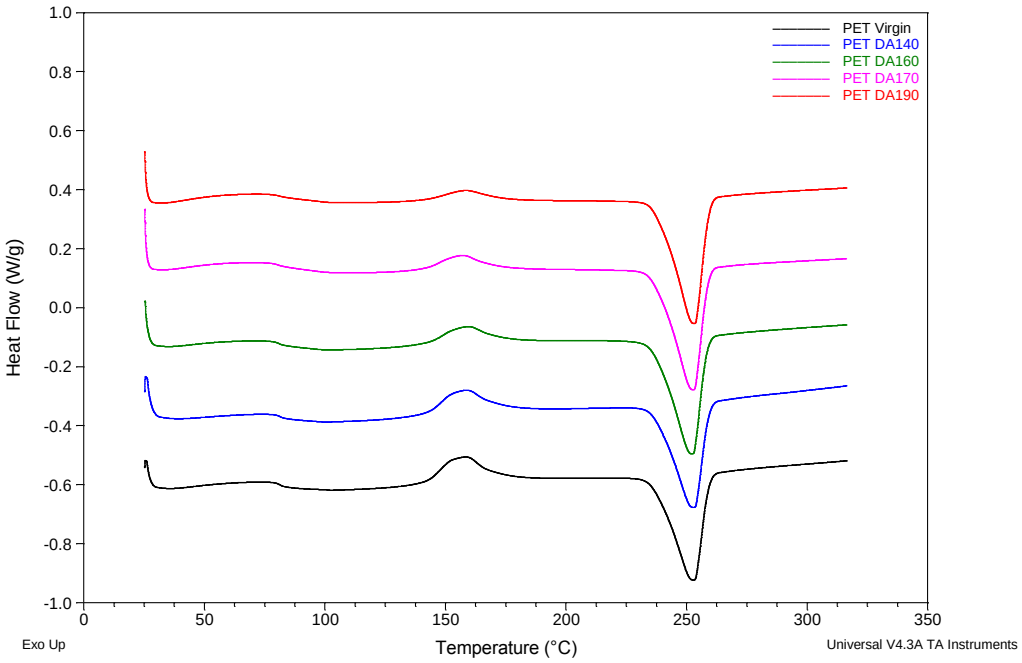

Figure 8.127 DSC of PET samples aged under dry air, cycle 3

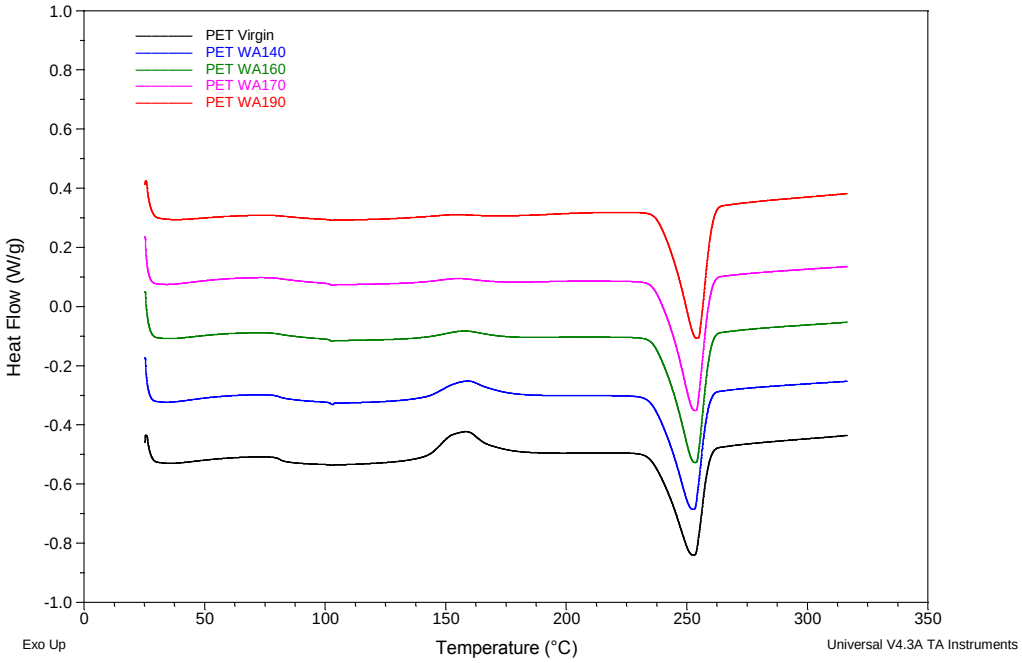

Figure 8.128 DSC of PET samples aged under wet (1.6% AH) air, cycle 3

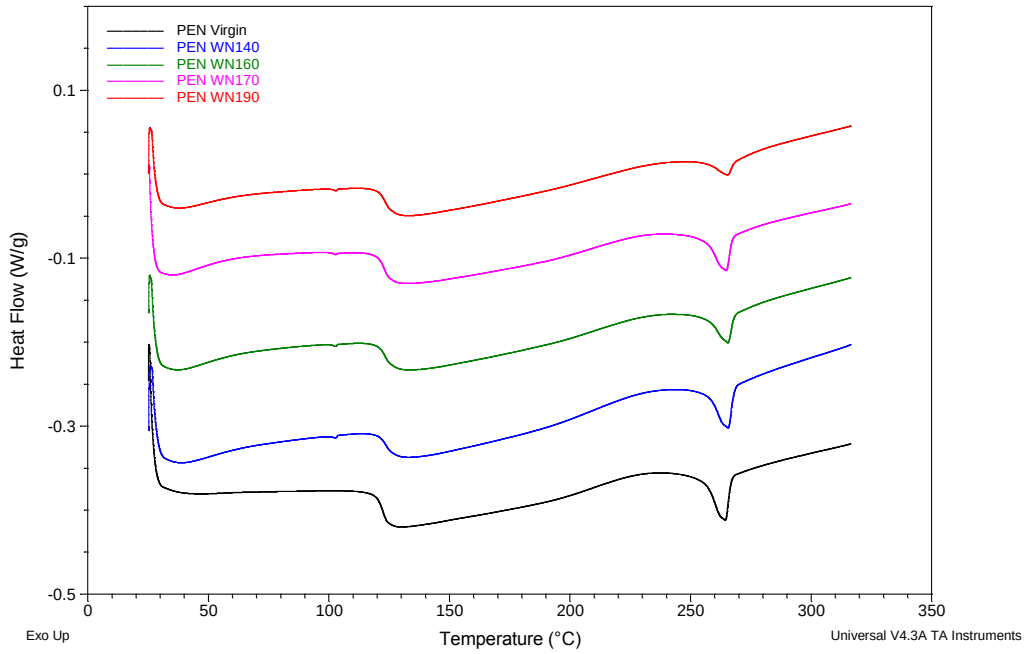

Figure 8.129 DSC of PEN samples aged under wet (1.6% AH) nitrogen, cycle 3

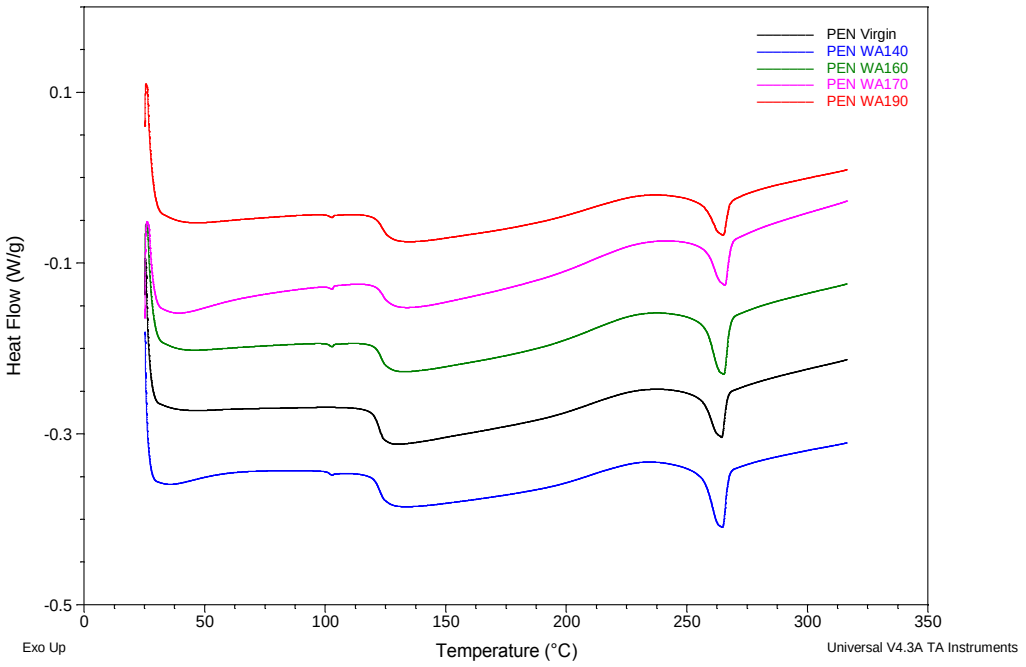

Figure 8.130 DSC of PEN samples aged under wet (1.6% AH) air, cycle 3

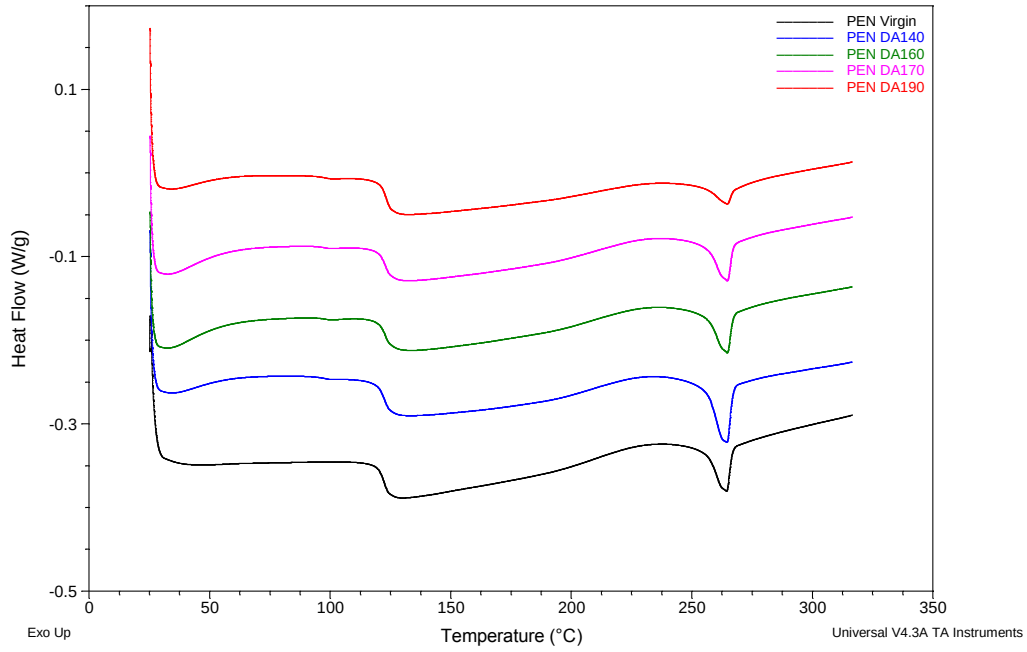

Figure 8.131 DSC thermal transitions in PEN samples aged under dry air, cycle 3