

# Ageing of Poly(ethylene terephthalate) and Poly(ethylene naphthalate) Under Moderately Accelerated Conditions

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**ABSTRACT:** PEN is thought to have increased thermal and hydrolytic resistance in comparison to PET. However, due to a lack of research, few studies have been published on the degradation of PEN. In our research, we report on the extent of degradation in PET and PEN after ageing under contrasting environments (dry nitrogen, dry air, wet nitrogen, and wet air) at temperatures between 140°C and 190°C. A combination of analysis techniques were employed in order to characterize and track the physical and chemical changes in the aged polyester samples, ena-

bling the effects of temperature, water, and oxygen to be mapped onto the resultant property changes of PET and PEN. The extent of degradation has been shown to differ between both polymers and the dominant degradation mechanism in PET was shown to differ with ageing temperature. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 4517–4529, 2012

**Key words:** degradation; polyesters; molecular weight distribution; thermal properties

## INTRODUCTION

### Introduction to polyesters

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

The first synthesis of linear aliphatic polyesters began in the 1930s by Carothers at DuPont, USA; however these aliphatic polyesters did not succeed commercially due to their low melting points and poor hydrolytic stability.<sup>1</sup> This research did, however, inspire other scientists to attempt the synthesis of polyesters from ethylene glycol and terephthalic acid monomers, leading to the synthesis of the first

linear aromatic polyester, poly(ethylene terephthalate) (PET), by Whinfield and Dickson in 1941.<sup>2,3</sup> Whinfield and Dickson identified PET as an excellent fiber forming polymer due to its low cost and thermal/mechanical properties, resulting in rapid expansion in the production of PET fibers. The development of polyester based films from PET followed thereafter. PET is now one of the leading commercial polymers, accounting for 8% of the total world plastic demand in 2009.<sup>4</sup> Its major commercial uses remain as a textile fiber, material for blow molded bottles and biaxially oriented film used for packaging, advanced photo systems, electrical and electronic applications.

Although the demand for PET remains very strong, applications exist which often require improved properties that PET cannot provide. These include increased mechanical strength for motor substrates, high temperature resistance for electronics and improved gaseous barrier properties for food packaging applications. One polymer that can provide such properties is poly(ethylene naphthalate) (PEN). PEN incorporates naphthalene rings into the polymer backbone as opposed to phenyl rings in PET. The naphthalene units stiffen the polymer backbone resulting in a higher glass transition temperature and improved thermal, mechanical, electrical, and barrier properties, in comparison to PET.<sup>5,6</sup> Although PEN was first produced in 1948, it is now only beginning to make a major appearance into the market place due to the lack of availability of the

Additional Supporting Information may be found in the online version of this article.

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starting monomer, dimethyl-2,6-naphthalenedicarboxylate (NDC). Large-scale production of NDC was only introduced in the early 1990s leading to a significant increase in the raw material feed stocks for the production of PEN, reducing the overall cost of PEN resin.<sup>1</sup> This led to a substantial increase in the production and applications of PEN, with PEN now competing with PET in certain performance-driven markets based on its superior strength, heat stability, and barrier properties.

### Degradation of polyesters

Degradation of polyesters, such as PET and PEN, is generally inevitable during synthesis and processing as the polyesters are exposed to high temperatures, both under non-oxidative and oxidative conditions in the presence of moisture. These conditions can result in a combination of thermal, thermo-oxidative, and hydrolytic degradation reactions leading to the evolution of volatile degradation products and significant loss of crucial polymer properties. Unfortunately, water uptake by polyester chips is particularly inevitable during post-polymerisation cooling processes and storage. The hydroxyl, carboxyl, and ester groups within the polyester network are likely to retain water and therefore if the polyester chips were to be processed directly, their molar mass would significantly decrease as a result of hydrolytic degradation. For this reason, polyester chips are crystallized, to avoid sintering during drying, and then dried for several hours to reduce the moisture content prior to processing.

The effect of this pre-processing drying treatment on the thermal degradation of PET polyester chips has been investigated. Villain et al.<sup>7</sup> examined the overall mass loss behavior of PET when dried under air and nitrogen at 160°C for 800 minutes, prior to thermal degradation at processing temperatures of 280°C and 310°C. The most significant mass loss was reported when drying and degradation were performed under air, due to oxidative degradation leading to a reduction in the overall length of the polymer chain. PEN is reported to have increased thermal<sup>1</sup> and hydrolytic<sup>8</sup> resistance in comparison to PET; however due to a lack of research on PEN, few studies have been published and no research has been conducted on the effects of drying on the degradation of PEN.

In our research, we report on the extent of degradation in PET and PEN after ageing under different drying conditions. PET and PEN polyester chips were aged under dry nitrogen, dry air, wet nitrogen and wet air environments at temperatures of 140, 160, 170, and 190°C. The ageing temperatures selected were based around the typical drying temperatures currently used during the pre-processing

treatment of PET. With increasing temperature, the degradation mechanism during ageing is thought to differ. Hydrolysis is believed to dominate over extended periods of time at lower ageing temperatures (i.e., 140–160°C) with oxidative degradation dominating at higher ageing temperatures (i.e., 190°C). This contrasting set of ageing conditions, at which the polyester samples were exposed to, enables the effects of temperature, water and oxygen to be mapped onto the resultant property changes of PET and PEN.

## EXPERIMENTAL

### Materials

Commercial samples of PET and PEN were kindly supplied by DuPont Teijin Films. Both PET and PEN were supplied as transparent chips with a weight average molar mass ( $M_w$ ) of  $24900 \pm 141 \text{ g mol}^{-1}$  and  $20,200 \pm 71 \text{ g mol}^{-1}$ , respectively. Prior to use, the polyester chips were stored for several hours in a vacuum desiccator at room temperature, to remove any surface water.

### Ageing apparatus

The purpose of the experimental apparatus was to age samples under contrasting environments; dry nitrogen, wet nitrogen, dry air, and wet air at elevated temperatures, over a period of 24 h. This enabled the effects of thermal, thermal-hydrolytic, thermo-oxidative, and thermo-oxidative-hydrolytic degradation to be studied in both polyesters. A schematic representation of the ageing apparatus is illustrated in Figure 1.

The apparatus consisted of a thermostatically controlled block heater capable of reaching temperatures of  $200^\circ\text{C} \pm 1.0^\circ\text{C}$ . 1 g of polymer chip sample was placed in each sample tube for ageing and dry/wet, nitrogen/air were fed individually into each sample chamber yielding dry non-oxidative, wet non-oxidative, dry oxidative, and wet oxidative conditions. Flowing gas through a dreschel bottle containing water created a wet atmosphere (1.6% absolute humidity) and silica gel created a dry atmosphere. The temperatures studied were 140, 160, 170, and 190°C and the gas flow was regulated using a flow meter, supplying  $50 \text{ mL min}^{-1}$  to each sample chamber. After the drying temperature was programmed on the block heater, the system was left to equilibrate for 30 minutes prior to starting the experiment time of 24 h. After completion, all samples were dried in a vacuum oven at 60°C for a period of 24 h to remove any surface water prior to analysis.

A combination of analysis techniques were employed in order to characterize and track the

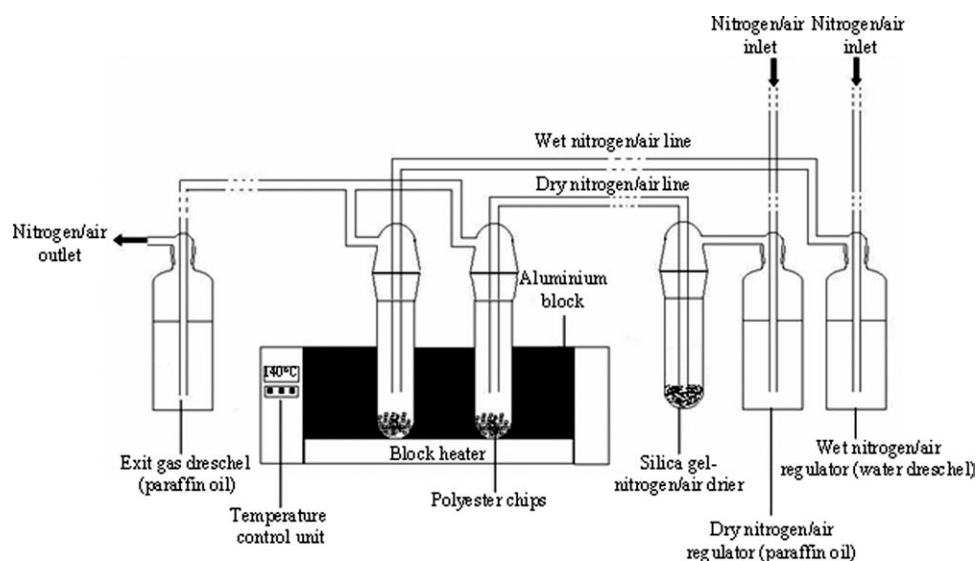


Figure 1 Apparatus for ageing PET and PEN.

physical and chemical changes in the aged polyester samples. Changes in the physical morphology of the samples as a result of ageing, such as crystalline content/behavior, were characterized primarily using differential scanning calorimetry (DSC). The high temperature stability of all samples was assessed using thermogravimetric analysis (TGA) to determine if the different ageing conditions had significant impact on the overall thermal stability of the material. The molar mass of the aged polyester samples was also expected to vary under the action of thermal, thermo-oxidative, and hydrolytic conditions. Therefore changes in the molar mass of the polyester samples were characterized using gel permeation chromatography (GPC).

#### Differential scanning calorimetry (DSC)

All samples were analyzed using a TA Q1000 DSC equipped with a RC90 refrigerated cooling system. The instrument was calibrated with a standard of indium and all samples were prepared in aluminum hermetic DSC pans. A heat-cool-reheat method was adopted, firstly heating the samples from 25°C to 320°C, at a rate of 10°C min<sup>-1</sup>, to destroy their thermal history. Secondly, the samples were cooled from 320°C to 25°C, at a rate of 10°C min<sup>-1</sup>, to impose a known thermal history on all samples. A second heating cycle was finally performed ramping from 25°C to 320°C, at a rate of 10°C min<sup>-1</sup>. The heat-cool-reheat DSC method was conducted under a flow of dry nitrogen (20 mL min<sup>-1</sup>) on 6 mg samples and all DSC data was processed using TA software. All temperature values quoted from the DSC curves are rounded to the nearest integral value, with an error of ±1°C.

#### Thermogravimetric analysis (TGA)

TGA studies were carried out using a Perkin Elmer TGA (TGA7), controlled using Windows based software on a bench-top PC. All experiments were carried out using 10 mg of sample under an inert atmosphere of helium. A heating profile of 50°C to 800°C was performed at a heating rate of 10°C min<sup>-1</sup> and all data was processed using Origin software. From the data obtained, the % mass loss was recorded as a function of temperature and the onset temperatures of degradation were determined at 5% mass loss. The temperature values quoted from the TGA curves are rounded to the nearest integral value, with an error of ±1°C.

#### Gel permeation chromatography (GPC)

All practical GPC work was kindly undertaken by Smithers Rapra based in Shrewsbury, UK. The molar mass and molar mass distribution of the aged polyester samples were determined on a Viscotek TDA model 301 GPC, equipped with PL hexafluoroisopropanol (HFIP) gel guard columns and a refractive index detector. Measurements were carried out at 40°C, using HFIP with 25 mM sodium trifluoroacetate (NaTFAc) as the eluent, at a rate of 0.8 mL min<sup>-1</sup>. Duplicate solutions of each sample were prepared by adding 10 mL of solvent to 20 mg of polymer and leaving overnight to dissolve. The solutions were thoroughly mixed and filtered through a 0.45 µm polytetrafluoroethylene (PTFE) filter prior to analysis. The GPC system was calibrated using polymethylmethacrylate (PMMA); therefore results are expressed as "PMMA equivalent" molar masses. Data was collected and analyzed using Polymer Laboratories 'Cirrus' software. For all samples,

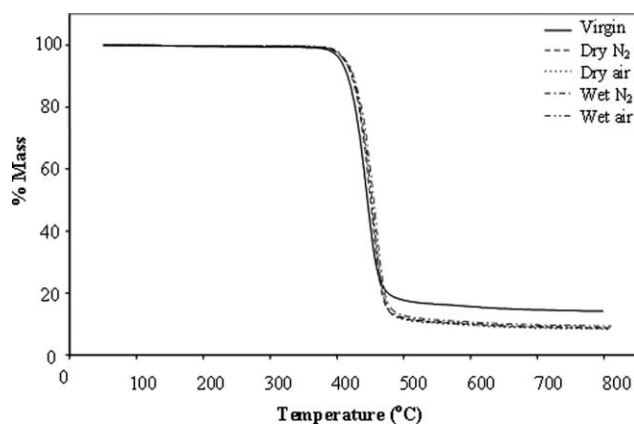
integration limits were selected to exclude any material with a PMMA equivalent molar mass of less than  $400 \text{ g mol}^{-1}$ . The results are summarized as the calculated molar mass averages and polydispersities ( $M_w/M_n$ ) and the graphs are all plotted to the same area, the y-axis being a function of mass fraction.

## RESULTS AND DISCUSSION

### Physical observations of PET and PEN after ageing

Prior to reporting DSC, TGA, and GPC results, it is important to consider the physical appearance of the polymers after ageing. In addition to a significant decrease in molar mass and subsequent loss in mechanical, physical, and chemical properties expected as a result of ageing, discoloration is also likely to be evident. Yellowing of polyesters is a severe problem in synthesis and melt processing and is thought to be a result of both thermal and thermo-oxidative degradation.<sup>1,9,10-13</sup> The transparency of both PET and PEN renders both polyesters suitable for the production of blow molded bottles and packaging materials; however discoloration can adversely affect the end use of the final product, making it suitable only for materials where color is not an issue.

All PET samples aged under dry nitrogen and dry air were found to be crystalline (i.e., white, opaque), with no hint of discoloration at any ageing temperature. Similarly, PET samples aged under wet nitrogen and wet air were also found to be crystalline; however discoloration (yellowing) was evident in PET samples aged at  $190^\circ\text{C}$ . Initially, on observation of the aged PEN samples, it was evident that all samples were not fully crystalline, in contrast to PET. Under all environments at  $140^\circ\text{C}$ , the PEN samples were found to be only partially crystalline (i.e., partly opaque). However, this is not entirely surprising as significant crystallization of PEN does not occur until  $180^\circ\text{C}$ , with the rate of maximum crystallization occurring around  $210^\circ\text{C}$ . With increased ageing temperature, under all environments, the PEN samples were found to anneal from transparent, amorphous polyester chips to white, crystalline polyester chips. No discoloration of PEN was evident under all environments at ageing temperatures of  $140^\circ\text{C}$  and  $160^\circ\text{C}$ . However, in contrast to PET, discoloration was evident in the PEN samples aged at  $170^\circ\text{C}$  under all environments. Of all PET and PEN samples aged, the most significant discoloration was evident in PEN samples aged under all environments at  $190^\circ\text{C}$ . This increased discoloration of PEN is in agreement with the studies completed by Botelho et al.<sup>14</sup> and Scheirs et al.<sup>15</sup> Both studies report that PEN discolors more rapidly than PET, suggesting that the discoloration is due to the formation of highly conjugated and highly



**Figure 2** TG curves of PET samples aged under different environments at  $140^\circ\text{C}$ .

absorbing naphthalene structures formed as a result of degradation.

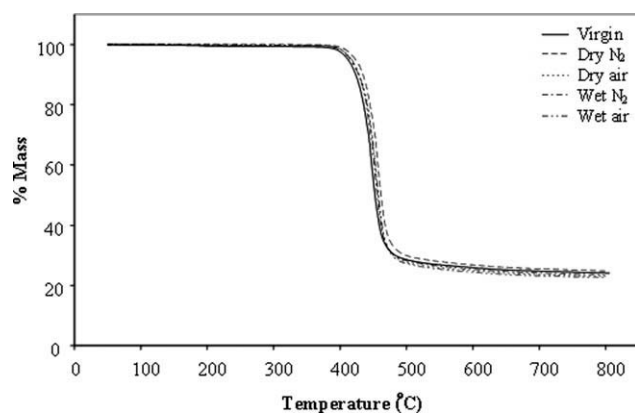
In addition to the discoloration of aged PET and PEN samples, a loss in mechanical strength was apparent. All PET samples aged at  $190^\circ\text{C}$  had reduced mechanical strength, in comparison to all other samples. These polyester chips became brittle after ageing and crumbled readily when pressure was exerted upon them. The most significant loss of mechanical strength was noted in PET samples aged under dry and wet air at  $190^\circ\text{C}$ . Similar to PET, a loss in mechanical strength was evident in PEN. All PEN samples aged at  $190^\circ\text{C}$  were found to have reduced mechanical strength, to the extent that the polyester chips became brittle and crumbled when pressure was exerted upon them. In contrast to PET, the PEN samples aged under wet air at  $170^\circ\text{C}$  were also found to be very brittle, indicating a more significant loss in mechanical strength in PEN than in PET aged under identical conditions. Of all PET and PEN samples aged, the most significant loss in mechanical properties was evident in PEN samples aged under wet air at  $190^\circ\text{C}$ .

### Thermal stability of PET and PEN after ageing

The thermal stability of all aged polyester samples was assessed using TGA to determine if there were any changes in the polyesters significant enough to impact on their degradation profile. Changes in the overall thermal stability of PET and PEN will be observed if significant degradation of the polyester chains (e.g., hydrolytic chain scission at the ester linkages or oxidative cross-linking) has occurred during ageing.

Figures 2–5 illustrate the thermal stability of PET and PEN samples aged under all environments at temperatures of  $140^\circ\text{C}$  and  $190^\circ\text{C}$ . Due to such minor changes observed in the overall thermal stability of all aged samples of PET and PEN, the TGA curves

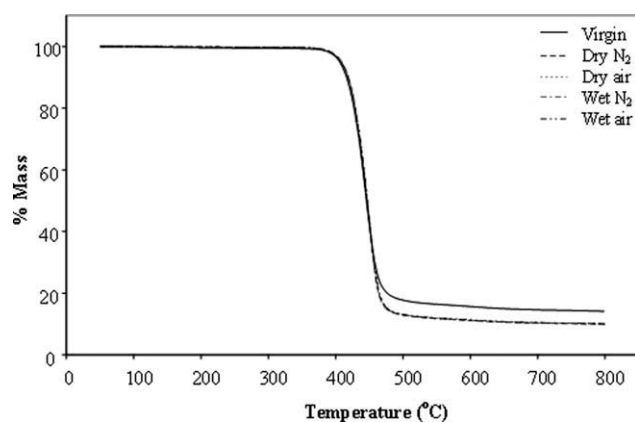




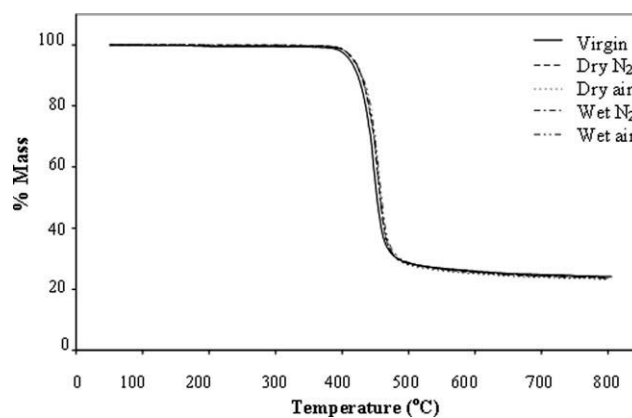
**Figure 3** TG curves of PEN samples aged under different environments at 140°C.

are only shown for the samples aged at the lowest and highest temperatures. All other TGA curves can be found in the Supporting Information. Table I presents the temperatures of degradation from the TGA curves illustrated in Figures 2–5. Comparison of the TGA results reveals no significant differences in the mass loss behavior and therefore overall thermal stability between the virgin and aged samples of PET and PEN.

All samples of PET appear to undergo only one significant mass loss step, starting around 406°C, due to thermal degradation of the polyester backbone, i.e., chain scission at the ester bonds. Small differences are evident in the % mass of PET remaining after degradation. All PET samples aged under dry and wet, inert and oxidative environments have a marginally lower % residual mass after degradation, in comparison to the virgin material. This suggests that the extent of chain scission prior to analysis is more significant in aged PET than virgin PET. Shorter polymer chains, formed as a result of chain scission degradation reactions during ageing, will volatilize faster, resulting in a lower overall % mass of polyester remaining. However, despite these dif-



**Figure 4** TG curves of PET samples aged under different environments at 190°C.



**Figure 5** TG curves of PEN samples aged under different environments at 190°C.

ferences in residual mass, the extent of degradation in all aged PET samples is not sufficient enough to change the overall thermal stability of the material. Therefore, regardless of changes in the overall physical appearance and mechanical strength of aged PET samples, in comparison to virgin PET, the overall thermal stability of the materials remains unchanged.

From Figures 3 and 5, it can be observed that aged samples of PEN also appear to undergo only one significant mass loss step, starting above 412°C. This is identical to PET and is again due to thermal degradation of the polymer backbone, i.e., chain scission at the ester bonds. It is also apparent that no distinct differences exist between the thermal stability of PEN samples aged under different environments between temperatures of 140°C and 190°C. However, the onset temperatures of degradation and temperatures of maximum mass loss are marginally higher for virgin and aged samples of PEN, in comparison to PET. This is thought to be a result of the enhanced delocalization of charge across the naphthalene ring units in PEN, increasing the stability of the ester linkages. Interestingly, no significant differences are evident in the % mass of original polymer remaining after the degradation of aged PEN samples, in comparison to virgin PEN. Degradation of PEN is therefore thought to be minimal under the ageing conditions studied.

#### Changes in molar mass of PET and PEN after ageing

Despite insignificant changes in the overall thermal stability of aged samples of PET and PEN, the molar mass is thought to vary under the action of thermal, thermo-oxidative, and hydrolytic conditions. Therefore, changes in the molar mass of virgin and aged samples of PET and PEN were characterized using GPC.

TABLE I  
Degradation Temperatures from TG Curves of PET and PEN Samples Aged at 140°C and 190°C

Polymer	Ageing environment	Ageing temperature, °C	Onset of degradation, °C	Temperature of maximum mass loss, °C	Mass remaining at 800°C, %
PET	Virgin	N/A	406	440	14
PET	Dry nitrogen	140	406	441	10
PET	Dry nitrogen	190	409	444	10
PET	Dry air	140	407	446	9
PET	Dry air	190	408	446	10
PET	Wet nitrogen	140	409	448	10
PET	Wet nitrogen	190	408	442	10
PET	Wet air	140	408	441	10
PET	Wet air	190	408	444	10
PEN	Virgin	N/A	412	443	24
PEN	Dry nitrogen	140	423	451	25
PEN	Dry nitrogen	190	418	449	24
PEN	Dry air	140	417	448	23
PEN	Dry air	190	418	450	23
PEN	Wet nitrogen	140	415	447	24
PEN	Wet nitrogen	190	417	447	24
PEN	Wet air	140	418	451	23
PEN	Wet air	190	417	450	24

Table II presents the number-average molar masses ( $M_n$ ), weight-average molar masses ( $M_w$ ), and polydispersity values determined for all aged samples of PET by GPC. Comparison of the GPC data presented indicates that thermal degradation of PET is minimal up to ageing temperatures of 190°C under dry nitrogen. A small decrease in  $M_w$  and  $M_n$  is noted only at 190°C under dry air indicating that the presence of oxygen is promoting the degradation of PET at the highest ageing temperature. Oxidative degradation of PET is initiated by heat and oxygen leading to the formation of hydroperoxides at methylene sites within the polymer chains.<sup>16</sup> These hydroperoxides are unstable and therefore undergo a series of chain scission degradation reactions. Degradation is further accelerated when ageing is performed under moist thermal conditions, with a decrease in molar mass noticeable from 140°C in wet nitrogen. This indicates that although significant degradation of PET does not occur under the influence of purely thermal conditions (i.e., dry nitrogen), the presence of water induces degradation of PET at lower ageing temperatures. Hydrolytic degradation of PET is reported to involve chain scission at the ester linkages. Each water molecule breaks down one ester bond, leading to the formation of one carboxyl and one hydroxyl group. During hydrolytic ageing of PET, it is believed that water diffuses into the amorphous regions of the polymer where hydrolysis occurs at a rate dependant on the sample shape, crystalline morphology of the sample, the relative humidity and temperature.<sup>12,13,17–20</sup> At temperatures below the glass transition temperature of PET, hydrolytic degradation is thought to be negligible. However, above the glass transition tempera-

ture, increased mobility of the polymer chains enables penetration of water into the amorphous regions, increasing the rate of hydrolytic degradation. Therefore, as the ageing temperature increases from 140°C to 190°C under thermal-hydrolytic conditions, more extensive degradation occurs with the most significant decrease in molar mass observed at 190°C. Similarly, the presence of water during the thermo-oxidative ageing of PET has significant impact on the molar mass distribution of PET. Samples aged under thermo-oxidative-hydrolytic conditions, at temperatures between 140°C and 190°C, all exhibit a pronounced decrease in the average molar mass with increased ageing temperature. A small decrease in the average molar mass values can be observed for PET samples aged under thermo-oxidative-hydrolytic conditions (i.e., wet air) at 140°C. The extent of this degradation is only marginally higher than that observed for degradation of PET under purely thermo-oxidative conditions (i.e., dry air) at 140°C. However, as the ageing temperature increases, the extent of degradation increases and a sharp decrease in the average molar mass can be observed for PET samples aged at 160, 170, and 190°C. All GPC curves for PET samples aged under all ageing environments can be found in the Supporting Information.

The GPC results therefore demonstrate that the dominant degradation reaction in PET differs with ageing temperature. At the lowest ageing temperature of 140°C, no significant changes in  $M_w$  are evident with contrasting ageing conditions and therefore it is impossible to deduce which degradation process is dominant. In contrast, the GPC results for PET indicate that hydrolytic degradation is the

**TABLE II**  
**GPC Average Molar Mass Results for PET Samples Aged Under Different Environments at Temperatures Between 140 and 190°C**

Ageing environment	Ageing temperature, °C	$M_w$ (g mol <sup>-1</sup> )	$M_n$ (g mol <sup>-1</sup> )	Polydispersity
Virgin	N/A	24900 ± 141	8725 ± 64	2.9
Dry nitrogen	140	24350 ± 71	8480 ± 57	2.9
Dry nitrogen	160	24200	8600 ± 57	2.8
Dry nitrogen	170	24650 ± 212	8660 ± 99	2.8
Dry nitrogen	190	24950 ± 71	8865 ± 78	2.8
Dry air	140	23800 ± 141	9120 ± 14	2.6
Dry air	160	24150 ± 212	9030 ± 71	2.7
Dry air	170	24550 ± 71	8830	2.8
Dry air	190	21300	7610 ± 14	2.8
Wet nitrogen	140	22950 ± 212	8310 ± 14	2.8
Wet nitrogen	160	22650 ± 354	8145 ± 21	2.8
Wet nitrogen	170	21600	8050 ± 42	2.7
Wet nitrogen	190	19350 ± 71	8000 ± 113	2.4
Wet air	140	23250 ± 212	8520 ± 14	2.7
Wet air	160	21100	7745 ± 50	2.7
Wet air	170	18800 ± 141	7025 ± 149	2.7
Wet air	190	16800 ± 141	6510 ± 156	2.6

dominant degradation reaction occurring between 160°C and 170°C. From Table II, it can be seen that degradation of PET is minimal under purely thermal and thermo-oxidative ageing conditions, indicating that even the presence of air is not enough to result in significant degradation of PET at 160°C and 170°C. However, significant changes in  $M_w$  can be observed in both PET samples aged under thermal-hydrolytic and thermo-oxidative-hydrolytic conditions indicating that hydrolytic degradation is likely to be the dominant degradation reaction occurring at 160°C and 170°C. Obviously, the decrease in molar mass is larger in PET samples aged at 170°C than 160°C indicating that progressively more hydrolytic degradation is occurring at 170°C due to increased mobility of the polymer chains. GPC results for PET aged under contrasting environments at 190°C illustrate that changes in  $M_w$  are not only influenced by the presence of water, but also oxygen. No significant changes in  $M_w$  can be observed under thermal conditions, indicating once again that thermal degradation of PET is minimal at temperatures up to 190°C. However, a large decrease in the molar mass of the aged system can be seen on the introduction of oxygen (i.e., dry air) at 190°C highlighting that the presence of oxygen, during ageing at increased temperatures, promotes the degradation of PET. The most significant decrease in  $M_w$  can be observed in PET samples aged under thermo-oxidative-hydrolytic conditions at 190°C. Therefore, as the temperature is increased, it is thought that oxidative degradation becomes the dominant degradation process, resulting in the largest changes in the molar mass of aged PET samples. The dominant degradation reaction in PET has therefore been shown to differ with ageing tempera-

ture. At lower temperatures, i.e., 140–170°C, it has been illustrated that hydrolysis is the dominant degradation reaction, with thermo-oxidative degradation dominating at the highest ageing temperature of 190°C.

Difficulties were experienced during the analysis of aged PEN samples by GPC due to the crystallinity that developed upon ageing. This was sufficient enough to render the polymer insoluble. As a consequence, all aged samples of PEN had to be rendered amorphous before dissolution was possible. This was performed simply by melting the samples at 320°C in a DSC and quenching to the amorphous state. While this involved imposing a new thermal history on all samples, it was hoped that the fact that all aged samples of PEN had the same thermal history superimposed, would still enable comparative use of the GPC data thus obtained.

Table III presents the  $M_n$ ,  $M_w$ , and polydispersity values determined by GPC for PEN samples aged under different environments at 190°C. The molar mass distribution curves for PEN can be found in the Supporting Information. Due to such minor changes observed in the overall molar mass distribution of PEN samples aged under the harshest conditions, i.e., 190°C, it was deemed unnecessary to analyze all other PEN samples by GPC. Comparison of the GPC data obtained for aged PEN samples reveals no significant changes in the overall molar mass of the aged PEN samples, in comparison to virgin PEN. Degradation of PEN, under all ageing conditions, is therefore minimal up to temperatures of 190°C. However, one question remains unanswered—why do the aged samples of PEN embrittle badly if the material has not degraded (i.e., no decrease in molar mass observed)?

TABLE III  
GPC Average Molar Mass Results for PEN Samples Aged Under Different Environments at 190°C

Ageing environment	Ageing temperature, °C	$M_w$ (g mol <sup>-1</sup> )	$M_n$ (g mol <sup>-1</sup> )	Polydispersity
Virgin	N/A	20200 ± 71	5455 ± 233	3.7
Dry nitrogen	190	20700 ± 283	5505 ± 276	3.8
Dry air	190	22950 ± 71	6490 ± 71	3.5
Wet nitrogen	190	19700 ± 141	4780 ± 0	4.1
Wet air	190	19650 ± 71	4760 ± 57	4.1

### Changes in physical morphology after ageing

Although distinct trends were evident in the molar mass distribution curves for aged PET, the overall thermal stability of the aged PET/PEN samples, assessed using TGA, was unchanged relative to the unaged samples. It was therefore of interest to determine if any significant changes in the physical morphology of PET and PEN could be observed as a result of ageing. Crystalline content and behavior was monitored in all samples using DSC.

#### Initial DSC heating cycle (cycle 1)

The initial DSC heating cycle was performed in order to destroy the thermal history of the samples prior to studying permanent morphological changes. However, it can also provide information on the extent of crystallinity in samples, formed as a result of ageing.

Figure 6 represents the initial DSC heating cycle obtained for PET samples aged under dry nitrogen between temperatures of 140°C and 190°C, in comparison to virgin PET. Table IV presents the temperatures of the DSC thermal transitions in all PET samples including the onset temperature of the crystalline melt ( $T_{\text{onset}}$ ), the maximum temperature of the crystalline melt ( $T_{\text{max}}$ ), and the enthalpy of the crystalline melt. Virgin PET shows a cold crystallization peak around 150°C, which is absent for the aged samples, indicating, as would be expected, that

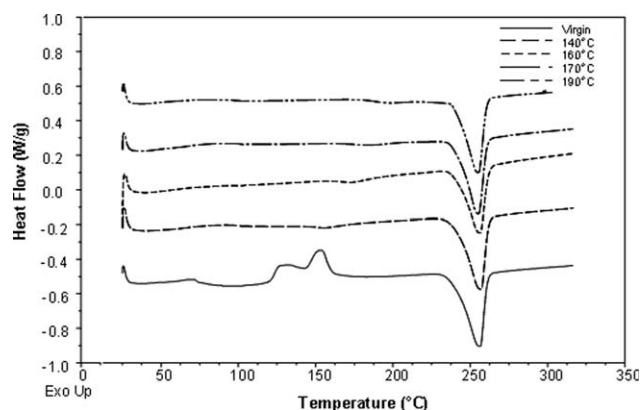


Figure 6 DSC curves of PET samples aged under dry nitrogen at temperatures between 140°C and 190°C, cycle 1.

they had crystallized during the ageing process. Small, so-called, annealing peaks are evident some 10–20°C above the ageing temperature in all aged samples of PET in addition to one crystalline melt peak. The  $T_{\text{onset}}$ ,  $T_{\text{max}}$ , and enthalpy of the crystalline melt peak were not found to differ significantly between samples of PET aged at 140, 160, and 170°C under dry nitrogen, in comparison to unaged PET. An increase in the enthalpy of the crystalline melt can be observed for PET aged at 190°C; however this is due to the annealing peak merging with the crystalline melt peak. The impact of thermo-oxidative, thermal-hydrolytic, and thermo-oxidative-hydrolytic ageing on the crystalline content/behavior of PET was found to be very similar to the results illustrated in Figure 6 for thermal ageing and can therefore be found in the Supporting Information.

The impact of thermal, thermo-oxidative, thermal-hydrolytic, and thermo-oxidative-hydrolytic ageing on the crystalline content/behavior of PEN samples was also found to be similar in all samples. Therefore only one example has been illustrated. Figure 7 represents the DSC curves obtained for PEN samples aged under dry nitrogen between temperatures of 140°C and 190°C, in comparison to unaged PEN. A glass transition can be observed at 117°C for unaged PEN and PEN aged at 140 °C; however as the glass transition phenomenon is purely an amorphous event, no glass transition temperatures can be observed in any PEN samples aged above 140°C due to the increased levels of crystallinity formed during ageing. Similarly, due to the increased levels of crystallinity in PEN samples aged above 140°C, no cold crystallization event is evident on heating and small annealing peaks become visible, identical to those observed in PET. Table V presents the temperatures of the DSC thermal transitions in all PEN samples including the  $T_{\text{onset}}$ ,  $T_{\text{max}}$ , and enthalpy of the crystalline melt. All DSC heating curves for PEN samples aged under dry air, wet nitrogen, and wet air can be found in the Supporting Information.

#### DSC cooling cycle (cycle 2)

The DSC cooling cycle provides useful information on the crystallization behavior of the polyesters.



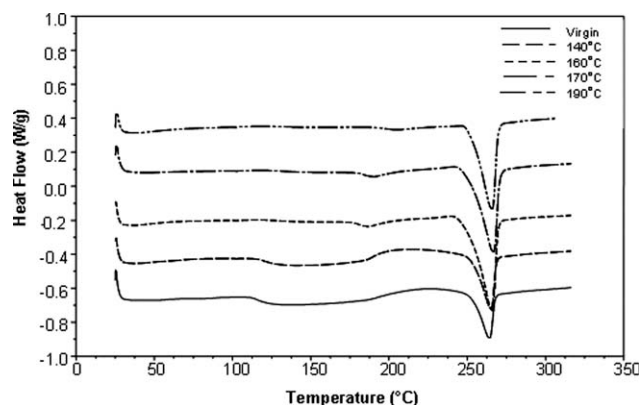
**TABLE IV**  
DSC Thermal Transitions in PET Samples Aged Under Different Environments at Temperatures Between 140°C and 190°C, Cycle 1

Ageing environment	Ageing temperature, °C	Enthalpy of crystalline melt, J g <sup>-1</sup>	T <sub>onset</sub> crystalline melt, °C	T <sub>max</sub> crystalline melt, °C
Virgin	N/A	35	241	256
Dry nitrogen	140	34	242	257
Dry nitrogen	160	30	242	256
Dry nitrogen	170	33	241	256
Dry nitrogen	190	42	244	254
Dry air	140	33	240	255
Dry air	160	36	241	255
Dry air	170	36	241	255
Dry air	190	43	240	255
Wet nitrogen	140	37	242	255
Wet nitrogen	160	38	241	255
Wet nitrogen	170	32	241	256
Wet nitrogen	190	41	244	258
Wet air	140	37	242	256
Wet air	160	36	241	256
Wet air	170	36	242	256
Wet air	190	34	242	256

Table VI presents the temperatures of the DSC transitions in all samples of PET including the  $T_{\text{onset}}$ ,  $T_{\text{max}}$ , and the enthalpy of crystallization. As can be seen, the PET samples aged in dry nitrogen are little different from virgin PET. A small increase in the enthalpy of crystallization can be observed for samples aged above 160°C; however the  $T_{\text{onset}}$  and  $T_{\text{max}}$  values for crystallization do not differ significantly. Interestingly, on observation of the DSC cooling cycles of PET samples aged under thermo-oxidative conditions (i.e., dry air), more significant variations in the crystalline behavior were identified. A distinct trend exists between the ageing temperature and extent of crystallization for PET samples aged above 140°C. On increasing the ageing temperature above 140°C, an increase in the enthalpy of crystallization is evident, indicating that samples aged above 140°C undergo crystallization at an increased rate in comparison to samples aged at 140°C and unaged PET. The onset temperature and temperature of maxi-

imum crystallization are highest for PET aged at 190°C, indicating that crystallization is occurring most readily in this sample as it is cooled. Such differences in the enthalpy of crystallization and thus rate of crystallization are thought to be due to increased mobility of the polymer chains as a result of degradation. On increasing the ageing temperature above 140°C, the extent of chain scission in amorphous regions progressively increases and thus results in formation of shorter chain fragments and free chain ends with increased conformational freedom. Subsequently, chain segments that were previously entangled can now readily crystallize, resulting in rapid crystallization and thus an increase in the overall enthalpy of crystallization. These results are in agreement with the decrease in molar mass observed from GPC as a result of thermo-oxidative degradation.

Under hydrolytic ageing conditions, degradation is also thought to occur rapidly, particularly at lower ageing temperatures. Therefore, it is expected that similar variations in the crystalline behavior will be observed from PET samples aged under a hydrolytic environment. On interpretation of the DSC cooling data, a clear trend exists once again between the extent of crystallization and ageing temperature of PET samples aged under hydrolytic conditions. On increasing the ageing temperature, an increase in the enthalpy of crystallization is evident, indicating that crystallization occurs at an increased rate, in comparison to unaged PET. The onset temperature and temperature maximum for crystallization are highest for PET aged under moist thermo-oxidative conditions at 190°C, indicating that crystallization is occurring most readily in this sample (i.e., the lowest molar mass sample) as it is cooled.



**Figure 7** DSC curves of PEN samples aged under dry nitrogen at temperatures between 140°C and 190°C, cycle 1.

**TABLE V**  
**DSC Thermal Transitions in PEN Samples Aged Under Different Environments at Temperatures Between 140°C and 190°C, Cycle 1**

Ageing environment	Ageing temperature, °C	Enthalpy of crystalline melt, J g <sup>-1</sup>	T <sub>onset</sub> crystalline melt, °C	T <sub>max</sub> crystalline melt, °C
Virgin	N/A	17	253	264
Dry nitrogen	140	18	254	265
Dry nitrogen	160	39	252	266
Dry nitrogen	170	36	252	267
Dry nitrogen	190	32	253	266
Dry air	140	37	252	265
Dry air	160	38	253	266
Dry air	170	38	252	265
Dry air	190	41	253	265
Wet nitrogen	140	35	253	267
Wet nitrogen	160	37	253	267
Wet nitrogen	170	37	252	265
Wet nitrogen	190	32	255	267
Wet air	140	39	252	266
Wet air	160	38	252	266
Wet air	170	34	253	267
Wet air	190	41	256	266

Therefore, this physical data illustrates that purely thermal degradation of PET is minimal up to temperatures of 190°C. In the presence of oxygen, however, significant changes in the enthalpy of crystallization were observed at ageing temperatures around 170–190°C, indicating that the presence of oxygen does significantly influence the degradation of PET at the highest ageing temperatures. This provides further evidence that the dominant degradation reaction at the highest ageing temperatures is thermo-oxidative degradation as previously suggested. Ageing of PET under hydrolytic conditions was found to have the most significant impact on the overall enthalpy of crystallization of PET at the lower age-

ing temperatures, indicating that hydrolysis is the dominant degradation reaction between 140°C and 160°C. Degradation was found to be most significant under thermo-oxidative-hydrolytic ageing conditions due to the combined effect of hydrolytic and oxidative reactions. These DSC results are thus in very good agreement with the GPC results reported previously.

In contrast to the results reported for aged samples of PET, no distinct changes in the crystallization behavior of PEN could be identified from the DSC cooling curves. All cooling curves were found to be identical for all PEN samples aged under different environments. Aged samples of PEN did not

**TABLE VI**  
**DSC Thermal Transitions in PET Samples Aged Under Different Environments at Temperatures Between 140°C and 190°C, Cycle 2**

Ageing environment	Ageing temperature, °C	Enthalpy of crystallization, J g <sup>-1</sup>	T <sub>onset</sub> crystallization, °C	T <sub>max</sub> crystallization, °C
Virgin	N/A	16	186	152
Dry nitrogen	140	16	189	155
Dry nitrogen	160	15	186	152
Dry nitrogen	170	21	188	154
Dry nitrogen	190	22	188	155
Dry air	140	16	183	151
Dry air	160	22	190	159
Dry air	170	25	188	157
Dry air	190	29	192	163
Wet nitrogen	140	22	191	159
Wet nitrogen	160	26	191	159
Wet nitrogen	170	27	189	159
Wet nitrogen	190	29	191	167
Wet air	140	22	189	156
Wet air	160	33	192	165
Wet air	170	35	193	166
Wet air	190	36	193	168

**TABLE VII**  
**DSC Thermal Transitions in PET Samples Aged Under Different Environments at Temperatures Between 140°C and 190°C, Cycle 3**

Ageing environment	Ageing temperature, °C	$T_g$ (°C)	Enthalpy of crystallization, $J g^{-1}$	$T_{onset}$ crystallization, °C	$T_{max}$ crystallization, °C	Enthalpy of crystalline melt, $J g^{-1}$	$T_{onset}$ crystalline melt, °C	$T_{max}$ crystalline melt, °C
Virgin	N/A	81	12	142	158	30	237	253
Dry nitrogen	140	81	8	143	160	29	238	253
Dry nitrogen	160	82	9	143	158	26	238	254
Dry nitrogen	170	82	9	140	161	32	236	251
Dry nitrogen	190	82	8	142	163	29	238	253
Dry air	140	82	10	142	158	29	237	253
Dry air	160	81	8	142	159	32	237	252
Dry air	170	81	7	141	157	33	238	253
Dry air	190	81	5	140	158	34	238	253
Wet nitrogen	140	81	9	141	160	32	237	253
Wet nitrogen	160	81	7	139	159	36	237	253
Wet nitrogen	170	82	5	138	160	32	238	253
Wet nitrogen	190	83	1	142	158	29	241	255
Wet air	140	81	8	141	159	32	238	253
Wet air	160	81	3	139	157	34	239	254
Wet air	170	82	2	137	155	35	239	254
Wet air	190	83	1	134	153	34	240	254

undergo crystallization on cooling, in contrast to the results reported previously for PET. Only a broad glass transition was observed in all PEN samples above 100°C. Due to the presence of bulky naphthalene groups in PEN, the ease at which PEN can arrange its polymer chains into regular domains is reduced, in comparison to PET. Additionally, the non-linear 2,6-substitution pattern of aromatic rings in PEN, compared to a 1,4 linear substitution of the phenyl group in PET, reduces its tendency to crystallize. Therefore no crystallization activity was observed from the DSC cooling curves of any aged samples of PEN. All DSC cooling curves for PET and PEN samples aged under thermal, thermo-oxidative, thermal-hydrolytic, and thermo-oxidative-hydrolytic environments can be found in the Supporting Information.

#### DSC second heating cycle (cycle 3)

Any permanent changes in morphology, as a result of ageing, can be observed in the second DSC heating cycle. Tables VII and VIII present the temperatures of the DSC thermal transitions in all aged samples of PET and PEN, respectively. All DSC reheat curves for PET and PEN samples aged under dry nitrogen, dry air, wet nitrogen, and wet air can be found in the Supporting Information.

The glass transition and cold crystallization processes remain unaltered between samples of PET aged under dry nitrogen and unaged PET. However, trends for PET samples aged under dry air are evident, where the amount of cold crystallization upon reheating decreases for samples aged under the most extreme conditions, as a simple consequence of

increased crystallisation during the cooling cycle. Generally, the melting process was found to be relatively constant between all aged samples of PET, suggesting that no gross morphological changes occurred as a result of ageing. Similarly, the glass transition temperature of PEN remains unaltered with ageing and the crystallization events all remain similar between aged and unaged samples of PEN. The enthalpy and maximum temperature for cold crystallization of PEN are all difficult to determine due to low levels of crystallinity in all samples.

#### Relationship between mechanical properties and ageing conditions

From the ageing studies, completed on PET and PEN, the extent of degradation has been shown to differ between both polymers. Degradation of PET was largely influenced by the ageing environment and temperature. Although the overall thermal stability of PET remained unchanged after ageing, variations in the molar mass and crystalline content/behavior were observed in aged PET samples, in addition to a loss in mechanical strength. The dominant degradation mechanism in PET was shown to differ with the ageing temperature. At lower ageing temperatures, i.e., 140–170°C, hydrolysis was revealed as the dominant degradation reaction, with thermo-oxidative degradation dominating at the highest ageing temperature of 190°C.

In contrast to PET, all ageing environments and temperatures were found to have no detrimental effect on the overall thermal stability, molar mass, or crystallization content/behavior of PEN. It is thought that this could be due to either one or a

**TABLE VIII**  
**DSC Thermal Transitions in PEN Samples Aged Under Different Environments at Temperatures Between 140°C and 190°C, Cycle 3**

Ageing environment	Ageing temperature, °C	$T_g$ (°C)	Enthalpy of crystalline melt, J g <sup>-1</sup>	$T_{\text{onset}}$ crystalline melt, °C	$T_{\text{max}}$ crystalline melt, °C
Virgin	N/A	122	3	255	264
Dry nitrogen	140	123	3	256	265
Dry nitrogen	160	122	3	256	265
Dry nitrogen	170	123	1	256	265
Dry nitrogen	190	123	1	256	265
Dry air	140	122	5	256	264
Dry air	160	123	3	256	265
Dry air	170	123	3	256	265
Dry air	190	123	2	254	265
Wet nitrogen	140	124	3	257	266
Wet nitrogen	160	123	3	256	265
Wet nitrogen	170	123	3	256	265
Wet nitrogen	190	123	1	257	265
Wet air	140	123	5	256	265
Wet air	160	123	4	257	265
Wet air	170	124	3	257	266
Wet air	190	123	3	256	265

combination of the following factors: (1) reduced chain mobility due to the significantly increased glass transition of PEN (122°C) in comparison to PET (80°C); (2) increased crystallinity of PEN, in comparison to PET. This could contribute to the lack of chain scission reactions and thus overall extent of degradation as crystallites are impermeable to water and can act as barriers to oxygen and water; (3) hydrophobicity effects—the lack of degradation observed could simply be a result of increased hydrophobicity effects in PEN, in comparison to PET. The overall mass fraction of non-polar, aromatic sequences in PEN is greatly increased, due to the presence of additional phenyl rings. This results in a material with increasing hydrophobic character. However, none of above factors provides an explanation as to why aged samples of PEN embrittle badly when no decrease in molar mass is observed.

This leads us onto believe that the embrittlement of both PET and PEN upon ageing seems to have a physical rather than a chemical origin. Although at the most extreme ageing conditions for PET, a drop in molar mass is observed, this is too small to account for the severe embrittlement. Instead, we propose that the change in mechanical properties, in both PET and PEN, is due to crystallization upon ageing, and secondary crystallization in particular. Separate experiments not included here, illustrate that the primary crystallization process of PET and PEN is complete within 25 minutes and 60 minutes, respectively, at 140°C. Therefore, over the 24 h of the ageing process, considerable secondary crystallization can occur. Such crystallization has been shown in the past to cause remarkable changes in mechanical properties. This is most notorious in the Biopol polyesters where secondary crystallization

upon room temperature storage embrittled moldings and extrusions, even when plasticized, to the extent that it threatened the commercial development of the polymers.<sup>21–27</sup> The degree of secondary crystallization, in the Biopol polyesters, was so small that it could not be readily detected by DSC, except through the presence of a low temperature so-called annealing melting peak as observed in the DSC curves of aged samples of PET and PEN.

## CONCLUSIONS

The extent of degradation in PET and PEN has been examined after ageing under contrasting drying conditions, enabling the effects of temperature, water, and oxygen to be mapped onto the resultant property changes. Degradation of PET was found to be largely influenced by the ageing environment and temperature and the dominant degradation mechanism was shown to differ with ageing temperature. In contrast to PET, the increased thermal and hydrolytic resistance of PEN has been illustrated with all ageing environments and temperatures having no detrimental effect on the overall thermal stability, molar mass, or crystallization content/behavior of PEN. Embrittlement of both PET and PEN after ageing has been proposed to originate from secondary crystallization developed upon ageing, causing remarkable changes to mechanical properties.

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