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The effect of thermal ageing on carbon fibre-reinforced polyetheretherketone (PEEK)

Part II *Morphological changes*

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The morphological properties of carbon fibre-reinforced PEEK (APC-2) laminates subjected to long-term thermal ageing and cycling treatments have been studied using differential scanning calorimetry and wide-angle X-ray diffraction techniques. This work sought provided a structural explanation for measured changes in mechanical properties. Annealing at 120° had no effect but significant changes in crystal content and crystal perfection occurred at 250° and 310 °C. At 250 °C, for short ageing periods, both crystal growth and perfection processes were observed. For longer ageing periods, there was a multiple increase in capital perfection. Initial ageing at 310 °C caused rapid crystal growth, but further ageing resulted in a reduction in measured crystal contents due to thermal degradation.

1. Introduction

Polyetheretherketone (PEEK) is a semicrystalline thermoplastic polymer with attractive properties for use in structural composites. One particular grade, APC-2, is reinforced, 68% by weight. PEEK can crystallize at temperatures between its glass transition temperature, T_g, 145 °C, and its melting temperature, T_m, 343 °C. With such a wide crystallization window, processing and any subsequent thermal treatment can cause significant crystal morphology changes which, in turn, affect the mechanical properties of PEEK and its composites [1, 2]. It has been demonstrated that although two different PEEK polymer samples contain the same degree of crystallinity, obtained by varying the cooling rate, they exhibited significantly different tensile behaviour [3]. Such a response is a result of differences in crystal size and size distribution in the respective samples. The strong dependence of mechanical properties on crystal morphology is well known from studies with other polymers [4].

It has been found that PEEK, similar to polyethyleneterephthalate (PET), shows multiple endothermic fusion peaks where the lower temperature peak was found to have been induced by all annealing processes [5, 6]. Although progress towards the understanding of PEEK's morphology and its effect on mechanical properties has been made, considerable controversy still exists over the origin of this double melting peak phenomenon [1]. In general, the two most important hypotheses are:

(a) the peaks are related to a melting and recrystallization phenomenon of a single-crystal morphology [5–7]. The small low-temperature peak is characteristic of the crystal structure prior to scanning and the high-temperature peak is a result of continuous melting, recrystallization, and reorganization processes which take place during the scan;

(b) the peaks are associated with separate crystal entities [3, 8, 9]. The crystallites that form first are associated with the upper melting peak while the crystals formed later are laid down in between the first-formed crystallites, i.e. they are different components of the morphology.

This paper reports the effect of long-term thermal ageing on the crystal morphology of various APC-2 laminates. It complements work on the effects of long-term thermal ageing on mechanical properties [10].

2. Experimental procedure

Laminate production and thermal ageing programmes were as described previously [10].

2.1. Wide-angle X-ray (WAXS) studies

WAXS scans were obtained using a Philips 1050 vertical goniometer with 1° divergence and convergence slits and a 0.2 mm scatter slit following techniques outlined elsewhere by other researchers [11]. Unidirectional laminate sections, 20 mm^2, were inserted into the sample holder and the diffraction profiles were recorded at a scanning rate of $1° \ 2\theta \ min^{-1}$ over an angular range of $4° < 2\theta < 40°$.

2.2. Differential scanning calorimetry (DSC)

A Du Pont differential scanning calorimeter coupled to a 1090 data collection and analysis station was used to assess the crystal morphology of the APC-2 laminates. Samples were scanned from room temperature

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(RT) to 400 °C at 10 °C min^{-1} under a continuous nitrogen gas flow. Using a value of 130 mJ mg^{-1} for the enthalpy of melting for 100% crystalline [12] PEEK, the percentage crystallinities of the laminates were obtained.

3. Results

A number of DSC scans of amorphous APC-2 laminates were generated. There is a T_g step at 145 °C, followed by a crystallization exothermic peak at 175 °C and the associated melting endotherm at 343 °C. The area underneath the crystallization peak is only 75% of the area underneath the corresponding melting peak. Similar differences have been reported previously [12]. There are two possible explanations for this. First, assuming that the composite is perfectly amorphous, there is a continuous increase in crystallinity during the scan which is not detectable in the DSC baseline. Secondly, it is also possible, because semicrystalline polymers are difficult to obtain in a fully amorphous state, that a certain amount of crystallinity existed at room temperature prior to scanning.

Fig. 1 displays the DSC scan for both unidirectional and cross-ply laminate geometries prior to ageing. As previously mentioned, both laminates were isothermally crystallized at 210 °C and the corresponding broad endotherm indicates a broad distribution of crystal sizes present in the composite. The responses appeared to be geometry independent. Ageing at the lower temperature of 120 °C, which is below the polymer's T_g, does not affect the crystalline component, and therefore the melting behaviour as monitored by DSC remains unaltered.

Fig. 2 shows scans for a unidirectional laminate aged at 250 °C for periods of up to 76 weeks. Their traces are characterized by two melting processes. A smaller low-temperature melting endotherm occurs above the ageing temperature and a large high-melting peak whose profile is identical to that previously found for control laminates. Ageing for longer periods causes the small peak to shift to higher temperatures and become part of the main melting endotherm. This process occurs rapidly for short ageing periods while prolonged ageing continues the process but at a much slower rate. However, when the small peak becomes a shoulder on the main endotherm, the process is not interrupted. The onset temperature continues to shift to higher temperatures although the position of the main melting peak is not influenced, i.e. its offset and peak temperatures remain constant. It is also noted that the size of the small peak goes through a maximum after 3 days and decreases thereafter as it shifts into the main endotherm. These trends are common for both laminate geometries and thermally aged and cycled laminates exhibit similar responses.

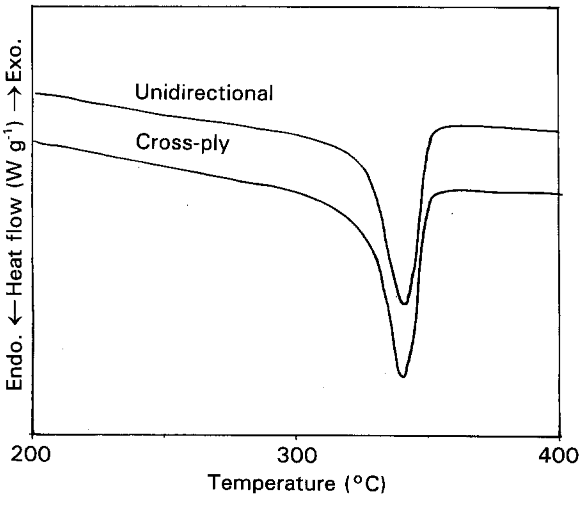

Figure 1 DSC response for control unidirectional and cross-ply laminates.

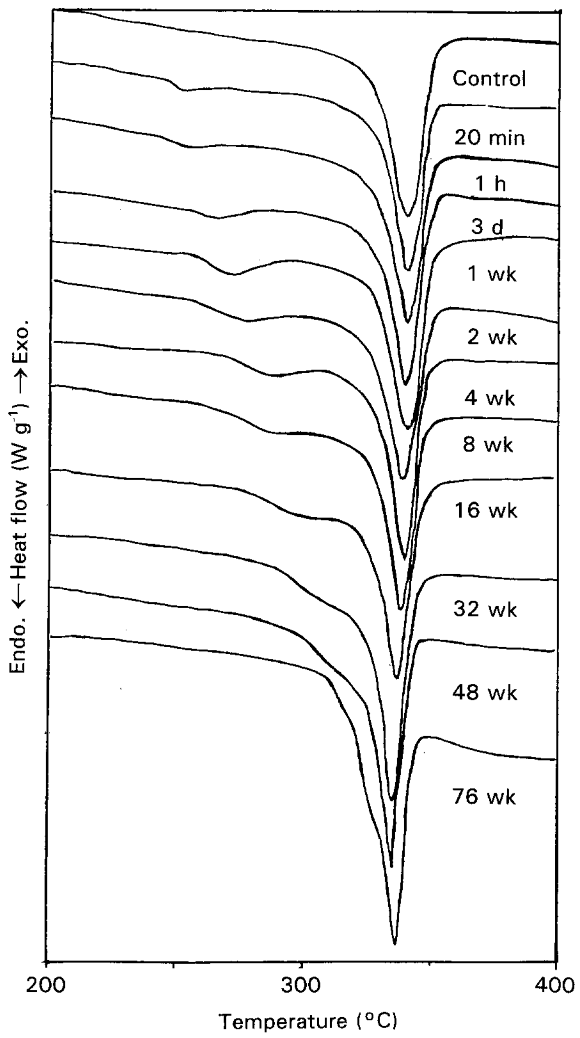

Figure 2 Effect of ageing time at 250 °C on the DSC response of unidirectional laminates.

When ageing at 310 °C, two endothermic peaks appear after short annealing times (3 days cross-ply) whereas longer annealing leads to one peak only, Fig. 3. The size of the main peak initially increases. Further ageing causes a continuous reduction in its size although the peak itself becomes narrower and sharper and moves to higher temperatures for longer ageing periods. Both geometries exhibit similar trends.

Typical WAXS scans for laminates stored at 250 °C are shown in Fig. 4. Using the technique outlined by Blundell *et al.* [11], the measured per cent crystallinity of the unidirectional control laminate is 18% which is

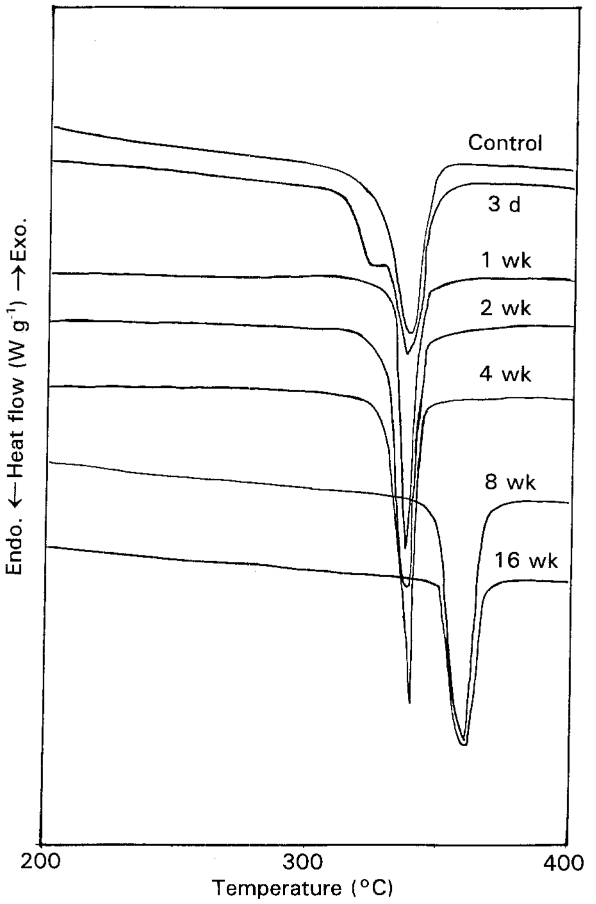

Figure 3 Effect of ageing time at 310 °C on the DSC response of laminates.

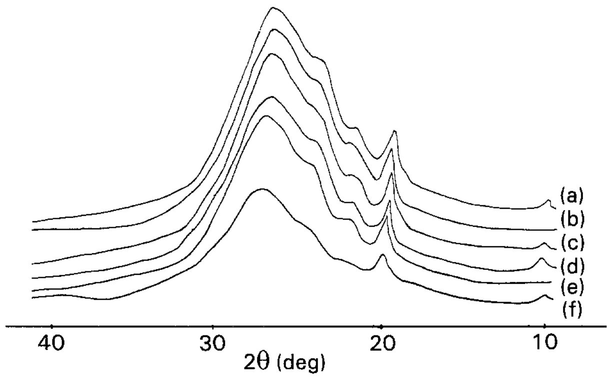

Figure 4 Effect of ageing time at 250 °C on the WAXS response of laminates. (a) Control, (b) 8 wk, (c) 16 wk, (d) 32 wk, (e) 48 wk, (f) 76 wk.

much lower than that measured by DSC, Table I. On ageing at 250 °C, the crystalline component increased to 24% after short ageing periods and equilibrated at this level. The measured degree of orientation of the polymer crystals was found to be 0.4, which is believed to be relatively weak. Randomly oriented pure PEEK exhibits a ratio of about 0.3. The degree of orientation initially increased on ageing but decreased thereafter. Thermal cycling at 250 °C showed similar trends. Ageing at 310 °C showed an initial heightening of the crystal reflection, and as degradation took place, the peaks diminished and disappeared fully; finally after 14 weeks, only the carbon halo remained, see Table II.

TABLE I The effect of ageing unidirectional APC-2 laminates at 250 °C on its crystalline phases as measured by WAXS

Time (wk)	Crystallinity (%) (h1 1 0/hc × 127)	Degree of orientation (h2 0 0/h1 0 0)
0	18.7 (29%DSC)	0.35
8	24.9	0.5
16	25.4	0.42
32	24.9	0.46
48	27.2	0.42
76	25.0	0.38

TABLE II The effect of ageing unidirectional APC-2 laminates at 310 °C on its crystalline phases as measured by WAXS

Time (wk)	Crystallinity (%)	Degree of orientation
Control	24	0.41
3 d	45.7	0.41
1	30.4	0
2	22.7	0
4	9.76	0
8	2.38	0

4. Discussion

Both DSC and WAXS analytical techniques involve uncertainties in assessing polymer crystallinity. X-ray diffraction affords a direct determination of three-dimensional order. While it is regarded as the foremost method in assessing crystallinity, separating the amorphous and crystalline scattering is not absolute and constructing a baseline can be difficult. DSC measures properties related to the degree of crystallinity through calculations involving heats of fusion. The main drawbacks are again the definition of a proper baseline and that crystallization takes place during the heating scan. Therefore, if hypothesis (a) is correct, then the crystal content, as measured by DSC, is not necessarily that of the sample at room temperature before testing. Owing to these difficulties, it was decided that DSC analysis be used to monitor morphological changes (double melting peak) and WAXS analysis to quantify these changes.

In order to confirm the origin of the multiple melting peaks found on annealing APC-2, it is important to establish the dependence of the peaks position and size on the heating rate during DSC analysis. A superheating effect has been observed for secondary melting in a number of polymers as indicated by a shift in the lower melting peak to higher temperatures as the thermal scanning rate increases. This has been explained as follows. In general, at fast scan rates, no recrystallization can take place and the position of the peaks is characteristic of the melting of the crystal structure. At low scan rates, reorganization will occur and the thermal response is due to competing melting and crystallization processes. It has been shown [6, 13] that the heating-rate dependence for PET is consistent with that of a melting/recrystallization phenomenon that occurs during the DSC scan. Other

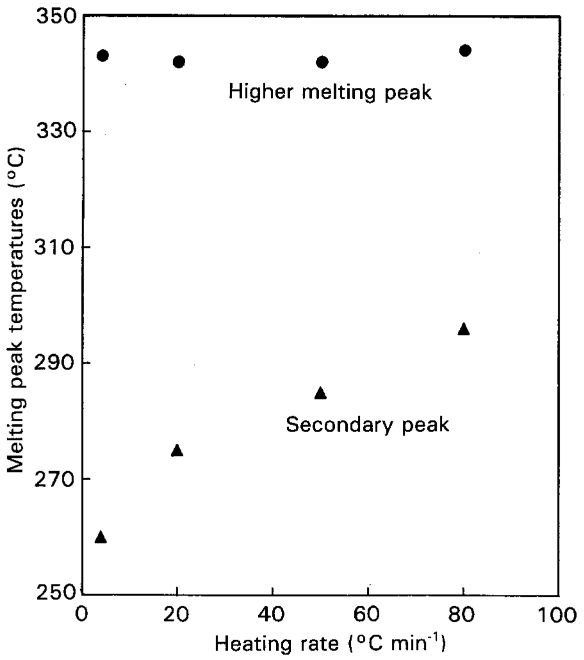

Figure 5 Effect of heating rate on melting temperature.

workers [5, 14] have suggested that continuous melting/recrystallization occurs during calorimetry for both PEEK and APC-2 between the annealing temperature and T_m by showing that crystallinity changes occur when measured using WAXS and density techniques. There were disparities in measured crystallinities between these two techniques used, but this was attributed to the theoretical bases of the individual measuring techniques and the assumptions used therein. Bassett *et al.* [8] found that the variations in peak size and position for PEEK polymers are small when measured at various scanning rates and then concluded that the two peaks are related to different textural components within the structure. However, these results are questionable, because thinner samples were used at faster heating rates; such a geometry change can significantly affect the resulting melting scans.

A heating-rate experiment was carried out in this investigation for APC-2 [15]. A "superheating" effect was observed for the small melting peak as both the size and position of the secondary peak was found to be dependent on heating rate, Fig. 5. However, the position of the higher melting peak did not exhibit any such dependency. This is contrary to the findings of other workers [14]. These effects support the thesis of reorganization occurring during a DSC scan of crystallized APC-2.

However, WAXS analysis shows that during ageing the overall crystal content increases from 18% to 24% after 16 weeks which may correspond to the onset, growth and movement of the secondary endotherm into the larger melting endotherm. Heat treatment of PET is believed to result in the formation of crystallites in the amorphous interlamellar material, although the resulting X-ray reflections were relatively insensitive [6]. This phenomenon was also observed for PEEK where the introduction of the secondary endotherm was assigned to the infilling of the dominant lamellae by subsidiary lamellae which crystallized in increasingly restricted circumstances [8]. Under the conditions of annealing imposed in this project, that is, a relatively low annealing temperature of 250 °C, it is difficult to perceive how the lower melting endotherm, which by hypothesis (a) corresponds to the majority of the crystal prior to scanning, could change so dramatically on ageing.

It is perhaps more plausible that hypothesis (b) is applicable to APC-2. Holding laminates at 250 °C may cause a continuous melting and recrystallization process to occur. When this process is interrupted by the removal of the samples from the oven and slowly cooling to room temperature, the process is discontinued. Upon rescanning, a melting endotherm is found above the ageing temperature corresponding to the crystals that formed and perfected isothermally on annealing, Fig. 2. As the scan proceeds, the melting/recrystallization process is re-established, displaying a main endothermic melting peak similar to that of the control laminate. Further ageing causes a continuous growth and perfection process to occur shifting the smaller endotherm to higher temperatures and becoming part of the main endotherms after ageing for 16 weeks. This growth process is confirmed from WAXS analysis where the crystal content increases from 18% to 24% over this time period. Initially as the ageing proceeds the size of the small endotherm increases to a maximum after 3 days. Further ageing causes a continuous perfection and growth process to occur, shifting the more perfect and stable crystals to higher temperatures which subsequently melt as part of the main endotherm. This is revealed by a reduction in the size of the small endotherm on ageing. These trends are common for both laminate geometries, and thermally aged and cycled laminates exhibit similar responses.

Ageing at 310 °C corresponds to a temperature close to the onset of melting (326 °C) of the crystals initially isothermally formed at 210 °C. Therefore, melting and recrystallization of the majority of these crystals can occur to form more perfect entities. This occurs by a lamellar thickening and interlamellar growth process. When the ageing process is interrupted, the melting process of the highly perfect and stable crystals occurs at such a high temperature that the melting/recrystallization process is unable to be, or is only partly, re-established. This is illustrated by unidirectional and cross-ply laminates, respectively. In general, a single endothermic peak is evident and, on ageing, further crystal perfection causes the melting endotherm to become narrower and sharper and move to higher temperatures (Fig. 3). The size of the peak initially increases owing to the crystal growth process; however, longer ageing times cause matrix degradation and therefore a reduction in the crystal content.

5. Conclusion

Significant changes in crystallinity occurred in thermally aged PEEK laminates as measured by both DSC and WAXS techniques. Experimental results suggest that for short ageing times at 250 °C, both crystal growth and perfection processes were in operation, while at longer ageing periods, crystal growth processes diminished and the average perfection of the formed crystals increased. Initial ageing at the higher temperature of 310 °C caused rapid crystal growth. However, further ageing caused a reduction in the measured crystallinity probably associated with matrix degradation but an increase in the perfection of the remaining crystal structure.

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