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Fabrication characteristics of a carbon fibre-reinforced thermoplastic resin

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Investigations are described which were designed to identify the origin of the phenomenon of kinking in carbon fibre-reinforced polyetheretherketone (PEEK). Preliminary observations upon the production and subsequent behaviour of specimens of the pure matrix resin led to the recognition of the inducement and subsequent relaxation of preferred molecular orientations, which could result from changes of temperature and pressure. These observations were followed by a series of experiments upon commercial prepreg, from which some of the critical parameters in kink formation were identified.

1. Introduction

High-performance fibre-reinforced composites are sometimes fabricated from continuous fibre and fabric reinforcements embedded in a thermosetting resin matrix. Thermoplastic resins are currently receiving considerable attention as potential composite matrices because of the attractions of their fabrication process compared with that of thermoset-based composites, e.g. short cycle time, absence of post cure, low level of volatiles, etc., and because of the physical properties of the finished product, e.g. higher resistance to penetration by water [1, 2]. Thermoplastic prepreg also has better storage properties than thermoset prepreg, because the resin matrix is in the fully cured condition. However, detailed examination of composite panels based upon thermoplastic matrix resins has revealed localized areas of fibres displaying a wavy appearance. These characteristics, which have been noted in studies of other properties, e.g. [3], are not present in the prepreg from which the panels were fabricated and they frequently extend through the thickness of the panel, thereby resulting in a degradation of mechanical properties. The present enquiry aimed to investigate the origin of this phenomenon and is related to that of an earlier study [4], which was concerned with the occurrence of kinks in fibres of composites based upon a thermoset matrix. However, the two systems are different in a number of important respects and there is no a priori reason for irregularities in fibre geometry within them to have the same origin.

2. Materials of the investigation

The thermoplastic resin system which forms the matrix of the composite system under study is ICI's aromatic polymer polyetheretherketone, known commercially as Victrex PEEK [5, 6]. The carbon fibre within the composite is designated AS-4. The two together make up a composite known as Aromatic Polymer Composite (APC-2).

3. Thermal cycling behaviour of the resin matrix

PEEK, which is available in pellet form, is designated 45 G. One plate of resin, plate 1, was produced by subjecting PEEK (grade 380 P) granules to heat and pressure and another, plate 2, by injection moulding PEEK (grade 450 P).

Specimens measuring approximately 40 mm long × 20 mm wide × 3 mm thick were cut from the plates with a lubricated stainless steel diamond-loaded disc saw. The preparation was completed by hand grinding. After mounting the specimens in an oven, temperature-induced dimensional changes in the specimens were measured with the aid of the quartz push rod dilatometer, further details of which are given elsewhere [7].

Fig. 1 shows results of in-plane fractional length changes observed in specimens cut from plate 1, as these were heated from ambient at a rate similar to that employed in composite manufacture, i.e. $5^\circ C\,min^{-1}$ and subsequently allowed to cool naturally. Clear evidence of a length reduction resulting from the cycling was evident and this led to a subsequent temperature excursion of a second specimen cut in the same in-plane orientation from plate 1, this time at the rate of $1^\circ C\,min^{-1}$. Subsequent temperature excursions to 330° C established that the contraction resulting from the slower cycle had produced a stable physical form of the resin, as shown in Fig. 2. The temperature-dependent dimensional behaviour in the thickness direction, obtained by cycling a specimen cut perpendicular to the plane of plate 1 at the rate of $1^\circ C\,min^{-1}$, is also illustrated in Fig. 2. The

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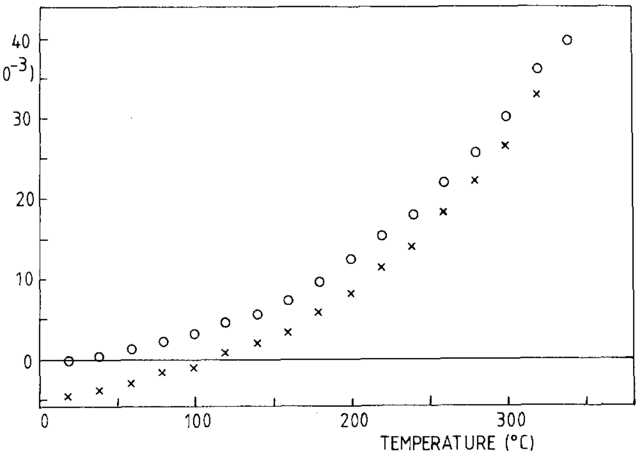

Figure 1 The fractional in-plane dimensional change of plate 1 resulting from (○) heating from ambient at the rate of 5° C min^{-1} and (×) subsequent cooling without constraint.

expansion resulting from the cycling is evident. The corresponding volume changes calculated from the linear changes displayed in Fig. 2 show an overall volume reduction of approximately 1%. There is evidence in Fig. 2 of a change of slope in the results in the neighbourhood of the glass transition temperature, $T_g \simeq 145°$ C. There is also evidence of a change of slope near the crystallisation temperature $T_c \simeq 180°$ C. Taken together, these results suggest that a preferential aligning of molecules of the resin had resulted from the fabrication process and that subsequent slow heating had allowed the molecules to change their orientation. By contrast, although the results for specimens prepared from plate 2, shown in Figs 3 and 4 are not identical for the in-plane and out-of-plane direction, they are qualitatively similar and both display a dimensional reduction of some 1.5% as a result of cycling, leading to an overall volume reduction of more than 4%. It appears that plates of resin produced by injection moulding are more nearly isotropic than those produced by heating and pressing, but they are less well consolidated.

4. Thermal cycling behaviour of the preimpregnated carbon fibres

Turning attention to the prepreg from which the CFRP panels were later fabricated, the temperature-dependent behaviour of the tape described in Table I, was examined. The temperatures employed within the manufacturer's recommended production cycle for fabricating laminates are achieved by heating at a rate of 6° C min^{-1} to a temperature of 390° C, cooling rapidly to 246° C, following by a further cooling to room temperature at a rate of 5° C min^{-1}. Strips of the prepreg were subjected to this sequence of temperature changes and it was found that waves in the fibres first appeared at a temperature of approximately 356° C, increasing in number as the temperature rose to 370° C. The waves in the prepreg tape were distributed fairly evenly over the area of a specimen.

The effect of tensioning specimens of prepreg during temperature cycling was examined by hanging a mass of approximately 650 g from the ends of strips of prepreg measuring approximately 270 mm long × 15 mm wide. The loaded specimens were heated at a rate of approximately 6° C min^{-1} to 390° C, after which they were allowed to cool naturally to room temperature. A marked improvement in straightness of the fibres was observed in the strips cycled with a tensile stress of approximately 2 MPa. Subsequent rapid heating to 400° C, without application of a tensile stress, followed by natural cooling, produced no further changes in the appearance of the specimens.

It was demonstrated that the dimensions of a specimen of prepreg were important in determining the occurrence of kinks. Tests were conducted by placing specimens of different sizes in an oven which had been pre-heated to 400° C, leaving them for 10 min and then examining them for kinks. An increase in surface roughness was noted as a result of the heat treatment, suggesting some lateral movement of resin and/or fibre. Up to a specimen length of 30 mm there was no evidence of kink formation. The first signs of kinking appeared in 40 mm long specimens and the effect increased with specimen length. Examination of the specimens revealed no evidence of a critical width for

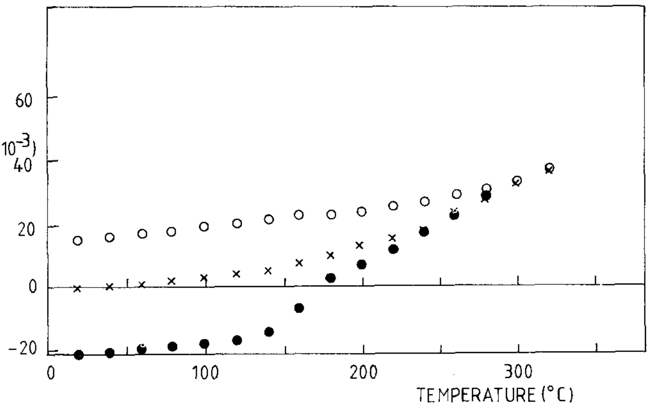

Figure 2 The fractional dimensional changes of plate 1 resulting from heating from ambient at the rate of 1° C min^{-1} (○) in-plane, (●) out-of-plane; subsequent cooling without constraint, re-heating and cooling for a second time, both in-plane and out-of-plane (×).

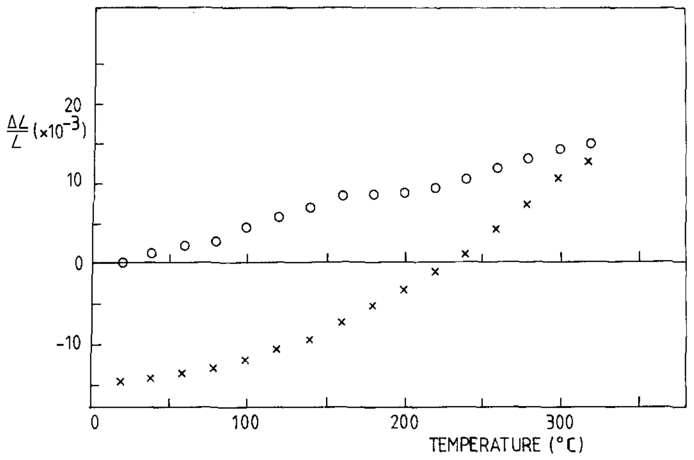

Figure 3 The fractional in-plane dimensional change of plate 2 resulting from (○) heating from ambient at the rate of 1° C min^{-1}; (×) subsequently cooling without constraint, re-heating and cooling for a second time.

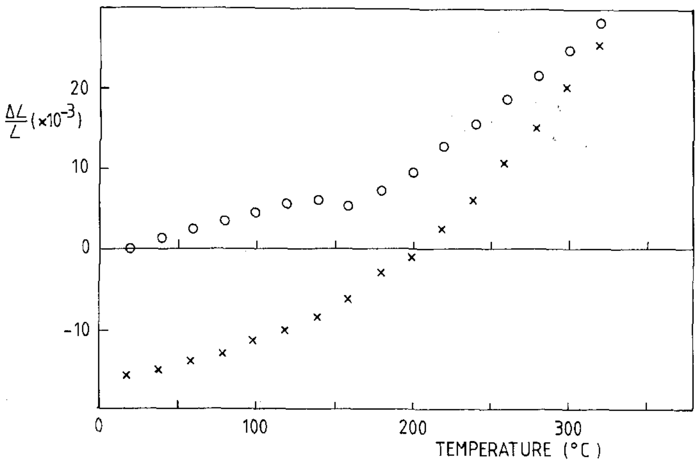

Figure 4 The fractional out-of-plane dimensional change of plate 2 resulting from (○) heating from ambient at the rate of 1° C min^{-1}; (×) subsequently cooling without constraint, re-heating and cooling for a second time.

the formation of kinks in a series of specimens whose length, 270 mm, was well in excess of the critical value.

The earlier observation that kinks formed at 356° C led to the investigation of the effects of the heating cycles 1 and 2 in Table II. It was considered that by more slowly traversing the temperature region in which kinking had been observed to occur, the molecular reorientation in the PEEK and the release of strain in the fibres might take place without displacing the fibres. However, this was not borne out and both heating cycles produced kinking in the prepreg. It was therefore decided to use a much slower heating rate from room temperature and to reduce the rate to 1° C h^{-1} over a larger range of temperature, from 330 to 370° C. This procedure, cycle 3 in Table II, resulted in the specimens arriving at 370° C in a kink-free condition, after which they were cooled rapidly to 246° C and then more slowly, at approximately 5° C min^{-1}, to room temperature.

Although cycle 3 produced a prepreg which would not kink when reheated to 370° C, it was found that a consolidated laminate could not be made from it. During the initial slow heating it was thought that the outer surface of the PEEK was oxidized, and it is suggested that this skin prevents the matrix flowing to consolidate the laminate. It would have been of much interest to have subjected prepreg to cycle 3 in an inert atmosphere.

TABLE I Properties of the prepreg tape

Standard width	140 mm
Nominal thickness	0.2 mm
Weight of carbon per unit area	145 g m^{-2}
Fibre content (by volume)	62%
Fibre content (by weight)	68%
Average number of fibres per tow	6000

5. Moulding characteristics of laminates

The recommended cure cycle for panels of CFRP manufactured from prepreg APC-2, i.e. carbon fibre in a matrix of PEEK, is summarized in Table III. An attempt was made to produce kink-free laminates by processing at somewhat lower temperatures, compensating for the lower temperatures by applying increased pressures for longer times. Details of the revised cycle are summarized in Table III. The intention was to keep below the critical temperature region in which

TABLE II Heating cycles

Cycle	Heating rate (° C h^{-1})	Temperature range (° C)
1	300	20–350
	10	350–370
	300	370–390
2	420	20–350
	1	350–370
	300	370–390
3	10	20–330
	1	330–370
	10	370–390

TABLE III Details of the production of test panels

	ICI cycle	Revised cycle	Vacuum-bag moulding cycle
1st stage	380° C 0.48 MPa 10 min	350° C 0.55 MPa 10 min	400° C 0.10 MPa 10 min
2nd stage	1.38 MPa 5 min	1.52 MPa 8 min	Cooled to 20° C and 0.10 MPa at 5° C min^{-1}
3rd stage	190° C 2.07 MPa 5 min Allowed to cool naturally on the bench	140° C 2.21 MPa 8 min Allowed to cool naturally on the bench	

kinks were believed to form. An additional experiment was conducted employing a higher upper temperature and a reduced pressure, obtained by using a vacuum-bag mould. Details of this cycle are included in Table III and details of the fibre lay-up of specimen plates are collected in Table IV. However, none of the plates produced by these different processes proved to be significantly better than plates produced employing standard procedures.

6. Conclusions

The most promising way to produce a kink-free laminate would seen to be to pretreat the prepreg so as to allow molecules of matrix resin to achieve an equilibrium configuration and to allow for the relief of any residual fibre stresses, without laterally displacing the fibres. This might best be achieved by approaching the important temperature region, between approximately 330 and 370° C, at an acceptably rapid rate which is commensurate with the absence of kink formation, passing through this region sufficiently slowly to allow the equilibrium processes to occur and then return to room temperature. The whole process should be undertaken in an inert gas atmosphere in order to prevent oxidation, with the prepreg under tension. The final product would be expected to be stress-free prepreg, from which kink-free laminates might be manufactured. Details of the exact sequence of events in the thermal conditioning process require further study.

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TABLE IV Lamina configurations in test panels

	Lay-up
ICI cycle	0°, +45°, −45°, 0°, 0°, −45°, +45°, 0° 90°, 0°, 90°, 0°, 0°, 90°, 0°, 90° −45°, +45°, −45°, +45°, +45°, −45°, +45°, −45°
Revised cycle	0, +45°, −45°, 0°, 0°, −45°, +45°, 0° 90°, 0°, 90°, 0°, 0°, 90°, 0°, 90° −45°, +45°, −45°, +45°, +45°, −45°, +45°, −45°
Vacuum-bag moulding cycle	Unidirectional
	−45°, +45°, −45°, +45°, +45°, −45°, +45°, −45°