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

Part I *Static and dynamic flexural properties*

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The static and dynamic mechanical properties of carbon fibre-reinforced PEEK (APC-2) laminates subjected to long-term thermal ageing and cycling treatments have been studied using three-point bend flexure tests. Results are discussed with respect to morphological changes and degradation analysis. S/N curves were modelled using fatigue modulus degradation data. Ageing laminates at high temperatures, for long time periods, between the glass transition temperature, T_g, and the melting temperature, T_m, caused a significant reduction in mechanical properties. However, for short ageing periods, a crystal-perfection process occurs which enhanced the low stress level fatigue resistance of both laminate geometries.

1. Introduction

APC-2 is a thermoplastic-based composite reinforced with carbon fibres. The matrix material polyetheretherketone (PEEK) is a semicrystalline polymer whose micro-structure and, therefore, its mechanical properties are influenced by the composite's previous thermal history and manufacturing process [1, 2]. Changes in the overall crystal content, spherulitic size and distribution and crystal orientation have been reported for various processing routes [3]. A marked reduction in delamination toughness was exhibited by AS4/PEEK for cooling rates below $3\,^{\circ}\mathrm{C\,min^{-1}}$ [4]. This is believed to be a result of weak regions (uncrystallized) between highly ordered transcrystalline layers [5]. Others found that the rate of cooling from the melt is a much more important indicator of tensile properties than measured per cent crystallinity values [6]. Slow cooling and cooling more quickly from the melt resulted in the same degree of crystallinity but produced large differences in mechanical properties. This highlights the importance of understanding and controlling the matrix crystal structure.

Barton *et al.* [7] suggested that the performance of APC-2 is not greatly dependent on thermal history provided the matrix is adequately crystallized, i.e. 30%. However, post-annealing (ageing) improved the transverse flexural properties slightly. Thermal analysis of these laminates revealed the introduction of a secondary endothermic melting peak positioned just above the annealing temperature [8, 9]. A number of investigations into annealing effects on the mechanical properties of PEEK have revealed the beneficial effects of annealing and suggest that annealing enhanced the growth of secondary crystals corresponding to the lower melting endotherm previously mentioned [10, 11]. However, the interpretation of this secondary endothermic peak remains unclear [12, 13].

The present work examined the effect of long-term thermal ageing and cycling on the flexural properties of various APC-2 laminate geometries. Results are discussed with respect to morphological changes and degradation data [12].

2. Experimental procedure

Laminates were produced by a two-stage compression-moulding process recommended by ICI [14] in order to achieve optimum crystallinity. Statically tested laminates measured 50 mm × 12 mm × 1 mm and both $(0)_8$ and $(0/90)_{2s}$ laminate geometries were tested. Flexural testing was performed on an Instron 4302 at a crosshead speed of $1.3\,\mathrm{mm\,min^{-1}}$ and an aspect ratio of 32/1. Flexural fatigue laminates measured 30 mm × 40 mm × 2 mm and both $(0)_{16}$ and $(0/90)_{4s}$ geometries were tested. Static strengths were measured. Fatigue testing was carried out at stress levels of between 70% and 95% static strength. A stress ratio of 0.1 and a test frequency of 5 Hz were used in all cases and a number of tests were carried out at each stress level. Fatigue testing was performed on a Dartec M100RE servohydraulic straining frame using a 50 kN load cell controlled by a 9500 Texas Instruments computer. Jig dimensions conformed to British standards BS 2782: Part 3; Method 304E and all tests were carried out at room temperature (RT).

Ageing temperatures of 120, 250 and 310 °C were selected. The lower temperature of 120 °C was chosen because it allows physical ageing of the polymer to occur [15] and because it is considered to represent

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the upper limit for under-the-bonnet temperatures in the auto industry [16]. Ageing at the higher temperature of 250 °C allow the reported upper service temperature limit (UST) [14] to be re-evaluated while also monitoring how reported morphological changes [8], as revealed by multiple melting peaks, affect the composite's mechanical properties. At 310 °C, approaching the matrix melt temperature, both degradation and crystal morphology changes are expected to occur. At all temperatures laminates were aged for time periods of up to 76 weeks.

Composites are frequently subjected to thermal cycling/spiking when in service [17]. Therefore, in order to complete the thermal ageing programme, laminates were also cycled from RT to 250 °C. This involved heating the laminates quickly from RT to 250 °C, holding for 17 h and subsequent slow cooling to RT where they are held for an additional 6 h. This cycle was repeated every 24 h.

3. Results and discussion

Static laminate flexural properties were calculated using classical beam equations and the values compare favourably with previously published data, see Table I [18]. Thermal ageing at 120 °C allows the polymer matrix to undergo a physical ageing process which is usually manifested by the material becoming stiffer and more brittle [15]. In general, laminate flexural modulus and strength values do not change appreciably on ageing. However, the flexural strain (strain at first peak load) shows a slight decrease on ageing for time periods of up to 16 weeks, upon which it stabilizes at this value. The above trend is common for both laminate geometries.

In general, laminate flexural strengths remain unchanged on ageing at 250 °C for up to 16 weeks but further ageing causes a dramatic loss in strength, Fig. 1. Similar trends are found for both geometries and for both thermal ageing and cycling at 250 °C, Tables II and III. During ageing, flexural property changes result from one or a combination of: (a) matrix degradation, (b) crystal morphology changes [12], or (c) reduced fabrication stresses. Although ageing causes continuous changes to occur in (a), (b) and (c) the critical time span after which the laminate flexural strength is first found to occur is between the 16 and 32 week testing periods, Fig. 1. A summary of monitored property changes which occur during this time span is given in Table IV. A 400% increase in weight loss results in a 25% decrease in flexural strain. This is emphasized by reduced ductility and an increased tensile fracture surface as indicated by SEM. In conclusion, it is believed that matrix degradation is the controlling factor affecting the abrupt reduction in mechanical properties during this time period. The poor dependence of laminate properties on morphological changes is attributed to the dominant role played by the carbon fibres in laminate fracture behaviour. In general, progressive thermal ageing causes further matrix degradation and a continual decline of mechanical properties.

TABLE I Flexural properties of experimental laminates

	Geometry	
	$(0)_8$	$(0/90)_{2S}$
Flexural strength (GPa)	2.30	1.67
Flexural modulus (GPa)	106	69.5
Strain	0.024	0.024

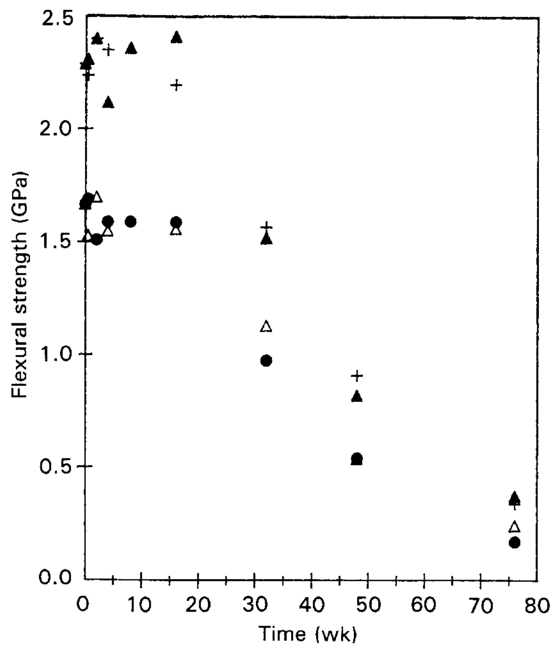

Figure 1 Variation in flexural strength of laminates with time, thermally aged at 250 °C. (▲, +) unidirectional, (●, △) cross-ply; (▲, ●) stored continually, (+ , △) thermally cycled.

Thermal ageing at the higher temperature of 310 °C causes rapid and extensive matrix degradation and correspondingly large decreases in mechanical properties, Table V. Despite the initial overall percentage crystallinity increase [12], rapid matrix degradation causes a dramatic decline of mechanical properties. The greater strength decay found for cross-ply laminates is due to more extensive interply damage despite exhibiting a similar degree of matrix loss to that of its unidirectional counterpart.

3.1. Fatigue

A fatigue modulus degradation model developed by Hwang and Han [19], was directly applied to flexural fatigue results generated by Dillon and Buggy [20], for APC-2 laminates. This mathematical model was also applied to laminates tested in this paper. As previously reported [20], cross-ply laminates appear to have a higher fatigue resistance up to 10^5–10^6 cycles compared with unidirectional laminates, when their S/N curves are normalized with respect to flexural strength, Fig. 2. This is believed to result from greater loading nose stress intensification in the unidirectional system causing a rapid build-up of compressive matrix damage. In general, the shape of the S/N curves suggest that the fatigue properties are heavily fibre dominated, especially for unidirectional laminates.

TABLE II The effects of ageing of APC-2 laminates at 250 °C on the mechanical properties

Time (wk)	Flexural modulus (GPa)		Flexural strength (MPa)		Flexural strain	
	Unidir.	Cross-ply	Unidir.	Cross-ply	Unidir.	Cross-ply
0	106.0	69.5	2296	1670	0.024	0.024
0.5	100.3	68.3	2311	1690	0.022	0.024
1	–	–	–	–	–	–
2	97.6	70.3	2409	1561	0.024	0.022
4	98.9	67.6	2120	1592	0.022	0.023
8	113.1	74.2	2364	1594	0.020	0.021
16	113.5	77.3	2446	1597	0.021	0.020
32	111.9	76.8	1523	976	0.014	0.013
48	98.6	68.6	826	543	0.008	0.007
76	63.8	38.9	373	172	0.006	0.005

TABLE III The effects of thermal cycling APC-2 laminates from room temperature to 250 °C on their mechanical properties

Time (wk)	Flexural modulus (GPa)		Flexural strength (MPa)		Flexural strain	
	Unidir.	Cross-ply	Unidir.	Cross-ply	Unidir.	Cross-ply
0	106.0	69.5	2296	1670	0.024	0.024
0.5	99.7	70.8	2240	1535	0.022	0.021
1	–	–	–	–	–	–
2	97.7	71.3	2406	1702	0.025	0.024
4	98.5	67.9	2356	1550	0.028	0.023
8	–	–	–	–	–	–
16	112.6	76.1	2209	1565	0.020	0.019
32	108.7	75.0	1574	1135	0.015	0.015
48	100.8	71.0	913	543	0.009	0.008
76	59.7	45.6	346	243	0.005	0.005

TABLE IV The effect of thermal ageing at 250 °C on laminate properties

	Time at 250 °C	
	16 wk	32 wk
Weight loss of composite (%)	0.2 (= 0.6 matrix)	0.8 (= 2.4 matrix)
Flexural strength (MPa)	2446	1523
Flexural modulus (GPa)	113.5	111.9
Crystallinity (%) (DSC)	25	42
Crystallinity (%) (XRD)	25	26
Strain	0.20	0.14
Fractography	Ductility excellent	Reduced ductility
	Neutral axis is central	Neutral axis shifted towards compressive surface
	Tensile zone and compressive zones equal	Tensile zone much larger than compressive zone

Cross-ply laminates exhibit a higher matrix dependence at low stress-levels as indicated by a sharper fall in the S/N curves.

In general, the fatigue response of laminates aged at 120 °C is unaffected except for a slight increase at lower stress levels, Fig. 3. Fig. 4 shows the effect of ageing at 250 °C on the fatigue behaviour of cross-ply laminates. They exhibit a general increase in fatigue lives especially at lower stress levels when aged for time periods of up to 16 weeks, whereas the curves generated for unidirectional laminates do not change when aged over the same time scale. At lower stress levels, the fatigue behaviour becomes more matrix dependent and therefore any changes in fatigue behaviour resulting from thermal ageing would be highlighted in this region. For ageing periods of up to 16 weeks, the observed increase in fatigue resistance results from a slight crystallinity increase, crystal perfection [12], and a reduction in laminate residual stresses [21]. Thereafter, matrix degradation becomes the over-riding factor as with statically tested specimens.

Two general trends were noted from SEM fractographic analysis of the dynamically tested thermally aged laminates: firstly, a reduction in matrix ductility throughout the sample with increased ageing time, and secondly an increased degree of delamination cracking. In cross-ply APC-2 laminates, damage development appears very late, just before the final failure, highlighting the plastic behaviour of the PEEK matrix. It is believed that this matrix toughness is a handicap as it suppresses the development of 90° ply cracking which would allow redistribution of stress concentrations [22]. The observed reduction in matrix ductility may be a result of polymer degradation or an increase in both the per cent crystallinity and the average crystal perfection. This causes a loss in matrix toughness which lowers the delamination

TABLE V The effects of ageing of APC-2 laminates at 310 °C on the mechanical properties

Time (wk)	Flexural modulus (GPa)		Flexural strength (MPa)		Flexural strain	
	Unidir.	Cross-ply	Unidir.	Cross-ply	Unidir.	Cross-ply
0	106.0	69.5	2296	1670	0.024	0.024
0.5	96.7	66.2	2252	1600	0.022	0.023
1	74.2	65.2	1575	1513	0.022	0.023
2	88.2	67.8	984	626	0.016	0.010
4	64.6	31.0	976	413	0.015	0.005
7	20.0	12.3	527	289	0.028	0.016
8	12.8	–	386	–	–	–

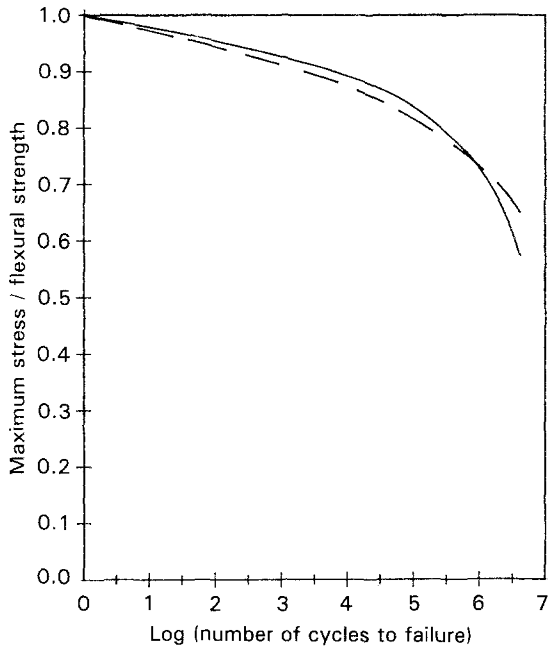

Figure 2 Flexural fatigue performance of (– – –) control unidirectional and (——) cross-ply laminates.

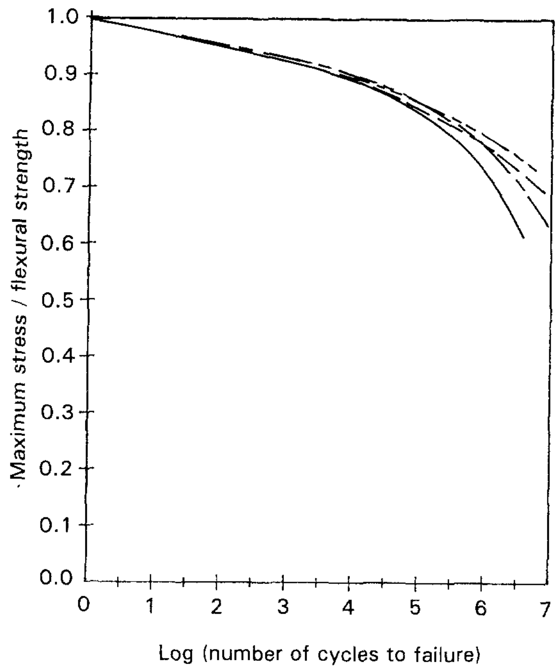

Figure 4 Flexural fatigue performance of cross-ply laminates aged at 250 °C, for (– – –) 4 wk, (- - - -) 8 wk, (— - —) 16 wk; (——) control.

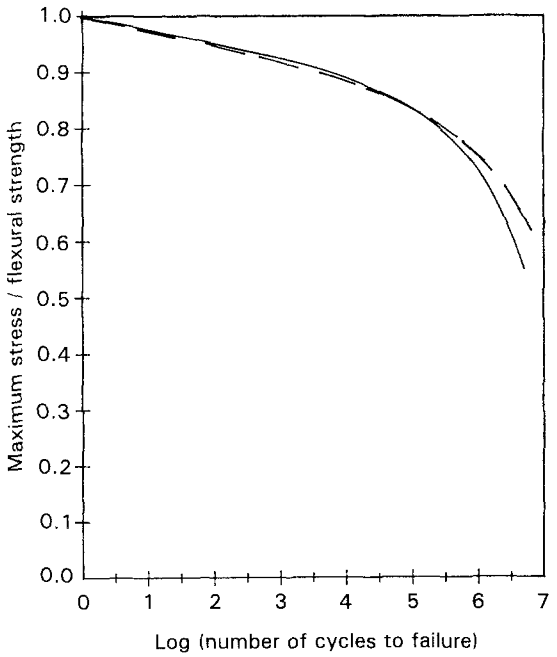

Figure 3 Flexural fatigue performance of (– – –) cross-ply laminates aged at 120 °C, for 48 wk; (——) control.

fatigue threshold and therefore allows a reduction in delamination resistance. The increased degree of delamination cracking found in aged laminates provides an effective energy absorption mechanism which allows for any overall increase in fatigue resistance. In the case of unidirectional laminates, post- and pre-failure delamination as well as a reduction in matrix ductility were observed, but the fibre's dominant fatigue behaviour masked any significant matrix property changes that occur on ageing.

In common with other semicrystalline polymers and their composites, rapid cooling of APC-2 or PEEK from the melt causes the introduction of residual thermal stresses [21, 23]. Annealing above the matrix T_g was found to reduce such effects. Although residual fabrication stresses were not monitored with ageing, it is presumed that stress relief on annealing did occur. In general, this can be expected to be most significant in cross-ply laminates where the build up of fabrication stresses is more pronounced [21].

Fig. 5 shows the effect of ageing cross-ply laminates at the higher temperature of 310 °C. Trends similar to those found for 250 °C samples are noted especially for

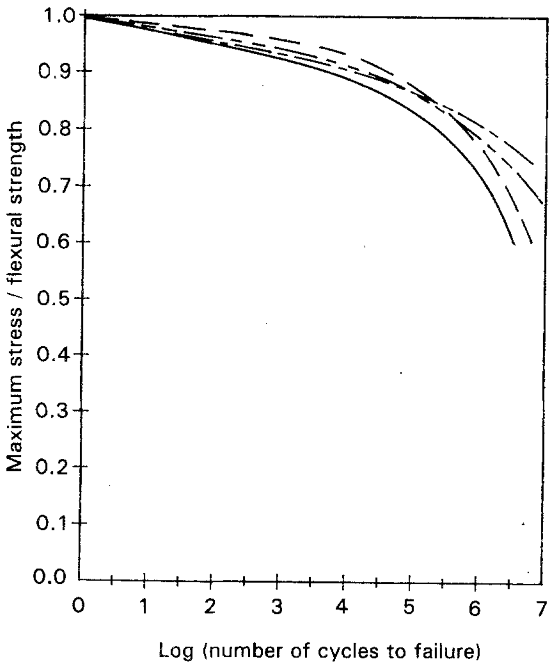

Figure 5 Flexural fatigue performance of cross-ply laminates aged at 310 °C, for (— - - —) 1 wk, (- - -) 2 wk, (— — —) 4 wk; (——) control.

cross-ply laminates when held for time periods of up to 4 weeks at 310 °C. It is believed that the same factors contribute to the increased fatigue resistance as found in the previous case.

On further ageing, a large reduction in strength occurred. This is again a result of extensive matrix degradation.

4. Conclusion

Ageing laminates at a temperature below the T_g of the matrix revealed no significant property changes. Ageing at higher temperatures between T_g and T_m, caused a marked reduction in flexural properties. This is considered to result from matrix degradation. However, ageing for short time periods enhanced the low stress level fatigue resistance of the composite. Thermal cycling at such temperatures exhibits similar trends but at a slower rate.

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References

1. M. DAY, T. SUPRUNCHUK, J. D. COONEY and D. M. WILES, in "20th International SAMPE Technical Conference", 27–29 September 1988, Minneapolis, US (SAMPE) pp. 132–43.
2. C. M. TUNG and P. J. DYNES, *J. Appl. Polym. Sci.* **33** (1987) 505.
3. L. YOUNGCHUL and R. S. PORTER, *Polym. Eng. Sci.* **26** (1986) 633.
4. P. T. CURTIS, P. DAVIES, I. K. PARTRIDGE and J. P. SAINTY, in "Proceedings of ICCM6-ECCM2" edited by F. L. Matthews, N. C. R. Bushell, J. M. Hodgkinson and J. Morton (Elsevier Applied Science, London, 1987) pp. 4401–12.
5. A. J. WADDON, M. J. HILL, A. KELLER and P. BLUNDELL, *J. Mater. Sci.* **22** (1987) 1773.
6. P. CEBE, S. D. HONG, S. CHUNG and A. GUPTA, "Toughened Composites", ASTM STP937 (American Society for Testing and Materials, Philadelphia, PA, 1987) p. 342.
7. J. M. BARTON, J. R. LLOYD, A. A. GOODWIN and J. N. HAY, *Br. Polym. J.* **23** (1990) 101.
8. D. J. BLUNDELL, *Polymer* **28** (1987) 2248.
9. P. CEBE and S. D. HONG, *ibid.* **27** (1986) 1183.
10. P. Y. JAR, H. H. KAUSCH, W. J. CANTWELL, P. DAVIES and H. RICHARD, *Polym. Bull.* **24** (1990) 657.
11. P. Y. JAR and H. H. KAUSCH, *J. Polym. Sci. Part B* **30** (1992) 775.
12. A. CAREW, PhD thesis, University of Limerick (1992).
13. D. C. BASSETT, R. H. OLLEY and I. A. M. RAHEIL, *Polymer* **29** (1988) 1745.
14. ICI "Aromatic Polymer Composites, Date Sheet 1-5" (ICI plc, Welwyn Garden City, 1987).
15. L. C. E. STRUIK, "Physical Ageing in Amorphous Polymers and Other Materials" (Elsevier, New York, 1978).
16. P. BEARDMORE and C. F. JOHNSON, *Compos. Sci. Technol.* **26**(4) (1986) 251.
17. G. PRICHARD and K. STANSFIELD, in "Proceedings of ICCM6-ECCM2", Vol. 4 (Elsevier Applied Science, London, 1987) pp. 190–9.
18. G. C. McGRATH, D. W. LEGG and A. A. COLLYER, *Composites* **19** (1988) 211.
19. W. HWANG and K. S. HAN, *J. Compos. Mater.* **20** (1986) 154.
20. G. DILLON and M. BUGGY, *Composites* **22** (1991) 191.
21. J. A. NAIRN and P. ZOLLER, *J. Mater. Sci.* **20** (1985) 367.
22. C. HENAFT-GARDIN and M. C. LAFARIE-FRENOT, *Composites* **23** (1992) 109.
23. P. CEBE, L. LOWRY, S. Y. CHUNG, A. YAVROVIAN and A. GUPTA, *J. Appl. Polym. Sci.* **34** (1987) 2273.

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