EFFECT OF MATRIX MORPHOLOGY ON FATIGUE BEHAVIOUR OF CARBON/PEEK COMPOSITES

M.C. Lafarie-Frenot*, J. Denault**, I. Goupillaud*, H. El Kadi**

The purpose of this work is to compare the quasi static and fatigue tensile strengths of several carbon/PEEK composites materials, with different PEEK matrix morphology. Effect of fibre/matrix interface is also discussed, using scanning electron micrographs. The present paper reports the potential improvement of the fatigue behaviour of carbon/PEEK laminates by different molding procedures.

INTRODUCTION

Continuous carbon fibre reinforced thermoplastic have received considerable attention since a few years due to greater toughness and impact tolerance than usual thermoset composites. However a lower fatigue resistance has been already observed that partly puts a check on potential applications (Henaff-Gardin and Lafarie-Frenot (1)).

It can be reminded that PEEK is a semicrystalline polymer with a low glass transition temperature. Thermal history during molding process, therefore modifies matrix and fibre/matrix interface morphology by way of crystallisation rate (Talbott et al (4)). The processing conditions induce specific matrix microstructures which can influence greatly mechanical properties (Cottenot et al (2); Denault and Vu-Khan (3)).

* Laboratoire de Mécanique et de Physique des Matériaux, URA CNRS 863, ENSMA, BP 109 Chasseneuil du Poitou, 86960 FUTUROSCOPE CEDEX, FRANCE
** Institut des Matériaux Industriels, CNRC, 75 de Mortagne, Boucherville, Québec, CANADA, J4B6Y4

In this context, the aim of this study is to compare the fatigue resistance of five carbon/PEEK composite materials obtained with different molding procedures. Effect of PEEK matrix morphology and interfacial strength is discussed.

MATERIALS

Angle ply laminates of APC-2 prepeg consisting of 'VITREX' PEEK reinforced with unidirectionnal AS4 graphique fibers obtained from ICI were compression molded with a $[(+45°)_2/(-45°_2)]_{2s}$stacking sequence. Square plates of 150 mm*150mm*2mm thick were compression molded in a matched mold using a programmable Wabash press permitting reproducible molding cycles. Heating was done without pressure and when the molding temperature was reached, high pressure was applied. After a residence time of 10 minutes at the molding temperature, the laminates were cooled to room temperature at controlled rates. The temperature of the melt was measured with a thermocouple inserted in the laminates. The plates were molded under five different molding conditions in order to obtain PEEK/carbon composite with various matrix morphologies and interfacial strenghts. Samples A, C and D were molded at 400°C and cooled respectively at 0.6, 20 and 70°C/min. Sample E was obtained under the same conditions than sample D, but cooling was followed by an annealing treatment of 4 hours at 300°C. Finally, B was molded at 365°C and cooled at 20°C/min. These molding procedures were found to confer different matrix microstructures and interfacial strenghts to the PEEK/carbon composites. Crystalline structure of the matrix was revealed by a permanganate etching technique and the crystallinity was evaluated by differential scanning calorimetry. Short beam shear tests were carried out to evaluate the interfacial strenght in the composites following the ASTM-D2344 method. Morphological characteristics and interfacial properties of the molded samples are presented in Table 1.

MECHANICAL BEHAVIOUR AND OBSERVATIONS

I) Mechanical tests

Experimental conditions. Quasi-static and fatigue tensile tests were performed on angle ply laminates $[(+45°)_2/(-45°)_2]_{2s}$, using 150*15*2 mm specimens, with end-tabs 30 mm long for gripping in the testing

machine. Quasi-static tensile experiments were realised on an Instron machine with a constant cross-head displacement rate of 1 mm/min. Strains were measured by a strain gage extensometer with a gage length of 25,4 mm. Fatigue tests were conducted on an Instron servo-hydraulic machine, with a sinusoidal load controlled testing mode and a stress ratio of R=0.1. To avoid material autogenous over heating (Curtis et al (5)), a low frequency of 0,5 Hz was chosen. All laminate coupons were loaded up to fatigue failure, providing fracture surfaces for microscopic observations.

Quasi-static tensile behaviour. Stress-strain curves were determined for all five materials. Figure 1 points out three types of behaviour related to the three different cooling rates. Specimen A exhibits a quasi linear elastic stress-strain curve with a very low ultimate strain value, whereas D and E show an important plastic behaviour with a high strain hardening. The intermediate cooling rate leads to a medium behaviour : B and C materials have both the lowest yield strength with moderate plasticity. The ultimate tensile strengths of A, D and E materials are similar and very high, about twice higher than the B and C maximal stress values .

Fatigue behaviour. The maximal stress imposed, equal to 130 MPa, corresponds approximately to 55% of A, D and E static ultimate stress and 89% of B, C one. Table 2 gives extreme values of ultimate cycle numbers and displays the molding procedure influence on fatigue resistance. Despite of an important scattering, the fatigue life of B and C laminates is at least ten times longer than other ones whereas the applied relative stress level is much higher. This result shows that extreme values of cooling rates entails the fatigue resistance of such laminates.

Previous investigations using X Ray technique, have revealed numerous initial damages in D and E laminates, due to severe molding conditions. These defects can affect the material fatigue resistance as they are preferential sites for cracking and delamination development. Moreover, the fatigue damage mechanisms concern all the composite components : fibre, matrix and fibre/matrix interface. The microstructure of this interface seems to result from several complex mechanisms such as matrix adsorption on the fibre surface, fibre matrix reaction leading to chemical bonding and particular crystallization (Denault and Vu-Khan (6)). Though SEM fracture surfaces analyses don't fit to characterise this microstructure, such observations let us connect fracture features to different fibre/matrix adhesion quality and matrix spherulitic structure.

II)Microscopic observations

Figure 2 shows micrographs of fatigue fracture surfaces and puts in light the leading part of cooling rate on matrix crystallinity and fibre/matrix bonding. On figure 2.a, the matrix A presents a dense aspect due to a great crystallinity level and some matrix remains bonded to fibres. The same characteristics, but much more marked, are present on B and C fracture surfaces (fig.2b). On higher enlargement (fig 2c) white traces are visible on fibre surface and are identified with spherulitic structures. The poor fatigue resistance of D and E composite materials can be linked to the presence of an amorphous matrix, detached from fibres and without trace of interface (fig 2d).

CONCLUSION AND PERSPECTIVES

Following tests and observations, it's clear that cooling rate and molding temperature, modifying the matrix microstructure around the fibre as well as the residual stresses, are both important for the quality of the fibre/matrix bonding. Opposite mechanical behaviour, under quasi-static and cyclic tensile loading, have been put in light. In particular, intermediate molding parameters induce the most fatigue resistant materials (B and C). This result could be due to an initial neat laminate and a strong fibre/matrix interface.

Detailed investigations are necessary to confirm these first results. More cyclic tests must be performed to have a better characterisation of the material fatigue resistance. As part of the work in progress, chemical attack of fatigue loaded specimens would let us to describe the spherulitic structure (size, shape) and establish if crack path is related to these microstructural entities

(1) Henaff-Gardin , C. and Lafarie-Frenot, M.C., J. of Composite, Vol. 23., 1992, pp. 109-116.
(2) Cottenot, C., Vautey, P., Marais, and C. Sigety, P., Annales des Composites, Vol. 1/2, 1989, pp 145-155.
(3) Denault, J. and Vu-Khan, T., J. of Thermoplastic Composite Materials, vol. 4, 1991, pp. 363-376.
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(5) Curtis, D.C., Davies., H., Moore, D.R. and Slater, B., Vol. ASTM STP 1110, 1991, pp. 581-595.
(6) Denault, J. and Vu-Khan, T., J. of Thermoplastic Composite Materials, 1993, Vol. 6, pp. 190-204.

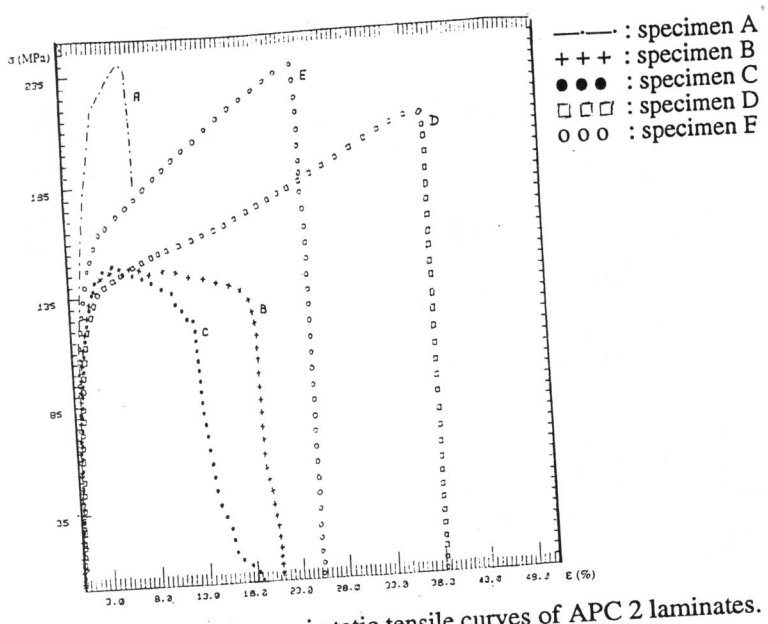


Figure 1 Strain- stress quasi-static tensile curves of APC 2 laminates.

samples	A	B	C	D	E
crystalline struture	spherulitic	non spherulitic	spherulitic	non spherulitic	non spherulitic
cristallinity (%)	40	33	32	28	39
interfacial strength (MPa)	90	85	86	74	87

Table 1 : Morphological characteristics of the molded samples

	A	B	C	D	E
tested specimens	5	3	3	3	5
extreme values of ultimate cycle numbers	2500 to 12500	12000 to 177000	7000 to 156000	1400 to 2600	7000 to 23000

Table 2 : APC2, fatigue, σ_{max}= 130 MPa : ultimate cycle numbers

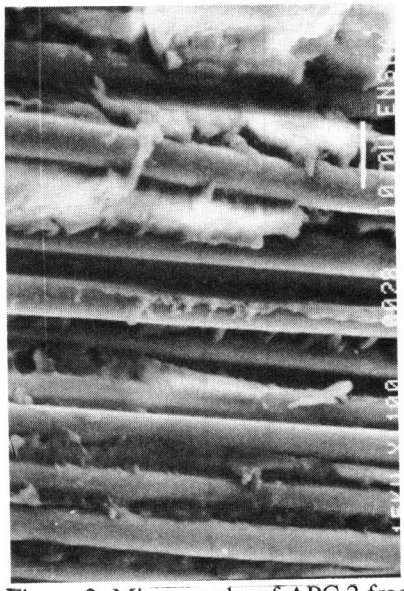
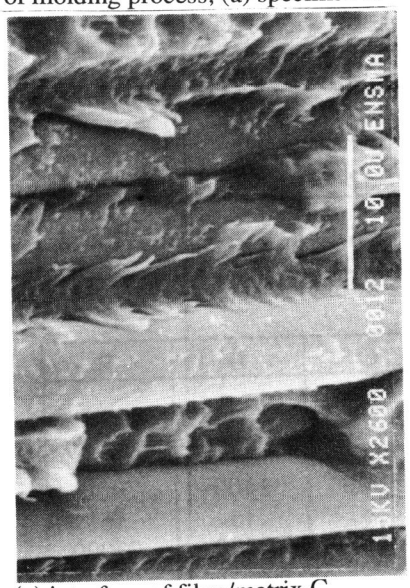
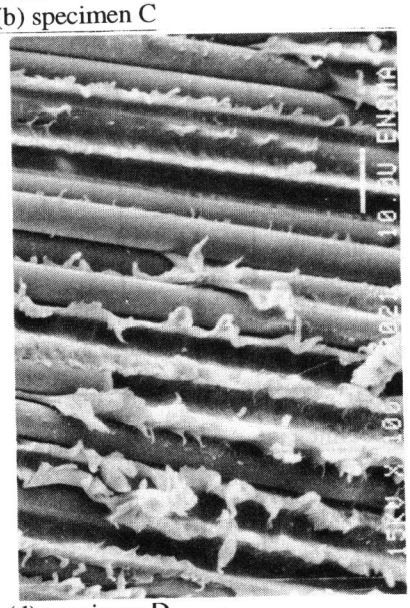


Figure 2: Micrographs of APC 2 fracture surfaces as a fonction of molding process; (a) specimen A (b) specimen C



(c) interface of fibre/matrix C



(d) specimen D