POSTER

THE EFFECT OF PITCH AIR-BLOWING ON THE MICROSTRUCTURE AND PROPERTIES OF C/C COMPOSITES

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INTRODUCTION

The main disadvantages of pitches for C/C composites are their low carbon yields and a significant pore volume after carbonization which produces undesirable effects on physical and mechanical properties. Several further impregnation and carbonization cycles are necessary to produce a dense matrix carbon. Pitch oxidation by air-blowing promises to be effective in order to optimize pitch utilization. Molecular cross-linking induced by oxygen functionality [1,2] at low temperatures, increases the molecular weight of some molecules, preventing their distillation and removal during carbonization and resulting in a significant increase of carbon yield. The objective of this paper is to study the potential of air-blowing of pitch on the improvement of pitch properties as a matrix precursor for C/C composites.

EXPERIMENTAL

A series of four pitches made up of the untreated pitch (an impregnating pitch, 3 wt% QI) and three air-blown pitches, obtained at 250, 275, 300°C, and PAN fibres (AS4-12K) of high strength, high strain and a filament diameter of 7 μm, were used as starting materials. The oxidation treatment of pitches and its effect on their chemical composition has been previously described [2]. Table 1 shows some selected properties of the studied pitches. Previous to the preparation of the composites, in order to determine the effect of air-blowing on the carbon matrix structure and properties, pitches were carbonized to 1000°C at 1°C min^{-1} and maintained at the maximum temperature for 30 min. Cokes were characterized in terms of their optical texture, pore content (determined by optical microscopy), He density (true density), bulk density and microstrength [3].

Plate-shaped unidirectionally reinforced composites were prepared by the wet-winding technique using a tetrahydrofuran suspension of pitch. Solvent was removed by keeping the structure so formed overnight under hot air at about 60°C. An initial pre-pressing of the prepreg was performed at this temperature under vacuum. Laminates of 170 mm x 70 mm were then cut and heated at a rate of 4°C min^{-1} to 450°C under a pressure of 4.5 MPa, except in the first two composites of the series, which was of 1.5 MPa, before being pyrolysed at a heating rate of 1°C min^{-1} to 750°C, under a nitrogen pressure of 10 MPa. In a subsequent pyrolysis, laminates of 150 mm x 45 mm were heated to 1200°C under argon at atmospheric pressure. Characterization of composites (undensified) was made by optical microscopy in terms of their porosity and the optical texture of the matrix. Interlaminar shearing and flexural strength tests were performed on the composites according to ISO 04585/ASTM D2344-84 and ASTM D790-86, respectively. Fracture surfaces of composites were characterized by SEM.

RESULTS AND DISCUSSION

The polymerization of the volatile components of pitch promoted by air-blowing [2] prevented pitch from swelling and resulted in an increase in carbon yield, a decrease of the porosity of cokes and a significant increase in the bulk density at initial stages of the treatment (250°C) followed by a slight increase (275 and 300°C), as observed in Table 2. Air-blowing also produced a substantial increase in coke strength and a decrease of coke optical texture (domains of smaller size and higher amount of mosaics). From these results an improvement on the mechanical properties and density of composites from air-blown pitches should be expected. The composite from 250°C/air pitch exhibits a considerably higher value of flexural strength (644 MPa) than that obtained from the untreated pitch (486 MPa). This increase can be related to the absence of shrinkage cracks, interface located, which were present in the untreated pitch composite and the increased amount of intramatrix mosaics brought about by the oxidation treatment (Figure 1). However, the flexural strength value unexpectly, according to the results obtained on the cokes, fell to 609 MPa and 432 MPa with 275°C/air and 300°C/air treatment, respectively. Although the three composites have very similar values of porosity, between 13-18%, and also similar matrix microstructure, being even slightly higher in amounts of mosaics with more severe treatment, the low value of 300°C/air composite can be explained from the loss of wettability of the pitch and the high volumetric contraction of the matrix. Both are due to the high viscosity of the system on pyrolysis, caused by the extensive polymerization in the air-blowing treatment. In the same way, the resultant low fibre content (42%) compared to the rest which was about 57%, can also contribute to the decrease of the flexural strength. The bulk density of composites increased from 1.53 g cm^{-3} for the untreated pitch composite to 1.59 g cm^{-3} for those from the treated ones. The beneficial effect of air-blowing on fibre/matrix bonding is confirmed by the increase of the interlaminar shear strength value, from 19 MPa for the untreated pitch composite to values in the range of 32-36 MPa for those from the air-blown pitches.

Table 1. Properties of pitches.

Treatment	Elemental Analysis (wt%)					SP	CY	TI
	C	H	N	S	O*	(°C)	(wt%)	(wt%)
–	92.0	4.5	1.1	0.5†	1.9	54	35.2	20.8
250°C/air	92.7	4.0	1.1	0.4	1.8	148	62.4	52.7
275°C/air	93.1	4.1	1.2	0.4	1.2	164	64.4	53.8
300°C/air	92.7	4.0	1.1	0.6	1.6	219	67.9	60.5

*, By difference
†, Sulfur and oxygen
SP, softening point TMA
CY, carbon yield (1000°C)
TI, toluene insolubles

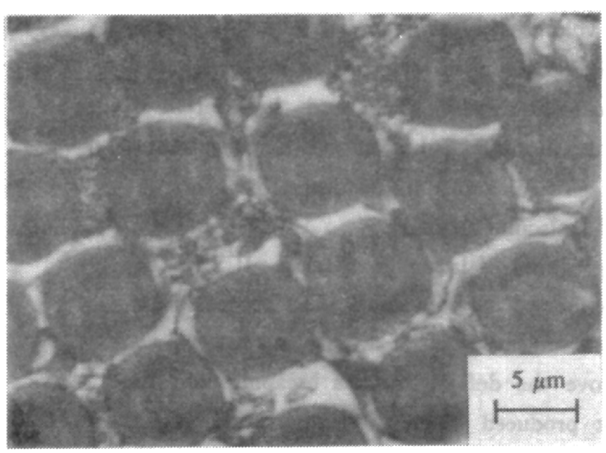

Figure 1. Optical micrograph of 275°C/air composite.

Figure 2 is a SEM micrograph of a fracture surface of 300°C/air composite showing an excellent adhesion between the carbon matrix and the fibres.

ACKNOWLEDGEMENTS

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REFERENCES

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Table 2. Properties of carbonaceous matrices.

Pitch Treatment	p (vol %)	d (g cm^{-3})	r_1/r_3
-	97.2	0.05	0.0
250°C/air	56.5	0.87	1.42
275°C/air	52.7	0.95	3.47
300°C/air	46.8	1.06	3.69

p, porosity (determined by microscopy)
d, bulk density
r_1/r_3, microstrength index

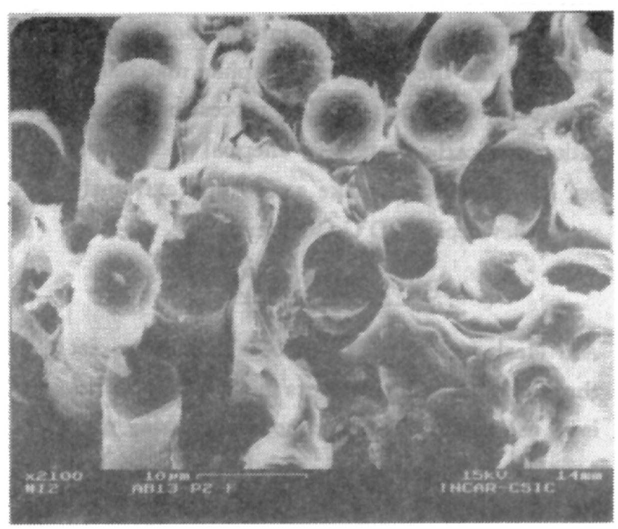

Figure 2. SEM micrograph of a fracture surface of 300°C/air composite.