POSTER

STRUCTURE AND PROPERTIES OF CARBON BLACK/PITCH BASED MATRICES IN C/C COMPOSITES

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INTRODUCTION

A problem with pitch in the preparation of carbon materials, is the development of porosity on carbonization. This makes necessary a further densification of the material with subsequent economical implications. Different treatments of pitch prior to carbonization, i.e. thermal treatment, air-blowing and carbon-black addition, are beneficial [1,2]. Kanno et al. [3] observed that carbon black produced a reduction in volumetric expansion on carbonization of mesophase pitches and a decrease of the optical texture of resultant cokes, due to an enhancement of gas removal and the hindering of association of mesogen molecules, respectively. Moreover, the presence of carbon black promotes the retention of the light components within the pitch with a subsequent increase in carbon yield. From this experience it seems that carbon black addition to pitch followed by thermal treatment could substantially improve pitch properties as matrix precursor of C/C composites. The objective of this paper is to study the influence of carbon black on the structure and mechanical properties of unidirectional C/C composites from a coal-tar pitch with Ketchem Black, thermally treated at different temperatures in the range of 400-450°C, and PAN fibres.

EXPERIMENTAL

A commercial coal-tar pitch (3 wt% QI) was blended with 3 wt% of a carbon black (Ketchem Black, 30 nm particle size, 800 m^2 g^{-1} of BET surface area, 360 ml/100 g of DBP value and 9 in pH), and then thermally treated to 400, 425, 430 and 450°C, at 5°C min^{-1}, for 5 h, with the exception of 430°C which was for 10 h, under vigorous stirring. Pitches were characterized in terms of their softening point, elemental composition (Table 1) and solubility in different solvents [1]. Pitches were carbonized to 900°C at 1°C min^{-1}, for 1 h, under nitrogen and resultant cokes characterized by optical microscopy in terms of their porosity (vol%) and optical texture.

Plate-shaped unidirectionally reinforced composites were prepared by the wet-winding technique using the original pitch and treated pitches and PAN fibres (AS4-12K) of high strength, high strain and a filament diameter of 7 μm. Laminates of prepreg were heated at 4°C min^{-1} to 450°C and moulded under a pressure of 4.5 MPa, before being pyrolysed to 750°C at 1°C min^{-1}, under argon at 10 MPa. Composites were further carbonized in a subsequent pyrolysis at 1200°C under nitrogen at atmospheric pressure. Characterization of composites (undensified) was performed by optical microscopy and SEM. Interlaminar shear tests were performed on the composites according to ISO 4585 and ASTM D2344-84, and flexural strength tests were carried out according to ASTM D790-86 standards.

RESULTS AND DISCUSSION

As with mesophase pitches [3], carbon black additions to the studied coal tar pitch produced an increase of pitch yield after heat treatment due to the retention of low molecular weight compounds, and an important increase of carbon yield which means that such molecules remain in the system during carbonization (Table 1). Porosity of coke, as determined by optical microscopy, dramatically decreased with carbon black addition at 400°C, 5 h of thermal treatment, from about 97% to 52%, to keep almost invariable for 425°C and 430°C, and then to increase for 450°C to 65%. This final increase could be due to the generation of a high viscosity system as a consequence of the large size molecules which makes difficult the evolution of gases generated on carbonization. The optical texture of cokes was of mosaics due to the presence of carbon black particles. No significant variations were observed with the different heat treatment temperatures.

Table 2 shows the values of the bulk density, fibre content and the results of the mechanical testing of the composites. A preparation of the composite from the pitch/carbon black treated at 450°C was not possible due to the high pitch viscosity. The interlaminar shear strength of composites from treated pitches was considerably improved when compared to that of composites using untreated pitch, and increases with the severity of the treatment. This is explained in terms of a better fibre/matrix bonding. The interface cracks present in the untreated pitch composite almost disappear with the treatment (Figure 1a). The decrease in size of the optical texture from flow domains (untreated pitch) to mosaics with some domains could also contribute to this effect. Flexural strength of composites also increased with carbon black addition at 400 and 425°C, being higher in the case of 400°C. At 430°C the value of the flexural strength is similar to that of the untreated pitch composite. The increase at the initial stage of treatment can be related to the lower porosity of the composite and the decrease of the optical texture of the matrix produced by the carbon black (fibre content is very similar in the two composites). The substantial decrease of the flexural strength from 400°C and 425°C to 430°C might be associated to the loss of wettability of pitch, the development of porosity (Figure 1b) and the increase of the matrix volume (Table 2), all these due to the generation of a high viscosity system promoted by the high polymerization degree.

ACKNOWLEDGEMENTS

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Table 1. Main characteristics of pitches.

Treatment	CY[1]	SP[2]	Elemental Analysis (wt%)			
			C	H	N	S+O[3]
-	35.2	54	92.4	4.5	1.0	2.1
KB 400, 5 h	46.1	59	93.0	4.5	1.0	1.5
KB 425, 5 h	54.3	67	93.3	4.3	1.0	1.5
KB 430, 10 h	71.1	101	94.0	4.0	1.0	1.0
KB 450, 5 h	72.3	167	94.0	3.8	0.9	1.3

[1] Coke yield, 1000°C, 1 K min^{-1} (wt%) [3] By difference
[2] Softening point, TMA (°C)

Table 2. Properties of composites.

Treatment	ILLS[1] (MPa)	FS[2] (MPa)	d[3] (g cm^{-3})	FC[4] (% vol)
None	14	486	1.53	57
KB 400, 5 h	20	736	1.52	53
KB 425, 5 h	26	676	1.59	50
KB 430, 10 h	33	484	-	41

[1] Interlaminar Shear Strength [3] Bulk density
[2] Flexural Strength [4] Fiber content

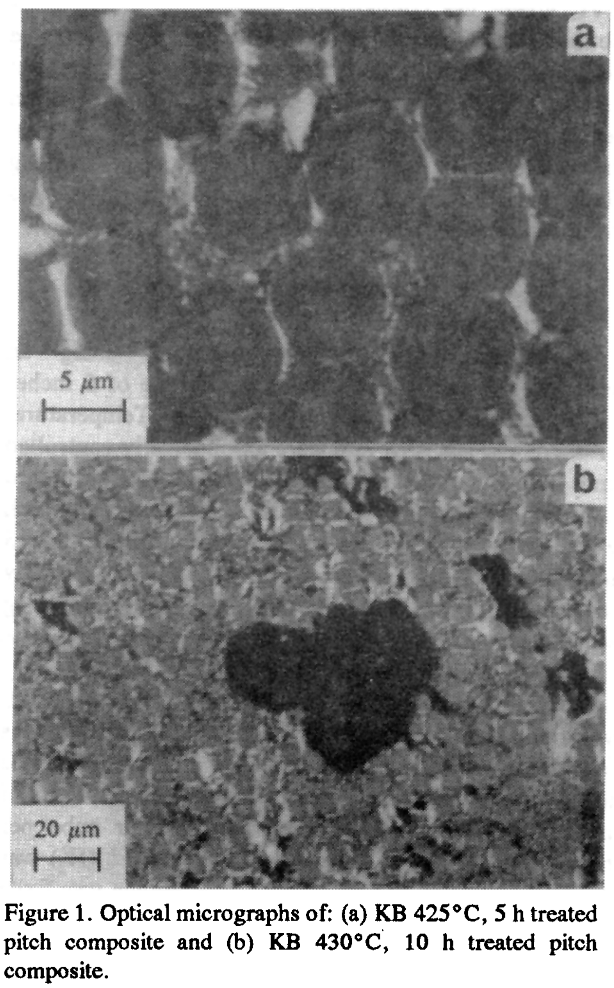

Figure 1. Optical micrographs of: (a) KB 425°C, 5 h treated pitch composite and (b) KB 430°C, 10 h treated pitch composite.