INFLUENCE OF PRIMARY QI MATERIAL ON THE STRUCTURE AND PROPERTIES OF PITCH-BASED UNIDIRECTIONAL C/C COMPOSITES

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Introduction

Properties of C/C composites are closely related to carbon matrix structure (voids and matrix microstructure) and fibre/matrix interaction. Coal-tar pitch is unique among carbon matrix precursors because of its low price and its flexibility to produce carbons with very different microstructures. Carbon matrix microstructure is mainly controlled by process conditions and pitch chemical composition. The presence of solid particles in pitches (primary QI) is also a contributing factor.

Several studies report on the behaviour of C/C composites prepared from different pitches differing in their primary QI content [1-3]; however, it is difficult to distinguish between the role of primary QI and other pitch components.

This paper reports on the influence of primary QI content, of four pitches with the same chemical composition, on their pyrolysis behaviour and how it affects unidirectional C/C composites when pitches are used as carbon matrix precursors.

Experimental

A series of four pitches of increasing QI content was prepared by blending, in different proportions, a commercial binder coal-tar pitch with varying amounts of the same filtered pitch .The pyrolysis behaviour of these pitches was studied by hot-stage microscopy and thermogravimetric analysis. Pyrolysis products of the pitches, obtained at 450°C and 30 min of soak time were characterized by polarized-light microscopy.

Unidirectional C/C composites were prepared by a wet-winding procedure [2], using the four pitches and PAN-based carbon fibres (Hercules, AS-4K). Composites were characterized in terms of their optical texture, porosity, fibre/matrix bonding, bulk density, and mechanical properties (flexural and interlaminar shear strength).

Results and Discussion

Influence of primary QI content on pitch properties

Variations of carbon yield, softening point and toluene insolubles of pitches (Table 1) may be attributed to their different primary QI contents. Pitch chemical composition was not altered during filtration.

Results obtained from TGA and DTG curves of the four pitches show that there are no significant differences in the values of initial temperature of weight loss (~ 170°C), temperature of maximum weight loss rate (~ 350°C) and final temperature of weight loss (~ 550°C), which means that for pitches with the same chemical composition, these thermogravimetric parameters are not QI dependent.

Table1. Properties of the pitches.

Pitch	Elemental Analysis (wt %)					SP[2]	CY[3]	TI[4]	QI[5]
	C	H	N	S	O[1]				
CTP0	93.8	4.3	1.0	0.6	0.3	114	50.0	35.6	11.0
CTP1	93.5	4.8	1.0	0.6	0.1	114	49.5	34.9	9.1
CTP2	93.4	4.9	1.0	0.6	0.1	111	45.5	31.8	5.5
CTP3	93.5	4.8	1.0	0.6	0.1	111	44.5	31.3	0.5
QI	93.4	1.8	0.9	0.8	3.1	-	95.0	-	-

[1] Determined by difference [4] Toluene insolubles (wt %)
[2] Softening point (°C) [5] Quinoline insolubles (wt %)
[3] Coke yield (5°C min^{-1}, 900°C, 30 min)

Mesophase development within the parent pitch (CTP0) and filtered pitch (CTP3,) controlled by hot-stage microscopy, shows that there are significant differences between the two pitches. CTP3 shows the formation of mesophase 10°C lower than for CTP0. Moreover, coalescence of spheres is more advanced in CTP3 than in CTP0. The structure of the spheres is also affected by the primary QI content. In CTP3 spheres are homogeneously distributed within the isotropic phase and are almost spherical, while in CTP0 spheres are distorted and of irregular shape. This different behaviour is because pitches with high primary QI content generate high viscosity systems on pyrolysis which adversely affect the mobility of the mesogenic molecules, making more difficult the mass transfer from the isotropic phase to the anisotropic phase.

Pyrolysis products of pitches, obtained at 450°C and 30 min of soak time, corroborate hot-stage microscopy observations. CTP0 pyrolysis product shows large coalesced mesophase regions, 50-170 µm, irregular in shape and distorted mesophase spheres (< 80 µm). At the same temperature and soak time, CTP3 developed higher amounts of mesophase and spheres almost undistorted of 2-120 µm. Large regions of coalesced mesophase (~ 300 µm) are also present. In both pyrolysis products, primary QI particles are associated with mesophase, appearing around the surface of the spheres. In CTP0, where the QI content is high, aggregates of QI are observed .

It is established that primary QI particles during mesophase development represent a point of interruption in the layer plane structure. Regions with continuous and well-ordered layer plane structures become progressively smaller as QI content in the pitch increases. This fact was observed in cokes obtained from the series of filtered pitches. Optical textures of pitch cokes vary from domains with aggregates of QI engulfed by the anisotropic material (CTP0 and CTP1 cokes), to flow domains (CTP2 coke) and elongated flow domains (CTP3 coke).

Influence of primary QI content on the structure and properties of composites

Variations in the optical texture of carbon matrices are similar to those observed in pitch cokes. Composite from parent pitch, CC0 (Figure 1), shows an optical texture of mosacis, mainly intramatrix located, and domains, orientated around the fibres. The presence of QI in this composite not only produces the formation of mosaics but also produces a non-homogeneous distribution of the fibres. As the QI content of pitches decreases, corresponding composites show a larger and more orientated optical texture. Thus, composite from filtered pitch, CC3 (Figure 1) exhibits an optical texture of domains. This higher contribution of domains is accompanied by a higher generation of cracks, intramatrix and interface located.

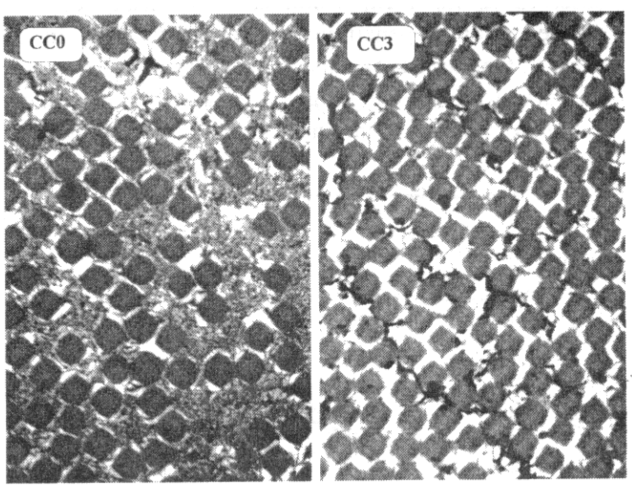

Figure 1. Optical micrographs of the composites CC0 and CC3.

Selected properties of composites are given in Table 2. As the pitch QI content decreases, carbon fibre content and porosity increase, while bulk density decreases. This could be attributed to a higher pitch fluidity and consequently a higher ability to be exudated, and a lower coke yield of pitches with the decrease of QI content.

Table 2. Properties of the composites.

Composite	FC[1]	d[2]	P[3]	FS[4]	ILSS[5]
CC0	51.2	1.5	13.7	514	20.2
CC1	51.9	1.5	16.5	425	18.3
CC2	52.0	1.4	15.7	477	18.2
CC3	53.0	1.4	17.5	335	9.1

[1] Carbon fibre content (vol %)
[2] Bulk density (g cm^{-3})
[3] Total porosity (vol %)
[4] Flexural strength (MPa)
[5] Interlaminar shear strength (MPa)

Mechanical properties of composites are strongly affected by the presence of QI particles. ILSS values for CC0, CC1 and CC2 duplicate those of CC3 (Table 2). This is in agreement with polarized-light microscopy observations which showed a very compact material, without fissuring, with a good fibre/matrix bonding and the presence of intramatrix mosaics. A similar trend is observed for the FS values, which decrease with increasing of porosity, which is closely related to the QI content as previously mentioned. These results are corroborated by composite flexural fracture behaviour. CC0, CC1 and CC2 exhibit a brittle failure, indicative of their relatively high fibre/matrix adhesion. In contrast CC3, with a weak fibre/matrix bonding, shows a more pseudoplastic behaviour.

Conclusions

The presence of primary QI particles in pitches, with the same chemical composition, strongly affects their pyrolysis behaviour, especially the development of mesophase and the optical texture of cokes and composites. Structure and properties of C/C composites were improved by the presence of primary QI.

Acknowledgments

The authors of this work would like to thank CICYT (Project MAT94-0715) for the financial support.

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