THE EFFECT OF COAL-TAR PITCH THERMAL TREATMENT ON THE MECHANICAL BEHAVIOUR OF C/C COMPOSITES

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Introduction

Pitches have proved to be adequate precursors of graphitizable carbon materials; however, when used as matrix precursors for C/C composites the development of porosity on carbonization makes necessary the densification of the material. Pitch pre-treatment [1-2] could reduce the number of densification cycles or at best to avoid them. Thermal treatment of coal-tar pitches is commom practice by industry to increase pitch softening point and carbon yield. Volatile removal and polymerization of some components are the two main effects of this treatment. The aim of this paper is to study the effect of thermal treatment on the properties of an impregnating coal-tar pitch and on the structure and properties of subsequent unidirectional C/C composites.

Experimental

An impregnating coal-tar pitch was thermally treated at 400°C-5h, 425°C-5h nd 430°C-10h, in an inert atmosphere. Resultant pitches were characterized in terms of their softening point, coke yield and solubility. Pitch solubility was determined by sequential extraction with hexane, benzene and pyridine [3]. Cokes obtained from pitches at 900°C were characterized by polarized-light microscopy (optical texture and porosity).

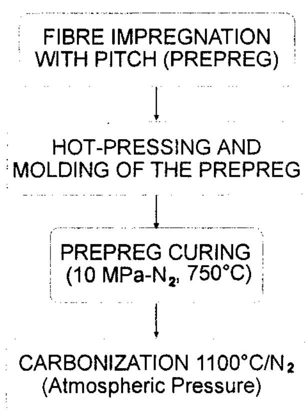

Figure 1. Diagram of the laboratory process of composites preparation.

Unidirectional C/C composites were prepared using parent and thermally treated pitches and commercial PAN-based carbon fibres (Hercules, AS-4K) according to Figueiras *et al.* [4], Figure 1. Characterization of composites was performed by optical microscopy (fibre content, porosity, matrix optical texture). Flexural and interlaminar shear strength of composites were determined according to ASTM D790-86 and ASTM D2344-84 standards, respectively.

Results and Discussion

Influence of thermal treatment on pitch properties

Thermal treament of pitch causes a significant increase in softening point and carbon yield, and produces and substantial change in its solubility in hexane, benzene and pyridine, Table 1. The effect of the temperature on pitch solubility was to decrease the HS fraction from 32 wt %, for TT0, to 23 wt %, for TT2, and to increase the PI fraction from 10 wt %, for TT0, to 31 wt %, for TT2. These variations are mainly due to the distillation and polymerization of pitch light components. In TT3, HS and BS decrease to 23 and 47 wt %, respectively, while PI increases to 47 wt%, which suggests that as the temperature and time of treatment increase, polymerization reactions become more important producing the transformation of HS and BS components in PI. Moreover, pitches obtained at the most severe treatments (425°C-5h and 430°C-10h) contain mesophase, 54 and 66 vol %, respectively.

Table 1. Properties of pitches.

Pitch	Treatment	SP	CY	HS	HI-BS	BS	BI-PS	PI
TT0	None	50	35	32	44	76	14	10
TT1	400°C-5h	70	44	31	39	70	9	21
TT2	425°C-5h	80	53	23	38	61	8	31
TT3	430°C-10h	92	66	23	24	47	6	47

SP, softening point (TMA, °C)
CY, coke yield (wt %, 900°C)
HS, hexane solubles (wt %)
HI, hexane insolubles (wt %)
BS, benzene solubles (wt %)
BI, benzene insolubles (wt %)
PS, pyridine solubles (wt %)
PI, pyridine insolubles (wt %)

Influence of thermal treatment on coke properties

Thermal treatments of pitch did not produce substantial changes in the optical texture of cokes.This is in agreement with previous studies [5] which show that the removal of part of pitch volatile components influences temperatures of mesophase generation and solidification, but only small variations in cokes optical texture are observed. Porosity of cokes, as determined by polarized-light microscopy, slightly decreases with pitch treatments at 400°C-5h and 425°C-5h. However, at 430°C-10h there is a considerable decrease of porosity, from 98 vol % (parent pitch coke) to 54 vol % which means that extensive devolatilization and polymerization are necessary to produce a significant decrease in coke porosity.

Influence of thermal treatment on composite microstructure and properties

Figure 2 shows optical micrographs of representative areas of cross-sections of composites CC-TT0, CC-TT1 and CC-TT3. Matrix microstructural changes correspond to those observed for the individual cokes. Composite from parent pitch (CC-TT0) has a dominant optical texture of domains with only small amounts of mosaics. Mesophase aligns with the fibre surface, producing a region of preferred orientation which extends to the surrounding matrix. Intramatrix cracks narrower than 2 μm were also observed in this composite, together with fibre/matrix debonding cracks, the later representing 2.6 vol % of the composite. With pitch thermal treatment (CC-TT1 and CC-TT3), interface and intramatrix cracks almost disappear (Figure 2).

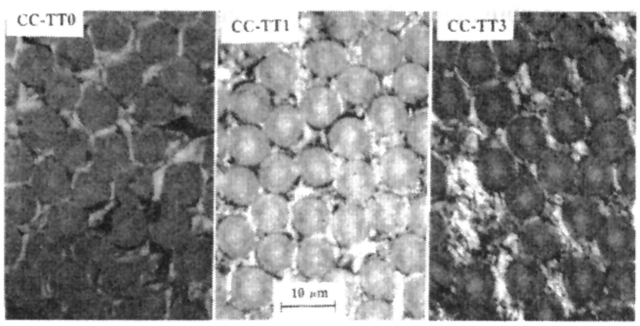

Figure 2. Optical micrographs of composites CC-TT0, CC-TT1 and CC-TT3.

Table 2. Properties of composites.

Composite	FC[1]	d[2]	FS[3]	ILSS[4]	fs[5]
CC-TT0	57	1.53	486	14	8.5
CC-TT1	57	1.54	674	19	11.8
CC-TT2	-	-	783	25	-
CC-TT3	44	-	583	28	13.2

[1] Carbon fibre content (vol %) [3] Flexural strength (MPa)
[2] Bulk density (g cm^{-3}) [4] Interlaminar shear strength (MPa)
[5] Specific flexural strength (MPa/Fibre, vol %)

Thermal treatment of pitch results in a considerable improvement in the strength of composites (Table 2). Interlaminar shear strength increases with the severity of the treatment from 14 MPa, for CC-TT0, to 28 MPa, for CC-TT3. A similar trend is observed for the values of flexural strength. Composite CC-TT1 has a higher flexural strength value (674 MPa) than composite from parent pitch (486 MPa). This improvement continued for CC-TT2 (783 MPa), to then decrease to 583 MPa for CC-TT3. The increase of the strength of the composites can be a consequence of a better fibre/matrix bonding and a more compact carbonaceous matrix material. The polymerization of molecules, which generates a high viscosity system, seems to be responsible for the low fibre content (44 vol %) and the lower flexural strength value of CC-TT3. However, specific flexural strength of this composite increases (Table 2), which is indicative of a material of improved properties.

Conclusions

Heat treatment at 400-430°C of an impregnating coal-tar pitch, causes a significant increase of carbon yield as a consequence of the distillation and polymerization of light components. Cokes from thermally treated pitches do not show substantial variations of optical texture. Porosity of cokes decreases with treatment.

Pitch thermal treatment improves mechanical properties of composites. Fibre/matrix bonding and a more compact carbonaceous matrix seem to be the main responsible. The lower fibre content and lower flexural strength of composite from the pitch treated at 430°C-10h is explained in terms of a high viscosity of the system on carbonization. However, the higher value of the specific flexural strength of this composite compared with that from parent pitch is indicative of an improved matrix.

Acknowledgements

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