PITCH-BASED CARBON/CARBON COMPOSITES WITH DISCONTINUOUS REINFORCEMENTS

C. Blanco, R. Santamaría, J.S. Canga, J. Bermejo and R. Menéndez
Instituto Nacional del Carbón, La Corredoria s/n, Oviedo-33011, Spain

Introduction

One of the main disadvantages of C/C composites is their high cost. The use of coal-tar pitches, granular carbons, i.e. graphites, anthracites, metallurgical coke, and short fibers would substantially reduce the cost of the precursors, allowing the application of more simple and less expensive processing techniques. Volatile components of pitch need to be initially removed or polymerized in order to avoid the development of porosity during carbonization [1,2]. The objective of this study is the preparation of high density C/C composites not requiring further densification. In a first stage, different pitches, obtained by air-blowing and thermal treatments of a commercial coal-tar pitch, are tested as possible binders of amorphous graphite.

Experimental

Pitch treatment conditions and relevant properties of resultant pitches are summarized in Table 1.

Amorphous graphite (Asbury 9985, < 100 μm) was mixed with pitch at temperatures which ensure a good wettability. Initially, different proportions of pitch were tested, 30 wt % of pitch being most suitable. 10 grams of pitch/graphite was used to prepare pellets of 3 cm diameter by pressing the sample at 400 kg cm^{-2} . A total of 5 pellets of each pitch were prepared for different tests. Pellets from parent pitch were obtained at room temperature, and others at temperatures which vary from 50 °C to 100 °C, with increasing pitch softening point. 4 pellets of each pitch were carbonized at 1 °C min^{-1} to 1000 °C under nitrogen, and percentage of carbonaceous residue, final amount of binder and volumetric contraction were determined. Apparent density and open porosity of the pellets, before and after heat treatment, were calculated according to DIN 51 918 standard; real density in He was measured in a Micromeritics AccPyc 1330 picnometer. Binder distribution and optical texture of heat treated samples were characterized by optical microscopy. Compressive strength tests were performed according to ASTM C 695-81 standard.

Results and Discussion

Pitches prepared for this study show different degree of polymerization/condensation, as deduced from their softening points and solubility values (Table 1), which increase with the severity of the treatments. Moreover, pitches obtained by air-blowing are all isotropic, while those obtained by thermal treatment contain some mesophase (10.5 and 21.6 %), although the degree of polymerization seems to be similar.

Table 1.- Pitch properties

Pitch	SP (°C)	CY (%)	TI (%)	NMPI (%)	Mesoph. (%)	C/H
PARENT, none	95	41.0	21.0	6.3	0	1.65
AB10, air/ 275°C/ 10 h	139	48.0	36.6	13.6	0	1.82
AB18, air/ 275°C/ 18 h	168	57.6	44.6	18.9	0	1.83
AB25, air/ 275°C/ 25 h	197	61.8	51.8	24.9	0	1.86
TT7, N_2/ 430°C/ 1 h	152	53.8	39.2	17.8	10.5	1.80
TT3, N_2/ 430°C/ 2 h	159	56.3	44.4	22.4	21.6	1.82

SP, Softening point Mettler; CY, Coke yield; TI, Toluene insolubles; NMPI, N-methylpyrrolidone insolubles; Mesoph., Mesophase content; C/H, Atomic ratio

For the preparation of pitch/graphite pellets, a proportion of 30 wt % of pitch was selected, because lower amounts of pitch were not enough to bind the graphite and with higher amounts, pellets were distorted. Mixing operation became more difficult as the softening point of pitches increased. Neither air-blowing nor thermal treatment of pitch caused any problem at the pressing/forming process. Carbonization of pellets at 1000 °C generated macroscopic cracks in AB25, which are absent in the others. Optical microscopy showed that pitch/binder distribution was very homogeneous, except for AB25 pellets.

Higher pitch carbon yields resulted in an increase in the pellet yield after carbonization and also in a higher binder content. Further, as a consequence of the graphite presence, pitch carbon yield in the pellet increased in comparison with the value obtained from the carbonization of pitch itself (Table 2).

Apparent density of green pellets slightly decreased with the severity of pitch treatments (Figure 1). This could be a consequence of the increased elasticity shown by the polymerized pitches [3]. Apparent density of carbonized pellets is lower than that of the green pellets (Figure 1), due to volatile release, although volumetric contraction occurred during carbonization (Table 2). However, differences between both densities diminish for the most polymerized pitches. The slight increase of the real density of green pellets (Figure 1) with treatments can be a consequence of the increase of pitch density, which varies from 1.305 g cm^{-3} for parent pitch to 1.349 g cm^{-3} for that most treated. On the contrary, the decrease of real density of the carbonized pellets with increasing severity of pitch treatment can be due to the higher amount of binder, which has a lower density than graphite.

Optical microscopy shows that pitches AB18 and AB25 developed a completely isotropic texture in the pellet, even though they produced anisotropic cokes (domains and small domains) when carbonized singly. The other pitches developed anisotropic textures. A possible explanation for the different behaviour of AB18 and AB25 could be the high viscosity of the pitch/graphite system on carbonization due to the high polymerization degree of these pitches, which diminish pitch fluidity and consequently pitch ability to form mesophase.

Compressive strength of pellets increased with the severity of pitch treatments, except for AB25 pellets which confirms the unsuitable processing conditions for this pitch. The highest value.of TT3 pellets could be a consequence of the combination of a high pitch carbon yield with a low softening point, and the anisotropic texture of the resultant binder.

Conclusions

Thermal treatment of pitches yields products with a better CY/SP for their use as carbon matrix precursors.

The presence of graphite influences pitch carbonization processes, through an increase of carbon yield and a modification of the optical texture in the final carbon.

Thermal and air-blowing treatments of pitch improve the compressive strength of pitch/graphite composites.

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Table 2.-Carbonized pellets characteristics

Pitch	Pellet yield (wt %)	Binder (%)	Δ CY (wt %)	VC (vol %)	OP (vol %)
PARENT	81.2	17.2	5.7	5	33
AB10	83.8	19.8	7.4	6	29
AB18	87.0	22.7	8.3	5	23
AB25	87.7	23.4	6.7	2	24
TT7	86.1	21.9	9.0	3	30
TT3	87.3	23.0	10.6	5	30

Δ CY, change in pitch carbon yield in pellet compared to its carbon yield when carbonized singly
VC, % volume difference between green and carbonized pellets.
OP, open porosity in carbonized pellets.

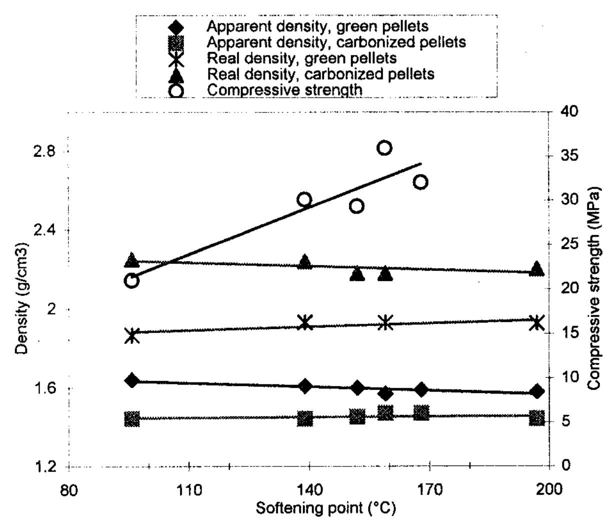

Figure 1-. Densities and mechanical properties of pellets.