PITCH PYROLYSIS BEHAVIOUR IN THE PRESENCE OF VARIOUS GRANULAR CARBONS

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Introduction

Coal-tar pitches are often used as matrix precursors in carbon composites. The properties of the final material depend on the characteristics of the pitch coke formed during the carbonization process. The presence of granular carbon, used as a filler in the manufacture of the carbon composites, affects mesophase formation during pitch carbonization and the development of porosity. In this study, four different pitches were mixed with four granular carbons in order to study the influence of the different fillers on pitch pyrolysis during carbonization. After moulding, the green pellets were heated to 350, 500, 700 and 1000 ºC. Properties of the resultant pellets were then measured for each stage of heat treatment.

Experimental

The four pitches used as matrix precursors were: (i) a commercial coal-tar pitch (D0), (ii) the same pitch air-blown for 18 h (G18), (iii) thermally treated for three (D3) and (iv) thermally treated for five hours (D5). The fillers used were a commercial graphite (GR), a Spanish anthracite (AT), a foundry coke (FC) and a green petroleum coke (PC).

Each pitch was mixed with the different carbon particles in the proportion of 30/70. The mixtures were heated to a temperature 100 ºC higher than the softening point of the pitch in order to ensure a good impregnation of the carbon particles by the pitch.

Mixtures were sieved to below 1mm and five pellets from each pitch/filler system were molded in a conventional way (axial pressing at 80 MPa). After removing the mixture from the mold, the resultant pellets were heated up to 350, 500, 700 and 1000 ºC at the constant rate of 1 ºCmin^{-1}.

The materials obtained were characterized by apparent density, open porosity, carbon yield, volume variation and optical texture. Apparent density and open porosity were determined by water immersion in accordance with the ASTM C20-83 standard.

Results and Discussion

Table 1 summarizes the main properties of pitches used as matrix precursor. Modified pitches, D3, G18 and D5 have higher softening points and higher IT, C/H and carbon yields than D0, as a consequence of their previous treatments and resultant polymerization. Thermally treated pitches, D3 and D5 contain mesophase, D0 and G18 being entirely isotropic.

Table 1. Main properties of pitches

Pitch	C	H	C/H	SP	Mes	TI	CY
D0	92.5	4.5	1.7	97	0	21.8	37.6
D3	94.1	4.0	2.0	169	30	51.6	61.3
D5	94.3	3.8	2.1	336	50	65.0	69.7
G18	92.8	4.2	1.9	180	0	46.7	53.7

C: Carbon content
H: Hydrogen content
C/H: Carbon/hydrogen atomic ratio
SP: Softening point (ºC)
Mes: Mesophase content (vol %)
TI: Toluene insoluble content (wt %)
CY: Carbon yield (wt %)

With respect to the characteristics of the carbon fillers it is relevant to note the high sulfur content of green petroleum coke and the high ash content of the graphite and the anthracite (Table 2).

Table 2. Main properties of granular carbon used as filler

Filler	Moist.	Ash	C	S	O	dHe
AT	3.41	11.4	82.3	1.0	3.0	1.70
GR	0.08	11.5	88.5	0.2	0.8	2.35
PC	0.13	1.4	86.3	5.8	1.4	1.47
FC	0.10	5.8	92.2	0.5	0.4	2.02

Moist.: Moisture content (wt %)
Ash: Ash content (wt %)
C: Carbon content
S: Sulfur content
O: Oxygen content
d_{He}: Helium density (gcm^{-1})

Weight losses with increasing heat treatment temperature of the petroleum coke and foundry coke composites are in Figures 1.a and 1.b, respectively. For petroleum coke, weight loss depends on the carbon filler and on the pitch. The D0 pellets commence to lose weight below 350 ºC, while for the modified pitches, the most important variations occurs between 350 and 500 ºC. Petroleum coke composites lose weight above 500 ºC because of the further pyrolysis reactions of the green coke.

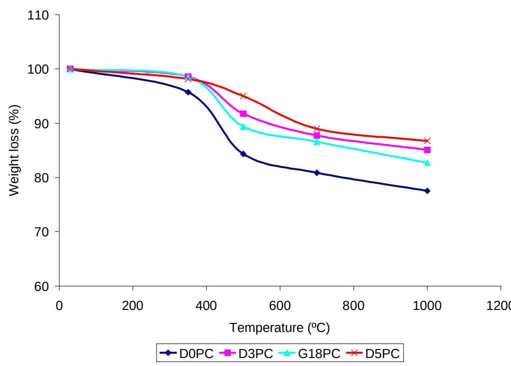

Figure 1.a. Weight loss of PC composites during carbonization

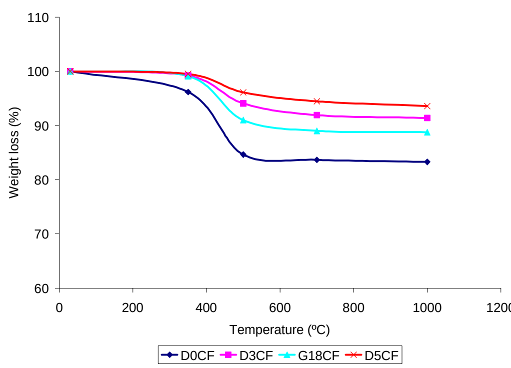

Figure 1.b. Weight loss of FC composites during carbonization

The volume of the composite changes during carbonization. Volume variations of petroleum coke composites are shown in Figure 2. These carbon composites undergo significant volume variations during carbonization without pellet deformation. The curves are similar for the different pitches. It seems that the petroleum coke controls these variations. During the first heat treatment at 350 ºC, the volume increases significantly, while from 500 ºC a considerable volume contraction occurs.

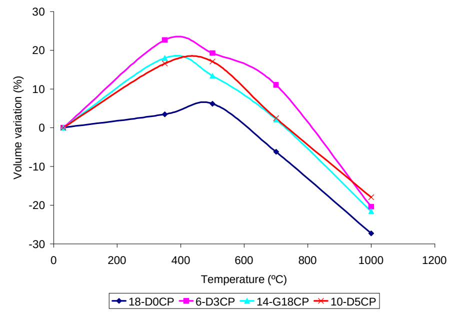

Figure 2. Volume variation of PC composites during carbonization

Related to volume and weight variations, densities and porosities of carbon composites also change during carbonization. Figures 3.a and 3.b show open porosity evolution during carbonization of anthracite and graphite composites, respectively. In both cases the porosity of D0 pellets increases up to 500 ºC, to remain constant at higher temperatures. The most important difference between the two types of composites is found with the modified pitches. Graphite appears to delay the evolution of porosity, especially for the thermally treated pitches. D5 pellet starts to develop porosity at temperatures higher than 500 ºC and continues to do so up to 700 ºC when non-plastic pitch coke is form.

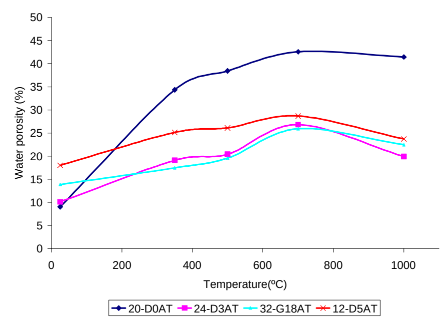

Figure 3.a. Open porosity evolution of AT composites during carbonization

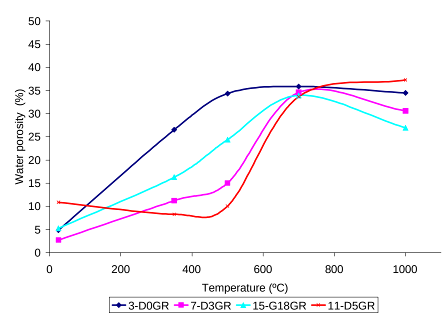

Figure 3.b. Open porosity evolution of GR composites during carbonization

Optical microscopy of surfaces of graphite composites treated at 500 and 700 ºC (Figure 4) confirm the porosity data of these pellets. Optical micrographs show that the initial isotropy of D5 and D3 remains entirely at 500 ºC. At 700 ºC the pitch coke has an anisotropic structure. On the other hand, when petroleum coke is used as a filler, opposite effects are observed. Figure 5 shows that the matrix carbon from the pitch is fully anisotropic at 500 ºC, except for G18 that develops isotropic coke. The other two fillers used, anthracite and foundry coke, had a smaller effect on the optical texture of the pitch during co-carbonization. The remarkable effect that graphite has on pitch pyrolysis agrees with the results discussed above for the evolution of porosity. These results indicate a strong interaction between the graphite particles and the pitch, especially those that have been thermally treated.

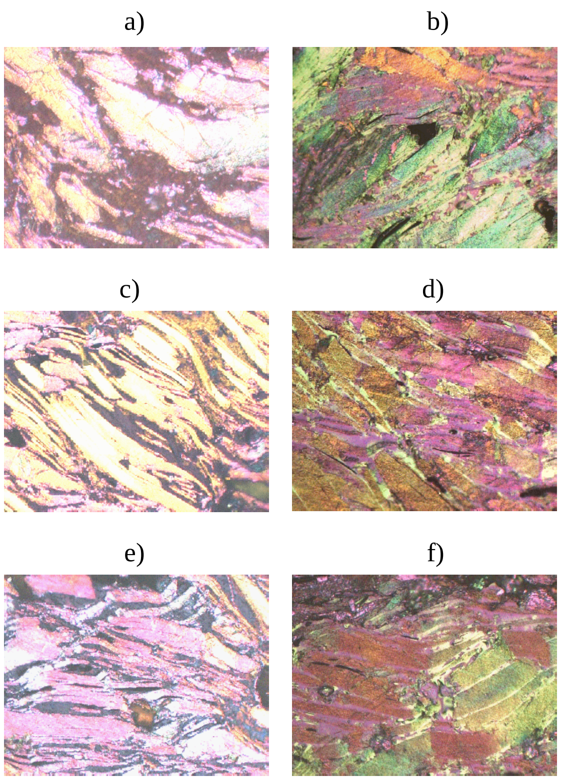

Figure 4. Optical micrographs of GR composites: a)G18GR(500ºC), b)G18GR(700ºC), c)D3GR(500ºC), d)D3GR(700ºC), e)D5GR(500ºC) and g)D5GR(700ºC)

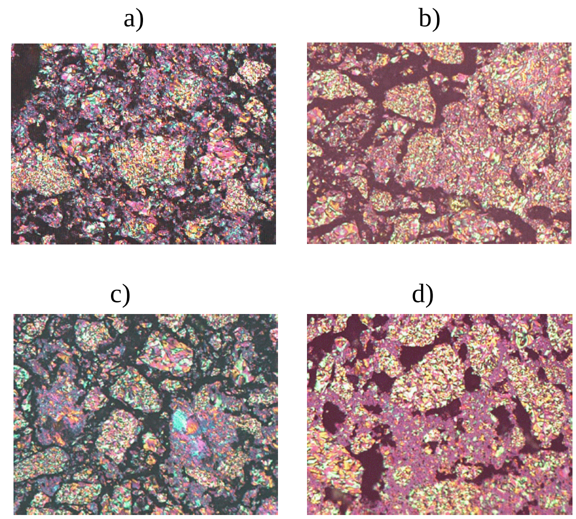

Figure 5. Optical microghraphs of PC composites: a)D0PC(500ºC), b)D3PC(700ºC), c)D5PC(500ºC) and d)G18PC(700ºC),

Conclusions

The type of granular carbons used as fillers has a major influence over pitch behavior during carbonization process. Green petroleum coke accelerates pitch pyrolysis and undergoes significant volume variations during carbonization, while graphite delays pitch pyrolysis especially with thermally treated pitches.