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Structural changes during pitch-based carbon granular composites carbonisation

**Ana Méndez · Ricardo Santamaría ·
Marcos Granda · Rosa Menéndez**

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Abstract This article deals with the study of carbon composites behavior during their carbonization. Composites were prepared using four granular carbons (graphite, anthracite, green petroleum coke, and foundry coke) and four pitches (a commercial impregnating coal-tar pitch, an air-blown and two thermally treated pitches). The evolution of the optical microstructure, porosity, volume, and weight of carbon composites was monitored at different intermediate carbonization temperatures (350, 500, 700, and finally 1000 °C). The porosity of composites increases with carbonization due to volume changes and weight loss of pitches. Weight loss of carbon composites during their carbonization mainly depends on the pitch characteristics and it was slightly influenced by the presence of granular carbon. On the other hand, carbon composites with the commercial coal-tar pitch and foundry coke, anthracite, or graphite deform in the initial stages of carbonization (<350 °C) probably due to the lower porosity of the green pellets and the high amount of low-molecular weight compounds of the pitch. Carbon composites with green petroleum coke underwent important dimensional changes during their carbonization, expanding initially and then shrinking at temperatures above 700 °C. The type of granular carbon strongly influenced the microstructure of the final carbon composite, as a result of its effect on the development of mesophase. Graphite, anthracite and foundry coke delays mesophase development, whereas green petroleum coke accelerates mesophase formation.

Introduction

Carbon composites play an important role in brake systems due to their unique combination of properties [1]. These materials are normally manufactured using a carbon-fiber preform, which is densified with a matrix precursor. The most widely used densification processes are chemical vapor deposition of carbon, CVD [2, 3] and liquid impregnation with an organic precursor [4]. In both cases, precursors and processes are expensive leading to high-cost materials. This fact limits their use to high-technological applications where the cost is only justified by the improved performance. The use of cheaper precursors and more simple fabrication processes could reduce the cost of carbon composites and make them competitive in conventional applications [5]. For example, granular carbons could serve as an alternative to carbon fibers and coal-tar pitches could be used as carbon matrix precursors [5]. Both are currently used in the manufacture of electrodes [6], briquettes [7], electrical brushes [8], and other carbon materials [9].

Coal-tar pitches are suitable carbon matrix precursors due to their low cost, their ability to generate graphitisable carbons and their relatively high carbon yield [10]. Moreover, the carbon yield of pitches can be improved and the porosity of pitch-based materials reduced by air-blowing [11] and thermal treatments [12]. These treatments involved the release of volatile compounds and condensation/polymerization reactions of pitch components, producing an increase of carbon yield and softening point. It is generally

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A. Méndez · R. Santamaría · M. Granda · R. Menéndez
Instituto Nacional del Carbón, INCAR, CSIC, C/ Francisco
Pintado Fe, n°26, 33011 Oviedo, Spain

Present Address:
A. Méndez (✉)
Dpto. Ingeniería de Materiales, E.T.S.I.Minas-Universidad
Politécnica de Madrid, C/Alenza n°4, 28003 Madrid, Spain
e-mail: anamaria.mendez@upm.es

accepted that air-blowing yields cross-linked structures, with a bridged bonded molecules via formation of the oxi-radical, whereas thermal treatments generate more planar and condensed structures usually accompanied by mesophase generation [13].

The transformation of a pitch into a carbon matrix requires a carbonization process [14]. Pitch behavior during this thermal treatment and consequently, the microstructure and properties of the final carbon matrix depend on the properties of pitches and the experimental conditions used during carbonization [15]. Moreover, when pitch is used in carbon composites manufacture, the presence of granular carbons greatly influences the pyrolysis behavior of the pitch [16, 17] and consequently, the microstructure and properties of the final composite [18, 19]. Previous research carried out elsewhere has showed that carbon composites exhibit different mechanical and tribological properties depending on the type of pitch and properties of the granular carbons [5, 20]. On the other hand, it was found that the characteristics of the granular carbons and their interaction with the pitch play an important role during the mixing and molding processes [20]. However, it is during the carbonization of carbon composites where the presence of granular carbons seems to have the greatest influence [20]. For this reason, a wide study of carbon composite carbonization was performed for the optimization of preparation conditions.

Experimental

Raw materials

The four coal-tar pitches used as carbon matrix precursors were a commercial impregnating coal-tar pitch (D0) supplied by Industrial Química del Nalón S.A. and the same pitch subjected to air-blowing at 275 °C during 18 h (G18) and thermally treated at 430 °C during 3 and 5 h (D3 and D5, respectively). Detailed experimental conditions for the preparation of G18, D3 and D5 were given elsewhere [21]. Prior to their use as carbon precursors, the pitches were ground and sieved to a particle size < 0.4 mm. Table 1 summarizes the main characteristics of four pitches.

The four granular carbons used were: green petroleum coke (PC) supplied by REPSOL YPF; foundry coke (FC) supplied by Industrial Química del Nalón, S.A., natural graphite (GR) provided by ISMAF; and anthracite (AT) obtained from the North of Spain. All carbons were grounded and sieved to a particle size <0.1 mm. A wide characterization of these granular carbons was performed elsewhere [21]. Main properties are summarized in Table 2.

Carbonization of individual raw materials

In order to achieve a better understanding of the influence of the precursors on the carbonization of the composites, raw materials (pitches and granular carbons) were individually carbonized at 350, 500, 700, and 1000 °C. Two grams of sample were placed in a ceramic crucible and put in the middle of a horizontal furnace. The temperature was raised to 350, 500, 750, and 1000 °C, depending on the experiment, at a heating rate of 1 °C min^{-1}, under nitrogen flow of 25 L h^{-1}.

Carbon yield

The carbon yield of raw materials (pitch and granular carbons) was determined from the weight of the carbonaceous residues obtained at the different intermediate carbonization temperatures.

Light microscopy

The optical texture of granular carbons and pitch-bases carbons during carbonization was analyzed in a Zeiss Axioplan optical microscope. Samples were ground and sieved to a particle size < 0.4 mm, embedded in a epoxy resin, successively ground on two grades of silicon-carbide paper (600 and 1200 grits) and polished successively with two different grades of alumina (1 and 0.05 μm). Microscopic analysis was conducted on each sample using a microscope equipped with adjusted oculars (10 and 5×) fitted with a cross-wire, oil-immersion infinity-corrected objective (50 and 100×) and a one-wave retarder plate to generate interference colors.

Carbon composites preparation

The carbon composites were prepared using the same pitch/granular carbon weight ratio of 30:70 to facilitate the comparison of experimental results, even though this was not the optimum pitch/granular carbon ratio. The preparation of these materials involved three steps: the mixing of pitch/granular carbon systems, the molding of the blend to obtain the green composite pellets and carbonization of green pellet [5, 20]. Five green pellets of each pitch/granular carbon were prepared. One of them was kept as green pellet; the other four were carbonized at 350, 500, 700, and 1000 °C. A flow diagram of the experimental process is given in Fig. 1.

Table 1 Main properties of pitches

Pitch	Elemental analysis (dry basis, wt%)					C/H[a]	SP[b]	CY[c]	TI[d]	MC[e]
	C	H	N	S	O					
D0	92.47	4.53	1.12	0.56	1.61	1.70	97	39.9	21.8	0
D3	94.05	3.98	1.11	0.46	1.05	1.98	169	59.2	51.6	30
D5	94.33	3.79	1.08	0.44	0.96	2.07	336	68.7	65.0	50
G18	92.81	4.15	1.15	0.56	1.79	1.86	180	54.8	46.7	0

[a] Carbon/hydrogen atomic ratio

[b] Softening point (°C)

[c] Carbon yield (wt%)

[d] Toluene insoluble content (wt%)

[e] Mesophase content, determined by light microscopy (vol%)

Table 2 Main characteristics of granular carbons

Granular carbon	Elemental analysis (dry basis, wt%)					Moisture (wt%)	Ash (wt%)	CY[a]	d_{He}^{b}
	C	H	N	S	O				
AT	82.04	1.69	0.95	1.00	2.96	3.41	11.37	91.6	1.70
GR	87.45	0.05	0.00	0.25	0.75	0.08	11.50	98.4	2.35
PC	86.62	2.89	1.83	5.84	1.44	0.13	1.39	90.0	1.47
FC	92.10	0.11	1.06	0.52	0.42	0.10	5.79	99.1	2.02

[a] Carbon yield (wt%)

[b] Helium density (g cm^{-3})

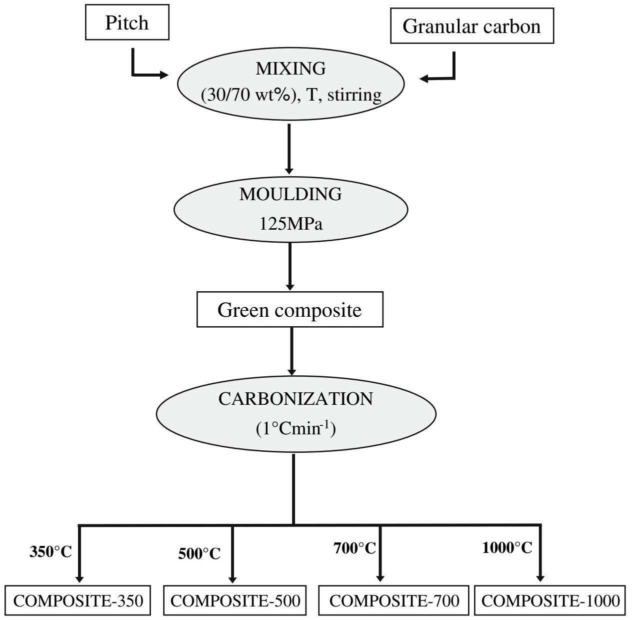


Fig. 1 Flow diagram of the experimental process of carbon composites processing

Mixing process

The first step in the preparation of carbon composites was the mixture of the two components (pitch and granular carbon). In order to ensure an adequate fluidity and a good impregnation of the granular carbons, the mixing process was performed at temperatures of about 100 °C above the softening point of the pitches. Thus, according with pitch properties showed in Table 1, a temperature of 190 °C was used for pitch D0, 270 °C for G18 and D3 and 300 °C for D5. In each case, 100 g of mixture were prepared in a 0.5L stainless steel reactor heated with an electrical furnace under continuous stirring and nitrogen atmosphere. Once the mixing process was accomplished, the mixture was cooled and sieved below 1 mm.

Molding process

The molding of the mixture was performed in a uniaxial press. 10 g of the mixture were placed in a cylindrical stainless steel mould with an inner diameter of 30 mm. The sample was heated to a temperature slightly below the softening point of the pitch in order to prevent the pellet from springing back during demolding. For this purpose, a small furnace was placed around the mould. The furnace was connected to a temperature controller and a thermocouple was inserted inside the mould. According to previous works, the temperature used was 40 °C for D0, 140 °C for D3 and G18 pitches and 180 °C for D5 [5, 20].

Once the temperature was achieved, 125 MPa of uniaxial pressure was applied to the mixture for 3 min.

Carbonization process

Green carbon-composite pellets were carbonized at 350, 500, 700, and 1000 °C. Green pellets were placed in a crucible covered with zircon (particle size <100 μm). The crucible was placed in the middle of a horizontal furnace and the temperature was raised to the desired temperature at a rate of 1°C min^{-1}, under nitrogen flow of 25 L s^{-1}.

Carbon composites characterization

Carbon pellets obtained at intermediate carbonization temperatures were characterized as follows.

Carbon yield

The carbon yield of pellets obtained at each intermediate carbonization temperature was determined from the weight of the carbonaceous residues at 350, 500, 700 and 1000 °C.

Density and porosity of the composites

Bulk density of the green and pellets obtains at intermediate carbonization temperatures were calculated by measuring the weight and volume of the specimens.

The water density and open porosity on the green and carbonized pellets were determined by water immersion in accordance to the ASTM C20-83 standard.

The helium density was determined by helium pycnometry using a Micromeritics AccPyc 1330 equipment.

Light microscopy

Light microscopy was used to study the microstructure evolution of composites during their carbonization. The green and intermediate carbonized pellets were cut in two pieces and embedded in an epoxy resin. Samples were prepared in a similar way to that described above (section "Light microscopy"). Representative photographs were taken at different magnifications (50, 250, 500, and 1000×).

Results and discussion

Effect of carbonization temperature on the properties of the composite precursor

In order to study the effect that each composite component (pitch and granular carbon) has over each other, the four pitches were individually carbonized at 350, 500, 700, and 1000 °C, under the same experimental conditions than corresponding composites. The parent pitch (D0) loses 34, 57, 59, and 60 wt% at 350, 500, 700, and 1000 °C, respectively (Table 3). This indicates that D0 mainly loses weight below 500 °C, whereas the loss above 500 °C being negligible. It is well known that pitches pass through a fluid stage during which pitch molecules are associated producing an anisotropic crystal phase called mesophase [22]. During the development of this fluid stage pitches lose important amounts of volatile, mainly due to the removal of compounds that are present in the initial pitch (compounds that distil before reacting) and low-weight molecules generated as by-products during the multiple and complex reactions that take place on pitch carbonization. Above 500 °C, the pitch is already transformed in carbon material (coke) and weight loses are due to the removal of gases (e.g., hydrogen) generated as the result of cyclation/aromatization reactions that lead to a larger pregraphitic order in the coke [22]. When the parent pitch (D0) is subjected to air-blowing (G18) or thermal treatment (D3 and D5) previously to its carbonization, part of the polymerization, condensation and distillation reactions that occur on carbonization take place during the pitch pretreatment. The modifications produced in the parent pitch by the treatments are not only reflected in the pitch composition and pitch characterization parameters (enrichment in C and increase in softening point, toluene-insoluble content, carbon yield, Table 1), but also in the way that weight loss (Table 3). In fact, the capacity of the pitches to lose weight below 500 °C is significantly reduced, giving rise to cokes at 1000 °C with a yield of 54.9, 59.3, and 68.8 wt% for G18 D3 and D5, respectively. The mitigation of the weight loss in the temperature range in which pitch/filler interactions are established might contribute to enhance the structure and properties of the composite.

The molecular growth of pitch components follows different mechanism depending on the treatment applied. Thermal treatment promotes molecular growth via polymerization/condensation reactions that lead to planar aromatic macromolecules while the air-blowing yields cross-linked structures, with bridged-bonded molecules via formation of the oxi-radical [13]. It is not surprising, therefore, that D3 and D5 contain mesophase (Fig. 2a, b, and c) while G18 is entirely isotropic (Fig. 2d). Figure 3 shows optical micrographs of carbonaceous residues obtained at 350, 500, and 700 °C. At 350 °C, D0 and G18 pitches rest as isotropic systems, whereas initial isotropic phase of D3 and D5 generates small mesophase spheres of different sizes, without QI particles in their surface (Fig. 3a, part A). This mesophase formation al tower temperatures (<350 °C) could be related with the presence of large molecules on the isotropic phase of thermally

Table 3 Weight loss (%wt) of pitches at intermediate carbonisation temperatures

Pitch	350 °C	500 °C	700 °C	1000 °C
D0	33.65	56.67	59.56	60.09
D3	13.56	30.51	37.67	40.75
G18	15.16	40.04	41.81	45.16
D5	4.60	25.75	30.67	31.25

treated pitches [12, 13]. This fact could easily promote mesophase development at lower temperatures. On the other hand, QI particles rest in the initial mesophase surface (Fig. 3a, part B) leading to spheres with different sizes. At 500 °C, all pitches yield to semi-coke systems of different light microstructure and any isotropic pitch were found (Fig. 3b, c). Semi-cokes from thermally treated pitches, D3 and D5 show large light texture (Fig. 3b) than semi-coke from G18 (Fig. 3c). At 700 °C, similar to 500 °C, microstructure of cokes generated was greatly influenced by the pitch properties [15]. In the case of thermally treated and commercial coal tar pitch, the light texture of the coke is very similar, predominantly composed of domains associated with the QI (Fig. 3d, e, and f). The coke obtained from the air-blown pitch, G18, shows a light texture of a smaller size that the others mainly composed of small domains and mosaics (Fig. 3g).

Table 4 summarizes the weight loss of four granular carbons at intermediate carbonization temperatures. Graphite and foundry coke do not undergo important weight changes. The moisture content of anthracite showed in Table 2 was responsible of their weight reduction at temperatures lowest than 350 °C (1.47 wt%). On the other hand, anthracite, and green petroleum coke undergo pyrolysis reactions at temperatures highest than 500 °C, leading to 8.38 and 9.99 wt% weight losses at 1000 °C, respectively.

Weight loss of carbon composites during their carbonization

Figure 4 shows carbonization weight loss of the 16 different carbon composites. Usually, carbon composites with D0 pitch showed the highest weight loss that start at temperatures lower than 350 °C. This fact is in agreement with the small carbon yield of D0 pitch (Table 1) due to their low-mean molecular size. Carbon composites with D3, D5, and G18 pitches show small weight loss at temperatures lowest than 350 °C, according with results showed above (Tables 1 and 3). In all cases, the highest weight variations of pellets were produced at temperatures from 350 to 500 °C, where main pyrolysis reactions were produced [16, 17]. At higher temperatures (>500 °C), carbon composites with anthracite and green petroleum coke continue their weight changes (Fig. 4a, b respectively) as a result of pitch pyrolysis but specially, anthracite and green petroleum coke transformations (Table 4). This fact could have a negative effect on their final mechanical properties and

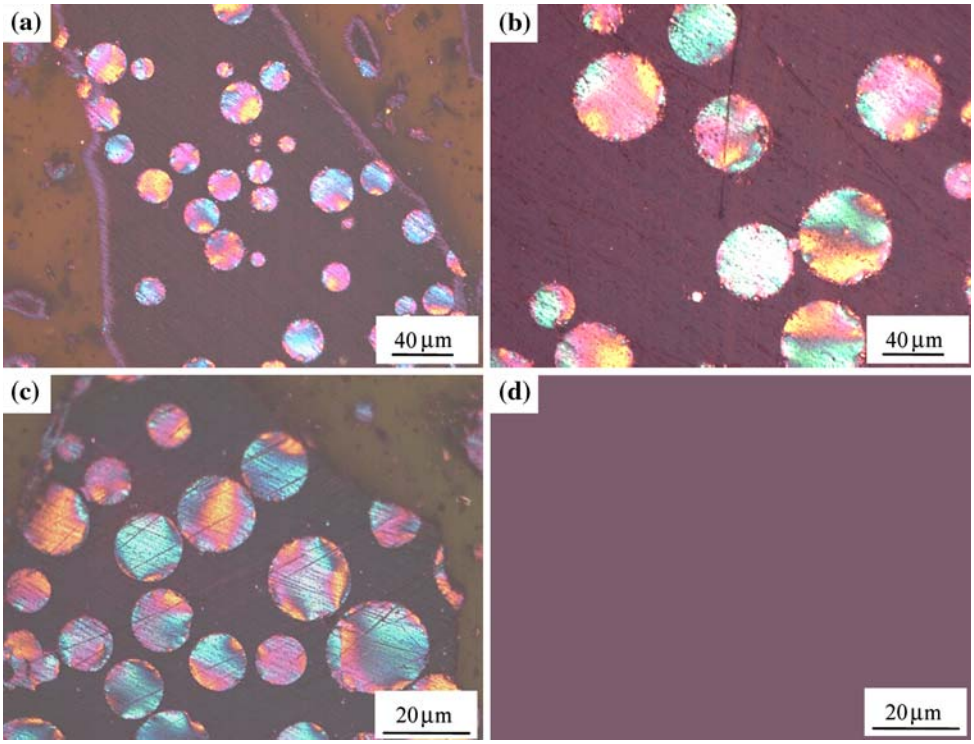


Fig. 2 Optical micrographs of pitches: (**a**) and (**b**) D3, (**c**) D5 and (**d**) G18

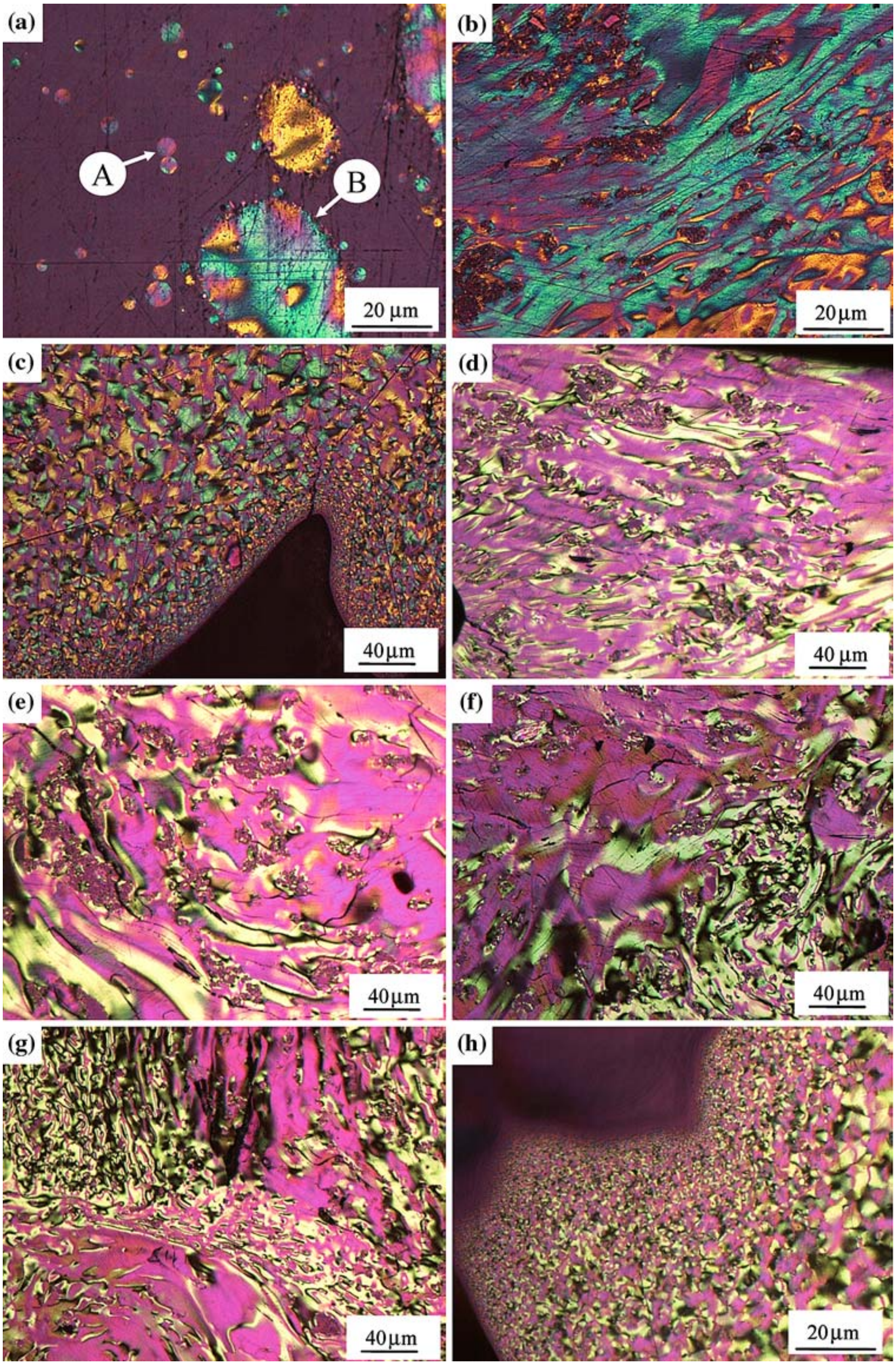


Fig. 3 Optical micrographs of pitches treated at intermediate carbonisation temperatures: (**a**) D3 (350 °C); (**b**) D3 (500 °C); (**c**) G18 (500 °C); (**d**) D0 (700 °C); (**e**) D3 (700 °C); (**f**) D5 (700 °C); (**g**) and (**h**) G18 (700 °C)

consequently, heat rate need to be controlled in order to provide an adequate volatile release.

Foundry coke and graphite do not undergo important variations during their carbonization (Table 4). Consequently, it is normal that carbon composites with foundry coke (Fig. 4c) undergo main weight changes at lower temperatures (<500 °C). However, graphite composites show an interesting behavior (Fig. 4d). At elevated temperatures, even higher than 700 °C, graphite composites with modified pitches (D3, D5, and G18) undergo significant weight losses. This result could indicate that pitch pyrolysis was delayed and continues at highest temperatures. Previous works have showed that presence of granular carbons play an important role in the pyrolysis

Table 4 Weight loss (wt%) of granular carbons at intermediate carbonization temperatures

Granular carbon	350 °C	500 °C	700 °C	1000 °C
AT	1.47	1.85	5.59	8.38
FC	0.43	0.64	0.75	0.88
PC	0.65	1.24	3.67	9.99
GR	0.14	0.70	0.99	1.59

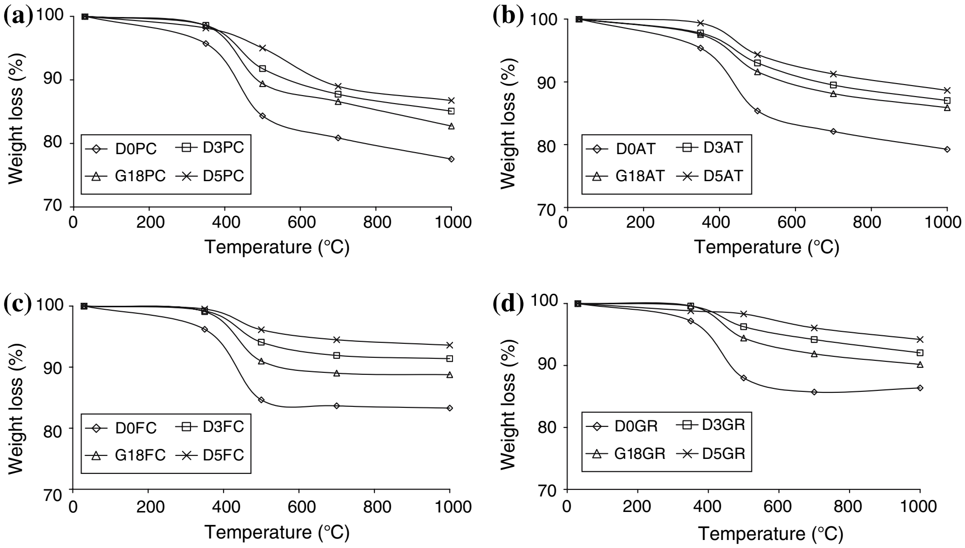


Fig. 4 Weight loss (%) during carbonisation of carbon composites reinforced with: (**a**) petroleum coke; (**b**) anthracite; (**c**) foundry coke (**d**) graphite

behavior of coal-tar pitches, whereas green petroleum coke accelerates pyrolysis reactions, graphite particles seems to delay these reactions [16, 17].

Dimensional variations of carbon composites during their carbonization

Previous works have showed that pitch-based carbon composites undergo considerable dimensional changes after their carbonization [18, 20]. An expansion is usually found in the early stages of pitch carbonization followed by shrinkage at higher temperatures (>700 °C). It is known that anthracite and green petroleum coke considerably shrink, when temperature increases above 600 °C, whereas foundry coke and graphite do not undergo dimensional changes with thermal treatments. The overall volume changes of pellets would be the result of these individual changes in addition to the pitch/granular carbon interactions.

Figure 5 shows volume variations of carbon composites during their carbonization. It is interesting to note that composites with green petroleum coke showed important volume changes (Fig. 5a) without any external deformation of pellets. Pellets with modified pitches undergo volumetric expansion during first stages of carbonization (15–20 wt%), that could be due to several factors like: the relaxation of internal stresses presents in the green pellet originated in the molding process, the expansion of gases occluded during molding of the blend or the release of volatile compounds with thermal treatment. In this way, previous works have showed the high difficulty of some green petroleum coke mixtures to compact forming the pellets [18, 20]. This fact could originate high internal stresses on the pellet that relax during the first steps of carbonization. The D0 pitch has an elevated content of volatile compounds but corresponding pellet not undergo important volume expansions at first stages of carbonization, probably due to the elevated porosity of green pellet (25.36 vol%, as will be comment in Section “Helium and water porosity evolution of carbon composites during their carbonization”). At temperatures highest than 500 °C, pellets undergo important volume reductions (20–30 vol%) due to carbon matrix and green petroleum coke shrinkages.

Carbon composites with anthracite showed important variations in their volume during carbonization process (Fig. 5b). At first stages of carbonization, only pellet with D0 swell and expand whereas not important volume changes were observed with modified pitches. In a different way to pellets with green petroleum coke, expansion of pellet with anthracite and D0 pitch was accompanied with external deformation. The elevated content of D0 pitch on

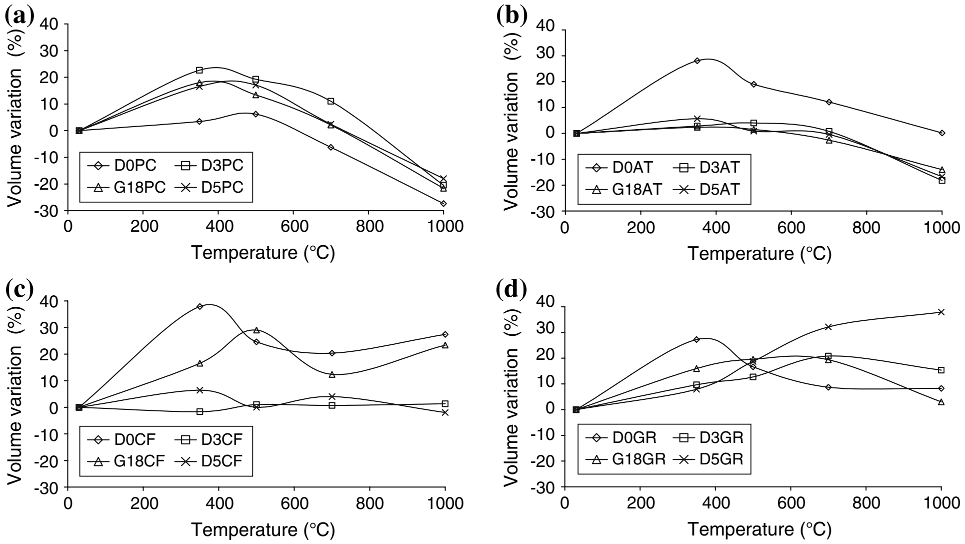


Fig. 5 Volume variation (%) during carbonisation of carbon composites reinforced with: (**a**) petroleum coke; (**b**) anthracite; (**c**) foundry coke and (**d**) graphite composites

volatile compounds that release at temperatures below 350 °C and the lower porosity of green pellet in comparison with petroleum coke (Section "Helium and water porosity evolution of carbon composites during their carbonization") seem to be responsible of this fact [20]. On this hand, modified pitches showed a lower content of volatile compounds that could release by the porosity of pellet. At highest temperatures (>700 °C), an important volume reduction of pellets with modified pitches (G18, D3 and D5) was observed due to the shrinkage of pitches and the anthracite particles.

Figure 5c shows volume variations during carbonization of carbon composites with foundry coke. The main volume changes correspond to D0 and G18 pitches, whereas small variations were observed in pellets with thermally treated pitches (D3 and D5). Pellets prepared with D0 and G18 pitches showed an important volume expansion at first stages of carbonization followed by a lightly shrinkage and subsequent expansion at temperatures highest than 700 °C.

Finally, Fig. 5d shows volume variations of carbon composites with graphite. An important expansion was produced at temperatures lowest than 350 °C, especially with D0 pitch. This expansion was accompanied with small pellet deformations. This fact could be due to lower porosity of pellets prepared with graphite (5–10 vol% as will be comment in Section "Helium and water porosity evolution of carbon composites during their carbonization") [20]. Carbon composites with modified pitches (D3, D5 and G18) show an interesting behavior during their carbonization. Pellets seem to be a plastic system at temperatures highest than 500 (or 700 °C in case of D5 pitch). Previous works have showed that presence of graphite particles delays pitch pyrolysis reactions, especially with thermally treated pitches (D3 and D5) [17]. In this way, section 3.2 has showed that weight loss of pellets with modified pitches and graphite starts at elevated temperatures (>500 °C). Green pellets with graphite have a low porosity and volatile compounds would rest inside the pellet leading to plastic systems at elevated temperatures.

Bulk density evolution of carbon composites reinforced with green petroleum coke

Pitch-based carbon composites develop a large number of pores during their carbonization [18, 20]. It is generally accepted, that porosity developed below 400 °C was mostly due to an important release of volatile compounds from pitches. At highest temperatures, porosity variations could be due to the shrinkage of carbon matrix and granular carbons such as anthracite or green petroleum coke. In this work, previous sections have showed that carbon composites with green petroleum coke undergo important volume and weight variations during their carbonization. Figure 6 shows their bulk density evolution during carbonization. It is interesting to note that all pellets showed the same trend, independently on the pitch use. This fact indicates that it is the green petroleum coke, which seems to control the porosity evolution of corresponding carbon composites. Weight loss (Fig. 4a) and expansion of pellets (Fig. 5a) in the first stages of carbonization cause the corresponding density reduction from 1.01–1.09 g·cm^{-3} to 0.85–0.89 g cm^{-3} at 350 °C (Fig. 6). Then, an important density increases was observed from 0.80–0.83 g cm^{-3} at 500 °C to 1.08–1.19 g cm^{-3} at 1000°C, due to the elevated shrinkage of pellets observed in the Fig. 5a.

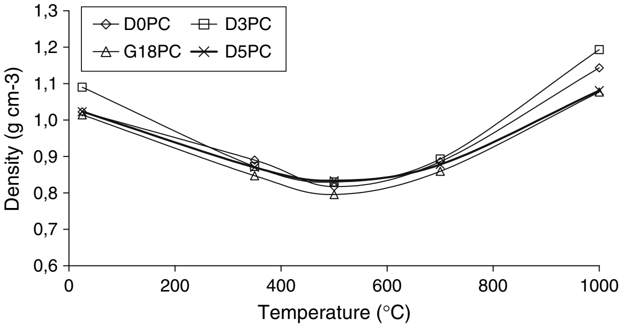


Fig. 6 Bulk density evolution during carbonisation of carbon composites reinforced with green petroleum coke

Helium and water porosity evolution of carbon composites during their carbonization

Figure 7a shows the helium porosity evolution during carbonization of carbon composites reinforced with petroleum coke. Generally, all pellets with green petroleum coke show a similar trend. First, it is necessary to note that green pellets had an elevated porosity (22–29 vol%), which probably will provide the release of pitch volatile compounds during their carbonization without external deformation. Nevertheless, pellets underwent an increase of porosity with carbonization at 350°C. Figure 4a has showed that these composites do not undergo important weight loss during thermal treatment at 350 °C. However, at first stages of carbonization, carbon composites with green petroleum coke underwent an important volume expansion that could be responsible of the observed highest porosity increases (Fig. 7a). The porosity of pellets rises with carbonization temperature and only decreases at temperatures highest than 700 °C due to the high shrinkage of green petroleum coke at these temperatures.

Figure 7b shows the helium porosity evolution of carbon composites with foundry coke. In this case, pellets show a different evolution depending of the pitch used. Green pellet with G18 has an elevated porosity (24.06 vol%) that slightly decreases with carbonization at 350 °C (21.57 vol%). This fact was produced whereas volume of pellet increases (Fig. 5d) and could be due to a reorganization of pitch around the pellet during the first stages of carbonization. Carbon composites with D0 and D3 pitches show a continuous increase of porosity during their carbonization. In case of D5 pitch, the porosity decreases at temperatures highest than 700 °C probably due to the carbon-matrix shrinkage at these temperatures.

Figure 7c, d show helium and water evolution of anthracite carbon composites, respectively. In a similar way to other carbon composites, pellet with D0 shows an elevated porosity increase during their carbonization at 350 °C. This pellet swells and deforms in a similar way that

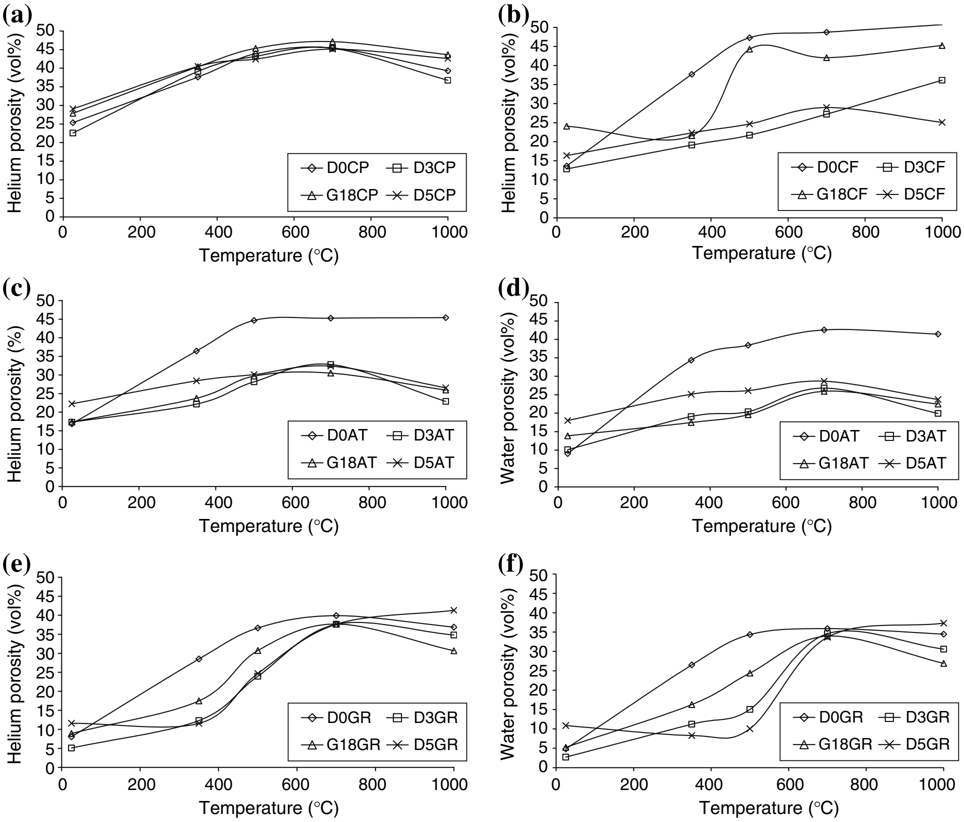


Fig. 7 Porosity evolution during carbonisation of carbon composites reinforced with: (**a**) petroleum coke; (**b**) foundry coke; (**c**) and (**d**) anthracite; (**e**) and (**f**) graphite

pellet with D0 and foundry coke, leading to the elevated porosity formation (from 16.84 vol% in green pellet to 36.43 vol% at 350 °C). It was interesting to note that water porosity of pellets (Fig. 7d) starts their increase at higher temperature that helium porosity (Fig. 7c). This fact proves that firstly small pores accessible to helium atoms were formed and during subsequent heat treatment, their size increases leading to large pores accessible to water molecules. From 700 to 1000 °C, the porosity of pellets decreases due to their shrinkage of botch components, pitch and anthracite.

Carbon composites with graphite and modified pitches show an interesting weight loss (Fig. 4c) and volume evolution (Fig. 5c) during their carbonization that consequently, will influence on their porosity evolution. Figure 7e, f show helium and water porosity evolution, respectively. An elevated increase of porosity with carbonization at 500 °C was observed for pellets with D0. Carbon composites with graphite and modified pitches (G18, D3 and D5) have an interesting behavior. Pellets with D3 and G18 undergo a lower-porosity increase with treatment at 350 °C, whereas pellet with D5 slightly decreases their porosity. From 350 to 500 °C, helium porosity of these pellets increases. In case of water porosity evolution, the most significant increase was produced at temperatures between 500 and 700 °C leading to pellets with similar porosity values (35 vol% and 37 vol% for water and helium porosity, respectively). In case of pellets with D5, the porosity continues to increase at temperatures highest than 700 °C. According to weight loss (Fig. 4c), volume variation (Fig. 5c) and porosity evolution (Fig. 7c, d) of carbon composites with graphite and modified pitches, experimental results indicate that an important pyrolysis delays of D3, D5 and G18 pitches was produced in the carbon composites reinforced with graphite. These results were according with that showed previously for pitch/granular carbons mixtures [16, 17].

Microstructure evolution of carbon composites during their carbonization

Previous works have showed that light texture evolution of carbon matrix was strongly influenced by the properties of granular carbons used as reinforcing material [18]. It has showed that D0 and G18 pitches lead to homogeneous mixtures, whereas thermally treated pitches (D3 and D5), which contain mesophase, undergo a different behavior during the mixing and molding process depending on the nature of the granular carbon used leading generally, to more heterogeneous samples [21].

Figure 8 shows optical micrographs of carbon composites with green petroleum coke at intermediate carbonization temperatures. First, it could be observed that pellets do not show good compaction of both components at all intermediate carbonization temperatures. Previous works have showed that green petroleum coke needs an elevated pitch weight ratio on the mixture to provide a compacted pellet [20]. Figure 8a, b and c show optical micrographs of pellets with green petroleum coke heat treated at 350 °C. D0 and G18 pitches lead to homogeneous samples with an isotropic-pitch-carbon matrix (Fig. 8a) whereas D3 and D5 showed the isotropic (Fig. 8b) and anisotropic phase (Fig. 8c) well differenced. In case of D5 pitch, pellet was heterogeneous with mesophase separated from the isotropic phase and petroleum particles (Fig. 8c). This fact was originated by the high softening point of D5 pitch that difficult their mixture with the granular carbon. Important variations were produced on pellets with carbonization from 350 to 500 °C. Figure 8d, e, and f show that different pitches were transformed into a semi-coke material. At 500 °C, air-blow pitch (G18), generates a light texture of coarse mosaics and fine mosaics with isotropic coke (Fig. 8d, e). In case of thermally treated pitches, D5 and D3 (Fig. 8f, g, respectively), the isotropic and anisotropic phases lead to different carbon-matrices, the former shows a light texture of mosaics (Fig. 8f, part A and Fig. 8g) and the latter preserves its original texture (Fig. 8f, part B). Comparison of Figs. 2 and 8 shows the great influence of green petroleum coke on the pyrolysis of pitches. So, it could be observed the high volume of pores that carbon composites with petroleum coke develop with carbonization at 500 °C, especially when D0 pitch was used as carbon matrix precursor. Light texture generates at 500 °C was kept up at higher temperatures and not important changes were produced (Fig. 8h, i, and j show optical micrographs at 700 °C).

Figure 9 shows optical micrographs of carbon composites with anthracite at intermediate carbonization temperatures. At 350 °C, pellets with D0 and G18 were homogeneous samples (Fig. 9a), whereas D3 and D5 leads to more heterogeneous pellets with many coalesced mesophase (Fig. 9b). One of the aspects that distinguish coal-tar pitches from pitches obtained for other sources is the presence of solid particles insoluble in quinoline, called primary quinoline insolubles (QI). During pitch carbonization, these particles are found on the surfaces of the spheres at the initial stages of mesophase and it is generally accepted that they restrict the development and coalescence of mesophase. Previous works have showed that anthracite particles interact with QI of pitches [21] and mesophase spheres mixed with anthracite deformed and coalesced during the mixing step due to QI particles affinity for anthracite surface [17, 21]. At 500 °C, pellets with D0 and G18 pitches show similar characteristics with low mesophase development (Fig. 9c). Initial mesophase from D3 pitch have generated large pores (Fig. 9d), whereas the initial isotropic phase has generated deformed

Fig. 8 Optical micrographs of carbon composites with petroleum coke carbonised at intermediate temperatures: (**a**) G18PC (350 °C); (**b**) D3PC (350 °C); (**c**) D5PC (350 °C); (**d**) G18PC (500 °C); (**e**) G18PC (500 °C); (**f**) D5PC (500 °C); (**g**) D3PC (500 °C); (**h**) D0PC (700 °C); (**i**) G18PC (700 °C); (**j**) D3PC (700 °C)

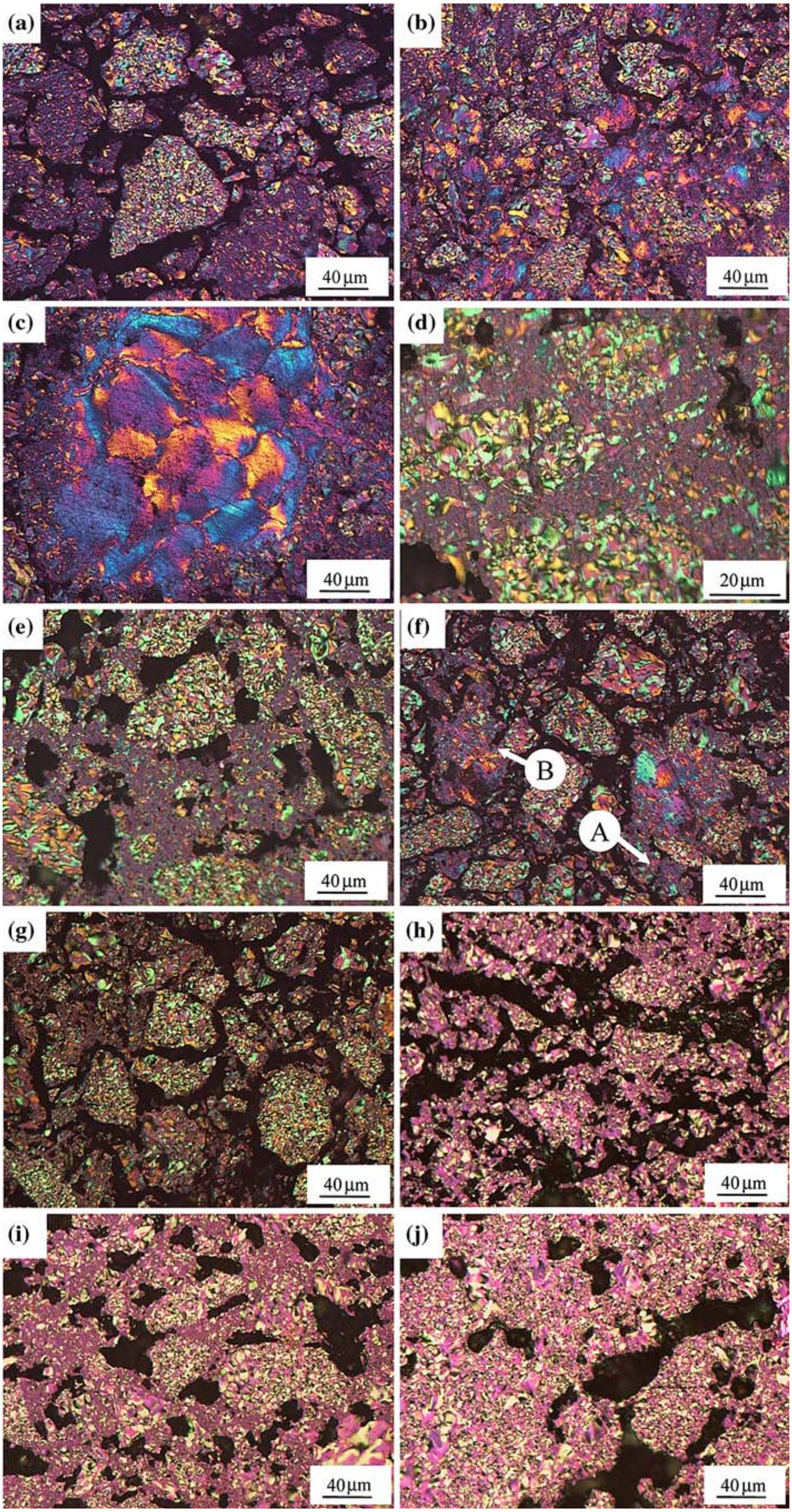
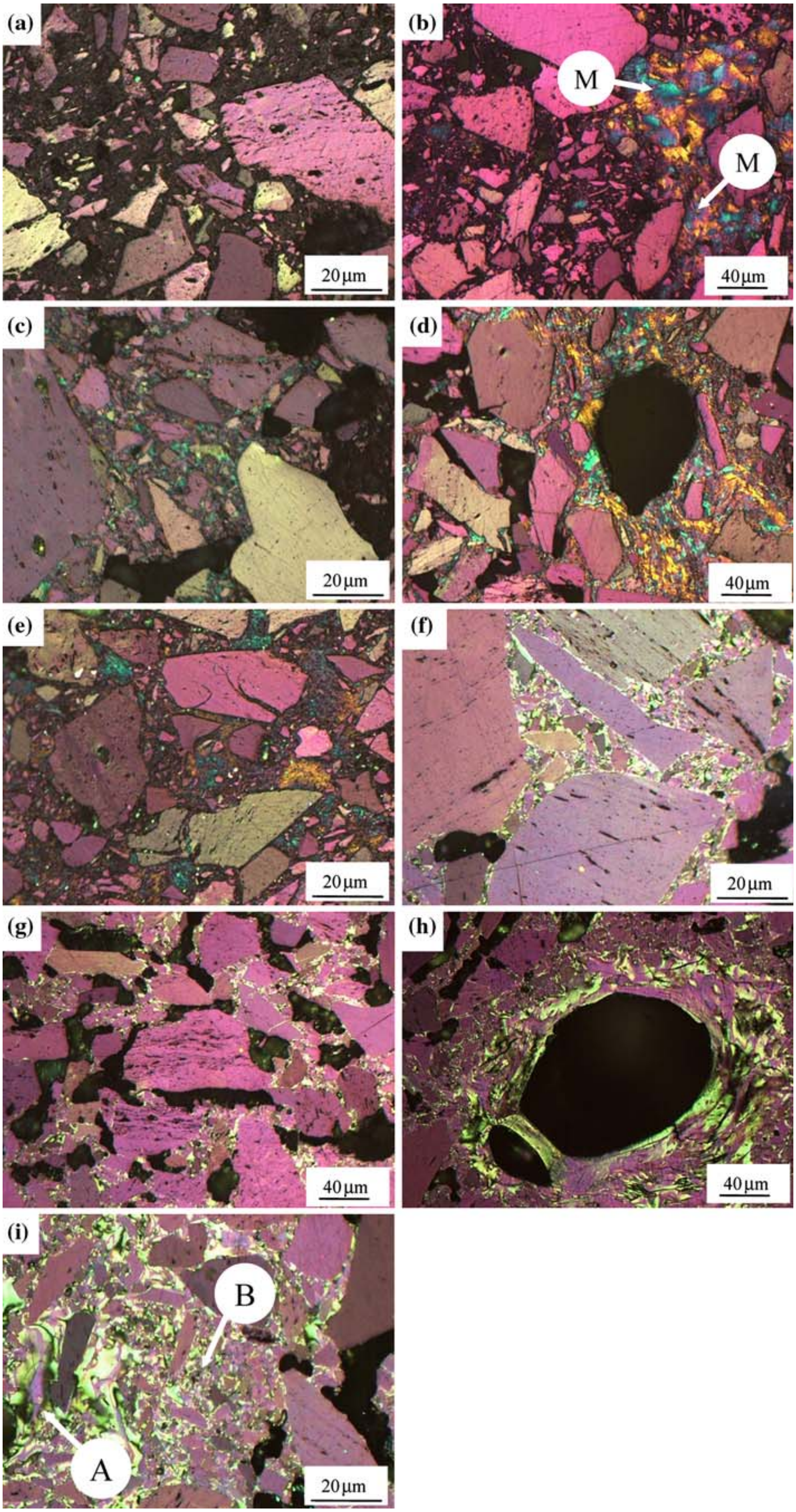


Fig. 9 Optical micrographs of carbon composites with anthracite carbonised at intermediate temperatures: (**a**) G18AT (350 °C); (**b**) D3AT (350 °C); (**c**) G18AT (500 °C); (**d**) D3AT (500 °C); (**e**) D3AT (500 °C); (**f**) G18AT (700 °C); (**g**) D3AT (700 °C); (**h**) D5AT (700 °C); (**i**) D5AT (700 °C)



spheres (Fig. 9e) in a similar way to D0 and G18 pitches (Fig. 9c) due to the absence of QI particles inside the pitch [17]. It could be observed that some isotropic phase is present at 500 °C and not semi-coke systems were formed. So, it could be proposed that anthracite particles delay mesophase growth. From 500 to 700 °C, pellets underwent important changes on their light texture (Fig. 9f, g, h and i). Great porosity was generated with carbonization at 700 °C and different pitches originated cokes with very different light textures. D0 and G18 pitches lead to homogeneous samples with the same light texture inside the pellet (Fig. 9f). So, it could be observed the great porosity of pellets with treated pitches (Fig. 9g, h and i). Furthermore, pellet with D5 shows pores of a large size developed in the regions where the initial mesophase of the pitch was accumulated (Fig. 9h). The use of thermally treated pitches (D3 and D5) leads to heterogeneous samples. As in case of petroleum coke, light texture generated by the initial mesophase of pitch (Fig. 9i, part A) was different to that of the isotropic phase (Fig. 9i, part B). Comparison of Figs. 2 and 9 show that size of coke domains in the carbon composites with anthracite was smallest that them generated by individual pitches. This fact could be related with the increase of pitch viscosity and the pyrolysis delay observed at 500 °C.

Figure 10 shows optical micrographs of carbon composites with foundry coke at intermediate carbonization temperatures. At 350 °C, similar to carbon composites with anthracite or green petroleum coke, pellets with D0 and G18 pitches were homogeneous (Fig. 10a). In carbon composite with D3 not all mesophase (M) is well dispersed among foundry coke particles (Fig. 10b). In a similar way to pellets with green petroleum coke and anthracite, D5 leads to poor mixtures due to their elevated mesophase content (Fig. 10c). At 500 °C, foundry coke seems to delay mesophase development (Fig. 10d). Pellets show a small growth of mesophase, some pitch rest as isotropic phase (I)

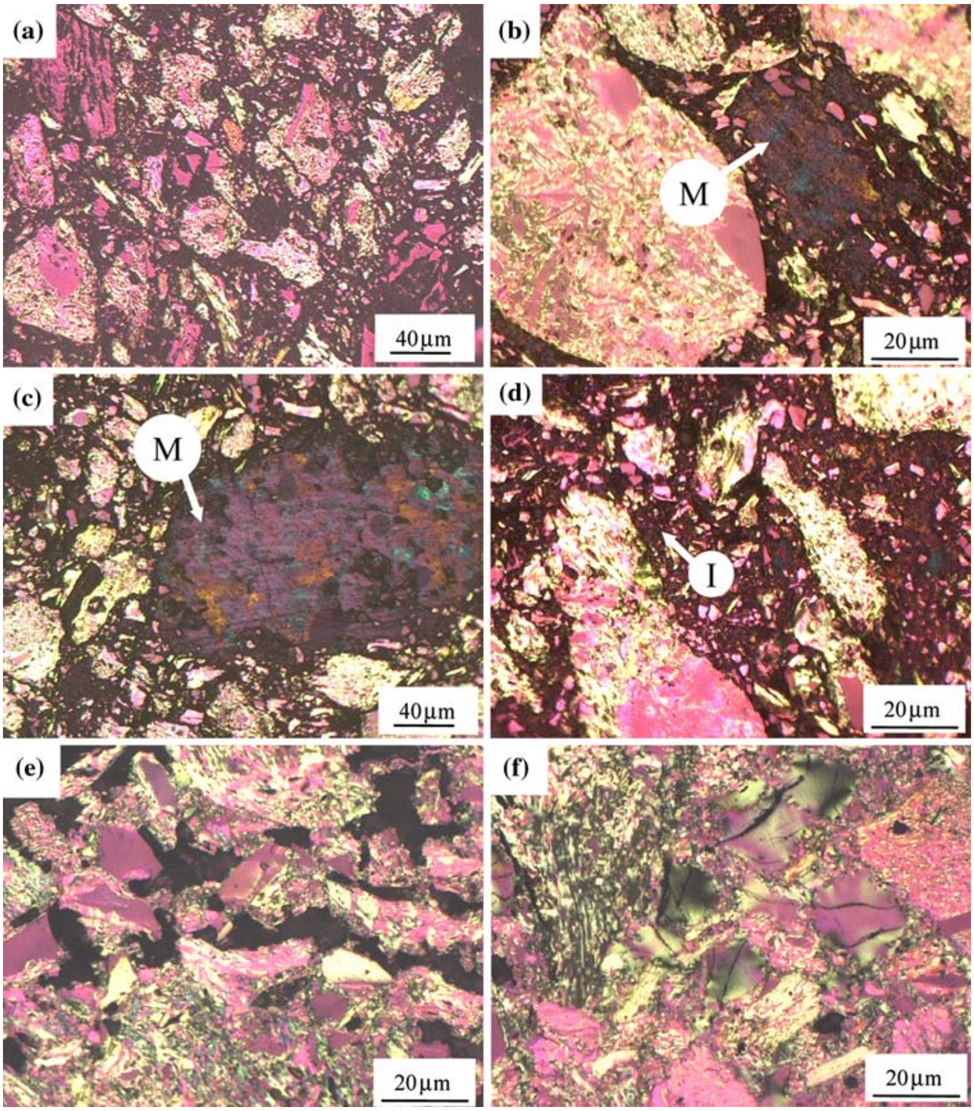


Fig. 10 Optical micrographs of carbon composites with foundry coke carbonised at intermediate temperatures: (**a**) G18FC (350 °C); (**b**) D3FC (350 °C); (**c**) D5FC (350 °C); (**d**) D5FC (500 °C); (**e**) D0FC (700 °C); (**f**) D3FC (700 °C)

and not semi-coke systems were formed (Fig. 10d). At high temperatures (>700 °C), it was not possible to distinguish carbon matrix and foundry coke, due to similar light texture of both components.

Finally, carbon composites with graphite show an interesting light texture of carbon matrix evolution during their carbonization (Fig. 11). Similar to other granular carbons, at 350 °C, pellets with D0 and G18 are homogenous samples (Fig. 11a). In pellets with D3, isotropic phase is around graphite particles forming small films of pitch (Fig. 11b, part I) and mesophase leads to thicker films of pitch between graphite particles (Fig. 11b, part M). In a similar way to other granular carbons, D5 leads to heterogeneous samples where isotropic phase is well dispersed,

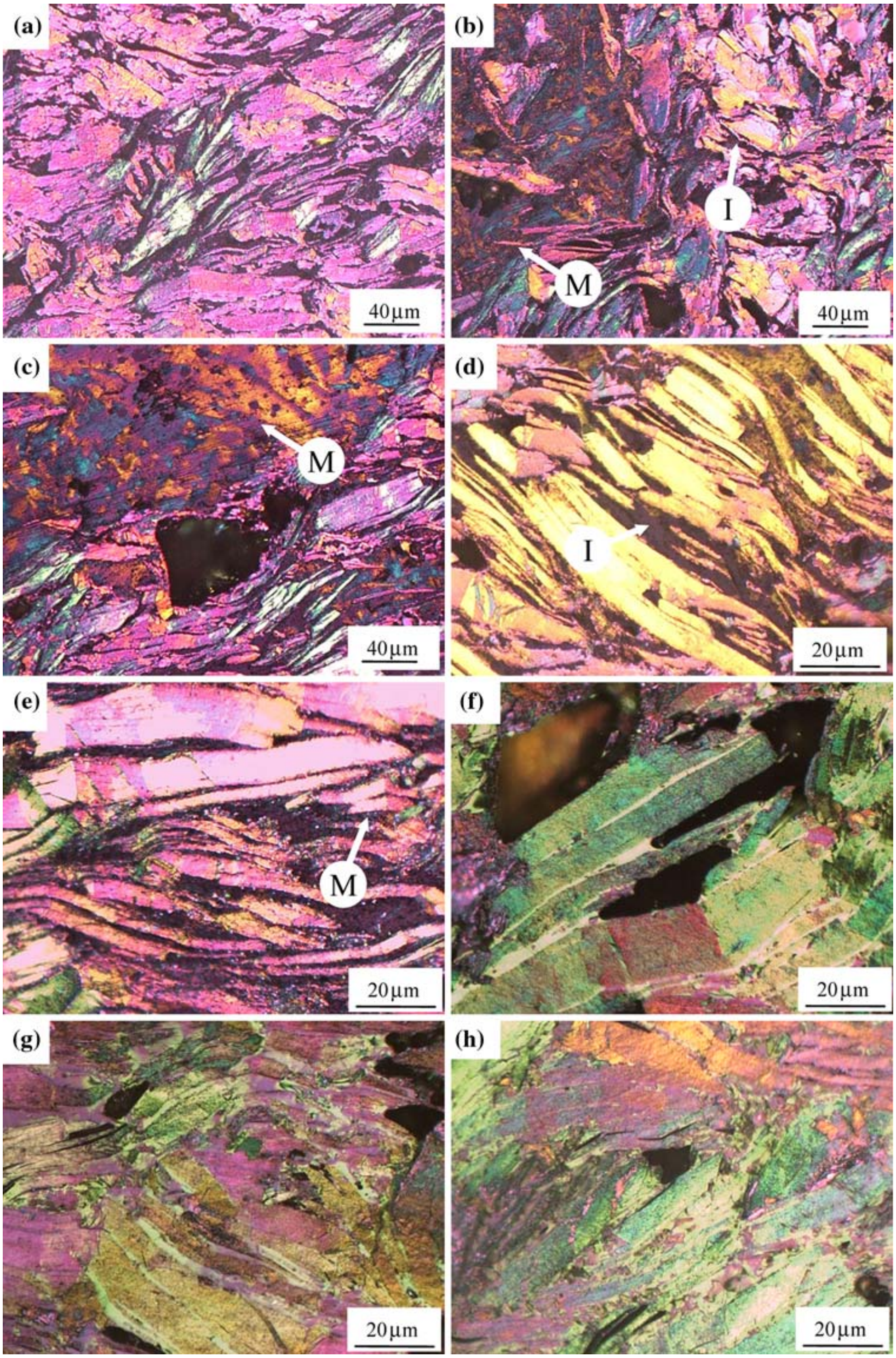


Fig. 11 Optical micrographs of carbon composites with graphite carbonised at intermediate temperatures: (**a**) G18GR (350 °C); (**b**) D3GR (350 °C); (**c**) D5GR (350 °C); (**d**) D3GR (500 °C); (**e**) G18GR (500 °C); (**f**) D5GR (700 °C); (**g**) D3GR (700 °C); (**h**) G18GR (700 °C)

whereas mesophase rests coalesced without mixing with the graphite particles (Fig. 11c, part M). At 500 °C, isotropic phase of D3 and D5 pitches rest as isotropic systems, without any growth of mesophase (Fig. 11d, part I) whereas G18 and D0 pitches have developed some spheres (Fig. 11e, part M). Graphite particles clearly delay mesophase development of pitches, especially in case of thermally treated pitches (D3 and D5). However, at 700 °C, the initial isotropic phase of thermally treated pitches (D3 and D5) generates large domains oriented on the graphite lamella direction (Fig. 10f, g). Generally, pyrolysis reactions delay leads to cokes with light textures of low size, coarse mosaics and isotropic cokes [14] as was observed previously for carbon composites reinforced with anthracite. This surprising result could be explained by experimental results of porosity (Fig. 7e, f), volume (Fig. 5d) and weight evolution (Fig. 4d) of carbon composites with graphite and thermally treated pitches. According with lower weight loss (Fig. 4d), volatile compounds could seems to rest inside the pellet leading to fluidized systems at elevated temperatures (>500 °C). This fact makes possible the order of pitch molecular structures. QI particles seem to have an important effect on mesophase development. In case of thermally treated pitches, D3 and D5, QI particles were in the anisotropic phase, around mesophase. Consequently, the absence of QI particles in the isotropic phase allows the subsequent structural order of molecular structures. However, in case of G18 and D0 pitches, QI particles were dispersed in all the pitch and could difficult the necessary order, leading to less size of light textures (Fig. 11h).

Conclusions

The characteristics of the granular carbons and their interactions with the pitches play an important role during the carbonization of carbon composites.

Carbon composites with the commercial coal-tar pitch and foundry coke, anthracite or graphite deform in the initial stages of carbonization due to the lower porosity of the green pellets and the high amount of low molecular weight compounds of the pitch. In case of green petroleum coke, the elevated porosity of green pellet permits volatile compounds go out and any external deformation was produced.

Carbon composites with anthracite, green petroleum coke and graphite undergo important weight loss at elevated temperatures. This fact could have a negative effect on their mechanical properties and heat rate need to be controlled in order to provide an adequate volatile release.

Carbon composites with green petroleum coke show a similar carbonization behavior independent on the pitch properties (porosity evolution, weight loss and volume changes). The presence of green petroleum coke leads to light texture of mosaics and fine mosaics with isotropic coke, depending on the pith. These materials underwent important dimensional changes during their carbonization, without any apparent external deformation.

Anthracite delays the mesophase development of pitches leading to light textures lower that in the absence of granular carbons. At temperatures highest than 700 °C, all pellets reduce their volume due to the shrinkage of anthracite particles and pitches.

Graphite delays mesophase development of pitches. In addition, volatile compounds rest inside the pellets and lead to fluidized systems at elevated temperatures (>500 °C). Both factors play an important role in the final microstructure of carbon composites reinforced with graphite. In case of thermally treated pitches, D3 and D5, QI particles were in the anisotropic phase, around mesophase and the absence of QI particles in the isotropic phase allows the great structural order of molecular structures. However, in case of G18 and D0 pitches, QI particles were dispersed in all the pitch and could difficult the necessary order, leading to less size of light textures.

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