ANTHRACENE OIL AS A NOVEL PRECURSOR OF MESOPHASE-BASED CARBON MATERIALS

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Introduction

Flow mesophase is an attractive precursor for the preparation of many types of carbon materials (i.e., carbon fibers, polygranular graphites, foam materials, composites). This is because flow mesophase has superb physical and structural properties, which can be tailored according to the processing conditions and/or through the selection of a suitable precursor. In this regard, White *et al*. have established a processing window for mesophase manipulation, based on the variation of mesophase viscosity with temperature [1]. Thus, the flow properties of the mesophase can be used to produce spinnable materials [2], agents for use in liquid injection processes [1] or self-adhesive precursors for high-density carbons [3].

Flow mesophase has been traditionally produced from two main sources: coal-tar and petroleum pitches [4,5], and some pure aromatic hydrocarbons [6]. More recently, research carried out elsewhere has demonstrated that anthracene oil might also be a suitable precursor for preparing flow mesophase [7-9]. From a chemical point of view, anthracene oil can be considered as an intermediate product between pitches and pure aromatic hydrocarbons. In fact, anthracene oil is a coal tar fraction that distils between ~ 270-400 °C and consists of about one hundred polycyclic aromatic hydrocarbons (PAH) made up of 3-5 rings. The transformation of anthracene oil into flow mesophase is not feasible, at least by conventional thermal treatment at atmospheric pressure. However, when the thermal treatment is performed in the presence of polymerizing agents (i.e., Friedel Craft catalysts, sulfur, air) this transformation can be successfully achieved.

The present work is based on studies carried out by the authors on the preparation of anthracene-oil-based pitches and the use of these pitches for the production of different mesophase-based carbon materials.

Experimental

Anthracene-oil-based pitches were obtained from a commercial anthracene oil (250-370 °C coal tar distillation fraction) supplied by Industrial Química del Nalón, S.A. The anthracene oil was polymerized and converted into pitch by air-blowing [9] and thermal treatment in the presence of sulfur [7] and aluminum trichloride [8]. Flow mesophase and carbon materials were produced by the pyrolysis of anthracene-oil-based pitches at different temperatures (450, 900 °C).

Results and Discussion

Pitches from anthracene oil

The use of aluminum trichloride, sulfur and air causes the anthracene oil components to polymerize, giving rise to pitch-like materials. The mechanism of polymerization is dependant upon the treatment applied. Aluminum trichloride acts as a Fridel Craft catalyst, producing non-dehydrogenative polymerization with the formation of planar macromolecules that are easily transformed into flow mesophase. On the other hand, oxygen promotes a dehydrogenative polymerization which results in the formation of both planar and cross-linked structures. The contribution of each type of structure to the pitch depends on the severity of the treatment. Thus, high temperatures and/or long reaction times favor polymerization towards cross-linked structures. The reaction with sulfur follows a mechanism similar to that of air-blowing. However, the use of sulfur may cause the formation of sulfur-containing moieties, which adversely affect the graphitizability of the material.

Because anthracene oil is a distillation fraction, the anthracene-oil-based pitches are characterized by the total absence of metals and solid particles (primary quinoline insolubles, QI). Thus, anthracene-oil-based pitches might be considered as a hybrid system between coal-tar pitch (because of their composition and origin) and petroleum pitch (because they are metal-free and QI-free). Moreover, the degree of polymerization and the pregraphitic order attained during the transformation of the anthracene oil determines the ability of the pitches to develop mesophase and generate carbons with different microstructures.

Mesophase and carbons from anthracene oil based pitches

The air-blowing of anthracene oil at 350 °C for 6, 8 and 12 h and the subsequent treatment of the anthracene-oil-based pitches at 450 °C give rise to partially anisotropic materials, in which the mesophase is in the form of single spheres (Figure 1a) and large coalesced regions (Figure 1b). When the air-blowing is too severe, the contribution of cross-linked structures to the pitch prevents the mesophase from forming, and consequently, the resultant material is isotropic (Figure 1c).

The flexibility which enables anthracene-oil-based pitches to generate carbons with different microstructures is patent in the case of cokes obtained from anthracene oil treated with different sulfur concentrations (Figure 2). The optical texture of the carbons decreases with the increase in sulfur concentration, which is in agreement with what was previously said regarding the increase in the amount of sulfur incorporated into the molecular structure of the pitch components with the increase in the sulfur/anthracene oil ratio.

It should be noted that, when the air-blowing is not excessively severe, a significant amount of the cross-linked structures generated during the treatment can be broken and

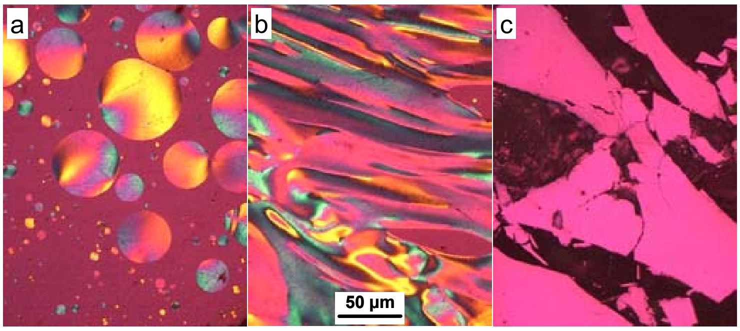

Figure 1. Optical micrographs of mesophase obtained from air-blown anthracene oil at 350 °C for (a) 6, (b) 8 and (c) 12 h.

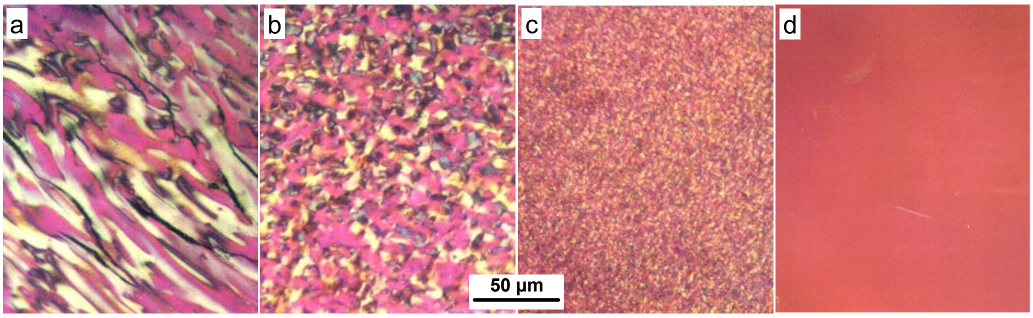

Figure 2. Optical micrographs of cokes obtained from anthracene oil treated with (a) 5, (b) 7.5, (c) 10 and (d) 20 wt.% of sulphur at 300 °C for 2 h.

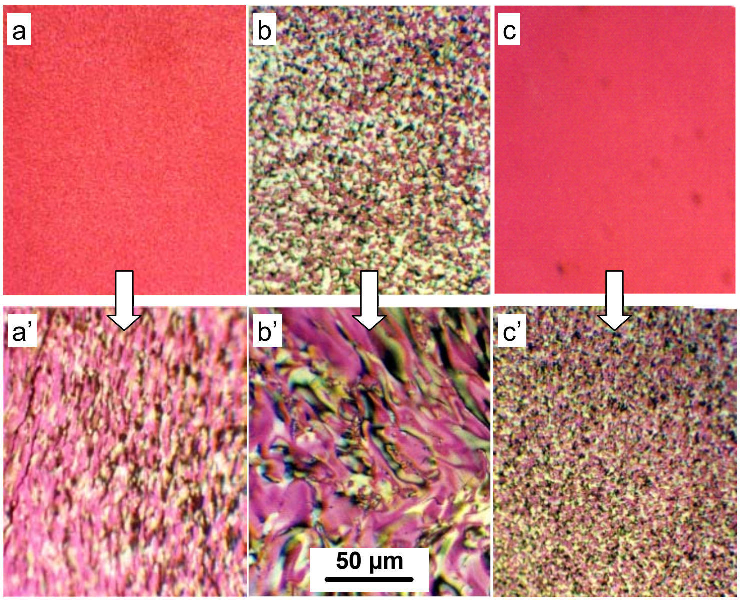

Figure 3. Optical micrographs of cokes obtained from air-blown anthracene oil (a,b,c) before and (a',b',c') after thermal treatment.

subsequently reorganized, giving rise to more planar structures via thermal treatment. Thus, air-blown pitches that give rise to granular flow carbons (Figure 3b) and even isotropic carbons (Figures 3a and 3c) can be transformed by thermal treatment into pitches that generate granular flow carbons (Figures 3a’ and 3c’) and flow domains (Figure 3b’).

Conclusions

The thermal treatment of anthracene oil in the presence of polymerizing agents allows pitches with different degrees of polymerization and different compositions to be tailored. These pitches are unique precursors for developing mesophase and carbons with a wide variety of microstructures, ranging from single spheres to coalesced regions, or from granular flow to flow domains.

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