CO-CARBONIZATION OF SULFUR WITH SYNTHETIC MESOPHASE PITCH

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Introduction

Synthetic mesophase pitch has been recognized to show excellent properties as a binder for carbon composites, having a great potential in the production of advanced composites because of its high fluidity, coke yield and graphitability. However, synthetic mesophase pitch from naphthalene suffers severe swelling during carbonization, this restricting its broad application for the production of advanced carbon composites. A previous work has reported that the addition of carbon black with large surface area can reduce the swelling [1]. Increasing the surface area of the carbon black by gasification was found to be effective to reduce swelling [2]. The co-carbonization of mesophase pitch with phenolic resin was another way to reduce swelling [3]. The mechanism for suppression of swelling is suggested to be the removal of hydrogen at the critical stage of the carbonization. It has also been suggested that the sulphur it is at good candidate to reduce the swelling [4].

The present study is a continuation of a previous research, focused now in the modification of the synthetic mesophase pitch for use in different applications, such as the manufacture of carbon foam.

Experimental

Mesophase pitch (AR) synthesized from naphthalene using a HF/BF3 catalyst was supplied by Mitsubishi Gas Chemical Co. The softening point of the pitch was measured by the flow tester method. Properties of the pitch are summarized in Table 1. Sulphur was sublimed grade, supplied by Izushu Pharmaceutical Co.
Powdered mixtures of mesophase pitch and sulphur with differents ratios (99/1, 95/5, 90/10, 85/15, 80/20 AR/S) were well blended in acetone slurry by an ultrasonic technique. After drying in vacuum the blend was molded under 20 Mpa at room temperature into disks of 20 mm in diameter and 2g weight. The disks were heat treated at 300 °C during 2 hours under a flow of nitrogen. The heat treated material was crushed and pelletized again under the same conditions. The disks were carbonized in a glass tube at 600 °C for 1 hour under a flow of nitrogen, and the heating rate used was 1 °C/min.

Extent of expansion during carbonization was evaluated by controlling the height of the produced carbon artifact. Optical texture was examined under reflected polarized microscope, after conventional mounting and polishing.

The X-ray diffraction profiles of calcined coke were obtained using CuKa with a wide angle X-ray diffractometer. Simultaneous thermogravimetric differential thermal analysis was carried out in an open system under nitrogen flow (200 ml/min, 3mg of sample, heating rate 5°C/min). The softening point of pitches was determined with a thermomechanical analyzer, with at section probe of 1 mm^2 and a penetrating load of 10 g. The experiments were carried out in nitrogen atmosphere (200 ml/min, heating rate 5°C/min). FTIR spectra were obtained in a Nicolet spectrometer using diffuse reflectance technique with a resolution of 2cm-1. XPS espectra were obtained using monochromatic Mg Kα radiation. Chemical shift was corrected to C(1s) peak position observed at 284.8 ±0.1 eV. The sulphur 2p signals were identified according to Kelemen et al. [5]. The distribution of molecular weight has been obtained in a MALDI TOF-MASS equipment (N_2 laser, 20kV).

Table 1.- Some analytical properties of mesophase pitch (AR).

AC	SP	BS	BI-PyI	PyI	H/C	fa
100	237	46	21	33	0.65	0.94

AC: anisotropy content (%); SP: softening point (°C); fa: aromaticity factor (measured by NMR)

Results and discussion

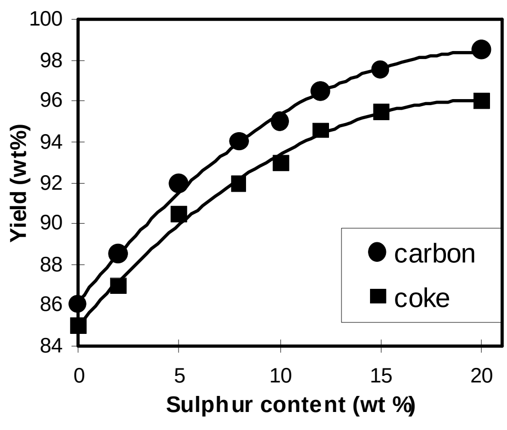

***Figure 1**. Effect of sulphur on the coke and carbon yield evolution at function of sulphur content (600 °C, 1 °C/min, N_2).*

Figure 1 includes the evolution of coke and carbon yield as a function of the sulphur content in the copirolysis at 600 °C. There is a clear increase in coke and carbon yield with increasing sulphur content in the blend.

Figure 2 shows the weight loss for different blends of AR with sulphur (already heat-treated at 300 °C). All samples show similar temperature profiles. The figure clearly shows that increasing the sulphur content decreases the volatile matter, and at the same time the start of weight loss shifts to higher temperature.

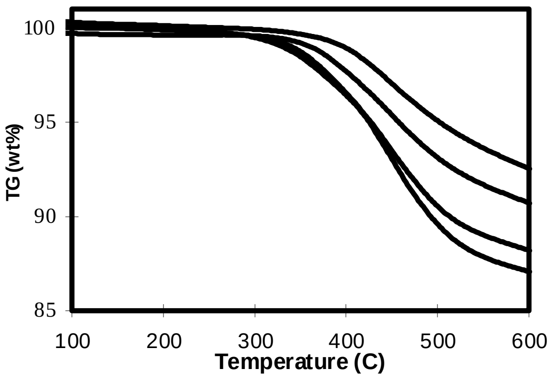

Figure 2. *TG weight change of AR mesophase blend with sulphur.*

Figure 3 shows the penetration curves obtained by TMA for two samples with different sulphur contents. Similar curves have been obtained for all samples. The softening point increases with sulphur content, and the slope decreases with sulphur content, indicating that the apparent viscosity also increases.

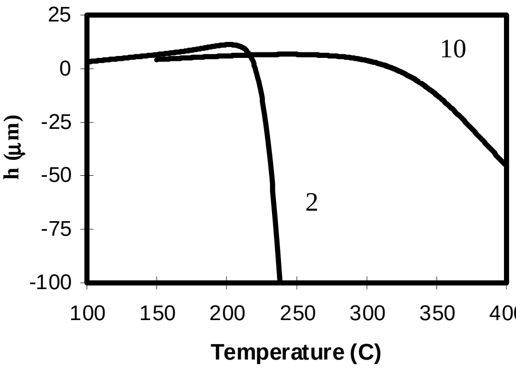

Figure 3*. Penetration curves of AR blended with 2 and 10% of sulphur.*

Figure 4 shows the evolution of the C/H ratio of a function of sulphur content. There is a clear linear relationship between the C/H ratio and the sulphur content.

The previous results show that sulphur promotes the polymerization of mesophase pitch. The reaction between sulphur and mesophase mainly produces H_2S that evolve off the system. The relationship between Har/Hal measured by FTIR increases with the sulphur content in the blend, indicating that sulphur reacts mainly with the linear chains and promotes the cyclation and the formation of mesogen molecules, by adition of small molecules. The increase in molecular weight has been showed by direct TOF measurements and by the reological properties.

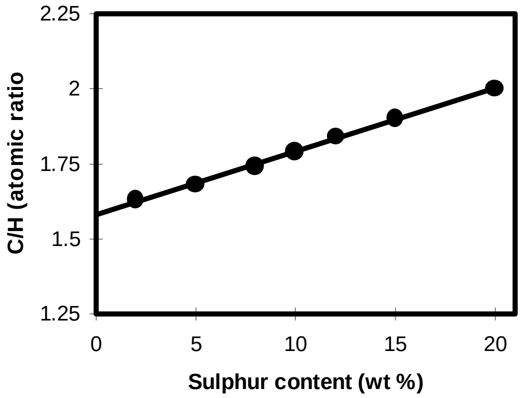

Figure 4. *Effect of sulphur contents on the evolution of carbon/hydrogen ratio. (600 °C, 1°C/min, N_2)*

The sulphur pretreatment increases the coke and carbon yield and the reduction in reological properties is not so significative. This is very important in traditional uses, like manufacture of C/C composites. However, there are other additional properties that can be controlled which are important for applications, such as manufacture of carbon foams.

The carbon foam is formed by the action of the gas trapped in the structure, because the viscosity of the material is appropriate for the bubble growth inside of the liquid phase. The cellular structure formed is basically a function of the gas evolved and the viscosity of the liquid. In the case of the undoped material (without sulphur), the volatile content is around 25%, but the viscosity is no high and the foam produced is brittle, because the wall thickness is very think.When the mesophase is treated with 15 or 20 % of sulphur the viscosity is too high and the volatile content is less of 10%, this meaning that the deformation of the fluid material and the porosity of the final carbon artifacts are small.

By controlling the proportion of sulphur in the synthetic mesophase it is possible to obtain carbon foams with adequate properties, without the need of using the sophisticated experimental system typical of carbon foam manufacture [6].

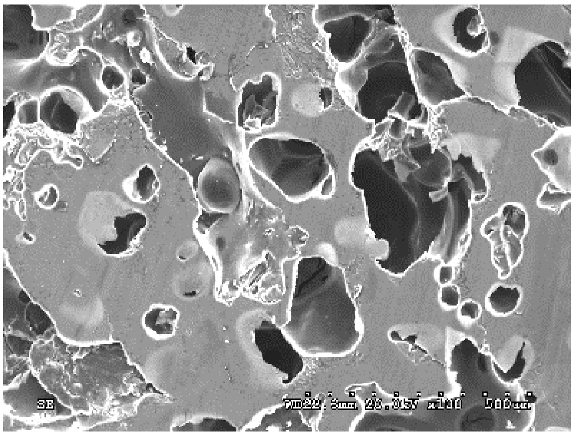

Figure 5. *Microphotograph of top surface of carbon foam.*

Figure 5 show a micrograph of carbon foam produced by AR blended with 10% of sulphur. The cellular structure it is a function of sulphur content and the heating rate mainly. The mechanical properties of the carbon foam is 3 MPa in compression test, and the density 0.54 g/cm^3.

Conclusions

The sulphur increase the carbon and coke yield in the pyrolisis of synthetic mesophase pitch, also increase the softening point and the viscosity of the pitch reducing the puffing in the carbon materials.

Co-carbonization of synthetic mesophase pitch with sulphur produce materials suitable to use in the manufacture of carbon foam.

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