

DEVELOPMENT OF MESOPHASE IN TARS OBTAINED FROM PETROLEUM RESIDUES

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INTRODUCTION

Mesophase formation and spinning ability determine the use of petroleum tars in the development of carbon fibers. These properties depend principally on the chemical composition and distribution of molecular weight, which also affect the viscosity and reactivity of the precursor fiber.

The organic compounds that form the petroleum tars are made up of rigid systems of condensed aromatic rings, intertwined or substituted with side chains [1-3]; also present are organometallic and sulfur-containing compounds that intervene in an indeterminate manner in the thermocondensation and dehydropolymerization reactions that are favorable in a pressurized pyrolytic treatment [4, 5].

The result of this heat treatment is an isotropic material, which when heated over temperatures of 625K, begins to form nematic liquid crystal spheres (mesophase) that grow, coalesce, and form great anisotropic areas, conserving a directional order as the structure of the liquid crystal is modified.

The growth and coalescence pattern of the mesophase determines the use of the tar as a precursor of carbon fibers. Even though it is now accepted that the nucleation that originates the mesophase is homogeneous, and its growth occurs by diffusion of the lamellae of the isotropic phase [3, 6], the effect of the organometallic and sulfur-containing compounds cannot be generalized, as an evaluation is necessary for each situation.

EXPERIMENTAL

Binary mixtures of gas oil (ICCO; LCCO) with heavy crude from an olefin plant (APPO), heavy crude (H) or vacuum residues (RH370; RH510), were characterized on the basis of their ash content (ASTM D482), elemental analysis (ASTM D3120 and AFNOR M03-032) and the proportion of species present (HPLC).

Subsequently, they were subjected to 8 hours of heat treatment in an autoclave at 625K and 1.75 MPa. The product was concentrated by distillation at 575K, 35KPa and characterized by chemical analysis, proportion of species present (ASTM D4124), TGA, polarized-light optical microscopy, was carried out on the residue carbonized at 673K, it was mounted in an epoxy resin. The formation, growth and coalescence processes of the mesophase in the heat-treated products were also observed using a microscope heating stage LEITZ 1350 [7].

RESULTS AND DISCUSSION

Table 1 summarizes the characterization of the mixtures before and after the heat treatment. The composition of the mixtures are indicated by the corresponding codes of each component and two digits representing the percentage in weight of the first.

The ash content reported, indicative of the presence of organometallic compounds, can influence the formation and growth of the mesophase [6], favoring the nucleation process when it is low, but hindering the growth and coalescence process when its proportion is high. This second effect could have been present in the APPO mixtures [3].

The major thermodesulfurization for the mixtures with H, RH370, and RH510 seems to indicate little stability of the sulfur-containing compounds present, which associated with the presence of V and Ni, has been reported as advantageous in the mesophase formation, due to a possible catalytic effect on the dehydropolymerization reactions [6].

The increase in the ratio C/H entails an increase in the average molecular weight which corresponds with the displacement of the TGA curves to higher temperatures. At the same time, the narrowing of the weight loss interval entails a greater stability and uniformity in average molecular size of the species present, which corresponds with a greater uniformity in

the size of the mesophase spheres. Fig. 1 indicates the development of the mesophase in the sample 50APPO:ICCO, heated at a controlled rate up to 700K, in which can be observed the formation of anisotropic spheres of uniform size from the isotropic mass, growing and coalescing to form fluid structures as the temperature and heat treatment time are increased.

The increase in the proportion of APPO up to a limit of 50% appears to favor the uniformity of the mesophase spheres which can be associated to the more complex asphaltene systems. This can be observed in samples with a high content of aromatics and as low content in asphaltenes, in which the mesophase spheres are little developed. The fraction of saturates does not seem to contribute directly to the mesophase formation, but appears to have an effect on the coalescence, because of its participation as a solvent in reducing the viscosity of the medium [3].

CONCLUSIONS

The pressurized heat treatment favors the reactions that lead to the mesophase formation, which can be favorably influenced by the organometallic and sulfur-containing compounds. However, its progress is strongly determined by the proportion of saturates, asphaltenes and aromatics present in the sample.

REFERENCES

- 1.- J. Donnet; R. Bansal. CARBON FIBERS. Menachem Lewin (Ed.) New York. 1990.
- 2.- H. Marsh; R. Mendez. FUEL PROCESSING TECHNOLOGY. 20: p. 269-296. 1988.
- 3.- H. Marsh; C. Latham. The chemistry of mesophase formation. In Petroleum-Derived Carbon. J. Bacha et. al (Ed.) p. 1-28. New York. 1986.
- 4.- I. Iim; I. Lee. JOURNAL OF MATERIAL SCIENCE. 26: p. 1039-1044. 1991.
- 5.- K. Huttlinger; J. Wang. CARBON 29 (3): p. 439-448. 1991.
- 6.- S. Oi; N. Onishi; Y. Yamada; H. Honda. CARBON. 16 (6): p. 445-452. 1978.
- 7.- A. Requena. MSc. Thesis USB. 1994.

TABLE 1: Characterization of the mixtures before and after the heat treatment.

SAMPLE	BEFORE				AFTER			
	% Ash	% S	% C	C/H	% Ash	% S	% C	C/H
50RH370:LCCO	0.05	2.15	85.9	0.607	0.06	1.86	87.7	0.803
50RH510:ICCO	0.05	2.6	85.9	0.663	0.06	2.19	86.6	0.714
50H:LCCO	0.04	2.26	86.0	0.666	0.09	1.81	87.2	0.616
70RH370:LCCO	0.06	2.91	85.1	0.622	0.09	2.84	87.2	0.790
30APPO:ICCO	0.05	0.57	84.8	0.660	0.15	0.48	92.4	1.08
50APPO:ICCO	0.08	0.41	82.2	0.753	0.18	0.47	89.4	1.31
70APPO:ICCO	0.11	0.26	84.5	0.880	0.26	0.33	93.7	1.45

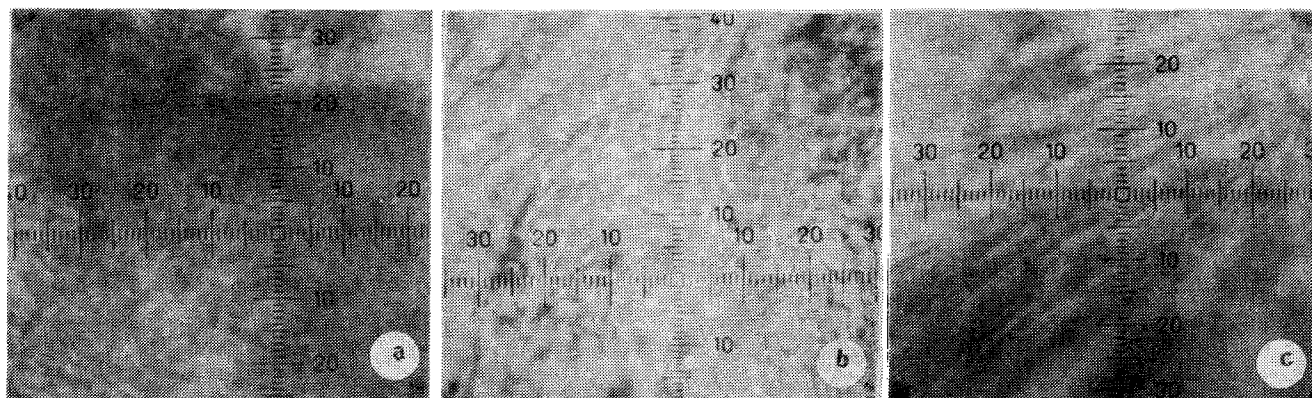


FIGURE 1: Development of mesophase in 50APPO:ICCO at 648K (a), 673K for 15 (b) and 30 min. (c) [1 div. = 1 μ m]