

ASPECTS OF FORMATION OF GRAPHITIZABLE CARBONS FROM BLENDS OF PITCH-LIKE SUBSTANCES

H. Marsh, I. Macefield and Janet Smith
Northern Carbon Research Laboratories, School of Chemistry,
University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, U.K.

Introduction

The establishment of the preferential, parallel stacking of lamellar molecules in anisotropic carbons, as distinct from quite random arrangements within isotropic carbons, is now accepted as being via the nematic liquid crystals and the mesophase (see references listed in Ref. 1 and 2). The origins of nematic liquid crystals, their nucleation, growth and stabilization, are still imperfectly understood. One aspect of growth concerns the chemical heterogeneity of pitch substances, and the almost dominant role of certain molecular constituents. Considering the wide range of molecular size, shape, weight and constitution of parent substances, it is somewhat of an enigma to understand how the mesophase can grow and yet contain such a high element of crystallographic order. This paper discusses the dominant role of certain molecular constituents.

Origins of Nematic Liquid Crystals

As the pitch parent material is subject to increasing carbonization temperatures then inter- and intra-molecular re-arrangements produce an increasing concentration of large, lamellar constituent molecules. In all liquids there exist statistical associations of molecules and no doubt this association also occurs in fluid pitch. When a critical condition of temperature, molecular weight and molecular concentration is established, these nucleation associations (homogeneous), instead of rapidly dissociating, continue to grow to establish a new phase, as seen in optical microscopy (Ref. 3). The formation of the nematic liquid-crystal probably is assisted by the high enthalpies of physical adsorption which are possible when two large lamellar molecules 'come together' flat surface to flat surface.

It is considered that the development of these liquid crystals is insensitive to the detail of chemical composition of molecular constituents, but is very sensitive to the size and shape of these constituent molecules. But once having been formed by an essentially physical process, then chemical processes within the liquid crystals immediately become dominant and dictate subsequent events. Extents of 'cross-linkage' between the lamellar constituent molecules influence the viscosity of the liquid crystal and mesophase and ultimately the optical texture of resultant anisotropic carbons.

As discussed by Marsh (Ref. 4) it is a known property of documented nematic liquid crystal systems that they can accommodate material which itself would not form nematic liquid crystals. This process probably occurs during the growth of liquid crystals from pitch systems. In fact, Crawford and Marsh (Ref. 5), using phase-contrast,

high resolution electron microscopy, were able to identify molecules contained (trapped) within the lamellar stacks. It is this aspect of the growth of mesophase which is reported here, using methods of extraction from single pitch-like substances and by blending pitches followed by the carbonization of the blends.

The Experimental Approach

An anthracene-oil coal extract (D112) was extracted with a range of solvents and the soluble and insoluble fractions carbonized. Resultant carbons were examined by optical microscopy. Also, in attempts to produce carbons with a range of optical texture, blends (binary) made up of A200 Ashland petroleum pitch, D112 coal-extract, Gilsonite pitch, asphaltenes and Orgreave coal-tar pitch, in varying ratios, were carbonized and resultant carbons examined by optical microscopy.

Discussion

The general conclusion of the study of carbonizations of pitch blends is that it is not possible to modify systematically and progressively, the size of optical texture (*i.e.* size of isochromatic areas as seen in polished sections) by co-carbonizing, in increasing percentage content, two pitches one of which would give large domains (*e.g.* A200 petroleum pitch), the second giving small mozaics (*e.g.* Gilsonite pitch). Small additions (<15%) of the A200 pitch to a pitch giving small mozaics had little effect upon the formation of the mozaics, but then over a further small increase in concentration the behaviour of the A200 pitch became dominant and large domains resulted (see Figure 1). It was as though the molecules of the Gilsonite pitch became trapped within the liquid crystals of the A200 pitch and it was the latter which controlled final properties. Separation (dilution) of the Gilsonite system may have prevented cross-linkage between the molecules of the Gilsonite pitch so preventing enhanced viscosity which produces the characteristic small mozaic structures.

Similarly, extraction by solvents of components of the pitch is capable of preventing the formation of nematic liquid crystal systems in the insoluble residues. These results into blending and solvent extraction are broadly in agreement with the recent findings of Mochida *et al.* (Ref. 5). These authors separated four SRC pitches with benzene into solvent-soluble: solvent-insoluble fractions and subsequently carbonized blends of soluble-insoluble fractions from different pitches. Two of the original pitches formed anisotropic flow structures, and two formed mozaic structures. All the insoluble fractions formed isotropic carbon; however, the anisotropic structures formed on blending were not predictable.

A thorough elemental, ^1H nmr and ^{13}C nmr analysis proved unrewarding.

It would appear as though the correlation of anisotropic structure (optical texture) with blend composition is of the form of Figure 1. The position of line AB may vary with the origins of pitch P_1 and P_2 . The analysis of Mochida et al. may be unrewarding because what is of major importance is not the chemistry of the pitch as obtained but its chemistry immediately prior to formation of the nematic liquid crystal systems. The complexity of pyrolysis chemistry is such that predictions from parent molecular systems in multi-component mixtures cannot be contemplated. What could be looked for is the development of large, lamellar aromatic molecules in sufficient concentration to act as the dominant partner and establish anisotropic flow structures.

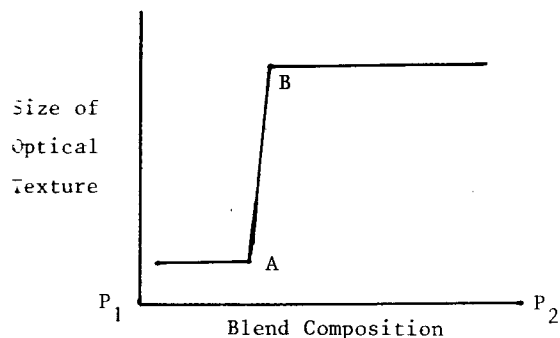


Figure 1.

References

1. Marsh H., Proc. 4th Conf. on Industrial Carbon and Graphites, S.C.I. London, pp. 2-38 (1976).
2. White J.L. and Zimmer J.E., "Surface and Defect Properties of Solids", Chem. Soc. London, 5, pp. 16-35 (1976).
3. Lewis R.T. Abstracts, 12th Conf. on Carbon, p. 215 (1975).
4. Marsh H., Fuel, London, 52, pp. 205-12 (1973).
5. Crawford D. and Marsh H., Carbon '76. Deutsche Keramische Gesellschaft, pp. 231-234 (1976).
6. Mochida I., et al., Fuel, London, 56, pp. 49-56 (1977).

Acknowledgement

We express our appreciation to the National Coal Board for financial support.