

A RHEOLOGICAL INVESTIGATION IN THE MESOPHASE REGION

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Introduction

The rheological behaviour of pitches during heat treatment is of considerable technological significance, both in the low temperature region where pitch/coke mixtures are formed and extruded and at higher temperatures where the mesophase grows and coalesces. The characteristic anisotropy of needle coke is a result of deformation of the mesophase during delayed coking and such structural orientation is also important in the initial stages of the manufacture of carbon fibres from pitch (1). It has also been suggested that internal reaction and rearrangement within the mesophase spheres themselves alters their rheological behaviour, which in turn is considered to influence the degree of coalescence (2). Didchenko *et al* (1) investigated the 'viscosities' of pitches containing mesophase and observed a peak in the 'viscosity'-temperature curves which appeared to be related to the mesophase content of the pitches. However, no explanation of this phenomenon has appeared in the literature. Didchenko *et al* (1) also reported that mesophase systems could be thixotropic or plastic, depending upon the temperature of measurement and molecular weight distribution of the pyridine soluble and insoluble fractions.

As a contribution to the understanding of the rheological properties of pitches containing mesophase, a rheological investigation has been undertaken using a concentric cylinder measuring system.

Experimental

All rheological observations were made with the Contraves Rheomat-30 viscometer which has a range of rotational speeds of 0.05-350 rev min⁻¹ and a rapid response to changes in torque in the measured system. Speed selection can be carried out manually and the torque signal fed to a recorder to follow time dependent phenomena, or with a programmed X-Y recorder attachment which enables flow curves to be determined automatically at predetermined rates of change of speed. Since only a fixed range of torque can be detected, measuring systems of different geometry must be designed for fluids of widely different viscosities.

Co-axial cylinder measuring systems were constructed in stainless steel. A flowing nitrogen atmosphere was maintained over the sample and the whole unit was heated electrically. Most experiments were carried out with a gap width of 1 mm as follows. The system containing the pitch was heated at 0.4°C min⁻¹ with the inner cylinder rotating continuously at a constant speed whilst the torque and temperature were displayed continuously on a two pen recorder. In selected experiments heating was arrested at certain temperatures and flow curves measured, and in others samples were removed from the fluid above the rotating bob. These samples had not been sheared during the heat treatment but gave an indication of the mesophase development. They were subjected to quinoline and toluene extraction and examined microscopically.

Orgreave binder and impregnation pitches were examined principally along with an Ashland petroleum pitch and Gilsonite. A thermogravimetric study of the pyrolysis of these materials is described elsewhere in the abstracts of this conference.

Results and Discussion

At temperatures below 250°C the coal tar pitches are Newtonian. Heating and cooling curves on the binder pitch established that below 240°C the apparent viscosity-temperature curve was reversible but above this temperature higher viscosities were obtained on cooling, indicating the onset of polymerisation. Volatilisation in this system was first observed at about 185°C.

At high temperatures the apparent viscosity increases markedly with temperature as the mesophase grows and coalesces. However, there are maxima in the apparent viscosity-temperature curves of the coal tar pitches but not the petroleum pitch (Fig.1). It is clear also that in this temperature region the system is shear thinning and the positions and magnitudes of the two peaks are influenced by the rate of shear. At a speed 1.03 rev min⁻¹ the largest peak occurs at a quinoline insoluble content of 65% and the smaller one at 57%, whilst at the faster speed both peaks are closer together occurring at QI levels of 50-53%. Microscopic examination of samples shows that the first signs of mesophase coalescence are at a QI of 53% and at the 65% value there are substantial areas of coalesced mesophase.

Nematic liquid crystals are known to be shear thinning due to the orientation of the molecules in the shear field (3) and maxima are often observed in one component systems at the transformation temperature because of the lower viscosity of the oriented phase. Hermans (4) showed that the apparent viscosities of solutions of poly- γ -benzyl-L-glutamate in m-cresol, measured at low shear stresses, exhibited maxima at a critical concentration above which the solution was birefringent. At higher shear stresses the effect was absent. The anisotropic phase was considered to be more easily oriented than the isotropic phase at low shear stresses, but in the high shear Newtonian region both phases could be oriented.

The behaviour of liquid crystals offers a possible explanation of the rheological properties of the carbonaceous mesophase in coal tar pitches. At temperatures above 400°C, shear thinning behaviour is apparent because the mesophase spheres can be elongated and partially oriented in the shear field along with the high molecular weight aromatic molecules in the isotropic liquid. Initially the mesophase probably remains as discrete particles because of surface tension effects. Hence, as the amount increases so does the apparent viscosity. An increase in the average molecular weight of the isotropic phase is also a possible contributory factor to the apparent viscosity. When coalescence sets in and the mesophase becomes the major phase, however, it can be

oriented more easily than the isotropic liquid at low rates of shear and the apparent viscosity at low rates decreases. Presumably the subsequent increase again at higher mesophase contents is a result of stronger intermolecular forces between the lamellar molecules restricting their motion.

The Ashland petroleum pitch has not yet been extensively investigated and it is not clear why no maxima are seen in the rheological behaviour of this pitch.

Optical micrographs of the 420°C impregnation pitch sample, cooled under shear, show elongated mesophase units oriented in a particular direction. On heating, they do not revert to spherical shape until a temperature of 300°C, indicating that this is the temperature at which the molecules within the mesophase of this particular sample become mobile. The sample which received a similar heat treatment but no shear, when examined rheologically at temperatures between 250 and 300°C, exhibited flow curves of the type shown in Fig. 2. After heating to a particular temperature under continuous shear conditions a Newtonian flow curve was obtained (A in Fig. 2), but on aging the sample at this temperature for various periods, flow curves of type B were observed, and the position of the 'bulge' shifted to higher values of shear stress with time. A second flow curve measured immediately after the first was Newtonian. This response is typical of a thixotropic material and since the mesophase in this temperature region has been shown to be 'solid-like', it is tentatively suggested that this thixotropic effect is due to a reversible sol-gel transformation.

These and other results will be presented in more detail at the conference.

References

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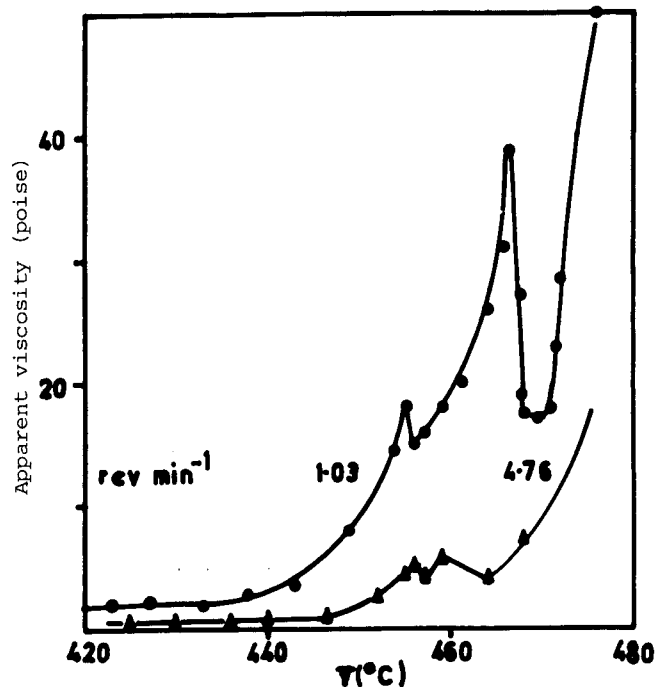


Fig.1 Rheological changes during mesophase growth in an Orgreave impregnation pitch

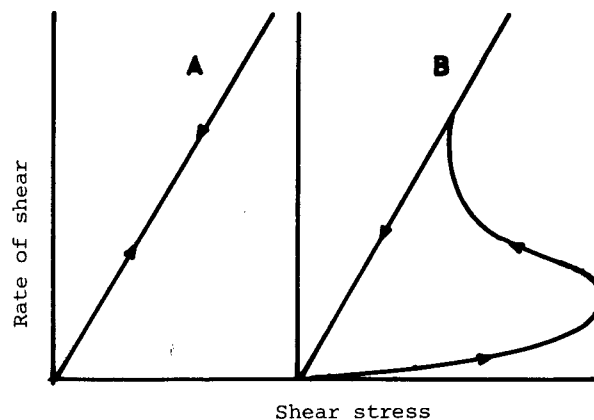


Fig.2 Flow curves in region 250-300°C of a 420°C Orgreave impregnation pitch
A - immediately after shearing
B - after time t under isothermal conditions