ELASTICITY OF ISOTROPIC PITCHES OBSERVED BY DYNAMIC AND CREEP RHEOLOGY

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Introduction

The flow behaviour of apparently single phase isotropic pitch, such as coal tar and petroleum pitch, at processing temperatures is generally considered to be Newtonian. However, two phase systems and 100% optical anisotropic content (AC) mesophase pitches (MP) show marked deviations from Newtonian behaviour. Due to the liquid crystalline nature of MP flow orientation can occur and their complex rheological behaviour involves time-dependent structural changes, depending on various parameters (e.g. temperature, shear rate, etc.), and this has been demonstrated by recent work[1-2].

It has been shown previously[1] that elastic effects are exhibited by MP at processing temperatures. This behaviour was tentatively attributed to the deformation of the liquid crystalline "domains" due to the time dependent relaxation process of the perturbed structure. Under comparable conditions, Ashland A240, a typical isotropic binder pitch, showed no such elasticity and was Newtonian in character.

More recently[3] it was shown that such elastic effects are not unique to the mesophase materials, but may also be exhibited by optically isotropic pitches, for example Aerocarb 75. This is illustrated in Figure 1, which shows a comparison of the Master curves (reduced to the softening temperature, T_s) of the shear storage modulus G', for Aerocarb 75 and A240. In the low reduced frequency region of 10^{-1} to 10^{-4} Hz (or higher temperatures), G' for Aerocarb 75 is 10-100 times greater in magnitude as compared to A240. Therefore, since G' represents the elastic component in dynamic oscillatory rheometry, this represents an increase in the elasticity of Aerocarb 75. Also, Aerocarb 75 in creep (constant stress) experiments showed clear evidence of elastic recovery.

In this work we present results which show that such elastic effects are also exhibited by other optically isotropic pitches, while there are some which show no such elastic effects. These pitches have been characterised by dynamic rheological measurements in the form of controlled stress oscillatory rheometry (CSOR) and dynamic mechanical thermal analysis (DMTA), and transient measurements in the form of creep experiments. The rheological characteristics and glass transition temperatures (T_g) of these pitches are determined. The possible origin of the elasticity is also discussed.

Experimental

Four commercially available optically isotropic pitches were used in this study, which were Carbores/1, Carbores/2 (provided by VFT, Germany), and MMC-36T and MMC-41T (provided by Repsol, Spain). Table 1 gives typical characteristic features. The Carbores materials are thermally treated pitches. Also a coal tar pitch (provided by Bitmac, UK) was prepared to give a 50% AC pitch (HTCTP) and ARA24 of 100% AC (provided by Mitsubishi Gas Chemical Company, Japan) were used for the DMTA analysis.

A Carrimed CSL500 rheometer was used to perform CSOR and creep measurements at temperatures of approximately 30-40°C above and below T_s. CSOR frequency sweep measurements in shear were performed and combined using Time-Temperature Superposition to give Master curves of the storage modulus G', loss modulus G", dynamic viscosity η' and phase angle δ at the reference temperature (T_r) of T_s. The detailed procedure has been outlined elsewhere[1]. DMTA was performed using a Polymer laboratories DMTA in the bending and shear mode. In bending the multiplexing technique was used at frequencies of 0.3, 1, 3, 10 and 30 Hz and T_g was determined from the E' modulus data. The shear mode was used to characterise pitch behaviour at the higher temperatures using a frequency of 1 Hz.

Results and Discussion

Table 1 gives some results determined along with some characteristic data. Figure 2 shows the G', G", η' and δ Master curves for Carbores/1, and is the pitch which showed the most elasticity. The MMC-41T showed no elastic effects, behaving very similar to A240. Carbores/2 approximately showed the same amount of elasticity as Aerocarb 75. MMC-36T having a comparatively low T_g to the other pitches in this study showed elastic effects. These results point to the fact that the elasticity observed is a characteristic of the particular pitch and is not unique to mesophase pitch.

DMTA multiplexing experiments in bending gave T_g for each pitch and the results are shown in table 1.

DMTA for the high T_g pitches in shear showed evidence of elasticity at the higher temperatures. In contrast, A240 and MMC-41T display no such elasticity at the higher temperatures with the G' function being lost, i.e. the decrease in G' (or E') with temperature is more rapid for the low T_g pitches. HTCTP was expected to give two T_g's due to its two-phase nature (the isotropic phase being the continuous phase), however the DMTA instrument failed to give reasonable data at the higher temperatures. It was found that DMTA is a very sensitive technique for determining 2nd order transitions (T_g) in pitches, where they cannot ordinarily be measured by DSC.

In creep experiments, the Carbores pitches and MMC-36T showed evidence of elastic recovery after a constant stress test and behaved as viscoelastic liquids (figure 3, where σ denotes stress used). Also, at very low stresses the Carbores pitches took longer to reach a steady state. Thus, during processing even gravity could affect the materials behaviour or structure after, say application to a surface or fibre. MMC-41T displayed Newtonian behaviour similar to A240.

The existence of a spectrum of relaxation times giving rise to the rheological characteristics observed is not due to any structure observable on the optical scale of sizes. It is possible that a sub-micron micellar structure exists, the perturbation of which provides the origin of the effect. Micellar models of pitch have been around for a long time, where the pitch is viewed as a colloidal system and have been described by Riggs and Diefendorf[4]. It was suggested that the aromatic moieties are solubilised by a sheath of polyaromatics and napthenics. If this outer sheath is eliminated by solvent fractionation, then the remnant material can show mesogenic character at elevated temperatures when the molecules are mobile. The preparation method for the high T_g pitches involves the evaporation of small molecules, which modifies severely any micellar structure. This may create a pitch of a more narrow molecular weight distribution with larger average molecular weights. Whilst the precise origins of the elasticity observed here are not known at the present time it seems likely that their explanation will lie in an understanding of how the volume fraction, size distribution and degree of coalescence of such micellar units is modified under shear and by temperature.

References

1.Turpin, M., Cheung, T., Rand, B., *Carbon*,1996,34,265

2.Fleurot, O., and Edie, D. D., in *Carbon '96 (Ext. Abstr. Euro. Carbon Conf.)*, Newcastle, 1996, p. 425

3.Daji, J. and Rand, B., in *Carbon '96 (Ext. Abstr. Euro. Carbon Conf.)*, Newcastle, 1996, p. 140.

4.Riggs, D.M. and Diefendorf, R.J., in *Carbon '79 (Ext. Abstr. 14th Biennial Conf. Carbon)*, PA, 1979, p. 407.

Table 1 Characteristics of pitches used in this study

Sample	Carbon Yield/%	T_s/°C	T_g/°C	QI/%	TI/%	AC/%
A240	50	119	58	0	8.0	0
CTP	58	116	52	5.7	27.6	0
Aero-75	75	234	156	0	26.0	0
Carb/1	89	290	198	11.5	70.0	<1
Carb/2	85	250	160	10.0	58.2	<1
M-36T	56	155	65	<0.2	23.0	0
M-41T	49	118	49	<0.2	<1.0	0
HTCTP	-	-	64	-	-	50
ARA24	84	238	192	-	65.0	100

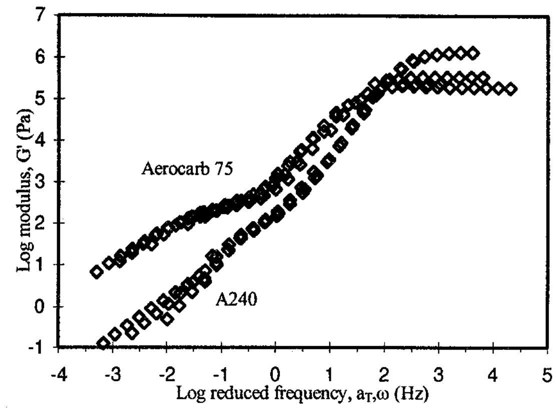

Figure 1. G' Master curves for A240 and Aerocarb 75.

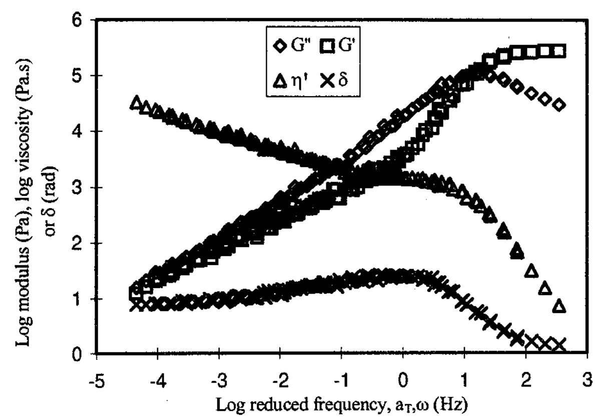

Figure 2. Master curves for Carbores/1 at T_r=290° C.

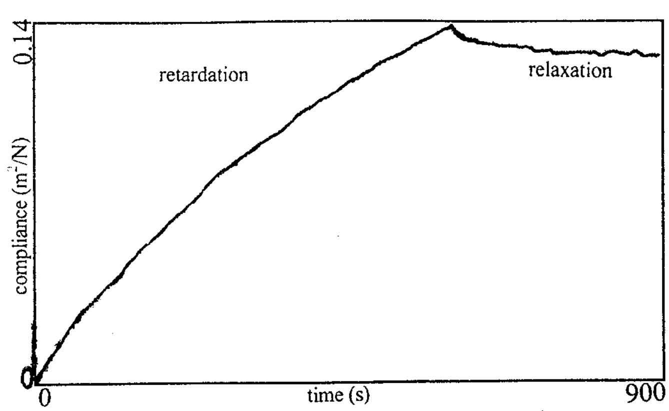

Figure 3. Creep curve of Carbores/1 at 310°C (σ=1Pa).