Viscosity and WLF-Type Behavior of Mesophase Pitches

by

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Introduction

The importance of rheological characterization of mesophase pitch has been described in several papers.[1-4] During the thermal polymerization process involved in the formation of mesophase, pitch undergoes substantial viscosity changes. The rheological behavior is related to both the mesophase content and molecular weight distribution of the mesophase pitch.

In order to clarify the flow behavior during the development of mesophase, a series of mesophase pitches made from a given precursor at rigidly controlled reaction conditions has now been utilized to investigate their viscosity dependence on isotropic content and temperature. From this study, a mathematical relationship between viscosity, temperature, and isotropic content is developed.

Experimental

The mesophase pitches used in this study were similar to those described by Chwastiak and Lewis.[5] They were all produced in the laboratory from a precursor petroleum pitch under highly controlled reaction conditions. The isotropic content of the mesophase pitches was varied from 4 to 34 percent by changing the reaction time without any changes in the remaining reaction conditions. The properties of these pitches including their Mettler softening points and calculated glass transition temperatures are listed in Table 1. The amount of isotropic phase was determined from polarized light photomicrographs.

Table 1. Properties of the Mesophase Pitches

Mesophase Pitch	Glass Transition Temperature Tg, °C*	Mettler Softening Point Ts, °C	Percent Isotropic Content
A	235	339	4
B	225	334	11
C	221	329	17
D	210	324	20
E	195	312	34

* Calculated Tg from $T_g = 0.8\ T_s$.[6]

Viscosity data for the pitches were measured with a modified concentric-cylinder viscometer. When the test specimen reached the desired steady-state temperature, it was sheared at a fixed shear rate sufficiently long to attain constant torque. The following equations were used to calculate the shear rate, $\dot{\gamma}$, and the viscosity, η:

$$\dot{\gamma} = \frac{\Omega}{1-K} \quad (1)$$

and

$$\eta = \frac{\tau\ (1-K)}{2\ \pi\ R^2\ \Omega\ (K^2L + K^3\ R/3)} \quad (2)$$

where τ is the steady state torque, K is the ratio of bob-to-cup radii, R is the bob radius, Ω is angular velocity, and L is the height of the bob in the concentric-cylinder region.

Viscosities were measured over a range of shear rates and at temperatures of 13°C, 18°C, and 23°C above the Mettler softening points of the pitches. A common temperature could not be used because of the different fluidity of the pitches.

Results and Discusson

Apparent Viscosity Versus Shear Rate

The apparent viscosity-shear rate plots for the five pitches at 23°C above the Mettler softening temperatures are shown in Figure 1. As can be seen, the pitches initially demonstrate a yield-type behavior followed by fairly "Pseudo-Newtonian" regions where the viscosities appear to be independent of shear rate. Similar behavior was observed at the other two measurement temperatures.

Viscosity Versus Isotropic Content

The "Pseudo-Newtonian" viscosities at each equivalent relative temperature are plotted against isotropic content in Figure 2. This plot illustrates that the viscosity of pitch at the same relative equivalent temperature (RET), increases with decreasing isotropic content.

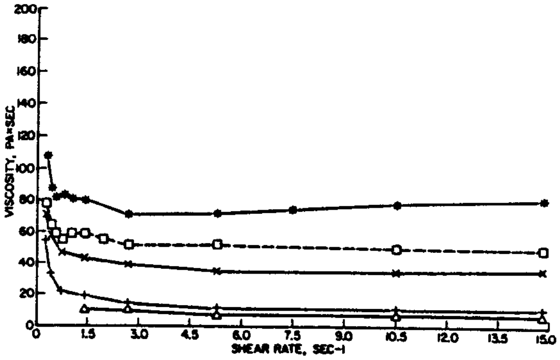

Figure 1. Viscosity Measurements at 23°C Above Softening Point. Pitch A = ✱, Pitch B = □, Pitch C = X, Pitch D = +, Pitch E = Δ

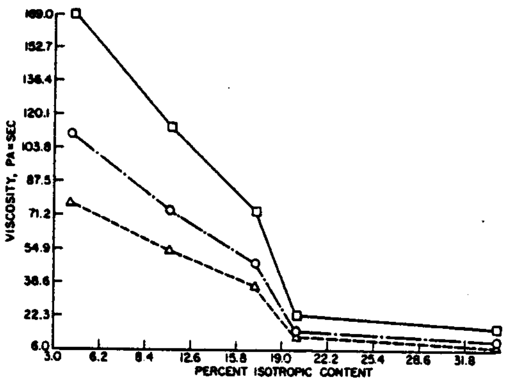

Figure 2. Viscosity Versus Pitch Isotropic Content as a Function of Relative Equivalent Temperature (RET). □ = at 13°C RET, o = at 18°C RET, and Δ = at 23°C RET.

Temperature Dependence of Viscosities

Arrhenius-type plots were used to determine activation energies for the five mesophase pitches. The data are presented in Table 2 and show a decreasing activation energy with increasing isotropic content.

Table 2. Activation Energies for the "Pseudo-Newtonian" Region of the Mesophase Pitches

Pitch	Percent Isotropic	ΔE, Activation Energy (Kcal/mole)
A	4	71.2
B	11	58.8
C	17	56.4
D	20	45.7
E	34	49.2

Application of William-Landel-Ferry (WLF) Plot to Mesophase Pitch

The procedure described by William, Landel, and Ferry[7] was applied to the rheological data for the five mesophase pitches. This procedure introduces a shift factor, A_T, which represents the ratio of relaxation times at two different temperatures. The reference temperature for the pitches was found to be Tg + 140°C. In Figure 3, the shift factor defined as $A_T = \eta T_r/\eta_r T$ is plotted versus $(T-T_r)$. The single correlation for all the viscosity data shows the WLF equation to be applicable to mesophase pitches.

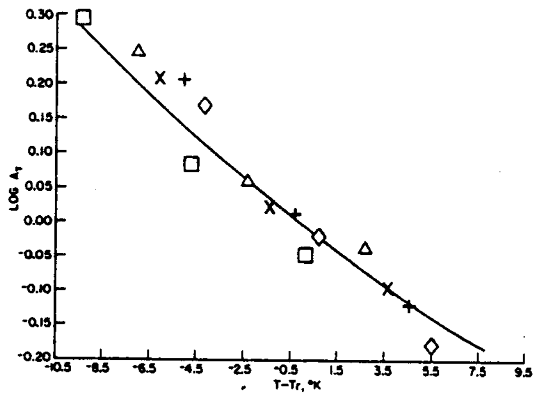

Figure 3. Shift Factor Plot for Mesophase Pitches. ◇ = Sample A, + = Sample B, X = Sample C, Δ = Sample D, and □ = Sample E.

Viscosity-Isotropic Content-Temperature Correlation

Using the WLF-type approach, one finds:

$$\log A_T = -2.3(T-T_r)/(90.3 + T-T_r) = \log \left(\frac{\eta\, T_r}{\eta_r T}\right) \quad (3)$$

The relationship between $\frac{\eta_r}{T_r}$ and the isotropic content, ϕ, can be represented as follows:

$$\frac{\eta_r}{T_r} = e^{-(1.36 + 0.09\,\phi)} \quad (4)$$

The correlation between the softening point and isotropic content is given below:

$$T_s = 528.5 + 0.89\,(100 - \phi) \quad (5)$$

Incorporating Equations (4) and (5) for the appropriate terms in Equation (3) provides the final expression (6) for viscosity in terms of isotropic content and temperature as:

$$\eta = T \exp\,(4097.3 - 6.7\,T + 45.3\,\phi - 0.09\,\phi T - 0.07\,\phi^2)/(-543.7 + T + 0.71\,\phi) \quad (6)$$

References

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