THE INFLUENCE OF THERMAL TREATMENT ON THE RHEOLOGY OF COAL TAR PITCHES

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INTRODUCTION

Thermal treatment of pitch is frequently used, prior to the preparation of carbon materials, to reduce the development of porosity during carbonization and consequently to increase density. The rheological behavior of treated pitches is of special interest for the selection of optimum processing conditions. Current studies are mainly concerned with treatments that generate a substantial amount of mesophase [1]. The objective of this study is to determine the rheological behavior of a series of pitches obtained by thermal treatment of a commercial impregnating coal tar pitch, little or no mesophase development. Rheological changes will be explained based on the chemical composition of pitches.

MATERIALS AND METHODS

Table 1 shows the experimental conditions followed for various thermal treatments of the starting impregnated pitch and the main characteristics of the pitches produced. Thermogravimetric analysis (TGA and DTG) of the pitches was performed at 10°C min^{-1} up to 1000°C, under nitrogen, using a Perkin Elmer TGA7 thermobalance. The aromaticity and ortho-sustitution indices of the pitches were obtained from the FTIR analysis of KBr pellets, following a procedure detailed by Guillén *et al.* [2]. The mesophase content in the pitches was determined by a point counting procedure, using a polarized light Leitz microscope.

A Rheometrics RDS II Dynamic Spectrometer, equipped with cone and plate fixtures (plate radius: 2.5 cm; cone angle: 0.1 rad), was used to characterize the viscoelastic behavior of the pitches. First, the rheometer was used in the steady mode of operation to measure the steady shear viscosities of the samples. Then, the samples again were tested in the steady mode and the transient shear stress response associated with inception of steady shear flow was recorded. The detailed procedure followed is described in [3]. Finally, the dynamic mode was used to analyze samples. In this mode a small oscillating strain was applied to the samples and the stress response was recorded. Loss modulus (G''), storage modulus (G') and phase angle (δ) were measured within the linear viscoelastic region of each pitch and over a range of temperatures. Master curves were generated by applying the time-temperature superposition principle to the data, as proposed by Turpin *et al.* [4].

RESULTS AND DISCUSSION

Pitch characterization. SP and CY of the pitches increased with the degree of thermal treatment (Table 1). This is a consequence of volatiles release and polymerization that occur during heat treatment. The latter is confirmed by the results of solubility tests which indicated that the TI content increased with increasing pitch treatment (Table 1). This also is in agreement with the results of the DTG analysis, which showed a shift of the initial temperature of weight loss to higher temperatures and the presence of new peaks of weight loss in the temperature range of 450-600°C for the most treated pitches. Even though the smallest components distilled with the thermal treatment, the aromaticity index increased (Table 1). This, together with the increase of the C/H atomic ratio, indicates that a significant amount of aliphatic hydrogen is lost during polymerization. The first two pitches of the series (400°C 2h and 400°C 5h) were purely isotropic. Those obtained at 400°C 7h and 425°C 5h contained 7 and 20 vol% mesophase, respectively.

Table 1. Properties of the pitches investigated.

Pitch	C/H[1]	I_{ar}[2]	SP[3]	CY 4	TI[5]	QI[6]
CTP2P	1.7	0.64	97	37	21.6	3.5
CTP2P 400°C 2h	1.8	0.68	112	38	30.2	4.1
CTP2P 400°C 5h	1.9	0.69	121	44	32.0	5.8
CTP2P 400°C 7h	1.9	1.70	126	49	36.8	8.1
CTP2P 425°C 5h	2.0	0.78	146	59	47.8	21.5

[1] C/H atomic ratio [4] Coke yield (wt %)
[2] Aromaticity index [5] Toluene insolubles (wt %)
[3] Softening point (°C) [6] Quinoline insolubles (wt %)

Steady Shear Rheology. Figure 1 shows flow curves obtained for the parent pitch (CTP2P), the least treated pitch (CTP2P 400°C 2h) and the most highly treated one (CTP2P 425°C 5h). In the range of shear rates investigated, both CTP2P and CTP2P 400°C 2h exhibited Newtonian flow behavior. By contrast, CTP2P 425°C 5h exhibited shear thinning behavior at low rates of shear (below 1 s^{-1}). However, its viscosity appeared to become constant at higher shear rates. Optical analysis of fragments of this pitch quenched before and during an experiment showed that the two-phase nature of the fluid was probably responsible for its non-Newtonian behavior. It was observed that the spheres of mesophase present in the pitch did not coalesce or deform during flow. Based on this observation, we concluded that for small rates of shear, the interference among mesophase spheres impeded the flow, resulting in a yield stress (shear thinning viscosity). For higher shear rates, sufficient energy was available to overcome this interference and a Newtonian behavior resulted.

Transient Shear Rheology. Next, the Rheometrics was again operated in the steady mode and the stress response of the samples was monitored during startup of flow. The results showed that only CTP2P exhibited a purely viscous response (no overshoot). As the degree of heat treatment increased, the pitches likely became more elastic resulting in larger overshoots of the transient shear stresses. Because this technique only provided a qualitative analysis of the elasticity of the pitches, oscillatory rheometry was performed to quantitatively characterize their viscoelastic behavior.

Oscillatory Rheometry. The master curves obtained for the most treated pitch (CTP2P 425°C 5h) are presented in Figure 2. The viscoelastic nature of CTP2P 425°C 5 h was evidenced by a phase angle, δ, between 55° and 76° over the range of frequencies studied. As illustrated in Figure2, δ steadily increased during the frequency sweep. Therefore, as one would expect, the pitch becomes more elastic at high frequencies.

Figure 3 allows a direct comparison of the elasticity of all pitches studied by showing their phase angle as a function of frequency. While CTP2P exhibited purely viscous behavior, all thermally treated pitches showed some elasticity. More precisely, increasing thermal treatment produced a more elastic pitch. This is probably a consequence of the polymerization of pitch components during thermal treatments. The result is a material with higher molecular weight and increased elasticity.

CONCLUSION

The polymerization of pitch by thermal treatment increased the size of the pitch molecules. These larger molecules can exhibit elastic behavior, even when mesophase is not formed.

ACKNOWLEDGMENTS

Authors would like to thank CICYT (Project MAT95-0206) for financial support. Rosa Menéndez gratefully acknowledges DGICYT for granting her stay at Clemson University.

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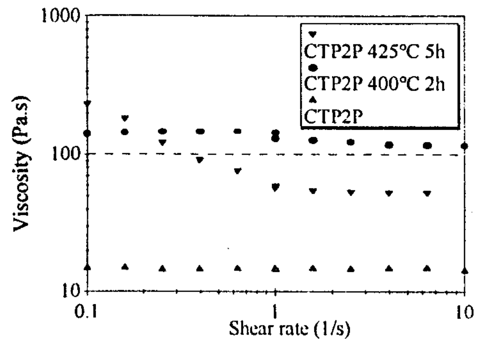

Figure 1. Flow curves for the starting impregnating pitch (CTP2P) and two thermally treated pitches.

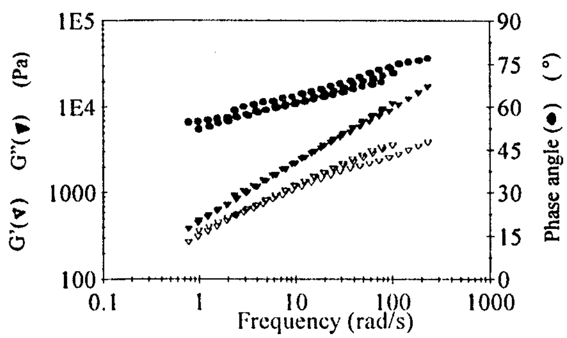

Figure 2. Master curves of loss modulus, G'', storage modulus, G', and phase angle, δ, for CTP2P 425°C 5h.

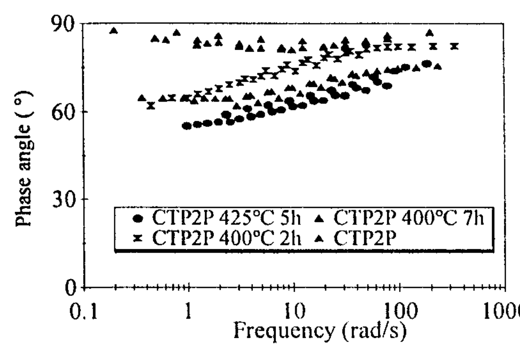

Figure 3. Master curves of phase angle for all pitches produced.