THE VISCOELASTIC BEHAVIOR OF AIR-BLOWN COAL-TAR PITCHES

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INTRODUCTION

Previous research has shown that pitch air-blowing was an effective treatment that could increase pitch carbon yield without destroying graphitizability [1]. Air-blown pitch cokes generally exhibit improved density and strength, and lower reactivity than those of the starting pitches [2]. Chemical changes due to the controlled polymerization of pitch components during air-blowing have been studied and possible reaction mechanisms proposed [1]. However, to our knowledge, the viscoelastic behavior of the pitches (which relates to the processing of the pitches and the properties of the final products) has never been investigated. Therefore, the objective of this study was to determine if the polymerization of a coal-tar pitch by air-blowing, at moderate temperatures and with no generation of mesophase, modified pitch elasticity.

EXPERIMENTAL

A series of five pitches were prepared by air-blowing an impregnating coal tar pitch (CTP) under the conditions shown in Table 1. Softening point (Mettler), carbon yield (5°C min^{-1}, 900°C, 30 min, nitrogen flow of 65 ml min^{-1}), solubility in toluene and N-methylpyrrolidone (NMP), and elemental analysis (O was directly determined) for each pitch are presented in Table 1. Pitch reflectance in air was measured on polished samples by optical microscopy following a procedure similar to that used for coal rank evaluation [3]. Note that reflectance relates to aromaticity of samples. In addition, aromaticity and ortho-sustitution indexes of pitches were determined from FT-IR spectra [4]. Extents of cross-linking caused by air-blowing polymerization were estimated by iodine sorption (up-take) [5].

The viscoelastic nature of the air-blown pitches was studied by performing both transient and oscillatory rheological experiments. We used a Rheometrics RDS II Dynamic Spectrometer equipped with cone and plate fixtures (plate radius: 2.5 cm; cone angle: 0.1 rad). The procedure followed to test the transient rheological behavior of the pitches is detailed elsewhere [6]. The measurement technique used to estimate loss modulus (G”), storage modulus (G’) and phase angle (δ) of the pitch samples during the oscillatory rheometry also is described elsewhere [7].

RESULTS AND DISCUSSION

Pitch characterization. As reported in Table 1, the softening point of the pitches ranged from 95 °C for the starting pitch to 210 °C for the one obtained under the most severe air-blowing conditions (275 °C, 30h). Carbon yield increased from 41 wt % for the parent pitch to about 63 wt % for the most treated one. These changes are due to the polymerization reactions occurring during pitch air-blowing, as confirmed by the increase in TI and NMPI. The increase of the aromaticity index (Figure 1) and C/H atomic ratio suggests that polymerization involves a significant loss of aliphatic hydrogen, along with the generation of large planar macromolecules through extensive ring condensation, as confirmed by the increase of reflectance (Table 1). The decrease in iodine up-take with the severity of treatment also suggested a formation of cross-linked structures (see Figure 1).

Transient Shear Rheology. The shear stress response upon start-up of steady shear flow was monitored for all five pitches, as a function of rest time between consecutive inceptions of plate rotation. The study focused on the magnitude of the stress overshoot which directly relates to the elasticity of the fluid.

As shown in Figure 2, the starting impregnating pitch showed a purely viscous behavior (no overshoot). In contrast, the air-blown pitches exhibited elastic behavior. As the degree of air-blowing increased, larger macromolecules, more cross-linked, were formed resulting in greater overshoots upon start-up of flow. These overshoots were higher than those observed for thermally treated pitches under inert atmosphere. However, this effect seemed to level-off for long air-blowing times. Therefore, the similar transient behavior of the two most treated pitches along with their comparable physical properties (as reported in Table 1) suggest that air-blowing of CTP 275 °C 25h for five additional hours did not significantly change the nature of this pitch, but merely its softening point.

Oscillatory Rheometry. Figure 3 shows the phase angle between the imposed strain and the measured stress for the pitches studied as a function of frequency. Note that Figure 3 does not show master curves. They will be presented later. The phase angles reported in the present abstract correspond to similar loss moduli curves for the pitches.

The viscoelastic nature of the air-blown pitches was evidenced by a phase angle different of 90°. The most treated pitches (CTP 275 °C 25h and 30h) appeared more elastic than the less treated ones. Their elastic behavior was not greatly affected by frequency. In contrast, the elasticity of CTP 18h and 10h decreased with increasing frequency. Therefore, increasing the speed of the process should decrease elastic effects for these two pitches.

CONCLUSION

Isotropic pitches produced by air-blowing of an impregnating coal tar pitch at 275 °C, for periods ranging from 10 to 30 hours showed elastic behaviour as a consequence of the generation of large aromatic macromolecules. The elastic behavior increased with time of treatment and eventually became constant for long air-blowing times.

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Table 1. Pitch properties.

Pitch treatment	SP (°C)	CY (wt %)	TI (wt %)	NMPI (wt %)	C/H	O (%)	Ra (%)
None	95	41	21.0	6.3	1.65	1.70	8.89
275 °C-10h	139	48	36.6	13.6	1.82	1.79	9.25
275 °C-18h	168	58	44.6	18.9	1.83	1.81	9.75
275 °C-25h	197	62	51.8	24.9	1.85	1.88	9.72
275 °C-30h	210	63	52.0	27.1	1.87	1.87	9.99

SP, softening point (Mettler)
CY, coke yield
TI, toluene insolubles
NMPI, N-methylpyrrolidone insolubles
C/H atomic ratio
O, oxygen content
Ra, air reflectance

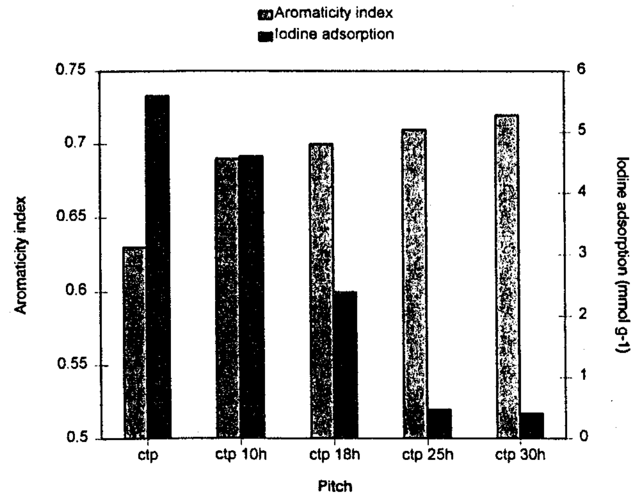

Figure 1. Aromaticity index and Iodine adsorption of pitches

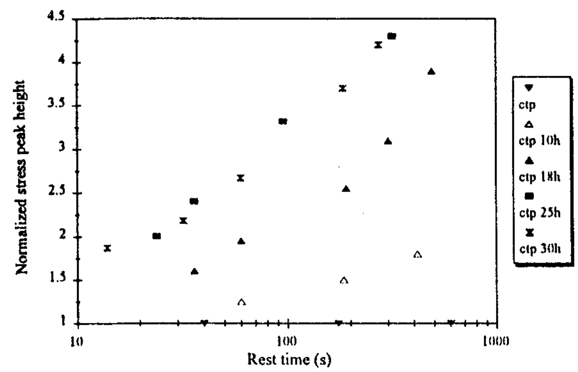

Figure 2. Normalized stress peak height vs. rest time before consecutive start-up of flow for the pitches produced.

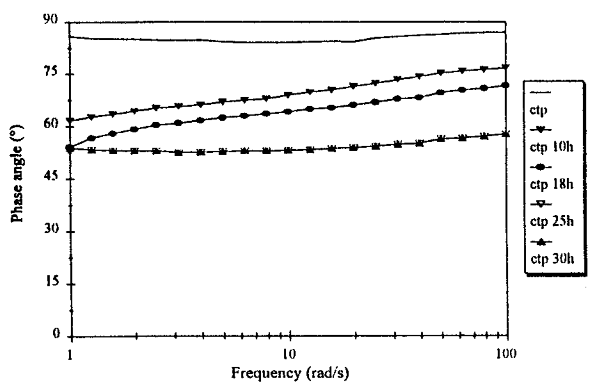

Figure 3. Phase angle vs. frequency for the pitches studied (reported for similar G").