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 (uptake) [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 (\(\delta\)) of the pitch samples during the oscillatory rheometry also is described elsewhere [7].
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.

**ACKNOWLEDGMENTS**

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**REFERENCES**


Table 1. Pitch properties.

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

SP, softening point (Metler)  
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°).