DEVELOPMENT OF SPINNABLE MESOPHASE PITCH USING ETHYLENE BOTTOM OIL WITHOUT HYDROGENATION

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Introduction
Mesophase pitch has various useful applications such as an effective precursor for graphitic anode of Li-ion battery and high-performance pitch-based carbon fiber. As an effective precursor of carbon fibers, its high price has been considered as a main obstacle to broaden the application areas of mesophase pitch-based carbon fiber. Spinnable mesophase pitch, which is used as a precursor for mesophase pitch-based carbon fiber, is usually prepared from petroleum heavy oils and coal tar pitch (CTP) through the purification, hydrogenation and other heat treatments with less than 10 wt.% pitch yield to its raw material. Hydrogenation lowers the softening point of the obtained mesophase pitch by introducing naphthenic structure and short-chain alkyl group (hydro and methyl group) to a raw material and coincidentally deceasing excess poly-aromaticity of heavy molecular components [1]. However, it is considered as main reasons for decreasing the pitch yield and high price. For example, the spinnable mesophase pitch derived from FCC decant oil (FCC-DO) prepared by hydrogenation and usual heat-treatment with nitrogen blowing usually showed the pitch yield of less than 10 wt.% [2]. Therefore, the development of the spinnable mesophase pitch without hydrogenation has been strongly required.

In this study, we have tried to prepare a spinnable mesophase pitch through the controlled bromination-dehydrobromination and continuous N2 blowing heat-treatment. The Bromination-dehydrobromination causes a reduction of alkyl groups and is also effective to conserve the light molecular components after heat-treatment [3]. N2 blowing heat-treatment accelerates to form aromatic molecular stacks. We investigated the effects of the addition of QI-free CTP and FCC-DO to help the mesophase formation.

Materials and Methods
Ethylene bottom oil (EBO) was pressurized at 370°C for 3 h under autogenous pressure (EBOp) because EBO included much asphaltene molecular which decrease the spinnability of pitch at melting spinning [4]. EBOp was heat-treated by bromination at 110°C for 2 h using bromine of 5.0 wt.% and dehydrobromination at 370°C for 3 h under Ar atmosphere (EBOp-Br). EBOp, QI-free CTP and FCC-DO were mixed at 1:1 (w/w) and heat-treated by bromination-dehydrobromination at same conditions ((EBOp/CTP)-Br and (EBOp/FCC-DO)-Br). The samples were heat-treated at 425°C for 1-3 h with N2 blowing heat-treatment. The N2 flow rate was 600 mL/min. The molecule structure, molecular weight distribution, crystal size, softening point and molten state of obtained pitches were estimated by 13C solid-state nuclear magnetic resonance spectroscopy (13C-NMR), time-of-flight mass spectrometry (TOF-MS), X-ray diffraction (XRD) and thermomechanical analysis (TMA).
Results and Discussion
Figure 1 and Table 1 showed the anisotropic structures and physical properties of EBOp-Br, (EBOp/CTP)-Br and (EBOp/FCC-DO)-Br heat-treated by N\textsubscript{2} blowing heat-treatment. The mesophase spheres of EBOp-Br derived pitch were not difficultly formed. The anisotropic structure of (EBO/FCC-DO)-Br derived pitch were more than EBOp-Br derived pitch. However, (EBOp/FCC-DO)-Br derived pitch could not be melted homogenously. (EBOp/CTP)-Br derived pitch showed high yield (27.0%), much mesophase spheres and homogeneous molten state. Mesophase spheres and isotropic matrix of (EBOp/CTP)-Br were high compatibility due to the anisotropic shape and crystal size.

![Figure 1](image1.png)

**Figure 1.** Anisotropic structure of the obtained pitches after N\textsubscript{2} blowing heat-treatment; (a) EBOp-Br, (b) (EBOp/CTP)-Br and (c) (EBOp/FCC-DO)-Br.

**Table 1.** Physical properties of obtained pitches

<table>
<thead>
<tr>
<th></th>
<th>Bromination</th>
<th>Dehydrobromination</th>
<th>N\textsubscript{2} blowing heat-treatment</th>
<th>Yield [wt%]</th>
<th>Soaking time [h]</th>
<th>Yield [wt%]</th>
<th>Softening point [µm]</th>
<th>L\textsubscript{c} [GPa]</th>
<th>f\textsubscript{s} [GPa]</th>
<th>Molten state</th>
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<tr>
<td>EBOp-Br</td>
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<td>65.8</td>
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<td>211</td>
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<td>(EBOp/CTP)-Br</td>
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<td></td>
<td></td>
<td>82.2</td>
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<td>27.0</td>
<td>256</td>
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<td>Homo</td>
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<tr>
<td>(EBOp/FCC-DO)-Br</td>
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<td>19.8</td>
<td>285</td>
<td>2.70</td>
<td>0.959</td>
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</tr>
</tbody>
</table>

Conclusions
The formation of mesophase texture was very enhanced through the addition of CTP with high yield. 5%-bromination was very effective to enhance the yield of mesophase pitch.

Acknowledgment
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References