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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 N_2 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]. N_2 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 N_2 blowing heat-treatment. The N_2 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 ^{13}C solid-state nuclear magnetic resonance spectroscopy (^{13}C-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_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.

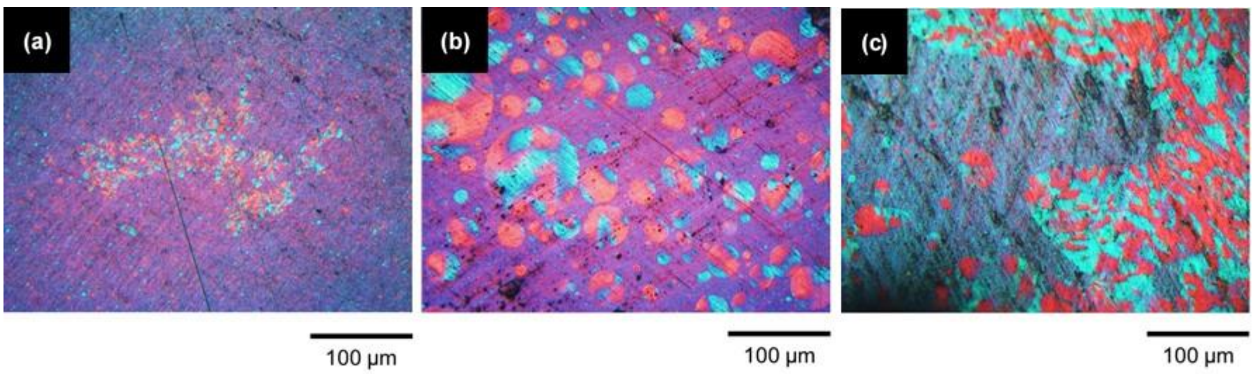

Figure 1. Anisotropic structure of the obtained pitches after N_2 blowing heat-treatment; (a) EBOp-Br, (b) (EBOp/CTP)-Br and (c) (EBOp/FCC-DO)-Br.

Table 1. Physical properties of obtained pitches

	Bromination Dehydrobromination	N_2 blowing heat-treatment					
	Yield [wt%]	Soaking time [h]	Yield [wt%]	Softening point [μm]	L_c [GPa]	f_a [GPa]	Molten state [%]
EBOp-Br	65.8	1	27.6	211	2.68	0.940	Homo
(EBOp/CTP)-Br	82.2	3	27.0	256	2.42	0.979	Homo
(EBOp/FCC-DO)-Br	80.8	3	19.8	285	2.70	0.959	Hetero

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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