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Eutectic effect during mesophase formation in co-carbonization of ethylene tar pitch and polystyrene

Cheng Xianglin *, Song Shulei

Key Laboratory of Coal Processing & Efficient Utilization, Ministry of Education, China University of Mining & Technology, Xuzhou 221116, China
High Tech Research Institution of China University of Mining & Technology & The City of Lianyungang Xuwei New Area, Xuzhou 221116, China

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ABSTRACT

Ethylene tar pitch was co-carbonized with waste polystyrene to prepare mesophase pitch. The characteristics of mesophase pitches were examined using polarized light optical microscopy, apparent viscometry, Fourier transform infrared spectrometry, ^1H nuclear magnetic resonance spectrometry, and X-ray diffractometry. The properties of the mesophase pitch were greatly improved because of the eutectic effect. The soluble content increased from 5% to 56%, the mesophase itself increased from 32% to 100%, and the optical texture was changed from a coarse mosaic into a flow domain after the waste polystyrene was added to the ethylene tar pitch. The apparent viscosity showed that the mesophase pitch changed from thixotropic to Newtonian suggesting improved rheological behavior during co-carbonization. The increased number of alkyl groups, which are mainly methylene groups, altered the molecular structure of the mesophase pitch in a way that resulted in the eutectic effect.

1. Introduction

Co-carbonization is believed to be a useful method for modifying the properties of mesophase pitch because of easier hydrogen transfer and the more favorable formation of a mesophase in such a system [1]. Marsh et al. have discussed the eutectic mixture and its formation mechanism in terms of coal carbonization [2]. A eutectic mixture was invoked to explain the formation of an anisotropic carbonaceous phase from a mixture of two compounds neither of which would individually form an anisotropic phase during carbonization. The formation temperature of the anisotropic carbonaceous phase decreased to a minimum and improved interfacial phenomena were observed in the co-carbonization of two different coals. The eutectic effect during co-carbonization is very important for the preparation of mesophase pitch of high quality from alternative materials. Mesophase pitch is the essential precursor for the manufacture of high performance carbon materials such as carbon foam, needle coke, or carbon fibers [3–5].

Ethylene tar pitch (ETP), which is obtained from naphtha and produced in large scale from ethylene crackers, is soluble in toluene, highly aromatic, and free from heteroatoms and inorganic matter. However, its application to the preparation of high performance carbon materials is very limited because its high carbonization reactivity results in the formation of mosaic textured coke under ordinary carbonization conditions [6]. Various methods have been used to modify ETP for preparation of a carbonaceous anisotropic mesophase [7,8]. Those investigations showed it was difficult to remove the byproducts from the carbonization system and the operating cost was high, which limits the wide application of these methods in industry.

The disposal of waste plastics is a major environment problem. Pyrolysis is one effective way to deal with the waste plastic. Co-carbonization of ETP and waste polystyrene (WPS) is assumed to be another method for dealing with the waste plastic and for implementing an economical way of manufacturing high performance carbon materials [9–12].

Only a few papers have described the eutectic effect during mesophase formation. Moreover, the influence of the eutectic effect on mesophase pitch properties and the reason for the eutectic effect are unknown, so far.

In the current work, ETP was co-carbonized with different proportions of WPS. The influence of the eutectic effect on the properties (including solubility, fluidity, optical texture, and molecular assembly) of the subsequently formed mesophase pitch was examined and the reason for the eutectic effect is discussed.

2. Experimental

2.1. Preparation of mesophase pitches

The ETP was from the Daqing Petroleum Chemical Corporation (China). Its primary properties are listed in Table 1. The WPS was selected from polystyrene packing waste.

* Corresponding author. Tel.: +86 516 83591066.
E-mail address: cxl8817@yahoo.com.cn (X. Cheng).

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Table 1
Primary properties of the ethylene tar pitch.

WC (%)	WH (%)	WN (%)	Wash (%)	H/C	WBS (%)	C_a
92.40	7.30	0.04	0.23	0.95	100	0.77

Note: BS, benzene soluble; C_a, carbon aromaticity.

The ETP was mixed and agitated at 170 °C with different proportions of WPS. The WPS concentrations were 10% and 20% and the reaction kettle was 1 L in size, heated, and purged by a continuous nitrogen flow. The heating rate was 2.5 °C/min to a temperature of 430 °C at which point it was then maintained at 430 °C for 4 h. Pure ETP was carbonized under the same conditions except that the maximum temperature was 450 °C. The resultant mesophase pitches were labeled MP, MP-10, or MP-20 according to the proportion of waste polystyrene.

2.2. Characterization of the mesophase pitches

Samples of the mesophase pitches were ground with KBr and pressed into tablets that were then analyzed by fourier transform infrared spectrometry (FTIS) (Tensor-27, Bruker Corp., Germany) at a resolution of 4 cm^{-1}.

^{1}H nuclear magnetic resonance (^{1}H NMR) spectra of pyridine soluble fractions of the MP, MP-10, and MP-20 samples were recorded with a Varian AS600 spectrometer. A ten percent solution of the pyridine soluble fraction was mixed (3:1) with $CDCl_3$ using tetramethylsilane as an internal standard.

The elemental analysis was performed with a VARIO EL III CHNS/O analyzer made in Germany. Polished specimens of MP, MP-10, and MP-20 were examined by polarized light microscopy (Nikon Eclipse E600 Pol, China). The mesophase content was obtained from the 'feature analysis' of these micrographs [13].

The rheological behavior of MP, MP-10, and MP-20 was investigated with a NXS-11 Viscometer (Chengdu analysis instrument factory, China) at a constant shear rate of 1 r/min. A nitrogen gas flow was maintained over the pitch during the viscosity experiments.

The crystallite size of the ground mesophase pitch, *Lc* (002) which represents the stacking thickness of the aromatic molecules, and the d_{002} parameter were calculated from the half width of the C (002) peak and the peak position measured by X-ray diffraction (X′ Pert Pro MPD, Holland, PAN analytical) [14].

3. Results and discussion

3.1. Eutectic effect in the co-carbonization of WPS and ETP

The polarized micrographs of the mesophase pitches are shown in Fig. 1. The optical texture of the MP is a coarse mosaic texture and the anisotropic content is 32%. However, MP-10 and MP-20 exhibit a flow domain texture with 100% mesophase after the WPS was added to the ETP.

Transformation to anisotropy occurs at a temperature of 430 °C in the WPS doped ETP, a lower temperature by 20 °C compared to the carbonization of pure ETP. Both ethylene tar pitch and waste polystyrene produce isotropic carbon when carbonized individually. However, mixed together they form anisotropic carbon at temperatures below the temperature where the individual components form isotropic carbon. This illustrates that the eutectic effect occurs during the co-carbonization of the ETP with WPS.

3.2. Changes of mesophase pitch properties during the cocarbonization

The mesophase includes pyridine insoluble materials, which are higher molecular weight components, and pyridine soluble ones, which are lower molecular weight species, i.e., a soluble mesophase [15]. Generally, the amount of soluble mesophase is determined from the difference in total mesophase and the pyridine insoluble content. The quantity of soluble mesophase may be one of the most influential properties of mesophase pitches. The pyridine soluble portion was determined with a Soxhlet extractor. As shown in Table 2 the soluble mesophase is 5% for MP, 49% for MP-10, and 56% for MP-20. The soluble mesophase concentration increases with the proportion of WPS. This greatly improves the characteristics of the mesophase pitch.

The main properties of the mesophase pitches are summarized in Table 3. The H/C ratios of MP, MP-10, and MP-20 are 0.442, 0.460, and 0.487. This indicates that alkyl groups in the polynuclear aromatic hydrocarbons (PAH) fraction was increased during the co-carbonization. The softening points are 320 °C for MP, 293 °C for MP-10, and 278 °C for MP-20.

The viscosity-temperature curves of MP, MP-10, and MP-20 are shown in Fig. 2. The apparent viscosity of pitch MP is higher than that of either MP-10 or MP-20 at a given temperature. The mesophase pitches lose their thixotropic nature during co-carbonization. The fluidity of MP-10 and MP-20 is higher than that of MP showing a change in rheological behavior after adding the WPS to the ETP. The high viscosity of the ETP carbonization system inhibits coalescence during the formation of a mesophase. The added WPS enhances mesophase coalescence because of the greater fluidity. This result is consistent with the results shown in Fig. 1.

X-ray C (002) diffraction profiles are shown in Fig. 3 and the X-ray C (002) diffraction parameters are listed in Table 4. The *Lc* value is 2.5 nm for MP, 4.7 nm for MP-10, and 4.9 nm for MP-20. The d_{002} values of MP, MP-10, and MP-20 are 0.3470, 0.3457, and 0.3455 nm. The increase in *Lc* value, and a decrease in d_{002} value, noted upon adding WPS shows that the molecular arrangement of the mesophase pitches is changed by co-carbonization with WPS.

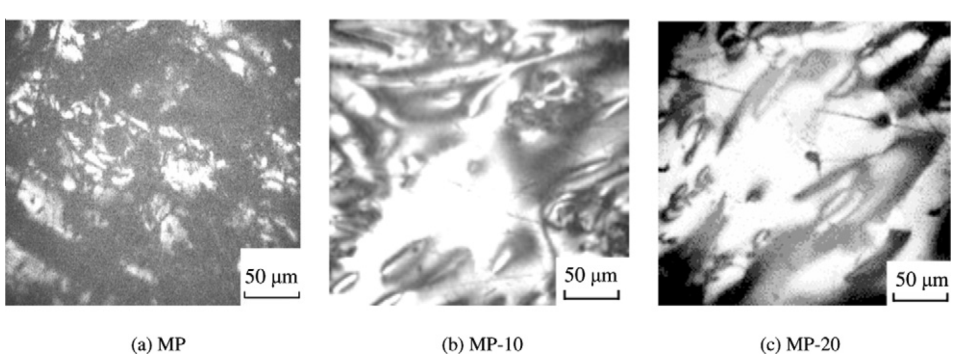

Fig. 1. Polarized micrographs of mesophase pitches.