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Carbonization behavior and mesophase conversion kinetics of coal tar pitch using a low temperature molten salt method

Youliang Cheng^a, Changqing Fang^{a,*}, Jian Su^a, Ruien Yu^a, Tiehu Li^b

^a School of Printing and Packaging Engineering, Xi'an University of Technology, Xi'an 710048, PR China

^b School of Materials Science and Engineering, Northwestern Polytechnical University, Xi'an 710072, PR China

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ABSTRACT

Mesophase pitch can be prepared from coal tar pitch (CTP) with AlCl_3 – NaCl molten salt mixture at low temperature via the molten salt method. The carbonized and mesophase products were characterized using polarized optical microscope, FTIR, XRD, ^{13}C NMR and TEM. The kinetic parameters of the mesophase conversion were calculated by isothermal kinetics. These experimental results demonstrated that the molten salt catalyzed the mesophase transition and the formation temperature of CTP was lowered to 250 °C. An abundance of mesophase spheres formed in the carbonized products when the CTP was treated with molten salt at 280 °C for 30 min (CTPS-280-30). The optical textures of these carbonized products exhibited mosaic anisotropy and the degree of order was reduced when the heating temperature and holding time were increased. It was found that the building units of CTPS-280-30 mesophase products were parallel molecular layers with a thickness of 0.6–2.5 nm, and the building units of CTPS-280-120 were 1–3.5 nm in thickness. Naphthene and methylene-bridge structures were found in the mesophase products. The kinetics study showed that the molten salt conversion of CTP to mesophase pitch was first-order kinetic with a low apparent activation energy (40.5 kJ/mol).

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1. Introduction

During the liquid phase carbonization of the pitch, the planar macromolecular compounds can form via pyrolysis, dehydrogenation, cyclization, aromatization and polycondensation reactions, which are considered as the nucleus for generating small mesophase spheres. The mesophase pitch product results from the subsequent growth and coalescence of these small spheres [1–4]. Mesophase pitch is an excellent precursor for carbon materials and has been widely used in the production of high performance carbon fiber, C/C composites, carbon foam, activated carbon, mesoporous carbon, lithium ion battery electrodes [5–10]. The conditions of the chemical reactions and the formation, accumulation and rearrangement of the planar macromolecular compounds in the mesophase building block units influence the development of the mesophase pitch and determine its final morphology [11,12]. Research has shown that the additives such as ferrocene, HF/BF_3 , carbon black, flake-like graphite, BMI resins, divinyl benzene and rosin have a significant influence on the growth, size and texture of pitch-based mesophase [13–19]. The formation temperature of

mesophase pitch is normally above 350 °C [17–19] and the apparent activation energy of the mesophase conversion by isothermal kinetics is greater than 100 kJ/mol [20–22]. Therefore, significant research emphasis has been focused on lowering the mesophase pitch conversion temperature to improve the energy efficiency of this process. It has been found that AlCl_3 is a good catalyst for the polymerization of model compounds such as naphthalene, anthracene, anthracene oil and ethylene tar, because it reduces the polycondensation reaction activation energy [23–26]. It is quite possible that this salt may also reduce the reaction activation energy of mesophase formation, thereby decreasing the quantity of thermal energy required to effect this reaction. Nevertheless, the modification of pitch and reactant preheating prior to mesophase formation are usually required in the AlCl_3 catalyzed reaction system.

Molten salt synthesis is often used to prepare inorganic materials [27]. In molten salt synthesis, the molten salt performs the roles of solvent and reactant. This improves the dispersion of reactants on the atomic scale and reduces the viscosity of the reaction system [28–30]. As a result, the chemical reaction occurs at a lower temperature and within shorter time [31]. Preparation of mesophase pitch by the molten salt method may significantly lower the process cost. In the past, researchers have used the molten salt method (AlCl_3 – NaCl – KCl , ZnCl_2 – KCl , NaOH – Na_2CO_3 molten salt, etc.) to

* Corresponding author. Tel.: +86 29 82312038; fax: +86 29 82312512.
E-mail address: funiy@163.com (C. Fang).

Table 1
The properties of coal tar pitch.

Average molecular weight	Ratio of C/H	Carbonized yield (wt%)	Softening point (°C)	Pyridine insoluble content (wt%)
470.0	1.73	50.79	82.0	12.16

prepare mesophase pitch under 300 °C with no pretreatment of pitch [32–34]. In addition, the carbonization kinetics of coal tar pitch have been studied systematically [13,20–22,35,36]. However, the carbonization behavior and mesophase kinetics of coal tar pitch conversion using AlCl₃–NaCl molten salt have received scant attention.

The molten salt melting temperature varies in different systems as does its wettability with pitch, both of which make product prediction difficult. In this reported study, the catalytic properties of AlCl₃ with coal tar pitch and the low melting temperature of AlCl₃–NaCl molten salt, were employed to explore the influence of this molten salt process on the mesophase formation of coal tar pitch at low temperature.

2. Experimental

2.1. Materials

The reagents NaCl, anhydrous AlCl₃ and pyridine were analytically grade. Medium temperature coal tar pitch (coal tar pitch, CTP) was provided by Wugang Coking Plant, and its properties are shown in Table 1.

2.2. Preparation of carbonized products and mesophase products

The salts AlCl₃ and NaCl were individually ground into powders and then mixed in a molar ratio of 3:2 to form the AlCl₃–NaCl salt mixture. The CTP was sieved through a 100 mesh screen and 5 g of this material was combined with 10 of the salt mixture and the two were thoroughly mixed together. Fifteen grams aliquots of this mixture (denoted CTPS) were then placed in individual glass test tubes for the reaction. Each individual test tube was sequentially placed in an oven and heated to a preset temperature under nitrogen at a ramp rate of 1 °C/min. The reaction temperatures ranged from 220 to 350 °C and once holding time at the set temperature was 1 h the oven was shut off and cooled under flowing nitrogen to room temperature. In a second set of experiments, individual test tubes containing 15 g of reaction mixture were each heated to 280 °C at the same ramp rate and then held there for various times ranging from 0 to 120 min. After holding for a specific time, the reaction was then cooled under N₂ flow to room temperature by shutting off the oven.

All of the experimental products were washed with 5 wt% diluted hydrochloric acid to remove the aluminum ions, followed by washing with deionized water to thoroughly remove chloride ions and sodium ions. Finally, each purified product was dried under high vacuum to obtain the carbonized products. The carbonized products obtained at different temperatures were labeled based on their reaction temperature (e.g. CTPS-220 to CTPS-350) and the products obtained from various different holding times at 280 °C were denoted from CTPS-280-0 to CTPS-280-120. The dried materials were extracted using pyridine until the filtrate turned colorless. The extracted materials were then dried at 90 °C, resulting in the mesophase products and labeled from MCTPS-0 to MCTPS-120 respectively.

2.3. Measurement and characterization

A series of analyses was conducted on the experimental pitch samples. Polarized micrographs of the samples were obtained using with a DMM-300C vertical metallographic microscope. The samples were placed in cylindrical paper molds, and the molds were filled with dental base acrylic resin powder, which was cured by adding methyl methacrylate. The mounted specimens were inspected with a polarized light microscope following surface polishing.

Thermogravimetric analysis (TGA) was carried out on a Perkin-Elmer thermogravimetric analyzer in the temperature range of 25–800 °C with a heating rate of 5 °C/min under N₂ flow.

X-ray diffraction (XRD) tests were performed on an X'Pert High-Score diffractometer (Netherlands Philips Company) with Cu K α radiation ($\lambda = 0.1541$ nm).

Transmission electron microscope (TEM) images were obtained using a JEM-3010 high resolution transmission electron microscope (operated at 160 kV).

Fourier transform infrared (FTIR) spectra were collected on an EQUINOX-55 FTIR spectrometer (EQUINOX Company) at a resolution of 0.2 cm⁻¹ using KBr pellets of solid samples. The pellets were formed of approximately 400 mg of KBr and approximately 3 mg of sample.

Solid state ¹³C nuclear magnetic resonance spectrum (¹³C NMR) was performed using an AVANCE III 400 MHz solid state NMR spectrometer (BRUKER Company, Switzerland) equipped with a BRUKER 4-mm CP/MAS probe.

3. Results and discussion

3.1. Influence of temperature on the optical texture of carbonized products

Fig. 1 shows the polarized micrographs of the carbonized CTPS products obtained at various temperatures for 1 h. In Fig. 1(a), few bright spots were observed, indicating little anisotropy in the CTPS-220 sample. It can be concluded from this that the mesophase formation temperature of coal tar pitch with molten salt is above 220 °C. In CTPS-250, a small number of bright anisotropic regions appeared in Fig. 1(b), meaning that a small amount of mesophase material formed at 250 °C. In CTPS-280, a large amount of small mesophase spheres are evident as can be seen in Fig. 1(c), where the diameter of the spheres is large and spherical coalescence has occurred. With the increase of temperature, CTPS-300 in Fig. 1(d) shows ultra-fine mosaic texture, while CTPS-320 in Fig. 1(e) shows the complex of fine mosaics and small domain-like textures. Eventually an elongated and domain-like texture existed in the carbonized products at 350 °C as shown in Fig. 1(f). The development of these polarized optical textures was directly related to the carbonized temperature indicates that the temperature of CTPS mesophase formation is low and the content of mesophase in carbonized product is high at 280 °C.

DTG curves of CTP and CTPS are shown in Fig. 2. The results show that the weight loss rate of the CTP and CTPS were different. The CTPS weight loss occurred in a lower temperature range than that of the CTP. Notice that there is a weight loss obvious peak at about 420 °C for CTP, while the peak for the CTPS is located at about 300 °C. This indicates that a significant polycondensation reaction

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