Journal of Materials Science & Technology 31 (2015) 857–863

Contents lists available at ScienceDirect

Journal of Materials Science & Technology

journal homepage: www.jmst.org

# Preparation and Characterization of Mesophase Pitch via Co-Carbonization of Waste Polyethylene/Petroleum Pitch

Youliang Cheng [1], Lu Yang [1], Tao Luo [2], Changqing Fang [1,*], Jian Su [1], Jian Hui [1]

[1] School of Printing and Packaging Engineering, Xi'an University of Technology, Xi'an 710048, China
[2] Petrochina Liaoyang Petrochemical Company, China National Petroleum Corporation, Liaoyang 111000, China

ARTICLE INFO

*Article history:*
Received 16 December 2014
Received in revised form
10 February 2015
Accepted 29 April 2015
Available online 14 July 2015

*Keywords:*
Polarized light microscopy
Microstructure
Property
Thermogravimetric analysis (TGA)
Formation mechanism

The low-cost petroleum pitch and waste polyethylene (WPE) were used as raw materials to prepare the mesophase pitch by co-carbonization method and the forming mechanization of mesophase pitch was also investigated. Polarized microscopy, softening point, Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) were used to characterize and analyze the properties and structure of the mesophase pitch. The results showed that the carbonization yield of the modified pitch was high when 1−2 wt% WPE was added and the property of mesophase pitch (MP1-450-4 and MP2-450-4) prepared by thermal polymerization was excellent. Moreover, when the treatment temperature was above 420 °C, the mesophase development of the modified pitch may be entire and 100% streamline texture mesophase can form. During the co-carbonization of WPE/petroleum pitch, a large number of naphthenic structures and methylene bridges may be generated, which can improve the properties of the obtained mesophase pitch.


## 1. Introduction

During the liquid phase carbonization of the pitch, thermal polymerization reaction occurred, which leads to the generation of mesophase sphere, and then bulk mesophase pitch was obtained due to the growth and coalescence of the small spheres[1–4]. Mesophase pitch is an excellent precursor for carbon materials and has been widely applied in the production of high performance carbon fiber, C/C composites, carbon foams and lithium ion battery electrodes[5–8].

The anisotropy content and rheology behavior of the mesophase pitch determine the graphitization, mechanical and spinning properties[9]. 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 properties[10,11]. As a result, the common precursor pitch is usually modified to improve its properties and then the co-carbonization method is used for the production of the mesophase pitch[12–14]. The excellent mesophase pitch was produced via the co-carbonization of the feedstocks with similar compositions (such as coal, maltene, coal tar pitch, petroleum pitch) under appropriate conditions[12,15–18]. It is worth mentioning that the addition of coal tar pitch to petroleum pitch can prevent the mesophase growth of the coke[19]. The same strategy also has been applied in the co-carbonization of coal tar pitch and/or petroleum pitch with various polymers to control the morphology, the structure and the properties of the cokes in producing the desired precursors of carbon materials[2,20–25].

## 2. Materials and Methods

### 2.1. Materials

NO.90A petroleum pitch was purchased from Xi'an Petrochemical Controlled Company and its properties are shown in Table 1. The randomly recycled waste polyethylene (WPE) was obtained from abandoned milk bags, and its properties are shown in Table 2.

### 2.2. Preparation of the mesophase pitch

The cleaned and dried WPE was melted and made into particles by using a comminutor for reserving. The preparation of modified pitch was reported in our previous work[26,27], and a typical process

* Corresponding author. Prof., Ph.D.; Tel.: +86 29 82312038; Fax: +86 29 82312512.
*E-mail address:* fcqxaut@163.com (C. Fang).

http://dx.doi.org/10.1016/j.jmst.2015.07.010

**Table 1**
Properties of petroleum pitch

| C/H | TI (wt%) | QI (wt%) | SP (°C) |
|---|---|---|---|
| 0.73 | 13.6 | 0.1% | 51 |

Note: C/H: atomic ratio, TI: toluene insoluble, QI: quinoline insoluble, SP: softening point.

**Table 2**
Properties of recycled abandoned milk bags

| Basis | Purity | Density (g/cm$^2$) | Softening point (°C) |
|---|---|---|---|
| PE | 92% | 0.93 | 125 |

was as follows: 500 g petroleum pitch was heated into fluid in an iron container and turned on the shearer at a speed of 3750 r/min. Then, the WPE was added into the petroleum pitch in 5 min (the contents of WPE were 0 wt%, 0.5 wt%, 1 wt%, 2 wt% and 5 wt%, respectively). More importantly, the modifying temperature of the petroleum must be measured to make sure that the temperature was constant. The sample was swelled for 10 min every 30 min until the set time for shearing, and then the modified pitch was obtained for reserving.

The modified pitch was put into the reactor vessel and the reaction system was heated to the set temperature at the rate of 1.5 °C min$^{-1}$ under $N_2$ flow, in which the stirring speed was 1000 r/min. After holding for a certain time, the reaction system naturally cooled to room temperature and the sample of mesophase pitch was obtained.

The names of all modified pitch and mesophase pitch samples obtained under different conditions are shown in Table 3.

### 2.3. Measurement and characterization

DMM-300C vertical metallographic microscope was used for the polarized microscopic test. The samples were placed in paper molds, injected with dental base acrylic resin powder, then methyl methacrylate was added for curing. Finally, the specimens were observed under polarized microscope after being grinded and polished.

X-ray diffraction (XRD) test was carried out by an X'Pert High Score Diffractometer (Philips Company, Netherlands) using Cu *Kα* radiation (λ = 0.1541 nm).

**Table 3**
Names of samples under different experimental conditions

| Samples | PE content (wt%) | Shearing temperature (°C) | Shearing time (h) | Heating temperature (°C) | Holding time (h) |
|---|---|---|---|---|---|
| MDP-0.5 | 0.5 | 150 | 1.5 | / | / |
| MDP-1 | 1 | 150 | 1.5 | / | / |
| MDP-2 | 2 | 150 | 1.5 | / | / |
| MDP-5 | 5 | 150 | 1.5 | / | / |
| MP-420-4 | 0 | / | / | 420 | 4 |
| MP-450-4 | 0 | / | / | 450 | 4 |
| MP0.5–450-4 | 0.5 | 150 | 1.5 | 450 | 4 |
| MP1-450-4 | 1 | 150 | 1.5 | 450 | 4 |
| MP2-450-4 | 2 | 150 | 1.5 | 450 | 4 |
| MP5-450-4 | 5 | 150 | 1.5 | 450 | 4 |
| MP5-420-4 | 5 | 150 | 1.5 | 420 | 4 |
| MP1-420-4 | 1 | 150 | 1.5 | 420 | 4 |
| MP1-400-4 | 1 | 150 | 1.5 | 400 | 4 |
| MP1-380-4 | 1 | 150 | 1.5 | 380 | 4 |

Fourier transform infrared spectroscopy (FTIR) test was carried out by 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 2 mg of sample.

The softening point (SP) of the samples was measured using a SLR-C type pitch softening point tester, and the digital display tester was made by Shuyang Expressway Instrument Ltd.

The rheological behavior of the samples MP-450-4 and MP2-450-4 was investigated using a NXS-11 Viscometer (Chengdu Analysis Instrument Factory) at a constant shear rate of 5 r/min under $N_2$ flow.

Thermogravimetric analysis (TGA) of the samples WPE, MDP-1 and MP1-450-4 was carried out using a PERKIN-ELMER Thermogravimetric Analyzer in the temperature range of 25–700 °C at a heating rate of 5 °C min$^{-1}$ under $N_2$ flow.

## 3. Results and Discussion

### 3.1. Influence of heat treatment temperature on the formation of mesophase pitch

Fig. 1 shows the polarizing micrographs of the co-carbonized products from modified pitch with 1 wt% WPE at a holding time of 4 h and various temperatures. In these micrographs, the brightest part is the anisotropy area, and the content of mesophase is determined by proportion of anisotropy area[3]. As shown in Fig. 1(a), the anisotropy area is very small and difficult to be found in sample MP1-380-4. The area of anisotropy increased in Fig. 1(b), but the mesophase content of sample MP1-400-4 was less than 30%. When the temperature was raised to 420 °C, the area of anisotropy in sample MP1-420-4 obviously increased and formed a streamline texture as shown in Fig. 1(c). When the temperature reached 450 °C, 100% bulk mesophase with domain-like texture was obtained as shown in Fig. 1(d). Consequently, in order to obtain the bulk mesophase pitch with high mesophase content, the heat treatment temperature should be above 420 °C.

### 3.2. Influence of WPE content on the optical structure of co-carbonized products from modified pitch

Fig. 2 shows the polarizing micrographs of carbonized products from modified pitch with different contents of WPE at 450 °C and holding time of 4 h. As shown in Fig. 2(a), the sample MP-450-4 was mostly bulk mesophase with mosaic texture. This is because mesophase spheres were formed before the bulk mesophase in the petroleum pitch and the viscosity of the reaction system decreased and mobility reduced with the increase of heat treatment temperature. As a result, these mesophase spheres may easily form a mosaic texture. When 0.5 wt% WPE was added, the sample MP0.5–450-4 turned into streamline bulk mesophase as shown in Fig. 2(b). Obviously, the samples MP1-450-4 and MP2-450-4 were also streamline bulk mesophases as shown in Fig. 1(d) and Fig. 2(c). Moreover, streamline texture is beneficial for the mesophase pitch spun into carbon fibers[5,25], and then the samples MP1-450-4 and MP2-450-4 may be used in the production of carbon fibers. However, the mesophase content of the sample MP5-450-4 reduced as shown in Fig. 2(d), which indicates that more WPE may block the development of mesophase and even lead to the appearance of isotropy. In this study, the streamline mesophase pitch may be obtained when 0.5–2.0 wt% WPE was added into the petroleum pitch according to the polarizing micrographs.