NEW CARBON MATERIALS
Volume 33, Issue 1, Feb 2018
Online English edition of the Chinese language journal

Available online at www.sciencedirect.com
ScienceDirect

Cite this article as: New Carbon Materials, 2018, 33(1): 71-81

RESEARCH PAPER

Preparation and characterization of high softening point and homogeneous isotropic pitches produced from distilled ethylene tar by a novel bromination method

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Abstract: Homogeneous isotropic pitches with high softening points were prepared from vacuum-distilled heavy residue ethylene tar (ET-HR) by a two-step method of bromination and subsequent dehydrobromination/polycondensation. The ET-HR was first brominated at 30 or 200 °C, and then heat-treated at 350 °C to enable the dehydrobromination/polycondensation reactions. GC/MS and LDI TOF/MS spectra indicated that the ET-HR was mainly composed of compounds containing 3- to 6-ring aromatic species with a considerable aliphatic chain content. Compared with thermal condensation alone, such a two-step method increased the softening point of the pitches from 152 to 264 °C with a yield in the range of 62 wt. %-67 wt.% and a coking value in the range of 57 wt. %-77 wt.%, depending on the bromination temperature and the bromine content. Structural characterization of the as-prepared pitches by elemental analysis, ^{1}H NMR, FT-IR and LDI-TOF/MS showed increased aromatization and polymerization of the precursor during the dehydrobromination/polycondensation. All the homogeneous isotropic pitches showed an ability to transform into an anisotropic texture after coking at 800 °C.

Key Words: Ethylene tar; Distillation; Bromination; Dehydrobromination; Properties

1 Introduction

High softening point isotropic pitches are complex mixtures of polycyclic aromatic hydrocarbon (PAH) oligomers which exhibit a high molecular weight, high coking value and high softening point of more than 200 °C. It is well-known that the high softening point isotropic pitches have been extensively used as precursors for making a variety of high-value added products and high performance carbonaceous materials in industrials such as general purpose carbon fibers (GPCF) [1], carbon foams [2], high density isotropic graphite [3], anode materials for lithium ion batteries [4], advanced C/C composites [5,6] and activated carbon materials [7].

Generally high softening point isotropic pitches can be prepared from various feed stocks, such as heavy oils, petroleum pitch or purified coal tar pitch, by methods of solvent extraction [8], air blowing[9,10], thermal treatment[11] and the polymerization of small molecules using catalysts [12,13]. Among these methods, air blowing and thermal treatment are the most efficient and economical ones. It is generally accepted that air blowing greatly increases the softening point by enabling the formation of oxy-radicals and gives cross-linked structures of the pitch [14]. However, the introduced oxygen in the pitch is unstable and would decompose during pyrolysis which will inevitably deteriorate the performance of the final carbon products. Whereas the thermal treatment, which needs to be held at high temperature for long reaction time, is likely to generate more planar and condensed molecules and thus gives rise to the formation of mesophase [15], which will leads to inhomogeneity of the pitch and badly destroys the spinning property of the isotropic pitch for the manufacture of carbon fibers. Moreover, most of the light components are distilled out during the heating treatment, which will results in a low pitch yield. Therefore, how to prepare high purity isotropic pitches with a high yield and softening point using a cheap raw material still remains to be a challenge task.

Ethylene tar (ET), a byproduct from naphtha cracking process, is produced on a large scale each year with the growing need of ethylene. This typical residual oil possesses advantage features of a high solvent solubility, high carbon/hydrogen ratio, high aromaticity and essentially free from heteroatoms and inorganic substances, which make it

Received date: 6 Jul 2017; **Revised date:** 12 Oct 2017
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DOI: 10.1016/S1872-5805(18)60327-0

suitable source for developing carbon materials [16,17]. In this paper, a new facile two-step method to produce a high softening point and homogeneous isotropic pitch from the vacuum distillated ET was developed and the obtained pitches were characterized. First, the vacuum distillated ET was modified via bromination, and then thermally treated under a relatively low temperature to induce dehydrobromination/ polycondensation reaction. The effect of bromination temperatures and the amount of the introduced bromine on the composition, physical properties and coking behaviors of the final pitches were investigated. This route should suggest a significant guidance for the effective utilization of ET and potential market can be stimulated by the developing of high-value-added carbon materials.

2 Experimental

2.1 Raw material and pretreatment

ET supplied by Sinopec Shanghai Petrochemical Co. Ltd. (PR China) was used as the starting material. The original ET was subsequently distillated at 250 °C under vacuum (0.025 mmHg) to remove the volatile fractions. The obtained solid heavy residue (ET-HR) which takes up ca. 49% of the entire ET was then used as the feed stock for the preparation of the novel high softening point isotropic pitches.

2.2 Pitch preparation

The novel high softening point pitches were prepared by a successive two-step method, the bromination of ET-HR under low temperatures and subsequent dehydrobromination/ polycondensation (DP) at 350 °C. The schematic diagram of the preparation process was shown in Fig. 1. In a typical run, about 120 g coarsely grounded ET-HR (<5 mm particle diameter) was re-melted in a 250 mL Pyrex reactor under vigorous stirring with an N_2 flow of 150 mL/min. Then the liquid bromine was added to the ET-HR under 200 °C at a dropping rate of 0.5 mL/min to form brominated products with a bromine content of 9.25 wt. % (labeled as BP1) and 13.35 wt. % (labeled as BP2). The ET-HR was also brominated at 30 °C to form a mixture with bromine content of 12.02 wt. % by using benzene as the solvent (labeled as LBP). After this, the second thermal treatment of BP1, BP2 and LBP were carried out at 350 °C for 6 h to induce the dehydrobromination/ polycondensation. The resultant pitches were denoted as DBP1, DBP2 and DLP, respectively. For comparison, the direct thermal treatment of ET-HR at 350 °C for 6 h in nitrogen atmosphere was also carried out to determine the effect of the thermal treatment itself on characteristics of pitch. This obtained pitch was denoted as TTP. All the pitches were further distillated at 330 °C for 20 min under vacuum to remove volatile components. The product yield was calculated by the following equation:

$$\text{Yield (\%)} = 100 \times \text{Mass of resultant pitch/ Mass of the used ET-HR}$$

As-prepared pitches were then carbonized at 800 °C using a horizontal tube furnace. About 5 g pitch samples were placed in a quartz crucible, which was then positioned in the constant temperature zone of the furnace. The samples were heated to 800 °C at 5 °C /min and held for 30 min under a nitrogen flow rate of 120 mL/min. The obtained cokes were noted as C-X, where X stands for the corresponding pitches.

2.3 Pitch characterization

The composition of ET-HR was determined by gas chromatography-mass spectrometry (GC-MS) on a Shimadzu GCMS-QP2010 plus instrument operating in an electron ionization (EI, 70 eV) mode. Sample injection (1 μL) was performed in split mode with a split ratio of 1:30. The oven temperature was initially held at 100 °C for 5 min, and then increased to 260 °C at a rate of 7 °C /min and held for 3 min. The ion source temperature was set at 250 °C, and the samples were scanned from 35 to 800 m/z in TIC mode. The separated components were determined by comparing their mass spectra with those recorded in the National Institute of Standards and Technology (NIST) database. Quantitative analysis of the main components was determined by peak area normalization method.

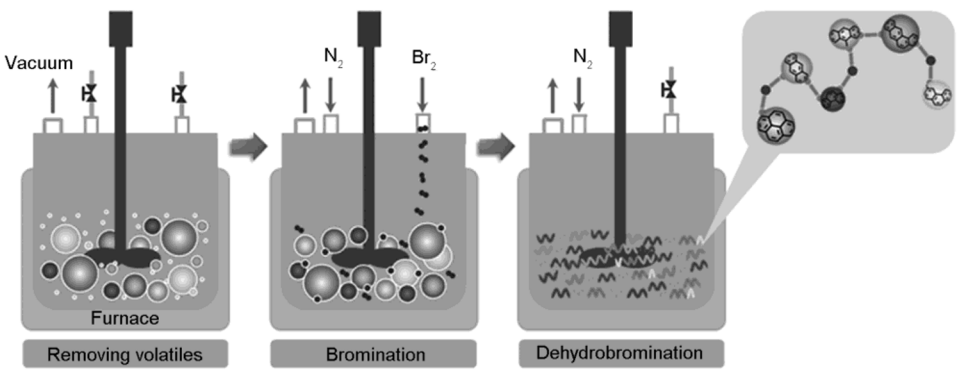

Fig. 1 Schematic diagram of the novel pitch preparation process.