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Enhanced oxidation performance of pitch fibers formed from a heterogeneous pitch blend

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ABSTRACT

The oxidation performance of heterogeneous pitch fibers formed by blending a coal tar-derived isotropic pitch (IPc) and a naphthalene-derived mesophase pitch (MPn) was studied. The role of IPc in affecting the oxidation performance of such heterogeneous fibers was illustrated. The IPc spherical domains distributed in the MPn matrix facilitate the reduction of oxidization time and the decrease of the gradient of oxygen distribution. As such, the MPn/IPc blends have been demonstrated to be a feasible approach for reducing the oxidation difficulties in producing large diameter carbon fibers. Further improvement on the oxidation efficiency and the suppression of deep stabilization in large diameter pitch fibers were observed, when the blend precursors were oxidized in pure oxygen atmosphere.

1. Introduction

As revealed by both simulation/modeling [1] and experimental observations [2], during the melt-spinning of mesophase pitch fiber, the rate at which the fibers are cooled is the main factor in controlling the degree of the molecule orientation in the pitch precursor fibers and thereafter the degree of preferred orientation of graphite layers in the resulting mesophase pitch-based carbon fibers (MPCFs). For large diameter precursor fibers, the slow cooling rate permits the mesophase molecules to reorient to a well-developed texture. Thus the large diameter precursor fibers are favored for obtaining the high degree of orientation of mesophase molecules along the fiber axis. This is critical to enhance the modulus, electrical and thermal transport properties of the resultant MPCFs [3,4].

However, there exist processing difficulties in the production of large diameter MPCFs [5]. First, the time required for optimum stabilization of large diameter pitch fiber is extremely long. Second, the resultant MPCF is prone to have a skin-core structure. To obtain large diameter MPCFs with optimized performance and reduce their manufacturing cost, it is crucial to carefully control the oxygen uptake, in terms of both quantity and distribution, during the oxidation of pitch fibers [6,7]. To this regard, modification of the mesophase pitch composition has been explored to adjust its properties as a suitable precursor for MPCFs [8]. Along the same line of thought, heterogeneous pitch precursors – a naphthalene based anisotropic sphere-containing precursor [9] and petroleum pitch precursors with different mesophase contents [10] have been synthesized and successfully used for continuous spinning of heterogeneous pitch precursors. It has been revealed that the synthetic heterogeneous pitches assure the similarity in the molecular composition between the anisotropic and isotropic portions [11]. In contrast, our own group has demonstrated using a heterogeneous pitch formed by blending two pitches with different origins – a coal tar-derived isotropic pitch (IPc) and a naphthalene-derived mesophase pitch (MPn) to mitigate the macro-crack formation and therefore to improve the tensile strength of MPCFs [12]. To further

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explore the MPn/IPc incompatible blend precursors developed by us, in this paper, we studied the oxidation performance of the pitch fibers formed by the IPc/MPn blend. The results show that the great chemical/physical difference between MPn and IPc molecules can be taken advantage in improving the oxidation efficiency in producing large diameter carbon fibers. In brief, the IPc, MPn and their incompatible blend with mass ratio of IPc/MPn = 30/70 were spun into precursor fibers with diameter of 30 and 50 μm. The precursor fibers of 30 μm in diameter formed from different precursors were oxidized in different oxidizing conditions. The formed oxidized fibers were subjected to electron probe micro-analyzer (EPMA) for determining the oxygen distribution across the fiber diameter. All the oxidized fibers were further carbonized at the same conditions for the formation of CFs, which were examined by scanning electron microscope (SEM) to observe the cross-sectional morphologies. The combined EPMA and SEM studies for 30 μm fibers are highly valuable in estimating the oxidative performance of pitch fibers that were spun from different precursors and clarifying the role of IPc in affecting the oxidation performance of pitch fibers formed from the IPc/MPn incompatible pitch blend. The acquired information was used to guide the study of the oxidation of 50 μm pitch fibers to demonstrate the feasibility of using the MPn/IPc blend approach for reducing the oxidation difficulties in producing large diameter MPCFs. For further understanding the oxidation mechanism of the IPc/MPn blends, we compared our results with the oxidation behavior of a compatible blending pitch based on the mixtures of a polyvinyl chloride (PVC) pitch and a coal tar-derived mesophase pitch [13,14]. The systematic studies on the oxidation behavior of MPn and IPc presented in this paper will shed light on the understanding the effect of composition and structure of the pitch precursors on the oxidative activity and stabilization rate – an intensively studied but still not fully understood subject [15–20].

2. Experimental

2.1. Materials

MPn and IPc were purchased from Mitsubishi Gas Chemical Co. (Japan) and Shanghai Dongdao Carbon Chemical Industry Co. Ltd. (China), respectively. The detailed chemical/physical characteristics of the parent pitches have been listed in [12]. The IPc/MPn blend precursor denoted by IPc-30 was prepared by mechanical stirring of an IPc/MPn mixture (mass ratio of 30/70) at 360 °C for 60 min in a 99.999% argon atmosphere. With IPc uniformly distributed in the mesophase matrix as spheres, IPc-30 has proved to show good spinnability and the macro-cracks along the fiber axis in the resultant MPCFs can be effectively suppressed [12].

2.2. Preparation of precursor fibers and carbon fibers

The precursor fibers based on IPc and IPc-30 were melt spun by using a spinning machine (MMCH05, Chemat, America) equipped with a single-hole spinneret ($L/D = 3$; $D = 0.3$ mm). The spinneret setup for the MPn precursor fibers was the same as in the previous study [21,22], which consists of a filter assembly with 50 layers of plain-weaved screen (2000-mesh), a pitch reservoir, and a capillary. This assembly located above the capillary has been tested in effectively disturbing the mesophase melt flow in the upper stream of the spinneret and thus preventing the macro-crack formation in the resultant MPCFs [21,22]. In spinning, the temperature was kept as 330 °C. The melt volumetric flow rate was controlled at 157 mm^3/min. Two different winding speed settings – 350 and 450 m/min were used to obtain fibers with diameter of 50 and 30 μm for subsequent studies.

The precursor fibers were oxidized in dry air or pure oxygen (200 cm^3/min) environment by heating the fiber to 230 or 280 °C at 5 °C/min and maintaining for varied duration. The carbonization was performed by heating the oxidized fibers in a 99.999% argon atmosphere to 1800 °C at 40 °C/min. The subsequent soaking time was 20 min.

2.3. Test and characterization method

Thermogravimetric analysis (TG) was performed by a thermal analyzer (Netzsch STA 409PC, Waldkaiburg, Germany) in both air and oxygen atmosphere at a heating rate of 5 °C/min from 25 up to 350 °C. The chemical composition of pitches was examined using an elemental analyzer (EA-MA1110, Carlo Erba, Italy). The powder sample used for both TG and elemental analysis was prepared by grinding the 30 μm PFs and sieving through a 400-mesh filter sieve. With the commonly used KBr pellet sample preparation method, the infrared spectra for 30 μm precursor fibers and oxidized fibers were collected with a Fourier transform infrared spectrometer (FTIR, Avatar360, Nicolet, US) to examine the oxidation induced chemical changes of the fibers. The cross-sectional morphologies of the MPCFs were examined by using SEM imaging (XL30, Philips-FEI, The Netherlands). The fibers were sputter coated with gold prior to SEM imaging. Oxygen distribution across the fiber diameter of oxidized fibers was measured with an EPMA (JXA-8100, Japan Electron Optics Laboratory, Japan). For EPMA measurement, the oxidized fibers were mounted in epoxy resin and polished and coated with a 2 nm thick gold film. Semi-quantitative analysis for oxygen was performed at 15 kV and 10 nA beam using a LDE2H-type multilayer crystal. Oxygen content was standardized on Al_2O_3, with no determination of peak shift. Count time was 20 s on peak and 10 s on background position. The electron beam at the focal position was estimated to be approximately 1 μm in diameter and the analysis interval was 2 μm.

3. Results and discussion

3.1. FTIR and TG assessment for the oxidation activity of different pitch precursors

The FTIR allows the examination of the precursor compositions and their chemical changes during the oxidation. Fig. 1 compares the results for MPn and IPc. The aromaticity index (I_{Ar}) is a measure of the fraction of aromatic component content. It can be semi-quantitatively determined by FITR according to $I_{Ar} = A_{(3150-2990)}/\left[A_{(3150-2990)} + A_{(2990-2800)}\right]$, where $A_{(3150-2990)}$ and $A_{(2990-2800)}$ are the band area due to C—H