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Thermal properties and thermal stabilization of lignosulfonate-acrylonitrile-itaconic acid terpolymer for preparation of carbon fiber

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ABSTRACT

Lignin, the most abundant aromatic biopolymer on the earth, is considered as a sustainable carbon fiber precursor. However, lignin-based carbon fibers face great challenges in the fiber spinning and thermal stabilization due to the complex structure of lignin. In this work, lignosulfonate-acrylonitrile-itaconic acid (LS-AN-IA) terpolymer with excellent spinnability was prepared as a novel precursor for carbon fibers, and the thermal properties and thermal stabilization of this precursor were studied. The introduced itaconic acid (IA) comonomer was found to play an important role in improving the thermal properties and promoting the thermal stabilization. The hindering effect of LS on the cyclization reaction of nitrile groups was overcome by the IA comonomer through changing free-radical reaction mechanism to an ionic one. The thermal stabilization of the LS-AN-IA terpolymer precursor fibers could be carried out at a lower temperature and required a shorter time, which helped to reduce the energy and time consumption. Carbon fibers with tensile strength and tensile modulus of 1.74 GPa and 210 GPa, respectively, were obtained from the LS-AN-IA terpolymer.

1. Introduction

Lignin, as the world's most abundant aromatic biomass, has prospective applications in carbon fibers, engineered plastics, fuels, chemicals and so on [1]. However, due to its complexity of the structure, lignin has not yet been utilized efficiently on a large-scale so far [2–4]. Lignin consists of three primary monomers, including p-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol [2]. The three monomers are linked by several types of bonds [5]. The relative contents of monomers and linkages of lignin vary with the resource plant species and extraction processes [6,7].

Owing to their lightweight characteristics and excellent mechanical properties, carbon fibers have been extensively applied in aviation, aerospace, and national defense [8]. Currently, carbon fibers are mainly produced from petroleum resources such as polyacrylonitrile (PAN) and pitch [4,9]. But the unsustainability and high price limit the use of petroleum-based carbon fibers into the narrow field of high-end products [10]. Lignin is considered as an ideal candidate for preparation of carbon fibers, because it is an abundant and environmentally friendly renewable resource [11,12]. In addition, lignin has a high carbon content and potentially high carbon yield after carbonization [13].

As an alternative precursor for carbon fibers, lignin has attracted increasing research attention during the last decades. Various purified lignins or blends of lignin with different polymers have been converted into precursor fibers by melt spinning [13–20]. But the mechanical properties of the carbon fibers are too low to be used as reinforcements for structural composites [9,21]. In addition, an extremely low heating rate and a long period of time for thermal stabilization must be adopted to prevent the melt-spun lignin fibers from fusion [22]. Blend of lignin with PAN has been studied as a low-cost precursor for carbon fibers by many researchers [23–27]. This precursor system could take advantages of the excellent spinnability and thermal stability of PAN. Zoltek and Weyerhaeuser together developed low-cost carbon fiber precursors from lignin/PAN blends of different proportions using a solution spinning process [28,29]. The carbon fibers produced had tensile strength and tensile modulus of 2.24 GPa and 217 GPa, respectively, which had exceeded the targets of low-cost carbon fibers for the automotive industry defined by the U.S. Department of Energy (DOE) [10]. However, with the increase of lignin content in the blend, unacceptable macro-voids were formed in the fibers; some lignin leaching occurred during the spinning process, which created production problems [29].

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In order to solve these problems, our team has prepared a lignosulfonate-acrylonitrile (LS-AN) copolymer [30,31]. The problem of spinnability was well resolved by using esterified LS as a macromer which was then grafted to AN segmer [31]. Carbon fibers with dense structure and free of any macro-voids were successfully obtained from the LS-AN copolymer. However, in the previous studies, the mechanical properties of the LS-AN copolymer-based carbon fibers were still not satisfied for practical applications. In addition, we found that the thermal properties of the LS-AN copolymer should be improved. The cyclization reaction of nitrile groups was constrained to some extent in the LS-AN copolymer, which did not meet the requirements of thermal stabilization [30].

In this work, we have prepared a novel lignosulfonate-acrylonitrile-itaconic acid (LS-AN-IA) terpolymer. IA was incorporated as another comonomer for improving the thermal properties of the LS-AN copolymer. The thermal properties of the LS-AN-IA terpolymer were assessed by simultaneous differential scanning calorimetry and thermogravimetry (DSC/TG) in nitrogen and air atmospheres. Thermal stabilization of the LS-AN-IA terpolymer precursor fibers was studied by Fourier transform infrared (FTIR) and densimetry. Carbon fibers with desired mechanical properties were finally obtained from the LS-AN-IA terpolymer precursor fibers.

2. Experimental

2.1. Materials

Calcium lignosulfonate (LS, 96%), acryloyl chloride (AC, AR), and itaconic acid (IA, 99%) were used as received (Aladdin Industrial Corporation, Shanghai, China). Diethyl ether, ethanol, dimethyl sulfoxide (DMSO), lithium bromide (LiBr) and N,N-dimethylformamide (DMF) were purchased from Sinapharm Chemical Reagent Co. Ltd. and used without further purification. α,α-Azoisobutyronitrile (AIBN) was purchased from No.4 Reagent & H.v Chemical Co. Ltd. (Shanghai, China) and purified by crystallization in ethanol. Acrylonitrile (AN) was obtained from Sinopec Shanghai Petrochemical Co. Ltd. and treated by vacuum distillation before use for removing the inhibitor.

2.2. Precursor polymer synthesis

LS-AN-IA terpolymer was synthesized by a free radical polymerization technique using AIBN as initiator. First, LS was esterified by reacting with AC. 120 g LS was dissolved in 300 g of DMSO in a three-necked round-bottomed flask at 60 °C under stirring. Then, the solution was cooled in an ice bath, and 30 g AC was added into the solution dropwisely for 1 h. The mixture was to react at 30 °C for 22 h. The product of the reaction was precipitated out in diethyl ether. The precipitate was centrifuged and washed several times with ethanol. Esterified LS was obtained after drying under vacuum at 60 °C. LS-AN-IA terpolymer was prepared by a free radical copolymerization technique in DMSO solvent. The total concentration of monomers in feed was 30 wt%. The mass ratio of esterified LS: AN: IA: AIBN is 20:80:2:1. The polymerization reaction was taken under nitrogen in a three-necked round-bottomed flask at 60 °C for 22 h with DMSO as solvent. LS-AN (20:80 w/w in feed) copolymer was synthesized under the same condition. AN-IA (100:2 w/w in feed) copolymer and PAN homopolymer were initiated by 0.7% of AIBN, and the total concentration of monomer(s) in solution was controlled to 22%. The polymerization dopes were precipitated in deionized water and the polymers were obtained by washing several times, and drying under vacuum at 60 °C.

The reaction equations for the synthesis of the above-mentioned polymers are shown in Scheme 1. The recipes and yield of all the polymers have been listed in Table 1.

2.3. Precursor fiber spinning

Polymers were dissolved in DMSO to produce homogeneous spinning solutions. For LS-AN-IA terpolymer and LS-AN copolymer, the concentration of spinning solution was controlled to 24%; while for PAN homopolymer and AN-IA copolymer, the concentration of spinning solution was controlled to 22%. All the spinning solutions were maintained at 60 °C before spinning. A wet spinning technique was used to prepare precursor fibers from the polymers. A schematic of the wet spinning process was shown in the Scheme S1 of Supporting Information.

Precursor fibers of LS-AN-IA terpolymer, LS-AN copolymer, and AN-IA copolymer were spun by a spinneret with 500 holes of 60 μm diameter. PAN fibers were spun by a spinneret with 50 holes of 100 μm diameter. Under nitrogen pressure of about 0.5 MPa, all the spinning solutions were extruded into a DMSO/H_2O (60:40 w/w, 60 °C) coagulation bath. The coagulated fibers were washed and drawn synchronously in three water baths at 70, 80 and 90 °C. The total draw ratio was 3. The drawn fibers were then coated with oil agent and dried on hot rollers of 100–130 °C. The fibers of LS-AN-IA terpolymer, LS-AN copolymer, and AN-IA copolymer were further drawn with a ratio of 2 in high-pressure steam. The total draw ratio of them was 6. Due to the poor spinnability, PAN fibers were only bear a total draw ratio of 3. All the precursor fibers were finally collected by a winding machine (kamitsu Co., Ltd.).

2.4. Stabilization and carbonization

Thermal stabilization of the precursor fibers was carried out in air atmosphere using an electric heat oven (NC-881-2, China). The precursor fibers were fixed on a self-made device and put into the oven which was already heated to 200 °C. A stepwise heating procedure from 200 °C to 270 °C was used. Each step increased by 10 °C and held for 20min. Thermo-stabilized fibers after treated at 230 °C, 240 °C, 250 °C, 260 °C, and 270 °C were collected for analysis.

Carbon fibers of LS-AN-IA terpolymer, LS-AN copolymer, and AN-IA copolymer were prepared by carbonized the thermo-stabilized fibers in a high temperature furnace (GSL-1700X) at 1400 °C for 10 min under nitrogen atmosphere. The heating rate during carbonization was 5 °C/min. The thermo-stabilized fibers of PAN homopolymer were too fragile and failed to carry out carbonization.

2.5. Characterization

2.5.1. Gel permeation chromatography (GPC)

The precursor polymers were characterized by TOSOH HLC-8320 GPC with a refractive index detector. A LiBr/DMF solution (0.01 mol L^{-1}) was used as the mobile phase. Solutions of the samples (1 mg mL^{-1}) were prepared by dissolving at 80 °C for 2 h and then filtered using 0.45 μm PTFE syringe filter prior to analysis.

2.5.2. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra of the precursor polymers and thermo-stabilized fibers were recorded on a ThermoNicolet Nexus 470 FTIR spectrometer in the range 4000-400 cm^{-1}. A KBr pellet technique was used and 32 scans were collected at a resolution of 4 cm^{-1}. The degree of cyclization reaction of the thermo-stabilized fibers was determined using the absorbance ratio (R_A) of the $C=N$ band and the $C\equiv N$ band.

2.5.3. Differential scanning calorimetry and thermogravimetry (DSC/TG)

Thermal properties of the precursor polymers were studied by a NETZSCH STA 449 thermal analyzer. About 5 mg of samples was placed in an aluminium oxide pan, and heated from room temperature up to 500 °C with a heating rate of 10 °C/min under air and nitrogen atmospheres. The DSC parameters of the exotherms, including initiation temperature (T_i), final temperature (T_f), their difference ($\Delta T = T_f - T_i$),