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RESEARCH PAPER

Preparation of carbon fibers from low-molecular-weight compounds obtained from low-rank coal and biomass by solvent extraction

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Abstract: The practical use of carbon fibers is limited by their high price mainly due to the high price of precursors. We have examined a high temperature solvent extraction method to prepare carbon fiber precursors from low-rank coals and biomass, using a lignite from Australia and rice straw. 1-methylnaphthalene at 350 °C was used for the extraction and some of the extract in the solvent was precipated at room temperature. The soluble fractions at room temperature were obtained for use as the precursors by solvent evaporation. They were spun into fibers by a centrifuge spinning system and were then were extracted by cyclohexane to increase the softening point, stabilized by a temperature-programmed thermal treatment in air from 80 °C to 330 °C and carbonized at 1 000 °C for 1 h in N_2 to obtain carbon fibers. The carbon and oxygen contents of the final carbon fibers were 92 and 6.0 wt%, respectively, similar to those of commercial carbon fibers. The fiber diameter was around 4-6 μm. The soluble fractions were found to be promising low-cost precursors for carbon fibers.

Key Words: Carbon fiber; Degradative solvent extraction; Low-rank coal; Biomass

1 Introduction

Carbon fiber, as a high value-added carbon material, can be used widely for various purposes, such as a raw material for aircraft manufacture, construction, automobile, sporting goods. However, the practical utilization of carbon fiber is limited by its high price which is caused by the high cost of its feedstocks as well as manufacturing cost. Conventional precursors for carbon fiber preparation are polyacrylonitrile (PAN) and pitch. In 2012, more than 96% of global carbon fiber was made from PAN [1], which is a rather expensive precursor for carbon fiber preparation. Coal tar pitch and petroleum asphalt pitch were also widely studied to prepare carbon fiber[2-4]. However, the pretreatment, preparation and purifying procedure for these precusors is complex and the produced carbon fiber generally have poor property compared with the PAN-based carbon fiber [5]. Biomass, as a renewable material, is expected to be a promissing raw material for carbon fiber preparation. However, the real precursor is just lignin, which accounts for less than 30% of the total biomass and has to be separated from raw biomass by some methods, such as steam explosion[6, 7], organic solvent treatment or chemical method [8-12]. However, the methods used were complex and not environment-friendly. Additionally, carbon fiber preparation process generally involves spinning, stabilization and carbonization. The precursor (except PAN) is spun at the temperature over its melting point to obtain spun fiber/precursor fiber, which is then stabilized generally at about 200 – 400 °C in air by oxidization to increase their softening points [13-15]. Therefore, the melting point must be low enough for the spinning and high enough for the stabilization to be completed in short time.

We have proposed a degradative solvent extraction method to separate various types of low-rank coals and biomasses into three solid fractions under mild conditions [16-18]. The extraction was performed by using a nonpolar solvent under the temperature lower than 350 °C. The solid fractions consisted of residue (termed as residue), high molecular wieght fraction which is extracted at the extraction tempetrature but precipitates at room temperature (termed as deposit), and low molecular weight fraction which is extracted at the extraction temperature and soluble in the solvent even at room temperature (termed as soluble). The utilization of the three fractions were studied for various purposes in our previous works[19-21]. The soluble was obtained with the yield of around 23-61%, which has a carbon content of 80-85% and

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an ash content of lower than 1.0%, and whose softening and melting points are at around 100-300 °C, similar to pitch. In this paper, a preliminary study was undertaken to examine the possibility of using the soluble as a low-cost precursor for carbon fiber preparation.

2 Experimental

2.1 Samples

Loy Yang coal (LY, lignite from Australia) and a rice straw (RS, from Thailand) were used in this work. Their properties are shown in Table 1.

2.2 Degradative solvent extraction

The degradative solvent extraction was performed at 350 °C in a 350 mL of batch reactor (autoclave). The schematic diagram of the apparatus is shown in Fig. 1. The procedure has been described in detail in our previous papers [20, 22]. A stainless filter was equipped at the bottom of the autoclave. The autoclave was charged with around 20 g of as-received raw material and 300 mL of 1-methylnaphthalene, purged by N_2, heated at a rate of 5 K/ min up to 350 °C, and kept at this temperature for 60 min. The extract along with the solvent was separated from the residue at the extraction temperature by opening the valve placed below the filter, which was connected to the autoclave and a stainless steel reservoir. The extract with the solvent was collected in the reservoir. The deposit precipitated as solid at room temperature was removed from the solvent by filtration. The soluble dissolved in the solvent at room temperature was recovered as solid by distilling the solvent out. The soluble thus prepared was used proposed as the precursor for carbon fiber prerparation.

2.3 Carbon fiber preparation

The soluble was spun to prapare "spun fibers" by a centrifuge spinning system as shown in Fig. 2. The spinning system consisted of a sample pot and a surrounding stainless mesh. The soluble in the sample pot was heated to around 200 °C and the spinning system rotated at around 3500 r/min to prepare spun fibers through the mesh. The spun fibers were then extracted by cyclohexane at room temperature for 24 h to remove the light molecular weight fraction to increase their softening point. The fibers thus obtained was termed "extracted fibers". The stabilization of the extracted fibers was performed by a temperature-programed thermal treatment in a thermobalance. About 20 mg of the extracted fibers placed in the sample basket of the thermobalance was heated in air stream with a flow rate of 50 mL/min. After many attempts the optimum heating profiles for the two precursors shown in Fig. 3 were obtained for the stabilization of the extracted fibers. The extracted fibers were heated up from 80 to 330 °C in around 9 h with several isothermal stages, and kept at 330 °C for 2 hours. The fibers obtained after the stabilization were termed as "stabilized fibers". At the end of the stabilization the air stream was switched to a N_2 stream and the temperature was increased at a heating rate of 10 K/min up to 1 000 °C, and kept for 1 h to carry out carbonization to obtain "carbon fibers". The weight loss during the stabilization and carbonization was recorded by the thermobalance for a detailed investigation of the both processes.

2.4 Product analyses

The raw materials, solubles and fibers were characterized by various analyses. The proximate analysis was performed by a thermogravimetric analyzer (Shimadzu, TGA50). The elemental analysis was performed by a CHN corder (Yanaco, CHN MT-6M). The softening/melting behavior was examined using a thermomechanical analyzer (Shimadzu, TMA50). The TMA estimates the relative displacement of the sample in a platinum pan (6 mm I.D. and 3 mm high) under 10 g of load in nitrogen atmosphere during heating. The appearance of the fiber surface was observed by SEM (Keyence VE-7800 SEM). The chemical structure of the solubles and fibers was investigated by FTIR using the pellet method. The FTIR spectra were obtained at 64 scans from 4000 to 600 cm^{-1} at 4 cm^{-1} interval.

3 Results and discussion

3.1 Yield and properties of the solubles

The carbon-based yields and analyses of the solubles prepared from the RS and LY are shown in Table 1. As high as 56.2 and 27.4 % of carbon were converted to solubles for RS and LY respectively. The soluble yield of RS was much higher than that of LY.

Table 1 Properties of raw materials and solubles.

Sample	Ultimate Analysis (%, d.a.f.)				Proximate Analysis (%, d.b.)			Yield[b]
	C	H	N	O [a]	VM	FC	Ash	(%)
RS	49.8	7.0	1.0	42.2	72.5	12.5	15.0	-
LY	66.7	4.7	0.9	27.7	51.5	47.0	1.5	-
RS-Soluble	80.1	6.4	1.4	12.1	74.8	24.4	0.8	56.2
LY- Soluble	81.8	7.5	0.5	10.2	83.4	16.3	0.3	27.4

Note: [a]: by difference; [b]: carbon basis.