

Preparation of Carbon Fiber from Low-Molecular-Weight Compounds Obtained from Biomass by Solvent Extraction

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Abstract: A possibility of carbon fiber production by using a novel precursor, a low-molecular-weight compound obtained from a solvent treatment process developed by the authors' research group, has been examined. This extract, called Soluble, was derived from an extraction of rice straw using 1-methylnaphthalene (1-MN). The Soluble precursors were heated in nitrogen atmosphere at 280-320°C to increase the softening point. Then, they were spun into fiber using a mono-hole spinning machine, and then they were stabilized in air at 300°C and were carbonized at 900°C in nitrogen atmosphere. SEM images of carbon fibers showed that the diameter of the fibers were around 10-15 µm were rather uniform. It was found that at pretreatment of 280°C and 60 min the fiber was non-hollow, whereas the pretreatment at 320°C and 30 min was hollow. These preliminary results showed a good potential for producing carbon fiber from Soluble.

Keywords: Carbon fiber, Biomass, Degradative solvent extraction, Soluble.

1. Introduction

Carbon fiber is an important engineering material with high stiffness, great tensile strength, low thermal expansion, and lightweight [1]. 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 production are polyacrylonitrile (PAN) and pitch. In 2012, more than 96% of global carbon fiber was made from PAN, which is a rather expensive precursor for carbon fiber production [2]. Coal tar pitch and petroleum pitch were also widely studied to prepare carbon fiber [3]. However, the pretreatment, preparation, and purifying procedure for these precursors are complex and the produced carbon fiber generally has poor property compared with the PAN-based carbon fiber. Biomass, as a renewable resource, is expected to be a promising raw material for carbon fiber preparation. Many studies have conducted to prepare carbon fiber from biomass derived lignin [4-6]. However, lignin, which accounts for less than 30% of the total biomass, has to be separated from raw biomass by some means such as organosolv technique or chemical method [7-8]. These methods used were rather complex and not environmental-friendly. So, the development of simple method that can use whole biomass to produce a precursor for carbon fiber is highly desired.

The authors have recently proposed a degradative solvent extraction method to separate low rank coals and biomasses into three solid fractions under mild condition [9-11]. The method treats biomass in a non-hydrogen donor at around 350°C, under pressure, using a batch autoclave to dewater without phase change, to remove oxygen functional groups, and to produce low-molecular-weight compounds. The core concept underlying this method involves exposing the entire sample to thermal reactions in a non-polar solvent at around 350°C. The upgraded product was fractionated into three solid fractions: Soluble, Deposit, and Residue. The carbon based yield of Soluble reached as high as 70% for some biomass. Soluble were free from water and mineral matters, and their physical and chemical properties were almost

independent of raw materials. Elemental compositions of Solubles, for example, were C = 81.8 – 84.8 wt%, H = 7.5 – 8.1 wt%, and O = 6.5 – 10.2 wt% [10]. The Solubles were composed of low-molecular-weight compounds having a molecular peak at ca. 300. complete melting of the Soluble occurred below 100°C, and 60 – 70 % of the Solubles were devolatilized below 400°C. These properties are therefore very attractive for the Soluble to be used as a precursor for making a carbon fiber. In this study, the conventional examination of the carbon fiber production from Soluble precursor without using any chemicals was conducted. The properties of the obtained carbon fiber were investigated.

2. Experimental

2.1. Raw material

Rice straw was used as a raw material in this work. The properties of rice straw are shown in Table 1.

2.2 Degradative solvent extraction

The extraction method treats biomass in a non-hydrogen donor at around 350°C under pressure using a batch autoclave to dewater without phase changes, to remove oxygen functional groups, and to produce low-molecular-weight compounds. The schematic diagram of the apparatus and the procedure has been described in detail in our previous papers [10-12]. Rice straw (20 g) on dry basis (d.b.) and 1-methylnaphthalene (400 mL) were conducted into the autoclave reactor. After adequately, the He was purging into the reactor. The reactor was heated at the rated of 5°C/min from ambient temperature up to 350°C and held for 60 min. Then, the extraction products along with the solvent through the stainless steel filter to the reservoir. The extract product was functioned into three solid fractions: Soluble (it dissolved in the solvent even at room temperature and can be recovered as a solid by removing the solvent by rotary vacuum evaporator at 150°C), Deposit, and Residue. The Soluble thus prepared was used as a precursor for carbon fiber production in this work. The properties of Soluble were shown in Table 1.

Table 1. Yield, ultimate analyses, and proximate analyses of rice straw and Soluble.

Sample	Ultimate analyses (wt%, d.a.f.)				Proximate analyses (wt%, d.b.)			Yield (wt%, d.a.f.)
	C	H	N	O (diff.)	VM	FC	Ash	
Rice straw	47.0	6.5	0.6	45.9	72.2	12.0	15.8	-
Soluble	80.3	6.8	1.7	11.2	66.4	33.6	0.0	31.0

2.3. Carbon fiber preparation

The conventional process for carbon fiber production used in this study was shown in Figure 1. Due to the relatively low softening point of Soluble, a pretreatment of Soluble prior to be introducing in the melt spinning system was conducted. Soluble was heated in nitrogen atmosphere at two pretreatment conditions: 280°C, 60 min and 320°C, 30 min. Then, the pretreated Soluble was spun by using a mono-hole continuous spinning machine shown in Figure 2. The Soluble was heated at 270°C and extruded through the nozzle to form a fiber at the winding speed of 180 m/min. The spun fiber was stabilized in air atmosphere by heating to 300°C at the rate of 0.5°C/min and held for 60 min at 300°C. The fibers obtained after the stabilization were termed “stabilized fibers”. Finally, the stabilized fibers were heated to 900°C at the rate of 10°C/min and held for 60 min at 900°C to prepare carbon fibers.

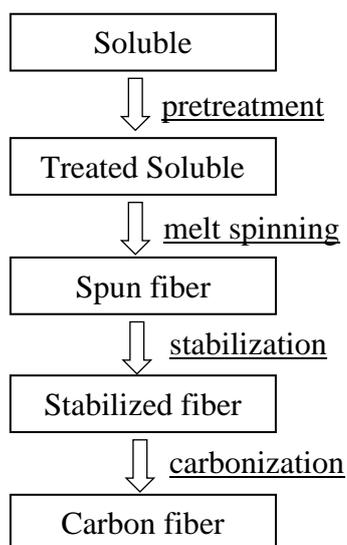


Figure 1 Conventional process for preparing of carbon fiber.



Figure 2 Mono-hole continuous spinning machine.

2.4 Analyses of Soluble and carbon fibers

Soluble, stabilized fibers, and carbon fibers were characterized by various analyses. The elemental analysis was performed by a CHN coder (J-Science, JM10 CHN). The softening/melting behavior was performed by using a thermomechanical analyzer (Shimadzu, TMA 60). 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 weight change behavior during the carbonization was examined by using a thermogravimetric analyzer (Shimadzu, TGA 50). The appearance of the fiber surface was observed by SEM (JEOL, JCM 6000). The nitrogen adsorption isotherms of the carbon fibers were measured at 77 K by the automated adsorption apparatus (BEL, Belsorp mini II) to estimate BET surface area of the carbon fiber.

3. Results and Discussion

3.1 Yield and properties of Soluble

Table 1 lists the yield, elemental analyses, proximate analyses, and atomic ratios of rice straw and Soluble. The carbon content of Soluble was as high as 80.3 wt%, while the oxygen content of Soluble was only 11.2 wt%. Soluble was free from ash and has high volatile matter. To examine the efficiency of the degradative solvent extraction, the carbon-based yield was calculated from the yield and elemental analyses of Soluble. It was found that as high as 53% of carbon in rice straw was converted to Soluble. More than 90% of oxygen in rice straw was removed by the degradative solvent extraction. These results showed that the degradative solvent extraction was very effective to upgrade biomass. Next, we will examine the thermal behaviors of Soluble. The TMA curves of Soluble compare with the oil pitch were shown in Figure 3. The TMA curve of Soluble shown that Soluble had very low softening point and it started to melt at temperature below 70°C and melt completely at 150°C. These results indicated that Soluble was composed of low-molecular-weight compounds.

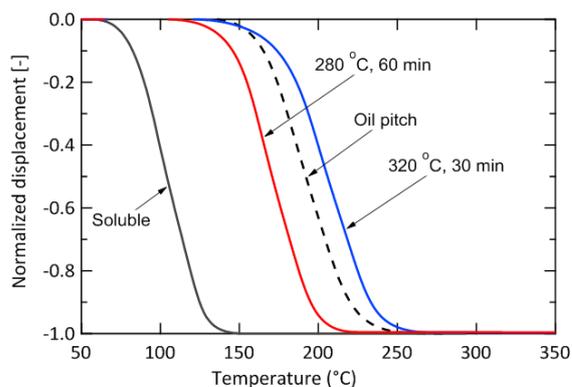


Figure 3. TMA profiles of Soluble and pretreated Soluble compare with oil pitch.

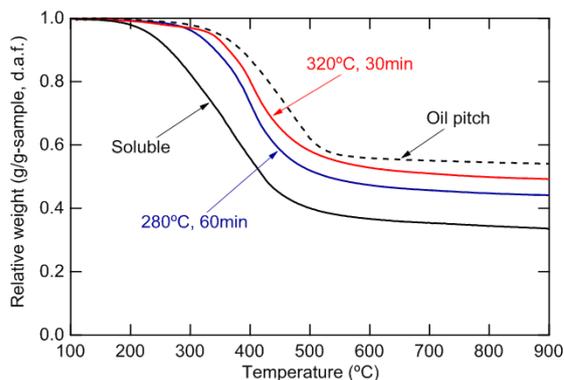


Figure 4. TGA profiles of Soluble and pretreated Soluble compare with oil pitch.

Figure 4 showed the TGA profile during the heating of Soluble in nitrogen atmosphere up to 900°C. The weight of Soluble started to decrease at around 200°C and decreased sharply at 250 – 450°C, and gradually decreased at temperature above 500°C. More than 70% of volatile matter in Soluble was devolatilized below 400°C. These results suggested that Soluble having such unique properties was expected to be utilized as raw materials of carbon materials.

3.2 Analyses of pretreated Soluble

In the previous session we found that Soluble had very low softening point and Soluble was composed of low-molecular-weight compounds. To prepare a carbon fiber by melt spinning method, it is necessary to increase the softening point of Soluble by removing low-molecular-weight compounds. So, Soluble was pretreated by thermal treatment in nitrogen atmosphere at two conditions: 280°C and held at 280°C for 60 min, and 320°C and held at 320°C for 30 min. The TMA curves of pretreated Solubles were shown in Figure 3. It was found that the TMA curves of the pretreated Soluble shifted to higher temperature with the increase in pretreatment temperature. For the pretreated Soluble at 280°C, 60 min, it started to melt at around 130°C and melted completely at 210°C. For the pretreated Soluble at 320°C, 30 min, it started to melt at around 150°C and melted completely at 250°C. These results indicated that the heat treatment of Soluble can raise its softening point. Generally, the softening point suitable for melt-spinning should be around 200-250°C. The TGA curves of the pretreated Solubles were shown in Figure 4. The TGA curves of pretreated Solubles shifted to higher temperature with the increase in pretreatment temperature. For the pretreated Soluble at 280°C, 60 min, its weight started to decrease at temperature higher than 220°C and decreased gradually at temperature higher than 500°C. The char yield at 900°C for the pretreated Soluble at 280°C, 60 min was 44 wt%. For the pretreated Soluble at 320°C, 30 min, its weight started to decrease at temperature higher than 250°C and decreased gradually at temperature higher than 500°C. The char yield at 900°C for the pretreated Soluble at 320°C, 30 min was 49 wt%. These results indicated that the thermal pretreatment can alter the thermal behaviors of Soluble. Or in other word, we can control the thermal behaviors of Soluble by changing the pretreatment temperature. Next, we will examine the carbon fiber production by using the pretreated Soluble.

3.3 Yield and analyses of stabilized fibers and carbon fibers.

The yield is one of the important factors to be considered for the carbon fiber production. The yields of pretreated Soluble, stabilized fiber, and carbon fiber based on the Soluble are shown in Table 2. It was found that around 20 % of light fraction was removed during the thermal pretreatment at 280°C, 60 min, and around 25% of light fraction was removed during the thermal pretreatment at 320°C, 30 min. The carbon content of the pretreated Soluble increased from 80.3 wt% to 82.0 – 82.6 wt%, whereas the oxygen content of the pretreated Soluble decreased from 11.2 wt% to 8.6 – 9.5 wt% after the pretreatment. The pretreated Soluble were successfully spun to form fibers using a mono-hole continuous spinning machine. Then, the spun fibers were stabilized

at 300°C in air atmosphere. The yields of stabilized fibers were 65.4 wt% and 63.9 wt% for the pretreated Soluble at 280°C, 60 min and at 320°C, 30 min, respectively. The carbon content of the stabilized fiber decreased to 61.3 wt% and 63.4 wt% for the pretreated Soluble at 280°C, 60 min and at 320°C, 30 min, respectively. On the other hand, the oxygen content of the stabilized fiber significantly increased to 34.3 wt% and 32.1 wt% for the pretreated Soluble at 280°C, 60 min and at 320°C, 30 min, respectively. These results indicated that the oxidation reaction indeed occurred during the stabilization at 300°C as expected. Next, the stabilized fibers were carbonized at 900°C in nitrogen atmosphere to produce carbon fibers. It was surprised that the yields of the carbon fibers were quite large: 31.6 wt% and 32.7 wt% for the pretreated Soluble at 280°C, 60 min and at 320°C, 30 min, respectively. The carbon content of the carbon fibers increased to 84.6 – 84.8 wt%, whereas the oxygen content decreased to 11.0 – 11.3 wt%. These results showed the potential of Soluble to be a promising precursor for carbon fiber production.

3.4 SEM images and adsorption isotherms of carbon fibers.

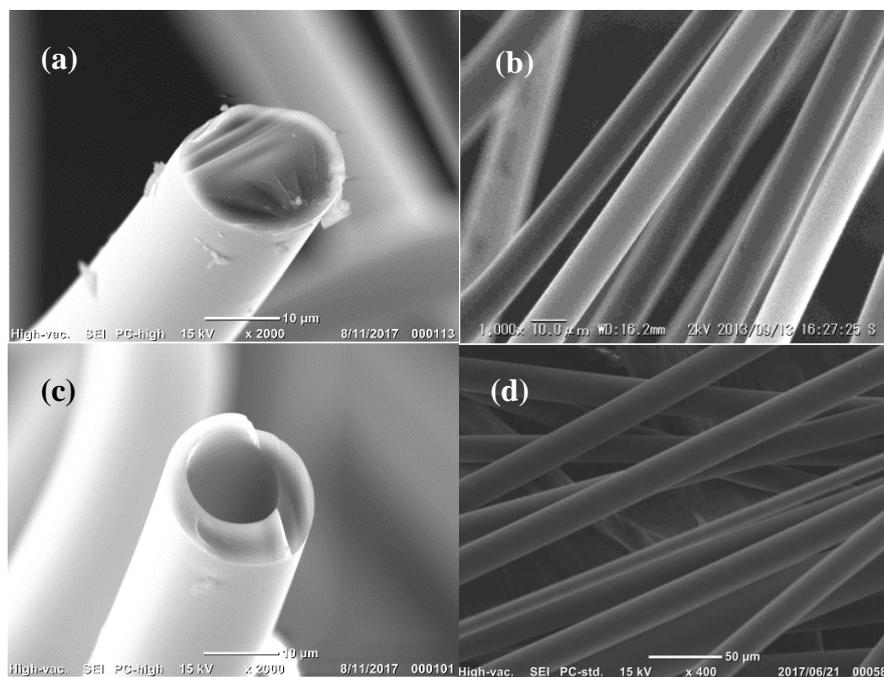
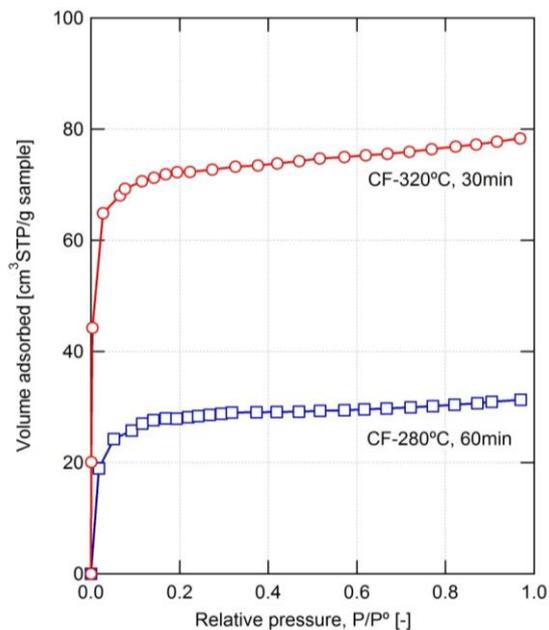
Figure 5 shows the SEM images of carbon fibers prepared from Soluble pretreated at 280°C, 60 min (a, b), and pretreated at 320°C, 30 min (c, d). It is shown the diameters of the carbon fibers are about 10 -15 μm for the carbon fibers prepared from both the Soluble pretreated at 280°C, 60 min and at 320°C, 30 min. A relatively smooth surface and a cross-section of the fiber are also observed. It was found that the carbon fibers prepared from the Soluble pretreated at 320°C, 30 min was hollow, whereas the carbon fibers prepared from the Soluble pretreated at 280°C, 60 min was non-hollow. These results suggested that we could control the hollow of the carbon fibers by changing the pretreatment temperature of the Soluble. Although it was not fully understood why the carbon fibers prepared from the Soluble pretreated at 320°C, 30 min had hollow, it was suggested that this result was brought about by the peculiarity of the Soluble. Figure 6 shows the nitrogen adsorption isotherms of carbon fibers prepared from pretreated Soluble at 280°C, 60 min, and at 320°C, 30 min. The nitrogen adsorption isotherms of the carbon fibers are type I of the IUPAC standard adsorption isotherms, which is a typical microporous carbon. The volume of nitrogen adsorbed for the carbon fibers prepared from pretreated Soluble at 320°C, 30 min was higher than that of the carbon fibers prepared from pretreated Soluble at 280°C, 60 min. The BET surface area of the carbon fibers prepared from pretreated Soluble at 320°C, 30 min was 216.6 m²/g, whereas the BET surface area of the carbon fibers prepared from pretreated Soluble at 280°C, 60 min was 90.3 m²/g. The higher BET surface area of the carbon fibers prepared from pretreated Soluble at 320°C, 30 min resulted from the fact that the carbon fibers were hollow. Moreover, these results showed that the carbon fibers prepared by the Soluble was hollow and had high surface area, and was expected to be applied in many applications such as production of activated carbon fibers. Table 3 shows the carbon content, oxygen content and BET surface area of carbon fibers produced from commercial carbon fibers. It was found that the properties of carbon fiber produced from Soluble were comparable to the commercial carbon fibers.

Table 2. Yield and ultimate analyses of pretreated Soluble, stabilized fiber, and carbon fibers.

Conditions	Ultimate analyses (% d.a.f.)				Yield (wt%)
	C	H	N	O (diff.)	
280°C, 60min					
Pretreated Soluble	82.6	6.7	2.1	8.6	80.7
Stabilized	61.3	2.3	2.1	34.3	65.4
Carbonized	84.6	1.2	2.1	12.1	31.6
320°C, 30min					
Pretreated Soluble	82.0	6.4	2.1	9.5	74.8
Stabilized	63.4	2.4	2.1	32.1	63.9
Carbonized	84.8	2.5	1.7	11.0	32.7

Table 3 properties of carbon fiber from different precursors.

Precursors	Carbon content (wt%)	Oxygen content (wt%)	Surface area (m ² /g)	Ref.
Phenolic resin	> 86.0	< 12.0	~640	[14]
Pitch	90.0-99.0	< 7.0	0.5-0.6	[15]
PAN	95.0-99.0	< 5.0	1.0-32.0	[16]

**Figure 5** SEM images of carbon fibers prepared from Soluble pretreated at 280 °C, 60 min (a, b), and pretreated at 320 °C, 30 min (c, d).**Figure 6.** Adsorption isotherms of carbon fibers prepared from pretreated Soluble at 280°C, 60 min, and 320°C, 30 min.

4. Conclusion

A possibility of carbon fiber production by using a novel precursor, a low-molecular-weight compound obtained from a solvent treatment process developed by the authors' research group, has been examined. This extract, called Soluble, was derived from an extraction of rice straw using 1-methylnaphthalene (1-MN). The Soluble precursors were heated in nitrogen atmosphere

at 280 – 320°C to increase the softening point. Then, they were spun into fiber using a mono-hole spinning machine, and then they were stabilized in air at 300°C and were carbonized at 900°C in nitrogen atmosphere. SEM images of carbon fibers showed that the diameter of the fibers were around 10 – 15 μm were rather uniform. It was found that at pretreatment of 280°C and 60 min the fiber was non-hollow, whereas the pretreatment at 320°C and 30 min was hollow. The BET surface area of the carbon fibers prepared from pretreated Soluble at 320°C, 30 min was 216.6 m²/g, whereas the BET surface area of the carbon fibers prepared from pretreated Soluble at 280°C, 60 min was 90.3 m²/g. The higher BET surface area of the carbon fibers prepared from pretreated Soluble at 320°C, 30 min resulted from the fact that the carbon fibers were hollow. These preliminary results showed a good potential for producing carbon fiber from Soluble.

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