No.4 穏和な溶剤処理により改質した低品位炭、バイオマスからの炭素繊維製造の試み

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Carbon fiber preparation by a new precursor obtained from low-rank coal or biomass extraction

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SYNOPSIS: In recent decades carbon fibers have been used widely from various purposes. However, the practical utilization of carbon fiber is limited by its high price which comes from the high cost of its feedstock as well as manufacturing cost. We have proposed a degradative solvent extraction method to separate various low-rank coals and biomasses to several fractions under mild conditions. The low-molecular-weight fractions, obtained in around 30 % yield, can soften and melt completely at around 100 ^{o}C. In this study, the low-molecular-weight fractions were proposed to be used as low-cost precursors for the carbon fiber. Preliminary experiments showed that the fractions can be easily spun to prepare spun fibers. The spun fibers were then extracted by cyclohexane to remove light compounds and stabilized by thermal treatment from 50 ^{o}C to 330 ^{o}C in air in 10 hours. The carbonization was performed at 1000 ^{o}C for 1 hour in N_2. The diameter of the carbon fiber obtained was around 5 μm. Thus, the low-molecular-weight fractions obtained by low-rank coal or biomass extraction can be promising precursors of low cost carbon fiber.

1. Introduction

In recent decades carbon fibers have been used widely from various purposes. However, the practical utilization of carbon fiber is limited by its high price which comes from the high cost of its feedstock as well as manufacturing cost. We have proposed a degradative solvent extraction method to separate various types of low-rank coals and biomasses into several fractions under mild conditions [1, 2]. The low-molecular-weight fractions, obtained in around 30 % yield, can soften and melt completely at around 100 ^{o}C. In this study, the low-molecular-weight fractions were proposed to be used as low-cost precursors for carbon fiber preparation.

2. Experimental

2.1 Degradative Solvent Extraction

Loy Yang coal (LY, lignite from Australia) and rice straw (RS, from Thailand) were upgraded and separated into three solid fractions by a batch reactor using 1-methylnaphthalene (1-MN) as solvent at 350 ℃. Three solid fractions obtained were residue which was not extracted by 1-MN, deposit which was extracted at extraction temperature but precipitated from 1-MN at room temperature, and soluble which was dissolved in 1-MN even at room temperature (termed Soluble). The solid soluble was obtained by removing solvent. The procedure of the extraction has been described in detail in our previous paper [1, 2]. The Soluble was the low-molecular-weight fraction which was to be used to prepare carbon fiber. The properties of raw materials and solubles were shown in **Table 1**.

2.2 Carbon Fibers Preparation

The Soluble was spun to prepare spun fiber by a specially modified Cotton Candy Machine (Asahisangyo). The spun fiber was extracted by cyclohexane at room temperature for 24 h to remove the light compounds, in order to increase the softening/melting point of the spun fiber (termed extracted fiber). Stabilization of the extracted fiber was performed by thermal treatment in flowing air (50 ml/min) using a thermogravimetric analyzer (Shimadzu, TGA50). After many attempts a suitable heating program was obtained for the extracted fiber stabilization. The extracted fiber was heated up from 50 ℃ to 330 ℃ in around 9 hours with several isothermal stages, and kept at 330 ℃ for 2 hours. The

heating profile of stabilization was shown in **Fig. 1**. After stabilization the flowing gas supplied to TG was switched to N_2 and the temperature was increased to 1000 °C and kept for 1 h to carbonize the stabilized fiber.

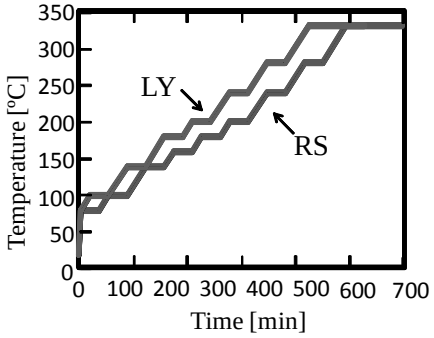

Fig. 1. Heating profile of extracted fiber stabilization

Table 1. Elemental compositions and yields of raw materials, solubles and fibers.

	Ultimate Analysis (%, d.a.f.)				Yield
	C	H	N	O (dif.)	wt%-Soluble
LY	66.7	4.7	0.9	27.7	
Soluble	81.8	7.5	0.5	12.1	100.0
Extracted fiber	81.4	7.0	0.6	11.0	61.9
Stabilized fiber	63.2	1.9	0.8	34.1	47.7
Carbon fiber	92.2	0.4	0.9	6.0	28.2
RS	46.2	1.6	6.7	45.5	
Soluble	80.0	6.8	1.3	11.9	100.0
Extracted fiber	79.7	5.9	1.6	12.7	78.0
Stabilized fiber	66.0	2.4	1.6	30.0	66.3
Carbon fiber	92.0	0.5	1.5	6.0	27.4

3. Results and Discussion

The Soluble yields of extraction were 56.2 % and 27.4 % on carbon basis respectively for RS and LY. The carbon contents of Solubles were higher than 80 %, much higher than those of the raw materials. Fig. 2 shows the softening/melting behaviors of Solubles examined by using a thermomechanical analyzer (Shimadzu, TMA). The figure clearly shows that the Solubles can melt completely at lower than 100 °C. This implies the Solubles can be spun easily. The diameters of the spun fibers were rather uniform and about 10 μm. The stabilized fibers were carbonized without melting and the SEM images of the final carbon fibers were shown in Fig. 3. The diameters of the carbon fibers were also rather uniform and about 5 μm. The elemental compositions and yields of the fibers obtained at each stage were shown in Table 1. The yields of extracted fibers were 78.0% and 61.9% on soluble weight basis respectively for RS and LY. The elemental compositions of the extracted fibers were similar to the solubles. The stabilized fibers had much higher oxygen contents. The yields of carbon fibers obtained from LY soluble and RS soluble were respectively 28.2% and 27.4%, and the carbon contents of them were as high as 92 %.

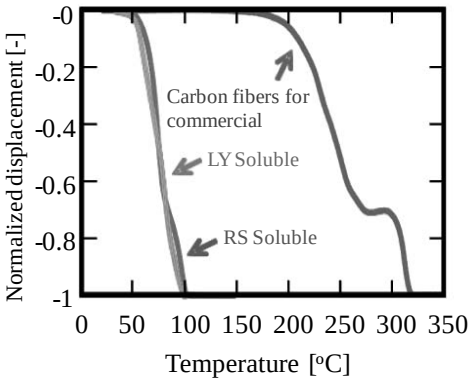

Fig. 2 TMA profiles of Solubles

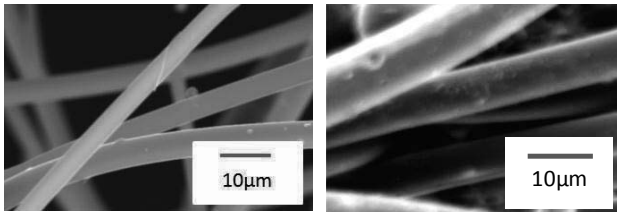

Fig. 3 SEM images of carbon fibers (left: LY; right: RS)

4. Conclusion

It was succeed to prepare carbon fibers by using Solubles obtained from LY and RS by degradative solvent extraction. The Soluble spinning can be performed easily because of the low softening/melting point of the Solubles. The spun fibers were extracted and stabilized by thermal treatment in air in around 10 h. The carbon fibers were finally obtained by carbonizing the stabilized fibers at 1000 °C for 1 h. This preparation method was conventional method for carbon fiber preparation. However, the precursor used was absolutely unique. The carbon fiber yields were 28.8% and 27.4% respectively for LY soluble and RS Soluble. Thus, the degradative solvent extraction should be a promising method to produce precursors for carbon fiber preparation from low-rank coals and biomasses.

References

[1] J. Wannapeera, et al. Energy & Fuels 26: 4521-4531, 2012.
[2] X. Li, et al. 第 47 回石炭科学会議, 京都, 2010.