

STRUCTURE AND PERFORMANCE OF SPINNING SOLUTION PREPARED FROM LIQUEFIED WOOD

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Abstract. A new spinning solution was synthesized from liquefied wood in phenol by adding hexamethylenetetramine (HMTA) as a synthesis agent, and was easily spun into fibers by melt-spinning. Structure evolution of the spinning solution from liquefied wood (LWS) was investigated by FTIR spectroscopy. Results show the functional groups of LWS were changed from that of liquefied wood by adding HMTA during synthesizing the spinning solution. The effects of various synthesis conditions on the properties of the spun fibers are discussed. Spun fibers with a tensile strength of 90–129 MPa and modulus of elasticity of 8–24 GPa were obtained at a phenol/wood ratio of 6, synthesis agent content of 5%, synthesis temperature of 120°C, and temperature-rising time of 40 min. It was also found that thermal stability of LWS is better than that of liquefied wood, and that the spun fibers from LWS could be a precursor for carbon fibers.

Keywords: Liquefied wood, spinning solution, fibers, chemical structure, mechanical properties, thermal analysis.

INTRODUCTION

In recent years, utilization of biomass resources has been gaining importance in environmental protection. Therefore, many techniques have been developed for using biomass resources effectively (Tatsuhiko and Hirokuni 2001). Wood liquefaction is one of those techniques for converting wood into useful liquid materials. As an alternative to fossil resources, liquefied wood (LW) has been applied in various chemical fields (Tsujimoto 1985; Lin et al 1995a 1995b; Yamada et al 1996; Alma et al 1996, 1998; Zhang et al 2004). To increase the use of LW and create “value-added” products, novel utilization methods must be developed, such as carbon fibers and nanostructure fibers. However, there are few studies of fibers from LW because

an appropriate spinning solution could not be easily obtained (Yoshida et al 2005; Ma and Zhao 2007).

It is well known that phenol-formaldehyde resin can be developed from LW (Lee et al 2000, 2002). Therefore, a liquefied wood spinning solution (LWS) could be synthesized according to the method of Kynol fibers (Liu et al 2005). The components in LW are rather complex after liquefaction. Therefore, the key to prepare fibers of high tensile strength is by synthesis of an optimal LWS. At the same time, more detailed studies on structure and performance of LWS are necessary.

In this study, the spinning solution, as raw material for carbon fiber precursors, was synthesized from LW in phenol. The structural evolution and thermal property of LWS was investigated by using FTIR spectroscopy and thermogravimetric (TG) analysis, respectively.

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The effects of the preparation parameters such as phenol/wood ratio, synthesis agent content, synthesis temperature, and temperature-rising time on mechanical properties of the spun fibers are also discussed.

MATERIALS AND METHODS

Materials

Wood meal (20–80 mesh) of Chinese fir (*Cunninghamia lanceolata* (Lamb.)) was oven-dried 105°C for 24 h and then kept in a desiccator at room temperature before use. A 37.5% H_3PO_4 aqueous solution was directly used as a catalyst. Phenol and hexamethylenetetramine (HMTA) were purchased from Beijing Chemical Company; 37% hydrochloric acid and 37% formaldehyde were obtained from Changchun Chemical Company. All other chemicals in the study were reagent grade and were used without further purification.

Liquefaction of Wood

Wood meal (20 g), phenol (60–120 g), and 37.5% aqueous phosphoric acid (8 wt% for phenol) catalyst were mixed together in a 500-mL three-neck glass flask. The glass flask was placed in an oil bath, and liquefaction was conducted at 160°C for 2.5 h using various liquid ratios (3, 4, 5, and 6 phenol/wood).

Synthesizing the Spinning Solution

LW (5 g), together with HMTA (3–6 wt% for LW) as a synthesis agent, were added in a reaction tube. Subsequently, according to the chosen temperature-rising time (20–50 min), the mixture was heated from room temperature to the setting synthesis temperature (110–125°C) then held for 5 min. LWS was thereby synthesized.

Preparation of Fibers from LWS

The LWS was placed in a spinning machine designed by our laboratory (Fig 1) and extruded in air through a pinhole under nitrogen pressure.

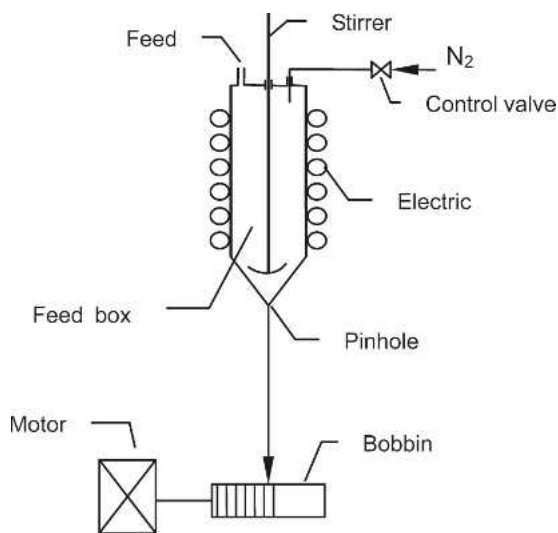


FIGURE 1. Schemes of the apparatus used for spinning.

The spun filaments were continuously wound on a bobbin at 36 rpm. The resultant fiber was cured by soaking in a solution containing hydrochloric acid and formaldehyde as main components at 95°C for 4 h at a heating rate of 10°C/h, washed with distilled water, and dried.

Analysis of the Samples

Structural changes of the LWS were traced with FTIR spectroscopy (Tensor27, Bruker company, France) by using the KBr disk technique. The samples were pulverized (150–200 mesh) and mixed with KBr before being pressed into a disk. The concentration of the sample in KBr was 2.5%, and 0.2 g of KBr was used in the preparation of the reference and sample disks.

The mechanical properties of fibers from liquefied wood (LWF) were measured by an electrical tensile strength apparatus (YG004N, Hongda spinning apparatus factory, China) with a span of 10 mm and crosshead speed of 2 mm/min. The data shown are average values for 20 samples of the fiber.

TG analysis was carried out with a Shimadzu TG-60 instrument. The sample (5–8 mg) was

heated in nitrogen from room temperature to 800°C at 10°C/min at a flow rate of 40 mL/min.

RESULTS AND DISCUSSION

FTIR Analysis

Figure 2 shows the FTIR spectra of Chinese fir, LW, and LWS. The absorption peak attributed to O-H is observed at 3406, 3408, and 3417 cm⁻¹ in Chinese fir, LW, and LWS, respectively (Zhang et al 2005). However, the decrease in intensity of these peaks, which is more in LWS than in LW, is due to the diminishing phenolic hydroxyl groups that have occurred as a result of the dehydration condensation reaction with phenolic hydroxide during synthesis of LWS. The bands at 1595, 1512, and 1454 cm⁻¹, which are assigned to aromatic ring stretch (Fengel and Wegener 1984; Liu et al 2005), are obviously weakened in LWS, while a new band appears at 1610 cm⁻¹ in LWS.

The peak found at 1101 cm⁻¹ in LW, which is associated with the presence of methylidene ether linkages, begins to intensify in LWS. At the same time, the band observed at 1015 cm⁻¹, attributed to the hydroxide methyl bond in LW, shifts to 1039 cm⁻¹ in LWS, and decreases in

intensity, indicating that the formation of methylidene ether in LWS is due to the condensation reaction with the hydroxymethyl group during synthesis of LWS (Ozaki et al 2000).

In addition, the bands at 692, 754, and 832 cm⁻¹, assigned to the out-of-plane CH deformation, appear in LW after liquefaction (Zhang et al 2005). However, the peak at 692 cm⁻¹ basically disappears while the bands at 832 and 754 cm⁻¹ decrease in intensity after synthesis of LWS, indicating that the amount of substituted benzene ring increases due to the appearance of a new addition reaction on the phenolic ring of LW, adding HMTA (Masahiko et al 2004).

Effects of Spinning Solution Factors on Mechanical Properties of Fibers

Figure 3 shows effects of the liquid ratio (phenol/wood) on mechanical properties of LWF. As shown in the figure, tensile strength and modulus of LWF linearly increase with increasing liquid ratio (phenol/wood). When the phenol/wood ratio increases from 3 to 6, tensile strength of LWF increases from 2.5 to 43 MPa while the modulus increases from 1.3 to 5.9 GPa. Under the same liquefaction condition, the greater the liquid ratio, the more crosslinking occurs in the curing reaction due to the unreacted phenol in liquefaction (Alma et al 1995). On the other hand, it was found that the higher the viscosity of the spinning solution, the lower the phenol/

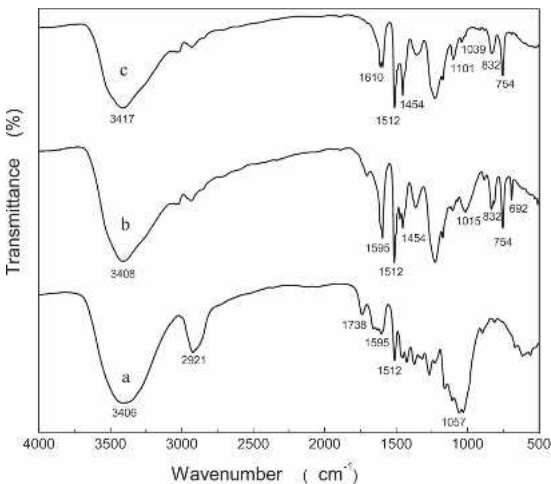


FIGURE 2. FTIR spectra of wood, LW, and LWS: (a) Chinese fir; (b) liquefied wood; (c) spinning solution from liquefied wood.

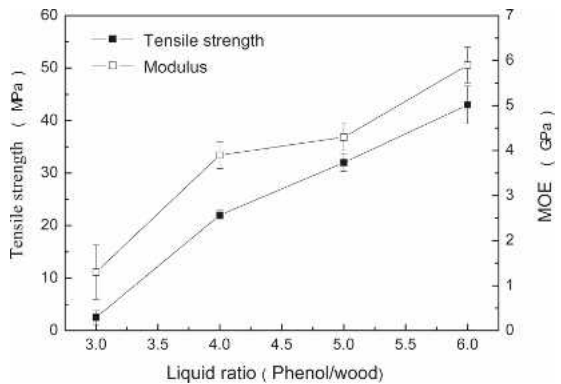


FIGURE 3. Effects of liquid ratio (phenol/wood) on mechanical properties of LWF.

wood ratio. The fibers have large diameters from the high viscosity of LWS and are difficult to spin, resulting in low crosslinkage and tensile strength of LWF.

Figure 4 shows effects of synthesis agent content on mechanical properties of LWF. With the increase of synthesis agent, tensile strength and modulus of LWF gradually decrease. In particular, when the synthesis agent content increases 5–6%, the changes of mechanical properties of LWF are the greatest. It has been known that high crosslinkage between phenolic rings in the network leads to good mechanical properties of fibers (Liu et al 2005). However, the number of crosslinked groups decreases in curing with the increase of synthesis agent content, indicating that phenolic rings react with the overuse of synthetic agent in the synthesization of LWS. As a result, tensile strength and modulus of LWF decrease with an increase of synthesis agent.

Figure 5 shows effects of synthesis temperature on mechanical properties of LWF. With increasing synthesis temperature from 110 to 125°C, tensile strength of LWF increases from 20 to 25 MPa while the modulus increases from 2.5 to 4.3 GPa. This indicates that mechanical properties of LWF increase only slightly over a small range of synthesis temperature. However, LWS is very sensitive to the change of synthesis temperature. It was found that synthesization of the spinning solution is difficult when the synthesis tempera-

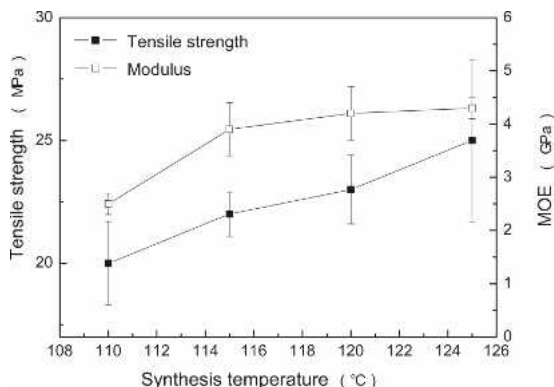


FIGURE 5. Effects of synthesis temperature on mechanical properties of LWF.

ture is below 100°C or above 130°C. In addition, the viscosity of LWS becomes increasingly low as the temperature rises.

Figure 6 shows effects of temperature-rising time on mechanical properties of LWF. Tensile strength and modulus of LWF reached a maximum of 49 MPa and 6.3 GPa, respectively, when the temperature-rising time was 40 min. Shorter or longer times lead to a decrease of tensile strength and modulus. It was found that micropores (see the arrow in Fig 7a) are developed due to the release of NH₃ gas during the shorter synthesis process of LWS (Ozaki et al 2000). Therefore, mechanical properties of LWF decrease due to these micropores.

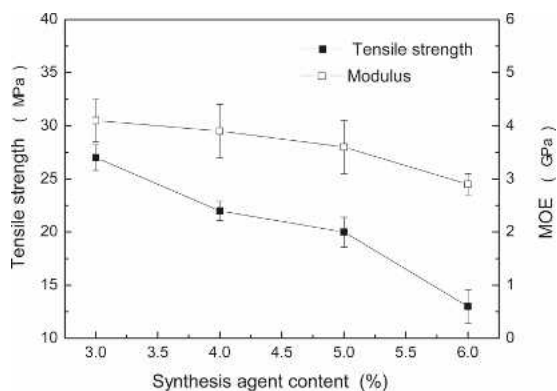


FIGURE 4. Effects of synthesis agent content on mechanical properties of LWF.

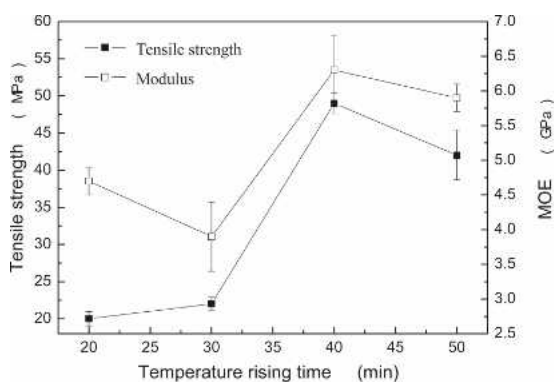


FIGURE 6. Effects of temperature-rising time on mechanical properties of LWF.

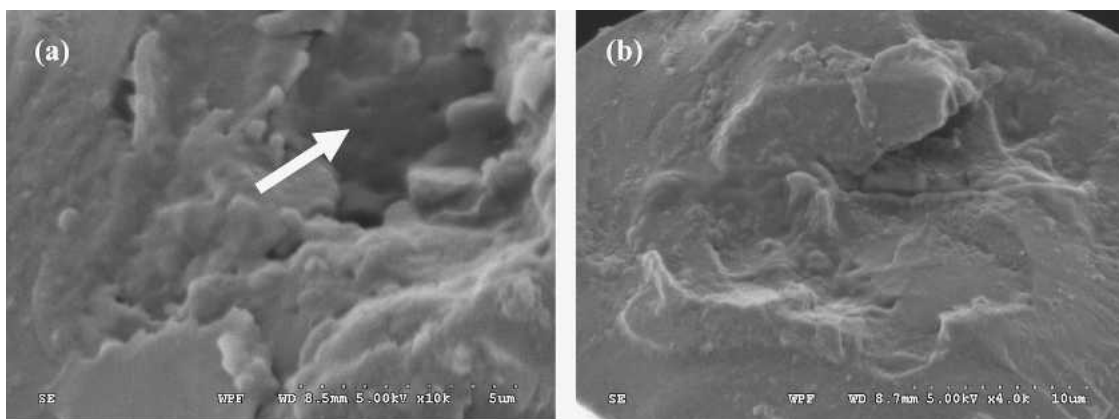


FIGURE 7. SEM photographs of LWF: (a) temperature-rising time of 30 min, (b) temperature-rising time of 50 min.

TG Analysis

As shown in Fig 8, both LW and LWS have similar TG curves. A small weight loss is observed below 200°C. However, LW shows slightly greater weight losses around 100°C than LWS, which is mainly due to most of the free phenol and moisture in LW. LWS rapidly decomposes between 200 and 400°C, corresponding to a weight loss of around 34.6% at 400°C. Meanwhile, a 40.1% weight loss of LW was recorded at 400°C. After this sharp weight loss, there was a gradual weight loss up to 800°C. Weight loss at 800°C is 62 and 58% for LW and LWS, respectively, indicating that thermal stability of LWS is better than that of LW.

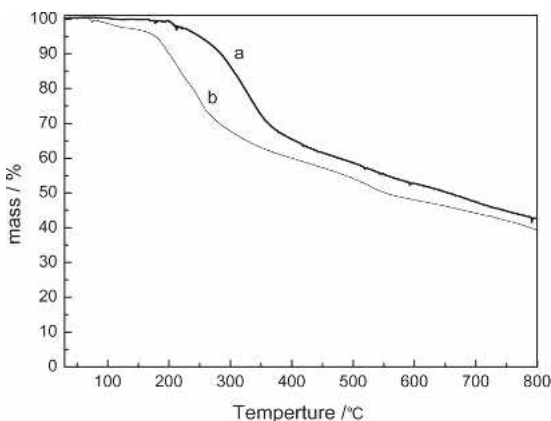


FIGURE 8. TG curves of (a) LW and (b) LWS.

CONCLUSIONS

Liquefied wood was converted to a spinning solution by adding HMTA. As carbon fiber precursors, the spun fibers were prepared from LWS after melt-spinning. It is clear that the functional groups of LWS have been changed from that of liquefied wood by adding HMTA during synthesis. As the phenol/wood ratio and synthesis temperature increase, tensile strength and modulus of the fibers from LWS increase. However, tensile strength and modulus of the fibers gradually decrease with the increase of synthesis agent content and temperature-rising time. Spun fibers with tensile strength of 90–129 MPa and modulus of 8–24 GPa are obtained from LWS at phenol/wood ratio of 6, synthesis agent content of 5%, synthesis temperature of 120°C, and temperature-rising time of 40 min. It is found that weight loss at 800°C was 62 and 58% for LW and LWS, respectively, indicating that the thermal stability of LWS is better than that of LW.

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REFERENCES

ALMA MH, YOSHIOKA M, YAO Y, SHIRAIISHI N (1995) Preparation and characterization of the phenolated wood using

- hydrochloric acid as a catalyst. *Wood Sci Technol* 30(1): 39–47.
- , ———, ———, ——— (1996) The preparation and flow properties of HCl catalyzed phenolated wood and its blends with commercial novolak. *Holzforschung* 50(1):85–90.
- , ———, ———, ——— (1998) Preparation of sulfuric acid-catalyzed phenolated wood resin. *Wood Sci Technol* 32(4):297–308.
- FENGEL D, WEGENER G (1984) *Wood - chemistry, ultrastructure, reactions*. W. de Gruyter, Berlin and NY. 613pp.
- LEE SH, TERAMOTO Y, SHIRAISHI N (2000) preparation and properties of phenolated corn bran (CB)/phenol/formaldehyde co-condensed resin. *J Appl Polym Sci* 77(13):2901–2907.
- , ———, ——— (2002) Resol-type phenolic from liquefied phenolated wood and its application to phenolic foam. *J Appl Polym Sci* 84(3):468–472.
- LIN L, YOSHIOKA M, YAO Y, SHIRAISHI N (1995a) Physical properties of moldings from liquefied wood resins. *J Appl Polym Sci* 55(11):1563–1571.
- , ———, ——— (1995b) Preparation and properties of phenolated wood/pheno/formaldehyde cocondensed resin. *J Appl Polym Sci* 58(8):1297–1304.
- LIU CL, GUO QG, SHI JL, LIU L (2005) A study on crosslinking of phenolic fibers. *Mater Chem Phys* 90(23):315–321.
- MA XJ, ZHAO GJ (2007) Preliminary study on preparation of carbon fiber from wood-phenol liquefaction products. *Chem Indu Fore Prod* 27(5):29–32.
- MASAHIKO K, TOSHIYUKI A, MIKIO K, BUNICHIRO T (2004) Analysis on residue formation during wood liquefaction with polyhydric alcohol. *J Wood Sci* 50(5):407–414.
- OZAKI J, OHIZUMI W, OYA A (2000) A TG-MS study of poly (vinyl butyral) /phenol-formaldehyde resin blend fiber. *Carbon* 38(10):1499–1524.
- TATSUHIKO Y, HIROKUNI O (2001) Characterization of the products resulting from ethylene glycol liquefaction of cellulose. *J Wood Sci* 47(5):458–464.
- TSUJIMOTO N (1985) Study on wood-phenol resin fiber. 1985 International Symposium on Wood and Pulping Chemistry. Pp. 19–20.
- YAMADA T, ONO H, OHARA S, YAMAGUCHI A (1996) Characterization of the products resulting from direct liquefaction of cellulose. *Mokuzai Gakkaishi* 42(11):1098–1104.
- YOSHIDA C, OKABE K, YAO T, SHIRAISHI N, OYA A (2005) Preparation of carbon fibers from biomass-based phenol formaldehyde resin. *J Mater Sci* 40(2):335–339.
- ZHANG QH, ZHAO GJ, JIE SJ (2004) Effects of phosphoric acid on liquefaction of wood in phenol and optimum liquefaction processing parameters. *For Stud Chin* 6(3): 50–54.
- , ———, ——— (2005) Liquefaction and product identification of main chemical compositions of wood in phenol. *For Stud Chin* 7(2):31–37.