

EFFECT OF THE SIZE OF SPINNERET ON THE THERMAL STABILITY OF CHEMICALLY LIQUEFIED WOOD

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ABSTRACT

Chemically cured fibers were prepared from liquefied wood in phenol by melt-spinning with different spinnerets of length/diameter ratio (L/D) (0, 2, and 4) and then chemical curing, to investigate the effect of the size of spinneret on the thermal stability of chemically cured fibers. High thermal transition temperatures and small weight loss percentages of resultant chemically cured fibers representing good thermal stability were obtained with the increase in L/D of spinneret. Besides, it was found that few defective structures with the total surface area of $5.3 \text{ m}^2 \cdot \text{g}^{-1}$ and total pore volume of $0.0013 \text{ mL} \cdot \text{g}^{-1}$ occurred on cross section and surface of chemically cured fibers, which was prepared with spinneret of L/D = 4. These improvements were mainly attributed to the larger amounts of three-dimensional network structures formed during chemical curing process.

KEYWORDS: Wood liquefaction; chemically cured fibers; length/diameter ratio; thermal stability; TGA/TMA.

INTRODUCTION

Carbon fibers (CFs), a type of lightweight and high performance fibrous carbon material, are generally processed as reinforcement materials utilized in area where lightweight and high strength are required. However, due to the high cost of production, CFs were limited to use in some aspects, such as parts in planes and luxury sports equipments (Ogawa 2000). Thus, many researchers have been conducting the studies directed at examining several types of potential materials as precursor for preparing the low-cost CFs (Kadla et al. 2002; Kubo et al. 1998; Ma and Zhao 2010; Sudo and Shimizu 1992; Uraki et al. 1995; Lin et al. 2012). In the case of liquefied wood in phenol as raw material, CFs with the tensile strength of 1.2-1.7 GPa and

modulus of 114–176 GPa were successfully processed, which could be classified as the fibers of general grade performance (Ma and Zhao 2010; Prauchner et al. 2005).

When preparing liquefied wood based CFs, chemical curing process was carried out after melt-spinning to convert primary fibers into infusible fibers which could maintain the fiber form during the subsequent carbonization. In previous study, we have discussed the distinct effect of spinneret size on the structure and thermal stability of primary fibers prepared from liquefied wood in phenol by melt-spinning (Lin et al. 2013). Accordingly, there may be also the relationships between spinneret size and some properties of chemically cured fibers. Besides, the various properties of CFs could be strongly affected by the qualities of precursor. Therefore, it is significantly to carry out the investigation on chemically cured fibers so as to provide useful information for fabricating precursor fibers with high quality and further obtaining CFs with high performance.

Especially, thermal stability is one of the most important properties for chemically cured fibers because they will be subsequently subjected to heat treatment. Not only the mechanical properties but also the yield of CFs was affected. However, there were few reports concerning the effect of melt-spinning parameters on the thermal stability of resultant liquefied wood based on chemically cured fibers. Therefore, in this article we would like to report the characterization and evaluation of chemically cured fibers derived from liquefied wood in phenol by melt-spinning process with different spinnerets and then chemical curing process.

MATERIAL AND METHODS

Preparation of liquefied wood based on chemically cured fibers

All chemicals were of analytical grade and used as received without further purification. The liquefied wood based primary fibers were prepared according to the previous study (Lin et al. 2013). The mixture of 20 g of dried wood powder, Chinese fir (*Cunninghamia lanceolata*) and 120 g of phenol as well as 9.6 g of phosphoric acid, loading in a round bottom flask, was heated in an oil bath at 160°C for 150 min. After heating and cooling, the resultant mixture was diluted with 0.75 L of acetone, and then filtrated through filter paper to separate filtrate and residue. The acetone in the filtrate was removed by evaporation to obtain the liquefied wood which was subsequently reacted with hexamethylenetetramine (HMTA) (5 wt % on the weight of liquefied wood) at 120°C for preparing spinning solution in different spinnerets with length/diameter ratio (L/D) = 0, 2, and 4, respectively (As shown in Fig. 1). The melt-spinning process was conducted to prepare the primary fibers from spinning solution at the nozzle temperature of 120°C and the winding rates of 14 m.min⁻¹ under a nitrogen pressure. Subsequently, the resultant primary fibers

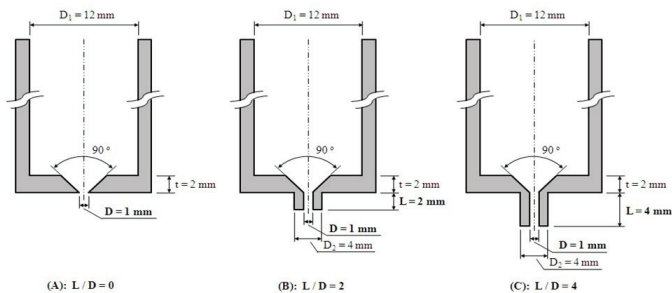


Fig. 1: Illustration of spinnerets with different L/D .

were converted into chemically cured fibers by immersing in the curing solution containing 18.5 % hydrochloric acid and 18.5 % formaldehyde, and then heating from room temperature to 95°C within 4 h as well as holding at this temperature for 2 h. Finally, these fibers were rinsed with distilled water and then dried at 105°C for overnight.

Characterizations

Morphology of chemically cured fibers were observed by scanning electronic microscopy (SEM; S-3400N, Hitachi, Japan) using gold-coated samples, at magnification factors of 1,000-3,000, and at an accelerating voltage of 10 kV, respectively. TMA was performed on a TMA-4000S System (MAC Science System 010, MAC Science, Yokohama, Japan) at the temperature ranging from 30 to 300°C under compression loading of 5 g under a N₂ stream at 0.15 L.min⁻¹. The glass transition temperature (T_g) was estimated as a first transition points in TMA profiles (Kubo et al. 1996). The weight loss behaviors and decomposition temperature (T_d) of liquefied wood based chemically cured fibers were measured by using thermogravimetric analysis (TGA) on a simultaneous thermal analyzer (DTG-60, Shimadzu, Japan) from room temperature to 800°C at the heating rate of 10°C.min⁻¹ in high pure nitrogen stream (30 ml.min⁻¹). Measurements of Fourier transform infrared (FT-IR) spectroscopy were carried out on an FT-IR spectrophotometer (SENSOR 27, Bruker, Germany), using the KBr disk method. Fiber pore structures were characterized by mercury porosimetry (AutoScan-33, Quantachrome, USA) with the pressure ranging from 0.2 to 60,000 psia and equilibration time of 10 s (Leon 1998).

RESULTS AND DISCUSSION

Liquefied wood based on chemically cured fibers were successfully prepared from wood liquefaction via melt-spinning process with different L/D spinnerets and then chemical curing process. The morphologies of chemically cured fibers were observed by SEM as shown in Fig. 2. Pores with various diameters in cross-section were observed obviously in addition to that splits existed on the fiber surface when spinneret of L/D = 0 was applied (Fig. 2 (A) and (B)). Contrarily, quite smooth fiber surface with no pores in cross-section were obtained under the condition of L/D = 4 (Fig. 2 (E) and (F)), while a little splits still remained on the fiber surface in the case of L/D = 2 (Fig. 2 (C) and (D)). The same phenomenon occurred in the corresponding primary

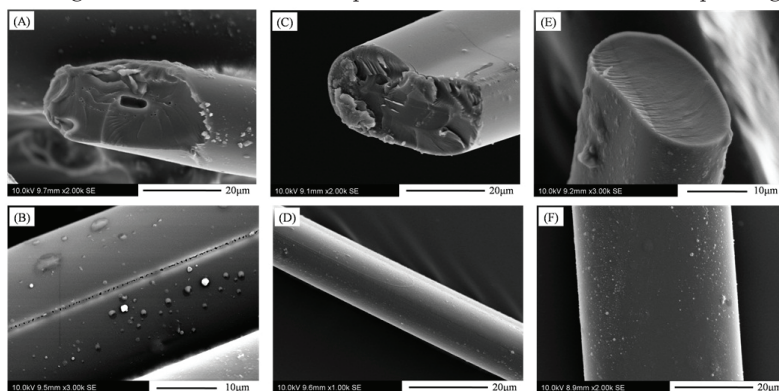


Fig. 2: SEM morphology of chemically cured fibers derived from primary fibers prepared with different L/D spinnerets. (Notes: (A and B) L/D = 0; (C and D) L/D = 2; (E and F) L/D = 4).

fibers, which were induced by nitrogen gas and spinning nozzle (Lin et al. 2013). Therefore, these results show the effect of spinneret size on the structure of chemically cured fibers even though the primary fibers were chemically cured.

The chemically cured fibers might exhibit significant differences in their thermal properties depending on their various structures. Accordingly, it is significant to determine the thermal properties of chemically cured fibers because these cured fibers as precursor would be carbonized at high temperature (generally 1000°C) for obtaining CFs. As shown in Fig. 3, TMA curves of chemically cured fibers showed only one transition point which corresponded to the T_g , indicating no thermal-flow starting temperature and infusible fibers. With an increase in the L/D, T_g of chemically cured fibers increased (Tab. 1), and all of them were higher than that of each primary fibers (Lin et al. 2001b), which might be caused by the conversion of fibers from thermoplastic character into thermosetting during chemical curing process (Ma and Zhao 2008). Furthermore, the TMA curves of chemically cured fibers prepared with spinneret of L/D = 0 still showed decreasing trend after 250°C, while almost no changes were observed in the TMA curves of chemically cured fibers prepared with spinneret of L/D = 2 and 4, suggesting that the thermal stability of chemically cured fibers were gradually enhanced with the spinneret of L/D increasing. These results can also be proved by TGA measurements.

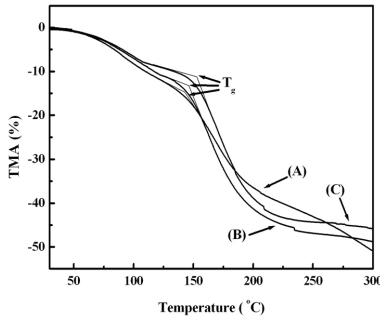


Fig. 3: TMA profiles of chemically cured fibers derived from primary fibers prepared with different L/D spinnerets. (Notes: (A) L/D = 0; (B) L/D = 2; (C) L/D = 4).

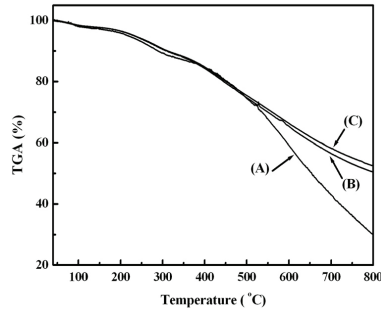


Fig. 4: TGA curves of chemical cured fibers derived from primary fibers prepared with different L/D spinnerets. (Notes: (A) L/D = 0; (B) L/D = 2; (C) L/D = 4).

Tab. 1: Thermal transition temperatures and residual ratio of chemically cured fibers derived from primary fibers prepared with different L/D spinnerets.

L/D _a	Transition temperature (°C) _b		Residual ratio (%)
	T_g	T_d	
0	144	261	29.9
2	147	269	50.5
4	153	272	52.5

^a L/D denotes length/diameter ratio of spinneret;

^b T_g and T_d denote glass transition temperature and decomposition temperature, respectively;

As shown in Fig. 4, with the temperature increasing, all the chemically cured fibers weights decreased to various degree, and the weight loss processes could be mainly partitioned into two stages (stage 1: slow weight loss varying from 150 to 327°C; stage 2: sharp weight loss ranging from 327 to 800°C), excluding the temperature lower than 150°C because of the loss of adsorbed water molecules, which are derived from ambient environment.

In the case of stage 1, weight loss percentages were quite similar (9.2, 8.6, and 8.4 % for L/D = 0, 2, and 4, respectively). These behaviors were mainly induced by the mild thermal degradation starting from the decomposition temperature (T_d), which was defined as a temperature that give a 5 % weight loss (Uraki et al. 1995). As shown in Tab. 1, high L/D of spinneret gave rise to the high T_d of the chemically cured fibers. For the L/D = 4, around 10°C increase of T_d was obtained in comparison with that of chemically cured fibers prepared with spinneret of L/D = 0. For stage 2, similarly, decreases in weight loss percentage took place with an increase in the L/D of spinneret, which was probably caused by the complete decomposition (Zheng et al. 2002). Especially for the case of L/D = 0, sharp decrease of 58.2 % occurred in comparison with that of 38.6 % for L/D = 2 and 37.7 % for L/D = 4, respectively. Accordingly, the highest residual ratio of 52.5 % was obtained by using the spinneret with L/D = 4, indicating that the thermal stability of chemically cured fibers could be improved and high yield would be obtained after carbonization process via increasing L/D of spinneret. These results are in good agreement with the TMA results of these fibers.

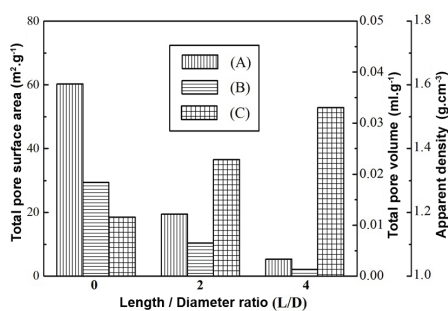


Fig. 5: Total pore surface area (A), total pore volume (B) and apparent density (C) of chemical cured fibers derived from primary fibers prepared with different L/D spinnerets.

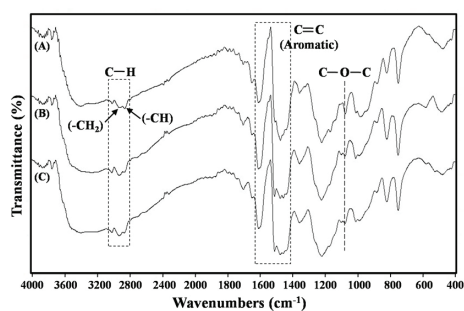


Fig. 6: FTIR spectra of chemical cured fibers derived from primary fibers prepared with different L/D spinnerets. (Notes: (A) L/D = 0; (B) L/D = 2; (C) L/D = 4).

MIP measurement is a relatively rapid and useful technique for evaluating the pore structure in many porous materials, with which the information including total surface area and wide pore diameter range as well as variety of porosity parameters can be obtained (Giesche 2006; Moura et al. 2005; Vennat et al. 2009; Tatsuo 2007). In this study, to confirm the various pore structures of chemically cured fibers derived from primary fibers prepared from liquefied wood with spinnerets of L/D = 0, 2, and 4, MIP measurements were conducted. Total pore surface area, total pore volume and apparent density of chemically cured fibers are shown in Fig. 5. It was obvious that the total pore surface area and total pore volume decreased with the L/D of spinneret increasing. Especially for L/D of 4, total pore surface area of 5.3 m²·g⁻¹ and total pore volume of 0.0013 cm³·g⁻¹ were obtained, respectively, indicated that there were almost no pore structures occurring in the corresponding chemically cured fibers. Meanwhile, the apparent density of chemically cured fibers showed the inverse trend in comparison with total pore surface area and total pore volume.

Therefore, chemically cured fibers prepared from spinneret with high L/D exhibited less porous structure and high apparent density. These results are extremely coincident to the results from morphologies observation of chemically cured fibers (Fig. 2), further suggesting that it is possible to improve the quality of chemically cured fibers through increasing the L/D of spinneret.

Additionally, FTIR measurements were carried out to investigate the chemical differences among the chemically cured fibers. Fig. 6 illustrates the FTIR spectra of chemically cured fibers prepared from different spinnerets of L/D. One can see that the peak intensity at around 2920 cm^{-1} of characteristics became stronger with spinneret of L/D increasing, indicating that more methylene groups are formed (Silverstein et al. 2005). The formation of these groups may be the result of the dehydration – condensation reaction between formaldehyde and phenolic moieties which were derived from free phenol and phenolated wood in the presence of hydrochloride acid as catalyst (Lin et al. 2001a; Lin et al. 2001b; Lin et al. 2004; Lin et al. 1994). During the condensation reaction, two carbon anions from different benzene rings of phenolic moieties successively attacked protonated formaldehyde ($^+\text{CH}_2\text{OH}$) to generate the methylene bridge between two benzene rings. Primary fibers prepared with higher spinneret of L/D exhibited smaller distance of molecular chains because of more hydrogen bonds (Lin et al. 2013), thus accelerating generating of more methylene groups. So, more cross-linkages occurred in the molecular chains of chemically cured fibers were prepared with spinneret of L/D=4. Besides, there were the decreasing trends upon the peak intensity of the ring C=C stretching vibration region ($1601\text{-}1478\text{ cm}^{-1}$) and symmetrical C-O-C stretching vibration (1046 cm^{-1}) with the increasing of L/D (Silverstein et al. 2005), which are also indicative of more three-dimensional network structures being formed and that the activities of molecules were limited. Therefore, being prepared with higher L/D spinneret, chemically cured primary fibers possessed more tight structures and good thermal stability.

CONCLUSIONS

The chemically cured fibers, prepared from liquefied wood in phenol by melt-spinning process with spinnerets of various L/D and then chemical curing process, exhibited extremely different thermal stability attributed to their various structures. With the L/D of spinneret increasing, prepared chemically cured fibers showed less defective structures on the cross section and surface, higher glass transition temperatures and decomposition temperatures, and less weight loss percentages, representing good thermal properties. Especially for L/D = 4, the residual ratio after thermal treatment reached to 52.5 %, which was approximately two times higher than that of chemically cured fibers prepared with spinneret of L/D = 0. Furthermore, there were total specific surface area of $5.3\text{ m}^2\cdot\text{g}^{-1}$ and total pore volume of $0.0013\text{ Ml}\cdot\text{g}^{-1}$ being determined. These improvements were the results of the formation of more cross-linkages during chemical curing process when spinneret with higher L/D was utilized. Accordingly, the properties of CFs prepared from chemically cured fibers as precursor could be enhanced by using spinneret with high L/D.

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