

**STUDY ON THE PYROLYSIS OF THE CURED FIBERS  
FROM LIQUEFIED WOOD (*CUNNINGHAMIA  
LANCEOLATA*) BY THERMOGRAVIMETRY-MASS  
SPECTROMERY**

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**ABSTRACT**

In this work, the cured fibers were prepared from wood (*Cunninghamia lanceolata* (Lumb.) Hook) by liquefaction, melt-spinning with the addition of hexamethylenetetra-mine, and soaking in the solution containing hydrochloric acid and formaldehyde as the main components. The pyrolysis of the cured fibers from liquefied wood was studied by thermogravimetry-mass spectrometry. The results showed that the pyrolysis of the cured fibers is not similar to that of other wood-derived rayon fiber, and could be divided into three phases. Most of the decomposition products are released at around 500°C. The decomposition product is mainly composed of H<sub>2</sub>O (m/z=18), CH<sub>4</sub> (m/z=16), CO (m/z = 28), CO<sub>2</sub> (m/z = 44), CH<sub>2</sub>O (m/z = 30), benzene (m/z = 78), toluene (m/z = 92) and macromolecular product. The pyrolysis of the cured fibers is not identical with that of cellulosic materials and phenolic fibers.

**KEYWORDS:** The cured fibers, liquefied wood, pyrolysis, TG-MS.

**INTRODUCTION**

Wood, as environmentally friendly renewable resource, is getting more and more attention with the rapid rise of oil energy prices. Wood has been used as the raw of fiber materials for many years, and some typical fiber materials (rayon fibers) are generated (Liu et al. 2005b). However, due to short fibers, poor spinning and the limited utilization of wood, which limits the development and application of wood fiber materials for carbon fibers (Ohshima et al. 2003, Higashihara et al. 2003, Li and Reeve 2004). In the current work, tensile strength of the cured fibers with 113 MPa was prepared from wood that was liquefied, spun and cured, and has become

superior precursor for the preparation of carbon fibers (Ma and Zhao 2008).

In order to further study the formation and evolution of the cured fibers, it is necessary to analyse the pyrolysis process of the cured fibers from liquefied wood. Thermogravimetry-mass spectrometry (TG-MS) has been a well-established technique for the analysis of evolved gases since the late 1970s. TG-MS has been used for the pyrolysis of rayon fibers, phenolic fibers and other materials (Ozaki et al. 2000, Liu et al. 2005b). In this work, the purpose of this research is to apply the technique of TG-MS analysis to study the pyrolysis process of the cured fibers from liquefied wood. The authors have provided a preliminary investigation of thermal degradation of the cured fibers. Moreover, the primary products from the pyrolysis of the cured fibers from liquefied wood are investigated and their formation reasons are discussed in detail.

## MATERIAL AND METHODS

A mixture composed of dried Chinese fir (*Cunninghamia lanceolata* (Lumb.) Hook) powder (20-80 mesh) and phenol at a mass ratio of 1:6 was liquefied for 2.5 h at 160°C with 8 % phosphoric acid (based on the mass ratio of phenol). The prepared liquefied wood was placed into a reaction tube with 5 % hexamethylenetetramine (based on the mass ratio of liquefied wood) as the synthetic material. The mixture was heated from room temperature to 115°C in 40 min to prepare the spinning solution. The spinning solution was placed into a spinning machine and the initial fibers were prepared by melt-spinning.

The prepared initial fibers were immediately immersed in a solution containing 18.5 % hydrochloric acid and 18.5 % formaldehyde. The fibers were then heated to 95°C at a rate of 10°C.h<sup>-1</sup>. After curing for 4 h, the fibers were washed with water and allowed to dry in a drying box for 40 min at 85°C to obtain the cured fibers (Fig. 1).



Fig. 1: The cured fibers prepared from liquefied wood.

The thermogravimetric analysis of the cured fibers prepared from liquefied wood during pyrogenation was performed using a Pyris Diamond TG/DTA/DSC thermal analyzer (PE Company, USA) with a Thermostar™ mass spectrometer (Switzerland) to detect the production of pyrolysis products. A 4-mg fraction of the precursor sample was placed into a small crucible and then heated to 800°C at a rate of 10°C.min<sup>-1</sup> in a N<sub>2</sub> atmosphere. The scanning range used was m/z = 1.6 to 200 with a scanning cycle of 20 ms.

## RESULTS AND DISCUSSION

As illustrated in Figs. 2 and 3, the TG curve shows that the thermal weight loss of the cured fibers from liquefied wood was relatively small at temperature lower than 300°C. The pyrolysis

products and fragments included  $m/z = 17$ ,  $m/z = 18$ ,  $m/z = 44$ , and  $m/z = 30$ . The product  $m/z = 18$ ,  $m/z = 30$ , and  $m/z = 44$  represented  $H_2O$ ,  $CH_2O$ , and  $CO_2$ , respectively. The peak of  $H_2O$  appears in the temperature range of 80–200°C, which means that the physical desorption of water mainly takes place at this stage. The formation of  $CO_2$  occurred because of the release of carbon in the cured fibers prepared from the liquefied wood. The formation of  $CH_2O$  was due to the scission of ether bonds that reacted between the -OH groups in the benzene ring and the formaldehyde in the curing solution and the dehydroxymethylation of the benzene rings that were not fully cross-linked during curing (Lin et al. 2001; Alma et al. 1995, 1998).

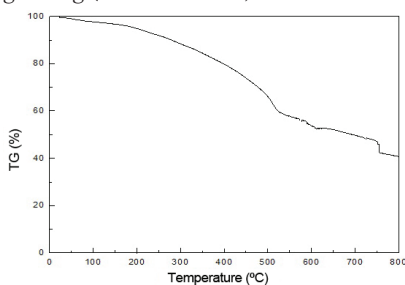


Fig. 2: TG diagram of the cured fibers prepared from liquefied wood.

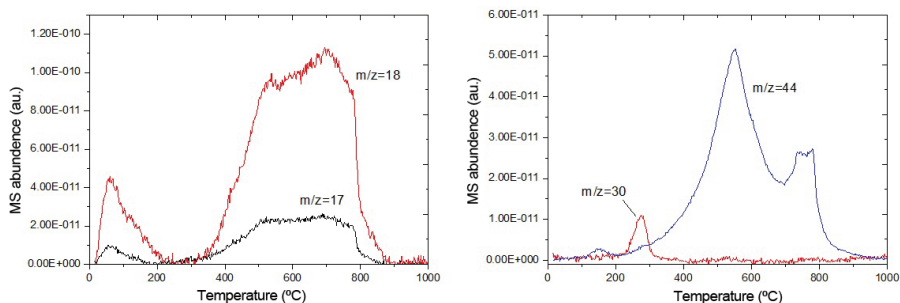


Fig. 3: Ms response of  $m/z = 17$ , 18, 30, 44 of TG-MS analysis of the cured fibers from liquefied wood.

As can be seen from Figs. 2, 3, and 4, the TG-MS curve showed that the maximum temperature for the release of most of the pyrolysis products of the cured fibers from liquefied wood was 500°C (Fig. 2). At temperature ranging from 300 to 600°C, the pyrolysis products contained  $CH_4$ , which was represented by  $m/z=16$ , and  $CO$  represented by  $m/z=28$ , as well as  $H_2O$  ( $m/z=18$ ),  $CO_2$  ( $m/z=44$ ), and other low-molecular-weight substances. Phenol at  $m/z=94$ , cresol at  $m/z = 108$ , and xylenol at  $m/z=122$ , typical pyrolysis products of phenolic substances, were the main decomposition products at this temperature. Furthermore,  $m/z = 68$  to 92 represented some macromolecular pyrolysis products also produced during this stage (Ozaki et al. 2000; Liu et al. 2005b). Specifically,  $m/z = 68$  may have been  $C_4H_4O^+$ ,  $m/z = 78$  may have been  $C_6H_6^+$  (benzene),  $m/z = 77$  may have been a fragment of  $C_6H_6^+$ ,  $m/z = 92$  may have been  $C_7H_8^+$  (toluene), and  $m/z = 110$  may have been  $C_6H_6O_2^+$  (5-methylfurfural). The products of polymer decomposition were probably represented by  $m/z = 132$  and  $m/z = 146$ . The presence of these substances may have been caused by partial cellulose, hemicellulose, lignin, and their liquefied derivatives, which were not completely decomposed in the precursor prepared from liquefied wood. Therefore, the decomposition products of this stage of pyrolysis seem to be more complicated than that of wood-derived rayon fiber (Lin et al. 2001; Liu et al. 2005a).

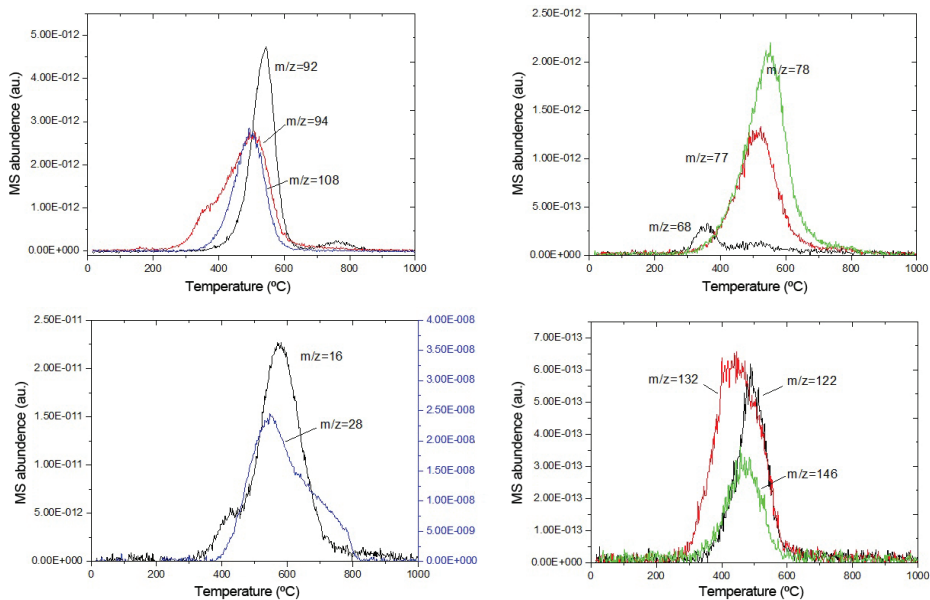


Fig. 4: MS response of  $m/z = 16, 28, 68, 77, 78, 92, 94, 108, 122, 132, 146$  of TG-MS analysis of the cured fibers from liquefied wood.

At temperature exceeding  $700^{\circ}\text{C}$ , the thermal weight loss of the cured fibers appears again. The TG-MS curve shows that the decomposition product was mainly  $\text{CO}_2$  ( $m/z = 44$ ) and its fragments ( $m/z = 43$ ), as well as  $\text{C}_7\text{H}_8^+$  (toluene), represented by  $m/z = 92$ . Therefore, at higher temperatures, the benzene fused-ring structure in the carbon filament continuously increased, secondary cracking of the molecular system was present.

It should be noted that water ( $m/z = 18$ ) was observed during the pyrolysis of the cured fibers, and the MS curve of water is very wide, which is different from the pyrolysis of wood-derived rayon fiber and cellulose (Liu et al. 2005b). On the other hand, due to liquefy by phenol, some typical pyrolysis products of phenolic substances are also observed. This observation is not identical with the pyrolysis of wood, phenolic fibers and other materials (Ozaki et al. 2000; Liu et al. 2005b).

## CONCLUSIONS

The cured fibers were prepared from wood (*Cunninghamia lanceolata* (Lumb.) Hook) by liquefaction, melt-spinning and soaking in the solution containing hydrochloric acid and formaldehyde as the main components. The pyrolysis of the cured fibers could be divided into three phases. Most of the decomposition products are released at about  $500^{\circ}\text{C}$ . The decomposition product is mainly composed of  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_2\text{O}$ , benzene, toluene and macromolecular product. The molecular structure of the carbon filament was secondarily adjusted at  $750^{\circ}\text{C}$ . The pyrolysis of the cured fibers is different from those of wood, phenolic fibers and cellulosic materials.

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