Front. For. China 2009, 4(3): 374–379
DOI 10.1007/s11461-009-0042-2

RESEARCH ARTICLE

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Dynamic viscoelastic behavior of wood under drying conditions

Abstract In this study heartwood from a Chinese fir [*Cunninghamia lanceolata* (Lamb.) Hook] plantation was treated using a high-temperature drying (HTD) method at 115°C, a low-temperature drying (LTD) method at 65°C, and freeze vacuum drying (FVD), respectively. The dynamic viscoelastic properties of dried wood specimens were investigated. The measurements were carried out at a temperature range of -120 to 250°C at four different frequencies (1, 2, 5, and 10 Hz) using dynamic mechanical analysis (DMA). We have drawn the following conclusions: 1) the storage modulus E' and loss modulus E'' are the highest for HTD wood and the lowest for FVD wood; 2) three relaxation processes were detected in HTD and LTD wood, attributed to the micro-Brownian motion of cell wall polymers in the non-crystalline region, the oscillations of the torso of cell wall polymers, and the motions of the methyl groups of cell wall polymers in the non-crystalline region in a decreasing order of temperatures at which they occurred; and 3) in FVD wood, four relaxation processes were observed. A newly added relaxation is attributed to the micro-Brownian motions of lignin molecules. This study suggests that both the HTD and the LTD methods restrict the micro-Brownian motion of lignin molecules somewhat by the cross-linking of chains due to their heating history.

Keywords high-temperature drying, low-temperature drying, freeze vacuum drying, viscoelasticity, relaxation processes, micro-Brownian motion

1 Introduction

Wood drying methods have been investigated by a number of scientists (Edvardsen and Sandland, 1999; Bengtsson and Betzold, 2000; Kang, 2001; Kang and Booker, 2002), but few reports have been found with respect to the effect of different drying methods on the physical and mechanical properties of wood, especially those concerning the viscoelasticities of wood dried by different drying methods. The purpose of our study was to determine the storage modulus E' and loss modulus E'' of high-temperature drying (HTD), low-temperature drying (LTD), and freeze vacuum drying (FVD) wood specimens and to investigate how the dynamic viscoelastic behavior varies among different dried woods.

2 Materials and methods

2.1 Materials

Wood specimens were obtained from the outer region of green Chinese fir [*Cunninghamia lanceolata* (Lamb.) Hook] heartwood. The initial moisture content of the samples was about 86% and their average basic density 0.272 g/cm^3. All clear and straight-grained specimens (6 mm longitudinal [L]×35 mm radial [R]×1.5 mm tangential [T]) were cut successively in the longitudinal and tangential directions from a wood stick with a cross-section of 120 mm (R) ×50 mm (T) (Fig. 1).

2.2 Drying conditions

Three kinds of drying conditions were applied. High-temperature drying (HTD) and low-temperature drying (LTD), in a constant temperature drying chamber, were carried out at 115°C for approximately 8 h and at 65°C for about 20 h, respectively. Freeze-vacuum drying (FVD) was carried out by a freeze-vacuum drying machine (FTS systems) with condensation temperature at -49°C and a vacuum degree at 124 mTorr (1 Torr = 0.1333 kPa) for

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Translated from *Journal of Beijing Forestry University*, 2008, 30(3): 96–100 [译自: 北京林业大学学报]

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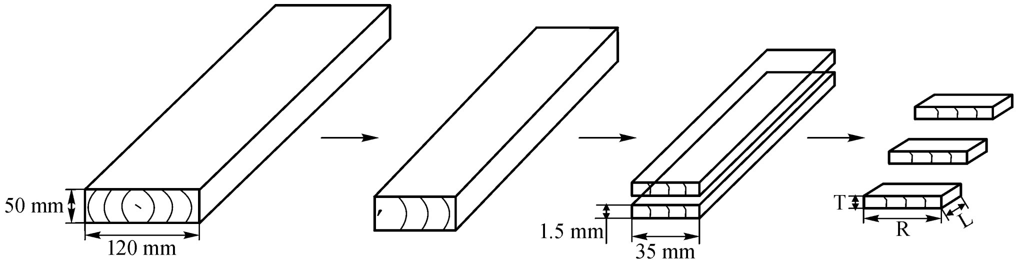

Fig. 1 Sawing method for test specimens

24 h. After these treatments, all specimens were thoroughly dried. Before dynamic mechanical analysis (DMA) measurements, the samples were enclosed in sealed plastic bags and kept in a silica gel desiccator.

2.3 Measurements of dynamic viscoelastic properties

The dynamic viscoelastic behavior was measured using a TA instrument, DMA 2980, in the temperature range of −120 to 250°C with a programmed heating rate of 2°C/min. The cooling system utilizes liquid nitrogen. A tension mode, i.e., the distance between clamping midpoints, of 17.65 mm was used (Fig. 2). The measurement frequencies were 1, 2, 5, and 10 Hz. In the tension tests, the specimens were fixed vertically by means of two clamps. Specimens were clamped on the tangential surfaces and tension occurred in the radial direction. These experiments were performed under a preload force of 0.01 N and a force track of 125%, in order to prevent buckling during the testing process.

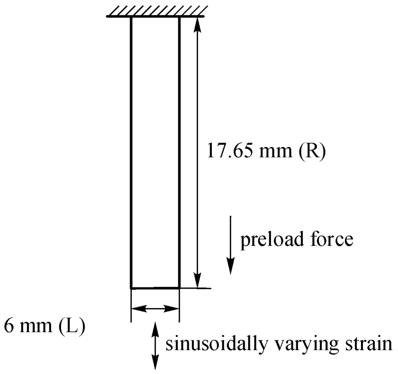

Fig. 2 Sketch map of tension

3 Results and discussion

3.1 Storage modulus

Figure 3 shows the temperature spectra of the storage modulus *E*′ for HTD, LTD, and FVD wood samples at 1, 2, 5, and 10 Hz. From the *E*′ vs. temperature plot, a generally declining trend of *E*′ with temperature is easily observed for all specimens. This phenomenon can be explained by the fact that the kinetic energy of wood molecules is very low under low temperature conditions; only the motion of some small units such as side-chains, branched-chains, and functional groups can be observed under exterior forces, hence the high *E*′ value. With increasing temperature, the thermal motion energy of wood molecules increases and a segmented motion occurs, leading to a low *E*′ value (He, 2000). In the temperature range between −120 and 20°C, the *E*′ of HTD wood was higher than that of LTD wood. In the temperature range between 20 and 250°C, the curve of the HTD wood was much closer to that of the LTD wood, regardless of the applied frequencies. Over the entire range of test temperatures, the *E*′ was the highest for HTD wood. This was probably due to the fact that the cellulose in the non-crystalline region of the cell wall may, to a certain extent, become crystallized during the HTD process (Hirai et al., 1972). Therefore, HTD wood displayed a higher stiffness than the other two kinds of dried wood. The *E*′ of FVD wood was always found to be the lowest. When the green wood was cooled below the freezing point, ice formed in the cell lumen. As the temperature dropped further, more water emerged from the cell wall by sublimation. The wood cell walls shrank at the same time as the ice lens in the lumen was expanding. Consequently, some physical damage probably occurred in wood cell walls during the FVD drying process (Erickson et al., 1966a, 1966b; Choong et al., 1973; Lu et al., 2005). This damage effectively decreased the stiffness of wood and led to a low *E*′.

Table 1 shows the frequency dependencies of *E*′ at 20°C for HTD, LTD, and FVD specimens. Generally, the *E*′ values of HTD wood were a little higher than those of LTD wood. The values of *E*′ for FVD wood were markedly much lower than those for the HTD and LTD samples. This indicates that the wood, after being dried by a high temperature method, would have a better mechanical performance in an environment at room temperature. For the comparison of *E*′ among the different frequencies, a slight increase in *E*′ with an increase in measurement frequency was observed. This result could be explained by the fact that by increasing the measurement frequency, the segmental motion of the main wood chain lagged behind the change of the exterior force and resulted in a relatively

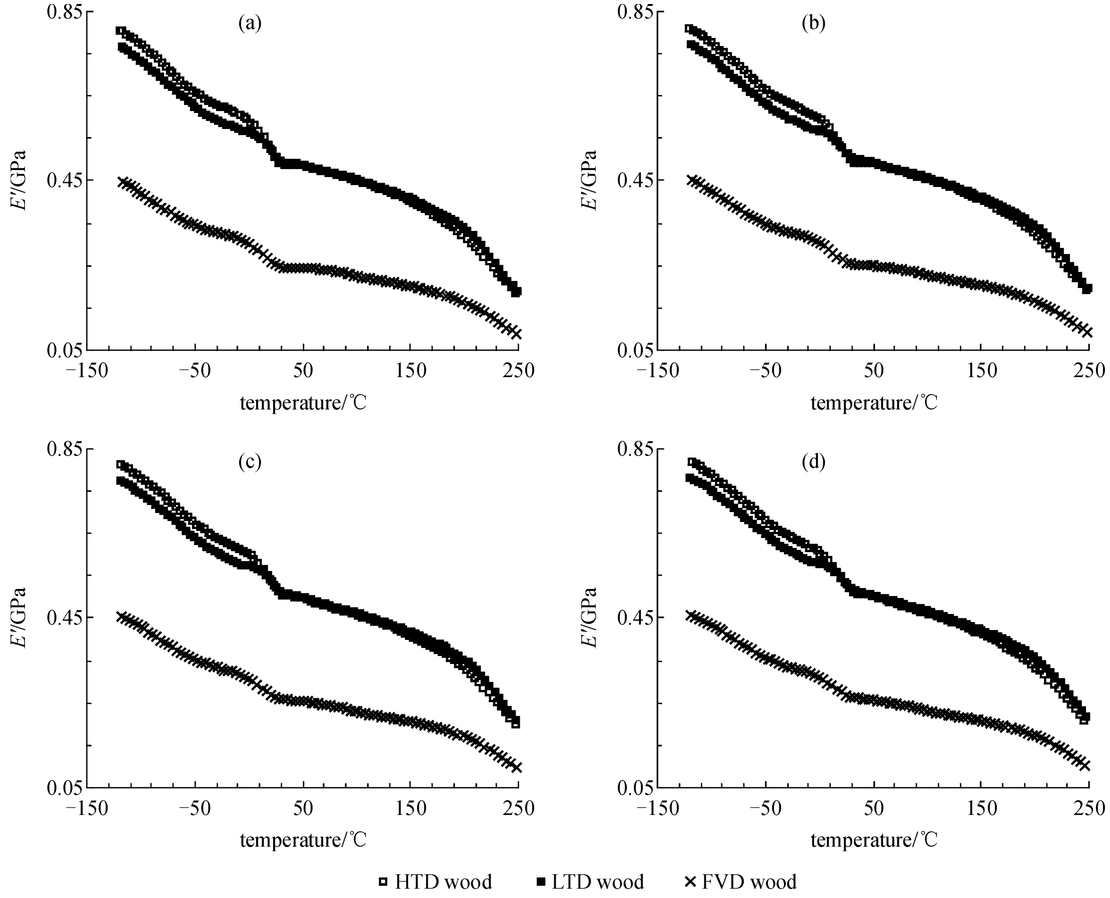

Fig. 3 Temperature spectra of storage modulus for dried wood. (a) 1 Hz; (b) 2 Hz; (c) 5 Hz; (d) 10 Hz.

small interior friction. Therefore, wood showed a rigid behavior.

Table 1 Storage modulus of dried wood measured at 20°C (unit: GPa)

sample	frequency/Hz			
	1	2	5	10
HTD wood	0.54	0.54	0.55	0.56
LTD wood	0.52	0.53	0.54	0.55
FVD wood	0.26	0.27	0.27	0.28

3.2 Loss modulus

Figure 4 shows the temperature spectrum of the loss modulus E'' for HTD, LTD, and FVD samples at 1, 2, 5, and 10 Hz. The highest value of the loss modulus was found for HTD wood and the lowest for FVD wood. Three relaxation processes were observed for both HTD and LTD wood. The loss peak temperatures at around 230, 30, and −70°C were labeled as an α relaxation process, a γ relaxation process, and a δ relaxation process, respectively. In general, it is reported that the thermal-softening temperature range of lignin is about 130–205°C, that of hemicellulose 150–220°C, and for cellulose about 200–250°C (Back and Salmen, 1982). Meanwhile, thermal degradation in the crystalline region of cellulose occurred at about 250–400°C (Chow and Pickeles, 1971). Therefore, the α relaxation process could be attributed to the micro-Brownian motions of wood cell wall polymers in the non-crystalline region (Sugiyama and Norimoto, 1996; Sugiyama et al., 1998). With respect to the γ relaxation process, a few references to a loss peak similar to that transition were found (Nakano et al., 1990; Backman and Lindberg, 2001; Mano, 2002). Nakano et al. (1990) observed a relaxation process at about 10°C and attributed it to the local mode of wood components related to water. Backman and Lindberg (2001) detected a loss peak around −7 to 34°C; their relaxation process related to a glass transition of hemicellulose with low molecular weight. Mano (2002) considered that a relaxation process at 20°C could probably be attributed to a similar glass transition of certain wood components. However, the mechanism of molecular motion for the γ relaxation process is still not clear. The δ relaxation process can be considered as caused by the motions of methyl groups in the amorphous region of cell walls (Kelly et al., 1987). Four relaxation processes were observed for FVD wood. A newly added loss peak at around 120°C was labeled as a *β* relaxation process and attributed to the micro-Brownian motions of lignin molecules (Furuta et al., 2000; Obataya et al., 2003). A *β* relaxation process was not found in HTD wood and LTD wood. The possible reasons for this absence were that both HTD and LTD samples underwent a heating process, and formation of intermolecular cross-linking probably occurred to a certain extent, hence the motion of lignin molecules was restricted. Table 2 shows the frequency dependencies of E'' at 20°C for HTD, LTD, and FVD specimens. The E'' decreased with an increase in measurement frequency.

Table 2 Loss modulus of dried wood measured at 20°C (unit: MPa)

sample	frequency/Hz			
	1	2	5	10
HTD wood	24.14	22.80	20.90	20.12
LTD wood	23.11	21.10	18.97	17.89
FVD wood	13.21	11.98	10.34	9.49

3.3 Loss peak temperature

Table 3 shows the loss peak temperatures for HTD, LTD, and FVD wood at 1, 2, 5, and 10 Hz. A comparison of the *α* loss peak temperature among the three kinds of dried woods shows that the loss peak temperature of HTD wood was much higher than that of LTD and FVD wood, regardless of testing frequency. This indicates that the HTD wood possesses a higher damping and thus more energy is dissipated when molecular motions occur. In general, when wood is heated in the temperature range of 100–200°C, the crystallinity of cellulose increases at its initial stage (Hirai et al., 1972; Kubojima et al., 1998). In our study, HTD was performed at a temperature of 115°C for about 8 h. Therefore, cellulose in the non-crystalline region of the cell walls may become crystallized to some extent during the HTD process. Consequently, HTD wood showed a higher *α* loss peak temperature. For the comparison of the *γ* loss peak temperature in this study, no significant differences and tendencies of loss peak temperature were found among our three kinds of dried wood. A comparison of the *δ* loss peak temperature among

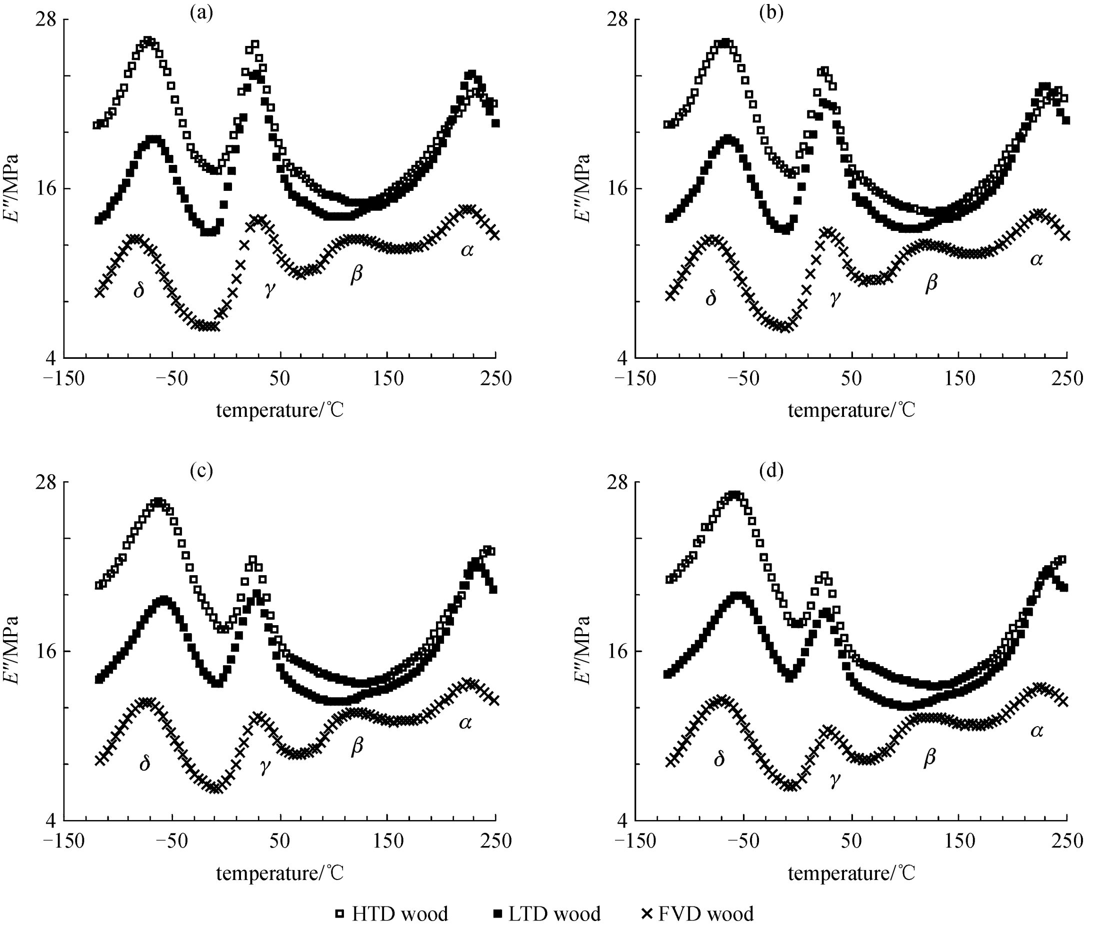

Fig. 4 Temperature spectra of loss modulus for dried wood. (a) 1 Hz; (b) 2 Hz; (c) 5 Hz; (d) 10 Hz.

Table 3 Loss peak temperature for dried wood (unit: °C)

sample	1 Hz				2 Hz				5 Hz				10 Hz			
	α	β	γ	δ	α	β	γ	δ	α	β	γ	δ	α	β	γ	δ
HTD wood	231.5	–	26.9	−72.7	243.4	–	26.6	−65.8	245.1	–	26.2	−62.5	246.9	–	25.9	−59.2
LTD wood	229.0	–	29.2	−70.4	232.7	–	24.7	−63.5	233.4	–	28.5	−56.5	232.1	–	28.1	−53.2
FVD wood	223.2	116.2	33.1	−80.3	222.9	119.6	29.0	−80.7	225.5	122.9	28.7	−73.5	226.3	126.2	28.4	−70.0

HTD, LTD, and FVD wood indicates that the loss peak temperature of FVD wood was much lower than that of HTD and LTD wood.

Given the effect of frequencies on loss peak temperature for HTD, LTD, and FVD wood, all α, β, and δ loss peak temperatures increased with the increase of measurement frequency. For the γ loss peak temperature, no notable regularity of loss peak temperature, with a change in frequency, was found for the three kinds of dried wood. Therefore, the γ relaxation process can be considered as a sub-relaxation process, which needs less molecular motion energy. The mechanism of molecular motion for the γ relaxation process may be attributed to the oscillations of the torso of wood cell wall polymers (Sugiyama et al., 1998).

4 Conclusions

The dynamic viscoelasticities of HTD, LTD, and FVD wood were measured at 1, 2, 5, and 10 Hz over a temperature range of −120 to 250°C. From the results of our tests, we arrive at the following, major conclusions:

1) The storage modulus E' and loss modulus E'' of HTD wood were the highest among three kinds of dried wood, which suggests that HTD wood displays more stiffness than the other two kinds of dried specimens. It was probably due to the cross-linking action or cellulose crystallization during the HTD process. Damage to the wood cell walls during the freeze vacuum drying process probably caused the lowest E' and E'' of FVD wood.

2) Three relaxation processes were detected in the HTD and LTD wood. These were attributed to the micro-Brownian motion of the cell wall polymers in the non-crystalline region, the oscillations of the torso of cell wall polymers, and the motions of the methyl groups of the cell wall polymers in the non-crystalline region in a decreasing order of temperatures at which these occurred. Four relaxation processes were observed for FVD wood. The newly added relaxation was attributed to the micro-Brownian motion of lignin molecules.

3) With respect to different relaxation processes, notable differences of loss peak temperatures were found among the three kinds of dried wood. The effect of measurement frequency on loss peak temperature also showed differences among HTD, LTD, and FVD wood.

Acknowledgement This study was supported by the National Natural Science Foundation of China (Grant No. 30671635).

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