DYNAMIC VISCOELASTIC PROPERTIES OF WOOD TREATED BY THREE DRYING METHODS MEASURED AT HIGH-TEMPERATURE RANGE

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ABSTRACT

The heartwood of Chinese fir was dried by high-temperature drying (HTD), low-temperature drying (LTD), and freeze-vacuum drying (FVD), respectively. The dynamic viscoelastic properties were investigated at a temperature range from 30 to 280°C at frequencies of 0.5–10 Hz using the technique of Dynamic Mechanical Analysis (DMA). The results showed that two relaxations labeled as α and β were detected in the order of the decreasing temperatures at which they occurred, attributed to the micro-Brownian motion of the amorphous cell-wall polymers and the molecular motion of lignin, respectively. The loss peak temperature in β relaxation of HTD wood was the lowest, probably because of the degradation of hemicellulose in the amorphous region. The highest apparent activation energy (ΔE) of HTD wood suggested that more bonds among molecular chains were broken in its segmental motion.

Keywords: Chinese fir, dynamic viscoelastic properties, different drying methods, micro-Brownian motion, apparent activation energy.

INTRODUCTION

Wood, as one of the most important biomaterials, is a bio-composite consisting of three structural components: cellulose, hemicellulose, and lignin. From the point of its structure, wood is composed of highly elongated cells whose walls have a complex multi-layered structure. In each layer, cellulose molecules are grouped together in long filaments called microfibrils embedded in a matrix substance composed of lignin, and hemicelluloses with some amorphous cellulose around the surface of the microfibrils (Sugiyama et al. 1998).

High-temperature drying (HTD) of timber has been used for several years. Drying at temperatures over 100°C is usually referred to as HTD, which is a faster and more economical drying way compared with conventional low-temperature drying (LTD) (Bengtsson and Kliger 2003). It was reported that HTD wood was more dimensionally stable compared with LTD timber (Edvardsen and Sandland 1999). However, it was also reported that HTD decreased the strength of wood and wood materials (Bengtsson and Betzold 2000). Freeze-vacuum

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drying (FVD), widely used in many industries, can preserve the nutritional components and biological properties of dried materials. However, because of the low velocity of mass and heat transfer during FVD process, the energy consumption is large and the drying time is long; thus the research on using FVD method to dry wood was limited.

Besides dimensional stability and strength, viscoelastic properties are of importance for dried timber. Dynamic viscoelastic properties, also known as dynamic mechanical properties, are defined as mechanical behavior occurring under a periodically varying stress or strain. Dynamic viscoelastic properties of wood have been investigated by a number of researchers. Most of their reports focused on dynamic viscoelastic behavior of chemically treated woods (Nakano et al. 1990; Korai and Suzuki 1995; Sugiyama and Norimoto 1996; Obataya et al. 2003; Jiang et al. 2006), and the effects of wood structure (Norimoto 1982; Furuta et al. 1997a; Backman and Lindberg 2001; Mano 2002) and chemical components (Hillis and Rosa 1978; Salmèn 1984; Iida 1986; Furuta et al. 1997b, 2001) on dynamic viscoelastic properties. Based on these studies, it was believed that the chemical components were the most important factor affecting dynamic viscoelasticities. In the meantime, it was reported that wood could undergo changes in chemical components during the drying process (Price and Koch 1980; Hinterstoisser et al. 1992). This implied that the wood chemical components would vary with different drying methods, which would lead to different viscoelasticities of wood. However, to the best of our knowledge, no one has specifically reported the dynamic viscoelastic properties of woods dried by different drying methods. Therefore, the main objective of the current study was to investigate the dynamic viscoelastic behavior of HTD, LTD, and FVD woods with different frequencies and temperature, and to compare the performances of wood dried using different methods. Moreover, the Arrhenius relationship was applied to calculate the apparent activation energy of relaxation processes.

EXPERIMENTAL

Materials and drying procedure

Chinese fir [*Cunninghamia lanceolata* (Lamb.) Hook] green heartwood specimens (moisture content: 70–85%) with dimension of 35 mm × 12 mm × 1 mm (longitudinal × radial × tangential) were examined. All specimens were cut successively in the longitudinal and tangential direction from a wood stick with a cross-section of 120 mm (R) × 50 mm (T) (Fig. 1).

Three kinds of drying methods were applied. HTD and LTD, done in a constant temperature drying chamber, were performed at 115°C for approximately 42 h and at 65°C over 84 h, respectively. FVD was carried out by a freeze-vacuum drying machine (FTS systems) with condensation temperature at −49°C and vacuum degree at 158 mTorr for 25 h. After the treatments mentioned above, all specimens were absolutely dried. Before DMA measurements, the specimens were enclosed in sealed plastic bags and kept in a silica gel desiccator.

Measurements of the dynamic viscoelastic properties

The dynamic viscoelastic properties were measured using a TA instruments® DMA 2980

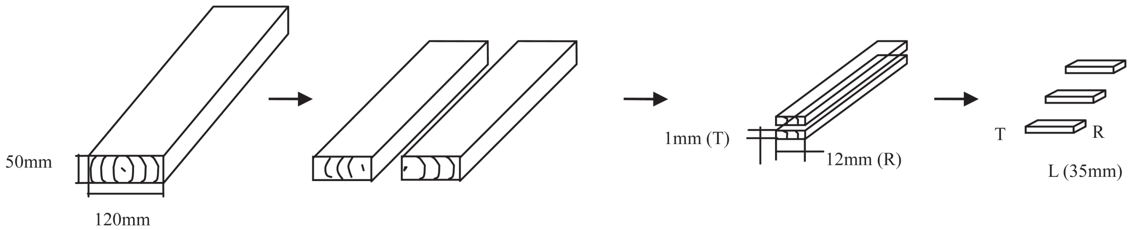

FIG. 1. Sawing method for test specimens.

at a temperature range from 30 to 280°C with a programmed heating rate of 2°C/min. Single cantilever bending mode (distance between clamping midpoints, 17.65 mm) was used. The measurement frequencies were 0.5, 1, 2, 5, and 10 Hz. The displacement amplitude was 15 μm. Specimens were clamped on the radial surfaces and bending occurred in the tangential direction. All experiments were replicated three or five times to confirm the results presented.

When dynamic mechanical analysis (DMA) was performed, the specimens underwent repeated small-amplitude strains in a cyclic manner. Molecules perturbed in this way store a portion of the imparted energy elastically and dissipate a portion in the form of heat. The modulus acquired in this case shows a complex form, $E^* = E' + iE''$. The quantity of E', the storage modulus, is a measure of the energy stored elastically, whereas E'', the loss modulus, is a measure of the energy lost as heat.

RESULTS AND DISCUSSION

Dynamic viscoelastic properties measured at single frequency

Because of wood inhomogeneity, the initial real value of E' and E'' for the specimens could not be the same, even though specimens were prepared by adjacent pairs in order to reduce variation of slices in this study. Therefore, the comparative results of dynamic viscoelastic properties among three kinds of dried woods may be affected. For this reason, the relative E' and the relative E'' normalized with reference to E' and E'' at 30°C were used instead of the real values of E' and E'', respectively, in this paper for comparative study of three dried woods.

Figure 2 shows the temperature dependencies of the relative E' and the relative E'' for HTD, LTD, and FVD woods at 1 Hz. From the relative E' vs. T plot, it can be observed that the relative E' decreased with increasing temperature due to the softening of the material. In the early stage (ca. 30–60°C) and last stage (ca. 220–280°C) of the experiments, strong decreases of relative E' were detected, irrespective of drying methods. In fact, this phenomenon was related with the occurrence of two relaxation processes. In the medium stage (ca. 60–220°C) of the temperature measured, the degree of decrease in relative E' was different among three kinds of dried woods.

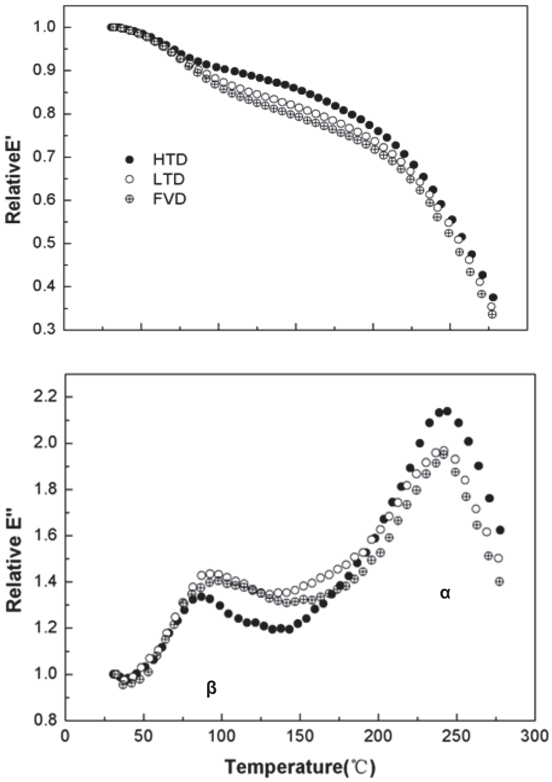

FIG. 2. Temperature dependencies of relative storage modulus E' and relative loss modulus E'' at 1 Hz for three kinds of dried woods. **Notes**: relative E': $E'/E_0' \times 100$, where E' and E_0' represent storage modulus at T and 30°C, respectively. Relative E'': $E''/E_0'' \times 100$, where E'' and E_0'' represent loss modulus at T and 30°C, respectively.

Taniguchi and Nakato (1966) reported that during the heating in the presence of air, the decomposition of cellulose crystal started at about 210°C and proceeded rapidly at 270°C. Chow and Pickeles (1971) studied softening and thermal degradation of wood, and reported the decomposition of cellulose crystals at 250–400°C. In this study, the relative E' of dried woods decreased strongly at 220–280°C; it may indicate that cellulose crystallinity decrease occurred in this temperature range.

In the medium stage (ca. 60–220°C) of experiments, the largest and the smallest decrease in relative E′ was found for FVD wood and HTD wood, respectively (Fig. 2). In general, when wood was heated at the temperature range of 100–200°C, the crystallinity of cellulose increased at the initial stage (Hirai et al. 1972; Kubojima et al. 1998). Hirai et al. (1972) found that the wood dynamic elastic modulus slightly increased after about 100 hours' heating at the relatively low temperature of 100°C, corresponding with the increase in the cellulose crystallinity. In this study, HTD was performed at the temperature of 115°C. Therefore, cellulose in the non-crystalline region of the cell wall may get a crystallized form to a certain extent during HTD process. This could explain the results mentioned above, that is, a smaller decrease in relative E′ for HTD wood than that for LTD and FVD woods (Fig. 2).

From the relative E″ vs. T plot, two relaxation processes were observed for wood dried by three drying methods. The loss peak temperature at around 240°C and 90°C was labeled as α relaxation process and β relaxation process, respectively. The α relaxation process has been observed by many investigators who assigned it to the micro-Brownian motions of wood cell-wall polymers in the non-crystalline region (Sugiyama and Norimoto 1996; Sugiyama et al. 1998). Meanwhile, it was reported that cellulose crystallinity began to decrease in this temperature range (Taniguchi and Nakato 1966; Chow and Pickeles 1971; Schaffer 1973; Moraes et al. 2004). The β relaxation process was attributed to the molecular motion of lignin (Furuta et al. 2000; Obataya et al. 2003).

With respect to comparison of α relaxation process among three dried woods, the intensity of α loss peak of HTD wood was much higher than that of LTD and FVD woods. The possible reasons for the differences in the intensity of α loss peak were that LTD and FVD woods did not undergo high temperature heating process, FVD especially wood was not subjected to any heating history. Therefore, chemical components in FVD wood and their interior crosslink were well protected, and the motion of wood matrix substance was restricted, which resulted in lower intensity in α relaxation of relative E″ than that of HTD wood. Table 1 shows that the α loss peak temperature of HTD, LTD, and FVD woods was about 244.0°C, 241.9°C and 241.7°C, respectively. The α loss peak temperatures of three kinds of dried woods were observed at the similar temperature location; this suggested that micro-Brownian motion of cell-wall polymers in the non-crystalline region occurred almost at the same time for dried woods, irrespective of drying methods.

For the comparison of β relaxation process in this study, the β loss peak temperature of HTD wood was obviously lower than that of the other two kinds of dried woods. According to the results shown in Table 1, the β loss peak temperatures of HTD, LTD, and FVD woods were about 87.0°C, 92.6°C, and 97.8°C, respectively. The difference of loss peak temperature among three kinds of dried woods could be explained by the fact that when wood was heated under a wet condition, thermal deterioration occurred due to degradation of hemicellulose. Hillis (1984) reported that heating wet wood led to thermal degradation and strength loss, probably because of the increase of acetic acid derived from the loss and chemical changes of hemicelluloses during heating. In general, the amorphous region is

TABLE 1. *Loss peak temperatures and apparent activation energy (ΔE_α, ΔE_β) at 0.5~10 Hz with coefficient of determination (R^2_α, R^2_β) of three kinds of dried woods.*

	α (°C)							β (°C)						
Drying methods	0.5 Hz	1 Hz	2 Hz	5 Hz	10 Hz	ΔE_α KJ/mol	R^2_α	0.5 Hz	1 Hz	2 Hz	5 Hz	10 Hz	ΔE_β KJ/mol	R^2_β
HTD	242.3	244.0	244.5	247.0	249.7	906.78	0.96	85.5	87.0	88.5	93.1	98.5	244.13	0.94
LTD	240.1	241.9	242.4	245.9	247.5	859.93	0.97	90.0	92.6	97.6	102.5	106.1	201.01	0.99
FVD	239.3	241.7	242.4	244.9	247.6	835.25	0.98	95.1	97.8	100.3	107.9	118.3	148.63	0.93

HTD: high-temperature drying (115°C); LTD: low-temperature drying (65°C); FVD: freeze-vacuum drying.

composed of the disordered fibers of cellulose, hemicellulose, and lignin molecule, and may retain lower bonding energy, which contributes to the easier thermal degradation in this region than that in crystalline region. The degradation of hemicellulose in the amorphous region released the molecular motion of lignin. Consequently, the β loss peak temperature of HTD wood was observed in the lower temperature region.

Dynamic viscoelastic properties measured at multi-frequency

Figures 3, 4, and 5 show the temperature dependencies of E′ and E″ at 0.5 to 10 Hz for HTD, LTD, and FVD woods, respectively. When the measurement frequency was increased, an increase in E′ and a decrease in E″ were observed, and at the same time, the loss peak temperature location of α relaxation process and β relaxation process shifted to the higher temperature range (Table 1). This result was in agreement with the earlier study (Furuta et al. 2001). In general, molecular motion was influenced by frequency and temperature (He and Chen 2003). Increasing the measurement frequency, the segmental motion of wood main chain lagged behind the change of exterior force, and it would result in a relatively small interior friction. Therefore, wood showed a rigid behavior, and higher temperature was needed to improve the chain segmental motion.

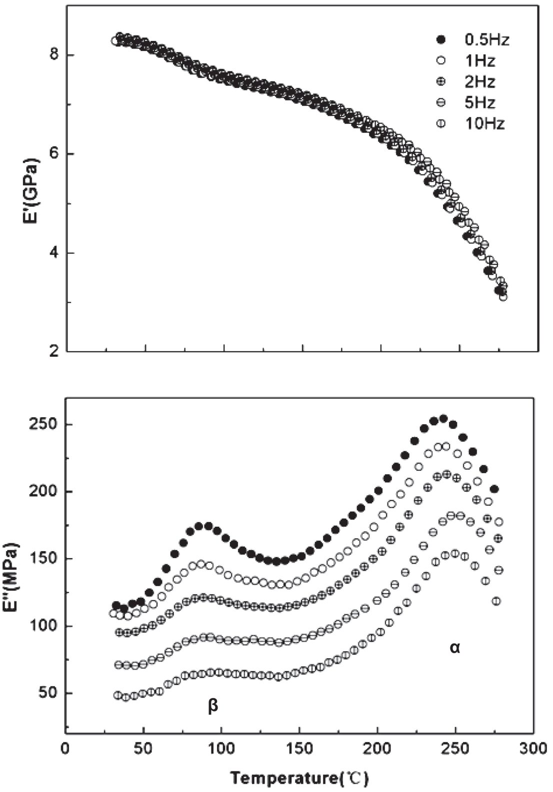

FIG. 3. Temperature dependencies of storage modulus E′ and loss modulus E″ at 0.5, 1, 2, 5, and 10 Hz for HTD wood.

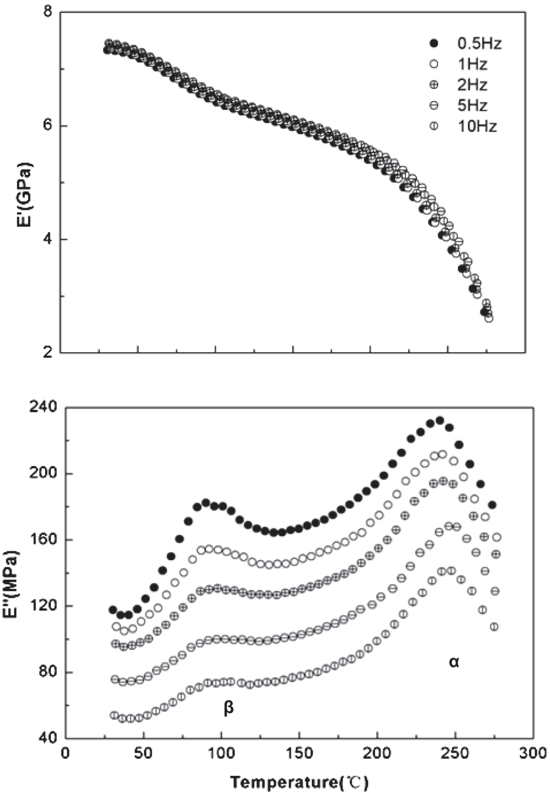

FIG. 4. Temperature dependencies of storage modulus E′ and loss modulus E″ at 0.5, 1, 2, 5, and 10 Hz for LTD wood.

Figure 6 shows the relationship between frequency and change of loss peak temperature (ΔT) for HTD, LTD, and FVD woods. For α relaxation process, when the measurement frequency increased from 0.5 Hz to 10 Hz, ΔT for

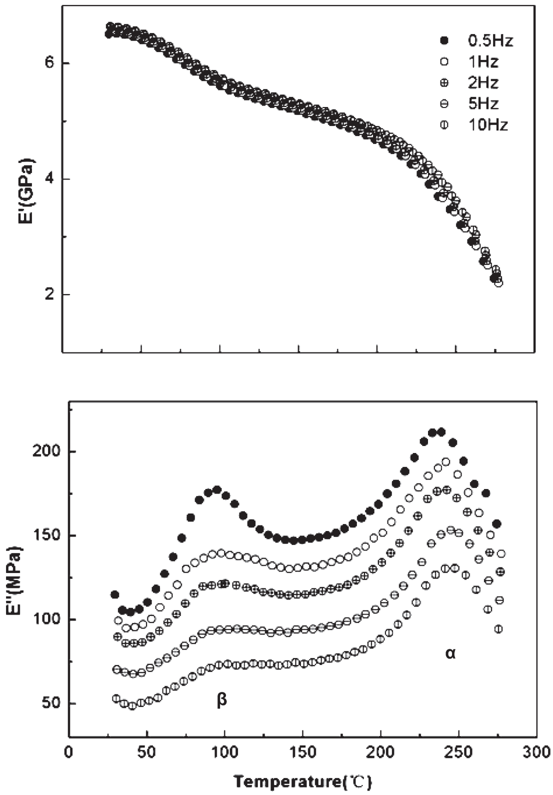

FIG. 5. Temperature dependencies of storage modulus E′ and loss modulus E″ at 0.5, 1, 2, 5, and 10 Hz for FVD wood.

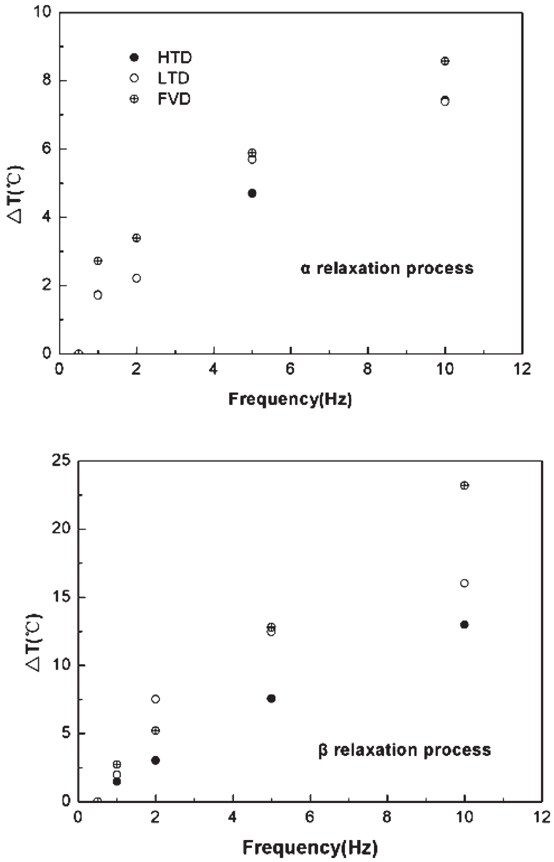

FIG. 6. Relationship between frequency and change of loss peak temperature (ΔT) for three kinds of dried woods.

three kinds of dried woods was about 8°C. As for β relaxation process, notable differences of ΔT were found among dried woods, the ΔT of HTD, LTD, and FVD woods was about 13.0°C, 16.0°C, and 23.2°C, respectively. With the increase of measurement frequency, ΔT of HTD wood was lower than that of the other two kinds of dried woods. It suggested that after high temperature treatments, bonding among wood molecules was released to a certain extent, which led to the acceleration of chain segmental motion. As a result, the temperature range of β relaxation process measured at multi-frequency for HTD wood was narrow. Conversely, wood chemical components and their interior crosslink were well protected after FVD; therefore, broad temperature range dependence on frequency of β relaxation process was observed.

Calculation of apparent activation energy

According to Figs. 3, 4, and 5, considering the relationship between the reciprocal of the absolute temperature (1/T) for the E″ peak and the logarithmic frequency (logf), the value of apparent activation energy (ΔE) was calculated in this study. This method was based on an Arrhenius interpretation of time-temperature equivalence. By using the Arrhenius relation, the value of ΔE can be calculated from the slope of the regression line (Fig. 7). The ΔE values of α and β relaxation processes and the coefficient of determination (R^2) are shown in Table 1. The ΔE value of HTD wood was higher than that of the other two kinds of dried woods. This could be explained by the following points: 1) the relative degree of crystallinity increased due to the crys-

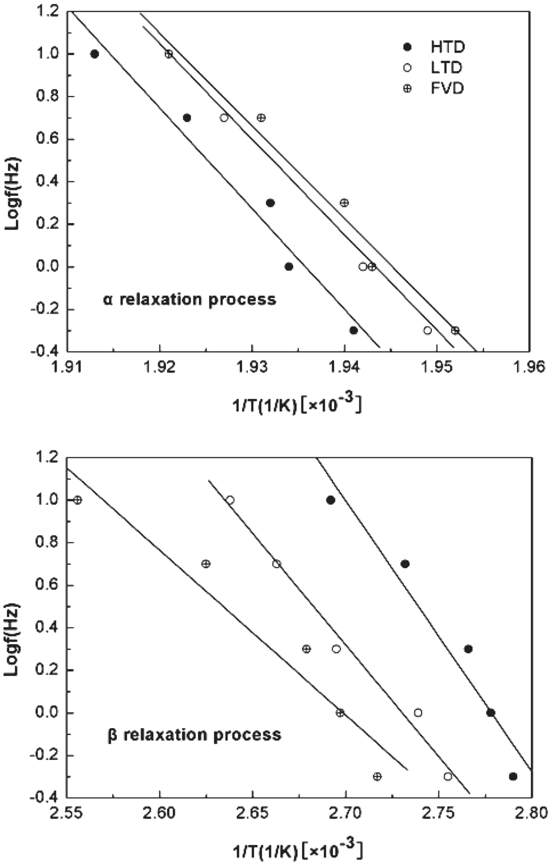

FIG. 7. Relationship between logarithm of frequency (logf) at loss maximum and reciprocal of absolute temperature (1/T) for three kinds of dried woods.

tallization in cellulose amorphous region during HTD process, 2) the formation of intermolecular cross-linking or the aggregation of cellulose molecule accompanied with the decomposition of cell-wall components by high-temperature heating probably occurred (Inoue and Norimoto 1991). Therefore, the segmental motion in HTD wood would be required to break more bonds among molecular chains.

CONCLUSIONS

The dynamic viscoelastic properties of HTD, LTD, and FVD woods were measured at single frequency (1Hz) and multi-frequency (0.5, 1, 2, 5, and 10 Hz) at temperature range from 30 to 280°C, respectively. The apparent activation energy of three kinds of dried woods was calculated using an Arrhenius relationship. The results of these tests led to the following main conclusions:

1. Two relaxation processes were detected in this temperature range. The relaxation process in the higher temperature range was labeled as α process, which was assigned to micro-Brownian motion of cell-wall polymers in the non-crystalline region. The relaxation process in the lower temperature range was labeled as β process, which was attributed to molecular motion of lignin.
2. With respect to single frequency measurement, α loss peak temperature of HTD, LTD, and FVD woods was about 244.0°C, 241.9°C, and 241.7°C, respectively, suggesting that the micro-Brownian motion of cell-wall polymers in the non-crystalline region occurred at a similar temperature location for three kinds of dried woods. β loss peak temperature of HTD, LTD, and FVD woods was about 87.0°C, 92.6°C, and 97.8°C, respectively. HTD wood showed the lowest loss peak temperature in β process due to the degradation of hemicellulose during drying process.
3. In the multi-frequency measurement, with the increase of measurement frequency, loss peak temperature location shifted to a higher temperature range. Apparent activation energy of α process for HTD, LTD, and FVD woods was about 906.78KJ/mol, 859.93 KJ/mol, and 835.25KJ/mol, respectively. Apparent activation energy of β process for HTD, LTD, and FVD woods was about 244.13KJ/mol, 201.01 KJ/mol, and 148.63KJ/mol, respectively. The value of apparent activation energy was higher in HTD wood, which suggested that HTD wood displayed more stiffness than LTD and FVD woods, indicating that more bonds among molecular chains were broken for the segmental motion in HTD wood.

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