Effect of Thermal History on Mechanical Relaxations of Dry Wood Determined in Tensile Mode at Temperatures from −136°C to 120°C

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Abstract

The influence of thermal history on the viscoelastic behavior of Chinese fir wood (*Cunninghamia lanceolata*) was investigated in the temperature range between −136°C and 120°C. The storage modulus (E'), loss modulus (E''), and loss factor (tan δ) of the radial specimens dried over P_2O_5 were determined in tensile mode at multiple frequencies ranging from 0.5 to 10 Hz. Results showed that the E' values of specimens were negatively correlated with the measured temperature. Moreover, δ-relaxation, γ-relaxation, and β-relaxation were detected in the E'' or tan δ spectrum. Wood specimens with thermal history exhibited δ-relaxation, with a corresponding temperature range of −129.3°C to −107.4°C, which has not been previously reported or discussed. The γ-relaxation was also influenced by thermal history; its peak temperature shifted to a higher range. Furthermore, clear differences in the viscoelastic behavior of wood were found between cooling and heating runs. A comparison demonstrated that β-relaxation at approximately 31.9°C to 37.6°C was only observed in the heating run. The β-relaxation peak temperature showed no frequency dependence, but the β-relaxation intensity significantly decreased with increasing frequency. In contrast, both the peak temperature and intensity of δ-relaxation and γ-relaxation showed significant frequency dependence. The apparent activation energy of δ-relaxation and γ-relaxation was 37.24 to 49.87 kJ/mol and 59.69 to 74.30 kJ/mol, respectively, which indicated that δ-relaxation was attributable to limited torsional vibration of groups in the amorphous wood cell walls.

With the advancement of dynamic mechanical analysis, a more refined and comprehensive understanding of the mechanical relaxations of wood has been achieved. The mechanical relaxations of wood, particularly when wet, have been extensively studied by numerous researchers (Salmén 1984, Placet et al. 2007, Havimo 2009, Furuta et al. 2010, Song et al. 2014, Salmén et al. 2016, Li et al. 2020a), as the softening of wood holds significance for many processing and manufacturing operations in the wood industry. This softening of wood is accompanied by a significant decrease in mechanical strength, which is widely attributed to the glass transition of lignin (Salmén 1984, Placet et al. 2007). In contrast, the secondary mechanical relaxations of wood at low temperatures or over short durations are much more complex, and their precise attribution to specific entities is still a subject of controversy.

The peak temperatures of secondary relaxations are closely correlated with wood species, grain orientation, moisture content (MC) of specimens, loading mode, and experiment measurement frequency, as presented in Table 1. In previous studies, the relaxation of completely dry wood specimens of Sitka spruce (*Picea sitchensis*) was determined using the free flexural vibration method and exhibited a single relaxation in the temperature range from −110°C to −93°C, referred to as γ-relaxation, attributed to the motion of methylol

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Table 1.—Summary of information contained in references from the literature on the peak temperature of secondary relaxations of wood.

References	Wood species	Loading mode[a]	Moisture [b]	Frequency	γ-relaxation[c]	β-relaxation[c]
Obataya et al. (1996)	Sitka spruce	Free flexural vibration mode	Absolutely dry; MC: 0.5%–3.2%	33 Hz	E'' peak: −100°C (dry)	E'' peak: around −40°C
Obataya et al. (1998)	Sitka spruce	Free flexural vibration mode	Absolutely dry; MC: 0.5%–3.2%	33 Hz	E'' peak: −100°C (dry)	E'' peak: around −40°C
Sugiyama et al. (1998)	Sitka spruce	Tension mode	Dried at 105°C for 24 hours	11 Hz	tan δ peak: around −110°C	tan δ peak: around −40°C
Backman and Lindberg (2001)	Scots pine	Tension mode	MC: 3%–7%	1 Hz	tan δ peak: −95 to −71°C	tan δ peak: −7°C to 34°C
Obataya et al. (2001)	Sitka spruce	Free flexural vibration mode	Absolutely dry; MC: 3.5%–25.7%	1–110 Hz	E'' peak: −93°C (dry)	E'' peak:−53to −33°C
Jiang and Lu (2006)	Chinese fir	Single-cantilever bending	MC: 4.83%–17.24%	0.5–10 Hz	E'' peak: −118°C to −100°C	E'' peak: 4°C to 32°C
Sun et al. (2007)	Yellow poplar, yellow pine	Single-cantilever bending	Dried over P_2O_5, MC: 0.7%	1 Hz	tan δ peak: −105°C (dry) tan δ peak: −120°C (0.7%)	tan δ peak: 25°C to 50°C (dry) tan δ peak: −50°C, 30°C (0.7%)
Jiang and Lu (2008)	Chinese fir	Single-cantilever bending	MC: 0%–17.5%	1 Hz	E'' peak: −115°C to −82°C	E'' peak: 4∼ 35°C
Jiang and Lu (2009a)	Chinese fir	Tension mode	Dried in a silica gel desiccator	1–10 Hz	E'' peak: −80.7°C to −53.2°C	E'' peak: 25.9°C to 33.1°C
Jiang and Lu (2009b)	Chinese fir	Tension, single-cantilever bending	MC: 3.3%–5.1%	1 Hz	tan δ peak: −95.8°C to −87.1°C	tan δ peak: 2.6°C to 36.1°C
Roig et al. (2017)	Rosewood, ebony, varongy	Torsion rectangular mode	Not mentioned	ω = 1 rad/s	tan δ peak: around −115°C	Not mentioned
Li et al. (2018)	Chinese fir	Tension mode	MC: 0.6%–14.1%	0.5–10 Hz	E'' peak: −113.0°C to −37.3°C	E'' peak: 21.5°C to 39.3°C
Li et al. (2019)	Chinese fir	Tension mode	Dried over P_2O_5	1–10 Hz	E'' peak: −64°C to −38°C	E'' peak: around 12°C
Ashaduzzamana et al. (2020)	Scots pine, obeche, gmelina, alstonia	Three-point bending mode	MC: 8%–9%	0.1–10 Hz	tan δ peak: −114.6°C to −82.7°C	tan δ peak: 4.7°C to 32.3°C
Li et al. (2020b)	Chinese fir	Tension mode	MC: 0.6%–22.0%	1 Hz	tan δ peak: −108.2°C to −84.9°C	Not mentioned
Li et al. (2023)	Chinese fir	Tension mode	MC: 4.4%–25.2%	10 Hz	E'' peak: −112.4°C to −35.0°C tan δ peak: −106.8°C to −27.8°C	Not mentioned

[a] Wood species: Sitka spruce (*Picea sitchensis*); Scots pine (*Pinus sylvestris*); Chinese fir (*Cunninghamia lanceolata*); yellow poplar (*Liriodendron tulipifera*); yellow pine (*Pinus* spp.); ebony (*Diospyros* spp.); obeche (*Triplochiton scleroxylon*); gmelina (*Gmelina arborea*); alstonia (*Alstonia scholaris*).

[b] MC = moisture content.

[c] E'' = loss modulus; tan δ = loss factor.

groups in the amorphous region of wood cell walls (Obataya et al. 1996, 2001). Studies have also reported that at a low MC of 0.7 percent, a new peak appeared at −40°C (33 Hz), and then this peak shifted to lower temperatures with increasing MC (Obataya et al. 1996, 1998). Jiang and coworkers examined the mechanical relaxations of Chinese fir (*Cunninghamia lanceolata*) with different MCs under tension mode in a low-temperature environment (Jiang and Lu 2009a, 2009b; Li et al. 2018, 2020b, 2023; Li et al. 2019). As shown in Table 1, they discovered that γ-relaxation ranged from −112.4°C to −27.8°C and was present across all orthotropic directions, regardless of the amount of adsorbed water. They attributed this γ-relaxation to the reorientation of methylol groups and adsorbed water molecules within the amorphous wood cell walls. While the damping properties of wood with increasing temperature are well investigated, less information is available about the mechanical relaxations of wood during cooling. Li et al. (2020b) investigated the effect of bound water and free water on orthotropic viscoelastic properties during the quenching process in the temperature range from 20°C to −120°C. Wood specimens with bound water in their cell walls exhibited a distinct γ-relaxation, whereas specimens with free water only displayed the high-temperature side of γ-relaxation in three anatomical directions. Further, some recent studies have investigated the viscoelastic behavior of wood during both cooling and heating (Li et al. 2020b, 2023), and these results revealed that the peak temperature of γ-relaxation during cooling was lower than that during heating, irrespective of the amount of adsorbed water. The mismatch in peak temperatures of γ-relaxation between heating and cooling scans might be attributable to physical aging and kinetic effects (Chowdhury et al. 2010, Wan et al. 2018).

Previous researchers have predominantly examined the mechanical relaxations of wood in a certain temperature range, while studies investigating the effect of quenching or heating history on wood mechanical relaxations are sparse. Several studies have investigated the quenching effect on the mechanical properties of wet wood (Furuta et al. 1995; Kudo et al. 2003; Nakano 2005; Iida et al. 2006; Wang et al. 2006, 2008; Miyoshi et al. 2020). Quenching induces structural changes at the molecular level, which, in turn, significantly alter the properties of the wood. Nakano (2005) attributed quenching-induced relaxation to the free volume temporarily created by freezing the molecular chain motion of wood components during the quenching process. Nevertheless, a few studies have investigated the effect of thermal history on the viscoelastic properties of dry wood (Takahashi et al. 2004, Kojiro et al. 2008). Kojiro et al. (2008) found that the unstable microstructure of dry wood was modified by activated molecular motion in the first heating process, and this phenomenon reoccurred after subsequent wetting and drying cycles. Takahashi et al. (2004) reported that wood exhibited greater creep immediately after drying compared with stable wood conditioned over a prolonged period. However, there have been few studies about the effect of thermal history on the mechanical relaxations of wood.

To date, studies on the mechanical relaxations of wood at low temperatures are few, and the effect of thermal history on the secondary relaxations remains unclear. Therefore, the purpose of this present research was to investigate the influence of thermal history on the viscoelastic behavior of dry wood determined in tensile mode between −136°C and 120°C. Additionally, dry wood specimens were subjected to different temperature procedures, including both cooling and heating runs, in order to analyze and parse the effects of different thermal histories on the mechanical relaxations of wood. The results were expected to broaden current knowledge of the secondary mechanical relaxations of dry wood under low-temperature conditions.

Materials and Methods

Wood material

Specimens were obtained from a single 25-year-old Chinese fir tree. The radial specimens were without any visual defects and knots and were cut to dimensions of 35 mm (radial) by 6 mm (longitudinal) by 1.5 mm (tangential) between the 6th and 14th growth rings in the heartwood zone. All wood specimens were dried in a sealed container with anhydrous phosphorus pentoxide (P_2O_5) at room temperature. When the weight variation did not exceed 0.2 percent of the specimen mass at an interval of 2 hours, the constant mass of the specimen was achieved. The corresponding equilibrium MC and basic density of the wood specimens were approximately 0.6 percent and 285 $kg \cdot m^{-3}$, respectively.

Experimental methods

The viscoelastic behavior of wood specimens was evaluated using a dynamic mechanical analyzer (DMA 2980, TA Instruments) with a cooling accessory. The viscoelastic parameters—storage modulus (E'), loss modulus (E''), and loss factor ($\tan \delta = E''/E'$)—were automatically recorded. The cooling system utilized cold nitrogen gas generated from controlled evaporation of liquid nitrogen. Specimens were secured in a tensile clamp with a distance of 18 mm between clamping midpoints. The force track was set to 125 percent, which was enabled to automatically adjust the combined static and dynamic force. The preload force was set at 0.01 N, and a sinusoidal displacement was applied with an amplitude of 15 μm. The measurement frequencies were 0.5, 1, 2, 5, and 10 Hz. After being mounted on the tensile clamp in the testing chamber, wood specimens were subjected to two temperature procedures: Procedure A (a sequential cool/heat/isothermal/cool/heat treatment) and Procedure B (a sequential heat/cool/heat/isothermal/cool/heat treatment), as detailed in Figure 1. Before Procedure B, wood specimens were treated again through an isothermal process at 103°C for 12 hours to obtain completely dry wood specimens.

Results and Discussion

Effect of thermal history on the viscoelastic behavior of dry wood at 10 Hz

Figure 2 shows the temperature dependencies of E', E'', and tan δ values at 10 Hz in the first cooling run in Procedure A with a programmed rate of 2°C/min. The E' value of the specimen at temperatures of 25°C and −136°C was 485.3 and 722.5 MPa, respectively. The E' value of specimens increased with decreasing temperature. Regarding both the E'' and tan δ peaks, a distinct relaxation of wood, labeled as the γ-relaxation, was observed at approximately −60.3°C and −54.4°C, respectively. These results are consistent with

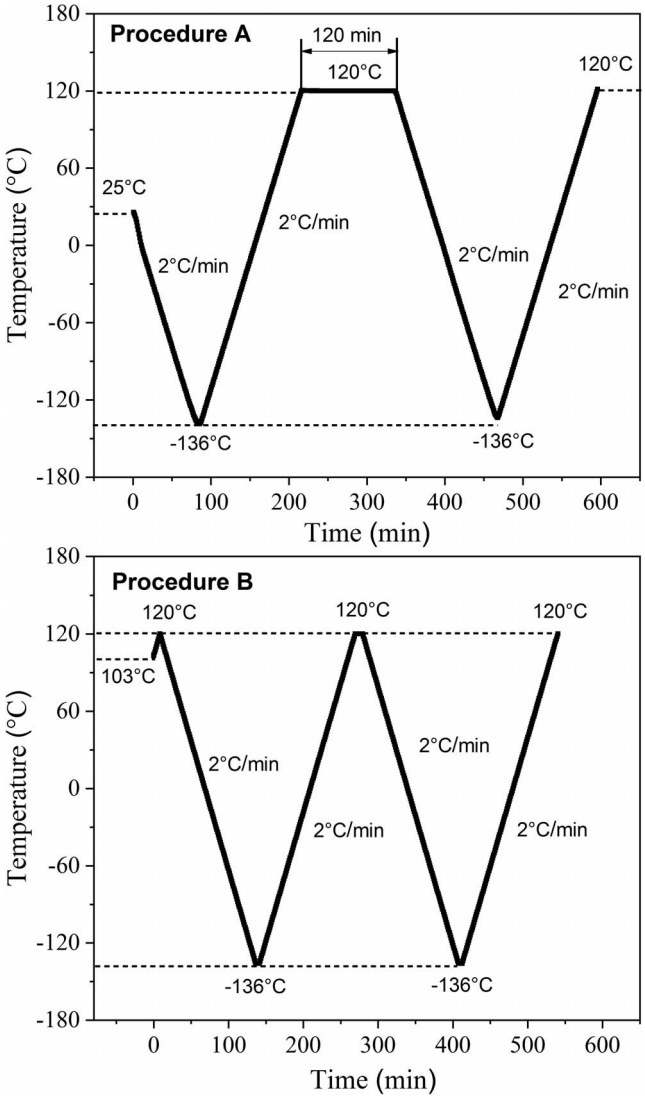

Figure 1.—Experimental setup for the temperature scan tests. Procedure A: sequential cool/heat/isothermal/cool/heat treatments; Procedure B: sequential heat/cool/heat/isothermal/cool/heat treatments. Before tests of Procedure B, wood specimens were treated again by an isothermal process of 103 °C for 12 hours.

those of previous studies (Backman and Lindberg 2001; Jiang and Lu 2009a, 2009b; Li et al. 2018, 2020b, 2023).

Figure 3 presents the subsequent heating run and the second cooling and heating scans of Procedure A for the same specimen. The E' values of specimens were negatively correlated with the measured temperature in the temperature range between −136°C and 120°C. According to the results shown in Figures 3a and 3b, the E' value was highly reproducible in the first and second heating runs of Procedure A. However, the locations of relaxations from the tan δ spectrum significantly differed between the first heating run and the second cooling run (Fig. 3a), and between the first and second heating runs of Procedure A (Figs. 3a and 3b). All tan δ relaxations of wood specimens were secondary, and the intensities of tan δ were below 0.04. In both the first and second heating runs, a distinct relaxation was observed at around 37.5°C, labeled as the β-relaxation, while none was observed in the cooling runs. As seen in Figure 3, the intensity of β-relaxation was larger than that of γ-relaxation. Alongside

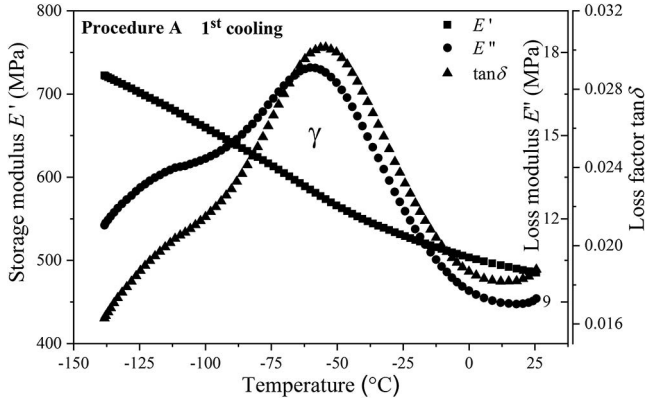

Figure 2.—Temperature dependencies of tensile storage modulus (E'), loss modulus (E''), and loss factor (tan δ) for the radial specimen at a frequency of 10 Hz in the first cooling run in Procedure A.

the occurrence of the β-relaxation, the E' values of specimens significantly decreased with increasing temperature. These facts indicated that the β-relaxation might be attributed to the motion of low-molecular-weight hemicellulose (Backman and Lindberg 2001, Placet et al. 2007, Li et al. 2019), which might be related to a small amount of adsorbed water at low

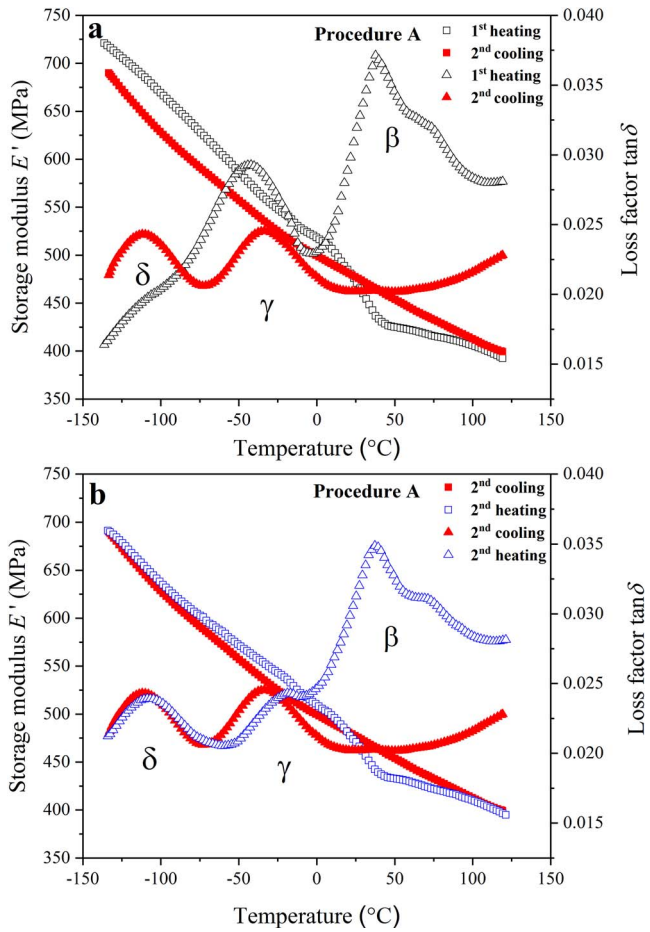

Figure 3.—Temperature dependencies of tensile storage modulus (E') and loss factor (tan δ) for the radial specimen at a frequency of 10 Hz in the first heating run and the second cooling and heating scans of Procedure A.

temperatures. Moreover, the E' value in the heating run was lower than that in the cooling run (Fig. 3b), particularly in the temperature range near the β-relaxation peak. Conversely, in the temperature range below 0°C, lower values of E' were observed in the cooling run compared with the heating run (Figs. 3a and 3b), consistent with previous studies (Li et al. 2023).

In the temperature range below 0°C, a tan δ relaxation at −42.2°C was observed in the first heating run (Fig. 3a), similar to the phenomenon observed in Figure 2. In both subsequent cooling and heating cycles, the specimens of dry wood exhibited two secondary mechanical relaxations (Fig. 3b). One relaxation was detected in the higher-temperature region (around −33.6°C or −18.8°C at 10 Hz), labeled as the γ-relaxation, which was ascribed to the reorientation of methylol groups in the amorphous wood cell walls (Obataya et al. 1996, Sugiyama et al. 1998). One additional relaxation was detected in the relatively lower temperature region (around −119.0°C or −108.9°C at 10 Hz), labeled δ-relaxation. The peak temperatures of both the δ-relaxation and γ-relaxation in the cooling run were lower than those in the heating run. Cooling causes wood polymers to move closer to each other, facilitating the formation of new secondary interactions (Chowdhury et al. 2010, Wan et al. 2018, Li et al. 2023). Once heating begins, extra thermal energy is required to break these new secondary bonds and expand free volume, resulting in the occurrence of these relaxations at relatively higher temperatures in the heating run.

To the best of our knowledge, the observation of the δ-relaxation of dry wood specimens with a corresponding temperature range of −111.9°C to −108.8°C has not been previously reported or discussed, and the mechanism behind it remains unclear. As shown in Table 1, Obataya et al. (2001) demonstrated that dry wood specimens exhibited only one relaxation at around −93°C, and wood specimens with 0.5 percent or 0.7 percent MC exhibited an additional relaxation at −40°C (33 Hz; Obataya et al. 1996, 1998). To exclude the effect of minor MC, wood specimens dried over P_2O_5 were treated again via an isothermal process at 120°C for 120 min (Fig. 1, Procedure A). The secondary relaxation of dry wood specimens has been widely investigated; however, the additional relaxation in the extremely low-temperature region (below −100°C) has not been previously discussed. These results suggest that the side chains, branch chains, and various kinds of functional groups in the amorphous wood cell walls were activated by the 120°C treatment for 120 minutes, making the additional δ-relaxation noticeable only under such conditions. Accordingly, a hypothesis for the thermal history mechanism related to the new secondary relaxation is proposed.

As mentioned in the previous section, the appearance of δ-relaxation is associated with the thermal history of the 120°C treatment for 120 minutes. To investigate the effect of minor variations in MC or the extended duration of the isothermal process, Figure 4 shows the temperature dependencies of E' and tan δ at 10 Hz with cyclical temperature variations between −136°C and 120°C in Procedure B. Before Procedure B tests, wood specimens were treated again through an isothermal process at 103°C for 12 hours to obtain dry wood specimens. As shown in Figure 4b, completely dry wood specimens from the first and second trials of Procedure B exhibited no difference in viscoelastic properties, and the observations were highly reproducible. The changes in E' and tan δ, as well as

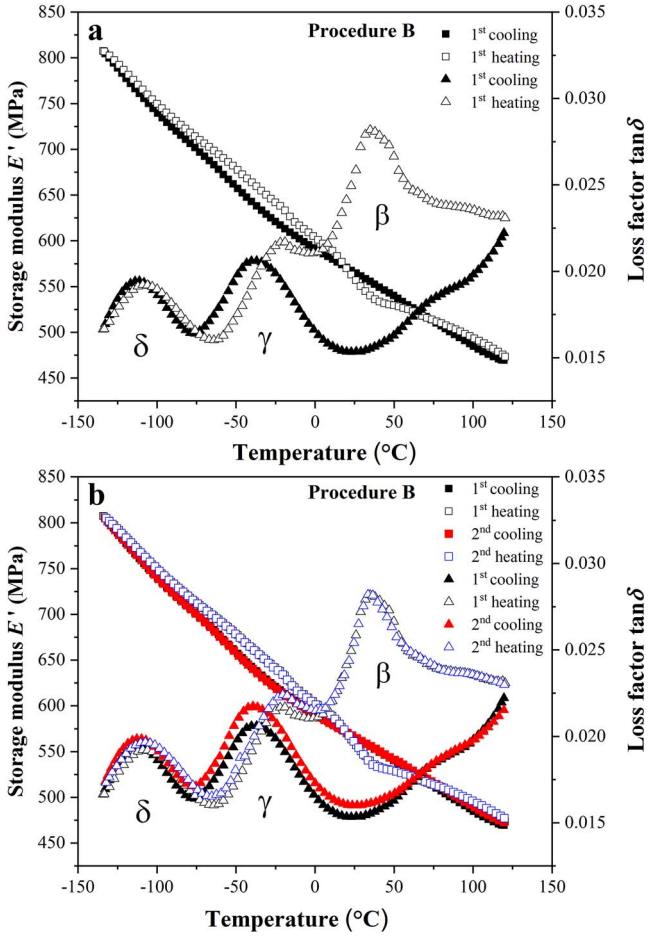

Figure 4.—Temperature dependencies of tensile storage modulus (E') and loss factor (tan δ) for the radial specimen at a frequency of 10 Hz with cyclical temperature variations between 120°C and −136°C in Procedure B.

some secondary relaxations of wood in Procedure B, were similar to those observed in the second cooling and heating runs of Procedure A. The tan δ versus temperature plot depicts three relaxations of wood throughout the −136°C to 120°C temperature range (Figs. 4a and 4b). The three distinct relaxations were labeled as the δ-relaxation, γ-relaxation, and β-relaxation, respectively. An additional new δ-relaxation with a corresponding temperature range of −111.1°C to −107.4°C was observed in the cooling and heating runs, when specimens in the radial direction were subjected to thermal history. This result clarifies that the occurrence of δ-relaxation was not related to minor changes in MC or prolonged thermal treatment. Furthermore, clear differences in γ-relaxation of wood were found between cooling and heating runs. The peak temperature of the γ-relaxation was at around −38.0°C and −20.0°C in the cooling run and heating run, respectively. The γ-relaxation was also influenced by thermal history; its peak temperature shifted to a higher range. Compared with the cooling run, the β-relaxation of wood at around 34.9°C was only observed in the heating run.

Effect of thermal history on the viscoelastic behavior of dry wood at multiple frequencies

Figure 5 depicts the dynamic viscoelastic properties of radial specimens of dry wood measured at 0.5, 1, 2, 5, and

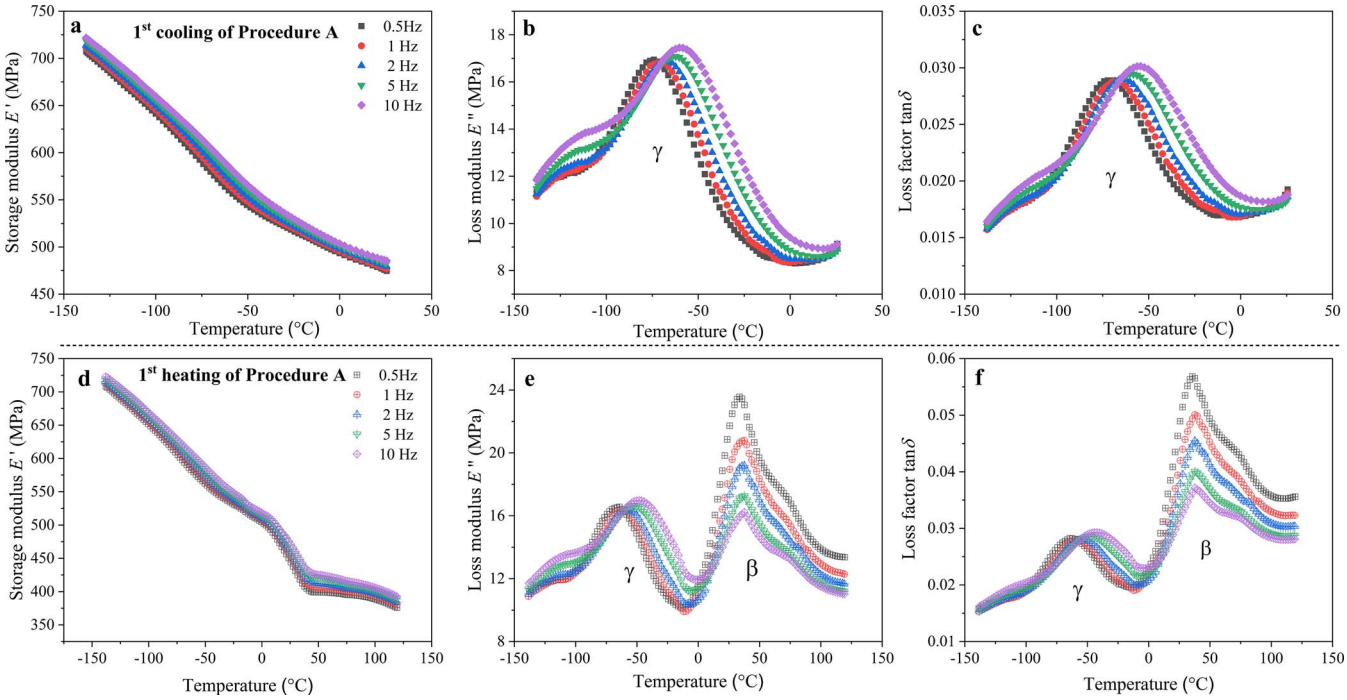

Figure 5.—Temperature dependencies of tensile storage modulus (E′), loss modulus (E″), and loss factor (tan δ) for the radial specimen measured at 0.5, 1, 2, 5, and 10 Hz in the first cooling and heating runs of Procedure A.

10 Hz in the first cooling and heating runs of Procedure A. As the measurement frequency increased, the E' values of wood specimens exhibited a slight increase, and the peak temperature of the γ-relaxation shifted to a higher temperature range (Figs. 5b, 5c, 5e, and 5f). These results agree with those of previous studies (Li et al. 2019, Ashaduzzamana et al. 2020). As the measurement frequency increased, the segmental motion of the wood main chain lagged behind the change in external force, leading to a relatively low internal friction (Jiang and Lu 2009a, Li et al. 2018). At higher frequencies, the movements of the main chain were likely frozen, and small-scale movements dominated, resulting in a stiffer material. Furthermore, the peak temperature of the β-relaxation did not change with frequency, while the intensity of the β-relaxation decreased significantly with increasing frequency. Li et al. (2018) pointed out that the peak temperature of relaxation at around 0°C in the E'' spectrum with different MCs did not change with frequency, which was related to the melting of frozen water. Li et al. (2019) also reported that the relaxation at around 12°C showed frequency independence for wood specimens in the longitudinal direction dried over P_2O_5.

As mentioned in the previous section, major differences in the viscoelastic properties at 10 Hz existed between specimens subjected to the first and second trials of Procedure A (Fig. 3). Accordingly, Figure 6 shows the viscoelastic behavior of radial specimens of dry wood measured at 0.5, 1, 2, 5, and 10 Hz in the second cooling and heating runs of Procedure A. The E' values and γ-relaxation and β-relaxation exhibited similar tendencies as the trends depicted in Figure 5. Moreover, the peak temperature and intensity of δ-relaxation showed frequency dependence. The dynamic viscoelastic properties at multiple frequencies in the first cooling and heating runs of Procedure B are also plotted in Figure 7. Similarly, E' and tan δ and secondary relaxations in Procedure B exhibited frequency dependencies, which were similar to those in the second cooling and heating runs of Procedure A.

Table 2 summarizes the peak temperatures of δ-relaxation and γ-relaxation for the radial specimens of dry wood at multiple frequencies ranging from 0.5 to 10 Hz in the cooling and heating runs of Procedure A and Procedure B. The peak temperatures of δ-relaxation and γ-relaxation ranged from −129.3°C to −107.4°C and from −74.1°C to −18.8°C, respectively. A comparison of the peak temperature of relaxations in the E'' and tan δ spectra revealed that the peak temperature in the E'' spectrum was lower than that in the tan δ spectrum, regardless of the change in temperature mode. Generally, with an increase in frequency, the peak temperatures of δ-relaxation and γ-relaxation of wood shifted to higher ranges, consistent with previous studies (Li et al. 2018, 2023; Li et al. 2019). Furthermore, regardless of the changes in temperature mode, the peak temperatures of both δ-relaxation and γ-relaxation in the cooling run were lower than those in the heating run.

According to the frequency dependence of the peak temperatures of δ-relaxation and γ-relaxation and the relationship between the reciprocal of the absolute relaxation-peak temperature ($1/T$) and the Napierian logarithmic frequency ($\ln f$), the apparent activation energy (ΔH) for the two relaxations of the E'' spectrum was calculated using an Arrhenius plot. The values of ΔH for δ-relaxation and γ-relaxation and the coefficient of determination (R^2) are presented in Table 3. The ΔH values for δ-relaxation and γ-relaxation of wood specimens were 37.24 to 49.87 kJ/mol and 59.69 to 74.30 kJ/mol, respectively, with R^2 values above 0.942. The ΔH for δ-relaxation was lower than that for γ-relaxation, indicating that the motion of the δ-relaxation process needed less

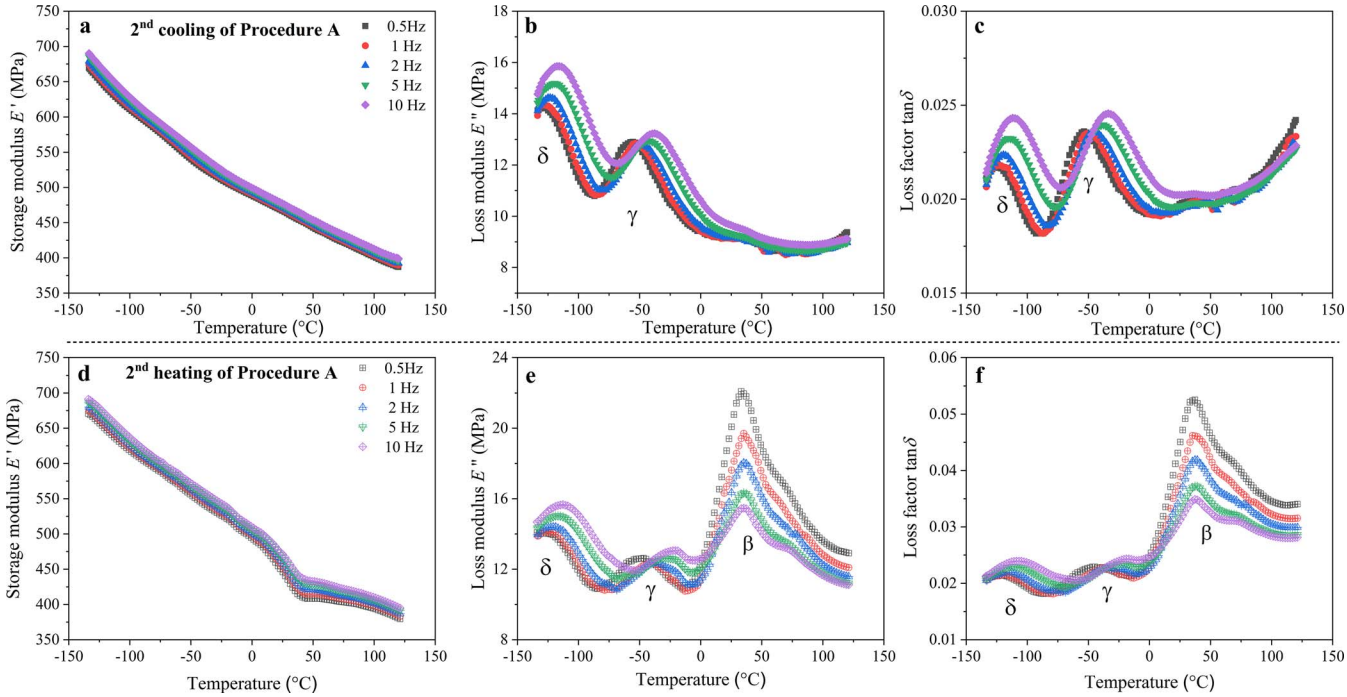

Figure 6.—Temperature dependencies of tensile storage modulus (E′), loss modulus (E″), and loss factor (tan δ) for the radial specimen measured at 0.5, 1, 2, 5, and 10 Hz in the second cooling and heating runs of Procedure A.

energy. As earlier mentioned, the γ-relaxation was attributed to the reorientation of the methylol groups in the wood cell walls (Sugiyama et al. 1998). In summary, the δ-relaxation might be attributable to limited torsional vibration of groups in the amorphous wood cell walls. Furthermore, the ΔH values of δ-relaxation and γ-relaxation in the cooling run were higher than those in the heating run, regardless of the changes in temperature mode, which could signify that the secondary relaxations of wood in the cooling run needed more energy to occur.

Conclusion

The tensile E' value of wood specimens was negatively correlated with the measured temperature. The δ-relaxation,

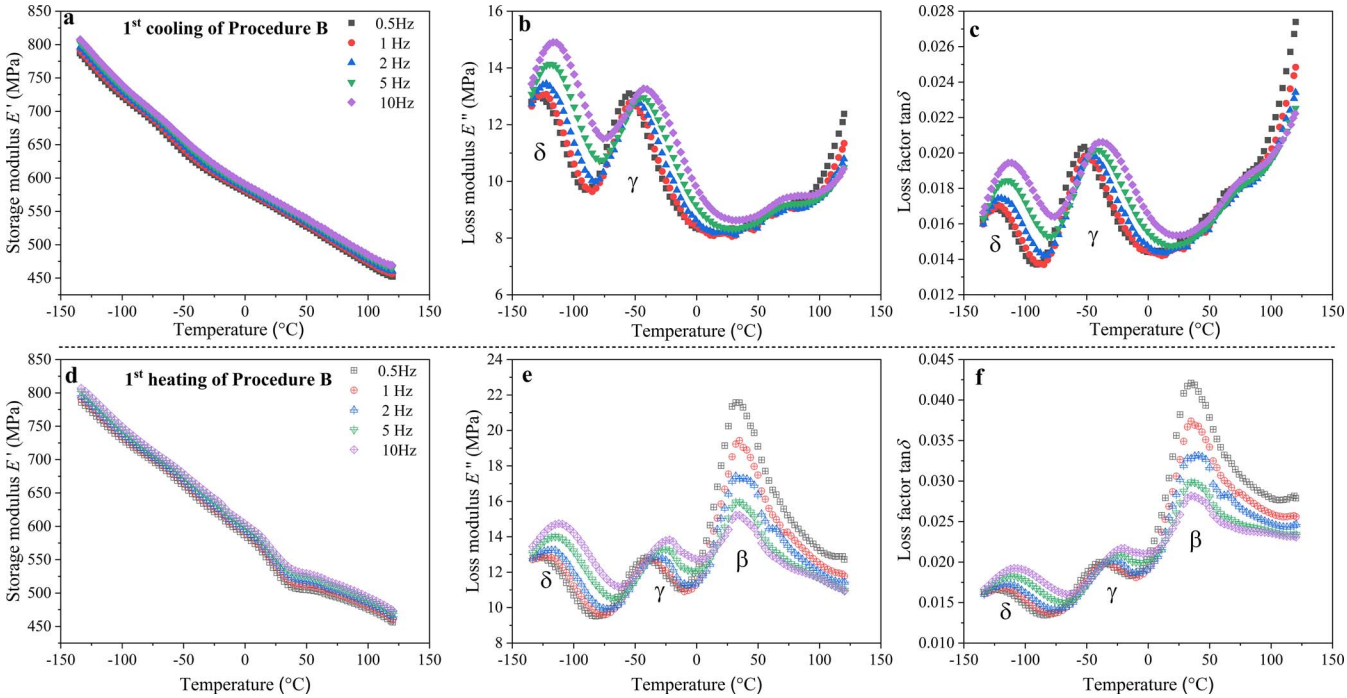

Figure 7.—Temperature dependencies of tensile storage modulus (E′), loss modulus (E″), and loss factor (tan δ) for the radial specimen measured at 0.5, 1, 2, 5, and 10 Hz in the first cooling and heating runs of Procedure B.

Table 2.—The peak temperature of relaxations for radial specimens of dry wood at multiple frequencies ranging from 0.5 to 10 Hz in the cooling and heating runs of Procedure A and Procedure B.

		Peak temperatures of relaxations (°C)									
		δ-relaxation					γ-relaxation				
Temperature spectrum	Test parameters	0.5 Hz	1 Hz	2 Hz	5 Hz	10 Hz	0.5 Hz	1 Hz	2 Hz	5 Hz	10 Hz
E'' spectrum	Procedure A										
	1st cooling	—	—	—	—	—	−74.1	−70.2	−68.2	−62.3	−60.3
	1st heating	—	—	—	—	—	−64.3	−62.3	−58.3	−52.2	−48.3
	2nd cooling	−128.5	−126.7	−123.2	−119.5	−115.8	−55.5	−53.6	−49.5	−41.7	−37.6
	2nd heating	—	−126.5	−120.7	−116.8	−112.8	−46.7	−38.7	−36.8	−28.7	−22.7
	Procedure B										
	1st cooling	−127.7	−124.1	−122.3	−118.9	−115.9	−54.6	−51.6	−46.2	−42.7	−36.6
	1st heating	−127.3	−124.1	−119.8	−116.8	−113.7	−44.6	−38.6	−32.7	−26.7	−22.0
	2nd cooling	−129.3	−126.5	−124.0	−118.4	−115.6	−57.2	−51.2	−49.7	−45.3	−39.3
	2nd heating	−128.3	−122.5	−119.5	−116.5	−113.5	−47.4	−38.4	−32.4	−29.4	−23.4
Tan δ spectrum	Procedure A										
	1st cooling	—	—	—	—	—	−70.2	−68.3	−64.2	−58.3	−54.4
	1st heating	—	—	—	—	—	−64.3	−58.3	−52.3	−48.3	−42.2
	2nd cooling	−124.9	−123.1	−119.5	−115.8	−111.9	−53.5	−51.6	−45.6	−37.6	−33.6
	2nd heating	−120.8	−118.8	−112.7	−110.8	−108.8	−44.7	−38.7	−34.8	−24.7	−18.8
	Procedure B										
	1st cooling	−127.7	−122.0	−119.5	−113.9	−111.1	−52.0	−49.1	−46.1	−43.2	−37.0
	1st heating	−124.0	−118.0	−115.0	−112.0	−109.0	−37.0	−34.0	−28.0	−22.0	−19.0
	2nd cooling	−124.9	−123.4	−121.3	−115.6	−109.8	−51.3	−50.2	−48.2	−42.3	−39.3
	2nd heating	−122.8	−122.5	−119.5	−110.5	−107.4	−47.4	−35.5	−29.3	−23.4	−20.4

γ-relaxation, and β-relaxation of the radial specimens dried over P_2O_5 were detected in the E'' or tan δ temperature spectra between −136°C and 120°C. Alongside the occurrence of β-relaxation, the E' value significantly decreased with increasing temperature. Specimens with thermal history exhibited δ-relaxation, with a corresponding temperature range of −129.3°C to −107.4°C, indicating that the occurrence of mechanical relaxation was not related to minor changes in MC or prolonged thermal treatment. Furthermore, the γ-relaxation was also influenced by thermal history—its peak temperature shifted to a higher temperature range.

Significant differences in viscoelastic behavior were found between specimens subjected to the cooling and heating runs. The peak temperatures of δ-relaxation and γ-relaxation in the cooling run were lower than those in the heating run, while the ΔH of the relaxations showed a contrary tendency.

Table 3.—The apparent activation energy (ΔH) with coefficient of determination (R^2) of δ -relaxation and γ-relaxation in the E' spectrum for radial specimens of dry wood in the cooling and heating runs of Procedure A and Procedure B.

	δ-relaxation		γ-relaxation	
Test parameters	ΔH (kJ/mol)	R^2	ΔH (kJ/mol)	R^2
Procedure A				
1st cooling	—	—	74.28	0.986
1st heating	—	—	69.30	0.989
2nd cooling	43.71	0.994	65.98	0.980
2nd heating	37.24	0.968	60.60	0.979
Procedure B				
1st cooling	49.87	0.991	71.87	0.987
1st heating	42.25	0.987	63.29	0.992
2nd cooling	39.95	0.994	74.30	0.968
2nd heating	39.57	0.953	59.69	0.942

A comparison revealed that the β-relaxation, which ranged from 31.9°C to 37.6°C, was only observed in the heating run. The peak temperature of β-relaxation showed no frequency dependence, but its intensity decreased significantly with increasing frequency. In contrast, the peak temperatures and intensities of δ-relaxation and γ-relaxation showed frequency dependence. The ΔH values of δ-relaxation and γ-relaxation for the radial specimens of dry wood were 37.24 to 49.87 kJ/mol and 59.69 to 74.30 kJ/mol, respectively. The ΔH of δ-relaxation was lower than that of γ-relaxation, indicating that δ-relaxation might be attributable to limited torsional vibration of groups in the amorphous wood cell walls. These mechanical relaxations attributed to specific substances in the wood cell walls and their mechanisms under the action of the external environment should be explored and investigated in depth to enrich the body of knowledge about relaxations of dry wood in low-temperature conditions.

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