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Effects of quenching on relaxation properties of wet wood

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Abstract A new relaxation property is discussed on the basis of creep behavior of wet wood specimens pretreated with heating at various temperatures followed by quenching. The treated samples showed more marked relaxation than that of an untreated sample. The relationship between relaxation time and heating history was represented by an equation $\ln(\lambda) = -(\gamma\alpha_t - k_1)\Delta T + [\ln(\lambda_g) + k_2]$, where $\ln(\lambda)$ is the logarithmic relaxation time of wet samples after quenching, ΔT is the difference between the heating temperature and the glass transition temperature (T_g), $\ln(\lambda_g)$ is the logarithmic relaxation time at T_g , γ is a constant, α_t is the coefficient of thermal bulk expansion, and k_1 and k_2 are constants. It was concluded from the analysis of experimental results that the change in the relaxation property caused by heating and the following quenching is due to the temporary free volume created by freezing of molecular chain motion of wood components, most probably lignin, during quenching.

Key words Heating · Quenching · Relaxation time · Free volume · Wood

Introduction

Mechanical relaxation of wood and wood components, especially when wet, has been examined by many researchers,^{1–6} because softening of wood is important for pulp and paper manufacturing processes. The mechanical properties of wood are not temporary but permanent and reappear in repeated viscoelastic measurements if no degradation oc-

curs by heating. Recently, Furuta et al.,^{7–9} Kudo et al.,^{10,11} and Kamei et al.¹² reported that a new relaxation process appeared following its heating history, especially quenching of wet wood. This relaxation process, which appeared at about 60°C in dynamic mechanical measurement, is completely different from the processes reported so far for wet wood components. The former is thus assumed to be a temporary relaxation process.

The mechanism of this interesting phenomenon has not been discussed in detail and is not yet clarified. A similar phenomenon caused by quenching, however, has already been found for various amorphous polymers and has been analyzed in detail.^{13,14} Amorphous polymers at temperatures below their T_g are to be regarded as solidified supercooled liquids, whose volume, enthalpy, and entropy are greater than those in the equilibrium state. Thus, the approach to equilibrium affects many properties over time such as mechanical relaxation, which is called “Physical aging.” This aging can be explained by the free volume concept.¹⁴ The change for wet wood also appears to be discussed on the basis of the free volume, considering the similarity of results reported so far. In this article, the mechanism of this new relaxation process was analyzed on the basis of the concept of free volume.

Experimental

Yezo spruce (*Picea jezoensis* Carr.) with no defects, which had been kiln-dried, was used as a sample having rectangular dimensions of 0.3 (L) × 8.5 (R) × 1.0 (T) cm, where L, R, and T denote longitudinal, radial, and tangential directions, respectively. All specimens were boiled for 1 h and then placed in water at room temperature for 1 week to remove internal stress.

Two heating treatments were conducted. In the first experiment, samples were quenched to the desired temperature below 60°C at the desired quenching rate after heating in water at various temperatures for 30 min, and then cooled at 25°C for 10 min. In the second experiment, the samples

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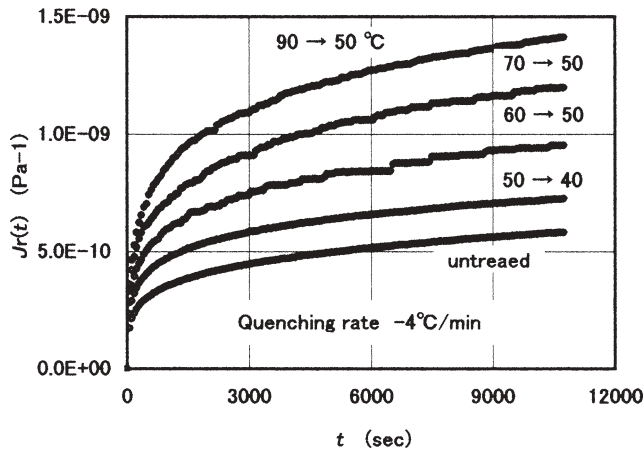


Fig. 1. Dependence of creep compliance at 25°C on heating temperature for heating followed by quenching to the desired temperature at a rate of $-4^\circ\text{C}/\text{min}$. Measurements were carried out immediately after samples were quenched to the desired temperature below 60°C at a rate of $-4^\circ\text{C}/\text{min}$ after heating in water at various temperatures for 30 min and then cooled at 25°C for 10 min

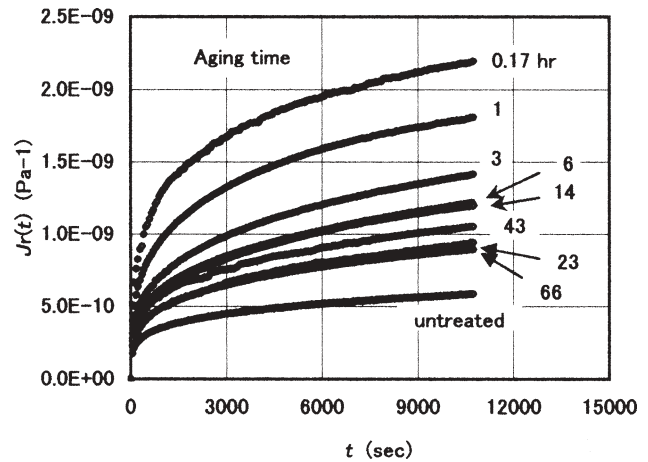


Fig. 2. Dependence of creep compliance at 25°C on aging time after heating at 100°C for 30 min followed by quenching to 25°C . Samples were quenched to 25°C at the desired quenching rate after heating at 100°C for 30 min

were quenched to 25°C at the desired quenching rate after heating at 100°C for 30 min. As such, the aging times of samples in the two experiments are different. Treated samples were subjected to creep measurements at 25°C while wet immediately after the above treatment.

Creep measurements were carried out in a chamber at 25°C by using a cantilever creep apparatus over a 0.06-m span under a load of 0.6 N, which was below 30% of the upper limit load of linearity. Samples were wrapped in polyethylene film to remain wet through the experiment.

Results and discussion

Creep behavior and quenching

Quenching scarcely influenced the instantaneous creep compliance J_0 , values of which varied from 1.8×10^{-9} to $1.9 \times 10^{-9} \text{ Pa}^{-1}$ through all quenching conditions, while the net creep compliance $J_r(t)$ subtracted J_0 from the total creep compliance did remarkably. Figure 1 shows the dependence of $J_r(t)$ on time for a series of samples heated at different temperatures and quenched to the prescribed temperatures at a rate of $-4^\circ\text{C}/\text{min}$. Higher heating temperatures caused a greater degree of relaxation. Creep, however, showed almost no temperature dependence below 50°C . In the relationship between heating temperature and $J_r(10^4)$, for the quenching rate $-4^\circ\text{C}/\text{min}$, $J_r(10^4)$ increased between 50° and 80°C and was constant in the regions less than 50°C and more than 80°C . These results agreed with the results of stress relaxation reported by Kudo et al.^{10,11} and Kamei et al.¹²

Aging time at 25°C after heating influenced the relaxation property as well as heating temperature. Figure 2 shows the dependence of creep compliance on aging time at 25°C for samples treated in boiled water at 100°C followed by quenching in water at 25°C , where $J_r(t)$ of a treated

sample approached that of an untreated sample with the aging time. This implied that the effect of the heating disappeared with the aging time, that is, it is temporary.

The above results suggest that a change of molecular motion of wood components takes place near 60°C , and this is related to the creation of free volume in accordance with an explanation that the relaxation process of amorphous polymers is generally caused by the free volume.¹⁵⁻¹⁷ This is because the effects of heating followed by quenching were related to both the aging time and heating temperature. It should be noted that the free volume creation by quenching is not permanent but temporary, so that the relaxation time is probably quite short.

Analysis of creep behavior by using universal functions

The mechanism of change in relaxation properties caused by heating and quenching of wood could not be quantitatively assessed in detail. We will, therefore, try to clarify the mechanism by using the short and long relaxation times, which are discussed on the basis of the assumption that the relaxation process for treated wood is approximately describable by the following two processes. That is, the relaxation process can be represented by a linear combination of a Kohlrausch-Williams-Watts (KWW) function and a Debye function.

Such a linear combination of the KWW function and Debye function have been used for analysis of various materials.¹⁸⁻²³ The resulting function gives three parameters, short and long relaxation times, and a parameter describing the shape of the time dependence of a relaxation process. It should be noted that this analysis is an approximate method that is based on the assumption that wood has only two relaxation times, which are regarded as the average relaxation times in the shorter and longer regions of the broad distribution of the relaxation time for wood.

This analysis is applied to the net creep compliance $J_r(t)$ without instantaneous creep compliance, because the instantaneous creep compliance J_0 does not vary with all quenching conditions as mentioned above. Then, $J_r(t)$ is represented by two processes which are $J_1(t)$ in the short time region and $J_2(t)$ in the long time region,

$$J_r(t) = J_1(t) + J_2(t) \quad (1)$$

with

$$J_1(t) = J_1(\infty) \left[1 - \exp\left(-\left(t/\lambda_1\right)^\beta\right) \right] \quad (2)$$

$$J_2(t) = J_2(\infty) \left[1 - \exp\left(-\left(t/\lambda_2\right)\right) \right] \quad (3)$$

where λ_1 , λ_2 , and β denote the relaxation time of the KWW function, the relaxation time of the Debye function, and a parameter describing the shape of the time dependence of the creep compliance, respectively. When the Debye function is valid in the longer time region,

$$y = \alpha + \gamma \exp[\mu t] \quad (3-a)$$

where $y = J_r(t)$, $\alpha = J_1(\infty) + J_2(\infty)$, $\gamma = -J_2(\infty)$, $\mu = -1/\lambda_2$. The constants are obtained from the regression curve of Eq. 3-a. We applied Eq. 3-a to $t > 2000$ s and then found the linearity of $\ln[\alpha - J_r(t)]$ versus t for all quenching conditions. We could, therefore, approximate the creep curves for $t > 2000$ s by the Debye function. $J_1(t)$ could be calculated by using $J_2(t)$ considering $J_1(t) = J_r(t) - J_2(t)$. Equation 2 held for $t < 2000$ s, because $\ln[-\ln[1 - J_1(t)/J_1(\infty)]]$ versus $\ln[t]$ for $t < 2000$ had good linearity. That is, the creep curves for $t < 2000$ s are suitably approximated by the KWW function.

Figure 3 shows the dependence of the parameters on aging time at 25°C, which were obtained by using the above procedure. Samples were boiled at 100°C and quenched at 25°C. Relaxation times λ_1 and λ_2 increased with aging time and then leveled off at 10h, while β decreased with aging time and leveled off at 10h when the value was about 0.5. From these results, we found that the relaxation behaviors in both the shorter and longer relaxation time regions were influenced by the heating history and that the effect disappeared after 10h of aging. In general, the distribution of relaxation time broadens with an increase in β and has only one relaxation time for $\beta = 1$. Considering that many polymers have $\beta = 0.5$ for stress relaxation and $\beta = 0.33$ for creep,²⁴ these results show that, in the shorter relaxation time region, the distribution for wet wood was relatively narrow and was broadened with aging.

The effects of heating temperature and quenching rate were not dealt with in the above discussion, although the above analysis clarified the effect of aging time. This is because the comparison of samples heated at different temperatures needed temperature correction for relaxation time, as is mentioned below.

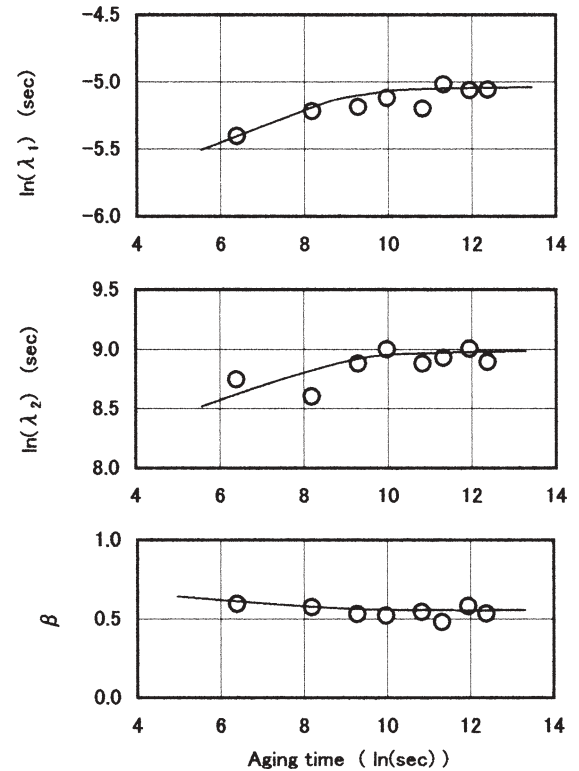


Fig. 3. Dependence of logarithmic relaxation times λ_1 , λ_2 , and β on aging time at 25°C after heating at 100°C followed by quenching to 25°C

Mechanism of change of relaxation property by quenching

The relaxation properties of wood and wood components, which are characterized by the glass transition temperature or softening temperature, have been examined.¹⁻⁶ According to Goring,¹ softening points of wet wood components are 54°–142°C for hemicellulose, 77°–128°C for lignin, and 222°–250°C for cellulose. They are not temporary and reappear in repeated viscoelastic measurements if no degradation occurs by heating, and hence they are different from the new temporary relaxation process in the present work as well as the ones reported by Furuta et al.,⁷⁻⁹ Kudo et al.,^{10,11} and Kamei et al.¹²

Furuta et al.,⁷ who first found the relaxation phenomenon for wood, reported results by dynamic viscoelastic measurements in the temperature region of 10°–95°C for green and wet samples impregnated with water after kiln drying. Their measurement consisted of two trials, that is, the first trial at a heating rate of 5°C/min carried out in the temperature region of 0° to 90°C and the second trial subsequent to the first done under the same conditions after gradual cooling for 15 min from 90° to 0°C. For samples swollen after kiln drying, there were two temperature peaks of $\tan \delta$ at around 50° and 80°C for the first trial and one peak at around 80°C for the second trial. That is, the peak near 50°C disappeared on the second trial. On the other hand, no difference between the first and second trials for the same measurement was observed for green wood. Furuta et al. speculated from the above results that the peak

near 50°C was not caused by wood components but related to strain stored by kiln drying which had not been released by swelling. Results obtained in the present work as well as those obtained by Kudo et al.^{10,11} and Kamei et al.¹² by using static viscoelastic measurements are regarded as the same phenomenon as that reported by Furuta et al.

There arises a question about the mechanism by which this relaxation process occurs. We should then note that quenching causes a change of the relaxation property, which is not permanent but temporary, and that its relaxation time is affected by both the heating temperature and the aging time after quenching.

For polymers, heating above the glass transition temperature (T_g) followed by quenching below T_g changes relaxation properties.^{13,14} Quenching flexible molecular chains heated above T_g influences their rearrangement below T_g so that the mechanical or dielectric relaxation properties change below T_g . The higher the temperature above T_g or the shorter the aging time, the shorter the relaxation time. This is because the free volume increases by heating above T_g and the nonequilibrium state after quenching below T_g approaches the equilibrium state with aging time.

Kovacs¹³ proposed the following equation to explain the above phenomena by the theory of isothermal volume relaxation,

$$\frac{dV_f}{dt} = -\frac{V_f - V_\infty}{\lambda} \quad (4)$$

where V_f , V_∞ , and λ are the momentary value of the free volume, the equilibrium value of the free volume, and the momentary value of the relaxation time, respectively, and t denotes the aging time. On the other hand, Struik¹⁴ assumed the following equation for the relationship between the relaxation time and free volume,

$$\ln(\lambda_\infty/\lambda) = \gamma(V_f - V_\infty) \quad (5)$$

where γ is constant, and λ_∞ is the relaxation time at equilibrium. The relationship between the relaxation time λ and the heating and quenching treatment is derived by using Eqs. 4 and 5.

We applied the above discussion to the aging of wet wood. From the left side of Eq. 4,

$$\frac{dV_f}{dt} = \frac{dV_f}{dT} \frac{dT}{dt} = \alpha_f v_c \quad (6)$$

where T is the absolute temperature, α_f is the coefficient of thermal bulk expansion of the free volume, and v_c is the quenching rate from the heating temperature to the aging one. The α_f is approximately equal to the coefficient of the whole sample. From Eqs. 4–6,

$$\frac{d \ln(\lambda_\infty/\lambda)}{dt} = -\gamma \alpha_f v_c \quad (7)$$

When the quenching rate is constant, from Eq. 7

$$\ln(\lambda) = -\gamma \alpha_f v_c t + \ln(\lambda_0) \quad (8)$$

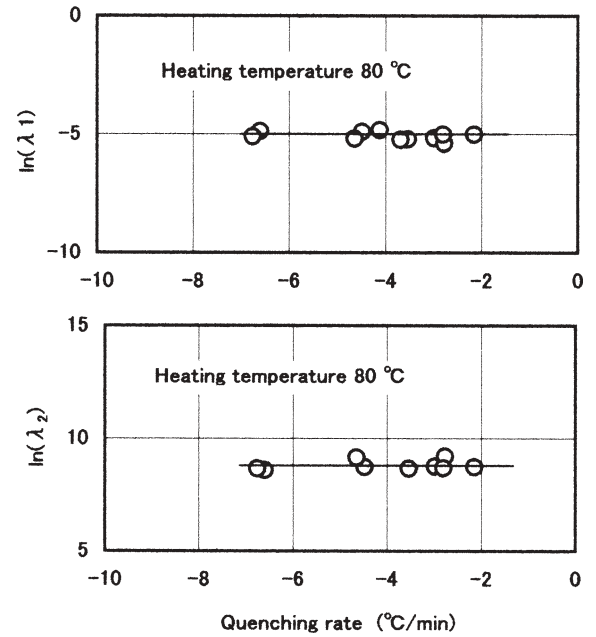


Fig. 4. Dependence of logarithmic relaxation times λ_1 and λ_2 on quenching rate for heating at 80°C followed by quenching to 25°C

where λ_0 is the relaxation time at $t = 0$, in other words, that at the heating temperature. Considering $\Delta T = v_c t$ because $v_c = \text{constant}$: t is the length of time required to quench a sample by ΔT ,

$$\ln(\lambda) = -\gamma \alpha_f \Delta T + \ln(\lambda_0) \quad (9)$$

where ΔT is the difference between the heating temperature and the aging temperature of molecular motion below T_g .

We now know the relationship between λ and ΔT . The above discussion for amorphous polymers probably holds for wet wood, considering Figs. 1 and 2, because the effects of heating followed by quenching on wet wood were closely related to both the aging time and heating temperature as were those of synthetic polymers. We can, therefore, expect that Eqs. 8 or 9 can be applied to quenching of wet wood, when $\ln(\lambda)$ versus ΔT must be linear for $\lambda = \lambda_1$ or λ_2 .

Figure 4 shows a plot of $\ln(\lambda_1)$ and $\ln(\lambda_2)$ versus v_c for samples heated at 80°C followed by quenching to 25°C. It does not show any dependence on the quenching rate. The same result was obtained for the other heating conditions. This is because $\Delta T (= v_c t)$ is constant even when quenching is conducted with a different rate after heating at a particular temperature. This supports the validity of Eq. 9.

It should be noted at this point that λ_0 is the relaxation time at $t = 0$ which is dependent on the heating temperature. Thus, Eq. 9 must be modified to deal with results obtained at different heating temperatures. Considering the result in Fig. 2 and various reports,^{1–6,8,25} the change in relaxation behavior at 60°C appears to be related to wet lignin whose molecular motion at the quenching temperature of 25°C is frozen, whereas wet hemicellulose molecular chains remain flexible according to Furuta et al.⁸

We will use the Williams–Landel–Ferry (WLF) equation to deal with the results at different heating temperatures. The WLF equation is represented as $\ln(a_T) = -c_1(T - T_g)/[c_2 + (T - T_g)]$, where a_T is the shift factor, $c_1 = 17.44$ and $c_2 = 51.6$ are the universal values for amorphous polymers. This equation is approximately applicable to our results, assuming that lignin can be treated as an analog of amorphous polymers, because the lignin chain length between cross-linking points is relatively long so that the molecular chains are flexible under wet conditions. Irvine⁶ discussed application of this principle to lignin. Applying the WLF to Eq. 9,

$$\ln(\lambda) = -\gamma\alpha_f\Delta T + \ln(a_T) + \ln(\lambda_g) \quad (10)$$

where λ_g is the relaxation time at T_g . Then, the heating temperature does not affect this equation. The shift factor can be simply represented by the following relation $\ln(a_T) = k_1\Delta T + k_2$ if $(T - T_g) < c_2$, where k_1 and k_2 are constants. In the present work, $(T - T_g) < c_2$. Thus, from Eq. 10 we have

$$\ln(\lambda) = -(\gamma\alpha_f - k_1)\Delta T + [\ln(\lambda_g) + k_2] \quad (11)$$

This is a conclusion from the discussion on the basis of the free volume concept.

Here, it must be considered whether Eq. 11 is usable for our experiment. It should be examined whether α_f and $[\ln(\lambda_g) + k_2]$ agree with the universal value for amorphous polymers and the value for an unheated sample, respectively. We obtained $\alpha_f = 1.23 \times 10^{-4}$ and $\ln(\lambda_g) = 6.20$ by using $\gamma = 1072$, $k_1 = -0.490$, and $k_2 = -0.777$. The derivation of γ is described in the Appendix. The constants k_1 and k_2 were calculated from the linear regression of $\ln(\lambda)$ versus ΔT . Considering that, according to Ferry,²⁶ the universal value of α_f is 2×10^{-4} to 5×10^{-4} and that the experimental values $[\ln(\lambda_g) + k_2]$ of the untreated sample were -4.76 and 8.67 for λ_1 and λ_2 , respectively, and relationships of $\ln\lambda_1$ and $\ln\lambda_2$ versus ΔT almost agreed with the regression line as shown in Fig. 5, application of Eq. 11 to our results appears to be reasonable.

The conclusion from the above discussion requires that the heating treatment should cause a volume expansion. In this connection, Furuta et al.⁹ reported no dimensional increase in any direction of treated block samples. Their result, however, is consistent with the creation of free volume in wood. The free volume for amorphous polymers is represented by $f = f_g + \alpha_f(T - T_g)$, where $f_g = 0.025$ and $\alpha_f = 2$ to 5×10^{-4} . A free volume increase immediately after heating at 100°C followed by quenching to 60°C was calculated by using this equation. When $T = 373\text{ K}$ (100°C), $T_g = 333\text{ K}$ (60°C), $f_g = 0.025$, and $\alpha_f = 2$ to 5×10^{-4} for lignin, $(f - f_g) = 0.008$ to 0.02 ($= 0.8\%$ to 2%), which is quite a small value. Additionally, lignin content is generally about 30% of wood components. Accordingly, the increase of volume fraction by the created free volume should be very small so that the increase can hardly be observed for a block sample without making an observation by precise microscopy of the wood cell wall.

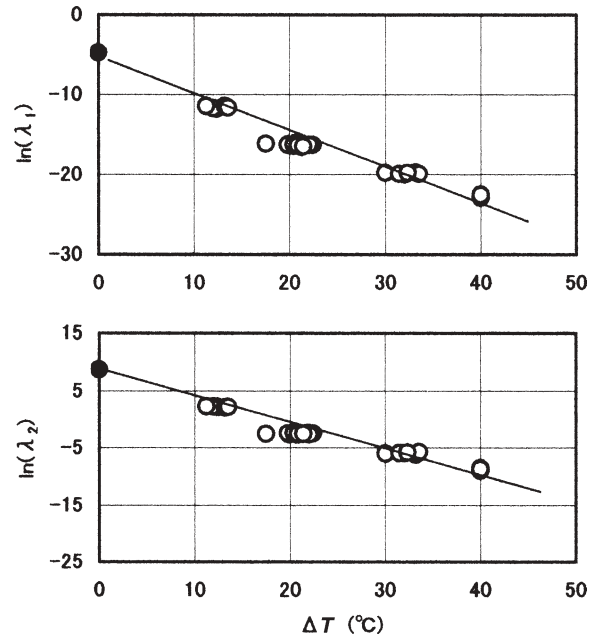


Fig. 5. Dependence of logarithmic relaxation times λ_1 and λ_2 on temperature difference ΔT between heating temperature and the glass transition temperature ($T_g = 60^\circ\text{C}$). Filled circles in the respective figures are for an unheated sample

Conclusions

We conclude for wet wood that an increase in the difference between heating temperature and the glass transition temperature T_g of one of the wood components, probably lignin, reduces the decrease in the relaxation time. In other words, the created free volume, which is temporarily created by freezing the molecular motion of wood components during quenching, decreases the relaxation time, which is proportional to the difference between the heating temperature and T_g . This is the reason why heating followed by quenching causes the characteristic change in relaxation behavior of wet wood.

In the present discussion, we did not consider the effects of the high-order structure of wood such as cell structure, lamella structure, and so on. More precise discussion will be made in the future on the effects of the high-order structure on the current phenomenon.

Appendix

The constant γ in the equation proposed by Struik¹⁴ is determined by the following procedure.

Now, consider a sample quenched after heating. The Struik equation is then represented by

$$\lambda = \lambda_\infty \exp[-\gamma(V - V_\infty)] \quad (a)$$

where V_∞ and V are the free volume long after and immediately after quenching, respectively, λ_∞ and λ are the

corresponding relaxation times, respectively, and γ is a constant. This equation is regarded as an approximation of the following equation which is derived from the Doolittle equation: $\lambda = \lambda_0 \exp[(1/f_0) - (1/f)]$, where f is the free volume ratio and $f = V_f/(V_0 + V_f) \approx V_f/V_0$, f_0 is the free volume at a certain temperature, V_0 is the specific volume. Here, replacing f_0 by f_∞ , we have the following equation as an approximation of the Struik equation.

$$\lambda = \lambda_\infty \exp[(1/f_\infty) - (1/f)] \quad (\text{b})$$

In this article, we consider f_g instead of f_∞ .

We find Eq. (b) is approximated by the linear line represented by Eq. (a) which passes through points $(f_\infty, 0)$ and $(\alpha f_\infty, \lambda_g \exp[(1/f_g) - (1/\alpha f_g)])$. The slope of the linear line is represented by

$$\gamma = \rho / (\alpha f_g^2) \quad (\text{c})$$

where $\rho = 1/V_0$, α is constant and $\alpha \geq 1$. The value of α is determined by the maximum of the free volume ratio. For amorphous polymers, $f_g = 0.025$ and $\alpha_f = 4.8 \times 10^{-4}$, and $f = f_g + \alpha_f (T - T_g)$, where α_f is the coefficient of thermal bulk expansion of the free volume.²⁶ When $T_g = 60^\circ\text{C}$ and the upper limit of temperature is 100°C as in the present work, $f = 0.044$ so that $\alpha \approx 2$. Accordingly, we have $\gamma = 1072$, considering $f_g = 0.025$ and $\rho = 1.34$ for lignin.

The difference between $\ln(\lambda/\lambda_\infty)$ in Eqs. (a) and (b), Δ , is given by

$$\Delta = \left(1 + \frac{1}{\alpha}\right) \frac{1}{f_g} - \left(\frac{1}{f} + \frac{f}{\alpha f_g^2}\right) \quad (\text{d})$$

where $f_0 = f_g$ in Eq. (c). The maximum of difference, Δ_{\max} , is represented by

$$\Delta_{\max} = \frac{(\sqrt{\alpha} - 1)^2}{\alpha} \frac{1}{f_g} \quad (\text{e})$$

when $f = \sqrt{\alpha} f_g$. Thus, we have the following equation as a ratio of the maximum error to the true value of δ .

$$\delta = 1 - \frac{1}{\sqrt{\alpha}} \quad (\text{f})$$

Accordingly, $\delta = 0.29$ from Eq. (f), when $\alpha = 2$. That is, the error obtained by using Eq. (a) under $\alpha = 2$ is 30% of the true value.

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