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Viscoelastic properties of the matrix substance of chemically treated wood

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The temperature variations of the storage modulus and the loss tangent along the grain for four kinds of chemically modified Sitka spruce (*Picea sitchensis* Carr.) woods were measured at 11 Hz over a temperature range of −150 to 200 °C. By using a cell-wall model in which the amorphous matrix substance is disposed parallel to the axis of cellulose fibrils inclined at an angle to the grain direction of the wood, the storage modulus, E_m, and the loss tangent, tan δ_m of the matrix substance were estimated, and the relaxation processes detected were discussed. In formalization, the restriction of the micro-Brownian motion of the main chains due to oxymethylene bridges between the hydroxyl groups resulted in a decrease in tan δ_m above 0 °C. In acetylation and propylene oxide treatment, a marked reduction in E_m was observed over the temperature range tested, by the introduction of bulky side chains, and the tan δ_m remarkably increased in the high-temperature range. In polyethylene glycol (PEG) impregnation, the E_m increased below 20 °C due to the freezing of the micro-Brownian motion of PEG molecules in the cell lumens as well as in the cell walls, while it was reduced above this temperature by the melting of PEG molecules. © *1998 Kluwer Academic Publishers*

1. Introduction

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. Some chemical treatments of wood reach the core of microfibrils, destroying the crystalline structure and eliminating most of the composite structures of wood. Consequently, the resulting material does not have any of the characteristic properties of wood, although it may provide other properties such as thermoplasticity [1]. The chemical treatment of wood presented in this study excludes such radical treatments. In most cases, it affects the amorphous components of the cell wall, the cell lumens sometimes being filled by resins or chemicals. It may reduce some defects relative to wood utilization, enhance the properties, and create new performance or functions, while keeping the bulk of the superior mechanical properties of wood. In order to study how chemical treatments change the properties of wood, it is important to have a clear understanding of the structural modifications of wood by the treatments.

In our previous study [2], the effects of several chemical treatments on the vibrational properties of wood along the grain were quantified through rheological uniaxial modelling. Comparison with experimental data allowed an estimate of the changes of rigidity and viscosity of the amorphous matrix substance in the cell wall at room temperature. However, the assumption that fibrils run along the grain predicted a value of storage modulus much larger than the measured one at high moisture contents or temperatures.

In the present study, the storage modulus and the loss tangent of four kinds of chemically treated woods were measured at 11 Hz over a temperature range of −150 to 200 °C. Furthermore, by using a cell-wall model in which the angle of fibrils was taken into consideration, the storage modulus and the loss tangent of the matrix substance were estimated and the relaxation processes detected were discussed.

2. Experimental procedure

2.1. Materials and treatment procedure

Heartwood of Sitka spruce (*Picea Sitchensis* Carr.) was used. The size of specimens was 70 mm(L) by 50 mm(R) by 1 mm(T). Four kinds of chemical treatments were employed. Formalization was done in a closed vessel with paraformaldehyde and SO_2 (catalyst) at 120 °C for 24 h. Acetylation was performed in neat acetic anhydride at 120 °C for 10 h. Propylene oxide (PO) treatment was done using PO and triethylamine (TEA) (catalyst) in an autoclave at 120 °C for 2 h. Polyethylene glycol (PEG) (molecular weight 1000) impregnation was done by saturating wood specimens first in water and then in a 25% aqueous solution at room temperature for 12 h.

2.2. Measurement of viscoelastic properties

Chemically treated specimens were cut into strips 4 mm wide along the radial direction. They were dried at 105 °C for 24 h, then subjected to viscoelastic measurements. The temperature variations of the storage modulus and the loss tangent along the grain of the treated specimens were measured by the tensile forced oscillation method using an automatic dynamic viscoelastometer (Orientec Co. Ltd., Rheovibron DDV-25FP). The measurements were conducted at 11 Hz over a temperature range of -150 to 200 °C with a programmed heating rate of 1 °C min^{-1}.

3. Results and discussion

3.1. Viscoelastic modelling

As the mechanical properties of the cell wall in the longitudinal (L) direction are mainly governed by those of the thickest S_2 layer, we adopted the simple cell-wall model shown in Fig. 1, in which an amorphous matrix substance composed of lignin and hemicelluloses, with some amorphous cellulose around the surface of microfibrils, is disposed parallel to the axis of mircofibrils (1 direction) inclined at θ to the grain direction of the wood. The complex dynamic modulus of the model along the grain, E_L^*, is expressed by

$$E_L^* = \left[\frac{1}{E_1^*}\cos^4\theta + \left(\frac{1}{G^*} - \frac{2\mu_{12}}{E_1^*}\right)\sin^2\theta\cos^2\theta + \frac{1}{E_2^*}\sin^4\theta\right]^{-1} \qquad (1)$$

where E_1^* and E_2^* are the complex dynamic moduli in the 1 and 2 directions, G^* is the complex shear modulus in the 1–2 plane, and μ_{12} is Poisson's ratio. If θ is small enough to ensure $\sin^4\theta \approx 0$, $\cos^4\theta \approx 1$, and $\sin^2\theta\cos^2\theta \approx \theta^2$, and μ_{12} is much smaller than the real part of E_1^*, the E' and the $\tan\delta$ of wood along the grain, as the first approximation, can be expressed by

$$E'_L \approx \frac{\Delta\gamma}{\gamma_w}\left(\frac{1}{E'_1} + \frac{\theta^2}{G'}\right)^{-1} \qquad (2a)$$

$$\tan\delta \approx \left(\frac{E''_1}{E'^2_1} + \frac{\theta^2 G''}{G'^2}\right)\left(\frac{1}{E'_1} + \frac{\theta^2}{G'}\right)^{-1} \qquad (2b)$$

where Δ is the volume fraction of the S_2 layer in the cell wall, γ and γ_w are the specific gravities of wood and the cell wall, E'_1 and E''_1 are the storage modulus and the loss modulus in the I direction, and G' and G'' the storage shear modulus and the loss shear modulus in the 1–2 plane, respectively. E'_1 and E''_1 are expressed by

$$E'_1 \approx \psi E_f \qquad (3a)$$

$$E''_1 \approx (1-\psi)E_m \tan\delta_m \qquad (3b)$$

where ψ is the volume fraction of the fibrils in the cell wall, E_f is the storage modulus of the fibrils, and E_m and $\tan\delta_m$ are the storage modulus and the loss tangent of the matrix substance, respectively. In the model, the fibrils with square cross-section are embedded in the matrix substance, so that the fibrils and the matrix substance are aligned partly in series and partly in parallel to the direction of shear force. According to the law of mixtures [3], G' and G'' can be expressed by

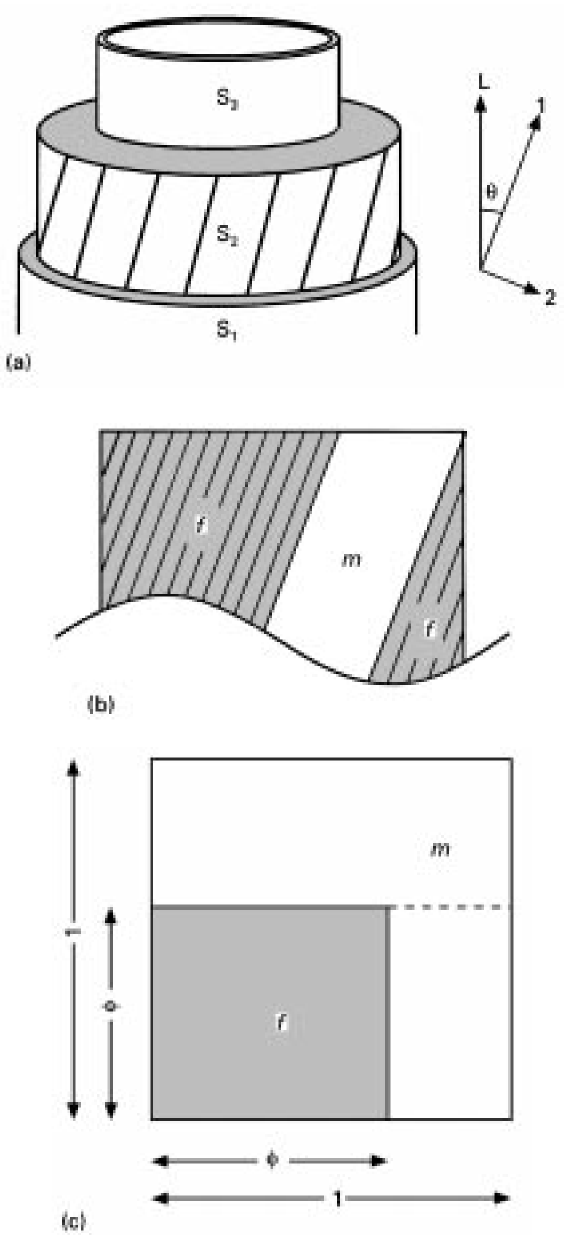

Figure 1 Schematical model for analogies. (a) Cell-wall structure, (b) side view of S_2 layer, (c) cross-section of S_2 layer. L, Longitudinal direction of wood; 1, direction of fibril axis in the S_2 layer; 2, direction perpendicular to the 1 direction; θ, fibril angle to the L direction; f, cellulosic fibrils; m, amorphous matrix substance; ϕ, side length of fibrils.

$$G' \approx G_m\left(1 + \frac{\psi}{1-\psi^{1/2}}\right) \qquad (4a)$$

$$G'' \approx G_m\left(1 + \frac{\psi}{1-\psi^{1/2}}\right)\tan\delta_m \qquad (4b)$$

The experimental values of E', $\tan\delta$, and γ for the untreated and chemically treated woods from -150 to 200 °C were fitted to the equations. For the

TABLE I The values of the volume fraction of fibrils, ψ, and the specific gravity, γ_w, of the cell wall

Treatment	ψ	γ_w
Untreated (U)	0.50	1.45
Formalised (F)	0.43	1.24
Acetylated (A)	0.34	1.06
Propylene oxide treated (PO)	0.31	1.09
Polyethylene glycol impregnated (PG)	0.39	1.54

untreated wood, $\psi = 0.5$, $\gamma_w = 1.45$, $\Delta = 0.84$, $\theta = 0.09$ rad, $E_f = 134$ GPa, and $E_m = 2$ GPa at 20 °C were used [4, 5]. Table I shows the values of ψ and γ_m. For the treated wood, $\psi = 0.32$–0.43 and $\gamma_w = 0.99$–1.62 were estimated from both weight gains and volume swellings.

3.2. Relaxation processes of the matrix substance

The E_m and $\tan\delta_m$ were quantified by eliminating the swelling contribution to the E' and $\tan\delta$ of four kinds of chemically treated woods as well as the untreated wood. The variations of E_m and $\tan\delta_m$ with temperature at 11 Hz for the untreated wood (U) and the formalized wood (F) in a dried condition are compared in Fig. 2. With respect to $\tan\delta_m$ for the untreated wood, four relaxation processes were detected. The relaxation process above 100 °C, labelled α_U, shifted to a lower temperature with increasing moisture content and exhibited a clear peak at high moisture contents below 100 °C [6]. This process was attributed to the micro-Brownian motions of the cell wall polymers in the non-crystalline region [7]. A small $\tan\delta_m$ peak at about 70 °C has been observed by many investigators who assigned it to the torsional oscillations of the cell-wall polymers. However, its location remained unchanged in the measurements at different frequencies. In addition, the peak was not observed in the absolutely dried specimens [8, 9]. It may be ascribed to the segmental motions of the matrix substance activated during the desorption of water. The loss peak at around −40 °C, labelled β_U, was not detected in the absolutely dried specimens and was attributed to the rotational motion of the adsorbed water itself [10]. The $\tan\delta_m$ peak at around −110 °C, labelled γ_U, has been reported to be due to the motions of the CH_2OH groups of the cell-wall polymers in the non-crystalline region [10, 11].

Formalization is a reaction involving the formation of oxymethylene bridges between the hydroxyl groups of the matrix substance by formaldehyde. The formalization of wood remarkably reduces its dimensional instability to moisture and biodegradability with a very small weight increase. An overall improvement to the sound quality of violins in which the sound board or bridge has been formalized, was reported [12]. In formalization, three relaxation processes were observed in $\tan\delta_m$ labelled α_F, β_F and γ_F in the order of decreasing temperature. The cross-linking of chains by OCH_2 bridges between the OH groups in the matrix substance, may restrict the micro-Brownian motion of the matrix substance to some extent, resulting in a decrease in $\tan\delta_m$ above 100 °C. The β_F process is comparable to the β_U process. The loss peak due to the motion of the OCH_2 groups was observed at almost the same temperature location for that of the CH_2OH groups [13]. Therefore, the γ_F process may involve both the motion of the remaining CH_2OH groups and that of the introduced OCH_2 groups.

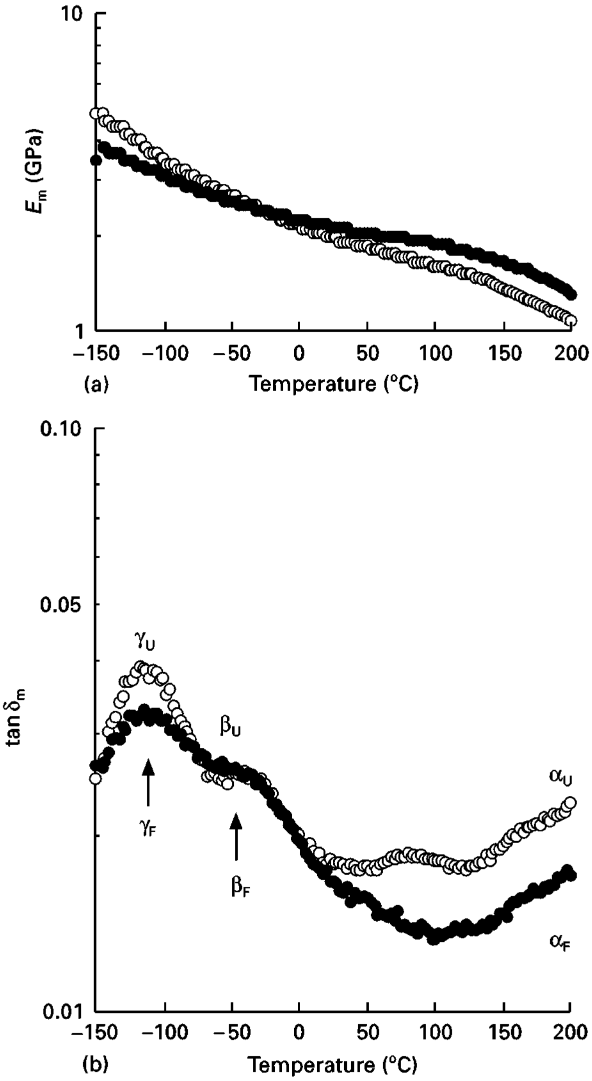

Figure 2 The temperature variations of (a) the storage modulus, E'_m, and (b) the loss tangent, $\tan\delta_m$, at 11 Hz for the matrix substance of the (●) formalized and (○) untreated woods.

In acetylation, hydrophilic hydroxyl groups of the matrix substance are substituted with hydrophobic and bulky acetyl groups. As this provides dimensional stability without toxicity, acetylation is used in bathtubs and on the internal walls of bathrooms, as well as for flooring materials in combination with the impregnation of vinyl polymers. It also improves the resistance to decay and termite attack. The results of the acetylated wood are compared to that of the untreated wood in Fig. 2. Two relaxation processes, labelled α_A and β_A, were recognised in $\tan\delta_m$. The introduction of bulky $OCOCH_3$ groups reduces the cohesive forces between the main chains of the matrix substance and probably facilitates their backbone motion. This effect is similar to that produced by the addition of a plasticizer and is usually known as internal plasticization.

A marked decrease in E_m and a marked increase in $\tan\delta_m$ above 100 °C may be ascribed to the internal plasticization. Thus, the α_A process is assigned to the micro-Brownian motion of the acetylated matrix substance. The loss peak comparable to the β_U process related to water desorption, was not recognized in the acetylated wood because of a reduction in hygroscopicity. As most of the OH groups in the matrix substance are replaced by the $OCOCH_3$ groups at about 20% WPG, the motions of the $OCOCH_3$ groups instead of the CH_2OH groups ought to occur. The β_A peak location agreed well with that due to the motions of the $OCOCH_3$ groups in cellulose acetate [14].

In propylene oxide treatment, hydroxyl groups of the matrix substance are substituted with hydrophilic and bulky $OCH_2CH(OH)C_2H_5$ groups. This treatment improves dimensional stability and, at the same time, yields high hygroscopicity. It also improves the resistance to decay. The results of the PO treated wood are shown in Fig. 3. The E_m was smaller than those of the untreated wood over the temperature range tested, especially above 100 °C. Three relaxation processes, labelled α_{PO} to γ_{PO}, were detected in $\tan\delta_m$. As the introduced $OCH_2CH(OH)C_2H_5$ groups are bulkier and more flexible than the $OCOCH_3$ groups, the matrix substance is much plasticized. So, the α_{PO} peak was observed within the temperature range tested. The treatment reduces hygroscopicity at low relative humidity levels, so the β_{PO} process due to the adsorbed water became less distinct. The introduced side chain contains the OCH_2 groups whose motion may be responsible for the γ_{PO} process as in the γ_F process.

Polyethylene glycol (PEG) molecules with molecular weights of 1000 can penetrate the cell wall [15] and this bulking of the cell wall leads to a decrease in additional swelling by moisture adsorption. The results of the PEG impregnated wood are shown in Fig. 5. The E_m was larger than that of the untreated wood below 0 °C, but became smaller above this temperature. Three peaks were observed in $\tan\delta_m$ labelled α_{PG}, β_{PG}, and γ_{PG} in order of decreasing temperature. PEG molecules in the cell wall act as plasticizers, which leads to an extreme reduction in the cohesive forces of the molecules. The α_{PG} was attributed to the

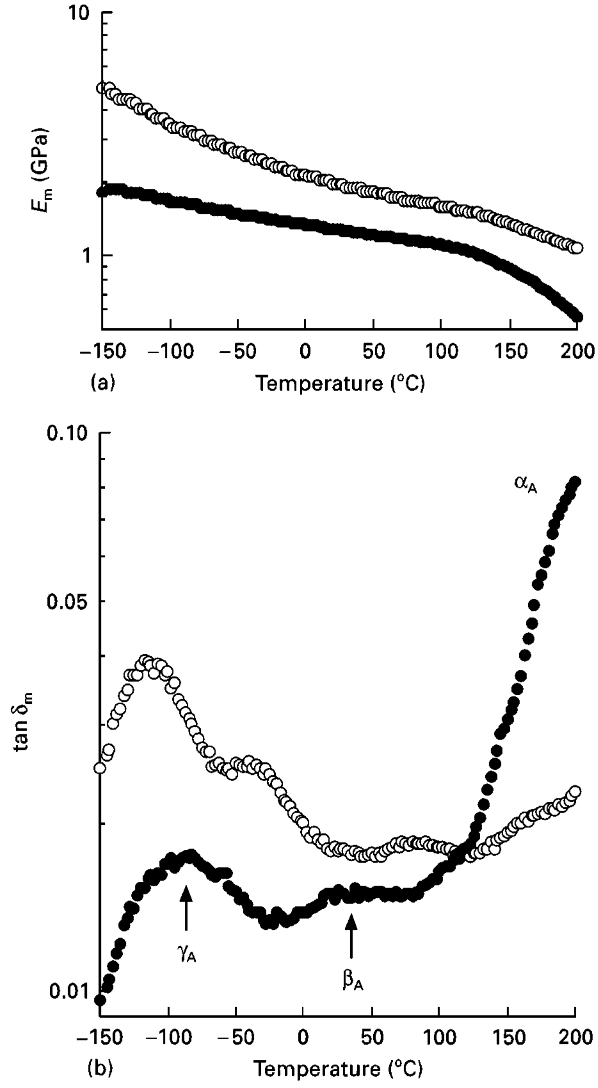

Figure 3 The temperature variations of (a) the storage modulus, E_m, and (b) the loss tangent, $\tan\delta_m$, at 11 Hz for the matrix substance of the (●) acetylated and (○) untreated woods.

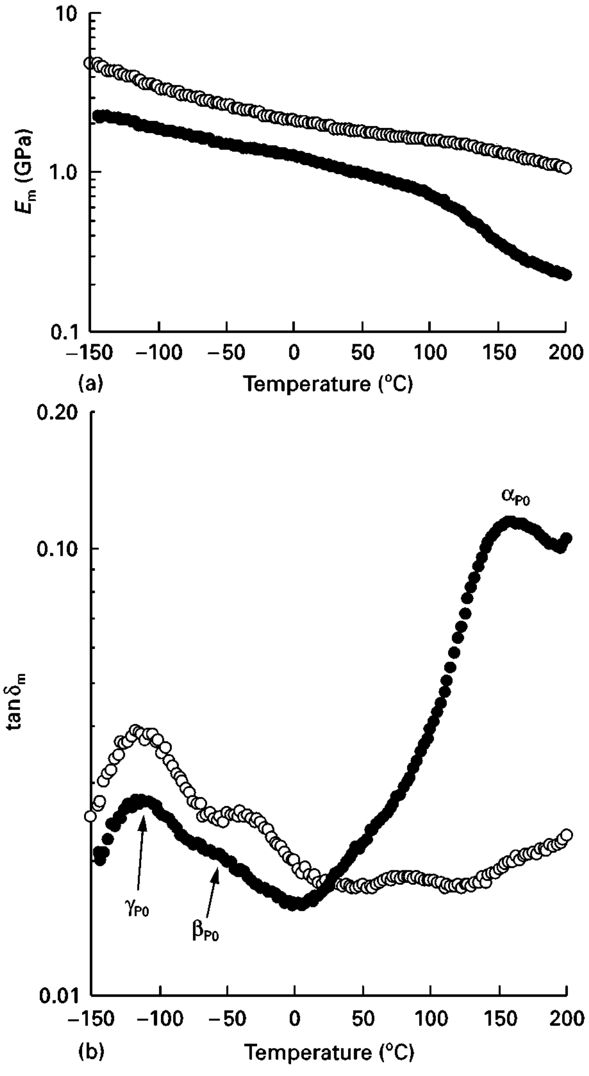

Figure 4 The temperature variations of (a) the storage modulus, E_m, and (b) the loss tangent, $\tan\delta_m$, at 11 Hz for the matrix substance of the (●) propylene oxide treated and (○) untreated woods.

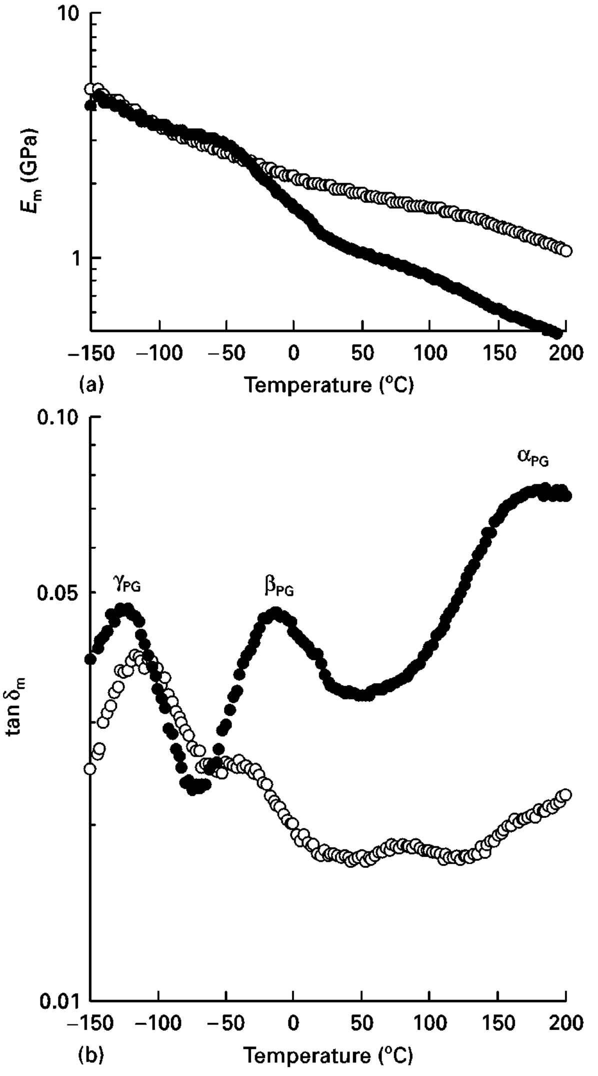

Figure 5 The temperature variations of (a) the storage modulus, E_m, and (b) the loss tangent, tan δ_m, at 11 Hz for the matrix substance of the (●) polyethylene glycol (1000) impregnated and (○) untreated woods.

micro-Brownian motion of the matrix substance plasticized with PEG molecules [15]. The tan δ_m of the glass fibres impregnated with PEG had a peak between −50 and 0 °C. The apparent activation energy for this process estimated from the measurement at five different frequencies was about 40 kcal mol^{-1}, which suggested a mechanism involving the chain backbone motion of PEG molecules. On the other hand, tan δ_m increased remarkably above 20 °C which corresponded almost to the melting point of PEG. Therefore, this sharp increase in tan δ_m may be related to the flow of PEG molecules. The β_{PG} process was not recognized in PEG. The PEG molecules in the cell wall plasticize the matrix substance, but at same time their micro-Brownian motion must be restricted to some extent by the matrix molecules. This may lead to a shift of the peak due to the micro-Brownian motion of PEG molecules to a higher temperature. The γ_{PG} peak occurred about 20 °C below the γ_U peak temperature and its value was rather large. This fact suggested that the mobility was considerably enhanced by the cell-wall swelling. The relationship between the logarithm of tan δ_m and the logarithm of E_m at 20 °C is shown in Fig. 6. The tan δ_m of the

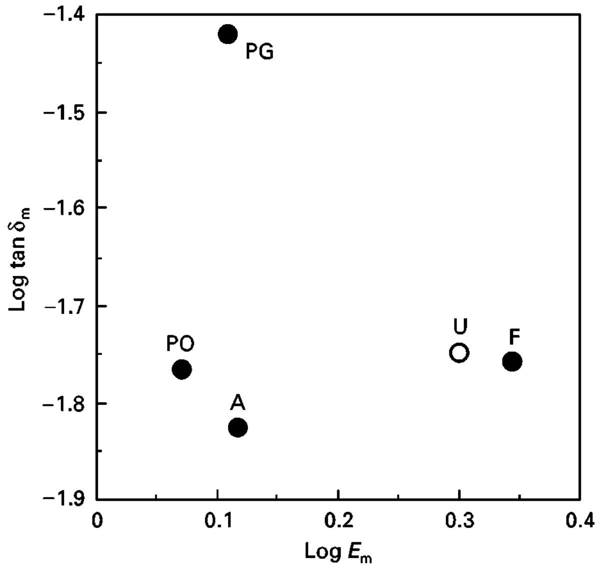

Figure 6 The relationships between the logarithms of loss tangent, log tan δ_m, and the logarithm of dynamic moduli, log E_m, of the matrix substances for the untreated and chemically modified woods at 11 Hz and 20 °C. For key, see Table I.

untreated wood and the treated woods, except the PEG-impregnated wood, showed almost the same values, because no relaxation process existed at this temperature. The large value of tan δ_m of the PEG-impregnated wood was attributed to the existence of the β_{PG} process. The smaller E_m of both the acetylated and propylene oxide treated woods was ascribed to the swelling of the matrix substance by the treatments. A slight increase of E_m by formalization was related to the cross-linking formation. In PEG treatment, E_m was larger than that of the untreated wood below 20 °C due to the freezing of the micro-Brownian motion of PEG molecules in the cell lumens, as well as in the cell walls, but it was reduced above this temperature by the melting of PEG molecules. The E_m of the PEG-impregnated wood was almost comparable to that of the untreated wood at 20 °C.

4. Conclusion

The viscoelastic properties along the grain for four kinds of chemically treated spruce woods as well as the untreated wood were measured at 11 Hz over a temperature range of −150 to 200 °C. The results were analysed by using the cell-wall model in which the matrix substance composed of lignin and hemicelluloses, with some amorphous cellulose around the surface of microfibrils, is disposed parallel to the axis of microfibrils inclined at an angle to the grain direction of the wood. The storage modulus and the loss tangent of the matrix substance were estimated by fitting the experimental values to the equations derived, and the relaxation processes detected were discussed. Two relaxation processes due to the micro-Brownian motion and the motion of the CH_2OH groups were observed in the absolutely dried untreated wood. In formalized wood, the micro-Brownian motion was restricted by the formation of

OCH_2 bridges between the main chains and the relaxation process due to the motion of OCH_2 groups was observed. The two relaxation processes due to the micro-Brownian motion and the motion of the $OCOCH_3$ groups were recognized in the acetylated wood. Two relaxation processes due to the micro-Brownian motion and the motion of the OCH_2 groups were detected in the propylene oxide treated wood. Three relaxation processes were observed in the PEG-impregnated wood, which were ascribed to the micro-Brownian motion of the matrix substance plasticized with PEG molecules, the micro-Brownian motion of PEG molecules in the cell wall and the motion of the CH_2OH groups.

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