

# Mechanical Relaxation Processes of Wood in the Low-Temperature Range

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**ABSTRACT:** The dynamic viscoelastic properties of untreated and chemically modified wood specimens were determined in the temperature range 123 to 293 K and at constant frequencies. Absolutely dry wood specimens exhibited one relaxation process labeled  $\gamma$  at around 180 K, being attributed to the motions of methylol groups in the amorphous region of the wood constituents. The changes in the  $\gamma$  process due to the chemical modifications were explained by the reduction in the original  $\gamma$  loss peak due to the decrease of methylol groups, and an additional relaxation induced by the other groups introduced. With moisture adsorption, an additional relaxation labeled  $\beta$  was induced at 220–240 K. It appeared only when the wood adsorbed moisture irrespective of chemical modifications, and its characteristics were not affected by the formaldehyde and PEG treatments involving the remarkable changes in the mobility of amorphous molecules. These results suggested that the dominant mechanism of  $\beta$  relaxation was not the segmental motions of the main chain, but the motion of the adsorbed water molecules. The positive activation entropy of the  $\beta$  relaxation was interpreted to reflect rearrangement of the adsorption sites required for the rotation of the adsorbed water molecules. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 3338–3347, 2001

**Key words:** wood; mechanical relaxation; low temperature; chemical modification; water

## INTRODUCTION

Wood is a popular natural polymer mainly consisting of cellulose, hemicellulose, and lignin. Because the physical properties of wood depend strongly on its moisture content, much attention has been paid to the behavior of water molecules adsorbed by the wood. In general, the adsorbed water acts as a plasticizer to decrease the glass-transition temperature of the wood constituents.<sup>1,2</sup> Consequently, the elastic constants of wood and its constituents decrease with water adsorption at room temperature or above.<sup>3–6</sup> At

an extremely low temperature, however, the Young's modulus of wood increases with increasing moisture content.<sup>7</sup> These reversed trends suggest the existence of some transition related to the motion of the adsorbed water. In fact, a clear mechanical, dielectric, or piezoelectric relaxation process occurs in wood and similar natural materials with water adsorption at low temperatures.<sup>8–13</sup> A similar relaxation also occurs in cellulose,<sup>14–18</sup> dextran,<sup>19</sup> amylose,<sup>20</sup> and lignin.<sup>21</sup> Although these “water” relaxations have been frequently attributed to the motions of the polymer–water complex,<sup>8,16</sup> our understanding of the mechanism involved remains incomplete.

Wood dried absolutely shows only one relaxation, often labeled  $\gamma$ , in the low-temperature range. This relaxation is simple and detectable

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mechanically,<sup>11</sup> dielectrically,<sup>22,23</sup> and piezoelectrically.<sup>9</sup> An analogous relaxation is observed in cellulose,<sup>15–18,23,24</sup> amylose,<sup>20</sup> mannan<sup>25,26</sup> and *p*-coumaryl alcohol,<sup>23</sup> but not in dextran,<sup>19</sup> xylan,<sup>25,26</sup> *p*-coumaric acid, or isoeugenol.<sup>23</sup> In addition, the dielectric  $\gamma$  relaxation of cellulose disappears completely when the methylol groups are selectively substituted by triphenylmethyl groups.<sup>27,28</sup> These findings strongly suggest that the  $\gamma$  relaxation is due to the motion of methylol groups. Montes and Cavaille recently reported that dry cellulose exhibited two relaxation processes due to the motions of methylol and hydroxyl groups.<sup>29</sup> They believed a clear dielectric relaxation detected in dry dextran is attributable to the motion of hydroxyl groups. Because the wood contains many active hydroxyl groups, the contribution of hydroxyl groups should be reconsidered to clarify the low-temperature relaxation phenomena of absolutely dry wood.

In this article, the viscoelastic profiles of natural and chemically modified wood specimens are determined in the temperature range 123 to 293 K, and the relaxation processes detected are attributed to the motions of polar groups in the wood constituents and those of the adsorbed water molecules.

## MATERIALS AND METHODS

One hundred Sitka spruce (*Picea Sitchensis* Carr.) specimens of 3 mm (T, tangential direction)  $\times$  15 mm (R, radial direction)  $\times$  150 mm (L, longitudinal direction) were prepared. After conditioning at 298 K and 60% relative humidity (RH) for more than a month, the dynamic Young's modulus ( $E$ ) and loss tangent ( $\tan \delta$ ) were determined using the free-free flexural vibration method. Next, 20 specimens with analogous dynamic viscoelastic properties were selected and divided into five groups. Of these, one group remained untreated and the other three were chemically modified by the following methods; Formaldehyde treatment (F), treated with formaldehyde with SO<sub>2</sub> at 393 K for 24 h; Acetylation (A), treated in acetic anhydride at 393 K for 8 h; Polyethylene glycol impregnation (P), soaked in a 25% aqueous solution of polyethylene glycol (PEG, molecular weight 1000) for a week. After drying under atmospheric conditions and subsequently at 333 K *in vacuo* for a few days, specimens were conditioned at 298 K and various RH levels, and their weight and dimensions were measured.

**Table I Weight Per Gain (WPG) and Swelling in Volume (Sw) of Wood Specimens Due to Chemical Modifications Under Absolutely Dry Conditions**

Treatments	WPG (%)	Sw (%)
Formaldehyde treatment (F)	5.6	1.8
Acetylation (A)	18.4	6.9
Polyethylene glycol impregnation (P)	31.6	11.3

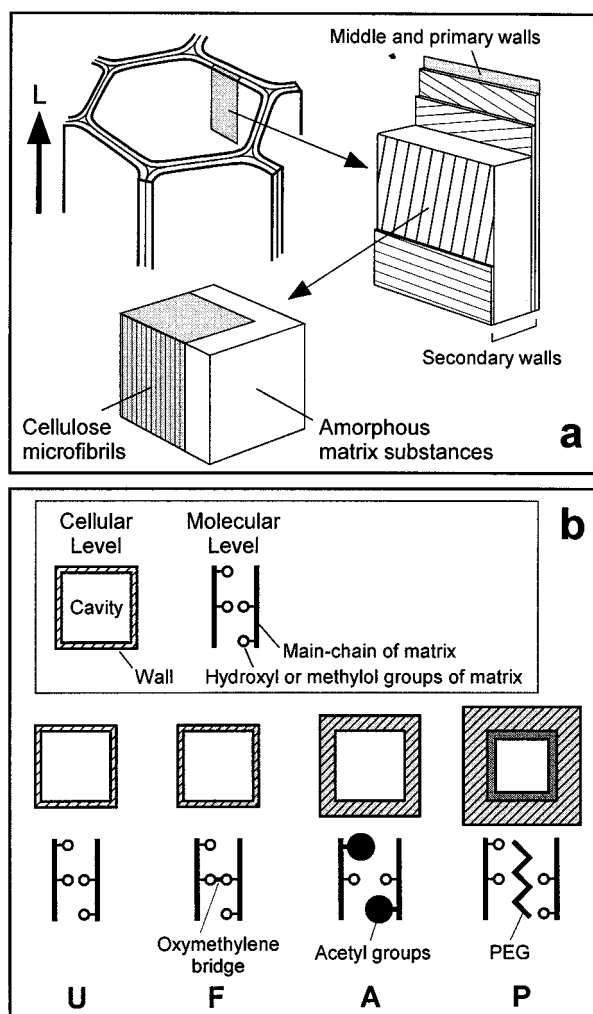
Next, the specimens were cut into strips of 1 mm (T)  $\times$  5 mm (R)  $\times$  70 mm (L). These samples were dried again and then conditioned at 298 K and various RH levels. Some of the samples were dried at 378 K for a day *in vacuo*, to complete the dehydration. Finally, the  $E$  and  $\tan \delta$  values of those samples in the L direction were determined in the temperature range from 123 to 293 K and at constant frequencies, 1, 3.5, 11, 33, and 110 Hz, by using a viscoelastometer, Rheovibron DDV-25FP. The programmed heating rate was 2 K/min. It had been confirmed that the changes in the moisture content of samples during measurement were negligibly small below 273 K. In the measurements of absolutely dry samples, the measuring bath was filled with the flow of dry N<sub>2</sub> gas to prevent the moisture sorption of samples during cooling.

## RESULTS

### Changes in the Structure and Hygroscopicity of Wood Due to Chemical Modifications

Table I lists the weight per gain (WPG) and swelling in volume (Sw) of wood specimens due to the chemical modifications. Both the weight and volume of wood increased with the introduction of chemicals. Figure 1 schematically illustrates the microscopic structure of wood and the structural changes in the amorphous region of its cell wall due to the chemical modifications.<sup>30</sup> The wood cell wall mainly consists of several layers in which crystallized cellulose microfibrils are embedded in amorphous matrix substances. The matrix substances include amorphous cellulose, hemicelluloses, and lignin. It is acknowledged that the water adsorption and the chemical modifications employed in this study do not affect the microfibrils but influence the matrix substances.

By the F treatment, the oxymethylene bridges are formed between a part of hydroxyl groups in



**Figure 1** Schematical illustrations for the microscopic structure of wood (a) and structural changes in the amorphous matrix substances of the wood cell wall due to chemical modifications (b).

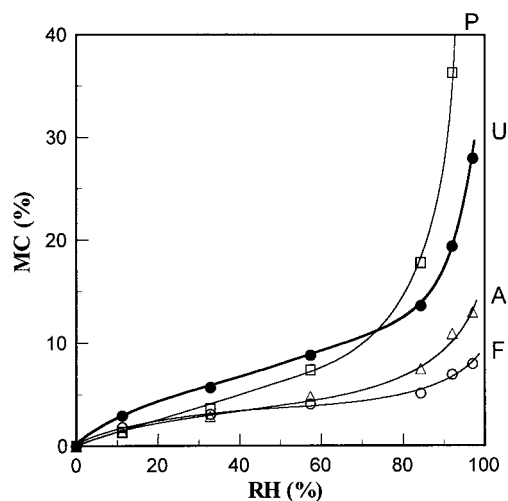
the matrix substances. As the molecular motions of the matrix substances are restricted by the crosslinking formation, the mechanical loss of wood is effectively reduced above 0°C at small WPGs.<sup>31,32</sup> Although little is known about the reactivity of different wood constituents with formaldehyde, it has been reported that the F treatment affects the relaxation phenomena of wood and cellulose in the same manner.<sup>33,34</sup>

In the A-treated wood, a part of hydroxyl groups are substituted by hydrophobic and bulky acetyl groups. The hydroxyl groups in lignin and hemicelluloses are substituted for readily at small WPGs.<sup>35–37</sup> The cellulose in wood is less reactive, but there is no difference in the reactivity of hydroxyl groups among their positions.<sup>36</sup> Thus, it was supposed that the substitution ratios

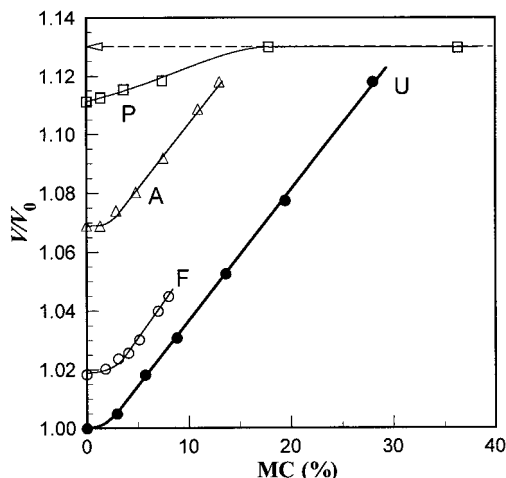
of hydroxyl and methylol groups are almost the same regardless of wood constituents. According to the relationships between the amount of methylol groups and WPG,<sup>38</sup> it was evaluated that 40 to 50% of hydroxyl and methylol groups were substituted by the acetyl groups in the A-treated wood specimen.

On P treatment, the matrix substances are highly swollen with penetration of PEG molecules, some of which remain in the cell cavities. However, there occurs no chemical reaction between the PEG and wood constituents. At room temperature or above, the PEG in the cell wall acts as a plasticizer to reduce the rigidity of wood and enhance its mechanical damping.<sup>32,39</sup>

The water sorption isotherms of the wood specimens at 298 K are represented in Figure 2. The moisture content of wood (MC) was fairly reduced by the F and A treatments at all RH levels examined, whereas it was remarkably increased by the P treatment above 80% RH. Figure 3 shows the relative volume of wood specimens ( $V/V_0$ ) plotted against the MC. By the F treatment, the maximum swelling level of wood was well restricted by the crosslinking formation in the matrix substances. The A treatment did not affect the maximum swelling level of wood, but suppressed the total amount of swelling with the introduction of bulky acetyl groups. Because the P-treated wood had been previously swollen with PEG, it reached its maximum swelling level at around 20% MC. Above 20% MC or 80% RH, the deliquescence of PEG in the cell cavities gave high MC values without additional swelling of wood.



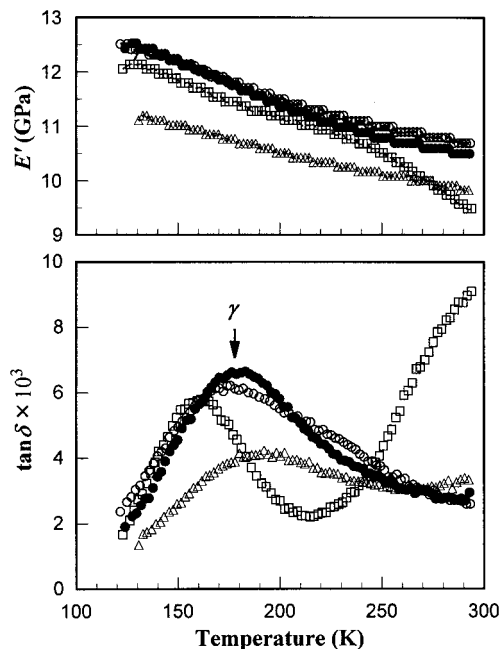
**Figure 2** Moisture content of wood specimens (MC) at 298 K and various relative humidities (RH). ●, Untreated (U); ○, formaldehyde treated (F); △, acetylated (A); □, polyethylene glycol impregnated (P).



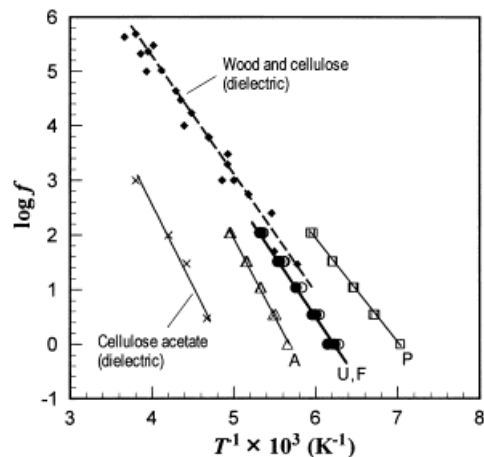
**Figure 3** Volume ratios of wood specimens based on the volume in their untreated state ( $V/V_0$ ) plotted against the moisture content (MC) at 298 K. Symbols, refer to Figure 2; the arrows indicate the maximum swelling level of wood in wet condition.

#### Relaxation Process of Absolutely Dry Wood

Figure 4 represents the temperature variations of  $E$  and  $\tan \delta$  values at 33 Hz for the untreated and chemically modified wood specimens in the absence of water. With respect to the  $\tan \delta$  peak, one relaxation process labeled  $\gamma$  was recognized in the



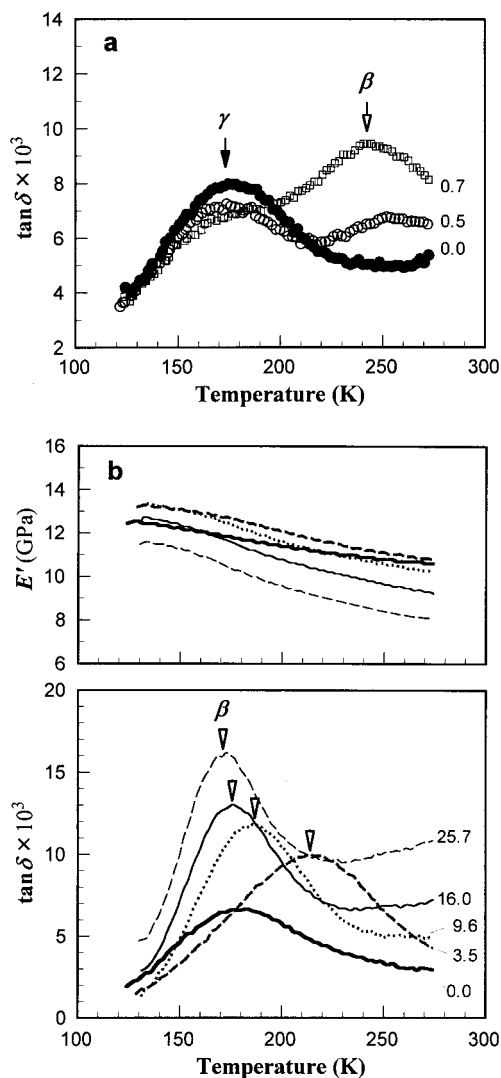
**Figure 4** Temperature variations of storage modulus ( $E$ ) and loss tangent ( $\tan \delta$ ) at 33 Hz for the untreated and chemically modified wood specimens dried absolutely. Symbols, refer to Figure 2.



**Figure 5** Relationships between the logarithms of measuring frequency ( $\log f$ ) and the reciprocals of absolute temperature ( $T^{-1}$ ) for the  $\gamma$  relaxation process observed in the wood specimens dried absolutely. Symbols, refer to Figure 2;  $\blacklozenge$ , dielectric  $\gamma$  relaxation in the untreated dry wood and cellulose available in the literature<sup>10,11,17,22,24,25</sup>;  $\times$ , dielectric  $\gamma$  relaxation observed in the dry cellulose acetate (DS = 2.5–2.9).<sup>17,18</sup>

untreated wood at around 180 K. In Figure 5, the logarithms of measuring frequency ( $\log f$ ) are plotted against the reciprocals of absolute temperature ( $T^{-1}$ ) at which the  $\gamma$  loss peak was detected. The frequency-temperature location of the  $\gamma$  relaxation was in good agreement with those available in the literature for the dielectric  $\gamma$  relaxation observed in wood and cellulose.<sup>10,11,17,22,24,25</sup> The apparent activation energy ( $\Delta E_a$ ) of the  $\gamma$  relaxation, 42 kJ/mol, was also comparable to that for the dielectric  $\gamma$  relaxation process. These facts indicated that both the mechanical and dielectric  $\gamma$  relaxations are attributable to the same mechanism, the motion of methylol groups.

As shown in Figure 4, the  $\gamma$  relaxation was also detected in the chemically modified wood specimens. Their frequency-temperature locations are plotted in Figure 5. By the F treatment, the amplitude and temperature location of the  $\gamma$  loss peak remained almost unchanged. It was suggested that the crosslinking formation did not affect the motion of methylol groups, while it fairly restricts the segmental motions of the main chain. The F-treated wood showed an obscure shoulder in its  $\tan \delta$  at around 220 K. This might be due to the motion of oxymethylene bridges.<sup>32</sup> The  $\gamma$  relaxation of the A-treated wood appeared at a higher temperature with a broader loss peak, and its  $\Delta E_a$  value, 56 kJ/mol, was larger than that of the untreated wood. In the A-treated wood, 40 to 50% of methylol groups were substituted by the



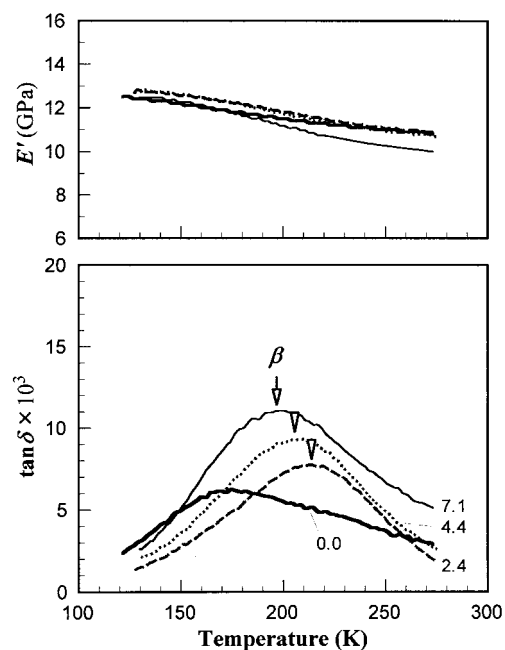
**Figure 6** Temperature variations of  $E'$  and  $\tan \delta$  for the untreated wood specimens at the indicated moisture contents (MC, %). (a) Low MC levels; ●, dried at 378 K *in vacuo* for a day; ○, dried at 378 K and atmospheric conditions for a day; □, dried absolutely and stored on dry silica-gel for 3 days; (b) high MC levels.

acetyl groups. Besides, it has been reported that the acetyl groups in dry cellulose acetate can induce a dielectric relaxation as shown in Figure 5.<sup>17,18</sup> Therefore, the  $\gamma$  relaxation of the A-treated wood must include two relaxation processes: the original  $\gamma$  relaxation reduced with the decrease of methylol groups, and an additional relaxation due to the acetyl groups introduced. These two relaxations may overlap to give the broader loss peak at a higher temperature. By the P treatment, the  $\gamma$  relaxation shifted to a lower temperature and its  $\Delta E_a$  value was decreased to 36 kJ/mol. These changes were interpreted from the plasticizing

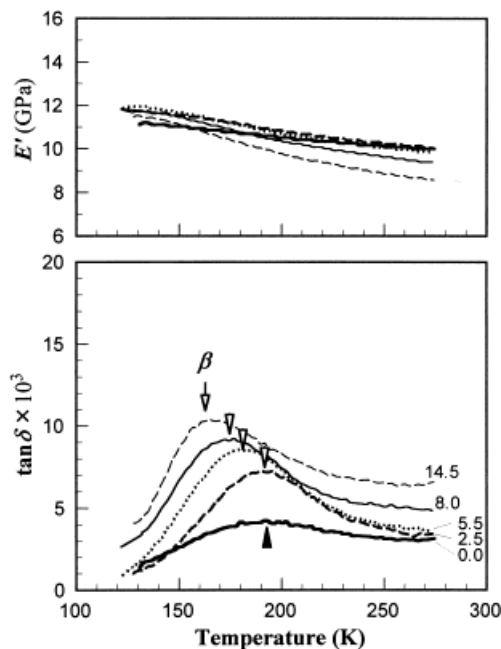
effect of the PEG molecules introduced. In the dried untreated wood, tight hydrogen bonds are formed between the hydroxyl and/or methylol groups in the matrix substances. However, the introduction of PEG molecules expands the distance between the amorphous molecules with the scission of hydrogen bonds. It must mobilize the methylol groups to shift the  $\gamma$  relaxation to a lower temperature, even when the motions of PEG molecules themselves are almost frozen. The backbone motions of PEG molecules may be responsible for the steep rise in  $\tan \delta$  and the marked decrease in  $E'$  above 230 K.

### Relaxation Process of Wood Containing Moisture

Figure 6 shows the viscoelastic profiles of wood containing moisture. As shown in Figure 6(a), an additional relaxation process labeled  $\beta$  is induced at 220–240 K with a small amount of water adsorption. The  $\beta$  loss peak is clearly detected even when the sample is dried at 378 K and under atmospheric conditions, but it disappears with complete drying *in vacuo*. And then, it appears again with water sorption during storage on the dry silica gel.<sup>11</sup> This reversible change indicates the  $\beta$  relaxation is not due to the irreversible degradation of wood constituents during drying but to the motions related to the adsorbed water.

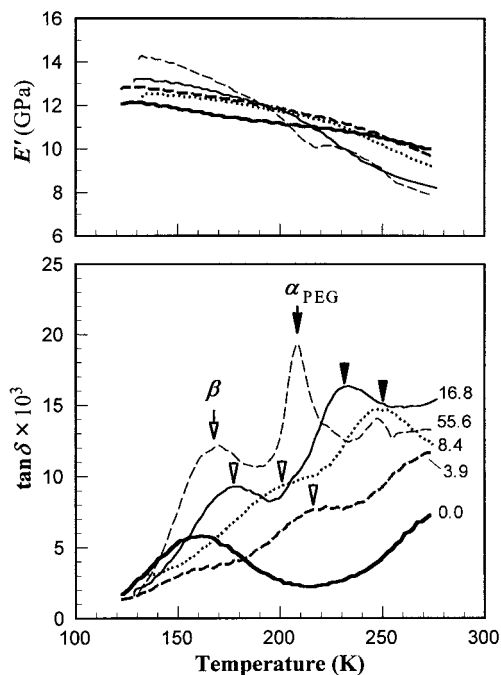


**Figure 7** Temperature variations of  $E'$  and  $\tan \delta$  for the formaldehyde-treated wood specimens at the indicated moisture contents (MC, %).

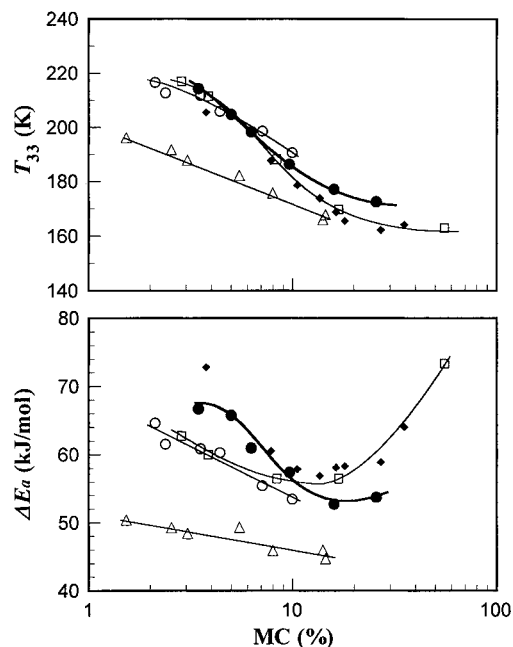


**Figure 8** Temperature variations of  $E'$  and  $\tan \delta$  for the acetylated wood specimens at the indicated moisture contents (MC, %).

The  $\beta$  loss peak increased and shifted to lower temperatures with increasing moisture content, as shown in Figure 6(b). These trends are quali-



**Figure 9** Temperature variations of  $E'$  and  $\tan \delta$  for the PEG impregnated wood specimens at the indicated moisture contents (MC, %).



**Figure 10** Temperature location of loss peaks detected at 33 Hz ( $T_{33}$ ) and apparent activation energy ( $\Delta E_a$ ) of the  $\beta$  relaxation process plotted against the moisture content (MC). Symbols, refer to Figure 2;  $\blacklozenge$ , dielectric  $\beta$  relaxation detected in wood.<sup>12</sup>

tatively analogous to those already reported for both the mechanical and dielectric  $\beta$  relaxations in wood and related materials.<sup>8-13</sup> Above a 10% moisture content, the  $\tan \delta$  of wood showed relatively high values at temperatures above 220 K. These were explained by the segmental motions of hemicellulose, lignin, and their complexes plasticized with moisture.<sup>40</sup>

Figures 7, 8, and 9 represent the viscoelastic profiles of F-, A-, and P-treated wood specimens, respectively. The  $\beta$  relaxation also appeared in all chemically modified woods with water adsorption. The smaller loss peaks of the F- and A-treated woods corresponded to their smaller moisture contents. The P-treated wood showed additional loss peaks in the range from 200 to 250 K. These loss peaks labeled  $\alpha_{\text{PEG}}$  were attributed to the motions of PEG molecules themselves or the complex motions of deliquesced PEG and water.

Figure 10 exhibits the temperature locations of  $\beta$  loss peaks observed at 33 Hz ( $T_{33}$ ) and  $\Delta E_a$  values plotted against the MC. The  $T_{33}$  and  $\Delta E_a$  values of the P-treated wood were determined after separating the peaks, to eliminate the apparent shift of peak temperatures with their overlapping. The  $\beta$  relaxation shifted to lower temperatures and its  $\Delta E_a$  values decreased up to 15% MC, irrespective of chemical modifications. These

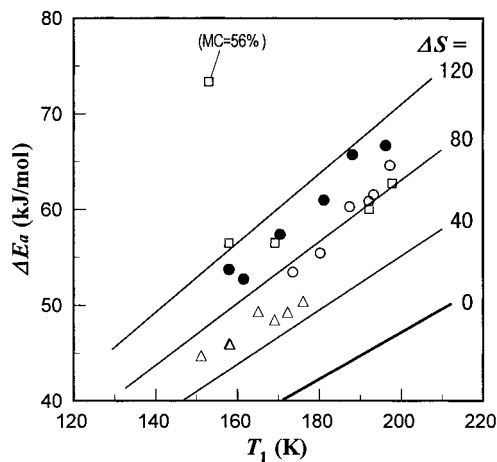
trends were in good agreement with those for the dielectric  $\beta$  relaxation.<sup>8,10,12</sup> However, the  $T_{33}$  and  $\Delta E_a$  values of A-treated wood were lower than those of the others. Above 15% MC, the  $\Delta E_a$  values for the untreated wood seemed to increase slightly with increasing MC, whereas temperature location remained almost unchanged. The P-treated wood recorded an extremely large  $\Delta E_a$  value at 56% MC. This may be associated with the moisture adsorption of PEG molecules deliquesced in the cell cavities.

### Activation Entropy of the $\beta$ Relaxation Process

Although the activation entropy of a relaxation ( $\Delta S$ ) provides useful information about the cooperativity of molecular motions, it is unfortunately difficult to determine accurately the  $\Delta S$  value of a mechanical relaxation because possible frequency range is fairly limited. Here we roughly evaluate  $\Delta S$  of the  $\beta$  relaxation process from its  $\Delta E_a$  value and temperature location. According to Starkweather, the relation between  $\Delta E_a$  and the relaxation temperature at 1 Hz ( $T_1$ ) is given by the following equation:<sup>41</sup>

$$\Delta E_a = RT_1[1 + \ln(kT_1/2\pi h)] + T_1\Delta S \quad (1)$$

Figure 11 represents the plots of  $\Delta E_a$  vs.  $T_1$  for the  $\beta$  relaxation detected in the wood specimens at various MC levels. Irrespective of chemical modifications, the  $\beta$  relaxation had a positive and quite large  $\Delta S$  value at all MC levels examined.



**Figure 11** Relationship between the  $\Delta E_a$  values and temperature locations at 1 Hz ( $T_1$ ) for the  $\beta$  relaxation process detected in wood. Symbols, refer to Figure 2, lines; calculated values at the indicated activation entropy ( $\Delta S$ , kJ/mol  $\cdot$  K).

Thus, the  $\beta$  is not a “simple” but a “complex” relaxation, according to the classification of Starkweather.

The changes in the  $\Delta S$  value due to the F treatment were small within the experimental uncertainty. On the other hand, the  $\Delta S$  values of the A-treated wood were slightly lower than those of the untreated wood. Although the  $\Delta S$  value of the P-treated wood was almost the same as that of the untreated wood at low moisture contents, it was extremely large at 56% MC.

## DISCUSSION

### The Mechanism of the $\gamma$ Relaxation Process

The  $\gamma$  relaxation is detectable only in the materials containing methylol groups, and disappears on substitution of the methylol groups with other groups. Therefore, it is generally accepted that the  $\gamma$  relaxation is due to the motion of methylol groups in the amorphous region of wood, cellulose, and related materials. So far, the mechanical and dielectric  $\gamma$  relaxations have been often observed at different frequency-temperature ranges.<sup>16</sup> Such a disagreement may be due to the effects of water remaining in the “dry” sample. In fact, the characteristics of mechanical  $\gamma$  relaxation agreed well with the dielectric  $\gamma$  relaxation when the sample was dried completely.

Montes and Cavaille have recently reported that dry cellulose exhibits two mechanical relaxations ( $\gamma_m$  and  $\beta_m$ ) and one dielectric relaxation with a broad loss peak ( $\gamma_d$ ) in the low-temperature range.<sup>29</sup> They suggested that the  $\gamma_d$  relaxation includes two relaxations,  $\gamma_{\text{CH}_2\text{OH}}$  and  $\gamma_{\text{OH}}$ , due to the motions of methylol and hydroxyl groups, respectively. In addition, they attributed the mechanical  $\beta_m$  relaxation to the motion of cellulose main chain. Their idea seems to be based on the fact that a dielectric  $\gamma_{\text{OH}}$  relaxation is detectable in dextran, which has no methylol groups. However, the dry wood showed only one simple  $\gamma$  relaxation due to the motion of methylol groups, and neither  $\beta_m$  nor  $\gamma_{\text{OH}}$  relaxation was detected, whereas the wood contains a large amount of cellulosic constituents. Actually, a lot of investigators have reported that only one relaxation is detectable in dry cellulose and related materials, and there is no indication that the simple relaxation consists of two processes. In addition, dextran exhibits no mechanical relaxation in the temperature range of “ $\gamma_{\text{OH}}$ ,” at extremely low (0.34%) moisture content.<sup>19</sup> Further-

more, both the mechanical and dielectric  $\gamma$  relaxations of cellulose disappear with the tritylation, whereas hydroxyl groups remain unreacted.<sup>27,28</sup> Thus, it is speculated that both the " $\gamma_{OH}$ " and " $\beta_m$ " relaxations observed by Montes and Cavaille were due to a trace amount of adsorbed water remaining in their "dehydrated" samples dried at 373 K for a day. It should be remembered that the trace of water induces both the mechanical and dielectric  $\beta$  relaxation processes. In fact, the wood specimen clearly shows double loss peaks,  $\gamma$  and  $\beta$ , even when it is dried at 378 K and 1atm for a day. These results suggest that careful drying is necessary to determine the relaxation phenomena of wood and related materials in their dried state.

The effects of chemical modifications on the  $\gamma$  relaxation process can be explained by the introduction of chemicals resulting in additional mechanical losses, or the plasticization of amorphous regions involving the mobilization of methylol groups.

### The Mechanism of the $\beta$ Relaxation Process

In the presence of water, the  $\beta$  relaxation generally appears in the wood and its major components, cellulose, hemicellulose, and lignin. Although a number of researchers have observed the  $\beta$  relaxation, its assignment is still incomplete. Here we reconsider the mechanisms of  $\beta$  relaxation already proposed.

Kimura and Nakano have attributed the  $\beta$  relaxation in cellulose to the motions of the methylol-water complex.<sup>16</sup> This interpretation has so far been supported by many investigators. However, further investigations found that the dielectric  $\beta$  relaxation also appeared in trityl cellulose with water sorption, trityl cellulose having no methylol groups. In addition, the characteristics of the dielectric  $\beta$  relaxation in trityl cellulose are analogous to those in the original cellulose.<sup>17</sup> These findings suggest that methylol groups are not required for the  $\beta$  relaxation process.

Bradley and Carr have found that a dielectric relaxation appeared with moisture adsorption in dextran as well as cellulose.<sup>19</sup> They attributed the  $\beta$  relaxation observed in cellulose to the motion of the methylol-water complex, but no sufficient explanation for the relaxation observed in dextran.

The  $\beta$  relaxation of cellulose acetate was assigned to the local-mode motions of the main chain by Scandola and Ceccolulli.<sup>42</sup> However, the segmental motions of the main chain is not a dominant factor for the  $\beta$  relaxation discussed here, because the characteristics of  $\beta$  relaxation

at low moisture content remained almost unchanged by the F treatment involving the restriction of segmental motions, or the P treatment resulting in the plasticization of amorphous molecules.

Handa et al. have found that the  $\beta$  relaxation appeared in wood with the adsorption of various organic diluents as well as water. They concluded that the  $\beta$  relaxation is not due to the motion of adsorbed water itself.<sup>8</sup> However, it is acknowledged that various organic diluents themselves can induce dielectric relaxations in the low temperature range.<sup>43-46</sup> Therefore, we can hardly exclude the motion of water molecule itself from the fact that the  $\beta$  process appeared with organic diluents other than water.

The motions of polar groups in the wood constituents are sometimes used to explain the behavior of the  $\beta$  relaxation process.<sup>8</sup> However, it should be remembered that the characteristics of  $\beta$  relaxation in wood are analogous to those in cellulose and amylose containing only two polar groups, methylol and hydroxyl groups. As mentioned above, the motion of methylol groups does not dominate the  $\beta$  relaxation process, and there is no indication that the motion of hydroxyl groups induces any relaxation process in the temperature-frequency range discussed here. Consequently, we have no evidence to attribute the  $\beta$  relaxation to the motion of "some" polar groups. If the  $\beta$  relaxation is governed by the motion of some polar groups, the P-treated wood should exhibit the  $\beta$  or similar relaxation process even in the absence of moisture because the polar groups in the P treated wood may be mobilized with the introduction of PEG molecules. However, the P-treated wood shows no  $\beta$ -like relaxation process unless it contains moisture.

These considerations lead us to focus on the motion of the adsorbed water molecule itself. Norimoto and coresearchers have found that the dielectric  $\beta$  relaxation processes in wood and related materials are very close to a relaxation due to the rotational motions of water molecules at defects in ice I.<sup>10,17,23</sup> They have suggested that the  $\beta$  relaxation is dominated by the motion of adsorbed water itself, which forms an ice-like structure. A similar concept has been proposed by Kapur et al. for the  $\beta$ -like relaxation process observed in nylon.<sup>47</sup>

Because there are many active adsorption sites in the amorphous region of wood, an adsorbed water molecule can form four hydrogen bonds at most, with the adjacent adsorption sites such as hydroxyl and methylol groups. At the tempera-



ture of the  $\beta$  process, the adsorbed water molecule might rotate with scission of hydrogen bonds to cause mechanical and dielectric relaxations. With increasing moisture content up to 15%, the possible hydrogen bonds of an adsorbed water molecule decrease, so that, the  $\beta$  relaxation shifts to lower temperatures and its  $\Delta E_a$  value decreases. At around 15% moisture, most of the adsorption sites are occupied by the water molecules and above 15%, multilayered water adsorption occurs. In this situation, the structure of adsorbed water molecules becomes homogeneous; consequently, the  $\beta$  relaxation temperature shifts only slightly with increasing moisture content. On the other hand, the slight increase in  $\Delta E_a$  above 15% moisture content might be due to the cooperative motions of clustered water molecules. The changes in the  $\beta$  relaxation due to the acetylation can be qualitatively explained by the decrease of possible hydrogen bonds with the introduction of acetyl groups, which can form only one hydrogen bond with the adsorbed water molecule.

Although more detailed investigations are needed, the most reasonable interpretation for the  $\beta$  relaxation process is the motions of the adsorbed water molecules. This interpretation has few contradictions in explaining the experimental results available at this time.

### Cooperative Molecular Motions in the $\beta$ Relaxation Process

The large  $\Delta S$  values of the  $\beta$  relaxation indicated the contribution of cooperative molecular motions. The large  $\Delta S$  value is sometimes understood as evidence of main-chain motions, because the local mode main-chain relaxations have generally positive and quite large  $\Delta S$  values. However, it should be emphasized that a large  $\Delta S$  value does not always indicate segmental motions of the main chain. As there is no clear evidence that the segmental motions of the main chain are the dominant mechanism of the  $\beta$  relaxation, here we discuss the cooperative molecular motions in the  $\beta$  relaxation considering the rotational motions of the adsorbed water molecules.

It is acknowledged that a mechanical or dielectric relaxation is observed in ice I at low temperatures, being attributed to the rotational motions of water molecules at the defects.<sup>48,49</sup> This is a quite simple relaxation, but it has a positive and large  $\Delta S$  value being comparable to that of the  $\beta$  relaxation discussed here. In this case, the positive  $\Delta S$  value may reflect a rearrangement of water molecules around one water molecule rotating

in the relaxation process. It must be remembered that the dielectric  $\beta$  relaxation resembles the relaxation in ice I, and the mechanical  $\beta$  relaxation is similar to the dielectric  $\beta$  relaxation at low moisture content. Thus, it is speculated that the rotation of one adsorbed water molecule requires the rearrangement of its adjacent adsorption sites, such as hydroxyl and methylol groups, to give the positive  $\Delta S$  values.

Because the  $\Delta S$  value remained almost unchanged by the F treatment, it was suggested that the mobility of the main chain had little influence on the rearrangement of the adsorption sites. The slightly lower  $\Delta S$  values for the A-treated wood might be due to the weaker interaction between the adsorbed water and acetyl groups. The extremely high  $\Delta S$  value for the highly moistened P-treated wood (56% MC) might be due to the cooperative motions of clustered water molecules that aggregate around the PEG molecules deliquesced in the cell cavities.

## CONCLUSIONS

The dynamic viscoelastic properties of untreated and chemically modified wood specimens were determined in the low temperature range, and the mechanical relaxation processes detected were attributed to the motions of polar groups in the wood constituents and those of the adsorbed water. The results are summarized as follows:

1. Absolutely dried wood specimens exhibited a relaxation process labeled  $\gamma$ . The  $\gamma$  relaxation was attributed to the motions of methylol groups in the amorphous region of the wood constituents, such as cellulose, hemicelluloses, and lignin. The characteristics of the  $\gamma$  relaxation remained almost unchanged by the formaldehyde treatment involving the formation of crosslinks in the amorphous substance. With the introduction of acetyl groups, the  $\gamma$  loss peak was reduced, and it apparently shifted to a higher temperature. These results were explained by the reduction in the original  $\gamma$  loss peak due to the decrease of methylol groups, and an additional relaxation induced by the acetyl groups introduced. The  $\gamma$  relaxation was shifted to lower temperatures with the introduction of polyethylene glycol, probably because of the mobilization of methylol groups.
2. With moisture adsorption, an additional re-

laxation process labeled  $\beta$  was induced. It shifted to lower temperatures, and its apparent activation energy was reduced with increasing moisture content up to 15%. These trends are in good agreement with those of the dielectric  $\beta$  relaxation already reported. At low moisture content, the characteristics of the  $\beta$  process remained almost unchanged by the formaldehyde treatment or polyethylene glycol impregnation. These results suggest that the  $\beta$  relaxation is almost independent of the segmental motions of the main chain. Thus, the  $\beta$  relaxation was attributed to the motion of the adsorbed water molecules. The positive activation entropy of the  $\beta$  relaxation was interpreted to reflect a rearrangement of the adsorption site with the rotation of adsorbed water molecules.

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