J Wood Sci (2003) 49:152–157

ORIGINAL ARTICLE

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Dynamic viscoelastic properties of wood acetylated with acetic anhydride solution of glucose pentaacetate

Received: March 29, 2002 / Accepted: May 21, 2002

Abstract Spruce wood specimens were acetylated with acetic anhydride (AA) solutions of glucose pentaacetate (GPA), and their viscoelastic properties along the radial direction were compared to those of the untreated and the normally acetylated specimens at various relative humidities and temperatures. Higher concentrations of the GPA/AA solution resulted in more swelling of wood when GPA was introducted into the wood cell wall. At room temperature the dynamic Young's modulus (E') of the acetylated wood was enhanced by 10% with the introduction of GPA, whereas its mechanical loss tangent ($\tan\delta$) remained almost unchanged. These changes were interpreted to be an antiplasticizing effect of the bulky GPA molecules in the wood cell wall. On heating in the absence of moisture, the GPA-acetylated wood exhibited a marked drop in E' and a clear $\tan\delta$ peak above 150°C, whereas the E' and $\tan\delta$ of the untreated wood were relatively stable up to 200°C. The $\tan\delta$ peak of the GPA-acetylated wood shifted to lower temperatures with increasing GPA content, and there was no $\tan\delta$ peak due to the melting of GPA itself. Thus the marked thermal softening of the GPA-acetylated wood was attributed to the softening of wood components plasticized with GPA.

Key words Acetylation · Glucose pentaacetate · Dynamic Young's modulus · Loss tangent · Antiplasticizer

Introduction

Acetylation is an excellent method for improving the dimensional stability of wood.[1] For further improvement of dimensional stability, an attempt has been made to treat wood with an acetic anhydride (AA) solution of glucose pentaacetate (GPA).[2] During this "GPA acetylation" the wood cell wall is swollen not only by the acetylation with AA but also by the introduction of GPA into the wood cell wall. Consequently, the bulking effect of GPA results in higher dimensional stability. As the GPA is hydrophobic and hardly dissolves in water, it remains in the wood cell wall even when it is boiled in water.

In general, wood is plasticized and softened when it is swollen with flexible, hydrophilic or low molecular weight substances (or both). After acetylation, however, the dynamic Young's modulus of wood does not markedly decrease and its mechanical damping remains almost unchanged despite marked swelling due to introduction of the acetyl groups.[3] This fact can be explained by the antiplasticizing effect of the bulky and hydrophobic acetyl groups introduced. Because the GPA molecule is also bulky and hydrophobic, it might act as an antiplasticizer in the wood cell wall at room temperature. On the other hand, it should be recalled that the GPA has melting points ranging from 110° to 130°C. Above those temperatures, the GPA might act as a plasticizer in the wood cell wall to reduce the softening temperature of the acetylated wood. In this article, the viscoelastic properties of the GPA-acetylated wood are compared to those of untreated and normally acetylated wood at various moisture conditions and temperatures to evaluate the plasticizing and antiplasticizing effects of GPA introduced into the wood cell wall.

Materials and methods

Measurement of dimensional stability

Sitka spruce (*Picea Sitchensis*) wood specimens of 1 cm (L, longitudinal direction) × 3 cm (R, radial direction) × 3 cm (T, tangential direction) were used. The specimens were previously soaked in water for 1 week to remove the water-soluble extractives. These specimens were then completely

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dried in vacuo at room temperature, and their weight and dimensions were measured. The density (ρ) of the completely dried specimen was 0.34 ± 0.01 g/cm^3.

The completely dried specimens were soaked in 0%, 3%, 5%, 10%, and 15% AA solutions of GPA overnight and heated in a flask at 120°C for 8 h. The specimens were immediately cooled at room temperature, and dried in vacuo to remove the AA and acetic acid (a by-product) remaining in the specimens. The specimens were then dried completely at 105°C for 12 h and heated at 160°C for 10 min. With this short heating at 160°C, some of the GPA remaining in the cell cavities penetrates the cell wall without serious degradation of wood components.[1] The specimens were then washed in water and completely dried in vacuo at room temperature.

The weights and dimensions of the unacetylated and acetylated specimens were measured at 11%, 33%, 57%, 75%, 92%, and 97% relative humidity (RH). The specimens were then soaked in water and boiled at around 95°C for 1 h to measure their wet volume. Five specimens were used for each treating condition.

Measurement of viscoelastic properties at room temperature

Sitka spruce wood specimens of 1.5 cm (L) × 12 cm (R) × 0.3 cm (T) were soaked in water for 1 week to remove the water-soluble extractives and then dried in vacuo at room temperature to measure their absolute dry weight and dimensions. Next, the specimens were conditioned at 20°C and 33% RH for 1 month, and their dynamic Young's modulus (E') and loss tangent ($\tan\delta$) along the R direction were measured. Thirty specimens with analogous ρ (0.46 ± 0.03 g/cm^3), E' (1.22 ± 0.16 GPa), and $\tan\delta$ (0.017 ± 0.001) values were selected and divided into six groups. Of them, one group remained untreated, and the other five were acetylated in the same manner as described above. After acetylation, all specimens were dried in vacuo at room temperature, and their E' and $\tan\delta$ values were measured at 20°C and 0%, 11%, 33%, 57%, 75%, 92%, and 97% RH using the free-free flexural vibration method.[4] The E' value was calculated from the resonance frequency of the first mode vibration and the $\tan\delta$ from the resonance curve. The specimens and equipment were kept in a closed box in which the humidity was controlled with various aqueous salt solutions.

Measurement of temperature dependence

Sitka spruce wood sheets of 10 cm (L) × 6 cm (R) × 0.07 cm (T) were washed in water and acetylated in the same manner as described above. The sheets were cut into strips of 4 cm (R) × 0.4–0.5 cm (L) and subjected to the following measurements: Part of each specimen was completely dried in vacuo at room temperature, and its E' and $\tan\delta$ values along the radial direction were measured over a temperature range of 20°–200°C; the other specimens were soaked in water for 1 week and their E' and $\tan\delta$ values measured in water over a temperature range of 5°–100°C. Both these measurements were carried out using a viscoelastometer DMS 6100 (Seiko Instruments) equipped with a temperature-controlled tube filled with dry air or water. The measuring frequency, programmed heating rate, and effective span of the specimens were 5 Hz, 2°C/min, and 2 cm, respectively.

Results and discussion

Effect of GPA on the dimensional stability of wood

Table 1 shows the weight percent gain (WPG) and swelling of the volume (SV) of wood specimens due to acetylation at 120°C for 8 h. The SV value was based on the volume of the specimen in its untreated and absolutely dried state. Because the WPG and SV values did not strongly depend on the shape of the specimen, we describe here the dimensional stability of the "block" specimens.

Table 1. Weight percent gain and swelling of the volume of spruce wood specimens due to acetylation at 120°C for 8 h

Acetylation	GPA/AA[a] (%)	WPG (%)			SV (%)	
		Block[b]	Beam[c]	Sheet[d]	Block[b]	Beam[c]
Normal	0	23.6	25.3	20.4	7.8	8.2
GPA	3	29.2	28.8	28.7	9.0	9.7
	5	30.6	32.0	30.5	10.6	11.1
	10	39.7	34.4	37.0	11.6	11.6
	15	49.3	41.5	51.1	11.8	12.8

GPA, glucose pentaacetate; AA, acetic anhydride; WPG, weight percent gain; SV, swelling of the volume

[a] Concentration of GPA in the AA solution used for acetylation

[b] Specimens measuring 1 cm (L) × 3 cm (R) × 3 cm (T)

[c] Specimens measuring 1.5 cm (L) × 12 cm (R) × 0.3 cm (T) used for viscoelastic measurements at room temperature

[d] Specimens measuring 10 cm (L) × 6 cm (R) × 0.07 cm (T) used for temperature dependence measurements

The WPG and SV values of the specimens are plotted in Fig. 1 against the concentration of GPA in the treating reagent. The WPG value increased linearly with increasing GPA concentration. The SV value also increased with increasing GPA concentration, but it leveled off at GPA concentrations above 5%. These results indicated that some of the GPA remaining in the cell cavities did not contribute to the swelling of wood at GPA concentrations above 5%.

Figure 2 shows the relation between the SV value and the equilibrium moisture contents of the untreated and acetylated wood specimens. After acetylation the wood specimens were swollen by the acetyl groups and GPA molecules that had been introduced, but their maximum volume remained almost unchanged. Consequently, the swelling of wood due to moisture absorption was effectively reduced. Figure 3 shows the antiswelling efficiency (ASE) of the acetylated wood plotted against the concentration of GPA in the treating reagent. The ASE value was derived from the following equation.

$$\mathrm{ASE}\ (\%) = 100(\mathrm{SV'_u} - \mathrm{SV'_a})/\mathrm{SV'_u} \qquad (1)$$

where SV′ is the swelling of the volume of the specimens due to soaking in water, and suffixes u and a indicate the untreated and acetylated specimens, respectively. The ASE value increased when the GPA concentration was increased up to 5%, above which it leveled off. Such a trend resembled to that of the SV value, because the ASE of the acetylated wood depends on the bulking effects of the acetyl groups and GPA molecules introduced into the cell wall.

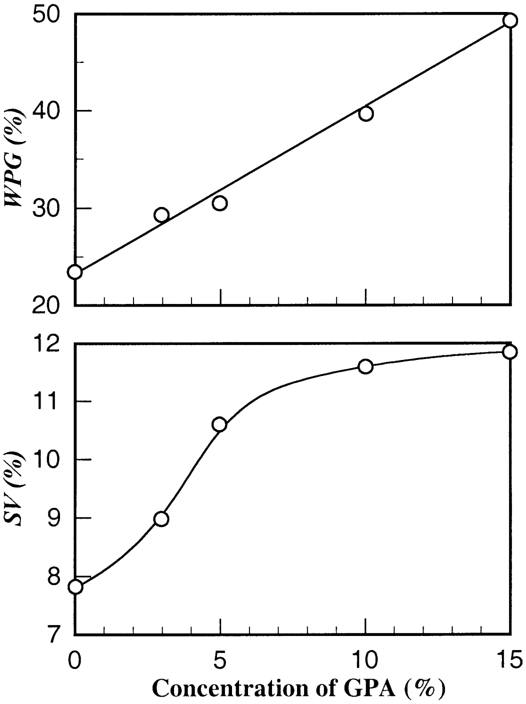

Fig. 1. Weight percent gain (*WPG*) and swelling of the volume (*SV*) of spruce wood specimens due to acetylation with acetic anhydride (AA) solutions of glucose pentaacetate (*GPA*) at 120°C for 8h plotted against the concentration of GPA in the treating reagent

These results confirmed that the GPA molecules were certainly introduced into the wood cell wall, though some GPA remained in the cell cavities.

Antiplasticizing effect of GPA at room temperature

Figure 4 shows the E' and $\tan\delta$ values of the untreated and the acetylated wood specimens along the radial direction at 20°C as a function of the RH. Above 40% RH, the E' of the untreated wood decreased and its $\tan\delta$ increased with an increase of RH. On the other hand, the E' and $\tan\delta$ values of the normally acetylated wood were quite stable against the RH change because of the marked reduction in hygroscopicity. The effects of GPA acetylation were qualitatively similar to those of normal acetylation, but it should be noted that the E' values of GPA-acetylated woods were

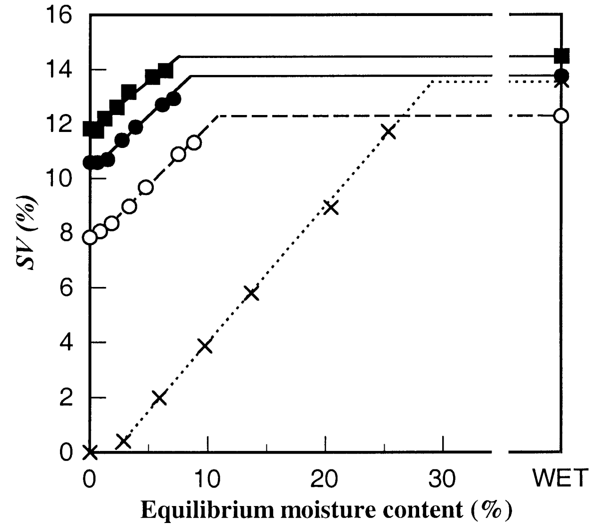

Fig. 2. Relations between the SV and the equilibrium moisture content of spruce wood specimens. *Crosses*, untreated; *open circles*, normal acetylation with AA; *filled circles*, acetylated with 5% GPA/AA solution; *squares*, acetylated with 15% GPA/AA solution

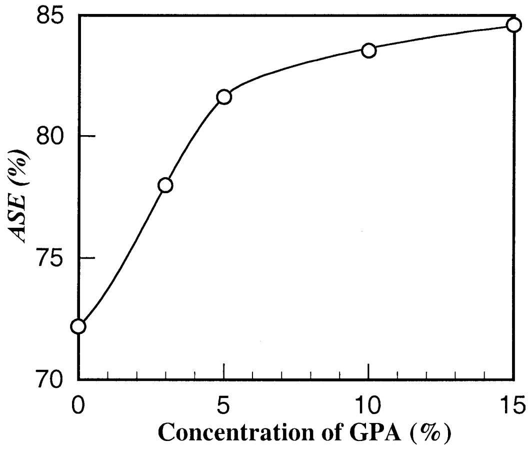

Fig. 3. Antiswelling efficiency (*ASE*) of acetylated wood specimens plotted against the concentration of GPA in the treating reagent

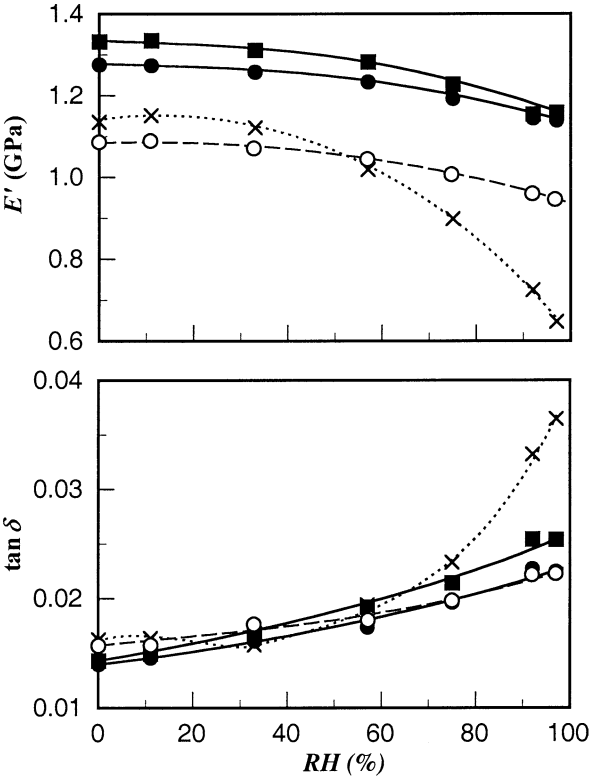

Fig. 4. Dynamic Young's modulus (E') and loss tangent (tan δ) of untreated and acetylated wood specimens along the radial direction at 20°C as a function of relative humidity (*RH*). For symbols, see Fig. 2

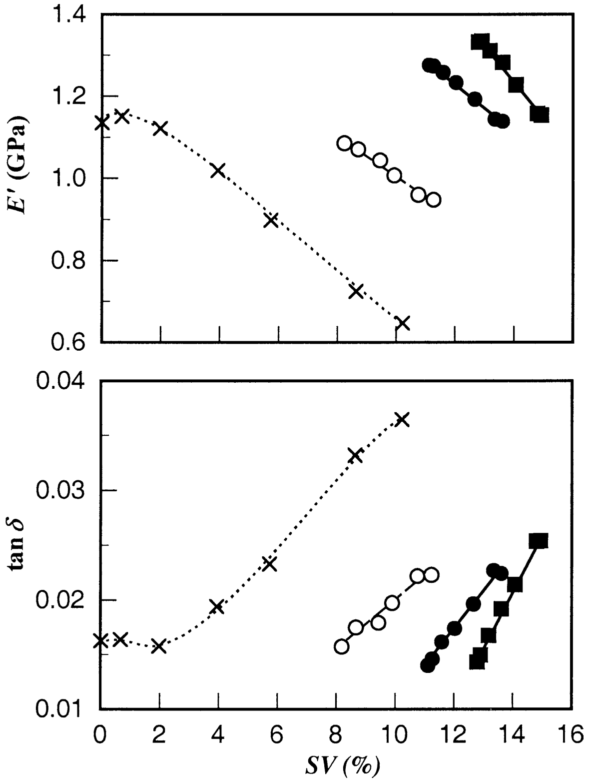

Fig. 5. Dynamic Young's modulus (E') and loss tangent (tan δ) of untreated and acetylated wood specimens along the radial direction at 20°C plotted against the SV due to acetylation and moisture adsorption. For symbols, see Fig. 2

always higher than those of the untreated and the normally acetylated ones.

The E' and tan δ values of the untreated and the acetylated wood specimens are plotted against the SV values in Fig. 5. In general, water and various chemicals are introduced into the amorphous region of the wood cell wall. Because the amorphous region is viscoelastic and its Young's modulus is much lower than that of the crystalline region of the cellulose microfibrils, the swelling of wood usually involves a reduction of E' and an increase of tan δ, unless a crosslinking structure is formed. However, as shown in Fig. 5, the normally acetylated and GPA-acetylated woods had higher E' and lower tan δ values than the untreated wood at the same SV level. Especially, the E' of the GPA-acetylated wood was about 10% higher than that of the normally acetylated wood despite the marked swelling due to GPA introduction. This fact suggested that the GPA acted as an antiplasticizer in the wood cell wall, probably because of their bulky nature.

Figure 6 shows the temperature variations of E' and tan δ for the untreated and the acetylated wood specimens along the radial direction in the wet condition. The untreated wood exhibited a marked drop in E' and a clear tan δ peak in the range of 60°–100°C. This transition was attributed to the glass–rubber transition of lignin.[5] On the other hand, the E' of the acetylated wood decreased only

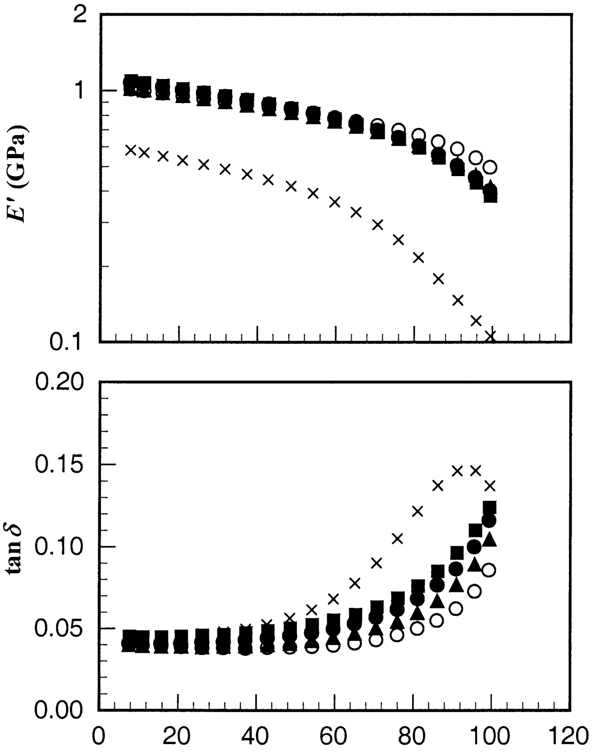

Fig. 6. Temperature variations of dynamic Young's modulus (E') and loss tangent (tan δ) at 5 Hz for untreated and acetylated wood specimens along the radial direction in the wet condition. *Crosses*, untreated; *open circles*, normal acetylation with AA; *triangles*, acetylated with 3% GPA/AA solution; *filled circles*, acetylated with 5% GPA/AA solution; *squares*, acetylated with 15% GPA/AA solution

slightly with increasing temperature, and its tan δ showed no peak in the temperature range examined. Among major components of the wood cell wall, lignin is highly reactive during acetylation.[6] After acetylation, there is less space for the water molecules involving the plasticization of lignin, and the mobility of lignin itself must be reduced by bulky acetyl groups. Thus the glass–rubber transition of lignin shifts to higher temperatures. These might be the reasons for the stable viscoelastic profile of the acetylated wood in water. The changes in E' and tan δ of the GPA-acetylated wood were slightly larger than those of normally acetylated wood but still smaller than those of untreated wood. It was thought that the antiplasticizing effects of GPA were maintained even in hot water owing to its hydrophobic nature.

Plasticizing effect of GPA at high temperatures

Figure 7 shows the temperature dependence of E' and tan δ in the untreated and acetylated wood specimens along the radial direction in the completely dried condition. The E' and tan δ of the untreated wood was relatively stable on heating. The normally acetylated wood showed a marked decrease in E' and a steep rise in tan δ above 150°C. These changes were not due to the thermal degradation of wood constituents but were attributable to some transition of wood components because the repeating measurements gave almost the same results. At room temperature the amorphous wood constituents are in a glassy state; they are not plasticized with the introduction of acetyl groups. However, the acetyl groups can act as an internal plasticizer at high temperatures, where the amorphous molecules in the wood cell wall are sufficiently mobile. Otherwise, some of the hydrogen bonds between the amorphous molecules are severed with the introduction of acetyl groups, thereby increasing the mobility of amorphous molecules.

After GPA acetylation the softening temperature of wood was markedly reduced. The temperature locations of the tan δ peaks ($T_{\delta\max}$) detected in the GPA-acetylated woods are plotted in Fig. 8 against the concentration of GPA in the treating reagent. The tan δ peak shifted to lower temperatures with an increase in GPA concentration, and it leveled off above 5%. Such a trend was similar to that of the SV value shown in Fig. 1. It was thought that only the GPA in the wood cell wall was responsible for the reduced softening temperature of wood.

If the marked softening of the GPA-acetylated wood was due to the melting of GPA itself, a clear loss peak should appear in the range of 110°–130°C. However, there was no such tan δ peak corresponding to the melting of GPA. Therefore, the considerable softening observed in the GPA-acetylated wood was not due to the melting of GPA but to the softening of wood components plasticized with GPA. It should be noted that the tan δ peak of the acetylated wood shifted smoothly with increasing GPA content while maintaining its magnitude. This fact indicated that the GPA and the acetylated wood components were well dissolved in each other; that is, the GPA worked well as a plasticizer in the wood cell wall.

Wood materials are easily softened with moisture but quite stable on heating in the absence of moisture. On the contrary, GPA-acetylated wood is not markedly softened with moisture, whereas it can be well softened on heating even in the absence of moisture. Hence GPA acetylation is an effective method for enhancing the thermal plasticity of the acetylated wood while maintaining its excellent antiwater property.

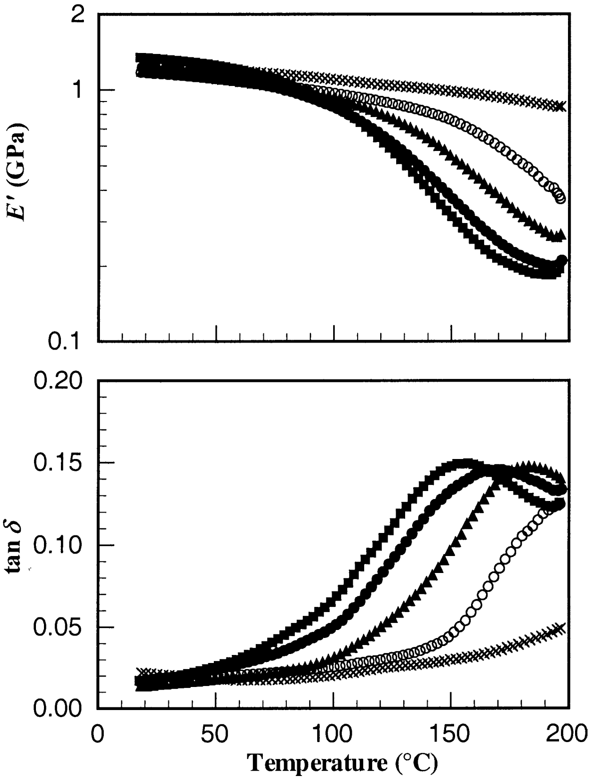

Fig. 7. Temperature variations of dynamic Young's modulus (E') and loss tangent (tan δ) at 5 Hz for untreated and acetylated wood specimens along the radial direction in the completely dried condition. For symbols, see Fig. 6

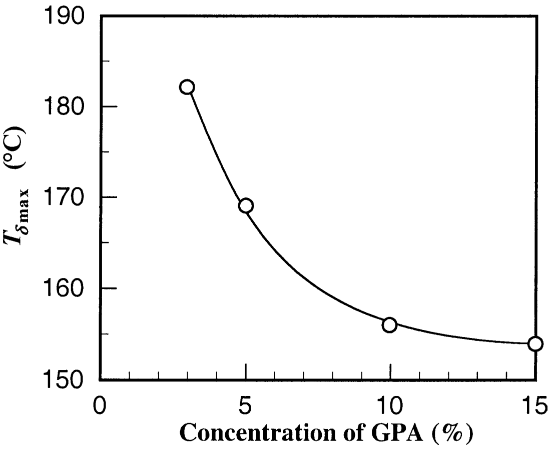

Fig. 8. Temperature location of the mechanical loss peak ($T_{\delta\max}$) detected in dry GPA-acetylated woods plotted against the concentration of GPA in the treating reagent

Conclusions

Spruce wood specimens were acetylated with an AA solution of GPA, and their viscoelastic properties were compared to those of the untreated and acetylated specimens. By using GPA/AA solutions instead of AA alone, the dynamic Young's modulus of the acetylated wood increased by 10%, and its mechanical loss tangent remained unchanged at room temperature. These changes were interpreted by the antiplasticizing effects of bulky GPA molecules introduced into the wood cell wall. On the other hand, the thermal softening temperature of the dry acetylated wood was markedly reduced with the introduction of GPA. Consequently, the GPA-acetylated wood was well softened above 150°C even in the absence of moisture. It was suggested that the GPA molecules acted as a plasticizer in the wood cell wall above its melting point.

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