EFFECT OF HUMIDITY ON VIBRATIONAL PROPERTIES OF CHEMICALLY MODIFIED WOOD

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ABSTRACT

Changes in vibrational properties of wood can be used to determine changes in the wood cell wall resulting from chemical modification. The dynamic Young's modulus to specific gravity ratio (E'/γ) and internal friction (tan δ) for chemically modified wood compared to those for untreated wood showed major differences in cell-wall modification and lumen filling modification. Increasing the moisture content of the cell wall also has a major effect on the vibrational properties of chemically modified wood. In general, treatments that resulted in lowering the moisture content of the cell wall also lowered internal friction within the cell wall. Vapor phase reactions with formaldehyde had the greatest effect in stabilizing the cell wall against changes in dynamic mechanical properties with increasing moisture content.

Keywords: Vibrational properties, dynamic Young's modulus, internal friction, moisture, chemical modification.

INTRODUCTION

This paper is part of a continuing study of the relationship between wood structure and wood properties. Most chemical and mechan-

ical properties of wood are a result of the chemistry of the cell-wall polymers and the matrix they are in. Because wood is a viscoelastic material, mechanical properties are highly dependent on the elasticity of, as well as the internal friction within, the cell-wall polymers and matrix.

One convenient way of studying viscoelastic properties of wood is through vibrational analysis. A simple harmonic stress results in a phase

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difference between stress and strain. The ratio of dynamic Young's modulus (E') to specific gravity (γ) (E'/γ = specific modulus) and internal friction (tangent of the phase angle, tan δ) measurements can be used to study the viscoelastic nature of wood. The E'/γ is related to sound velocity and tan δ to sound absorption or damping within the wood, so that in themselves, both quantities are important as far as technological applications are concerned. In addition to this practical purpose, however, we intend to show that changes in E'/γ and tan δ relative to those in untreated wood give valuable information on how a particular chemical treatment modified the structural nature of the wood cell wall. These data, in turn, can be used to predict change in physical properties.

A previous paper showed a linear relationship between logarithms of E'/γ and tan δ for untreated wood (Norimoto et al. 1986). This relationship was found regardless of wood species, vibrational measuring direction, or grain angle. It was also found that changes in ambient humidity did not change the linearity of the relationship but did change the magnitude (Sasaki et al. 1988).

Chemical modification of the wood cell-wall polymers has been shown to affect the vibrational properties of wood (Moore et al. 1983; Akitsu et al. 1991). The effect on vibrational properties was very dependent on the type of chemical modification at the cellular and molecular level. All these measurements were done at one level of relative humidity (60%). Change of vibrational properties, however, did not always depend on the type of molecule introduced. For example, if a hydrophilic polymer such as polyethylene glycol was introduced into the cell wall, tan δ values increased. However, in the case of maleic acid and glycerol treatments, which also introduce a hydrophilic molecule into the cell wall, tan δ values decreased. From this research, it was predicted not only that the vibrational properties are modified in various ways by chemical treatments but also that their sensitivity to changes in ambient humidity should occur according

to different patterns depending on the type of treatment.

The present approach differs basically from that of dynamic mechanical thermal analysis (DMTA) where the scanning over a large range of temperature and frequencies allows the detection of transitions and the estimation of apparent activation energies characterizing the molecular components involved in the viscoelastic processes (Kelley et al. 1987). In the range of temperature and frequency under consideration here, the material is expected to remain in a glassy state, so that the changes observed in E'/γ and tan δ are not affected by the crossing over glassy transitions and can be safely attributed to structural differences caused by chemical treatments or moisture adsorption. In the present work, the longitudinal vibrational properties of eight types of chemically modified wood were determined at four relative humidity (RH) levels.

EXPERIMENTAL

Glehn's spruce (*Picea glehnii*) specimens 200 by 10 by 2 mm (longitudinal by radial by tangential) were prepared from one piece of wood (air-dry specific gravity 0.46, average ring width 1.03 mm). All specimens were extracted with benzene/ethanol in a ratio of 1/1 (v/v) and oven-dried at 105 C overnight before chemical modification.

Chemical modification treatments

Fifteen chemical modification treatments were used:

FS Reaction with formaldehyde and sulfur dioxide in a vapor phase reaction.

FH Reaction with formaldehyde and hydrochloric acid in a vapor phase reaction.

FW Reaction with formaldehyde, acetic acid, and hydrochloric acid in a liquid phase reaction.

A Reaction with liquid acetic anhydride.

PF1 Impregnation with high molecular weight phenol-formaldehyde resin.

PF2 Impregnation with low molecular weight phenol-formaldehyde resin.

MG Reaction with maleic acid and glycerol.

PO Reaction with propylene oxide.

BO Reaction with butylene oxide.

WIC Formation of a wood-inorganic composite (barium chloride, boric acid, and diammonium phosphate).

PEG1 Impregnation with polyethylene glycol 10,000.

PEG2 Impregnation with polyethylene glycol 1,000.

PEG3 Impregnation with polyethylene glycol 600.

WM Formation of a wood-plastic composite using methyl methacrylate and oven-dry wood.

WWM Formation of a wood-plastic composite using methyl methacrylate and air-dry wood.

Formalization treatments were done with slight variations from the procedure previously published (Norimoto et al. 1992). The FS specimens were prepared in a closed vessel with 0.0215 mol/liter formaldehyde and 0.004 mol/liter SO_2 at 120 C for 24 h. The FH specimens were prepared in a vessel with 0.027 mol/liter formaldehyde and 0.0005 mol/liter HCl at 150 C for 4 h. The FW specimens were prepared by immersing the wood in an aqueous solution of 3.6% formaldehyde, 3.7% HCl, and 75% acetic acid for 6 days at 25 C, followed by water washing. All specimens were oven-dried overnight.

Acetylation (A) was done according to the procedure previously published (Rowell et al. 1986). Reactions were done in neat acetic anhydride at 120 C for 10 h, followed by leaching 10 h in boiling water and oven-drying overnight.

Impregnation with phenol-formaldehyde resin was done by soaking the specimens in a 20% aqueous solution of PF1 or a 20% aqueous solution of PF2 until complete saturation of

resin was achieved. The solution used for PF1 was obtained by leaving the resin solution more than 1 month at 5 C, whereas the solution for PF2 (average molecular weight 200) was used shortly after obtaining the product. The resin-impregnated wood was cured for 30 min at 130 C.

The MG specimens were prepared by impregnating the wood with a 20% aqueous solution of maleic acid and glycerol in a ratio of 2/1 (v/v), reacting at 180 C for 3 h, leaching 10 h in boiling water, and oven-drying overnight.

The PO specimens were prepared using propylene oxide and 5% triethylamine as catalyst. The reaction was done in a closed reactor at 120 C for 2 h. The BO specimens were prepared using butylene oxide and 5% triethylamine as catalyst. The reaction was done in a closed reactor at 120 C for 6 h. A vacuum was applied after both reactions to remove excess chemicals. Specimens were then oven-dried overnight.

The WIC specimens were prepared by immersing the wood in an aqueous solution containing 32.0% $BaCl_2$ and 7.2% boric acid at 50 C for 1 day. This was followed by a second immersion in an aqueous solution of 37.4% $(NH_4)_2HPO_4$ and 16.6% boric acid for 8 h at 50 C. All specimens were boiled in water for 12 h and then oven-dried overnight.

Impregnation with polyethylene glycol was done by first saturating the wood specimen in water and then in a 25% aqueous solution of PEG1, PEG2, or PEG3 for 12 h at room temperature. Following the soaking, the specimens were oven-dried overnight.

Wood-plastic composite specimens (WM and WWM) were prepared by impregnating the wood with a solution of methyl methacrylate containing 1% α,α'-azobis-isobutyronitrile as catalyst, wrapping the specimens in aluminum foil, and curing the polymer at 80 C for 3 h.

Weight percent gain resulting from each treatment was determined based on the oven-dry weight of the specimen before and after treatment.

Three specimens of each type were equilibrated at 0%, 35%, 60%, and 85% RH and their moisture content determined. Reduced moisture content M_R was calculated as follows:

$$M_R = \frac{M_2 - M_1}{M_0} \times 100 \tag{1}$$

where M_0 is oven-dry weight of specimen before treatment, M_1 is oven-dry weight of specimen after treatment, and M_2 is weight of specimen after treatment at the specified RH.

Contrary to the conventional moisture content, M_R allows a direct comparison of the amount of water adsorbed by the treated specimens with that of the untreated specimen placed in the same RH conditions. The specific gravity was also estimated based on measurements of the dimensions and the total weight of the specimens at each RH level.

Dynamic mechanical measurements

Dynamic mechanical properties were measured using a free-free beam method previously described (Ono and Norimoto 1983, 1984). The specimens were suspended horizontally with an iron piece at both ends by two fine threads at the nodal points; they were excited by an electromagnetic driver at one end, while the vibration was detected by an electromagnetic transducer at the other end. The E'/γ was calculated from the resonant frequency (200 to 400 Hz), and tan δ from the logarithmic decrease of the signal following a period of forced vibrations at the resonant frequency. Specimens were tested at 0%, 35%, 60%, and 85% RH at 20 C. Each specimen was first oven-dried, then cooled in a desiccator over phosphorus pentoxide and quickly tested. These specimens were designated 0-RH. After testing, the specimens were placed in another desiccator containing $MgCl_2 \cdot 6H_2O$ for at least 2 weeks. Each specimen was weighed to determine moisture content and then tested. These specimens were designated 35-RH. After testing, the specimens were placed in another desiccator containing sodium bromide for at least 2 weeks. The specimens were

weighed to determine moisture content and tested. These specimens were designated 60-RH. After testing, the specimens were placed in a final desiccator containing potassium chloride for at least 2 weeks. The specimens were weighed to determine moisture content and tested. These specimens were designated 85-RH. The minimum periods of 2 weeks allowed each specimen to reach an apparent equilibrium of moisture content, i.e., in all cases, the increase of weight per day did not exceed 0.1% of the oven-dry weight.

Dynamic Young's modulus per specific gravity (E'/γ) and internal friction (tan δ) were measured. An average of seven specimens per treatment were tested and the results averaged.

RESULTS AND DISCUSSION

Figure 1 shows the relationship between tan δ, E'/γ, and moisture content of untreated specimens at different relative humidity levels. The tan δ value decreased as the humidity changed from 0% to 35% RH and then rose with increasing humidity. The E'/γ remained about the same from 0% to 35% RH and then decreased with increasing humidity.

These results agree with those obtained by Kollmann and Krech (1960), James (1961, 1964), Matsumoto (1962), and Bradley and Carr (1976). They reported that at 8% moisture content, E' showed a maximum value and tan δ showed a minimum value. These phenomena can be explained by the hypothesis that in an oven-dry state, molecular chains in the amorphous regions of the cell wall are unnaturally distorted. Also, microvoids exist between the molecular chains. This unnatural structure of the cell wall in an oven-dry state causes a smaller E'/γ and a greater tan δ value. With increasing moisture content from oven-drying, water molecules are embedded in the microvoids and the distorted molecular chains are rearranged. As a result, at about 8% moisture content, a more stable state for the cell-wall structure is obtained. Above 8% moisture content, water acts as a plasticizer that allows more molecular movement and the cohesive forces between molecules are decreased, resulting in
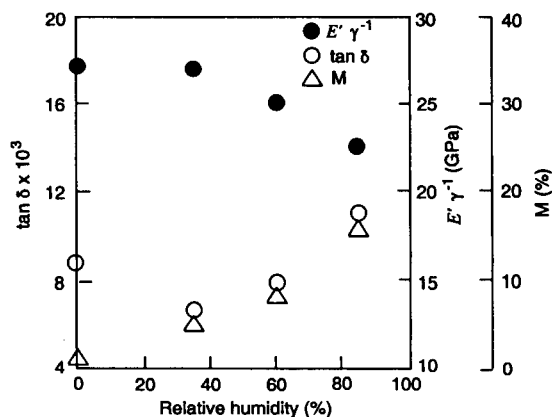
FIG. 1. Relationship between tan δ, E'/γ, and moisture content (M) for untreated wood resulting from change in relative humidity.

decreasing E'/γ values and increasing tan δ values.

Table 1 shows the specific gravity, moisture content, reduced moisture content, and weight percent gain of chemically modified wood at four RH conditions. Table 2 shows the vibrational properties of chemically modified wood at these RH conditions. The non-zero moisture content readings in Table 1 at the 0% RH level originate in the impossibility to obtain a

dry state equivalent to the oven-dry state with a desiccator. The moisture content data were consistent with those published in Norimoto et al. (1992). In the latter study, sorption isotherms were drawn by using the conventional definition of moisture content, based on the total oven-dry weight of the treated specimen. We suggest that for the present analysis, reduced moisture content should be used because it allows a direct comparison of the absolute of water adsorbed between treated and untreated wood. At 85% RH, the reduced moisture content for vapor phase formalization (FS, FH) was about 60% lower than that for untreated wood (U). For treatments such as FW, A, MG, BO, and PF2, reduced moisture content was about 30% lower than that of untreated wood. For PEG2 and PEG3, reduced moisture content was 80% higher than that for untreated wood.

Chemically induced structural changes

Because the moisture content of the cell wall has a direct effect on vibrational properties, part of the observed changes in E'/γ and tan δ values was due to the moisture held in the cell wall or cell lumen because of the chemical

TABLE 1. *Properties of chemically modified woods at various relative humidities.*

	Property at various levels of relative humidity (%)												
	Specific gravity				Moisture content				Reduced moisture content				Weight gain
Treatment[a]	0	35	60	85	0	35	60	85	0	35	60	85	(%)
U	0.45	0.46	0.47	0.48	1.0	5.0	8.5	16.4	1.0	5.0	8.5	—	—
FS	0.46	0.47	0.47	0.47	0.4	3.0	4.2	6.2	0.4	3.1	4.3	6.4	3.9
FH	0.47	0.44	0.45	0.45	0.1	2.1	3.2	5.5	0.1	2.2	3.3	5.7	2.9
FW	0.44	0.44	0.44	0.46	0.4	3.8	7.1	13.1	0.4	3.8	7.2	12.9	−1.2
A	0.49	0.49	0.49	0.51	0.7	2.4	4.3	8.4	0.9	2.9	5.1	10.1	20.4
PO	0.45	0.45	0.47	0.49	1.4	3.9	6.1	13.1	1.6	4.6	7.5	16.0	21.9
BO	0.47	0.47	0.49	0.50	1.3	3.5	5.7	10.7	1.5	4.1	6.7	12.8	18.7
MG	0.56	0.57	0.56	0.59	0.5	3.2	5.1	8.4	0.7	4.3	6.4	11.1	22.9
PF1	0.48	0.57	0.58	0.59	0.7	4.4	7.3	11.6	0.8	5.5	9.0	14.4	22.7
PF2	0.51	0.55	0.55	0.56	0.4	2.8	4.3	7.9	0.5	4.1	6.2	11.4	44.6
PEG1	0.54	0.52	0.54	0.55	0.6	3.1	5.2	11.6	0.9	4.2	7.0	15.8	37.3
PEG2	0.51	0.52	0.54	0.60	1.0	4.5	6.4	21.1	1.4	6.2	8.8	29.3	38.8
PEG3	0.54	0.56	0.59	0.66	1.5	7.1	9.1	21.6	2.2	10.2	13.6	32.2	48.9
WIC	0.68	0.69	0.68	0.69	0.8	4.4	7.0	11.3	1.2	6.5	10.5	16.8	47.2
WM	1.05	1.05	1.03	1.02	0.4	2.2	3.9	6.8	0.9	5.2	9.3	16.2	138.2
WWM	0.98	0.99	0.98	0.97	0.3	2.3	4.1	7.2	0.7	5.1	9.1	15.9	121.4

[a] U, untreated; see Chemical Modification Treatments section for other abbreviation definitions.

TABLE 2. *Dynamic mechanical properties of chemically modified woods at various levels of relative humidity.*

Treatment[a]	$E'/\gamma \times 10^{-11}$ (dyn/cm²)[b]				tan $\delta \times 10^{3}$[b]			
	0	35	60	85	0	35	60	85
U	2.72	2.71	2.52	2.26	8.71	6.65	7.70	11.01
FS	2.75	2.70	2.67	2.57	5.85	5.21	5.73	6.40
FH	3.16	2.94	2.83	2.74	4.77	4.57	5.26	5.82
FW	3.03	2.97	2.70	2.56	6.79	6.40	7.95	9.66
A	2.35	2.26	2.18	2.10	6.06	6.40	7.08	8.59
PO	2.64	2.48	2.29	1.87	5.88	6.45	11.51	17.45
BO	2.40	2.34	2.09	1.86	6.19	6.65	12.88	16.01
MG	2.12	2.07	1.93	1.84	6.82	5.92	6.91	10.82
PF1	2.15	1.98	1.88	1.71	8.83	8.81	9.51	11.95
PF2	2.55	2.50	2.44	2.28	5.10	5.14	5.52	6.58
PEG1	2.49	2.39	2.30	2.00	8.78	7.65	8.60	10.93
PEG2	2.34	2.17	2.09	1.61	14.24	15.49	15.80	19.01
PEG3	2.25	1.97	1.81	1.51	15.72	17.25	17.59	17.70
WIC	2.20	2.18	2.05	1.87	7.61	6.39	8.19	11.09
WM	1.68	1.63	1.53	1.42	14.99	14.64	15.16	17.73
WWM	1.75	1.74	1.65	1.50	14.77	14.48	15.29	16.87

[a] U, untreated; see Chemical Modification Treatments section for other abbreviation definitions.
[b] E'/γ, specific dynamic Young's modulus; tan δ, internal friction.

treatment. A previous paper (Sasaki et al. 1988) showed a linear regression line between log E'/γ and log tan δ for untreated wood at several relative humidity levels. At the 60% RH condition, the data points for wood modified with chemical that did not enter the cell wall, such as PEG1, PF1, and WIC, appeared on the same regression line as that for untreated wood at 60% RH (Akitsu et al. 1991). For the purpose of the present discussion, we will call the regression line derived from experimental plots of tan δ versus E'/γ in a log-log diagram for untreated wood the reference line of a given RH. On Figs. 2 to 5, the corresponding ref-
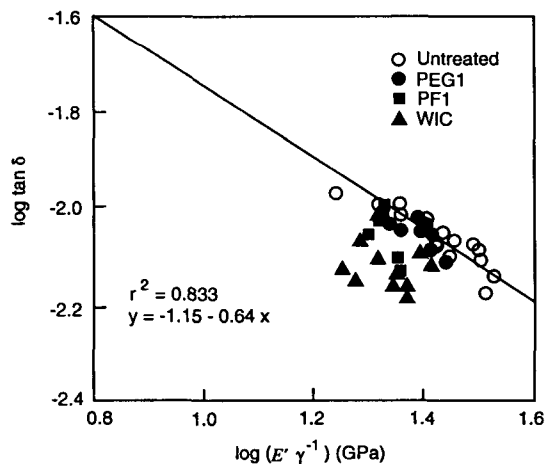
FIG. 2. Relationship between logarithm of E'/γ and logarithm of tan δ at 0% relative humidity for untreated wood and chemical modifications that do not enter the cell wall.
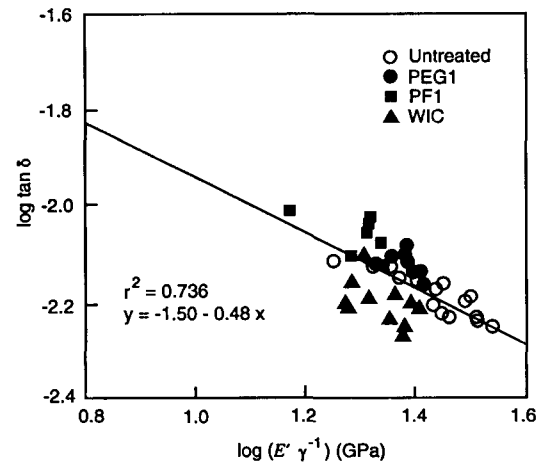
FIG. 3. Relationship between logarithm of E'/γ and logarithm of tan δ at 35% relative humidity for untreated wood and chemical modifications that do not enter the cell wall.
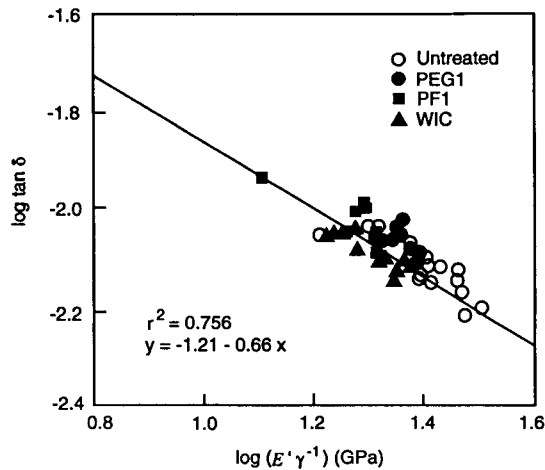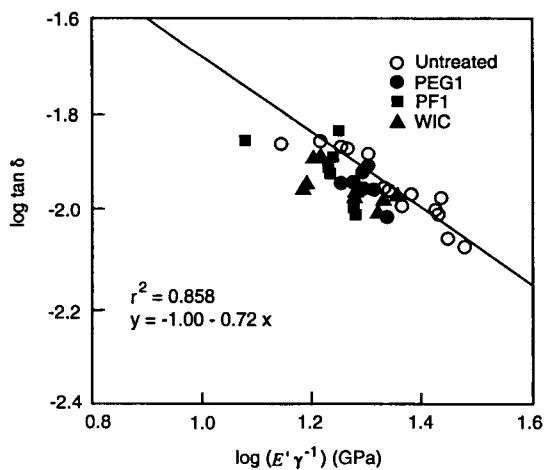
Fig. 4. Relationship between logarithm of E'/γ and logarithm of tan δ at 60% relative humidity for untreated wood and chemical modifications that do not enter the cell wall.

erence line was drawn together with the individual experimental results of untreated wood (U) and wood treated by PEG1, PF1, and WIC. In the case of 60% RH, the reference line was derived from a much larger set of data than that used in this paper. In the other cases (0% RH, 35% RH, and 85% RH), it was derived from the set of values shown on the graph only,

Fig. 5. Relationship between logarithm of E'/γ and logarithm of tan δ at 85% relative humidity for untreated wood and chemical modifications that do not enter the cell wall.

so that because of the small number of specimens measured, the quality of the regression was rather poor.

The existence of a correlation between E'/γ and tan δ for untreated wood is by no means accidental. Both quantities depend on the same microstructural and ultrastructural factors, among which the mean microfibrillar angle and the matrix rigidity have been shown to play the major role, at least in the longitudinal direction (Norimoto et al. 1986). According to this interpretation, a perfect correlation between E'/γ and tan δ at a given level of humidity corresponds to the ideal case where all structural parameters would be either constant or exactly correlated with the microfibrillar angle. The deviance of a given plot relative to the reference is thus explained by the disturbing action of these other structural parameters. Chemical treatments might in some cases provoke perturbations much more considerable than those that are caused by the natural variability of untreated wood. In the present approach, it is proposed that the deviance from the reference lines will give a first indication on the nature of the chemically induced structural changes. Figures 2 to 5 show that if only the lumen was filled or coated with chemical, there was no deviation from the untreated reference regardless of the humidity condition. An exception was the result for WIC at 0% and 35% RH. Because salt is much harder than wood in the dry state, tan δ was lower and E'/γ was higher than that of untreated wood at 0% RH. These differences were lost as water was introduced into the salt matrix, and as a consequence, the deviation from the reference line vanished with increasing humidity.

Figures 6 to 9 show the relationship between average values of log E'/γ and log tan δ for types of chemically cell-wall-modified wood used in this study at four RH levels, together with the corresponding reference lines. Treatments for which the average value on the graphs was significantly above or below the corresponding reference line gave valuable information about the change in the nature of the cell wall. Although this information in itself is
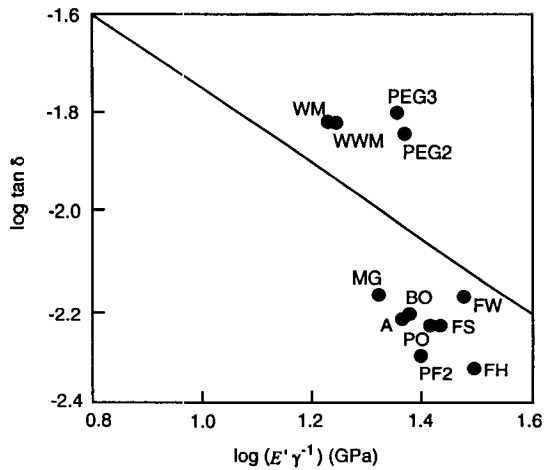
Fig. 6. Relationship between logarithm of E'/γ and logarithm of tan δ for chemically modified wood at 0% relative humidity. (Line on graph from Fig. 2. For abbreviation definitions, see Chemical Modification Treatments section in text.)
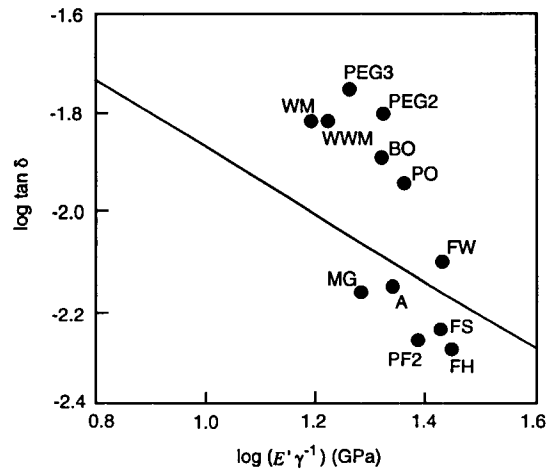

Fig. 8. Relationship between logarithm of E'/γ and logarithm of tan δ for chemically modified wood at 60% relative humidity. (Line on graph from Fig. 4.)

not sufficient and should be completed with a more detailed analysis, we will attempt to comment on the present results by suggesting possible interpretations of the structural changes involved.

Formalization introduced crosslinking as a result of the introduction of oxymethylene groups in the microfibril structure. At low

weight gain of added chemical, the reduced moisture content was much lower with very little effect on the specific gravity of the specimen. In the case of vapor phase formalization (FS, FH), crosslinking occurred in an unswollen state of the cell wall and prevented swelling. This decreased the mobility of the molecular chains, thus reducing tan δ at all humidity levels. In the case of liquid phase formalization
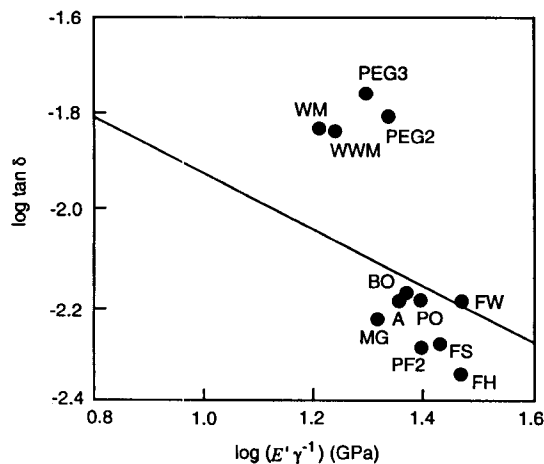

Fig. 7. Relationship between logarithm of E'/γ and logarithm of tan δ for chemically modified wood at 35% relative humidity. (Line on graph from Fig. 3.)
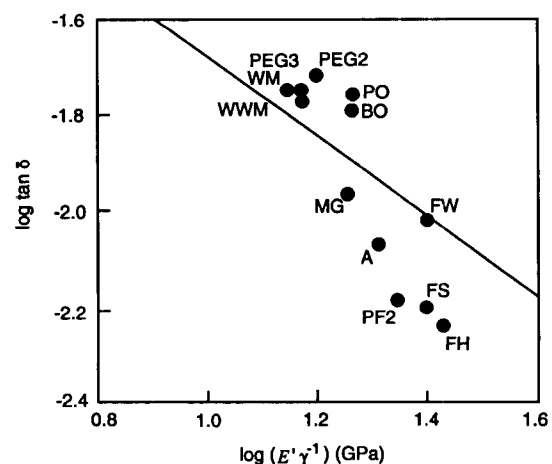

Fig. 9. Relationship between logarithm of E'/γ and logarithm of tan δ for chemically modified wood at 85% relative humidity. (Line on graph from Fig. 5.)
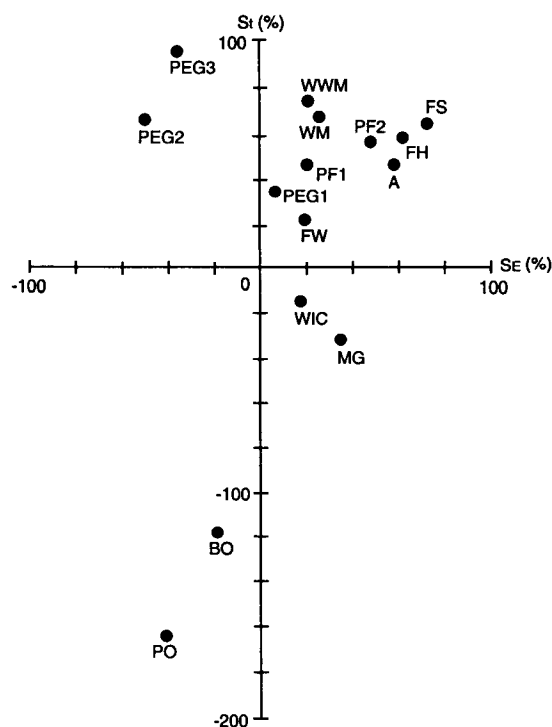
FIG. 10. Relationship between tan δ stability (S_t) and E'/γ stability (S_E) for chemically modified wood.

(FW), crosslinking occurred in a swollen state. One might expect that the mobility of molecular chains in wood constituent would become large compared to that for untreated wood. However, the tan δ value at 0% RH was lower than that for untreated wood, though the value was much larger than those for FS and FH. This lowering of tan δ may be ascribed to rearrangement of molecular chains during reaction. At 60% RH, tan δ for modified wood became greater than that for untreated wood. However, because the data points for FW at 85% RH appeared on the reference line, we suggest that the molecular motion in the highly swollen state is restricted by crosslinking.

For the reaction with acetic anhydride (A), E'/γ was slightly lower than for untreated specimens as a result of the slight increase in γ (about 5%) in acetylated wood. Hydrophobic acetyl groups were substituted for hydrogen atoms in the cell wall. This reduced tan δ because of the steric hindrance of the chain im-

posed by the bulky acetyl group. This effect was seen at all humidity levels. However, humidity-induced changes of E'/γ and tan δ values were greater than those for FS and FH. Because not all available hydroxyl groups were acetylated, water still was able to hydrogen bond with cell-wall polymers and act as a plasticizer.

Treatment with water-soluble, low molecular weight phenol-formaldehyde (PF2) introduced a bulky, hydrophobic group in the cell wall. A small amount of the resin possibly was bonded to the cell-wall hydroxyl groups. There was a large increase in specific gravity; E'/γ was lower for PF2 compared to that for untreated wood. Because of the presence of a rigid benzene ring in the resin backbone as well as reduced moisture sorption, molecular mobility was reduced, which lowered tan δ for all humidity levels tested.

Etherification with PO or BO resulted in bonded cell-wall bulking as in the case of acetylation, except the introduced group was hydrophilic. This made a big difference as the RH increased. At 0% RH (Fig. 6), PO and BO had slightly lower E'/γ because of the increase in specific gravity with etherification, and tan δ was lower than that for untreated wood. At 35% RH (Fig. 7), tan δ was almost the same as that for untreated wood, but at 60% and 85% RH (Figs. 8 and 9), tan δ was much larger. This was due to the flexibility introduced into the cell wall because the hydrophilic ether allowed water to act as a plasticizer.

The MG treatment resulted in a similar effect on E'/γ and tan δ as with PO and BO in that the group introduced into the cell wall is hydrophilic. Unlike PO and BO, the polymer formed with MG treatment is rigid in nature and some crosslinking may occur with the cell-wall hydroxyl groups. This results in less molecular motion in the cell wall, resulting in a lower tan δ than that of untreated wood. However, because of the hydrophilic nature of the polymer formed, tan δ increases at 85% RH (Fig. 9).

The PEG2 and PEG3 polymers are low molecular weight, hydrophilic polymers that enter

the cell wall. These very flexible, hydrophilic polymers swell and plasticize the cell wall even at 0% moisture content, resulting in very large tan δ in the dry condition. The hydrophilic nature of the cell wall does not change as the RH increases because it does not matter whether PEG or water is acting as a plasticizer.

The final treatment with methyl methacrylate (WM and WWM) indicates that a small amount of this polymer may enter the cell wall, but in general, this treatment only fills the lumen space. The increase in specific gravity reduces E'/γ. Water can still enter the cell wall and act as a plasticizer, so tan δ increases as the RH increases.

Thus, the sole deviation of the plots from the corresponding reference line allowed us to propose interpretations of the change in the nature of the cell wall induced by the various treatments. One could object here, especially for the group of treatments shown in Figs. 6 to 9, that as soon as the cell wall was modified, so was the amount of moisture adsorbed in it, as made clear by differences in the amount of reduced moisture content compared to that of untreated wood at the same RH level. Therefore, it would have made more sense to compare the plots to the reference line of untreated wood having reached a similar level of moisture content. However, differences in sorption behavior were themselves included in the change of cell-wall properties that constituted the object of the present discussion, so that the option of comparing the properties in the same RH condition remained founded. Actually, the correct analysis of chemically induced changes would require quantifying the action of a number of parameters, including moisture as well as density changes, which was not made possible with the limited set of parameters available here and was out of the scope of the present discussion.

The stabilizing action of chemical treatments

From a practical point of view, it is of first-hand importance to predict the differences in the reaction to humidity provided by chemical treatments. All these data can be used to derive a general relationship for sensitivity or stability to changes in humidity for chemically modified wood with respect to E'/γ and tan δ. An E'/γ stability S_E is calculated as follows:

$$S_E = \frac{\dfrac{\Delta(E'/\gamma)_u}{(E'/\gamma)_u} - \dfrac{\Delta(E'/\gamma)_T}{(E'/\gamma)_T}}{\dfrac{\Delta(E'/\gamma)_u}{(E'/\gamma)_u}} \times 100 \qquad (2)$$

where u is untreated, T is treated, and $\Delta(E'/\gamma)_u$ is change of E'/γ between 35% and 85% RH.

A tan δ stability S_t is calculated as follows:

$$S_t = \frac{\dfrac{\Delta(\tan\delta)_u}{(\tan\delta)_u} - \dfrac{\Delta(\tan\delta)_T}{(\tan\delta)_T}}{\dfrac{\Delta(\tan\delta)_u}{(\tan\delta)_u}} \times 100 \qquad (3)$$

where $\Delta\tan\delta$ is change of tan δ between 35% and 85% RH.

Figure 10 shows the results of these calculations. The S_E and S_t equations measure how E'/γ and tan δ changed with changing RH conditions. Figure 10 shows FS, FH, PF2, A, WWM, WM, PF1, PEG1, and FW have positive S_E and S_t; PEG2 and PEG3 have negative S_E and positive S_t; WIC and MG have positive S_E and negative S_t; and PO and BO have negative S_E and S_t.

These results show that the greatest stability to changes in vibrational properties with increasing RH is achieved with vapor phase crosslinking with formaldehyde, acetylation, and treatment with a water-soluble, low molecular weight phenol-formaldehyde resin.

CONCLUSIONS

Different molecules introduced into the wood cell wall resulted in different responses in dynamic mechanical properties as ambient humidity increased. Treatments that resulted in lowering of the cell-wall moisture content of the modified wood compared to that of untreated wood gave the greatest stability to changes in dynamic mechanical properties.

The results of this research indicate that treatments for wood, such as vapor phase reaction with formaldehyde, liquid phase reactions with acetic anhydride, and treatment of the cell wall with a water-soluble, low molecular weight phenol-formaldehyde solution and resin curing, result in greatly improved acoustical properties. Treatments for wood are presently under further investigation.

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