

Dielectric Relaxation Spectra of Chemically Treated Woods

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ABSTRACT: The changes in the dielectric properties of absolutely dried Sitka spruce (*Picea sitchensis* Carr.) wood caused by chemical treatments were investigated. Eight kinds of chemical treatments with various levels of weight percentage gain (WPG) were performed. Through the application of the Cole–Cole circular arc law to the results of the dielectric measurements in the frequency range of 1 kHz to 1 MHz at -60°C , the relaxation spectrum was calculated. The relaxation magnitude ($\epsilon_0 - \epsilon_{\infty}$) was reduced by formalization, acetylation, propylene oxide, and phenol–formaldehyde resin treatments, in which chemical reactions occurred between the OH groups in the cell wall and the added reagents. On the other hand, the generalized relaxation time (τ_m) decreased with increasing WPG, except for acetylation, for which τ_m decreased up to a WPG level of 20% and then

increased. In poly(ethylene glycol) impregnation, ($\epsilon_0 - \epsilon_{\infty}$) decreased with increasing WPG up to about 50% and then increased, whereas τ_m linearly decreased with increasing WPG. No significant changes in these parameters were recognized for the wood methyl methacrylate composite and heat treatment. With the steam treatment, τ_m increased. The distribution of the relaxation times was broad in acetylation and narrow in propylene oxide treatment and poly(ethylene glycol) impregnation. However, it remained almost unchanged in the other treatments. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 96: 37–43, 2005

Key words: dielectric properties; relaxation; structure-property relations

INTRODUCTION

The changes in the properties of wood caused by chemical treatments show characteristic behaviors depending on structural changes. The structures of chemically treated woods are divided into three types depending on the structural changes at the cellular level:¹ chemical modification or impregnation in the cell wall, impregnation in the cell wall and coating of the inner surface of the cell lumen, and filling of the cell lumen with a reagent while the cell wall remains untreated. In this study, the effects of eight kinds of typical chemical treatments on the dielectric properties were investigated with respect to structural changes due to the treatments. One of the best ways of understanding the dielectric properties of chemically treated woods is through the relaxation spectrum at a fixed temperature. However, it is very difficult to determine an accurate relaxation spectrum. If the Cole–Cole circular arc law can be applied to the results of dielectric measurements, an accurate spectrum can be obtained. In a previous article,² we reported that the Cole–Cole circular arc law could be satisfactorily applied to the results of chemically treated woods. This

article deals with changes in the relaxation spectra caused by typical types of chemical treatments, especially with respect to structural changes at various treatment levels.

EXPERIMENTAL

Preparation of chemically treated woods

Sitka spruce (*Picea sitchensis* Carr.) heartwood specimens, 50 mm (radial direction) by 50 mm (tangential direction) by 5 mm (longitudinal direction), were used. After extraction with a mixed solvent of ethanol and benzene (1:2 v/v) for 24 h with a Soxhlet extractor, they were air-dried and then absolutely dried by heating at 60°C for 24 h under reduced pressure. The average density of the extracted specimens under an absolutely dried condition was 0.45 g/cm^3 .

These specimens were subjected to eight kinds of chemical treatments. Formalization (F) was carried out in a sealed glass vessel with paraformaldehyde and SO_2 as catalysts at 120°C for 1, 4, 10, 24, or 48 h. Acetylation (A) was performed in neat acetic anhydride at 120°C for 0, 5, 15, 30, 60, 120, 240, 600, or 1440 min. After the reaction, the specimens were sufficiently rinsed in running water. Propylene oxide treatment (PO) was carried out in a pressure vessel containing a mixed solution of propylene oxide and triethylamine as a catalyst (95:5 v/v) at 120°C for 15, 30, 60, 120, or 180 min. The pressure inside the vessel was

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about 1 MPa. Poly(ethylene glycol) impregnation (PEG) was carried out by the saturation of the specimens first with water and then with 20, 40, 60, or 80% aqueous solutions of poly(ethylene glycol) (average molecular weight = 1000) or 100% poly(ethylene glycol) for 1 week. Phenol-formaldehyde resin treatment (PF) was carried out via the soaking of the specimens in 1, 3, 5, 10, or 15% aqueous solutions of a low-molecular-weight phenol-formaldehyde resin (average molecular weight = 270) under reduced pressure and then via the heating of resin-impregnated specimens for 90 min at 170°C. A wood methyl methacrylate composite (WPC) was created out by the impregnation of absolutely dried specimens with a solution of methyl methacrylate monomer containing 1% α, α' -azobisisobutyronitrile as an initiator under reduced pressure, the wrapping of the specimens in a Teflon sheet and aluminum foil, and polymerization at 80°C for 2 h. Heat treatment (H) was carried out by the heating of absolutely dried specimens at 180°C for 3, 6, 9, 12, 20, or 40 h in a vacuum oven. Steam treatment (S) was carried out in an autoclave at 140, 160, or 180°C for 60 min. After the treatments, the weights and dimensions of the treated specimens were measured. The weight percentage gain (WPG), density (γ), and volume change (V_c) of the treated specimens are shown in Table I.

Dielectric properties

Chemically treated specimens were cut into disks 49 mm in diameter. They were dried at 60°C for 24 h under vacuum pressure and then subjected to dielectric measurements. An LCR meter (HP4284A, Japan Hewlett-Packard Co., Ltd., Tokyo, Japan), an electrode (effective diameter = 38 mm; SE-30, Ando Electric Co., Ltd., Tokyo, Japan), and a bath (TO-3, Ando Electric) were used for the dielectric measurements. The dielectric constant (ϵ') and loss (ϵ'') of absolutely dried specimens along the grain were measured at 31 steps of frequency between 1 kHz and 1 MHz at -60°C.

RESULTS AND DISCUSSION

Cole-Cole circular arc law

Our previous study² showed that dielectric relaxation due to the motions of methylol groups occurred in chemically treated woods. To compare quantitative changes in the dielectric properties by treatments, we applied the Cole-Cole circular arc law to the results of dielectric measurements. The law is expressed as follows:³

$$\epsilon^* - \epsilon_\infty = (\epsilon_0 - \epsilon_\infty) \times \frac{1}{1 + (i\omega\tau_m)^\beta} \quad (1)$$

where ϵ^* is the complex dielectric constant ($\epsilon^* = \epsilon' - i\epsilon''$), ϵ_0 is the dielectric constant at the limiting low frequency, ϵ_∞ is the dielectric constant at the limiting high frequency, ω is the angular frequency ($\omega = 2\pi f$), τ_m is the generalized relaxation time, and β ($0 \leq \beta \leq 1$) is a parameter relating to the distribution of relaxation times. The broader the distribution of relaxation times becomes, the smaller β is. In the single-relaxation system, β is unity. $(\epsilon_0 - \epsilon_\infty)$ is the parameter relating to the magnitude of dipole orientation. The relaxation spectrum $H(s)$ or $H(\log \tau)$, obtained from the Cole-Cole circular arc law, can be expressed as follows:³

$$H(s) = \frac{1}{2\pi} \times \frac{\sin(\beta\pi)}{\cosh(\beta s) + \cos(\beta\pi)}$$

$$\times \int_{-\infty}^{\infty} H(s) \times ds = 1, s = \ln\left(\frac{\tau}{\tau_m}\right),$$

$$H(\log\tau) = 2.303H(\ln\tau) \quad (2)$$

The Cole-Cole circular arc law could be satisfactorily applied to the results. The parameters calculated from Cole-Cole plots are shown in Table I. The relaxation spectra were calculated by the substitution of these parameters in eq. (2).

Relaxation spectra of chemically treated woods

The relaxation spectra of untreated and formalized wood specimens are shown in Figure 1. A dielectric relaxation was recognized in both wood specimens. Dielectric measurements of the wood constituents have shown that the relaxation observed in untreated wood occurs in cellulose, mannan, and lignin, which have methylol groups, but not in xylan, which does not have methylol groups.⁴ The relaxation of cellulose is absolutely eliminated by tritylation, in which trityl groups are selectively introduced in primary hydroxyl groups.^{5,6} The relaxation magnitude of cellulose decreases as the degree of crystallinity increases.^{6,7} The apparent activation energy of this relaxation is about 42 kJ/mol.⁴ These facts show that the relaxation observed in the untreated wood was due to the motions of methylol groups in the noncrystalline region of the cell wall.⁴

F is a reaction involving the formation of OCH₂ bridges between OH groups of the cell wall components by formaldehyde. Short molecular bridges are made when the molecular chains of wood constituents are close to one another. The relaxation spectrum was greatly reduced with increasing WPG. The relaxation time at the maximum value of the spectrum (τ_0) was slightly reduced with increasing WPG. These results suggest that the motions of the remaining methylol groups were facilitated to some extent by the expan-

TABLE I
WPG, γ Under Absolutely Dried Conditions, V_c and Parameters in Cole-Cole Plots [$(\epsilon_0 - \epsilon_\infty)$, ϵ_∞ , β , τ_m]
of Untreated and Chemically Treated Wood Specimens

Treatment	Symbol	WPG (%)	γ (g/cm ³)	V_c (%)	$(\epsilon_0 - \epsilon_\infty)$	ϵ_∞	β	τ_m (10 ⁻⁵ s)
Untreated wood	U	—	0.45	—	1.01	1.74	0.26	3.66
Formalization	F	1.2	0.45	-0.1	0.79	1.73	0.26	1.47
		4.1	0.45	1.4	0.71	1.74	0.26	1.51
		5.4	0.45	2.3	0.59	1.73	0.27	0.93
		5.1	0.46	2.0	0.56	1.71	0.26	1.03
		5.9	0.45	2.1	0.54	1.71	0.26	1.15
Acetylation	A	0.2	0.46	-1.7	0.95	1.75	0.26	2.32
		3.6	0.47	0.0	0.81	1.77	0.26	1.57
		9.6	0.48	2.7	0.64	1.76	0.24	1.21
		12.6	0.48	4.2	0.53	1.79	0.23	1.99
		15.1	0.49	6.3	0.56	1.78	0.24	1.49
		17.3	0.50	6.7	0.59	1.78	0.24	1.20
		20.0	0.50	7.1	0.49	1.80	0.23	2.08
		22.3	0.51	7.1	0.49	1.81	0.22	5.20
		25.8	0.53	7.3	0.51	1.84	0.20	24.50
		Propylene oxide treatment	PO	1.6	0.46	0.4	0.90	1.74
3.0	0.46			0.8	0.86	1.74	0.27	2.07
8.7	0.46			5.1	0.79	1.77	0.28	1.99
15.3	0.48			8.1	0.74	1.76	0.29	1.72
40.1	0.54			16.5	0.62	1.85	0.29	0.77
47.8	0.56			20.5	0.64	1.90	0.30	0.71
Poly(ethylene glycol) impregnation	PEG	16.7	0.49	5.8	0.68	1.79	0.31	0.85
		48.7	0.59	11.8	0.59	1.94	0.34	0.45
		84.9	0.72	12.1	0.65	2.16	0.35	0.37
		147.6	0.97	10.3	0.77	2.51	0.37	0.31
		178.6	1.08	15.0	0.82	2.63	0.37	0.31
Phenol-formaldehyde resin treatment	PF	4.0	0.47	0.9	0.96	1.75	0.26	2.39
		11.1	0.49	5.0	0.82	1.80	0.27	1.15
		16.3	0.48	13.4	0.82	1.87	0.27	0.91
		26.5	0.53	9.5	0.75	1.87	0.27	0.68
		31.7	0.52	15.5	0.74	1.90	0.25	0.77
Wood methyl methacrylate composite	WPC	119.2	1.03	-3.0	1.05	2.43	0.26	2.36
Heat treatment	H	-0.6	0.44	0.0	1.01	1.73	0.26	3.64
		-0.7	0.44	-0.2	0.96	1.72	0.26	3.25
		-1.1	0.44	-0.5	1.00	1.72	0.25	4.00
		-1.3	0.44	-0.2	0.99	1.72	0.26	3.65
		-1.7	0.45	-0.8	1.05	1.71	0.25	5.56
Steam treatment	S	-2.0	0.45	-1.0	1.09	1.72	0.25	5.06
		-3.6	0.45	-4.9	0.99	1.75	0.26	3.32
		-9.8	0.44	-8.9	0.98	1.71	0.26	4.94
		-17.4	0.43	-12.8	1.11	1.69	0.25	10.65

sion of intramolecular space due to the introduction of OCH₂ groups. The volume increase of the specimen at 5.9% WPG was 2.1%.

Figure 2 shows the results for acetylated wood specimens. A is a reaction in which OH groups of the cell walls are replaced by hydrophobic and bulky OCOCH₃ groups. The spectra largely decreased in magnitude with increasing WPG, and the shape became broader. A distinct change in τ_0 was recognized above 22.3% WPG.

The spectra of PO are shown in Figure 3. In propylene oxide treated wood, OH groups are replaced by hydrophilic and bulky OCH₂CH(OH)C₂H₅ groups.

This treatment is similar to A, but the introduced side groups are hydrophilic. The spectrum magnitude gradually decreased with increasing WPG. However, the extent was smaller than that of F and A at the same WPG. The volume increase was 20.5% at 47.8% WPG, which was the largest of all the treatments. τ_0 decreased with increasing WPG.

The spectra of PEG are illustrated in Figure 4. In this treatment, bulky and extremely hydrophilic molecules are introduced not only in the cell walls without the formation of any stable bond but also in the cell lumens. τ_0 was reduced up to 49% WPG and then became almost constant. Hygroscopic poly(ethylene gly-

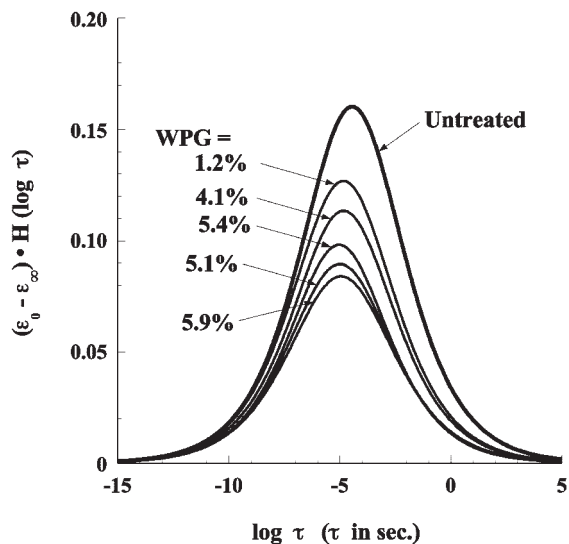


Figure 1 $(\epsilon_0 - \epsilon_\infty) \cdot H(\log \tau)$ relaxation spectra of untreated and formalized wood specimens with various WPG levels.

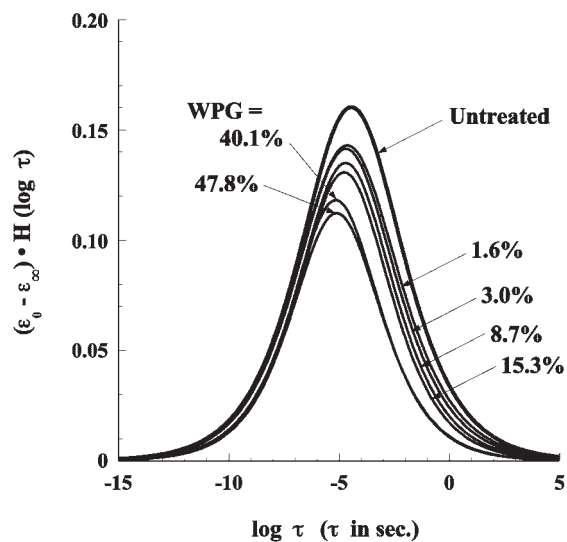


Figure 3 $(\epsilon_0 - \epsilon_\infty)H \cdot (\log \tau)$ relaxation spectra of untreated and propylene oxide treated wood specimens with various WPG levels.

col) molecules induced an extremely large swelling of the cell walls without any stable bonds and significantly facilitated the motions of cell wall polymers. Poly(ethylene glycol) molecules could be added to the cell walls, and a large swelling of the cell walls occurred. At the same time, they acted as a plasticizer, which led to an extreme reduction in the cohesive forces of the cell-wall polymers, and this resulted in the reduction of τ_0 . On the other hand, it appears that poly(ethylene glycol) molecules were added mainly to the cell lumens because of a slight change in the volume of the specimens above 49% WPG.

The spectra of PF are shown in Figure 5. In this treatment, only a limited amount of the resin is in the

cell walls, and excess resin is in the lumens. The resin added to the cell walls is hydrophobic and acts as a bulking agent. PF is different from PEG in the point at which the introduced resin is hydrophobic, and some chemical bonds may be formed between the resin and the cell wall components.⁸ V_c due to the treatment was relatively large, as shown in Table I. As WPG increased, both the spectrum magnitude and τ_0 decreased. These results showed that although the number of methylol groups involved in a unit of volume of the cell walls decreased, the motions of the remaining methylol groups were facilitated to reduce τ_0 by cell-wall swelling.

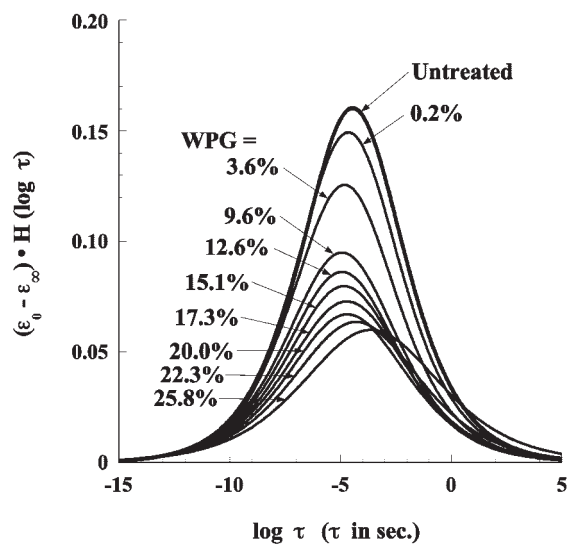


Figure 2 $(\epsilon_0 - \epsilon_\infty) \cdot H(\log \tau)$ relaxation spectra of untreated and acetylated wood specimens with various WPG levels.

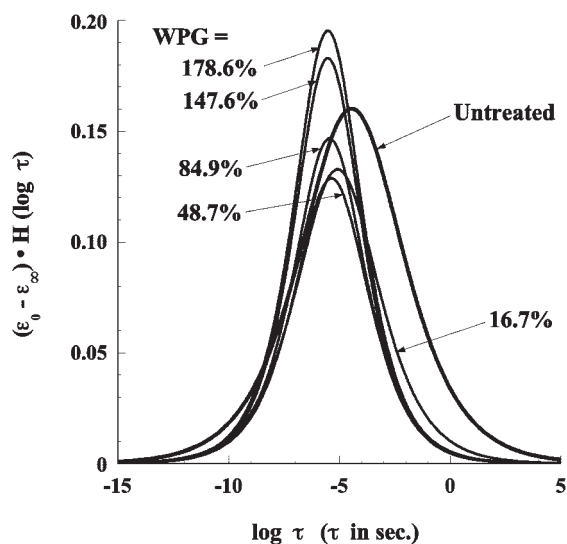


Figure 4 $(\epsilon_0 - \epsilon_\infty) \cdot H(\log \tau)$ relaxation spectra of untreated and poly(ethylene glycol) impregnated wood specimens with various WPG levels.

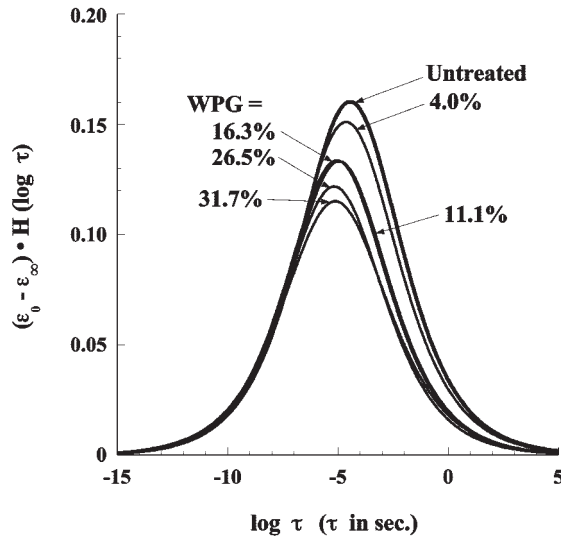


Figure 5 $(\epsilon_0 - \epsilon_\infty) \cdot H(\log \tau)$ relaxation spectra of untreated and phenol-formaldehyde resin treated wood specimens with various WPG levels.

The spectra of WPC are shown in Figure 6. Because methyl methacrylate is a nonpolar liquid, it cannot be added to the cell walls. The cell walls remain almost untreated, whereas the resin partially or totally fills the lumens. V_c of a specimen with 119.2% WPG showed a negative value of -3.0% . It appears that this negative V_c was caused by the contraction of poly(methyl methacrylate) polymers, which filled the cell lumens. No perceivable changes in the spectra were observed.

The spectra of H are shown in Figure 7. This treatment changes water-reactive polysaccharides into hydrophobic furfural polymers. The thermodegradation

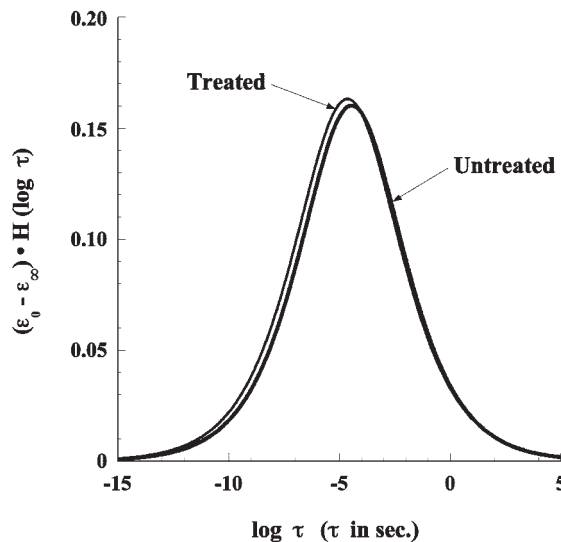


Figure 6 $(\epsilon_0 - \epsilon_\infty) \cdot H(\log \tau)$ relaxation spectra of untreated wood and WPC specimens.

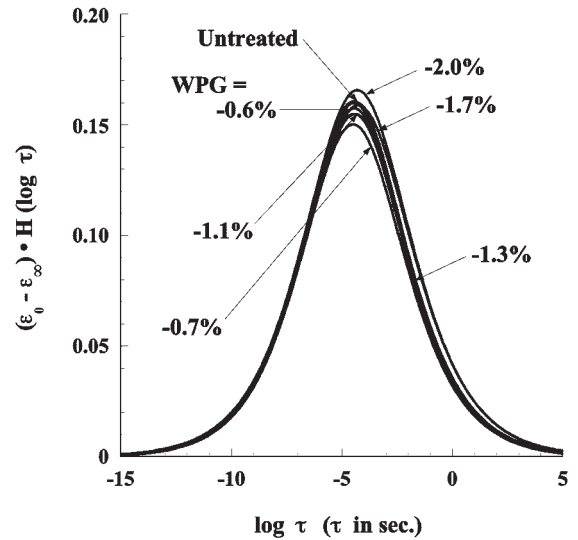


Figure 7 $(\epsilon_0 - \epsilon_\infty) \cdot H(\log \tau)$ relaxation spectra of untreated and heat-treated wood specimens with various WPG levels.

of hemicelluloses caused a slight weight loss as well as a slight V_c , as shown in Table I. The spectrum magnitude and τ_0 slightly changed.

The spectra of S are shown in Figure 8. This treatment induces the formation of cohesive structures in the matrix substance of the cell walls and the degradation of hemicelluloses.⁹ A large weight loss as well as a large volume decrease was caused by this treatment. A slight increase in the spectrum magnitude and τ_0 was observed.

Parameters in the Cole–Cole plots

To characterize changes in the dielectric relaxation by the treatments, we examined $(\epsilon_0 - \epsilon_\infty)$, ϵ_∞ , τ_m , and β

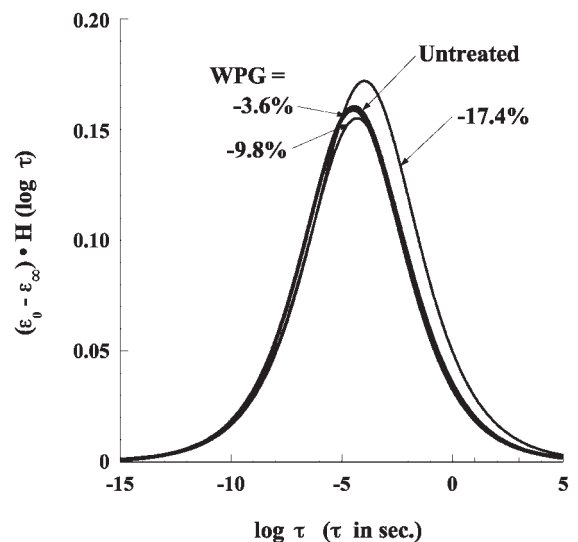


Figure 8 $(\epsilon_0 - \epsilon_\infty) \cdot H(\log \tau)$ relaxation spectra of untreated and steam-treated wood specimens with various WPG levels.

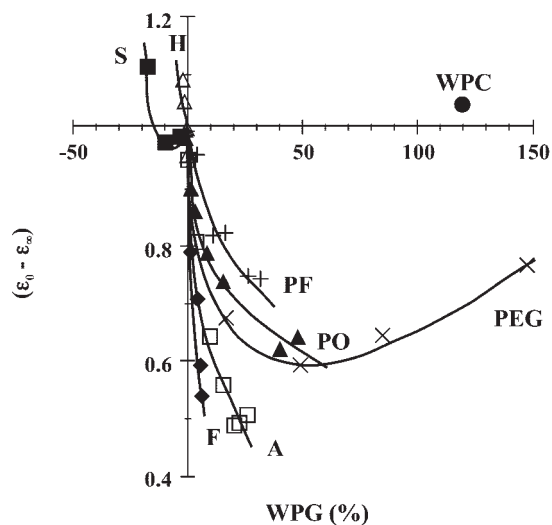


Figure 9 Magnitude of dipole orientation ($\epsilon_0 - \epsilon_\infty$) of chemically treated woods as a function of WPG: (\blacklozenge) F, (\square) A, (\blacktriangle) PO, (\times) PEG, ($+$) PF, (\bullet) WPC, (\triangle) H, and (\blacksquare) S.

from the Cole–Cole plots. ($\epsilon_0 - \epsilon_\infty$) is plotted against WPG in Figure 9. ($\epsilon_0 - \epsilon_\infty$) of F remarkably decreased with increasing WPG, suggesting a reduction in the number of methylol groups by the formation of OCH_2 bridges between OH groups. ϵ_∞ was not changed by the treatment, as shown in Table I.

ϵ_∞ is the dielectric constant due to optical polarization from the displacement of electrons and due to infrared polarization from the displacement of atoms or groups of atoms, and ϵ_∞ increases with γ of a specimen. ($\epsilon_0 - \epsilon_\infty$) of A remarkably decreased with increasing WPG. This occurred because the methylol groups had been replaced by OCOCH_3 groups. ϵ_∞ was increased in proportion to WPG, whereas ($\epsilon_0 - \epsilon_\infty$) of PO decreased with increasing WPG. However, the extent was smaller than that of F and A at the same WPG. This likely occurred because the reduction of methylol groups was counterbalanced by the added polar side chains of $\text{OCH}_2\text{CH}(\text{OH})\text{C}_2\text{H}_5$ groups, which contributed to the relaxation.

ϵ_∞ increased with WPG. It is reported that propylene oxide reaction continues beyond the cell wall rupture.¹⁰ This fact suggests that the motions of the remaining methylol groups were facilitated by a continuous increase in the intramolecular space at higher WPGs. ($\epsilon_0 - \epsilon_\infty$) of PEG decreased up to 49% WPG and then slightly increased. The number of methylol groups involved in a unit of volume of the cell walls decreased with increasing WPG, and this resulted in a decrease in ($\epsilon_0 - \epsilon_\infty$). On the other hand, the motions of methylol groups may have been facilitated with WPG by the introduction of bulky and extremely hydrophilic molecules into the cell walls, which increased the spectrum magnitude. It is speculated that the latter effect became dominant at higher WPGs. ϵ_∞

increased up to 2.63 with increasing WPG. ($\epsilon_0 - \epsilon_\infty$) of PF decreased with a decrease in the number of methylol groups involved in a unit of volume of the cell wall, whereas ϵ_∞ increased with increasing WPG. No significant changes in ($\epsilon_0 - \epsilon_\infty$) were induced by the WPC, H, and S treatments. However, ϵ_∞ of WPC showed a large value of 2.43 at 119.2% WPG. On the other hand, ϵ_∞ of S decreased with weight loss, and that of H remained unchanged.

The relationship between $\log \tau_m$ and WPG is shown in Figure 10. τ_m , identical to τ_0 , decreased in A, PO, PEG, and PF with increasing WPG. However, that of A decreased with increasing WPG up to 20% WPG and then increased. τ_m above 22.2% WPG exceeded that of the untreated specimen. It appears that the motions of the methylol groups were facilitated by the introduction of a small amount of bulky OCOCH_3 groups into the cell walls. However, when a large number of bulky groups were added to the cell walls, the swelling of the S_2 layer may have been restricted by the hoop effect of the S_1 layer. This restraint may have restricted the motions of the remaining methylol groups. τ_m of S increased with prolonged treatment. This result can be explained by the formation of cohesive structures in the matrix substance of the cell walls and the degradation of hemicelluloses.

Figure 11 shows the relationship between β and WPG. β increased with increasing WPG in F, PO, and PEG but decreased in PF and A. On the other hand, β slightly decreased with the treatment time in H and S.

CONCLUSIONS

Changes in the dielectric relaxation of wood (*Picea sitchensis* Carr) related to the motions of methylol

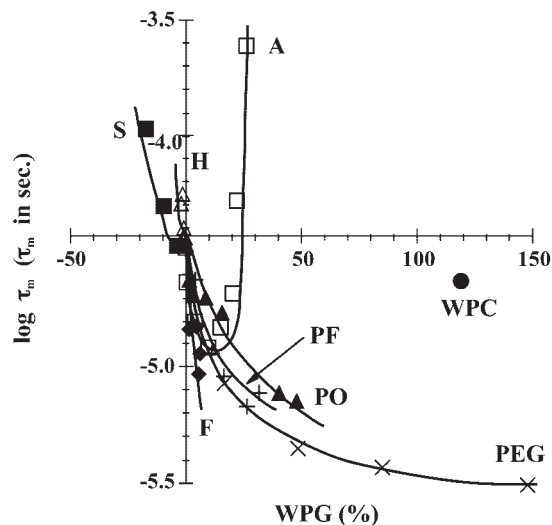


Figure 10 $\log \tau_m$ of chemically treated woods as a function of WPG: (\blacklozenge) F, (\square) A, (\blacktriangle) PO, (\times) PEG, ($+$) PF, (\bullet) WPC, (\triangle) H, and (\blacksquare) S.

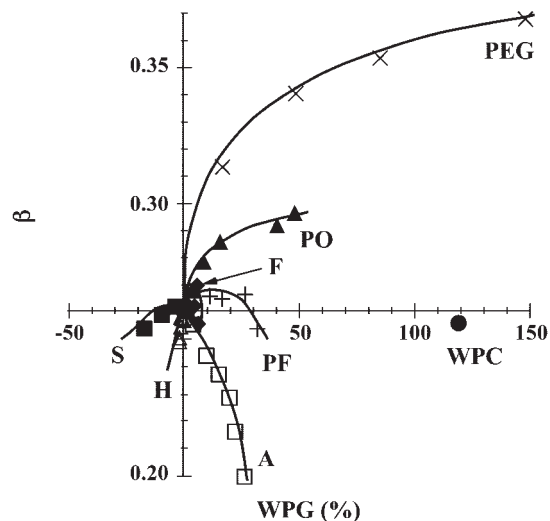


Figure 11 β of chemically treated woods as a function of WPG: (\blacklozenge) F, (\square) A, (\blacktriangle) PO, (\times) PEG, ($+$) PF, (\bullet) WPC, (\triangle) H, and (\blacksquare) S.

groups by eight kinds of chemical treatments were investigated. The Cole–Cole circular arc law was applied to the results of the dielectric measurements at -60°C , and the relaxation spectra were calculated. The following results were obtained.

$(\epsilon_0 - \epsilon_\infty)$ decreased with F, A, PO, and PF, in which chemical reactions occurred between the OH groups in the cell wall and the added reagents.

τ_m of F, PO, and PF decreased with increasing WPG. τ_m of A decreased up to 20% WPG and then increased. It appears that the motions of the methylol groups were facilitated by the addition of a small amount of bulky OCOCH_3 groups to the cell walls. However, when a large number of bulky groups were added to

the cell walls, the swelling of the S_2 layer may have been restricted by the hoop effect of the S_1 layer. This restraint may have restricted the motions of the remaining methylol groups.

$(\epsilon_0 - \epsilon_\infty)$ of PEG decreased up to about 50% WPG and then increased. The number of methylol groups involved in a unit of volume of the cell walls decreased with increasing WPG, and this resulted in a decrease in $(\epsilon_0 - \epsilon_\infty)$. On the other hand, the motions of the methylol groups may have been facilitated with WPG by the addition of bulky and extremely hydrophilic molecules into the cell walls, which increased the spectrum magnitude. τ_m of PEG decreased with WPG. However, no significant changes in τ_m were observed in WPC and H. In S, τ_m increased. This result can be explained by the formation of cohesive structures in the matrix substance of the cell walls and the degradation of hemicelluloses.

β became broad in A but narrow in PO and PEG. In the other treatments, it remained almost constant.

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