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Dielectric properties of chemically treated wood

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Dielectric properties along the grain for absolutely dried untreated and seven kinds of chemically treated Sitka spruce (*Picea sitchensis* Carr.) woods were measured. Cole-Cole's circular arc law was applied to the results of the relaxation due to the motions of methylol groups. The following changes were caused by chemical treatments. In polyethylene glycol (PEG) impregnation, the distribution of relaxation times became very narrow, the generalized relaxation time (τ_m) was considerably decreased, and the relaxation magnitude ($\varepsilon_0 - \varepsilon_\infty$) was slightly increased. In acetylation, the distribution of relaxation times became very broad, τ_m was considerably increased, and ($\varepsilon_0 - \varepsilon_\infty$) was remarkably decreased. In propylene oxide treatment, the distribution of relaxation times became slightly narrow and τ_m was decreased. τ_m was slightly decreased in formalization, phenol-formaldehyde (PF) resin treatment and wood methyl methacrylate (MMA) composite. ($\varepsilon_0 - \varepsilon_\infty$) was decreased in formalization and PF-resin treatment and was hardly changed in wood-MMA composite and heat treatment. The distribution of relaxation times was almost unchanged in formalization, PF-resin treatment, wood-MMA composite and heat treatment.

1. Introduction

Chemical treatments of wood are effective to improve various properties. Some treatments destroy the composite and cellular structures of wood. Consequently, the resulting material does not have any of the characteristic properties of wood. Chemical treatments of wood as discussed in this paper exclude such radical ones. It may reduce some defects relative to wood utilization and enhance its properties, while keeping the bulk of superior mechanical properties of wood.

To understand how chemical treatments change properties of wood, it is important to have a clear understanding of their structural modifications of wood. At the cellular level of wood, there are three types of treatments: (1) Only cell walls are treated; (2) Cell walls are treated with a deposit of a resin or any other products in cell lumens; and (3) Cell walls are untreated with a deposit of a resin or any other products in cell lumens. At the molecular level, there are four types of treatments: (1) Molecular bridges are formed between adjacent hydroxyl groups of cell wall polymers; (2) Hydroxyl groups of cell wall polymers are replaced with bulky and hydrophobic or hydrophilic groups; (3) Resin or other products are introduced into the cell wall without the formation of any stable bond; and (4) Some structural changes of cell wall polymers are induced. All types of chemical treatments can be characterized by a combination of structural changes at the cellular and molecular levels [1].

The aim of this paper is not to develop new chemical treatments of wood, but to investigate systematically the relationship between the structure and properties of typical chemically treated woods. In a previous paper, viscoelastic properties of chemically treated woods were analyzed in relation to their structure [2–4]. In this paper, the relationships between dielectric properties and the structure for seven kinds of chemically treated woods are investigated.

2. Experimental procedure

2.1. Materials and chemical treatments

Sitka spruce (*Picea sitchensis* Carr.) heartwood specimens of 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 (volume ratio = 1:2) for 24 h using a Soxhlet extractor, they were air-dried and then absolutely dried by heating at 60°C for 24 h under a reduced pressure. The average density of extracted specimens in an absolutely dried condition was 0.45 gcm^{-1}. These specimens were subjected to the following seven kinds of chemical treatments.

Formalization was carried out in a sealed glass vessel with paraformaldehyde and sulfur dioxide as a catalyst at 120°C for 48 h. Acetylation was performed in neat acetic anhydride at 120°C for 24 h. After the reaction, the specimens were sufficiently leached in running water. Propylene oxide treatment was carried out in a pressure vessel containing a mixed solution of propylene oxide and triethylamine as a catalyst (volume ratio = 95:5) at 120°C for 3 h. Polyethylene glycol (PEG) impregnation was carried out by immersing specimens successively into 20, 40, 60, 80 and 100% aqueous solution of PEG (average molecular weight = 1,000) for one week. Phenol-formaldehyde (PF) resin treatment was carried out by soaking specimens in 15% aqueous solution of a low molecular weight of PF-resin (average molecular weight = 270) under a reduced pressure and then by heating resin-impregnated specimens for 90 min at 170°C. Wood methyl methacrylate (MMA) composite treatment was carried out by impregnating absolutely dried specimens with a solution of MMA containing 1% α, α'-azobisisobutyronitrile as an initiator under a reduced pressure, wrapping specimens in aluminum foil and polymerizing for 2 h at 80°C. Heat treatment was carried out by heating absolutely dried specimens at 180°C for 40 h in a vacuum oven. After treatments, the weights and dimensions of treated specimens were measured.

2.2. Measurement of dielectric properties

LCR-meter (Japan Hewlett-Packard Co. Ltd., HP4284A), electrode (Ando Electric Co. Ltd., SE-3O, effective diameter = 38 mm) and bath (Ando Electric Co. Ltd., TO-3) were used for 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 over a temperature range of -150 to 20°C with a heating rate of less than 1°C min^{-1}.

3. Results and discussion

3.1. Contour diagrams of dielectric constant and loss

Weight percent gains (WPG) and densities (γ) of chemically treated woods are shown in Table I. Dimensional changes of specimens due to chemical treatments were much smaller in the longitudinal direction than in the radial and tangential directions. The percent dimensional change in the tangential direction (l_T) was larger than that in the radial direction (l_R) in all treatments, and the relationship between l_R and l_T was expressed by $l_R = 0.426\, l_T$.

Figs 1 and 2 show contour diagrams of ε' and ε'' in a wide range of temperature and frequency for the untreated and treated woods. A dielectric relaxation was found in the contour diagram of ε'' for the untreated wood. Dielectric measurements of wood constituents have shown that the same relaxation occurs in cellulose, mannan and lignin which have methylol groups, but not in xylan which does not have methylol groups [5]. The relaxation of cellulose is absolutely eliminated by tritylation in which trityl groups are selectively introduced in primary hydroxyl groups [6, 7]. The relaxation magnitude of cellulose decreases with increasing the degree of crystallinity [7, 8]. The apparent activation energy of this relaxation is about 42 kJ/mol [5]. These facts show that the relaxation observed in the untreated wood was due to motions of methylol groups in the non-crystalline region of the cell wall [5].

Formalization is a reaction involving the formation of oxymethylene bridges between hydroxyl groups of cell wall polymers by formaldehyde. Since short inflexible molecular bridges are formed while chains are close to each other, this treatment improves dimensional stability for very small weight and dimensional increase. Although relaxation due to motions of methylol groups was recognized, ε' and ε'' values considerably decreased.

In acetylation, hydroxyl groups are substituted with hydrophobic and bulky acetyl groups. Consequently, this treatment decreases hygroscopicity and improves dimensional stability. Weight and dimensional increase by the treatment were relatively large. Although the relaxation due to methylol groups was observed in the contour diagram of ε'', ε'' values were very small and the location of the relaxation moved to a higher temperature.

In propylene oxide treatment, the hydroxyl groups are replaced with hydrophilic and bulky groups, so that this treatment increases both dimensional stability and hygroscopicity [10]. The WPG was 47.8% and the dimensional increase was the largest among treatments. By the treatment, the magnitude of the relaxation due to the methylol groups slightly decreased and a new relaxation appeared in the low frequency and high temperature range. This new relaxation may be related to motions of $OCH_2CH(OH)C_2H_5$ groups.

PEG molecules are introduced not only in the cell walls, but also in the cell lumens. As PEG molecules introduced into the cell walls are bulky and extremely hydrophilic, cell wall polymers are remarkably plasticized. Both ε' and ε'' values increased in the frequency and temperature range tested by the PEG impregnation. The location of the relaxation due to methylol groups moved to a higher frequency and a lower temperature.

TABLE I Results of densities in absolutely dried condition (γ), weight percent gains (WPG), ($\varepsilon_0 - \varepsilon_\infty$),$\varepsilon_\infty$, β and τ_m for chemically treated woods

Treatment	(symbol)	γ(g cm^{-3})	WPG (%)	($\varepsilon_0 - \varepsilon_\infty$)	ε_∞	β	τ_m (10^{-5} sec)
Untreated wood	(U)	0.45	–	1.01	1.74	0.26	3.7
Formalization	(F)	0.45	5.9	0.54	1.71	0.26	1.1
Acetylation	(A)	0.53	25.8	0.51	1.84	0.20	24.5
Propylene oxide treatment	(PO)	0.56	47.8	0.64	1.90	0.30	0.7
PEG impregnation	(PEG)	1.08	178.6	0.82	2.63	0.37	0.3
PF-resin impregnation	(PF)	0.52	31.7	0.74	1.90	0.25	0.8
Wood-MMA composite	(WPC)	1.03	119.2	1.05	2.43	0.26	2.4
Heat treatment	(H)	0.45	−2.0	1.09	1.72	0.25	5.1

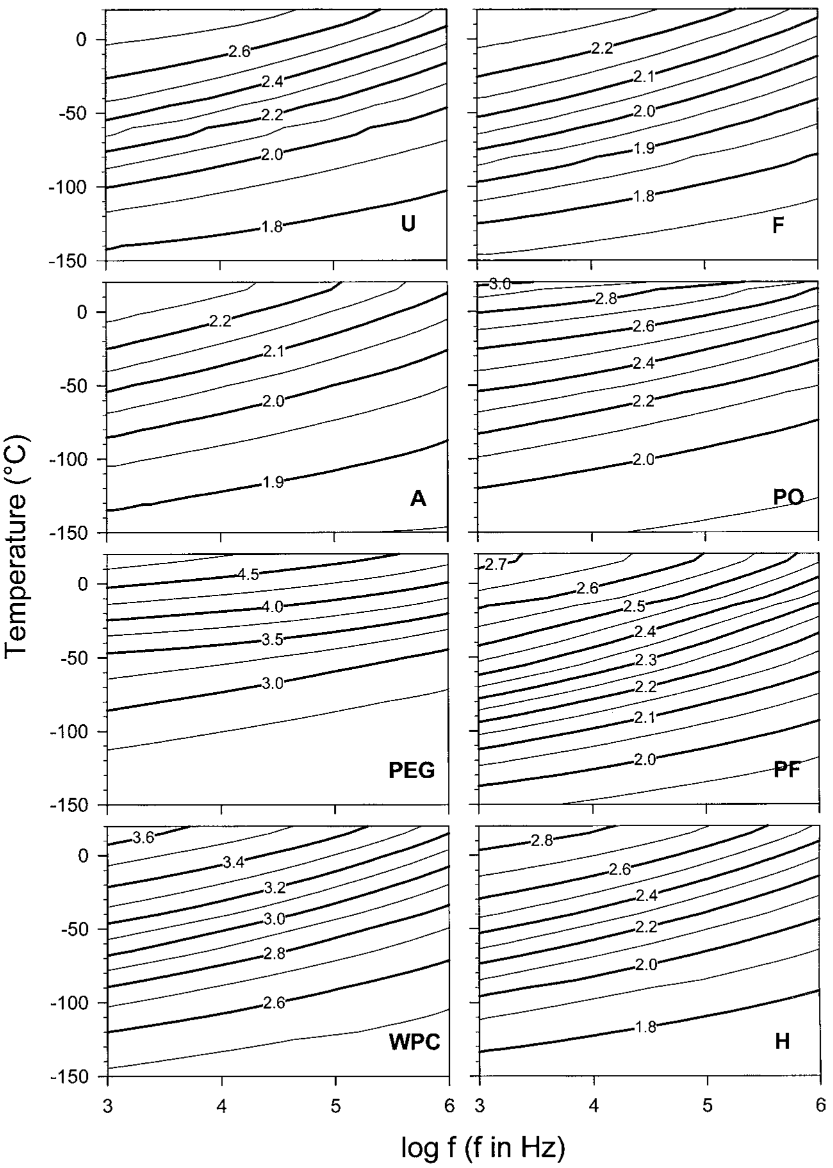

Figure 1 Relationship between temperature and logarithm of frequency, log f, for dielectric constant (contour diagrams) of untreated and chemically treated woods in absolutely dried condition. Symbols: refer to Table I.

On the other hand, a new relaxation, which may be attributed to PEG molecules, appeared in a lower frequency region.

In PF-resin treatment, only a limited amount of resin is in the cell walls acting as a bulking agent and there is excess resin in the lumens. ε'' values of the treated wood were slightly smaller than those of the untreated wood in the frequency and temperature ranges tested. This result suggested that the number of methylol groups was decreased by the chemical reaction and the number of methylol groups involving in unit volume of the cell wall is decreased by the introduction of PF-resin.

Wood-MMA composite is a treatment with no modification of the cell walls and poly-MMA molecules totally fill the cell lumens. By this treatment, the properties such as strength, hardness and abrasion resistance are remarkably increased, but the dimensional stability is not improved. ε' value was increased by the introduction of the resin into the lumens. However, no change due to methylol groups was observed in the relaxation.

Heat treatment may induce the formation of cohesive structures of cell wall polymers, but it also causes chemical changes as well as degradation. The dimensional stability is enhanced by the decrease in hygroscopicity due to the formation of hydrophobic furfural polymer from hydrophilic hemicelluloses. Perceivable changes in dielectric properties were not observed by the treatment.

3.2. Cole-Cole plot and relaxation spectrum

To compare quantitatively dielectric property changes of wood induced by the seven kinds of chemical treatments, Cole-Cole's circular arc law was applied to the results of dielectric measurements. The law is expressed by the following equation [9].

$$\varepsilon^* - \varepsilon_\infty = (\varepsilon_0 - \varepsilon_\infty) \cdot \frac{1}{1 + (i\omega\tau_\mathrm{m})^\beta}. \qquad (1)$$

where ε^* is the complex dielectric constant ($\varepsilon^* = \varepsilon' - i\varepsilon''$), ε_0 is the dielectric constant at the limiting low

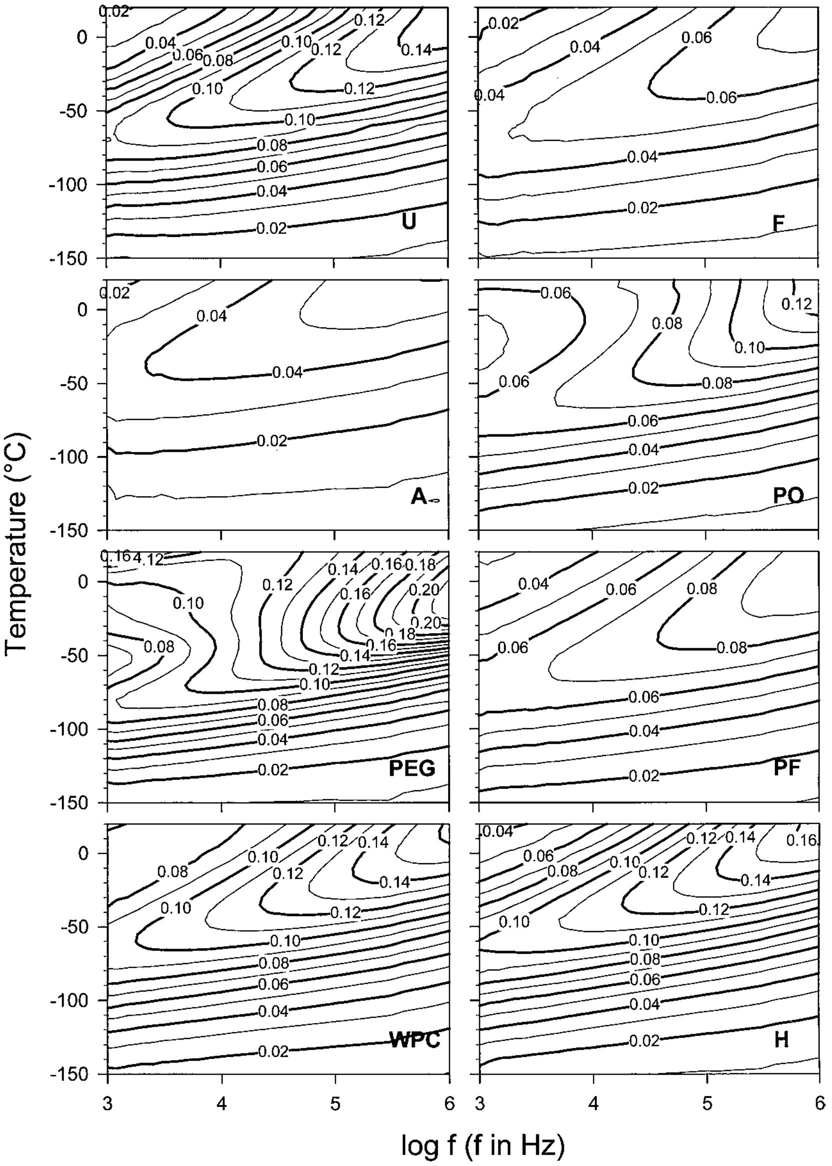

Figure 2 Relationship between temperature and logarithm of frequency, log f, for dielectric loss (contour diagrams) of untreated and chemically treated woods in absolutely dried condition. Symbols: refer to Table I.

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 the parameter relating to the distribution of relaxation times, when the angle between the radii of the arc drawn to the points ε_∞ and ε_0 from the center of the circle is given by $(1 - \beta)\pi/2$. The broader the distribution of relaxation times becomes, the smaller the β value. In the single relaxation system, β is unity. $(\varepsilon_0 - \varepsilon_\infty)$ is the parameter relating to the magnitude of dipole orientation.

The relaxation spectrum $H(s)$ or $H(\log \tau)$ obtained from Cole-Cole's circular arc law is expressed by the following equation [9].

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

$$\int_{-\infty}^{\infty} H(s) \cdot \mathrm{d}s = 1, \quad s = \ln\left(\frac{\tau}{\tau_m}\right), \qquad (2)$$

$$H(\log \tau) = 2.303 \cdot H(\ln \tau).$$

Cole-Cole's circular arc law could be satisfactorily applied to dielectric results at −60°C for untreated and treated woods as shown in Fig. 3. Parameters calculated from Cole-Cole's plots are shown in Table I.

$(\varepsilon_0 - \varepsilon_\infty)$ was decreased to about 1/2 by formalization. This was due to the decrease of the number of methylol groups by the treatment. On the other hand, τ_m was decreased to about 1/3. This fact suggests that cell wall polymer chains were cut during the reaction by sulfur dioxide used as a catalyst, so that motions of methylol groups were facilitated. No changes in ε_∞ and β were observed. By acetylation and propylene oxide treatment, $(\varepsilon_0 - \varepsilon_\infty)$ was remarkably decreased and ε_∞ was slightly increased depending on density increase. On the other hand, τ_m was largely increased and β was slightly decreased by the introduction of hydrophobic bulky groups in acetylation, while τ_m was decreased and β was slightly increased by the introduction of hydrophilic bulky groups in propylene oxide treatment. By PEG treatment, $(\varepsilon_0 - \varepsilon_\infty)$ was decreased by the decrease in the number of methylol groups involving in unit volume of the cell wall due to the swelling.

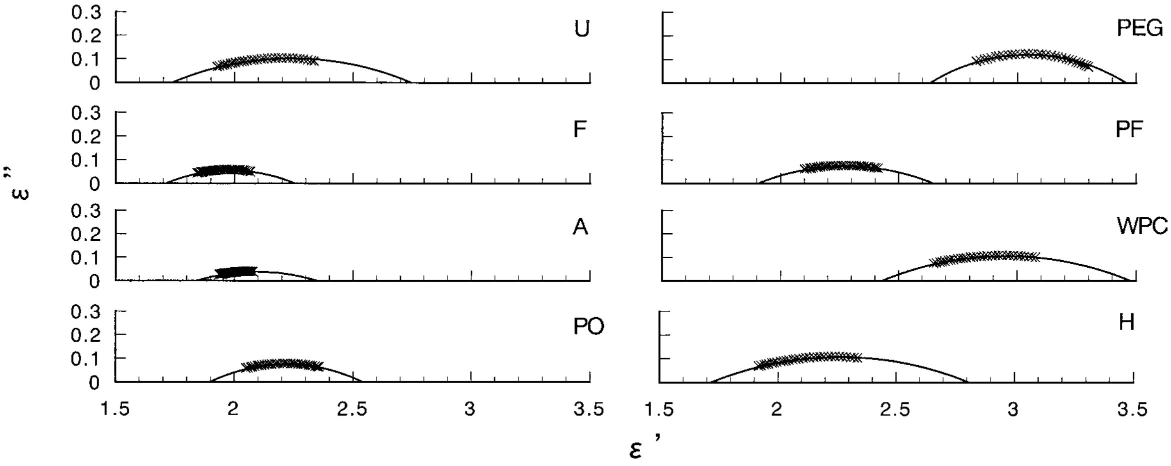

Figure 3 Cole-Cole plots at −60°C for untreated and chemically treated wood in absolutely dried condition. Symbols: refer to Table I.

ε_∞ was greatly increased by a large increase of density and τ_m was decreased by the plasticization of cell wall polymers. By PF-resin treatment, $(\varepsilon_0 - \varepsilon_\infty)$ was slightly decreased due to the expansion of the cell wall, β did not change and τ_m was slightly decreased. In wood-MMA composite, there occurred no structural change in the cell wall, so $(\varepsilon_0 - \varepsilon_\infty)$, β and τ_m did not change. However, since the density of the specimen was largely increased by the treatment, ε_∞ was extremely increased.

The relaxation spectra calculated using parameters in Table I and Equation 2 for untreated and treated woods are compared in Fig. 4. In PEG impregnation, the distribution of relaxation times was the narrowest, the peak value of the relaxation spectrum was the largest, and τ_m was the smallest. On the other hand, in acetylation, the distribution of relaxation times was the broadest, the peak value of the relaxation spectrum was the smallest, and τ_m was the largest. Compared to results of the untreated wood, τ_m was small for formalization, propylene oxide treatment, PEG impregnation and PF-resin treatment, almost the same for wood-MMA composite and heat treatment, and large for acetylation. The peak value of the spectrum was large for PEG impregnation, almost the same for wood-MMA composite and heat treatment, and small for propylene oxide treatment, PF-resin treatment, formalization and acetylation. β was small for PEG impregnation and propylene oxide treatment, almost the same for formalization, PF-resin treatment, wood-MMA composite and heat treatment, and large for acetylation.

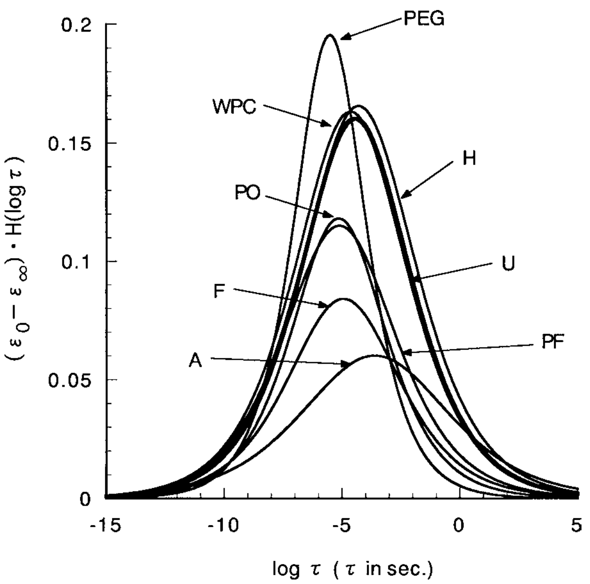

Figure 4 Relaxation spectra $(\varepsilon_0 - \varepsilon_\infty)\cdot H(\log\tau)$ at −60°C for untreated and chemically treated woods in absolutely dried condition. Symbols: refer to Table I.

4. Conclusion

The relationships between dielectric properties along the grain and structure for untreated and seven kinds of chemically treated Sitka spruce (*Picea sitchensis* Carr.) woods in absolutely-dried condition were investigated. The results obtained were as followed:

(1) Relaxation due to motions of methylol groups was observed in the contour diagram of ε'' for all results. Cole-Cole's circular arc law was applied to results of dielectric properties at −60°C and parameters such as the magnitude of dipole orientation $(\varepsilon_0 - \varepsilon_\infty)$, the generalized relaxation time (τ_m) and the distribution of relaxation times (β) were calculated.

(2) $(\varepsilon_0 - \varepsilon_\infty)$ and τ_m were decreased by formalization. In acetylation and propylene oxide treatment, $(\varepsilon_0 - \varepsilon_\infty)$ was remarkably decreased. τ_m was greatly increased and β was slightly decreased in acetylation, while τ_m was decreased and β was slightly increased in propylene oxide treatment. In PEG impregnation, $(\varepsilon_0 - \varepsilon_\infty)$ and τ_m were decreased. In PF-resin treatment, $(\varepsilon_0 - \varepsilon_\infty)$ and τ_m were slightly decreased, but β did not change. In wood-MMA composite and heat treatment, $(\varepsilon_0 - \varepsilon_\infty)$, β and τ_m did not change.

(3) In PEG impregnation, the distribution of relaxation times was the narrowest, the peak value of the relaxation spectrum was the largest, and τ_m was the smallest. On the other hand, in acetylation, the distribution of relaxation times was the broadest, the peak value of the relaxation spectrum was the smallest, and τ_m was the largest.

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