

Mechanical and Dielectric Properties of Cyanoethylated Wood

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Synopsis

The mechanical properties and dielectric properties of film specimens from cyanoethylated wood (CE-wood) which is a mixture of CE- (cellulose, hemicellulose, and lignin) were investigated and compared with those of cyanoethylated cellulose (CEC). From the dynamic mechanical measurement for CE-wood, it was observed distinctively that the segmental motions of the main chains were restrained by lignin. But these restraints were released with chlorination of CE-wood. The dynamic behavior for chlorinated CE-wood was similar to that for CEC. It was found that the CE-wood was plasticized effectively by blending with cyanoethylated poly(vinyl alcohol) (CE-PVA). The dynamic and static modulus of CE-wood decreased with increasing the CE-PVA fraction in the blended film, and the change of tensile strength at break for the CE-wood polyblends showed a maximum value at the CE-PVA fraction of ca. 40%. It was found that CE-wood which contained lignin showed very high values of dielectric constant comparable to those of CEC which was well known to be a high-performance dielectric materials. These dielectric properties were attributed to the segmental motion of the side chains, and it was thought that the behavior of the side chain was not so much influenced by the lignin as that of the main chain. CE-wood film specimens could be drawn to threefold the initial length in acetone aqueous solution. The degree of orientation measured by optical method increased rapidly at the early stage of drawing. The Young's modulus and the tensile strength at break of the high-drawn specimen increased to as much as three or four times those of the undrawn one, and the elongation at break changed little.

INTRODUCTION

It has been shown in our previous papers¹⁻³ that a chemically modified wood by cyanoethylation (CE-wood) demonstrated thermal flow and that the thermoplasticity and the solubility in organic solvent of CE-wood was considerably improved by chlorination. Thus CE-wood, especially chlorinated CE-wood (Cl-CE-wood) is moldable into many shapes by heating or dissolving it. These characteristics of CE-wood are of interest in connection with useful utilization of unused resources and wood waste products. Also, further development of higher performance woody materials may be expected.

Wood is composed of three polymeric components—namely, cellulose, hemicellulose, and lignin. Cellulose is semicrystalline, whereas hemicellulose and lignin are amorphous. These components intermix intimately, so that native woods show rigid characters. Hence moldings from CE-wood also show rigid characters. Considering the application of woody materials, it was desirable to give a variety of properties to them, e.g., plasticization by polymeric blending.

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A few studies⁴ were concerned with blending chemically modified woods with synthetic polymers, e.g., blending caprolated woods with polyester or polyethylene, etc. Such blends showed two-phase separation, though a difference of the miscibilities was seen for each polymer pairs. Generally speaking, it is difficult to gain a perfect compatibility for polymeric blending. It seemed important for polymeric blending to gain miscibility between phases. In this study, a plasticization effect by blending CE-wood with CE-PVA, which contained cyanoethyl groups, was investigated.

In recent years, various anhydrous solvent systems which dissolved cellulose have been developed,⁵⁻⁷ and the properties of cellulose and its derivatives have been studied. A variety of properties for cyanoethylated cellulose (CEC) also have been investigated⁸⁻¹² for a long time, including dielectric property, thermal stability, resistance to rot, etc. Especially, CEC was well known to exhibit unusual dielectric properties, namely, very high values of dielectric constant and relatively low values of dielectric loss factor at room temperature. CE-wood also could be expected to show good dielectric properties similar to those of CEC. This paper is concerned with the mechanical properties, the plasticization by blending with CE-PVA, and the dielectric properties for CE-woods.

EXPERIMENTAL

Preparation of Cyanoethylated Samples and Chlorination of CE-Wood

Preparation of CE-wood and its chlorination was carried out as described previously.¹ Wood meal of Buna (*Fagus Crenata* BL.) or bleached sulfite pulp were reacted with acrylonitrile in the presence of 4% sodium hydroxide solution approximately saturated with sodium thiocyanate at 40°C for 3 h. After the reaction, a slight excess of acetic acid was added to neutralize alkali catalyst. The product was thoroughly washed with water and then dried *in vacuo*. The nitrogen contents (N%) of products were analyzed by a Kjeldahl method. The N% of CE-wood and CE-pulp obtained were 9.7% and 11.5%, respectively.

CE-PVA was prepared from poly(vinyl alcohol) (degree of polymerization: 2000) in a homogeneous system according to the method described by Tsuda.¹³ The N% of CE-PVA obtained was 13.4%.

Chlorination of CE-wood was carried out with chlorine solution (concentration of 0.2%, w/v) for 2 h at ambient temperature. The chlorine content (Cl%) of product was analyzed by Schöniger's flask combustion method.¹⁴ The N% and Cl% of Cl-CE-wood obtained were 9.4% and 3.8%, respectively.

CEC (N: 11.4%) used as cellulose sample was purchased from Aldrich Co., Ltd.

Preparation of Film Specimens

Film specimens of CE-woods and the blends of CE-wood and CE-PVA were casted from the dimethylformamide (DMF) solution onto a glass surface. The initial concentration of each sample in DMF was about 10% (w/v). After the film was cast, 1 week of drying at 50°C under high vacuum was carried out slowly on the solid film.

Blending of Cl-CE-Wood and CE-PVA

DMF solution of Cl-CE-wood and CE-PVA were prepared separately at concentration of 10 wt %, and the two solutions were mixed in various proportions. Then blended films were prepared by the method as described above.

Measurement of Mechanical Properties

Dynamic mechanical measurement and static tensile tests were carried out to investigate mechanical properties.

Dynamic mechanical relaxation for the film specimens ($7_{(W)} \times 0.3_{(T)} \times 60_{(L)}$ mm) were measured with a torsional pendulum TPA-1 (Rhesca Co., Ltd., Japan) at the mean elevation rate of $2^{\circ}\text{C}/\text{min}$ in the temperature range from 20 to 200°C . The torsion pendulum permits a computation of a complex shear modulus (G^*). The real part of the modulus, G' , is calculated from the period of oscillation and the imaginary part, G'' , from the damping of the amplitude. The data were expressed in the form of G' , and the logarithmic decrement (loss) was given approximately by $\text{loss} = \pi(G''/G')$.

Static tensile tests for the film specimens ($3_{(W)} \times 0.3_{(T)} \times 20_{(L)}$ mm) were also carried out. The Young's modulus, the strength at break, and the elongation at break were obtained. Elongation was applied to the specimen with the constant speed of 1 mm/min.

Drawing

In general, the temperature range in the glassy transition region is most suitable for drawing of polymer in the dry state. But it is difficult for CE-wood film specimen to be drawn in the dry state. A swelling of this specimen with a suitable solvent system depressed the apparent transition temperature, and made the drawing easy at lower temperature. It was found that CE-pulp and Cl-CE-wood film specimens could be readily drawn in acetone aqueous solution (50 wt %). Drawing conditions were as follows;

temperature: 50°C

drawing speed: 20 mm/min

According to these conditions, uniaxial drawing was performed for film specimens of CE-pulp and Cl-CE-wood. Drawing ratio was expressed such as (length of drawn specimen/initial length).

Birefringence of the film specimen was measured by polarization microscope fitted with a Berek compensator at 20°C .

Measurement of Dielectric Properties

Using a transformer bridge TR-10C (Ando Denki Co., Ltd., Japan), dielectric constant, and dielectric loss factor were measured in the frequency range of 30 Hz to 3 MHz and the temperature range of -60 to 20°C .

RESULTS AND DISCUSSION

Dynamic Mechanical Properties for CEC, CE-Wood and Cl-CE-Wood

The thermoplasticity and the solubility in organic solvent of CE-wood was considerably improved by chlorination.² In order to examine the effect of chlorination on the behavior of CE-wood, the dynamic mechanical properties for CE-woods were investigated, comparing them with that for CEC.

The dynamic mechanical relaxations for CEC, CE-wood, and Cl-CE-wood are shown in Figure 1. The segmental motion of main chain was frozen at room temperature, and the values of G' of all specimens used were about the same, 7×10^9 dyn/cm², at about 30°C. It was seen that the segmental motion of main chain could be mobilized with the elevation of temperature, and that the values of G' and loss varied. The presence of loss peak was attributed to the segmental motion with the main chain (α process). A loss dispersion peak attributed to the local motion of the side chain (β process) was not observed, since it was below the temperature range measured.

For CEC, the values of G' decreased gradually with the elevation of temperature, and a sharp drop corresponding to the segmental motion of main chain was observed above 100°C. The temperature dependence of the values of loss agreed with that of G' , that is, loss showed a peak at about 100°C. The shoulder

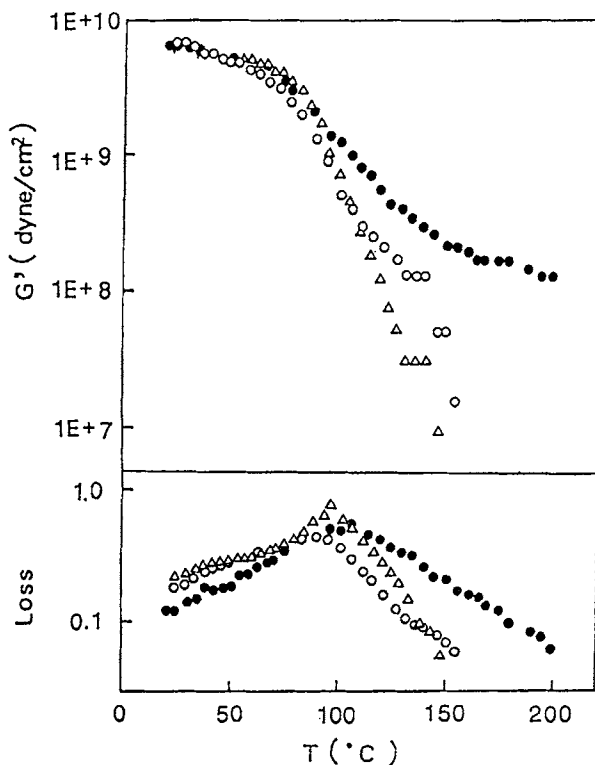


Fig. 1. The dynamic mechanical properties for CEC (Δ), CE-wood (\bullet), and Cl-CE-wood (\circ).

in the lower temperature side was thought to be attributed to a region of low restraint, e.g., an amorphous region. In this manner, the values of G' for CEC dropped to about 1/1000 corresponding to this glassy transition region.

On the other hand, for CE-wood, the temperature dependences of G' and the loss was slightly different from those of CEC. It was clearly seen that the slope of the decreasing G' became milder than that of CEC, and that the decreasing of the G' formed the shoulder at the higher temperature side. Corresponding to this, the loss peak became broader than that of CEC. Judging from the fact that wood is a multicomponent substance, it was thought that the segmental motions of CEC chains in CE-wood were restrained in places by the intimate interaction between components and that lignin macromolecules were mainly responsible for this restraint.

For Cl-CE-wood, both the temperature dependence of G' and loss were similar to those for CEC, considerably differing from those for CE-wood, e.g., the slope and the shoulder of the decreasing of G' at the higher temperature region and the width of the loss dispersion. It appeared that the CEC chains in Cl-CE-wood could mobilize more readily than those in CE-wood. The previous paper² reported that the lowering of the degree of polymerization of the cellulose fraction was small and that the structural modification of lignin moiety with chlorination may have played an important role on the improved thermoplasticity and the solubility. Judging from these dynamic behaviors, it was also reasonable to consider that such effects with chlorination were mainly due to the releasing the restraints of lignins against the CEC chains.

Mechanical Properties for Cl-CE-Wood/CE-PVA Blends

Both Cl-CE-wood and CE-PVA are similar in solubility, but the former is rigid while the latter is rubberlike at room temperature. The blended films of this polymer pair were prepared from solution in various proportions, and dynamic mechanical and static tensile properties were measured.

The temperature dependence of G' and loss for Cl-CE-wood/CE-PVA blended films are shown in Figure 2. When 10% CE-PVA was blended into the Cl-CE-wood film, the loss peak for Cl-CE-wood became broader. When 20% CE-PVA was blended, the loss peak for Cl-CE-wood depressed as a shoulder, and the position of the loss peak maximum shifted to the lower temperature side. From this proportion, the blended films began to show somewhat flexible character at room temperature. Furthermore, when 50% CE-PVA was blended, the dispersion for Cl-CE-wood disappeared completely, and the dispersion at the lower temperature region was increasing its height and sharpening in shape. In this manner, the dynamic behavior for blended films changed remarkably with increasing CE-PVA fraction, and it was hence thought that Cl-CE-wood was well dispersed with addition of CE-PVA.

The stress-strain diagrams for Cl-CE-wood/CE-PVA films are shown in Figure 3. It appeared that the blended films were gradually given a tenacity with increasing the CE-PVA fraction. The relationships between the blending ratio and the Young's modulus (E), strength at break (δ), and elongation at break (ϵ) are shown in Figure 4. The values of E decreased while the values of ϵ increased with increasing the CE-PVA fraction, whereas the values of δ increased slowly until the CE-PVA fraction of about 40 wt %, and subsequently

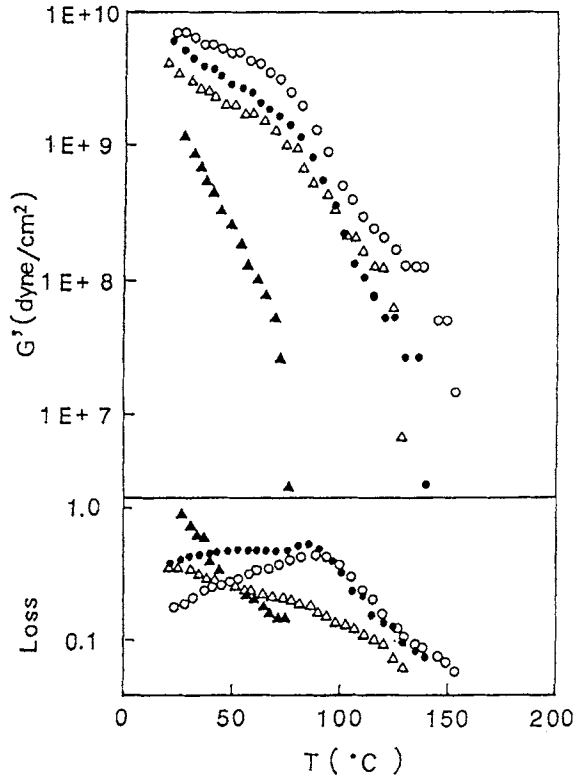


Fig. 2. The effect of blending on the dynamic mechanical properties for CI-CE-wood. CI-CE-wood/CE-PVA (wt ratio): (O) 10/0; (●) 9/1; (Δ) 8/2; (\blacktriangle) 5/5.

decreased with increasing the CE-PVA fraction. The values of E decreased remarkably in the vicinity of this proportion, and then the phase inversion had probably occurred in this vicinity. From these facts, it was thought that both polymers were well dispersed in blended films and this polymer pair was miscible. But the details of the miscibility are still uncertain. Continuing work on the miscibility of this polymer pair is in progress.

Lewis⁸ had reported that the values of dielectric constant of CE-PVA was higher than those of CEC above room temperature. Consequently, this polymer pair is of interest concerning its dielectric properties.

Changes of Mechanical Properties with Drawing for CE-Pulp and CI-CE-Wood

It is well known that molecular orientation has an important effect on the mechanical properties of polymeric materials. Under suitable conditions, the films of CE-pulp and CI-CE-wood were drawn uniaxially to fivefold and threefold of the initial length, respectively. The mechanical properties for drawn specimens were investigated by means of an optical method and static tensile tests. The partial alignment of polymer chains during linear orientation produces a difference between the electrical polarizability in the direction of stretch and that in the direction perpendicular to stretch. This polarization anisotropy

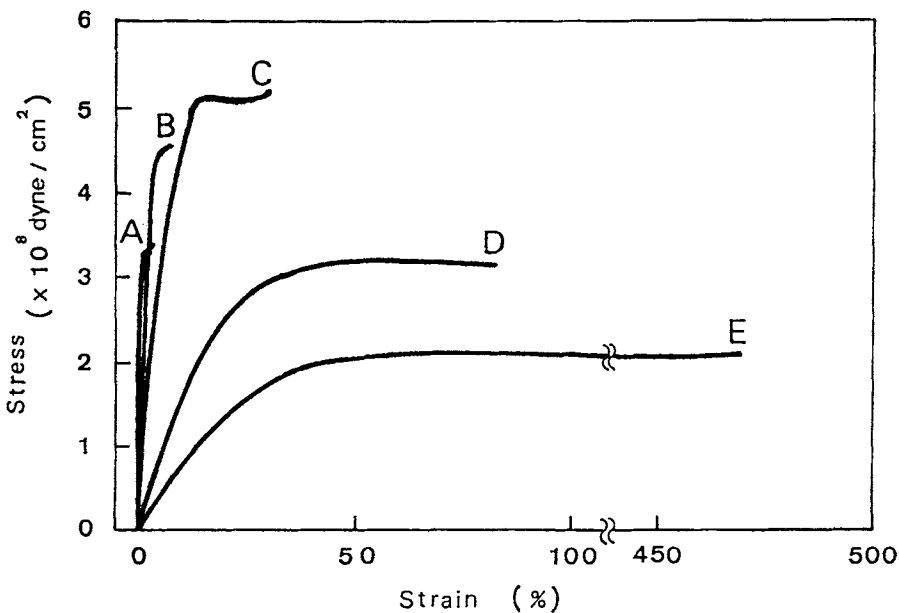


Fig. 3. The stress-strain diagrams at 20°C for blends of Cl-CE-wood/CE-PVA in various ratios: (A) 10/0; (B) 8/2; (C) 6/4; (D) 4/6; (E) 2/8.

gives rise to a difference between refractive indices in these directions, which is by definition the birefringence (Δn).

The relationships between drawing ratio and Δn , E , δ , and ϵ for CE-pulp are shown in Figure 5. Δn increased rapidly at the early stage of drawing, and

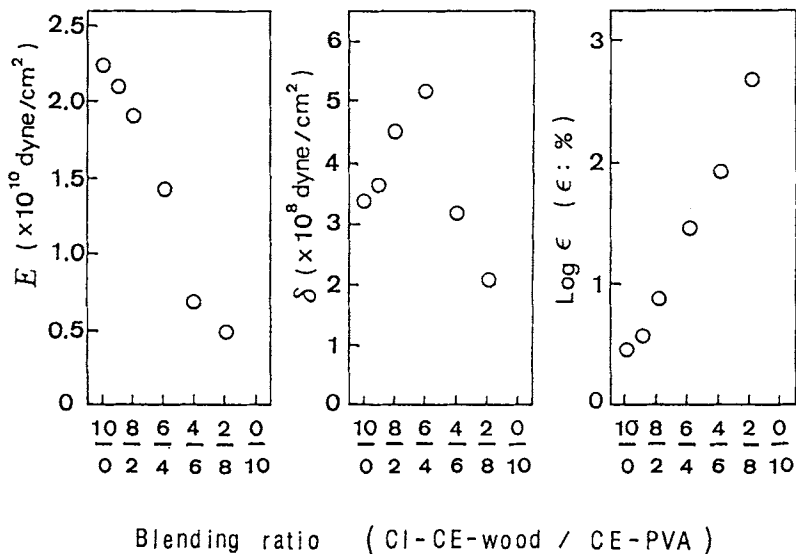


Fig. 4. The relationships between the blending ratio and E , δ , and ϵ for blends of Cl-CE-wood/CE-PVA at 20°C.

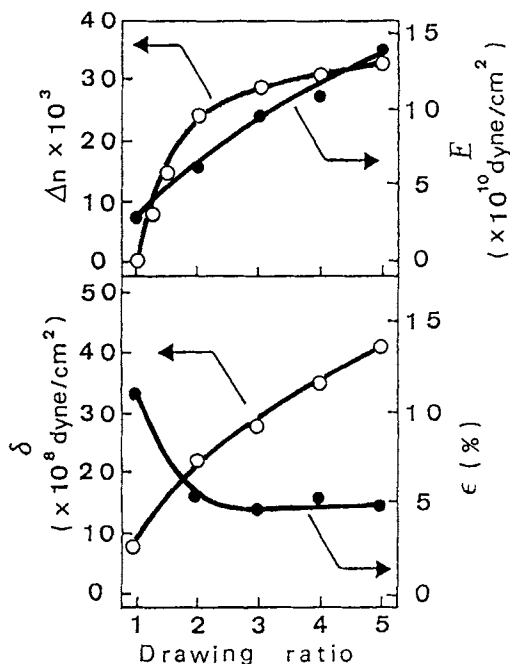


Fig. 5. The relationships between drawing ratio and Δn , E , δ , and ϵ at 20°C for CE-pulp.

changed slowly after the drawing ratio of 3. For undrawn specimens, e.g., drawing ratio of 0, the optical properties were isotropic, because of the random configuration of chains, even though the local polarizability of the specimen chain varied with direction. As the drawing was applied to the specimen, the values of E and δ also increased according to the changes of Δn . The values of E and δ for the films fivefold drawn were 14.0×10^{10} and 41.0×10^8 dyn/cm², respectively. There were about 4.6 times and 5.0 times as large as those of undrawn CE-pulp films.

On the other hand, the relationships between drawing ratio and Δn , E , δ , and ϵ for Cl-CE-wood are shown in Figure 6. Though Δn increased with drawing ratio similarly, it was difficult to draw highly. For film specimen threefold drawn, the values of E and δ were 5.8×10^{10} and 14.0×10^8 dyn/cm², respectively. These were about 3.1 times and 4.0 times as large as those of undrawn Cl-CE-wood films.

The difficulty of high drawing for Cl-CE-wood in this drawing condition was explained as follows. Cellulose is a linear polymer, but the lignin macromolecule is not, and the lignin-carbohydrate complexes (LCC) are localized. All these components do not swell uniformly. These factors were thought to interfere with the molecular alignments of cellulose chains.

Dielectric Properties for CEC, CE-Wood and Cl-CE-Wood

The dielectric properties for CEC, CE-wood, and Cl-CE-wood at 20°C are shown in Figure 7. As expected, the values of both dielectric constant (ϵ') and dielectric loss factor (ϵ'') for both CE-wood and Cl-CE-wood were comparable

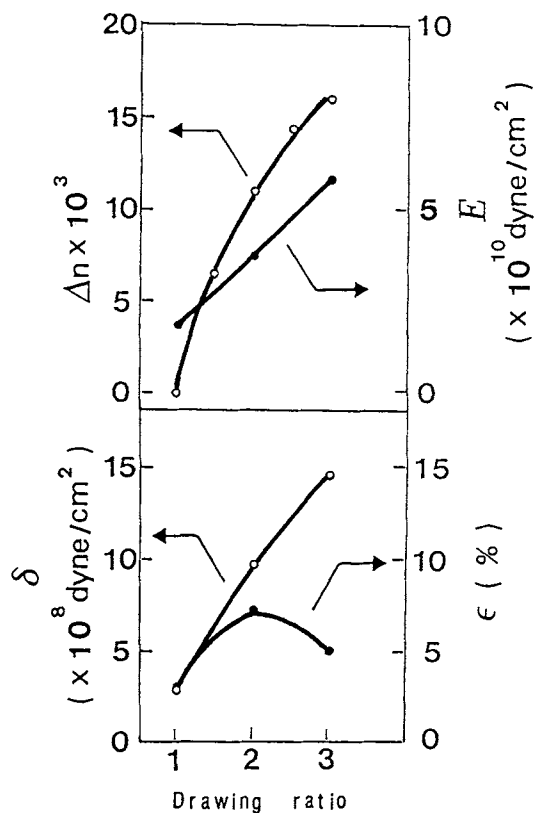


Fig. 6. The relationships between drawing ratio and Δn , E , δ , and ϵ at 20°C for Cl-CE-wood.

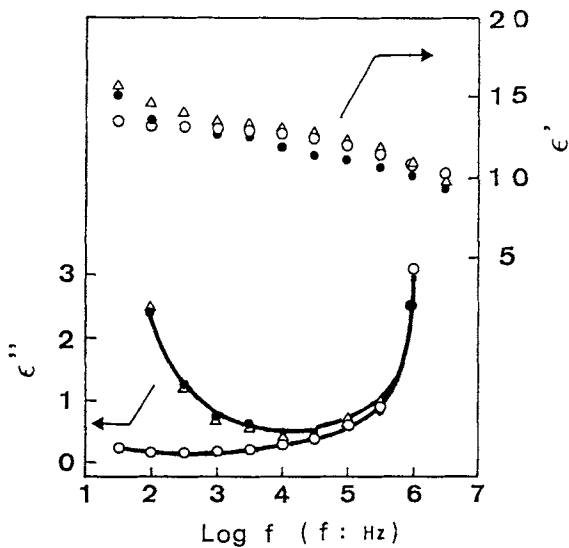


Fig. 7. The frequency dependences of dielectric properties at 20°C for CEC (Δ), CE-wood (\bullet), and Cl-CE-wood (\circ).

to those for CEC in all frequency range measured. The CE groups introduced into wood did orient in applied electric field at the room temperature. The increases of ϵ' and ϵ'' at the lower frequency region were due to ionic conductivities.

The dielectric properties for Cl-CE-wood at the lower temperature are shown in Figure 8. It is seen to display the phenomenon of dielectric dispersion in this frequency range, and there is a shift to the lower frequency region with the depression of temperature.

Cole and Cole¹⁵ have shown that the complex dielectric constant (ϵ^*) was given by the expression

$$\epsilon^* = \epsilon' - i\epsilon'' = \epsilon_\infty + (\epsilon_0 - \epsilon_\infty) / \{1 + (i\omega\tau)^{1-\alpha}\}$$

where ϵ_0 = dielectric constant extrapolated to zero frequency, ϵ_∞ = dielectric constant extrapolated to infinite frequency, $\omega = 2\pi f$, f = frequency of measurement, and τ = mean relaxation time for dielectric polarization due to dipole orientation. The quantity α is a measure of the broadness of the distribution of relaxation times, and has the value 0 for a single relaxation time, and the value 1 for a uniform distribution.

Cole-Cole plots for Cl-CE-wood are shown in Figure 9. In the high polymer, the resistances against each dipoles were not the same, that is, there is a distribution of relaxation times. The results were circular arcs whose centers are depressed below the horizontal axis by the amount of $\frac{1}{2}(\epsilon_0 - \epsilon_\infty)\tan(\alpha\pi/2)$. The magnitude of the dielectric dispersion ($\Delta\epsilon = \epsilon_0 - \epsilon_\infty$) and α determined by Cole-Cole plots are also shown in Figure 9. The value of $\Delta\epsilon$ decreased and α

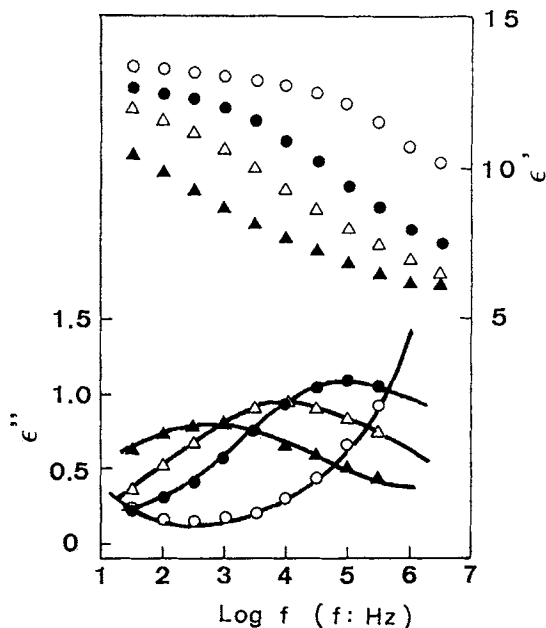
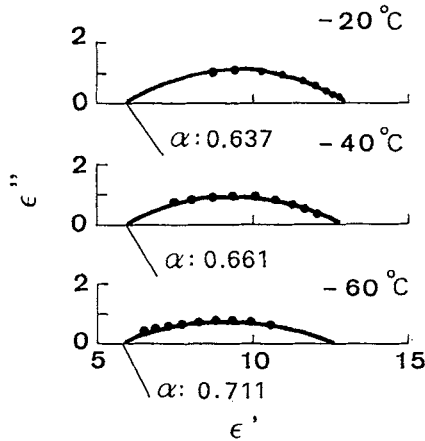


Fig. 8. The dielectric properties for Cl-CE-wood at various temperatures: (O) 20°C; (●) -20°C; (Δ) -40°C; (▲) -60°C.



	-20°C	-40°C	-60°C
$\Delta\epsilon$	7.09	6.91	6.84
α	0.637	0.661	0.711
ϵ_0	13.06	12.76	12.52
ϵ_∞	5.97	5.85	5.68

Fig. 9. Cole-Cole plots for CI-CE-wood.

increased with the depressing temperature, and that the decreasing of $\Delta\epsilon$ was mainly attributed to the decreasing of ϵ_0 .

For this dielectric relaxation, an normalized absorption curve (a reduced master curve) for CEC and CE-woods were constructed. The reduced master curve from plots of $\epsilon''/\epsilon''_{\max}$ vs. $\log(f/f_{\max})$ at temperature from -60 to -20°C are shown in Figure 10. ϵ''_{\max} is the maximum value at each temperature measured, and f_{\max} is the frequency at which ϵ''_{\max} occurs. Though CEC and CE-

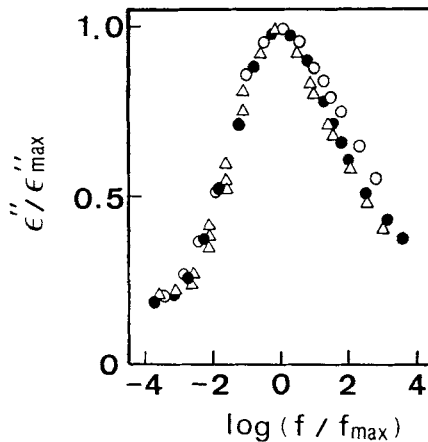


Fig. 10. An normalized absorption (the reduced master) curves of β process for CEC (Δ), CE-wood (\bullet), and CI-CE-wood (\circ).

wood differed in the dynamic behavior of main chain (Fig. 1), the behaviors of side chain was much the same.

The plots of $\log f_{\max}$ vs. $1/T$, that is, temperature dependences of position of the dielectric dispersion, for CEC, CE-wood, and Cl-CE-wood, are shown in Figure 11. The plots of $\log f_{\max}$ against $1/T$ gave a straight line, and the f_{\max} of both CEC and CE-woods were located on the same line. Apparent activation energy for this dielectric relaxation process was about 14.0 kcal/mol. From these results, as concerns the segmental motion of side chain, there is no remarkable difference between CE-woods and CEC, and hence it seems other components such as lignin do not hinder the rotation of dipoles. The CE-wood which contained lignin derivatives also shows good dielectric properties as well as CEC.

CONCLUSION

The mechanical properties and dielectric properties of film specimens from CE-wood were examined.

1. Dynamic mechanical properties: The CEC main chains in CE-wood were restrained by lignins, and that this restraint was released with chlorine treatment, and hence the dynamic behavior of chlorinated CE-wood was similar to that of CEC. From this fact, it was also explained that the thermoplasticity and the solubility in organic solvent for CE-wood was improved considerably with chlorine treatment.
2. Plasticization: CE-wood was plasticized effectively with CE-PVA, and the CE-wood film specimen showed a tenacity by polymeric blending. It was thought that both polymers were well dispersed with each other.
3. Drawing: It was found that CE-wood film specimens could be drawn to threefold of initial length in acetone aqueous solution, and that the Young's modulus of high drawn specimens were about 3.1 times as large as those

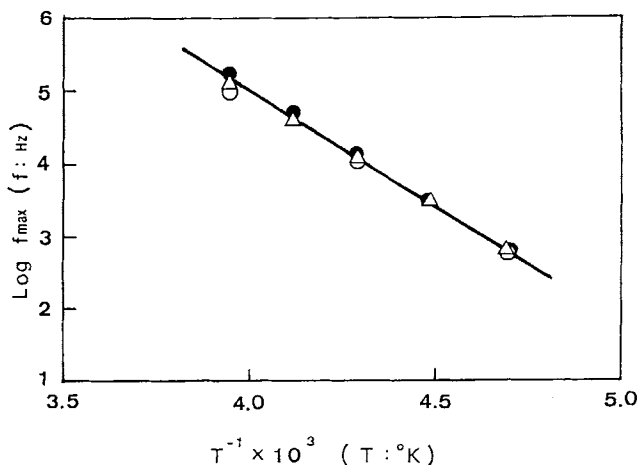


Fig. 11. Plots of $\log f_{\max}$ vs. $1/T$ for CEC (Δ) CE-wood (\bullet), and Cl-CE-wood (\circ).

of undrawn ones. But it was not possible for CE-wood to be drawn as highly as for CE-pulp. This was thought to be due to lignins, but this needs further studies.

4. Dielectric properties: CE-wood which contained lignins showed very high values of dielectric constant comparable to those of CEC at 20°C, and the segmental motion of side chain was not so restrained by lignins. These facts indicated that the woody materials which were not the pure cellulose had the capability to become high-performance dielectric materials.

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