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## Electrical properties of composite cyanoethylated pullulan film

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### Introduction

We have investigated the electrical properties of cyanoethylated cellulose to expand the field of wood utilization. Electrical properties of cyanoethylated cellulose that have been reported so far include dielectric properties, conductivity, and piezoelectricity.<sup>1–3</sup> Hirai et al.<sup>4</sup> reported that the high drawing cyanoethylated hydroxyethyl cellulose film had a high piezoelectric constant  $d$  that was 10–20 (pC/N) as large as that of PVDF film. Its ferroelectricity has not been determined.

The cyanoethyl groups contribute more to polarization than other groups, and their introduction has been effective in improving electrical properties. Chemical treatment alone is not able to improve the electrical properties. It has been necessary to apply an orientation method, such as drawing, to a film, but this is difficult because cyanoethylated film is extremely fragile.

In general, ferroelectric materials such as BaTiO<sub>3</sub> have a high dielectric constant, so they are combined with cellulose and this composite was expected to improve the electrical properties. A compound of cellulose and BaTiO<sub>3</sub> did not exhibit the ferroelectric phenomenon; but when samples were subjected to high voltage at high temperature, the electrical properties appear to have been markedly changed. We therefore tried to induce ferroelectricity of cyanoethylated pullulan with piezoelectric ceramics by applying high voltage at high temperature.

### Materials and methods

The samples for measuring the dielectric constant were prepared using a cyanoethylated pullulan (CEP), which is a derivative of polysaccharide, as shown in Fig. 1. It was manufactured by Shinetsu Kagaku Co. The melting point of CEP was not clear, but the weight decreased with increasing temperature up to about 150°C using a differential scanning calorimeter (DSC) (Rigaku Co).

The prepared powder (200#) of BaTiO<sub>3</sub> and PbZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub> (PZT) manufactured by Toshiba Seisaku Co. for improving the dielectric properties of cellulose was mixed with the CEP at a weight ratio of 10:1 or 10:2. The mixtures were blended in a chamber at 140°C and stirred at 50 rpm; they were then subjected to a pressure of 2 kgf/cm<sup>2</sup> at 150°C. The thickness of the films ranged from 100 to 500 μm. Gold was evaporated on both surfaces of the films, creating an electrode of about 1 cm<sup>2</sup>. A silver line was attached to the electrode as a lead.

A poling DC voltage of 1–5 kV was applied to the composite sample at 100°C for 1 min and repeated three times. After this treatment the samples were dried with a vacuum pump at room temperature for 24 h in a chamber and placed in a desiccator with P<sub>2</sub>O<sub>5</sub>.

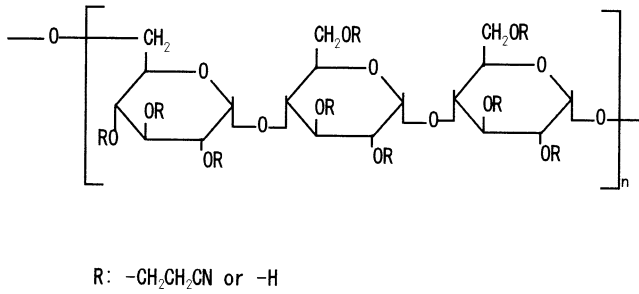
We examined a cross section of the film to verify its condition using a tapping mode atomic force microscope (AFM) (Nano Scope IIIa; Digital Instruments) to clarify the distribution of ceramic powder in the domain. An AFM image photograph, which is the phase detection image (PDI), is shown in Fig. 2.

The image area is 2 μm<sup>2</sup>. The white spots appear to be BaTiO<sub>3</sub> powder, and the dark area shows the CEP phase. The powder was not arranged in a cluster but was dispersed in a matrix of CEP.

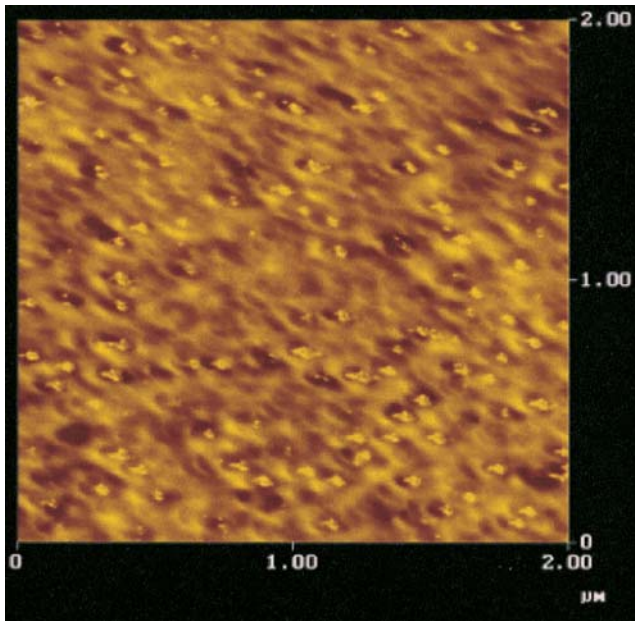
We investigated the dielectric and piezoelectric constants of the films using a Rheograph solid (Toyo Seiki Co.) at a temperature range of –150° to 100°C. The heating rate was about 2°C/min. Dry nitrogen gas was poured into the chamber to prevent water absorption during the measurement.

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## Cyanoethylated Pullulan (CEP)



**Fig. 1.** Chemical structure of cyanoethylated pullulan



**Fig. 2.** Atomic force microscopic (AFM) image (phase detection image) of a composite film with cyanoethylated pullulan and BaTiO<sub>3</sub>

When sinusoidal shear stress was applied to the specimen, polarization was observed on the surface of the specimen. The piezoelectric strain constant was denoted as  $d^* = d' + i d''$ .

The pyroelectric properties of some composite films were investigated using a thermal stimulated current apparatus (TSC; Toyo Seiki). The samples were placed in a chamber and heated at a rate of 1° or 2°C/min.

The ferroelectric properties were investigated at room temperature (18°C). The measuring apparatus consisted of a digital storage scope (DS-8606C; Iwatsu Co.), a synthesizer (1945; NF Electronic Instrument Co.), an amplifier (5325; NF Electronic Instrument Co.), and a high-voltage amplifier (Trek Co.). The digital data were transmitted to a personal computer (PC9821Xn, NEC) by a GPIB interface.

The two-phase system model consists of the piezoelectric phase (phase 2) and a nonpiezoelectric phase (phase 1). The

piezoelectric strain constant  $d$  was expressed in terms of the elastic constant  $c$  and the dielectric constant  $\epsilon$  as follows.<sup>5</sup>

$$d = d_2 \frac{5c_2}{3c_1 + 2c_2 - 3\phi(c_1 - c_2)} \cdot \frac{3\epsilon_1}{2\epsilon_1 + \epsilon_2 + \phi(\epsilon_1 - \epsilon_2)} \phi \quad (1)$$

where  $\phi$  is the volume fraction of phase 2, and subscripts 1 and 2 refer to the spherical piezoelectric phase and the nonpiezoelectric phase, respectively.

We calculated the piezoelectric constant  $d_2$  using the observed value of  $d$ . The details are reported in a previous paper.<sup>6</sup> We assumed that the volume fraction of the piezoelectric phases was nearly equal to the weight ratio of BaTiO<sub>3</sub> or PZT for the sample during the first step of the calculation.

We attempted to estimate the dielectric constant for the composite film using the two-phase disperse system model. Generally, the observed dielectric constant  $\epsilon$  can be expressed as follows:

$$\epsilon = \frac{2(1 - \phi)\epsilon_1 + (1 + 2\phi)\epsilon_2}{(2 + \phi)\epsilon_1 + (1 - \phi)\epsilon_2} \epsilon_1 \quad (2)$$

If  $\epsilon_2 \gg \epsilon_1$ , Eq. (2) can be expressed as follows.

$$\epsilon = \frac{(1 + 2\phi)}{(1 - \phi)} \epsilon_1 \quad (3)$$

## Results and discussion

The dielectric constant increased with increasing temperature for both CEP and the composite film. The dielectric constant  $\epsilon$  of the composite film was about 1.5 times higher than that of the CEP film at 0°C.

As with the dielectric constant, the piezoelectric constant  $d'$  increased with increasing temperature in the case of the composite film, whereas the piezoelectric constant  $d$  of CEP showed no distinct effect from the increasing temperature. Like the dielectric constant  $\epsilon$ , the piezoelectric constant  $d$  of the composite film was about 1.5 times than that of the CEP film at 0°C. The piezoelectric and dielectric constants at 20°, 50°, and 80°C are shown in Table 1. The piezoelectric constant  $d$  and dielectric constant  $\epsilon$  of the composite film without poling were not large, although they were larger than those of the CEP film.

As we had expected, the poling sample had a high dielectric constant, though the poling was not more than that of the control. Perhaps the reason the poling sample did not have a large  $\epsilon$  was that the applied voltage and temperature were not high enough to induce polarization.

Therefore, we speculated that the two-phase spherical disperse model could be applied to the estimation of dielectric and piezoelectric constants by being interpreted as uniform over the cross section of a film.

We estimated the dielectric constant  $\epsilon$  for the composite film to evaluate the performance using a two-phase system

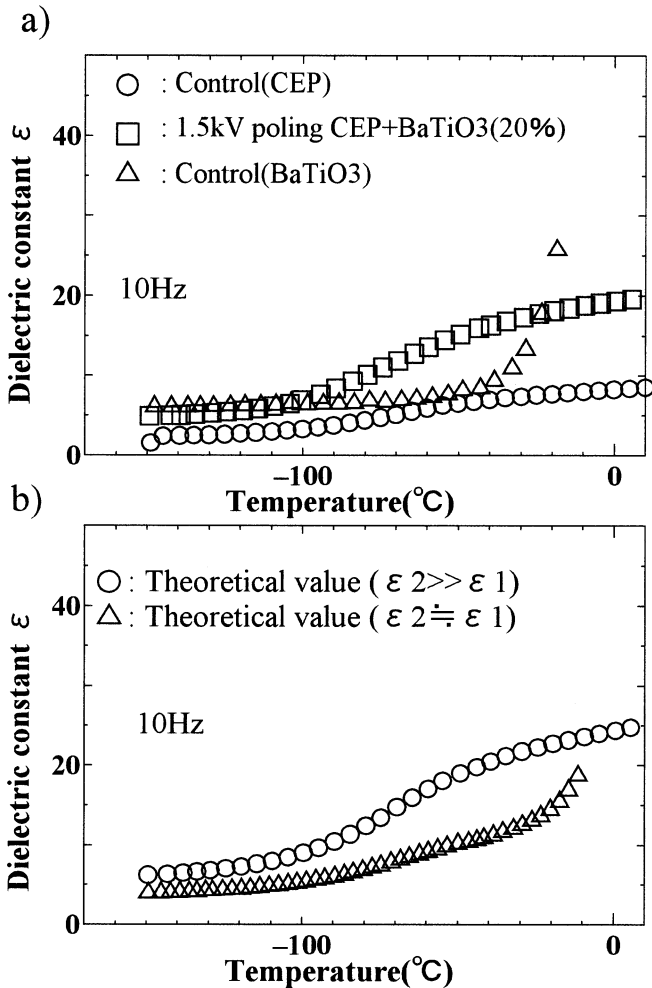
**Table 1.** Piezoelectric constant  $d$  and dielectric constant  $\epsilon$  at various temperatures

Parameter	20°C	50°C	80°C
$\epsilon'$ ( $\epsilon''$ )			
CEP (control)	14.7 (0.92)	18.3 (5.46)	23.7 (35.4)
CEP + PZT (1.5kV)	19.8 (0.24)	20.4 (0.91)	21.7 (6.72)
CEP + BaTiO <sub>3</sub> (1.5kV)	20.2 (0.34)	21.1 (2.14)	24.9 (13.8)
$d'$ ( $d''$ ) ( $\times 10^{-15}$ C/N)			
CEP (control)	2.2 (0.5)	4.7 (3.22)	19.2 (27.5)
CEP + PZT (1.5kV)	6.6 (1.38)	7.6 (2.65)	14.3 (2.25)
CEP + BaTiO <sub>3</sub> (1.5kV)	126.0 (1.05)	121.0 (6.4)	109.0 (59.8)

The results are given as the means (SD)

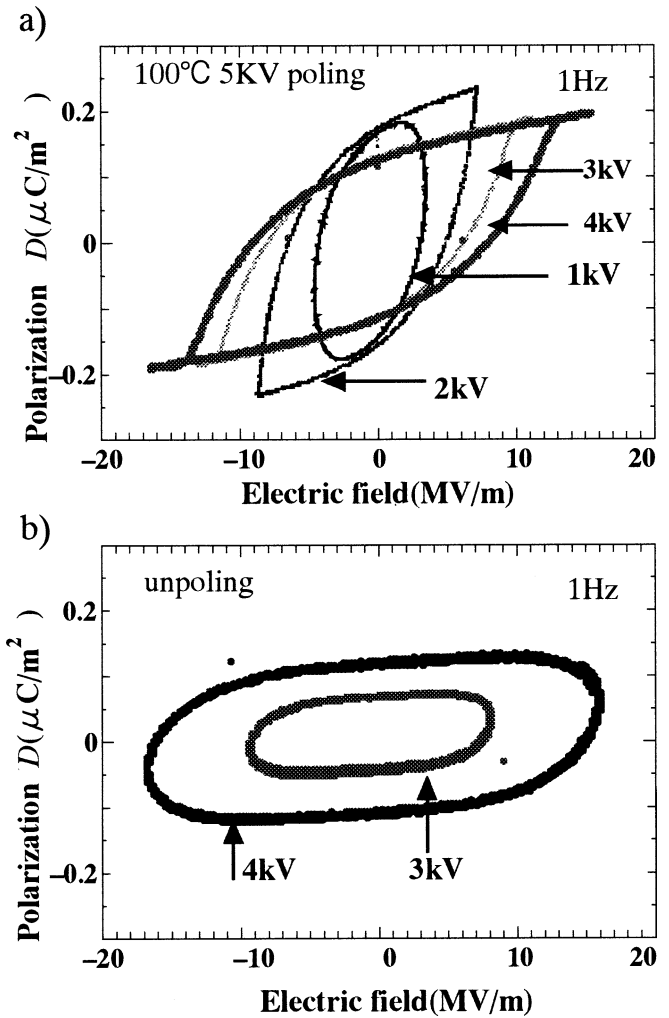
$\epsilon'$  and  $\epsilon''$  express, respectively, the real and imaginary parts of the dielectric constant  $\epsilon$ ;  $d'$  and  $d''$  express, respectively, the real and imaginary parts of the piezoelectric constant  $d$

CEP, cyanoethylated pullulan; PZT, PbZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub>

**Fig. 3.** Temperature dependence of the dielectric constants  $\epsilon$  **a** Observed values. **b** Calculated values

model to explain these phenomena. The dielectric constant  $\epsilon$  for BaTiO<sub>3</sub> and PZT were larger than that for CEP.

The dielectric constants for BaTiO<sub>3</sub> and PZT were measured in samples of about 1mm thickness. The dielectric constants of both of BaTiO<sub>3</sub> and PZT have an extremely wide range ( $-20^\circ$  to  $20^\circ$ C). It was thus necessary to deter-

**Fig. 4.**  $D$ - $E$  hysteresis loop of a composite film with cyanoethylated pullulan and BaTiO<sub>3</sub>. **a** Poling. **b** No treatment

mine the characteristics of the composite film using the two-phase disperse model.

From Eq. (3), we could estimate the values for BaTiO<sub>3</sub>, PZT, and CEP. Figure 3 shows the relation between the theoretical and the observed dielectric constants.

The observed value for the composite film that contained BaTiO<sub>3</sub> or PZT was larger than that for CEP but smaller than the theoretical value. When the dielectric constants  $\epsilon$  of the various phases of BaTiO<sub>3</sub> or PZT were nearly equal to the dielectric constant of phase 1 for CEP, the calculated dielectric constants were no larger than those for the control.

We concluded that it was not enough to do the poling properly. The dielectric constant could be obtained by poling using high voltage and high temperature. A poling voltage below 3kV was not sufficient, so we applied 5kV DC to each sample. The effect of temperature was investigated at temperatures of 75°, 100°, and 120°C, respectively. The most effective temperature for poling was about 100°C.

The next electrical property we investigated for the composite film was pyroelectricity in an attempt to clarify its effect on poling. The CEP film showed a pyroelectric

constant of about  $50\mu\text{C}/\text{m}^2$  at  $35^\circ\text{C}$ ; the value for the composite film was about five times higher.

The poling samples, composed of CEP and  $\text{BaTiO}_3$  (Fig. 4), exhibit a  $D$ - $E$  hysteresis loop at 1 Hz and  $20^\circ\text{C}$ . In this case, no distinct loop could be observed at voltages less than 2 kV; the hysteresis loop was observed above 3 kV. When the frequency increased with the voltage, the sample was broken by the electrical discharge. The sample then showed a remnant polarization of  $0.12$ – $0.13\mu\text{C}/\text{m}^2$  and a coercive field of 1–8 kV/m. This appears to have improved the ferroelectricity of the composite film. The films containing PZT also showed  $D$ - $E$  hysteresis loops with the same treatment.

Poling of the composite CEP film induced higher pyroelectricity and ferroelectricity when high-voltage DC (5 kV) was applied at  $100^\circ$ – $120^\circ\text{C}$ .

We concluded that poling the CEP composite film improved the piezoelectricity, pyroelectricity, and ferroelectricity. We also found ferroelectric phenomena, such a  $D$ - $E$  hysteresis loop, in cellulose material.

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