ORIGINAL ARTICLE

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Piezoelectric effect of cyanoethylated hydroxyethylcellulose

Abstract The piezoelectricity of cyanoethylated hydroxyethylcellulose was investigated. Elastic, piezoelectric, and dielectric relaxations were observed at $-80°$ to $-60°C$ and $0°$ to $20°C$ at a frequency of 10 Hz. The activation energy is about 9–15 kcal/mol in the low temperature region and about 30–45 kcal/mol at room temperature. These relaxations in the low temperature region may be caused by the motion of the cyanoethyl group and those at room temperature mostly by the motions of the main chain. Cyanoethylated hydroxyethylcellulose has a high piezoelectric strain constant (d_{25}), which is the largest value among the cellulose derivatives and is almost the same as the value for polyvinylidene fluoride. The electromechanical coupling factor for cyanoethylated hydroxyethylcellulose was small.

Key words Cyanoethylated hydroxyethylcellulose · High piezoelectric material · Functional cellulose derivative · Electromechanical coupling factor

Introduction

The purpose of our present investigation was to develop high-level piezoelectric materials from cellulose derivatives. It is recognized that among the cellulose derivatives, cyanoethylated cellulose has the largest piezoelectric constant, which is about 3×10^{-12} C/N at room temperature.[1] That of polyvinylidene fluoride is about 3×10^{-11} C/N at room temperature[2] and has been applied to the piezoelectric elements for electrodynamic transducers. If we can obtain

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piezoelectric cellulose derivatives with larger values than polyvinylidene fluoride, we can use them as electrodynamic transducers.

We have obtained a high-level piezoelectric cellulose derivative, cyanoethylated hydroxyethylcellulose (CEHEC). The value of its piezoelectric constant (d_{25}) is about $1–2 \times 10^{-11}$ C/N at 20°C. This constant is the largest for cellulose derivatives, and it is almost the same as that for polyvinylidene fluoride. It may be possible to use CEHEC as an industrial material with electrical functions by increasing the piezoelectric polarization.

Materials and method

Cyanoethylation

Cyanoethylation of hydroxyethylcellulose (Wako Pure Chemical Industries, Osaka, Japan), with a degree of polymerization (DP) of 400, a degree of substitution (DS) of 1.0, and 1.62 mol of ethylene oxide per anhydroglucose unit, (MS^3) was studied with acrylonitrile using sodium hydroxide as a catalyst.[4,5] Hydroxyethylcellulose (5 g) was added to 30 ml of a 2% sodium hydroxide solution at 30°C with stirring. It was completely dissolved within 2 h. Acrylonitrile (30 ml) was then added with stirring. The product precipitated within 1 h. The precipitate was transferred to a round-bottom flask and was refluxed at 80°C for 1 h after adding 60 ml acrylonitrile. The product was recovered by precipitation into a 50% ethanol solution. After removing the supernatant, the precipitate was washed thoroughly with distilled water and then redissolved in acetone. Again it was precipitated from a 50% ethanol solution. After this process was repeated three times, the polymer was vacuum-dried and the product analyzed for nitrogen content by the Kjeldahl method. The average DS value was about 1.5. A film of CEHEC was stretched uniaxially 30 times its original length at 60°C. After stretching, the crystalline orientation angles of the specimens were measured using the meridian curves of x-ray diffraction.[6]

Measurement of piezoelectric, dielectric,
and elastic constants

The Rheolosorid (Toyo Seiki, Tokyo, Japan) was used to measure the piezoelectric, dielectric, and elastic constants. Constants for the dried CEHEC film were measured by pouring dried nitrogen gas into the measuring chamber to avoid water adsorption during the measurement.

Measurement of electromechanical coupling factor

The electromechanical coupling factor of CEHEC was obtained by two methods. This factor is given by

$$k = d/\left(\varepsilon^{T} \cdot s^{E}\right)^{1/2} \qquad (1)$$

where d is the piezoelectric constant, ε^{T} the dielectric constant at a constant stress, and s^{E} the elastic compliance at a constant electric field. Therefore this factor is obtained from the values of d, ε^{T}, and s^{E}. The elastic constant depends

on the electrical condition when the strain/stress ratio is measured. If the electrical terminals are open-circuited, the elastic constant corresponds to zero electric displacement, whereas if the terminals are short-circuited it is obtained for a zero electric field. The ratio of these two constants is given by

$$s^{E}/s^{D} = 1/\left(1 - k^{2}\right) \qquad (2)$$

where s^{E} is the elastic compliance at zero electric field and s^{D} the elastic compliance at zero electric displacement.

Results and discussion

Temperature dependence of piezoelectric, dielectric, and elastic constants

The chemical structure of CEHEC is shown in Fig. 1. The temperature dependence of the piezoelectric, dielectric, and elastic constants measured at several frequencies for CEHEC are shown in Figs. 2–4. The real part of the piezoelectric strain constant (d') increased with increasing temperature. The imaginary component d'' reached a minimum at about $-75°C$ and $25°C$, which indicated piezoelectric relaxations. Elastic relaxations were observed at similar temperatures. In the case of dielectric behavior relaxation was observed at a low temperature ($-75°C$), but a peak was not recognized at the imaginary part of the dielectric constant (ε'') at a high temperature. It seems that there was an increase in electrical conductivity at this temperature, so the peak of ε'' at this temperature was hidden by the electrical conductivity. As shown in Figs. 2, 3, and 4, the temperature of these two relaxations shifted to the higher temperatures with increasing frequency. There were two relaxations for
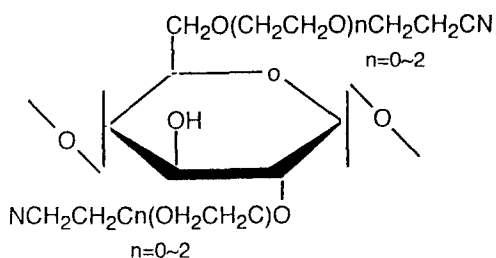

Fig. 1. Chemical structure of cyanoethylated hydroxyethylcellulose (CEHEC)
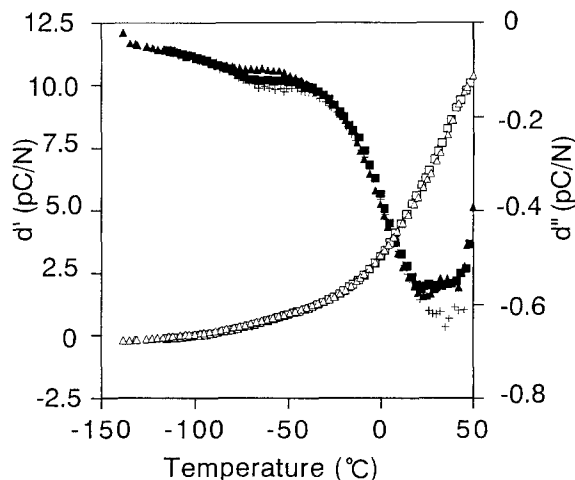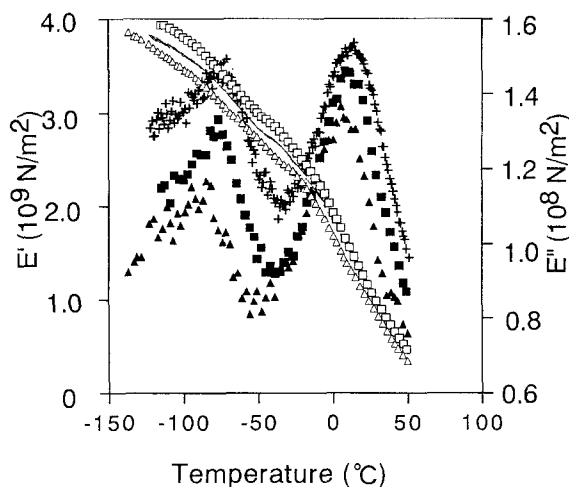

Fig. 2. Temperature dependence of the piezoelectric constants d' and d'' at frequencies of 5, 20, and 50 Hz for CEHEC. *Open triangles*, 5 Hz; *open squares*, 20 Hz; *crosses*, 50 Hz; *filled triangles*, 5 Hz; *filled squares*, 20 Hz; *plus sign*, 50 Hz. The first three signify the real part and the second three signify the imaginary part

Fig. 3. Temperature dependence of the elastic constants E' and E'' at frequencies of 5, 20, and 50 Hz for CEHEC
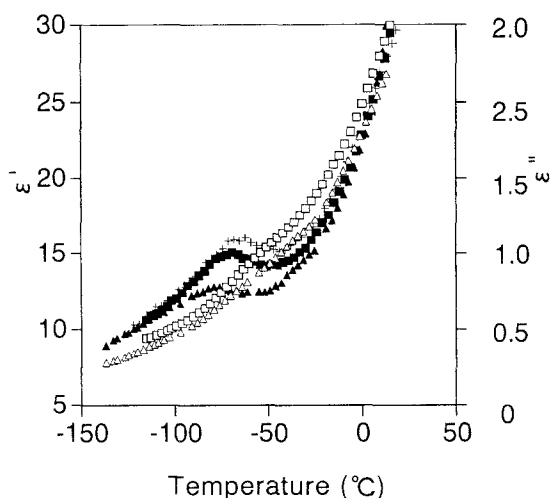
Fig. 4. Temperature dependence of the dielectric constants ε' and ε" at frequencies of 5, 20, and 50 Hz for cyanpethylated hydroxyethylcellulose

Fig. 5. Logarithm plots of frequency log *f* versus reciprocal absolute temperature of elastic, piezoelectric, and dielectric relaxations I for CEHEC. *Squares*, elasticity; *triangles*, piezoelectricity; *circles*, dielectricity

Table 1. Apparent activation energies of piezoelectric, dielectric, and elastic relaxations

Type of relaxation	Activation energy (kcal/mol)	
	Relaxation I	Relaxation II
Piezoelectric	12.2	32.9
Dielectric	9.3	–
Elastic	15.0	44.5

Fig. 6. Logarithm plots of frequency log f versus reciprocal absolute temperature of elastic, piezoelectric, and dielectric relaxations II for cyanoethylated hydroxyethylcellulose. *Squares*, elasticity; *triangles*, piezoelectricity; *circles*, dielectricity

the piezoelectric and elastic constants and one relaxation for the dielectric constant. Relaxations below about −50°C are called relaxations I in this paper, and relaxations at about 25°C are called relaxations II.

Apparent activation energies of piezoelectric, dielectric, and elastic relaxations for CEHEC

Figure 5 shows the relation between the reciprocal of absolute temperature and the logarithm of the frequency at the elastic, piezoelectric, and dielectric relaxations I in the temperature range below −50°C for CEHEC. The apparent activation energies estimated from Fig. 5 are listed in Table 1. These relaxations were observed within a narrow temperature range, and it may be that they are closely related. The temperature region and the activation energies for these relaxations approximately agree with the results of our previous study on CEHEC[7]; i.e., these relaxations are associated with the rotational motion of the cyanoethyl group in the cellulose derivative.

Figure 6 shows the relation in the case of relaxations II. The apparent energies for these relaxations are shown in
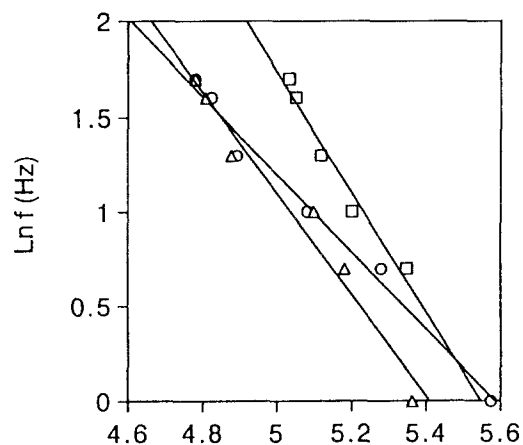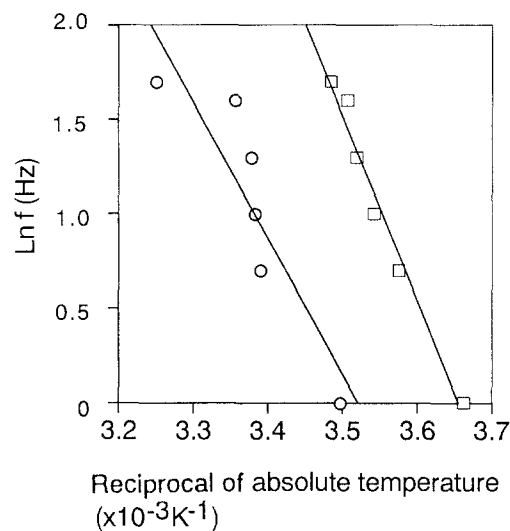
Table 1. Relaxations II have activation energies about twice as large as those of relaxations I. Relaxations II may be primarily associated with motions of the main chain, judging from the activation energies for relaxations II and the remarkable decrease in the elastic constant *E'* shown in Fig. 3.

CEHEC with high values of piezoelectric strain constant

It is difficult to obtain a film of cyanoethylated cellulose; it can be magnified about three times at most. In contrast, it is
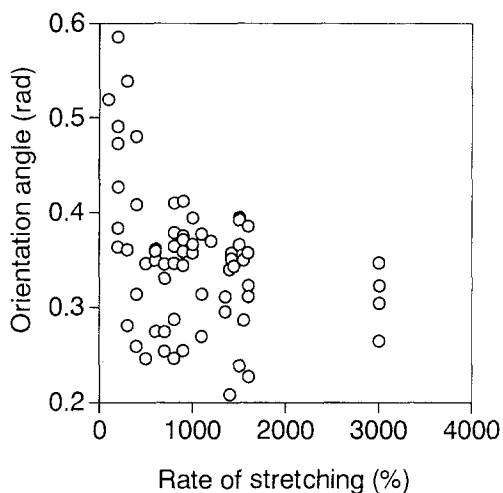
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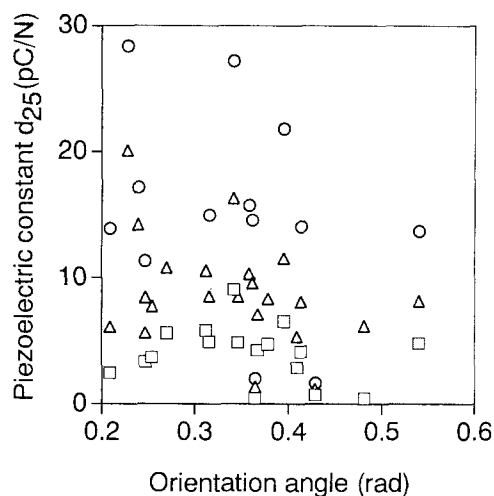Fig. 7. Relation between the rate of stretching and the orientation angle

Fig. 8. Relation between the orientation angle and the piezoelectric constant. *Squares*, 0°C; *triangles*, 20°C; *circles*, 50°C
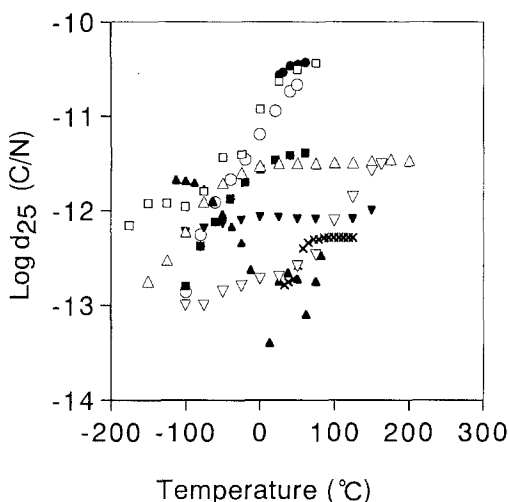

Fig. 9. Piezoelectric constants of cellulose derivatives. *Open squares*, PVDF (polyvinylidene fluoride); *inverted open triangles*, NC (nitrocellulose); *crosses*, EC (ethylcellulose); *upright open triangles/filled squares*, CEC (cyanoethylated cellulose); *inverted filled triangle*, DAC (cellulose diacetate); *upright filled triangles*, TAC (cellulose triacetate); *open/filled circles*, CEHEC (cyanoethylated hydroxethylcellulose)
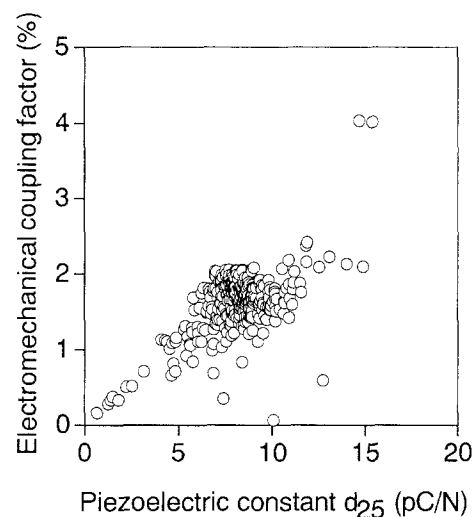

Fig. 10. Relation between piezoelectric constant and electromechanical coupling factor for CEHEC

easy to obtain a CEHEC film, which can be stretched 30-fold by applying tension at about 60°C. The presence of the hydroxyethyl group may facilitate stretching the molecular chains. Figure 7 shows the relation between the rate of stretching and the crystallite orientation angle of the CEHEC film. Figure 8 shows the relation between the orientation angle and the value of the real part of the piezoelectric constant (d'_{25}). Note that the orientation angles of specimens decrease with an increase in the rate of stretching up to about 500% and then disperse widely between 0.2 and 0.4 radian. The piezoelectric constant increases with a decrease in the orientation angle. The values of the real part of the piezoelectric strain constant (d'_{25}) reached about 2 × 10^{-11} C/N at 20°C.

Figure 9 shows the d_{25} of various cellulose derivatives and polyvinylidene fluoride. At room temperature CEHEC has a large piezoelectric constant, on the order of 10^{-11} C/N, which is almost same as that for polyvinylidene fluoride.

Until now, cyanoethylated cellulose has shown the largest piezoelectric strain constant (3 × 10^{-12} C/N) among the cellulose derivatives. However, the value of the CEHEC prepared here was about 2 × 10^{-11} C/N, which is now the largest for the cellulose derivatives, and can be compared with that for polyvinylidene fluoride. It may be that the high level of piezoelectricity of CEHEC is related to the orientation of the molecular chains, with the polar cyano group being stretched to some extent.

Electromechanical coupling factor

The electromechanical coupling factor (k) is considered important for estimating the properties of piezoelectric materials. The value of k is about 50% for PZT and about 20% for polyvinylidene fluoride. The k values for CEHEC are obtained from Eq. (1). Figure 10 shows the linear relation between the piezoelectric constant and the electromechanical coupling factor for CEHEC samples. Compared with the k value of polyvinylidene fluoride, that for CEHEC is small at less than 4%. The piezoelectric constant of CEHEC is high, but the electromechanical coupling factor is small owing to high dielectricity. We could not obtain reliable values with Eq. (2) because the magnitudes of s^E and s^D changed fractionally under tension during the measurement.

Cellulose is a rich natural resource, and it is expected to be a biodegradable polymer. Synthetic polymers such as polyvinylidene fluoride have some problems during the synthetic process, with much halogen and waste matter, so it may be important that cellulose, which is harmless to the human environment, can be used with industrial materials with electrical functions.

Conclusions

The piezoelectricity of CEHEC were investigated. The results obtained were as follows.

1. Dependence of the piezoelectric, dielectric, and elastic constants on temperature was measured. Elastic, piezoelectric, and dielectric relaxations were observed between $-80°$ and $-60°C$ and elastic and piezoelectric relaxations between $0°$ and $20°C$ at a frequency of 10 Hz. The activation energies are about 9–15 kcal/mol in the low-temperature region and about 30–45 kcal/mol in the higher temperature region. These relaxations may be caused by the motion of the cyanoethyl group at low temperature and mostly by motions of the main chain at room temperature.

2. At room temperature CEHEC has a large piezoelectric constant, approximately 10^{-11} C/N, which is similar to the constant for polyvinylidene fluoride. The high level of piezoelectricity of CEHEC may be related to the orientation of the molecular chains with the polar cyano group during stretching.

3. The electromechanical coupling factor for CEHEC was small ($<4\%$).

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