Preliminary Report

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Cyanoethylated Hydroxyethylcellulose with Great Piezoelectric Effect*1

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高圧電性シアノエチル化ヒドロキシエチルセルロース

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1. INTRODUCTION

The purpose of our present investigation is to develop high level piezoelectric materials of cellulose derivatives. It is recognized that cyanoethylated cellulose has the largest piezoelectric constant of the cellulose derivatives.[1] The value of the piezoeletric constant of cyanoethylated cellulose 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] which actually has been applied to the piezoelectric elements for electrodynamic transducers. If we can obtain larger piezoelectric cellulose derivatives than that of polyvinilidene fluoride, it will be possible to use them as electrodynamic transducers.

Now we have obtained a high level piezoelectric cellulose derivative, that is, cyanoethylated hydroxyethylcellulose. The value of this derivative is about $1\text{-}2\times10^{-11}$ C/N at 20°C. It is the largest value of cellulose derivatives, and it approaches the value of polyvinilidene fluoride. It may be possible to use it as an industrial material with electric functions by increasing the piezoelectric polarization.

2. MATERIALS AND METHODS

Cyanoethylation: Cyanoethylation of hydroxyethylcellulose (DP (degree of porimerization) = 400, DS (degree of substitution) = 1.0, MS (molecular substitution) = 1.62, Wako Pure Chemical Industries, Ltd.) was conducted with acrylonitrile using sodium hydroxide as a catalyst.[3,4] Five grams of hydroxyethylcellulose was added to 30 ml of a 2% sodium hydroxide solution at 30°C with stirring, and it was completely dissolved within two hours. Then 30 ml of acrylonitrile was added with stirring. The product was precipitated within one hour. The precipitate was transferred in a round bottom flask and was refluxed at 80°C for one hour after adding 60 ml of 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% eth-

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anol solution. After this process was repeated three times, the polymer was vacuum-dried, and the product was analyzed for nitrogen content by the Kjeldahl method. The average value of the DS was about 1.5. A film of cyanoethylated hydroxyethylcellulose was stretched uniaxially fifteen times the original length at 60°C.

Measurements: The Rheolosorid (Toyo Seiki Co. Ltd.) was used for measurements of the piezoelectric, dielectric, and elastic constants.

3. RESULTS AND DISCUSSION

The temperature dependence of the elastic, piezoelectric strain, and piezoelectric stress constant measured at a frequency of 10 Hz for the cyanoethylated hydroxyethylcellulose is shown in Figure 1. The value of the real part of the piezoelectric strain constant d' was about 1-2$\times10^{-11}$ C/N, although scattered at temperatures above 60°C. Until now, cyanoethylated cellulose has shown the largest value of a piezoelectric strain constant at 3$\times10^{-12}$ C/N for a cellulose derivative. However, the value of the cyanoethylated hydroxyethylcellulose prepared here was about 1-2$\times10^{-11}$ C/N, which is an order of magnitude larger and is the largest of the cellulose derivatives, approaching that of polyvinilidene fluoride.

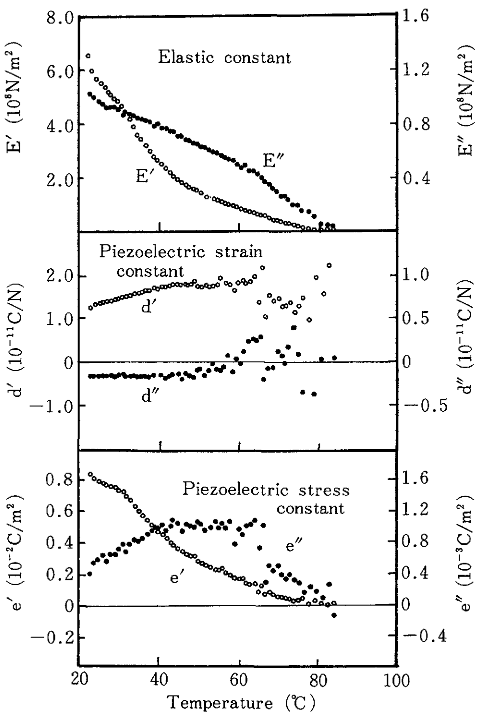

Fig. 1 Temperature dependence of the elastic constant, piezoelectric strain constant, and piezoelectric stress constant at a frequency of 10 Hz for cyanoethylated hydroxyethylcellulose.

It may be considered that the high level of piezoelectricity of the cyanoethylated hydroxyethylcellulose is related to the great orientation of the molecular chains with the polar cyano group by the fifteen times elongation. In the case of cyanoethylated cellulose, it is very difficult to elongate film, and the magnification of the elongation is about three times at most. The existence of the hydroxyethyl group may facilitate elongation of the molecular chains.

Cellulose is rich as a natural resource, and it is expected as a biodegradable polymer. While synthetic polymers such as polyvinilidene fluoride involve some problems in synthetic processes with much halogen and waste matter, it may be very important that cellulose, which is harmless to the human environment, has come to be used with industrial materials with electric functions.

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