

CONTRIBUTION OF MACROSCOPIC DIMENSION EFFECT TO PIEZOELCTRICITY IN POLYVINYLIDENE FLUORIDE

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ABSTRACT

In this paper, we have studied the piezoelectricity in the poled uniaxially drawn polyvinylidene fluoride. The piezoelectric constants d_{31} , d_{32} , d_{33}^* and Young's moduli $1/s_{11}$ and $1/s_{22}$ have been determined as a function of the remanent polarization P_r . The piezoelectric constants of the samples show a strong in-plane anisotropy. Such an anisotropy is mostly attributable to different Poisson's ratio. It is found that the piezoelectric activity mainly arises from macroscopic dimensional change.

The strong piezoelectricity of uniaxially drawn and poled polyvinylidene fluoride (PVDF) has prompted a number of researchers to make investigations on the underlying causes and applications in the industry^[1]. Reviews on the piezoelectricity which put emphasis on PVDF and its copolymers, have been published^[2-7]. Recent investigations have shown that PVDF and its copolymers are ferroelectric materials^[8-12]. Thus their piezoelectric activity can be ascribed to cooperative orientation of dipoles in the crystalline regions. However, there are distinction between the models suggested for piezoelectricity originated from cooperative alignment of dipoles. Among the various mechanisms, the largest contribution to the piezoelectric activity in PVDF has been shown to arise from macroscopic dimensional changes. That is, if the moments of rigid constituent dipoles are invariant upon deformation, the piezoelectric response can occur as a result of a change in macroscopic dimensions of the sample^[13]. In the previous papers^[13-15] we studied the piezoelectric and pyroelectric activities as a function of remanent polarization P_r in the copolymers of vinylidene fluoride-trifluoroethylene (PVDF/TrFE) and a copolymer of vinylidene fluoride-tetrafluoroethylene. We demonstrated that their piezoelectric activities primarily arise from the dimensional effect. However, the electrostriction can give the remaining contribution for piezoelectricity in some copolymers of vinylidene fluoride-trifluoroethylene having very low Curie point^[14,15].

In this paper, we present further experimental results on piezoelectricity and pyroelectricity in uniaxially drawn PVDF. In contrast to conventional high temperature poling, we carried out room temperature poling using a slowly changing high electric field and prepared samples with known values of remanent polarization P_r . The transverse and longitudinal piezoelectric constants as a function of P_r were measured. We discuss the contribution of the dimensional effect to piezoelectricity.

EXPERIMENTAL

Sample preparation.

The PVDF film used was supplied by Kureha Chemical Industry Co. The uniaxial drawing was performed at 35°C to 4 times their original length, followed at 135°C for 1 h. Rectangular pieces of samples were cut along the directions parallel and perpendicular to the orientation axis. Gold electrodes were along the directions parallel and perpendicular to the orientation axis. Gold electrodes were vacuum deposited onto both surfaces of these samples.

Measurements

The poling of samples was undertaken at room temperature by applying a sinusoidal high electric field of 10^{-2} Hz. By monitoring the induced charges, we obtained a typical hysteresis loop. The largest remanent polarization is created in the samples when the field is decreased to zero from its maximum. If we force the field to zero before reaching a maximum, we can impart various lower remanent polarizations in samples.

We studied two types of piezoelectric effects, the transverse effect and longitudinal effect. The transverse effects were observed at 10 Hz by the ratio of charge density generated on the electrode to the applied stress along the drawing direction and/or perpendicular to this direction in plane of a rectangular sample. Thus, we obtained d_{31} and d_{32} . At the same time, we measured the elastic compliance coefficients s_{11} and s_{22} . We used Cartesian coordinate system, where the 1 axis was taken along the drawn direction and the 3 axis, along the thickness (poling direction). Thus, s_{11} and s_{22} represent the elastic compliance coefficient of axis 1 and 2 respectively. The piezoelectric constants were measured at 25°C.

The longitudinal effect was measured by applying a quasi-static stress along the thickness direction to a sample sandwiched between a pair of glass plates. In this configuration, the in-plane deformation of the sample was restricted. Thus, we obtained apparent d_{33}^a rather than the true d_{33} .

The definition of these piezoelectric constants will be described in the following.

The most commonly used piezoelectric constants are defined by ^[16]

$$d_{3j} = \frac{1}{A} \left(\frac{\partial Q_3}{\partial X_j} \right)_{X_i \neq j} = 0 \quad (1)$$

$$e_{3j} = \frac{1}{A} \left(\frac{\partial Q_3}{\partial x_j} \right)_{x_i \neq j} = 0 \quad (2)$$

Where X_j is the stress, x_j the strain and Q_3 , the total charge induced on the electrodes of area A . Because of the restriction of the measuring boundary conditions, the following definitions must be used.

$$d_{3j}^a = \left(\frac{\partial P_3}{\partial X_j} \right)_{X_i \neq j} = 0 \quad (3)$$

$$e_{3j}^a = \left(\frac{\partial P_3}{\partial x_j} \right)_{X_i \neq j} = 0 \quad (4)$$

The P_3 is the remanent polarization of samples. The superscript "a" denotes the apparent value of these constants because they differ from d_{3i} and e_{3j} in eqs.1 and 2 in terms of mechanical boundary conditions^[13].

d_{3j} and e_{3j} are related to each other by

$$d_{3j} = \sum_{i=1}^3 e_{3i} s_{ij} \quad (5)$$

$$e_{3j} = \sum_{i=1}^3 d_{3i} c_{ij} \quad (6)$$

Corresponding to eq 3 and 4, we have

$$d_{3j}^a = e_{3j} / c_{jj} \quad (7)$$

$$e_{3j}^a = d_{3j} / s_{jj} \quad (8)$$

c_{ij} is the elastic stiffness constant.

We measured three constants d_{31} , d_{32} , d_{33}^a and elastic moduli $1/s_{11}$, $1/s_{22}$. The other constants were calculated using eqs. 3, 6, 7 and 8.

RESULTS

Figure 1 shows the dependence of the Young's moduli $1/s_{11}$, $1/s_{22}$ and the strain piezoelectric constants d_{31} , d_{32} on the remanent polarization Pr in the uniaxially drawn PVDF. We have noticed that Young's moduli $1/s_{11}$ and $1/s_{22}$ are identical to each other and independent of Pr . Both d_{31} and d_{32} are linearly proportional to Pr and increase with increasing remanent polarization Pr . Figure 1 also shows a strong in-plane anisotropy of the piezoelectric constants. The value of d_{31} is much larger than that of d_{32} at a given Pr , that is, $d_{31} = 10 d_{32}$.

Figure 2 shows the dependence of the longitudinal piezoelectric constant d_{33}^a on Pr in uniaxially drawn PVDF. The negative values of d_{33}^a are consistent with results reported by Sussner^[19] and their absolute values increase with increasing polarization Pr .

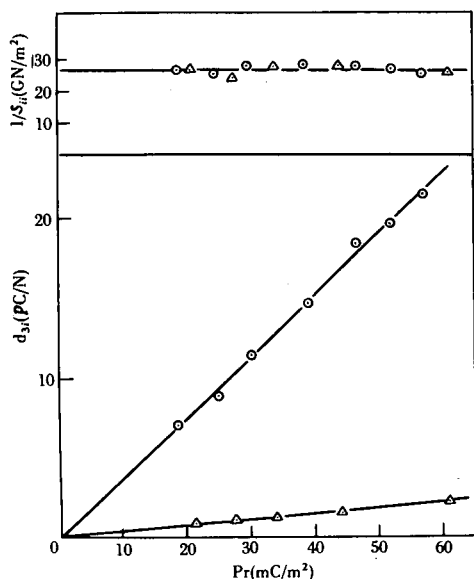


Figure 1 Dependence of d_{3j} and $1/s_{ii}$ on Pr in PVDF. $d_{31}(0)$, $d_{32}(\Delta)$, $1/s_{11}(0)$, $1/s_{22}(\Delta)$.

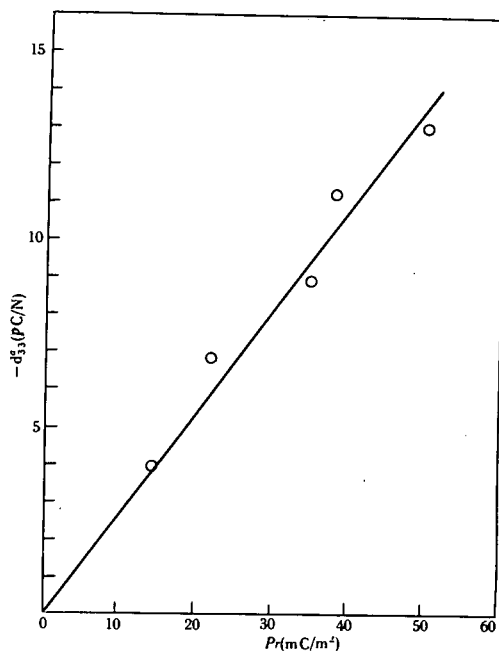


Figure 2 Dependence of d_{33}^a on Pr in PVDF.

Figure 3 shows the dependence of apparent stress piezoelectric constant e_{31}^a and e_{32}^a on Pr in the sample. Both e_{31}^a and e_{32}^a are linearly proportional to Pr and their values increase with increasing Pr . The ratios of e_{31}^a/Pr and e_{32}^a/Pr are 1.0 and about 0.1 respectively. The results are very important to the discussion on the contribution of the macroscopic dimensional effect.

Figure 4 shows the linear relationship between Pr and pyroelectric constant having the negative value. The absolute values of pyroelectric constants increase with increasing Pr .

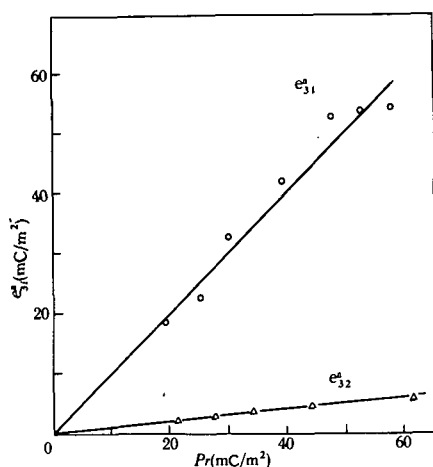


Figure 3 Dependence of e_{31}^a on Pr in PVDF

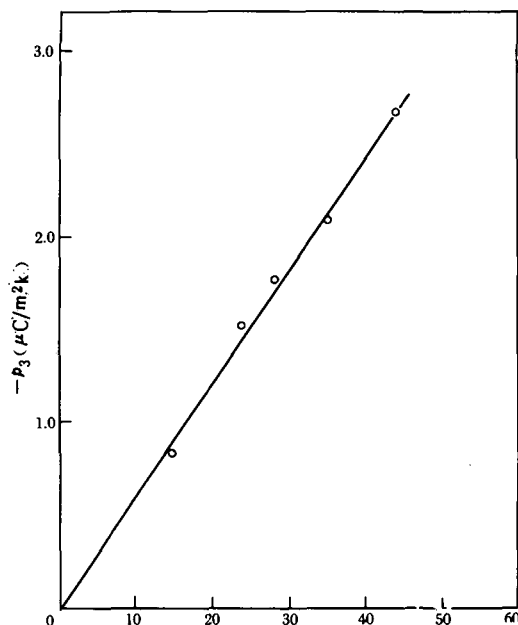


Figure 4 Dependence of pyroelectric constant p_3 on Pr

DISCUSSION

In order to elucidate the piezoelectric activities in PVDF, various physical models have been proposed. Broadhurst and his coworkers have considered a model consisting of polarizable and liberating dipoles^[1,7]. Wada and Hayakawa developed a theory on piezo- and pyroelectricity for semicrystalline polymer with polar crystals^[18,20]. Although their theoretical consideration is based on different models, they have derived a similar mechanism called the dimensional effect. The piezoelectric activity in PVDF primarily arises from the dimensional effect. In this paper, we consider further PVDF as a ferroelectric polymer. The piezoelectric constants have been determined as a function of the remanent polarization Pr . If the consistent dipoles oriented in the system are rigid when a sample is subjected to deformation, the expected change in induced charge on deformation may be proportional to the change in thickness. Therefore, the e constants are given as follows:^[4]

$$e_{31} = e_{32} = 0 \quad (9)$$

$$e_{33} = -Pr \quad (10)$$

Because there exist other mechanisms besides the dimensional effect, the values of e_{31} and e_{32} measured are not zero. For uniaxially drawn and poled PVDF having C_{2v} symmetry, we can

calculate the values of piezoelectric constants e_{31} , e_{32} and e_{33} using eqs. (5), (6). It has been shown that the Poisson's ratio ν_{31} of uniaxially drawn PVDF can exceed 0.5^[19].

Tasaka and Miyata reported a value of 0.7 for ν_{31} of PVDF^[20]. According to the Poisson's ratio of polyethylene^[22], we can assume the Poisson's ratio ν_{31} , ν_{21} and ν_{32} as 0.65, 0.3 and 0.3 respectively^[14]. Therefore, using the values of Poisson's ratio, we obtained the e constants at 50mC/m² of Pr as follows,

$$e_{ij} = \begin{pmatrix} 0 & 0 & 0 & 0 & e_{15} & 0 \\ 0 & 0 & 0 & e_{24} & 0 & 0 \\ -28 & -28 & -98 & 0 & 0 & 0 \end{pmatrix} \quad (\text{mC/m}^2) \quad (11)$$

$$\text{Where} \quad e_{ij} = \partial P_i / \partial x_j \quad (i = 1-3, j = 1-6) \quad (12)$$

We further discuss the results shown in Figure 3, which are the emphasis in this paper. For the values of e^a constants are independent of the values of Yong's moduli, the dependence of e^a constants on Pr can be used to study piezoelectric mechanism conveniently. The d constant can be determined by direct measurement. Therefore, e_{3j}^a constants can be calculated using eq (8). The dimensional effect leads to the expression for e^a as follows:^[14]

$$e_{31}^a = Pr \nu_{31} \quad (13)$$

$$e_{32}^a = Pr \nu_{32} \quad (14)$$

$$e_{33}^a = -Pr \quad (15)$$

It must be pointed that these expressions are independent of the choice of model. If the piezoelectric constants are measured as a function of macroscopic polarization Pr , the contribution of the dimensional effect is estimated by eqs. 13—15. At a given value of Pr in PVDF, the values of piezoelectric constants e_{31}^a , e_{32}^a only depend on the values of ν_{31} , ν_{32} , respectively. Figure 1 shows the difference between the values of d_{31} and d_{32} . For the elastic compliance s_{11} and s_{22} are identical to each other and independent of Pr , the strong in-plane anisotropy of e_{3j} constant appears, that is, e_{31}^a and e_{32}^a depend on the values of corresponding Poisson's ratios.

From Figure 3, we have the ratios, $e_{31}^a / Pr = 1.0$ and $e_{32}^a / Pr = 0.1$. By comparison of these values of the ratios, we can evaluate the contribution of the dimensional effect to piezoelectric activity in PVDF. Tasaka and Miyata reported a value of 0.7 for ν_{31} of PVDF^[20]. From the fact, we can suggest that e_{31}^a constants primarily arise from the dimensional effect. Since the values of ν_{32} is not available at the present, we tentatively assume that it is about 0.3. Because the existence of some effect rather than dimensional effect, the value 0.1 for e_{32}^a / Pr may also be consistent with the corresponding Poisson's ratio^[14].

The linear relationship between longitudinal piezoelectric constants d_{33}^a and Pr has been shown in Figure 2. d_{33}^a constants show the negative values and increase with increasing polarization Pr . These facts demonstrated that the dimensional effect is dominant in the orienting dipole system^[19].

Now we discuss the relationship between piezoelectricity and pyroelectricity. The pyroelectric constant p_3 for a mechanically free sample generally consists of two terms:

$$p_3 = \left(\frac{\partial P_3}{\partial T} \right)_{x_i} = 0 + \sum_{i=1}^3 e_{3i} \alpha_i \quad (16)$$

Where T is the temperature, α_i the thermal expansion coefficient and P_3 , the remanent polarization along thickness direction. The first term called the primary effect, expresses the intrinsic pyroelectricity which appears in a clamped sample. The second term expresses the coupling of the piezoelectricity and the thermal expansion and is called the secondary effect. Kepler and Anderson have discussed the primary and secondary effect and ascribed one half of the total activity to the latter in drawn PVDF^[21]. Comparison of Figure 4 with Figures 1, 2 and 3 indicates that there exists a similar dependence of pyroelectricity and piezoelectricity on Pr . Therefore, It leads a similar relationship between pyroelectricity and piezoelectricity. These results indicate the common origin for pyroelectricity and piezoelectricity.

Keywords:

Piezoelectricity; Pyroelectricity; Polyvinylidene fluoride.

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