

Piezoelectricity of Vinylidene fluoride–Trifluoroethylene Copolymer Films in Various Poling Conditions

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ABSTRACT: Piezoelectricity of ferroelectric thin polymer films strongly depends on the poling condition. We can classify them as conventional electrical and novel nonelectrical poling. These experiments show the comparative results on piezoelectricity induced from various poling processes (i.e., electrical corona poling, nonelectrical surface-energy poling, and a combination of both methods simultaneously in various poling conditions). The most in-

teresting result confirmed that the piezoelectricity increased significantly when the combination poling was applied with appropriate metal substrate and temperature decreasing rate. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 856–860, 2004

Key words: ferroelectricity; piezoelectricity; surfaces; poling; films

INTRODUCTION

Recently, high-performance ferroelectric polymers are required gradually for sensor and transducer applications.¹ Piezoelectricity of most ferroelectrics strongly depends on the poling process. In the case of polymer films, conventional electrical thermal or corona poling is usually applied for alignment and stabilization of dipoles to give rise to the piezoelectricity. However, dielectric breakdown, surface damage, and nonuniformity of remanent polarization are occasionally present. Several methods have been proposed^{2–4} to eliminate them but the problems could not be avoided completely.

Recently, Ide et al. successfully developed a novel method utilizing the energy difference between the surfaces of polycyanophenylenesulfides (PCPS).⁵ The film was sandwiched with an indium tin oxide coated glass (ITO glass) and dry air or poly(tetrafluoroethylene) (PTFE). The polymer was then heated to a temperature above the phase transition temperature (Curie point, T_c), which is nearly $1.2 \times T_g$ (glass transition temperature), and slowly cooled down to the room temperature. In such conditions, the surface molecules of the PCPS film reorient themselves to minimize the energy exerted by the high-energy surface (ITO glass) and the low-energy surface (dry air or PTFE). Other dipoles in the bulk thermally reorient up to a certain thickness because of high cooperation of dipoles, which are rotatable by thermal diffusion.

There are two advantages of this method. First, it requires no intensive electric field as does conventional electrical poling, which may cause surface problems. Another is that their pyroelectric devices seem to be stable because the remanent polarization is reversible with temperature. They referred to this new method as surface energy poling.⁵

In this article, we discuss preparation of piezoelectric films, utilizing copolymer of vinylidene fluoride with trifluoroethylene, P(VDF/TrFE), by various poling methods [i.e., electrical (corona poling), nonelectrical (surface-energy poling), and the novel combination of both methods simultaneously]. We also investigated the effects of the high surface energy of the metal substrates and the cooling rates on the piezoelectricity of the films in the case of surface energy and combination poling.

It should be noted that the presence of TrFE in the copolymer of the P(VDF/TrFE) films introduces two significant features to the PVDF homopolymer. It increases the tendency to crystallize in the polar β -phase without the requirement of stretching to transform the nonpolar α -phase to the polar β -phase as in the case of PVDF. Because of the random orientation of the unit cells in the semicrystalline film, the poling process is also essentially required to induce piezoelectricity to the untreated films.^{6–8} The other is that the transition between the ferroelectric and paraelectric phases in the crystalline region of P(VDF/TrFE) is clearly evident near the phase-transition temperature (T_c) in contrast to the PVDF homopolymer in which no transition temperature had been observed.^{9,10}

The polymer-containing cyanophenyl groups have been reported to have a large dipole moment (4.2 D)

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and have the possibility of providing ferroelectric behavior even in an amorphous state.¹¹ Although report of successful surface poling for a polymer containing cyanophenyl groups has been published,⁵ there are no reports for semicrystalline fluorinated polymers. It is of value to confirm the efficiency of the surface-energy poling to the P(VDF/TrFE) forwardly.

EXPERIMENTAL

Polymer and film preparation

The statistical copolymer of VDF and TrFE (VDF content of 52 mol %), supplied by Daikin Kogyo Co., Ltd. (Osaka, Japan), was used as a piezoelectric polymer.¹² From differential thermal analysis (DTA) and differential scanning calorimetry (DSC) measurement, the phase-transition temperature (T_c) and the melting point (T_m) are 60 and 163°C, respectively.

Polymer films were prepared by casting 4 wt % of *N,N*-dimethylformamide (DMF) (Wako Pure Chemical Industries, Ltd., Osaka, Japan) solution on different metal substrates and drying in vacuum at 25°C for 30 h or 35°C for 6 h. Film thickness determined by Sloan Dektak II profilometer (Sloan Technology Corp., Santa Barbara, CA) was around 60 μm . The IR spectrum of the samples clearly showed that there are no absorption peaks near 1680 cm^{-1} (carbonyl stretching band due to DMF),¹³ indicating the absence of the casting solvent.

The X-ray diffraction measurement (Rigaku, Tokyo, Japan) with $\text{CuK}\alpha$ beam ($\lambda = 1.542 \text{ \AA}$) was conducted on the cast film at room temperature. The sharp peak around $2\theta = 19^\circ$ can be attributed to (200) and (110) diffractions of the ferroelectric phase of the P(VDF/TrFE) and confirmed the present of the β -phase crystalline region according to a previous report.⁹

Indium tin oxide coated glass (ITO glass), copper plate (Cu), and vacuum-deposited Al, Ag, and Au thin films on the glass slides were used as substrates with high surface energies. To investigate the effect of contamination on the metal substrates between casting films, the other Au samples, called clean Au substrate (CAu), were directly deposited on the free-standing polymer films.

Poling condition

To confirm the efficiency of the surface poling, films cast on ITO glasses were poled by the following conditions.

- (1) Electrical corona poling by 33 kV/cm electric field at 25°C for 1 h with a needle and ITO as the anode and cathode, respectively.
- (2) Nonelectrical surface-energy poling using dry air and ITO as low- and high-energy surface,

respectively. The samples were annealed in dry air at 80°C for 1 h and temperature was decreased at the rate 1°C/min until 20°C.

- (3) In Combination poling, the sample was annealed in dry air at 80°C for 1 h, and then the temperature was decreased at the rate of 1°C/min until 20°C. Simultaneously, 33 kV/cm of electric field from the same corona poling apparatus was applied. In this case, the ITO surface was also used as the high-energy surface and the cathode.

Measurement

The surface energy of each sample on ITO substrate (called ITO sample in short) was determined by investigating the solid/liquid/vapor contact angle¹⁴ between a 2- μL drop of pure water and the film's low-energy surface (anode side). The water drops were left on the surfaces of the all samples at 20°C for 30 s before measuring by a contact angle meter (model AC-P) from Kyowa Interface Science Co., Ltd., Saitama, Japan. The contact angles for other metal substrates were measured in advance before casting film by the same process.

To evaluate the consequences of high surface energy and cooling rates, the other samples with different substrates were poled in the same way as the ITO samples but the electric field was reduced to 30 kV/cm. The temperature-decreasing rates were varied to 10, 5, 1, 0.5, 0.2, and 0.1°C/min, respectively.

The piezoelectric constants in thickness direction (d_{33}) for all samples were estimated from the variation of charge when instantaneously releasing a standard weight from the upper surface of the sample. The signal was measured by the ADVANTEST digital electrometer model TR8652 (Tokyo, Japan). Only a small and very slow decay was observed after releasing the weight. The advantage of this method was that it simply prevented uncontrollable shocking stress when the weight was immediately applied to the film.

RESULTS AND DISCUSSION

The contact angles measured on ITO samples (Table I) indicate the surface energy of the low-energy surface

TABLE I
Contact Angles for ITO Samples on P(VDF/TrFE) Surface

Poling method	Contact angle (deg)
Untreated film	75.5
Surface energy	76.0
Corona	77.6
Combination	78.1

TABLE II
Contact Angles, Surface Energies of the Substrates, and the Piezoelectricity
in Various Poling Methods

Substrate	Contact angle (deg)	Surface energy ^a (mN/m)	Piezoelectric constants d_{33} (pC/N)		
			Surface ^b	Corona	Combination ^b
ITO	76.9	—	0.93	1.21	1.32
Al	67.0	871.03	1.02	1.34	1.57
Ag	65.6	924.85	1.14	1.36	2.07
Cu	62.0	1330.16	1.39	1.78	2.43
Au	12.7	1145.38	2.36	3.10	5.28
CAu	12.3	1145.38	2.75	3.46	5.57

^a Ref. [16].

^b Temperature-decreasing rate was 1°C/min.

after poling. The lower angle means higher surface energy,¹⁵ so it is obviously seen that the contact angles after poling became higher compared to the untreated sample. Since the lower angle means higher surface energy,¹⁵ they indicate that the surface energy of the low-energy (anode) side decreased to some extent after poling by any of the methods. The corona poling increased the contact angle more so than for the surface-energy poling. However, the combination poling seems better than both those methods. It confirmed that the surface-energy poling was effective as well as electrical corona poling and the nonelectrical surface energy and combination poling is also effective for P(VDF/TrFE) polymer.

Table II shows the contact angles and surface tensions near the melting point for each metal substrate.¹⁶ It is reasonable to think that the surface tension at melting point can represent the surface energy in a solid because surface energy is relatively constant with temperature in the solid state.¹⁷ The table clearly shows the substrate of higher surface energy also had lower contact angle except the Cu plate, of which it is very difficult to control purity

and avoid contamination before experiment. The highest surface energies were afforded for the Au substrate. However, the surface of CAu, which was produced avoiding the adsorption of water and the other contaminated compounds, was higher because the surface energy of metals is significantly reduced when they adsorb water or other organic materials from the environment.¹⁸

According to Figure 1 and Table II, there are two factors which influenced the piezoelectricity induced by surface-energy poling. The factors are the substrate material and the temperature-decrease rate. The higher surface-energy substrate afforded higher piezoelectricity, especially in both Au samples. The difference between piezoelectricity of the Au and CAu films in surface poling (Fig. 1) and combination poling (Table II) implies the effect of contamination on surfaces of substrates as well as an anomaly of Cu samples.

Figure 1 shows that the samples with slower cooling rates gave higher piezoelectricity. The values changed abruptly when the films were cooled at the rates between 0.5 and 5.0°C/min but very small differences

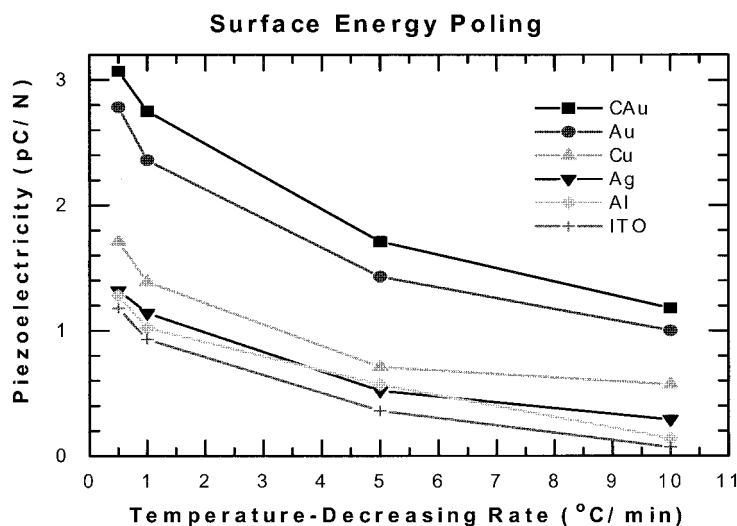


Figure 1 Piezoelectric constants d_{33} obtained from surface-energy poling with various temperature-decreasing rates.

appeared at the slower rate between 0.1 and 0.5°C/min (not shown in Fig. 1).

The piezoelectric constants d_{33} of the combination poling samples (Table II) increased significantly in all substrates compared to other poling methods. The highest piezoelectricity was obtained by the combination poling on the CAu surface with the cooling rate of 1°C/min.

Recently, the relationship between molecular motion and surface dynamics in polymer has been clarified by atomic force microscopy (AFM).^{19–21} The molecular motions in polymer samples are promoted by their thermal energy and opposed by the cohesive force between molecular segments. One can view the temperature-dependent transitions as occurring because, as temperature increases, there is more and more thermal energy in the polymer structure, which can activate motion and processes.²² In a glassy polymer, intermolecular dissociation occurs near the Curie point (T_c) [$1.2 \times T_g$].²³ Consequently, dipoles can rotate thermally to some degree around the molecular axis in the temperature range between the Curie point (T_c) and melting point (T_m).⁵

The thermally rotatable molecules have a tendency to rearrange themselves to reduce the surface energy as far as possible for energetic stabilization. The molecules at the interface have higher energy than the interior,¹⁴ so, if they can rotate thermally and are in contact with the other material, they are inclined to rearrange themselves to reduce their surface energy for more stability. Because more surface affinity brings less interfacial energy, the rotational molecules reorient themselves in the way that their parts with most affinity direct to the interface. In particular, the molecules of P(VDF/TrFE) at the lower energy surface (anode/air side) have a tendency to reorient their fluorine side toward the lower energy substrate and vice versa on another surface.

The other molecules in the bulk of the copolymer film are also activated by the thermal energy. In addition, increasing temperature leads to increased volume because of thermal expansion, providing greater volume in the bulk material that makes motion easier to achieve.²² They orient themselves according to the intermolecular forces, originating from both surfaces while the transformation of chain conformation and phase transition in the crystalline region occurs as temperature decreases. The total result is that most dipoles in the copolymer films were preferentially oriented by the thermal-energy and surface-energy difference between both substrates, and to some extent by thickness as well as the electrical poling.⁵

Time and temperature characteristics of the molecular motions are directly interrelated: the molecular segments may respond to the stimulus which is ap-

plied for only a short period of time at high temperature but would require a longer period at a lower temperature.²² In the case where cooling rate is faster than the relaxation time for molecules to rearrange themselves, the dipoles are unable to orient efficiently as we can see in the samples with fast cooling rates.

If the direction of an additional electric field is coincidentally applied to the surfaces [i.e., in the case of P(VDF/TrFE), the positive anode on lower energy surface (fluorine side) and the negative cathode on higher energy surface (hydrogen side)], piezoelectricity can be achieved more effectively because the thermal-activated dipoles in the bulk are additionally guided by the external electrical field rather than induced by intermolecular forces originated from the surfaces only.

CONCLUSION

Better piezoelectricity can be achieved by combination poling and also the limitation of thickness in the surface poling is improved by the aid of electric field. Moreover, the combination poling provides an alternative way to manufacture by using available equipment for the conventional electrical poling. The method can be easily applied by evaporating the metal electrode on one surface and then subjecting it to conventional poling above Curie temperature (T_c). By use of a proper temperature-decreasing rate, higher piezoelectricity will be accomplished.

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