

ENHANCEMENT OF PIEZOELECTRIC ACTIVITY IN P(VDF-TrFE) COPOLYMER USING TWO-STEP POLING

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Abstract

The piezoelectric property of thick P(VDF-TrFE) copolymer films could be enhanced by a two-step thermal poling method. Two weak resonance peaks were observed after the first poling, while only a single strong resonance was found after the two-step poling process. To study the mechanisms of the polarization process, X-ray diffraction (XRD) and differential scanning calorimetry (DSC) were used. The results were reported.

1. Introduction

Polyvinylidene fluoride (PVDF) and its copolymers with trifluoroethylene (TrFE) are important piezoelectric materials for transducer applications. 1-3 and 0-3 composites of P(VDF-TrFE) copolymers and piezoelectric ceramics have also attracted considerable interest [1,2]. The necessity to pole thick copolymer films arises from a piezoelectric ceramic/piezoelectric copolymer 1-3 composite project which we are currently undertaking. In that project [3], fired PZT rods were inserted into a pre-poled copolymer matrix to form a 1-3 composite and the ceramic rods were then poled at a much lower electric field. For studies of the 1-3 transducer resonance characteristics, it is essential to have the copolymer matrix as thick as possible. Thermal poling at temperatures above 100°C was chosen because we are also working on a 0-3 PZT/copolymer composite project, we have found that 0-3 composites can only be poled at high temperatures [4], so information on the high temperature poling characteristics of the copolymer obtained in the present study will help us to optimize the 0-3 composite poling conditions.

The starting materials were 0.8 mm thick extruded unpoled vinylidene fluoride-trifluoroethylene (80/20) copolymer sheets supplied by Atochem North America Inc.. The value of the thickness electromechanical coupling factor k_t was used as a figure of merit to indicate whether the copolymer was adequately poled. Copolymer of this VDF content, when poled, was reported to have the highest k_t values amongst copolymers of different compositions [5].

2. Effect of heat treatment on unpoled samples

Samples were either annealed at 120°C for 2 hours or melted and hot pressed at 180°C for 5 minutes. The endotherms for unpoled samples with different heat treatments obtained at a heating rate of 10°C/min using a DuPont 2000 Thermal Analyzer were given in Fig. 1. The Curie transition temperature for the first heating ($\uparrow T_c$) of the original sample was 124.4°C,

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which was close to but lower than the reported $\uparrow T_c$ value for this composition [6], indicating that the TrFE content may be slightly higher than 20%. Because of thermal hysteresis [7], the Curie temperature obtained from cooling ($\downarrow T_c$) of the original sample was 73°C. Annealing narrowed the transition peak and shifted it to higher temperature. In previous work [5,7], the copolymer samples were annealed above $\uparrow T_c$. However, annealing below $\uparrow T_c$ but above $\downarrow T_c$ was attempted here and effects similar to those reported for annealing above $\uparrow T_c$ was observed. The crystalline melting temperature T_m remained almost unchanged upon different heat treatments [5]. The melted and hot-pressed sample had a lower $\uparrow T_c$ compared to the original sample. This may be due to the fact that the as supplied extruded sheets have some chain orientations and melting has wiped out the orientation history of the sample.

XRD studies using a Philips X-ray diffractometer showed that the X-ray diffraction peaks of the annealed sample were essentially identical to those of the original sample, but there is a slight increase (about 0.5 degree) in the diffraction angle of the major peak (at $2\theta = 20$ deg, which is the $(200)\beta + (110)\beta$ peak) [8]. The original copolymer with 80% VDF had a diffractogram (Fig. 2(a)) similar to that reported for this composition [8]. After hot-pressing (Fig. 2(b)), the intensity of the $(200)\beta + (110)\beta$ peak decreased while the intensities of the $(001)\beta$ (at $2\theta = 35.06$ deg.) and the $(201)\beta$ (at $2\theta = 41$ deg.) increased. Further annealing of the hot-pressed sample at 120°C for another 2 hours did not change its diffractogram.

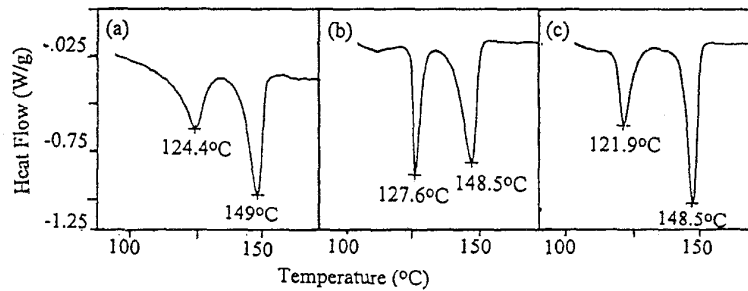


Fig. 1 DSC heating endotherms of unpoled P(VDF-TrFE) (80/20) samples (a) As supplied. (b) annealed at 120°C for two hours, (c) melted and hot-pressed at 180°C for 5 min..

Sample	k_t	$d_{33}(\text{pC/N}^{-1})$	Density(kgm^{-3})	$T_c(^{\circ}\text{C})$	$T_m(^{\circ}\text{C})$
As supplied	-----	-----	1864	124.4	149.0
Annealed	-----	-----	1872	127.6	148.5
Hot pressed	-----	-----	1884	121.9	148.5
(i)	0.20	30.5	1846	132.9	150.3
(ii)	0.25	32.1	1865	130.8	149.6
(iii)	0.27	36.2	1861	132	148.9
(iv)	0.21	28.5	1854	127.2	149.6
(v)	0.29	35.3	1878	128	149.6

Table 1. Properties of Copolymer Samples

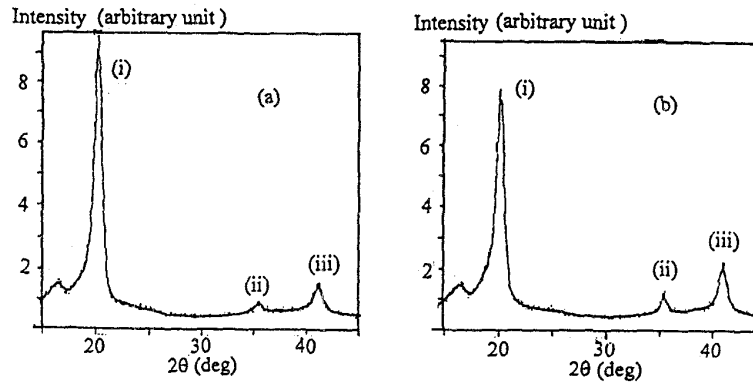


Fig.2 X-ray diffractograms of the unpoled copolymer samples
(a) As supplied, (b) melted and hot-pressed, (i) $(200)\beta+(110)\beta$, (ii) $(001)\beta$, (iii) $(201)\beta$.

3. Poling and resonance characteristics of samples after poling

Thermal poling was carried out in a temperature controlled oil bath. A two-side metalized (with silver paint) sample was exposed to a high poling field at an elevated temperature for a period of one to four hours. The sample was then cooled down to room temperature with the field applied to stabilize the dipole alignment. Several types of film samples were studied. Samples were first annealed at 120°C for 2 hours and then (i) poled at 105°C for two hours, (ii) poled at 105°C for four hours, (iii) poled using a two-step poling method: the sample was poled at 105°C for two hours and then cooled down to room temperature with the electric field kept on; the sample was then repoled at 105°C for another two hours. Samples were also melted and hot-pressed at 180°C for 5 minutes and then (iv) poled at 115°C for one hour (v) poled at 115°C using the two-step poling method.

The electric field applied to each sample was close to 30 MV/m. This is very close to its breakdown electric field and was higher than the reported high-temperature coercive field for the copolymer.[9] The annealed film cannot withstand such a high electric field if it was heated up to higher than 105°C , while the melted and hot-pressed film can be heated to higher temperature and can take a higher poling field without breakdown. This showed that the melt and hot-pressed process can improve the dielectric strength of the copolymer films as reported previously [6]. The poling field was 26 MV/m for the annealed film at 105°C and 30 MV/m for the hot-pressed film at 115°C .

Typical impedance vs frequency plots for samples (i) and (v) were shown in Fig. 3, and the values of k_t and d_{33} were given in Table 1. Values of k_t were evaluated using the method proposed by Sherrit et al [10] taking into account the high loss in the copolymer and using the first resonance to calculate k_t . d_{33} were measured using a Pennbaker model 8000 piezo d_{33} tester from American Piezo-Ceramics, Inc.. The not so well-poled samples, (i) and (iv), with lower k_t and d_{33} values, have two resonance peaks.(Fig. 3(a)) A major peak appeared at about 1.3 MHz while a secondary peak appeared at 2.6 MHz. Judging from the frequencies, the

secondary peak is the second harmonic of the first one. However, for thickness mode resonance, the boundary condition excludes the presence of even number harmonics and the second harmonic is usually missing. Poling the sample for longer time increases its piezoelectric activities. For example, sample (ii) has a weaker secondary peak than samples (i) and using two step poling completely eliminate the secondary peak (sample (iii) & (v)). Comparing the two samples poled using two step poling, the hot pressed sample (v) has the highest k_p .

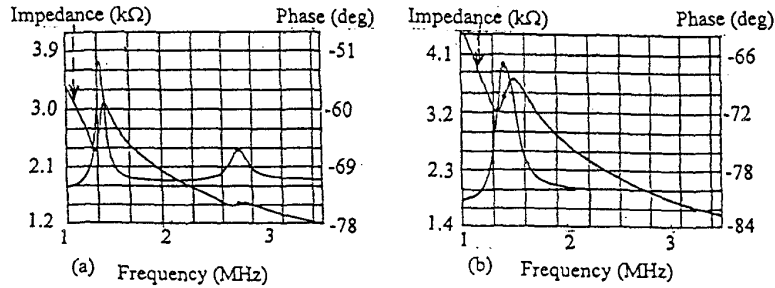


Fig.3 Impedance and phase vs frequency plot (a) annealed and poled sample (i)
(b) hot-pressed sample (v) after the two-step poling process.

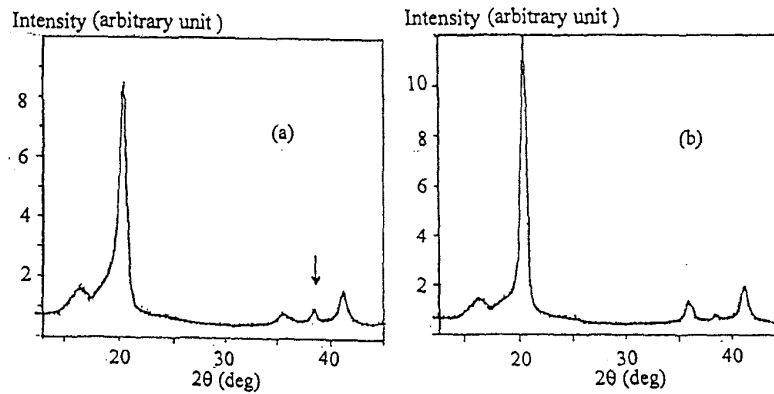


Fig. 4 X-ray diffractograms of the poled copolymer samples
(a) annealed and poled for one hour, (b) hot-pressed sample after the two-step poling process

X-ray diffractograms of samples (i) to (iv) were quite similar. Once the sample was poled at high temperature, an additional peak appeared at $2\theta = 38.55$ deg. (compare Fig.2(a) and 4(a)). However, for the most well-poled sample (v) with a single resonance peak, this extra X-ray peak is almost zero (Fig. 4(b)).

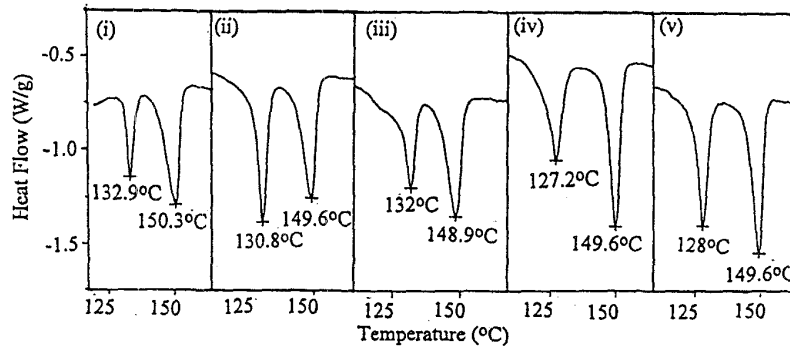


Fig.5 DSC heating endotherms of poled P(VDF-TrFE) (80/20) samples (i) annealed and poled for two hours (ii) annealed and poled for four hours (iii) annealed and poled in two steps (iv) hot-pressed and poled for one hour (v) hot-pressed sample after the two-step poling process.

DSC thermograms of samples (i) to (v) (Fig. 5) showed the following characteristics: for the annealed samples, poling shifted τT_c to higher temperature (Table 1) indicating the formation of a more ordered phase. The effect of poling was more pronounced in the hot-pressed samples. The transition peak not only shifted to higher temperature but also became sharper. The densities of the samples were shown in Table 1. Both types of heat treatments caused an increase in density, indicating an increase in the amount and perfection of the polar β -phase crystallites. During poling, the samples tended to swell and this accounted for the decrease in density. Amongst the five poled samples, the most well poled sample (v) has the highest density.

4. Conclusion and discussions

Thick films of P(VDF-TrFE) (80/20) copolymer with different heat treatments were poled at high temperature. To obtain high electromechanical coupling constants it is recommended to melt and hot-press the copolymer and then pole the film using a two-step poling procedure.

From DSC and XRD studies, the following were observed:

- (a) Analogous to annealing above τT_c , annealing the copolymer at a temperature below but close to τT_c led to a higher τT_c and a sharpening of the transition peak.
- (b) XRD studies showed that annealing caused little or no effect on the peaks associated with the polar β phase. However, hot pressing above melting temperature resulted in a significant

change in the magnitude of the diffraction peaks. Little change of the angle of diffraction (2θ) of the peaks was found after either heat treatment.

(c) Poling at high temperature produced a new peak in the X-ray diffractogram, which was located between the original $(201)\beta$ and $(001)\beta$ peaks. This peak was quite large for samples with low k_1 , and was accompanied by the appearance of a second harmonic resonance peak in the impedance vs frequency plot. Using a two-step poling technique, the second harmonic resonance peak as well as the XRD peak located at $2\theta \approx 38.55$ deg. were removed and a large k_1 was obtained. These experimental results cannot be explained as yet and further investigation is required.

In conclusion, we have developed an effective way to pole thick copolymer films using a high temperature, two-step poling method. The poled copolymer films with high k_1 are useful for fabricating 1-3 composites. We also intended to apply this two-step method to pole the 0-3 composites we have fabricated and the results will be reported in the near future.

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