Spontaneous Depolarization Current in Different Mole Ratio VDF/TrFE Ferroelectric Copolymers

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Abstract

Vinylidene fluoride (VDF)/trifluoroethylene (TrFE) ferroelectric copolymer samples with different mole ratio of 56/44, 70/30 and 77/23 were fabricated by casting from methyl ethyl ketone and followed by slowly cooling from melting state. Trapped delocalized charges during circulating thermo-stimulating have been observed as spontaneous depolarization current (SDC). For VDF(56)/TrFE(44) copolymer, SDC spectra show a positive current peak at 72 °C during heating and a negative peak at 58 °C during cooling. For VDF(70)/TrFE(30) copolymer, SDC spectra display a positive current peak at 114 °C during heating and present a negative peak at 58 °C and a positive one at 52 °C during cooling, respectively. As for VDF(77)/TrFE(23) sample, SDC show a negative peak at 71 °C and a positive one at 63 °C during cooling. By comparison with DSC measurements, the peaks are ascribed to the conformation change during ferro-to-paraelectric or para-to-ferroelectric phase transition at heating or cooling processes. This is also an evidence of two coexistent ferroelectric phases in the VDF/TrFE copolymers. Poling above Tc, the electric field can cause the sample an observable change.

1. Introduction

Thermally stimulated depolarization current (TSDC) was used to study ferroelectric materials for many years. Although the TSDC of VDF/TrFE copolymer has been studied by some authors [1-4], most of them poled the sample using a rather high electric field. Heating from room temperature to melting point, VDF/TrFE copolymer suffers an important phase transition. When the sample was poled using a lower electric field (e.g. 20 kV/cm) at different temperature from 50 °C to 130 °C with an increment of 10 °C, some new phenomena can be seen during TSDC measurements. Trapped delocalized charges were formed during thermo-forming or extrusion, which can be observed on reheating in a simple experiment of spontaneous depolarization current (SDC) [5]. In this paper, the decay current against cooling temperature was recorded for the copolymer sample after TSDC measurement. In general, the current will decay exponentially. However, if sample was poled above Tc, the decay curve will present a peak located at cooling Tc. And if the sample was reheated again without poling process, a small peak will appears at the heating Tc. This phenomenon implies that even poling at a rather low electric field (much less than the coercive field, ~500kV/cm), the sample has some change under the poling condition. This kind of the change may affect the use of VDF/TrFE copolymer as a ferroelectric material.

2. Experimental

Three kinds of VDF/TrFE copolymer pellets with different VDF contents (56, 70, 77 mole %) were supplied by Piezotech, France. The copolymer films (~60μm) were prepared by casting from methyl ethyl ketone solution. After melt at 170 °C, the film was cooled to room temperature slowly (the cooling rate<1 °C/min) and the slow-cooled sample was prepared. Aluminum electrodes (Φ10 mm) on two sides of the sample were made by evaporating in vacuum of 6.6×10^{-3} Pa. The TSDC measurements were carried out on a modified thermo-electric analyzer [6]. The current sensitivity of the apparatus is 10^{-13}A. Heating rate used in TSDC measurements was 4 °C /min. Poling field (Ep) was 20 kV/cm. Time of poling was 20 min. TSDC data were recorded from room temperature to 135 °C in order to avoid the melting of the copolymer. After TSDC measurements, sample cell was cooled by a fan and the SDC was

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recorded. The Curie points of the samples were measured by Perkin Elmer DSC 7 in a heating rate of 10 °C/min.

3. Results and Discussion

The differential scanning calorimetry (DSC) spectra of VDF(56)/TrFE(44) copolymer show a sharp peak of heating Tc at 63 °C and cooling Tc at 52 °C. The heating Curie transition of VDF(70)/TrFE(30) copolymer is rather broad comparing with VDF(56)/TrFE(44). Besides the Curie transition at 108 °C, a shoulder appears at the lower side of the peak at about 100 °C. The cooling process of the sample shows two peaks at 59, 52 °C and a shoulder at 48 °C, respectively. The result suggests that the multiple phase transitions exist in VDF(70)/TrFE(30) copolymer. For 77/23 sample, the heating and cooling Tc are 124 and 70 °C, respectively. Although its heating transition peak is also broad, the shoulder is not as clear as 70/30 sample.

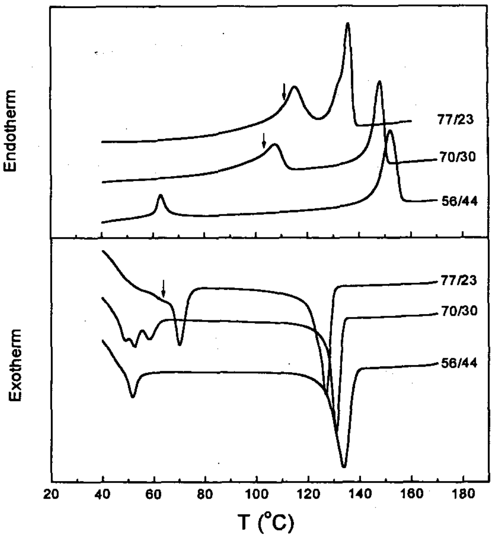

Figure 1. DSC spectra of VDF/TrFE (56/44, 70/30 and 77/23) copolymers.

From TSDC measurements, we have proved that the detrapped current peak represented the Curie transition of VDF/TrFE copolymer. Curve 1 in Fig. 2 is the TSDC spectrum of 56/44 sample poling at 130 °C. The peak located in 72 °C is the heating Tc. Curve 2 is the SDC of curve 1. A small peak appears at 58 °C. Curve 3 is obtained by reheating the sample after cooling without poling process. The peak position in curve 3 is the same as that in curve 1 but with an opposite current value. From 50 °C to 130 °C we poled the samples with an increment of 10 °C, the cooling results are shown in Fig. 3. If sample was poled at a temperature higher than Tc, a small current peak can be recorded in the cooling process after its TSDC measurement and its value increases with the poling temperature increases. In general, the amplitude of cooling peak is rather low.

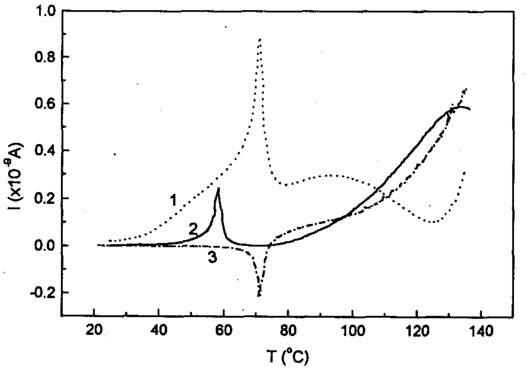

Figure 2. TSDC and SDC spectra for VDF(56)/TrFE(44) copolymer. 1. TSDC curve after poling at 130 °C; 2. cooling current of the sample; 3. reheating after cooling

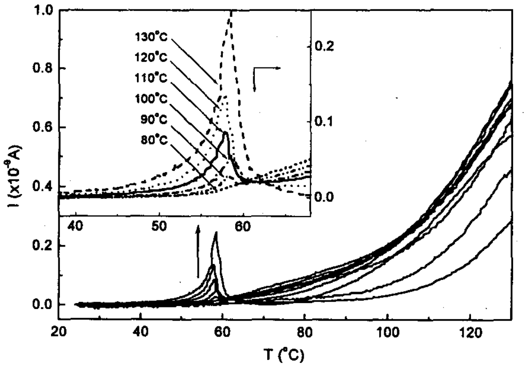

Figure 3. SDC spectra of VDF(56)/TrFE(44) copolymer during cooling after TSDC measurements with different poling temperature from 80-130 °C.

For 70/30 sample, if poling above Tc, its cooling current will present two peaks in opposite directions. In Fig. 4, curve 1 is the TSDC spectrum of the sample poled at 130 °C, showing two peaks located at 99 and 111 °C. Curve 2 is the cooling current with a negative peak at 58 °C and a positive peak at 52 °C. Curve 3 is the reheating result with a peak at 114 °C. The cooling current of the sample poled at different temperature is shown in Fig. 5. These peaks are also increased with the increase of poling temperature. Some authors believe that two ferroelectric phases coexist in 70/30 sample [7]. Our TSDC result has confirmed the conclusion. It can be assumed that the negative peak at 58 °C and positive peak at 52 °C represent two transitions similar to the results from DSC measurements.

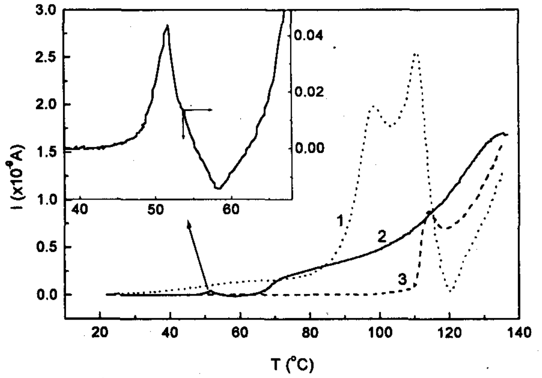

Figure 4. TSDC and SDC spectra of VDF(70)/TrFE(30) copolymer. 1. TSDC curve after poling at 130 °C; 2. cooling current of the sample; 3. reheating after cooling.

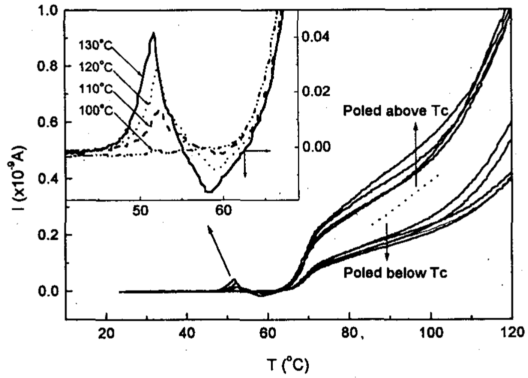

Figure 5. SDC spectra of VDF(70)/TrFE(30) copolymer during cooling after TSDC measurements with different poling temperature from 100 to 130 °C.

The TSDC spectra of 77/23 sample are shown in Fig. 6. Compare with 70/30 sample, 77/23 has only one broad peak when poling at 130 °C, similar to DSC results. It seems that the two peaks are overlapped. The two ferroelectric phases coexiting in 77/23 sample are not as clear as that in 70/30 sample. Because of the lower melting point of 77/23 copolymer (~145 °C), much data poling above Tc can not be obtained. Only one cooling curve with two peaks was recorded for the sample poled at 130 °C (Fig. 7). Though this peak is small, it still belongs to the behavior of a negative (~75 °C) and a positive peak (~63 °C). It also conforms the coexistence of the two ferroelectric phases in 77/23 sample.

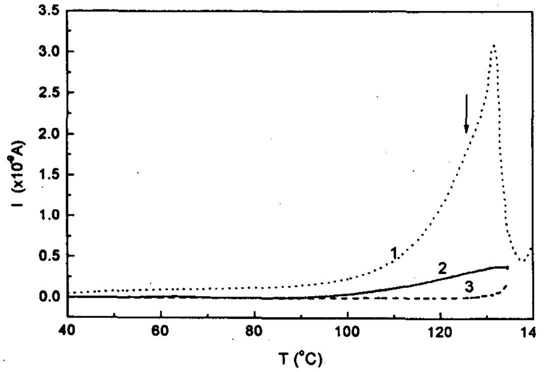

Figure 6. TSDC and SDC spectra of VDF(77)/TrFE(23) Copolymer. 1. TSDC curve after poling at 130 °C; 2. cooling current of the sample; 3. reheating after cooling.

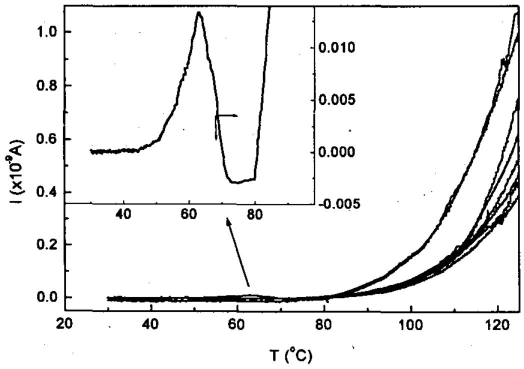

Figure 7. SDC spectra of VDF(77)/TrFE(23) copolymer during cooling after TSDC measurements with poling temperature of 130 °C.

Comparing these figures, we can find out that the cooling curves are separated into two groups. As shown in Fig.5, if the sample was poled at a temperature above Tc, the cooling current is high; if the sample was poled below Tc, the cooling current is low. Integrating positive peaks of Fig. 3, Fig. 5 and Fig. 7, the obtained relationship between the charge density against polarization temperature is shown in Fig. 8. Poling above Tc, the retrapped charges increase rapidly with poling temperature. We suppose that poling can cause the sample a little difference, the restore of non-equilibrium ferroelectric phase is the main reason of the cooling current peaks. Obviously, the poling field affects the samples remarkably when poling temperature higher than Tc.

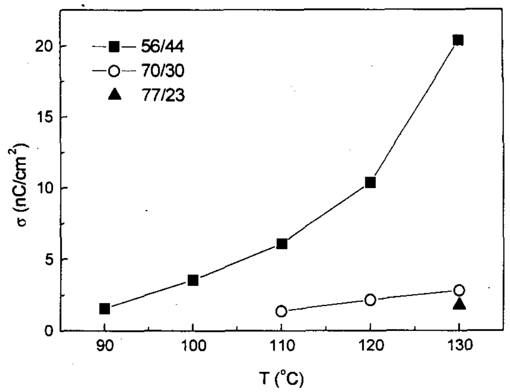

Figure 8. Plot of charge density of cooling current peaks against poling temperature.

It is known that SDC exists in many material even nonferroelectrics. Current peaks can be obtained in samples without prior exposing to any electric field. Ibar [5] believes that SDC are trapped delocalized charges formed during thermo-forming or extrusion. He reported a negative peak in biaxially stretched PET film and considered it as revealing a non-uniform draw ratio in the plane of biaxial stretch. Several explanations have also been given for SDC based on the nature of material and the method of sample preparation. For example, molecular orientation produced during film fabrication either as a direct consequence of extrusion, drawing or molding processes or, for solvent-cast materials as a result of charge gradient created during the unavoidably asymmetric evaporation process [8]; production of carriers during thermally induced chemical degradation taking place asymmetrically in regions near opposite surface of films [9], thermally generated electro-motive forces arising from a thermal gradient across the sample [10]. In our case, poling field may cause the sample a little difference as original. The charges trapped during poling can not be released completely in TSDC measurement. While cooling, sample suffers a para-to-ferroelectric phase transition. The restore of non-equilibrium ferroelectric phase at the temperature of phase transifion causes the current peaks. This part of charges can be released as an opposite peak if the sample is reheated. Because the delocalized charges arise from the electric field, perhaps the measured current can be called as field-induced spontaneous depolarization current.

Acknowledgments

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