Thermally Stimulated Depolarization Current of BaTiO₃/P[VDF(70)-TrFE(30)] 0-3 Ferroelectric Composites

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Abstract

0-3 ferroelectric composites of barium titanate (BT) and vinylidene fluoride-trifluoroethylene copolymer P[VDF(70)-TrFE(30)] with different volume fraction of BT were prepared by solution blending followed by compression-molding. The thermally stimulated depolarization current (TSDC) of the composites has been measured. Three detrapping charge and two phase transition peaks (one for copolymer and another for ceramic) are observed in TSDC spectra above room temperature. For the composite sample in which only ceramic phase is polarized, the detrapping charge peaks are disappeared, which indicates that the TSDC originates from the copolymer phase. According to the analysis of phase transition, the structural origin of TSDC peaks is proposed. The detrapping charge density increases as increasing BT content, which shows that ceramic inclusions enhance the ability of charge storage in the composites.

1. Introduction

Ferroelectric ceramic (PZT, PLZT, PT, PTCa)/polyvinylidene fluoride-trifluoroethylene [P(VDF-TrFE)] 0-3 composites have been designed to combine the superior electroactive properties of ceramic particles and high compliance, high electrical breakdown strength of copolymer matrix in recent years. The composites have been received considerable attention because of their good flexibility and formability, selective piezo- and pyroelectricity as well as their potential uses as transducer and sensor in smart systems [1-3]. In addition, space charges in insulating materials are well known to distort the local electric field and affect high-field conduction and other electrical properties. The importance of trapped charge carriers in PVDF and its derivative copolymer P(VDF-TrFE) has been discussed, and there is evidence to suggest that space charge may play an important role in the piezoelectric and pyroelectric behavior[4-7].

In this paper, we focus on the detrapping of trapped space charges in BaTiO₃(BT)/P[VDF(70)-TrFE(30)] thick films by the thermally stimulated depolarization current (TSDC) method. As a result, three prominent detrapping and two phase transition current peaks were observed in TSDC spectra above room temperature. Based on the analysis of phase transition of the copolymer and the ceramic, the structural origin for the peaks is proposed.

2. Experimental

In order to obtain the composites with different ceramic volume fraction ϕ, the copolymer P[VDF(70)/TrFE(30)] (the number is mole %) pellets produced by Piezotech, France were first dissolved in methyl ethyl ketone and a suitable amount of BT powder was blended into the solution. After evaporating the solvent, the mixture was crushed into small pieces and pressed into a cylinder in a stainless steel mould at 200 °C and then naturally cooled to ambient temperature. Cutting the cylinder using a high precision diamond saw, the disk composite samples (400 μm in thickness and 15 mm in diameter) were prepared.

Silver electrodes (130 mm² in area) were made by coating a quick drying silver paint onto both surfaces of the composite sample. TSDC measurements were carried out on the modified apparatus of thermo-electrical analyzer [8] from room temperature to 140 °C in order to avoid the melt of copolymer matrix

at a heating rate of 4 °C/min. Before TSDC measurements , the samples with ϕ from 0 to 0.4 were polarized for 20 min with an electric field intensity of 20 kV/cm at various temperatures (60-130 °C).

3. Results and Discussion

Fig. 1 shows the TSDC spectra for composite samples (ϕ = 0, 0.2 and 0.4). The sample had been previously polarized by an electric field (E) of 20 kV/cm at 90 °C. For the composites, four peaks are observed. These peaks have been named as ρ_1, ρ_2, ρ_3 and T_{c2}, respectively. As for the copolymer (ϕ = 0), only peaks ρ_1, ρ_2 and ρ_3 can be seen. Four peaks are also observed for the samples with ϕ = 0.1 and 0.3. Both the peak current and charges (the area under the TSDC curve) increase as increasing the applied field. This indicates that the increase of E can only increase the peak current and charges trapped in the composites.
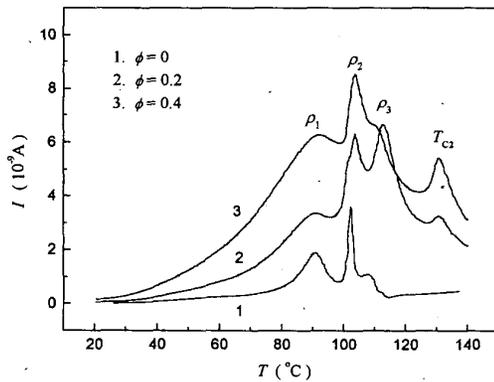
Figure 1. TSDC spectra of composites with different ϕ at a fixed T_p of 90 °C.

For probing into the dominant mechanism of polarization for the composite, samples are polarized at different temperatures. The TSDC spectra of the composite polarized at various temperatures (from 60 to 120 °C) are shown in Fig. 2. In general, ρ_1-, ρ_2-, ρ_3- and T_{c2}-peaks can be observed as T_p rises to 60 °C from room temperature, but the peak current is low ($\sim 1 \times 10^{-9}$A) when T_p is less than 60 °C. As increasing in T_p, ρ_1- and ρ_2-peaks shift towards higher temperature, the peak magnitude increases gradually. ρ_3-peak position (located at about 110 °C) and its relative magnitude almost do not change until T_p increases to 100 °C. The increase of T_p from 60 °C to 100 °C leads to the shift of ρ_1-peak from 80 °C to 100 °C. When T_p increases to over 105 °C, ρ_1-peak shifted into ρ_3-peak and doesn't move any more even if polarizing at higher temperature from 110 °C to 130 °C. With the increase of T_p, ρ_2-peak position also increases from 96 °C (T_p = 60 °C) to 119 °C (T_p = 105 °C), then as T_p increases from 105 °C to 108 °C, ρ_2-peak shifts to higher temperature continuously, while its magnitude decreases gradually and at last, disappears when T_p higher than 108 °C. It is noted that when T_p is over 100 °C, the magnitude of ρ_3-peak increases sharply, until T_p arrives at 110 °C. When T_p varies from 110 °C to 130 °C, the position and the magnitude of ρ_3-peak are unchanged. In addition, T_{c2}-peak position located at 132 °C can not be changed when T_p varies between 60 °C and 130 °C, but its magnitude increases as the increase of T_p, which shows that T_{c2}-peak is originated from the Curie point of BT.
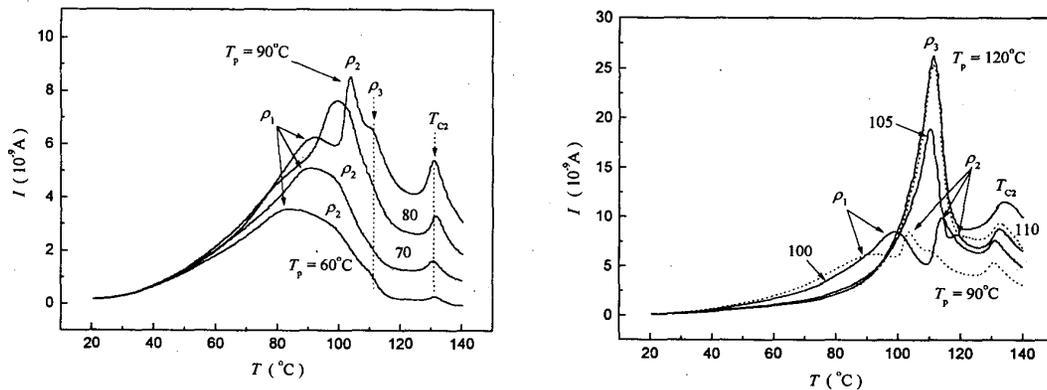
Figure 2. TSDC spectra of the composite with ϕ = 0.4 for different T_p.

In order to know the origin of the current peaks, different methods for polarizing composite samples are used [2]. The results are shown in Fig. 3. Curve 1 is TSDC spectrum of the composite with $\phi = 0.4$, which can be considered as two phases were polarized (before TSDC measurements, the sample was subjected to an electric field of 20 kV/cm at $T_p = 120$ °C for 20 min and subsequently cooled to ambient temperature with the electric field kept on). Curve 2 is the spectrum of the composite in which only ceramic phase was polarized (before TSDC measurements, the sample was charged at same condition as curve 1, but the electric field was switched off when the sample was cooed to ambient temperature). Curve 3 is obtained by measuring the sample being cooled to room temperature slowly after measuring curve 1. It can be considered as that no any phase was polarized in the composite. Comparing curve 1 and 2, it can be found that the TSDC is mainly contributed by copolymer phase, the ceramic phase can only give a less current. Curves 2 and 3 show two small peak (named as peaks T_{c1} and T_{c2}) that located at about 111 °C and 132 °C, respectively. After finishing measurement of curve 3, cooling the sample to the room temperature, and then measuring the sample repeatedly, the same shape curve can still be observed, only the current magnitude decreases a little, the peaks T_{c1} and T_{c2} do not vanish completely. Combined the DSC analysis, it can be concluded that small peak T_{c1} located at 111 °C is related to the phase transition of the copolymer matrix and peak T_{c2} located at 132 °C is ascribed to the Curie point of BT inclusions.
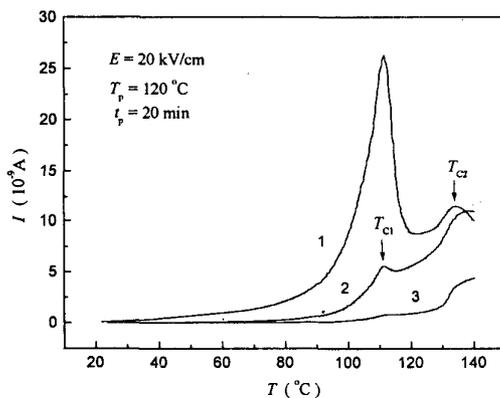
Figure 3. TSDC spectra of the composite with $\phi = 0.4$ for different polarizing methods.
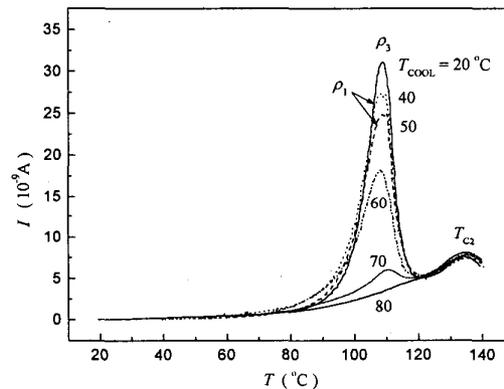
Figure 4. TSDC spectra of the composite with $\phi = 0.2$ for different T_{cool}.

Based on X-ray diffraction, infrared and Raman spectra as well as DSC data, the existence of two distinct ferroelectric phases, less ordered (Ferro I) and more ordered (Ferro II), has been suggested for P(VDF-TrFE) copolymers [5-7]. Changing the polarizing procedure, various cooling temperatures that the sample was cooled to (T_{cool}) are chosen after polarization for 20 min. The result for the composite with $\phi = 0.2$ is shown in Fig. 4. It can be seen that ρ_1-peak vanishes when T_{cool} is over 50 °C, while ρ_3-peak disappears when T_{cool} is over 70 °C. Same result for ρ_1-peak is also observed for the cases of T_p increasing from 70 to 130 °C. In all TSDC spectra, ρ_2-peak always appears except T_p is over 110 °C whatever T_{cool} equals 70, 80, 90 or 100 °C.

Practically, when the copolymer is heated up to a certain T_p (>105 °C), the paraelectric phase will be produced, then when the sample is cooled after polarization, the para-to-Ferro II transition will be taken place at about 70 °C. As the temperature further decreases, the Ferro II-to-Ferro I phase transition will also be in progress. As a result, Ferro II and Ferro I phase are coexisted in the sample because the Ferro II can not be transformed completely into the Ferro I phase. It is known that every TSDC peak is corresponding to a certain structural default (trap level) which can trap the charges injected from the electrode during polarization. Due to ρ_3-peak appears rapidly when T_p >105 °C and T_{cool} < 70 °C, according to the process that sample was first heated to T_p for polarization and then cooled to T_{cool} for

TSDC measurement, ρ_3-peak can be attributed to the ferro- to paraelectric phase transition. Moreover, ρ_1-peak can be ascribed to the charge detrapping from the Ferro I phase arisen from the cooling during polarization. As for ρ_2-peak, because it always appears until $T_p' > 108$ °C (Ferro-to-paraelectric transition can be taken place), it can be considered as the contribution of the Ferro II phase which is formed during cooling and is more stable (the original sample is cooled slowly from high temperature of 135 °C). According to the above discussions, further deduction indicates that the Ferro II-to-Ferro I phase transition is taken place at about 50 °C or more.

In general, the released charge density follows from the integrating of TSDC spectra [9].

$$Q = \int j(t)\, dt = \frac{1}{\beta} \int J(T)\, dT \qquad (1)$$

Integrating experimental TSDC curves of the composites, the obtained relationships between the detrapping density of trapped charges and polarization temperature T_p are shown in Fig. 5. In order to compare the contribution of the ceramic inclusions, the data for the composite lead titanate (PT)/P[VDF(70)-TrFE(30)] is also shown in the figure. The detrapping charge density σ increases as T_p rises from 60 °C to about 105°C, expressing the amount of trapped charge carrier increases. On the other hand, the detrapping charge density σ increases with the increase of BT content. For all range of polarization temperature, ceramic inclusions enhanced the ability of charge storage in the composite. But it can be seen that the ability for PT is much less than that of BT. Further deduction is that a suitable high temperature is of benefit to the injection of charges. When T_p is over 110 °C, σ decreases with rising T_p, which can be considered as the trapping ability goes to weakness because of the strong temperature vibration at high temperature.
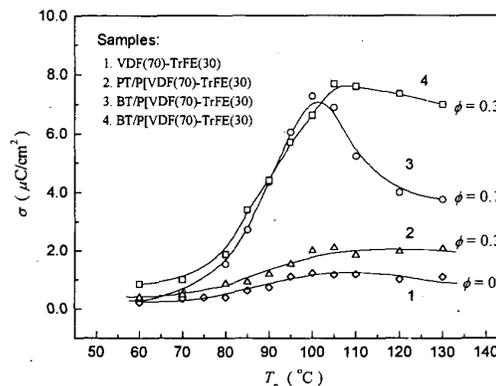
Figure 5. Plots the detrapping charge density as functions of polarization temperature.

Acknowledgments

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