Detrapping Behavior of Trapped Space Charges in Ferroelectric Copolymers of Vinylidene Fluoride with Trifluoroethylene

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Abstract

Three kinds of slowly-cooled ferroelectric VDF/TrFE copolymer samples with different VDF contents (56, 70, 77 mole %) were prepared by casting from methyl ethyl ketone solution and followed by cooling slowly from melting state to room temperature. The thermally stimulated depolarization current (TSDC) of the copolymer has been measured at various polarization temperatures (60-130°C). In the TSDC spectra, three peaks of detrapping charges for VDF(70)/TrFE(30) and VDF(77)/TrFE(23), two peaks for VDF(56)/TrFE(44) are observed. According to the peaks appeared at different cooling temperature during polarization and the analysis of phase transition, the structural origin of the TSDC peaks is proposed. The detrapping density of trapped charges shows that the ability of charge storage for VDF(70)/TrFE(30) is higher than that for other two copolymers.

1. Introduction

Copolymers of vinylidene fluoride and trifluoroethylene (VDF/TrFE) have been studied about two decades for their interesting ferroelectric properties and potential uses of piezoelectric and pyroelectric activities. Space charges in insulating materials are well known to distort the local electric field and affect high-field conduction and other electric properties. The importance of trapped space charges in PVDF and its derivative copolymer VDF/TrFE has been discussed, and there is evidence to suggest that space charges may play an important role in the piezoelectric and pyroelectric behavior [1-4]. As a very sensitive method, the thermally stimulated depolarization current (TSDC) has been widely used to investigate the relaxation, transition and motion of space charges in polymers. However, though detrapping of space charges for VDF/TrFE copolymer has been measured by several authors using TSDC, mainly the relaxation properties are involved [3-8]. This paper is intended to investigate the detrapping behavior of trapped charges in VDF/TrFE copolymers with different mole ratio using TSDC method. In TSDC spectra, three peaks of detrapping charges for VDF(70)/TrFE(30) and VDF(77)/TrFE(23), and two peaks for VDF(56)/TrFE(44) are observed above room temperature. The structural origin for these peaks is proposed according to the analysis of phase transition. In addition, the ability of charge storage for three copolymers is also discussed.

2. Experimental

Three kinds of VDF/TrFE copolymer pellets with VDF content of 56, 70, 77 (mole %) were supplied by Piezotech, France. The pellets were first dissolved in methyl ethyl ketone. After evaporating the solvent very slowly, as-cast film of the copolymer was fabricated. The film was heated to 170 °C and then cooled to room temperature slowly (cooling rate<1 °C/min), the slow-cooled sample was prepared (60 μm in thickness and 12 mm in diameter).

Aluminum electrodes (80 mm² in area) were vacuum deposited (6.6×10³ Pa) onto both surfaces of the sample. Before TSDC measurements, the sample was polarized for 20 min with an electric field of 20 kV/cm (strictly speaking, it should be so-called polarization because the applied field would not be expected to pole the sample to a significant extent since the coercive field is large than 500 kV/cm). TSDC was recorded on a modified thermo-electrical analyzer (current sensitivity is 10⁻¹³A) [9]
using a heating rate of 4 °C/min from room temperature to 135°C in order to avoid the melt of the copolymer.

3. Results and Discussion

The ferro- to paraelectric transition of VDF/TrFE copolymer is a first order transition because of its thermal hysteresis property. Heating and cooling processes present different phase transition temperature $T_c$. Heating $T_h$ and cooling $T_c$ given by differential scanning calorimetry (DSC) measurements (heating rate 10 °C/min) for VDF/TrFE copolymers are shown in Tab. 1.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Heating $T_h$ (°C)</th>
<th>Cooling $T_c$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VDF(56)/TrFE(44)</td>
<td>63</td>
<td>52</td>
</tr>
<tr>
<td>VDF(70)/TrFE(30)</td>
<td>108</td>
<td>59</td>
</tr>
<tr>
<td>VDF(77)/TrFE(23)</td>
<td>124</td>
<td>70</td>
</tr>
</tbody>
</table>

Fig. 1 shows some typical TSDC spectra of the copolymers with different mole ratio of VDF. Two peaks, peaks 1 and 2 or peaks 2 and 3, are observed for VDF(56)/TrFE(44) copolymer [Fig.1(a)] in each curve. When polarization temperature $T_p$ is 50 °C, peak 1 and peak 2 located at 62 °C and 70 °C are observed. As $T_p$ increases to 60 °C (near heating $T_h$), the peak 1 disappears, only peak 2 can be seen in the spectra. As $T_p$ increases to 80 °C or above, another wide peak, peak 3 located between 90 and 95 °C appears. For VDF(70)/TrFE(30) sample [Fig.1(b)], three well-separated peaks 1, 2 and 3 located at 92 °C, 102 °C and 112 °C are observed when $T_p$ equals 90 °C, but only two peaks 2 and 3 located at 97 °C and 112 °C can be seen when $T_p$ increases to 120 °C. As $T_p$ increases to 80 °C or above, another wide peak, peak 3 located between 90 and 95 °C appears. For VDF(77)/TrFE(23) [Fig.1(c)], three peaks located at 112 °C, 126 °C and 132 °C, respectively can also be observed when $T_p$ equals 110 °C. As $T_p$ increases to heating $T_h$ or above, peaks 1 and 2 move to peak 3, forming a wide peak located at 132 °C. Similar to other polymer samples, the current observed from these peaks increases as the increase of polarization field, and peak position is shifted towards higher temperature as increasing in heating rate.

Comparing with 56/44 copolymer, the TSDC spectra for 70/30 and 77/23 copolymer at different $T_p$ are more complex. As an example, TSDC spectra for 70/30 sample polarized at various temperatures (from 50 to 130 °C) are shown in Fig. 2. In general, peaks 1, 2 and 3 can be observed when $T_p$ rises from 50 °C up to 100 °C. As increasing in $T_p$, peak 1 shifts towards higher temperature, and the peak magnitude increases gradually [Fig.2(a)]. However, peak 2 located at about 97 °C almost do not change for $T_p = 50$–$70$ °C and 110–130 °C. When $T_p$ increases from 80 to 100 °C, peak 2 shows an
obvious shift from 95 °C to 102 °C. Following the moving of peak 2, the peak current also has a sharp increase. As for peak 3, Fig. 2 shows that it always appears in the position of 112 °C even though \( T_p \) varies between 50 °C and 130 °C. It is noted that when \( T_p \) is over 100 °C, the magnitude of peak 3 decreases gradually with the increase of \( T_p \). Similar behavior of peak shift when \( T_p \) increases from 60 °C to 130 °C are also observed for 77/23 copolymer.

The ferroelectric crystallites in copolymer transform into a paraelectric phase when the copolymer is heated to above 108 °C for 70/30 sample. Upon cooling, the paraelectric to ferroelectric phase transition occurs in the range of 50~70 °C because of hysteresis effect. Therefore, if the applied field acting on the sample is turned on at above heating \( T_o \) and then is not turned off during cooling until a temperature \( T_0 \) is reached, it is expected that the TSDC spectrum would depend on \( T_0 \). TSDC curves (\( T_p = 120 \) °C) measured for different \( T_0 \) are shown in Fig. 3. It can be seen that if \( T_0 \) is over 90 °C, no current peak can be found in the spectra. With the decrease of \( T_0 \), peak 3 appears clearly and the magnitude increases greatly. When \( T_0 \) decreases to 50 °C, peak 2 appears in the spectrum. With \( T_0 \) further decreases until 20 °C, the current of peak 2 only shows a small increase. Similar behavior can also be observed in the curves for other \( T_p \). It can be considered as that the sample is still in paraelectric phase when \( T_0 \) is higher than 70 °C, no considerable charges can be trapped stably. With the decrease of \( T_0 \), some ferroelectric phase forms and injected charges are trapped. Then the trapped charges are released during TSDC measurement.

The forming of peak 1 can be seen in TSDC spectra for \( T_p = 90 \) °C. In this case, when \( T_0 \) decreases from 80 °C to 60 °C, no clear peak 1 can be found. If \( T_0 \) decrease to 50 °C, peak 1 emerges. With the further decrease of \( T_0 \), the current of peak 1 increases gradually until a constant value at room temperature. According to 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 VDF-TrFE copolymers [2-4]. If the copolymer is heated
up to a certain $T_p$ which is higher than $T_c$, the paraelectric phase will be produced, then when the sample is cooled during 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. It is known that every TSDC peak is corresponding to a certain structural defect (trap level) which can trap the charges injected from the electrode during polarization. Therefore, based on the process that sample was first heated to $T_p$ for polarization and then cooled to $T_0$ for TSDC measurement, peak 1 can be attributed to the charge detrapping from the Ferro I and peak 2 to the Ferro II phase for 70/30 and 77/23 copolymers. As for peak 3, because it always appears at 112 °C, it can be considered as the contribution of ferro-to-paraelectric transition. For 56/44 sample, peak 1 can be ascribed to the charge detrapping from ferroelectric phase, and peak 2 to the ferro-to-paraelectric transition. Due to peak 3 is always appeared in the range of 90–95 °C, it can be considered as the release of charges trapped in the paraelectric phase. Moreover, it can be found that even paraelectric phase can trap some charges, but the amount is very low. Because the paraelectric phase for 70/30 and 77/23 copolymers is in high temperature, no any peak arisen from paraelectric phase similar to peak 3 for 56/44 copolymer was found.

It is well known that the released charge density follows from integrating of TSDC spectra [10]

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

Integrating experimental TSDC curves of the copolymer samples with different mole ratio VDF, the obtained relationships between the detrapping density of trapped charges and polarization temperature $T_p$ are shown in Fig. 4. It can be seen that the detrapping charge density $\sigma$ increases as the increase of $T_p$ until it near heating $T_c$. The increase of $\sigma$ expresses the amount of trapped charge increases. When $T_p$ is over $T_c$, $\sigma$ shows a decrease trend. In addition, every curve in Fig. 4 presents a peak which located at around the heating $T_c$ of the copolymer, which showing a suitable high temperature (near $T_c$) is of benefit to the storage of charges. Comparing $\sigma$ of three copolymer samples, it is found that 70/30 copolymer has a large charge storage when $T_p$ is in the range of 90–120 °C.

Acknowledgments

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References