Effect of heating treatment on trap level distribution in polyamide 66 film electrets*

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The effect of heating treatment on the trap level distribution in polyamide 66 film electret is studied by thermally stimulated depolarization current (TSDC) technique. For annealed polyamide 66, there are three trap levels that respectively originate from space charge trapped in amorphous phase, interphase and crystalline phase. There is one peak that originates from space charge trapped in amorphous phase for quenched one. Using multi-point method to fit the experimental curves, the detrapping current peaks can be separated and the trap depth is obtained. The shallower trap levels trapped in amorphous phase and interphase are obviously close to the deeper trap level trapped in crystalline phase for annealed polyamide 66 as the polarization temperature increases, while the trap level distribution remains unaffected by polarization temperature for quenched one.

Keywords: polyamide 66, film electret, thermally stimulated depolarization current, heating treatment

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1. Introduction

Polymers acquire persistent polarization due to the alignment of dipoles and the migration of space charges over macroscopic distances.[1,2] Information about charge storage and transport phenomena in polymer electrets is of great interest for several industrial applications. The space charge in a polymer is now one of the most serious problems that the electrical insulation technology confronts. Due to the relative simplicity of the experimental setup and the high resolution of the method, thermally stimulated depolarization current (TSDC) has been used to understand dipole relaxation, charge storage, and charge decay processes in electrets.[3–5] Two aspects of the physical mechanism of the relaxation process, i.e., dipole relaxation and space charge detrapping, and their characteristic parameters must be considered in TSDC investigations.[6]

The TSDC analysis has been widely used to study polymer relaxations. In the case of nylons, TSDC has been used mostly to examine polyamide 11.[7,8] Polyamide 66 is one of the most important polyamide engineering plastics and has been widely used in industry. Moreover, like other polyamides, polyamide 66 is a typical semi-crystalline polymer with different microstructures under various thermal histories and thermo-mechanical treatments.[9,10] The investigations of chain segment motion, charge trapping, and detrapping in polyamide 66 are important from both the fundamental and technological point of view.[11,12]

In this paper, the trap level distribution, charge trapping, and detrapping in polyamide 66 films are investigated by TSDC. The research point is to elucidate which physical mechanism gives rise to each peak in TSDC spectra and to determine the characteristic parameters of the relaxation processes.

2. Experiments

A granule sample of polyamide 66 was obtained from Yixing Chemicals. Quenched films with a thickness of 0.15 mm were prepared by quenching melt-pressed films in an ice-water bath. An annealed sample was obtained by annealing the quenched film at 200 °C under vacuum for 2 h. The two sides of the sample were coated with a silver electrode 10 mm in diameter for TSDC measurements. The film was first polarized with an electric field $E_p = 40$ kV/cm at different polarization temperatures for a polarization time of 10 min. Then, the polarized sample was cooled down to room temperature. Afterwards, the sample was heated at a constant rate of 3.6 °C/min while it was short-circuited through an ammeter and the current was recorded as a function of temperature.

3. Results and discussion

WAXD (wide-angle X-ray diffraction) intensity curves for polyamide 66 are shown in Fig. 1. The crystal form of annealed polyamide 66 belongs to the triclinic system.[13] For the annealed sample that is semi-crystalline material, two characteristic peaks at $2\theta = 20°$ and 24° corresponding to (100) and (010, 110) planes can be observed clearly. For the quenched

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sample that is primarily amorphous material, only one wide peak corresponding to the amorphous phase appears at about $2\theta = 21.5°$.

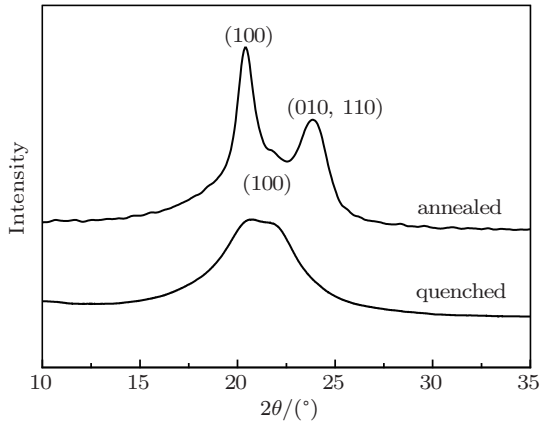


Fig. 1. WAXD curves of polyamide 66.

Experimental TSDC spectra for annealed polyamide 66 films at different polarization temperatures are shown in Fig. 2. The α peak corresponding to the glass transition temperature in the amorphous phase is not shown here. The TSDC spectrum has three space charge detrapping processes, corresponding current peaks appear at 124 °C (ρ_{a1} peak), 159 °C (ρ_{a2} peak), and 190 °C (ρ_{a3} peak), respectively when the polarization temperature is 80 °C. The TSDC spectrum has three space charge detrapping processes, corresponding current peaks appear at 159 °C (ρ_{a1} peak), 181 °C (ρ_{a2} peak), and 228 °C (ρ_{a3} peak), respectively, when the polarization temperature is 140 °C. The ρ_{a1} and ρ_{a2} peaks are shoulder peaks, and the two peak intensities are weaker than the ρ_{a3} peak intensity. Because the glass transition in the amorphous phase of annealed polyamide 66 is around 55 °C and the ρ_{a1} peak is above the temperature range of the glass transition, following the thermal-relaxation of frozen-in segmental dipoles the detrapping of charge carriers trapped in the amorphous phase can occur.[14] Therefore, the ρ_{a1} peak is attributed to space charge trapped in the amorphous phase. The second ρ_{a2} peak between 160 °C and 180 °C relates to the interphase. It is confirmed that the ρ_{a2} peak originates from the detrapping of space charge trapped in the interphase.[14] The temperature of the ρ_{a3} peak is lower than the melting temperature that is about 260 °C because more crystal defects mean poorer crystals. Thus, we suggest that the ρ_{a3} peak originates from the detrapping of space charges that were trapped in crystalline regions.

The increase of polarization temperature induces more stimulated space charges to form spontaneous current and space charge trapped in ρ peaks but can appear at higher temperatures. Therefore, the temperature of ρ peaks increases remarkably with the increase of polarization temperature. The increase of ρ_1 at 35 °C is more than that of ρ_2 at 22 °C, and the increase of ρ_3 at 38 °C is the same as that of ρ_1 at 35 °C. The amorphous phase and crystalline phase can bring more spontaneous current than the interphase because the areas of amorphous phase and crystalline phase are each more than the area of the interphase. With the increase of polarization temperature the crystal defects in the crystalline phase increase and the intensity of the ρ peak increases because of more space charges that are trapped in crystal defects in the crystalline phase.

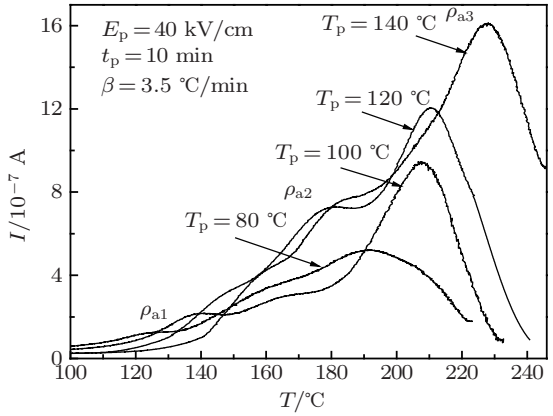


Fig. 2. Experimental TSDC spectra for annealed polyamide 66 at different polarization temperatures.

Figure 3 shows the TSDC spectra of annealed polyamide 66 measured for six different polarization fields. In the whole measuring temperature range three current peaks are observed. The complicated chain structure and condensed state structure of the polymer may both lead to various localized state distributions. Structure defects in the amorphous phase, and interphase state and crystal disfigurement in the crystalline phase can influence localized state distributions.[15] The current magnitudes of the three peaks increase with the increase of polarization field because more space charges are trapped in all phases.

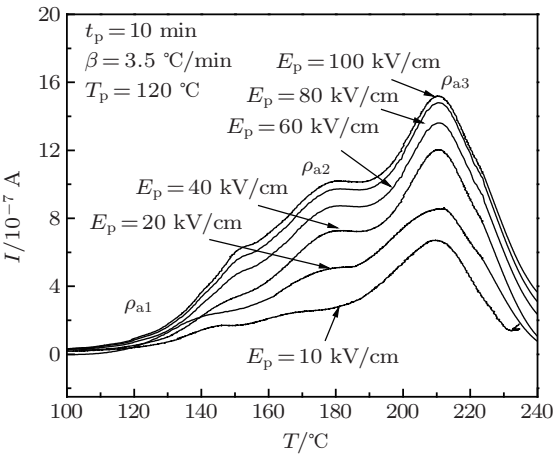


Fig. 3. TSDC spectra of annealed polyamide 66 poled with different polarization fields.

The ρ peak can be attributed to the detrapping of space charge in the thermal stimulation heating process. In fact, when the sample is polarized, not only can the dipoles of the

chain segment orient under the action of electric field and then become trapped in the traps, the charge carriers can also. On heating the trapped carriers, they will be detrapped from the localized energy state and produce the space charge peaks in the TSDC spectra. It can be seen from Fig. 3 that the increase of the ρ peak current becomes slower as the polarization field increases, which is correlated with the space charge detrapping mechanism.[15]

As shown in Fig. 4, the TSDC spectrum has one space charge detrapping process that corresponds to the ρ_q peak for the quenched film. Figure 5 gives the effect of polarization temperature on the peak temperature of polyamide 66. Compared with the ρ_{a3} peak of the annealed film, the ρ_q peak moves toward lower temperature, and compared with the ρ_{a1} peak of the annealed film, the ρ_q peak moves toward higher temperature. At the point of peak temperature, ρ_q is more similar to the ρ_{a2} peak.

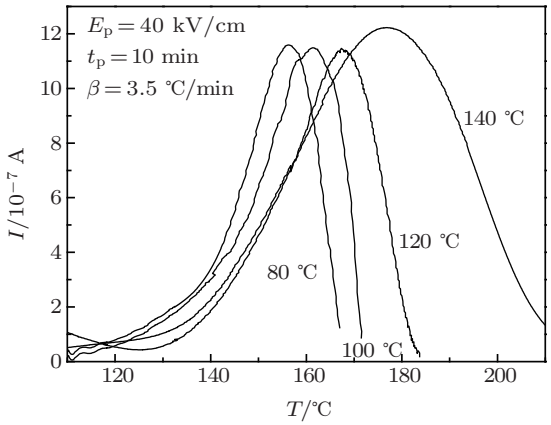


Fig. 4. Experimental TSDC spectra for quenched polyamide 66.

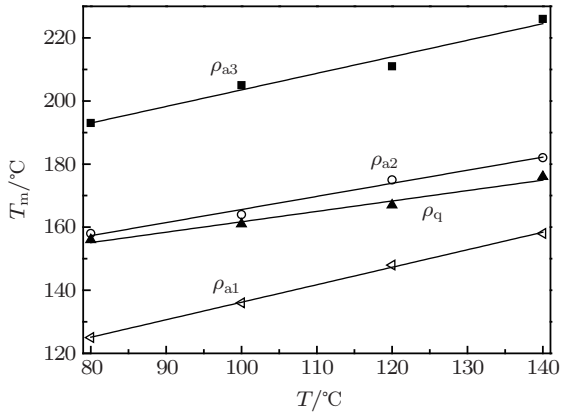


Fig. 5. Effect of polarization temperature on the peak temperature of polyamide 66.

In order to further elucidate the effects of heat treatment on charge storage and trap level distribution for polyamide 66 film electrets, it is necessary to analyze the characteristic parameters of the detrapping process. The general order kinetic model is used to describe the depolarization current. In the general order kinetic model, the current intensity is assumed to follow the empirical law[16]

$$I(t) = -\frac{\mathrm{d}n}{\mathrm{d}t} = n^b s \exp(-E/kT), \tag{1}$$

where n is the trapped charge at time t, E is the activation energy (the depth of the trapping sites in this model), T is the absolute temperature, k is Boltzmann's constant, s is a pre-exponential factor in units of $\mathrm{C}^{1-b}\cdot\mathrm{s}^{-1}$, and b is the kinetic order, an empirically determined parameter. In the case of a constant heating rate β, the solution of the equation is

$$I(T) = n_0 s \exp(-E/kT) \exp\left[(-s/\beta)\int_{T_0}^{T} \mathrm{e}^{-\frac{E}{kT'}}\,\mathrm{d}T'\right], \quad (b=1), \tag{2}$$

$$I(T) = n_0 s \exp(-E/kT) \times \left[1+(b-1)(s/\beta)\int_{T_0}^{T} \mathrm{e}^{-\frac{E}{kT'}}\,\mathrm{d}T'\right]^{b/(1-b)}, \quad (b\neq 1), \tag{3}$$

where n_0 is the initial trapped charge and $s_0 = s_0' n_0^{(b-1)}$ is a frequency factor. It reduces to the Randall and Wilkins equation in the limit b tending to 1 (first-order kinetics, which is valid in the case where the recombination is most likely to be a relaxation process in space charge detrapping). In the case of $b = 2$, this equation reduces to the Garlick and Gibson equation (second-order kinetics, which is valid in the case where retrapping is the prevailing relaxation mechanism). Although b is not in correspondence with physical reality, the equation allows the description of a wide variety of kinetic phenomena and b can be interpreted as the balance between the two extreme cases (1 or 2) considered. The activation energy calculated using this model is very close to its true value. Following the above TSDC theoretical equations, the TSDC experimental results can be fitted theoretically and then the values of TSDC parameters, such as frequency factor and trap level, can be obtained by the multi-point method.[15] Figure 6 gives the fitting results of theoretical TSDC spectra for annealed polyamide 66. The solid line refers to experimental TSDC spectrum at polarization temperature 140 °C, and the broken lines denote theoretical TSDC spectra. Figure 6 shows good agreement between the calculated data and the theoretical spectra.

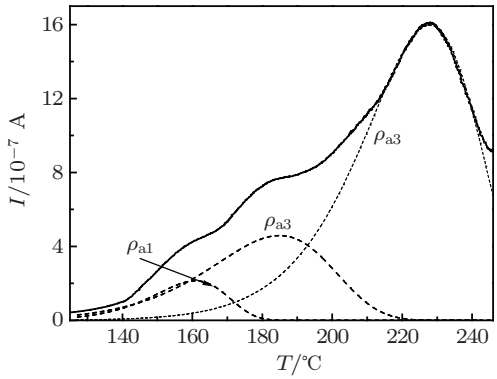


Fig. 6. Theoretical TSDC spectra for annealed polyamide 66.

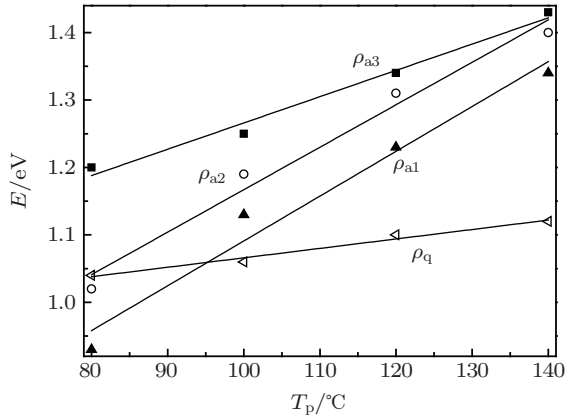


Fig. 7. The effect of polarization temperature on trap depth of polyamide 66.

Figure 7 shows the effect of heat treatment on trap depth of polyamide 66. The trap depth for the ρ_q peak of quenched polyamide 66, which is 1.1 eV, does not change with polarization temperature. The trap depths for the ρ_{a1}, ρ_{a2}, and ρ_{a3} peaks of annealed polyamide 66 all increase linearly with the increase of polarization temperature, indicating the trap depth becomes deeper and the detrapping process is more difficult in thermal stimulation for the film electret. For the annealed sample, because the chain arrangement in the crystal region is imperfect and then the crystalline lamellas are also imperfect, there are structural defects formed in the crystalline lamellas. Charge carriers are trapped in localized energy levels produced by these defects (ρ_{a1}, ρ_{a2}, and ρ_{a3} peaks). With the increase of polarization temperature, the quantity of imperfect crystalline lamellas becomes more than the quantity of the imperfect amorphous phase and interphase. The results also show that the shallower trap levels trapped in the amorphous phase and the interphase were obviously close to the deeper trap level trapped in the crystalline phase when the polarization temperature increases. However, crystalline lamellas, the interphase, and these defects formed in crystalline lamellas will disappear for the quenched sample, so the corresponding detrapping process in TSDC spectra will disappear. Such a change will lead to the invariability of trap depth of the ρ_q peak against the increase of polarization temperature.

4. Conclusion

In this study, three trap levels of space charge are found in the annealed film electret. The shallower trap levels trapped in the amorphous phase and the interphase are obviously close to the deeper trap level trapped in the crystalline phase for annealed polyamide 66 as the polarization temperature increases. There is only one trap level in the quenched one and the trap level distribution remains unaffected by polarization temperature.

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