Annealing Effect on Chain Segment Motion and Charge Detrapping in Polyamide 610

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ABSTRACT: The chain segment motion and charge detrapping in polyamide 610 films have been investigated by means of thermally stimulated depolarization current (TSDC) and wide-angle X-ray diffraction. There are three current peaks (namely α, ρ_1, and ρ_2 peaks) in the TSDC spectra above room temperature. α peak is attributed to a dipole relaxation by the motion of chain segments ρ_1 peak is caused by space charge trapped in amorphous phase and the interphase between crystalline and amorphous phases, and ρ_2 peak is brought about by space charge trapped in crystalline phase. By analyzing the characteristic parameters of these peaks, it is found that annealing induces the decrease of chain segment mobility and promotes the creation of structural traps in polyamide 610. The decrease of chain segment mobility in amorphous phase makes intensity of α peak weak and activation energy increscent. The higher the annealing temperature, the higher the degree of crystallinity, the more the charge carriers trapped in crystalline phase. So, the increase of degree of crystallinity makes intensity of ρ_2 peak strong and increases the stability of trapped charge in the crystalline phase. The increase of annealing temperature makes intensity of ρ_1 peak strong and decreases the stability of trapped charge in the amorphous phase and interphase. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4486–4490, 2012

Key words: polyamide 610; thermally stimulated depolarization current; dipole relaxation; space charge; annealing

INTRODUCTION

Polymers acquire persistent polarization due to the alignment of dipoles and migration of space charges over macroscopic distance.[1,2] Information on charge storage and transport phenomena in polymer electrets is of great interest for several industrial applications. The space charge in polymer is now one of the most serious problems confronting electrical insulation technology. Because of the relative simplicity of the experimental setup and the high resolution of the method, the thermally stimulated depolarization current (TSDC) technology has been used to study dipole relaxation, charge storage, and charge decay processes in electrets.[3–12] Two aspects of physical mechanism of relaxation process, dipole relaxation and space charge detrapping, and their characteristic parameters must be considered in TSDC investigations.[1,2,13–15]

TSDC analysis has been widely applied to study the polymer relaxations. In the case of polyamides,[16–23] TSDC has been applied mostly to examine polyamide 6 and polyamide 11. Polyamide 610, which has a molecular structure analogous to polyamide 66, is one of the important polyamide engineering plastics and has been widely used in industry. Moreover, like other polyamides, polyamide 610 is a typical semicrystalline polymer with different microstructure under various thermal histories and thermomechanical treatment.[24–28] The investigation of chain segment motion, charge trapping and detrapping in polyamide 610 is important both from the fundamental and technological point of view.

In this article, the chain segment motion and charge detrapping in polyamide 610 films are investigated by TSDC and wide-angle X-ray diffraction (WAXD). The research point is to elucidate which physical mechanism gives rise to each peak in TSDC spectra and to determine the characteristic parameters of relaxation process.

EXPERIMENTAL

Materials

A granule sample of polyamide 610 was obtained from Yixing Chemicals. Quenched film with thickness of 0.15 mm was prepared by quenching melt-pressed film in an ice-water bath. Annealed sample
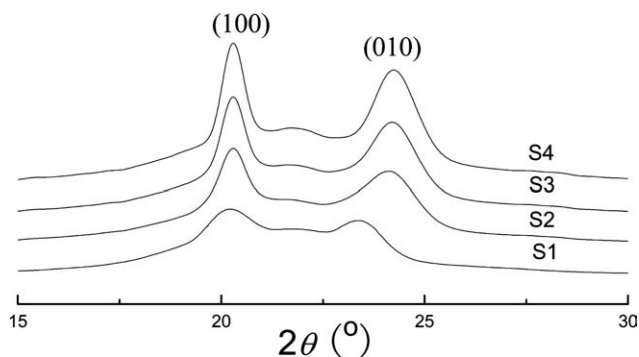
Figure 1 WAXD curves of polyamide 610.

was obtained by annealing the quenched film at four different temperatures (80, 110, 140 and 180°C) under vacuum condition for 2 h. Annealed sample was removed from oven and quickly cooled down to room temperature. The two sides of annealed sample were coated with a silver electrode of 10 mm in diameter for TSDC measurement. The number of sample for repeated experiments is three. Traces of solvent were removed by vacuum evaporation at room temperature for 24 h.

WAXD measurement

WAXD measurement was carried out on a Philips Dual X'Pert diffractometer with Cu K$_\alpha$ radiation over the diffraction angle (2θ) range of 15–35°. The degree of crystallinity of sample was determined based on WAXD patterns.

TSDC measurement

TSDC measurements were carried out on a modified thermal electric analyzer.[7] The film was first polarized with an electric field of 40 kV/cm at a polarization temperature of 80°C for a polarization time of 10 min. Then, polarized sample is cooled down to room temperature. Afterward, 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.

RESULTS AND DISCUSSION

Wide-angle X-ray diffraction

WAXD is commonly used for comparative studies of the crystal form, unit cell, the degree of crystallinity (X_c) and crystallite dimension of crystallized polymer under various conditions. The crystal form of polyamide 610 belongs to the triclinic system.[28] WAXD intensity curves for polyamide 610 are shown in Figure 1. Curves S1, S2, S3, and S4 show the structure of polyamide 610 films annealed at 80,

110, 140 and 180°C, respectively. For all the samples, two crystal characteristic peaks at 2θ = 20° and 24° corresponding to the reflection of (100) and (010) planes can be observed clearly and the intensity of diffraction peaks increases gradually with the increase of annealing temperature. The wide peak corresponding to amorphous phase appears at about 2θ = 21.5° and the intensity of diffraction peaks keeps immobile with the increase of annealing temperature. Based on X-radial diffraction intensity theory and the graphic multipeak resolution method,[25] taking into account different spontaneous interfere and approximate equation of atom scatter parameter, X_c of the samples could be calculated using the formula:

$$X_c = \frac{I_{010} + 0.32 I_{100}}{I_{010} + 0.32 I_{100} + 0.78 I_a} \times 100\%, \qquad (1)$$

where I_{hkl} is the area under the diffraction peak and I_a is the area under the peak corresponding to amorphous phase. Changing the annealed temperature, a series of polyamide 610 films with X_c of 8, 15, 26, and 43% were fabricated, and named S1, S2, S3, S4, respectively. It can be seen that X_c for the sample annealed at 180°C is about 43%, while that annealed at 80°C is about 8%. The degree of crystallinity of polyamide 610 increases with the increase of annealing temperature.

Experimental TSDC of polyamide 610

Experimental TSDC spectra for polyamide 610 films are shown in Figure 2. Only three distinguished peaks can be found apparently above room temperature. The first peak usually called α peak located at about 53°C corresponds with the glass transition temperature in the amorphous phase, which is
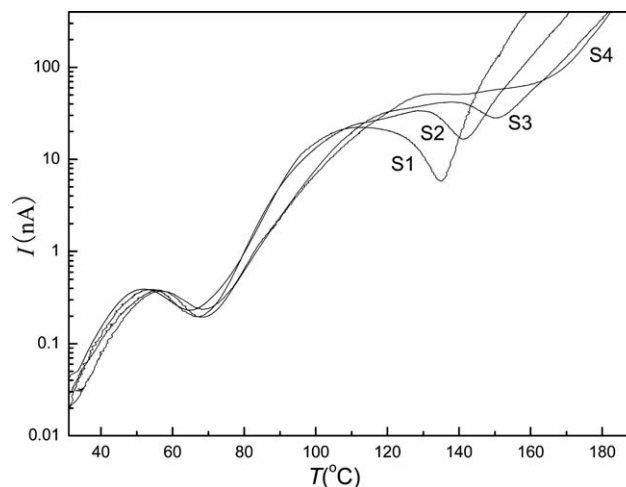

Figure 2 Experimental TSDC spectra for polyamide 610 above room temperature.

caused by the thermorelaxation of frozen-in dipole of segments. The temperature of α peak is little dependent on the annealing condition. The other peaks denoted as ρ peaks located at well above the temperature of α peak are due to space charge relaxation contributed by detrapping of trapped charge carriers. The intensity, shape, and temperature of ρ peaks are markedly dependent on the annealing condition. As temperature increase to above 140°C, it can be seen that the spectra show a sharp increscent current, which is a common feature to many polymers.[18,29] This current called spontaneous current is caused by thermal degradation, internally created charged gradients along the thickness direction, thermoelectric effects, contact electrification, or small electrochemical potential differences between the two electrodes.[30] The existence of spontaneous current can interfere with the analysis of TSDC spectra, especially for space charge relaxation.

In order to study well the dipolar relaxation and space charge detrapping, contribution of the spontaneous current should be deducted. The spontaneous current I_s in TSDC spectra at high temperature follows the equation

$$I_s = A \exp\left(-\frac{E}{kT}\right) + C, \qquad (2)$$

where A is a constant factor, E is activation energy, k is Boltzmann's constant, and C is a constant related to the baseline of experimental data. The spontaneous current can be deducted by the method based on eq. (2) proposed by Peng et al.[31]

Theoretical analysis of TSDC spectra of polyamide 610

To further elucidate the effect of annealing temperature on chain segment motion and charge detrapping in polyamide 610, it is necessary to analyze the characteristic parameters of three relaxation peaks. In the temperature range considered in this article, the relaxation mechanisms can be elucidated by dipole relaxation or space charge detrapping. If the depolarization current originates from dipole relaxation with an Arrhenius relaxation time, the current obtained during depolarization follows the equation form[13]:

$$I(T) = \frac{P_0}{\tau_0} \exp\left[-\frac{E_a}{kT} - \frac{1}{\beta\tau_0} \int_{T_0}^{T} \exp\left(-\frac{E_a}{kT'}\right) dT'\right], \quad (3)$$

where E_α is activation energy of the process, T is absolute temperature, k is Boltzmann's constant, T_0 represents the initial temperature of heating process, β is heating rate, P_0 is initial polarization in the sample, and t_0 is pre-exponential factor,

which is a characteristic time constant for the process.

If depolarization current arises from the detrapping of space charge, the general kinetic order model can be used to describe the depolarization current. In the general order kinetics model, the current intensity is assumed to follow the empirical law[13]:

$$I(t) = -\frac{dn}{dt} = n^b s \exp(-E/kT), \qquad (4)$$

where n is trapped charge at time t, E is the depth of trapping sites in this model, s is a pre-exponential factor, and b is kinetic order, an empirically determined parameter. In the case of a constant heating rate β, the solution of the equation is:

$$I(T) = n_0 s \exp(-E/kT) \exp\left[(-s/\beta) \int_{T_0}^{T} e^{-\frac{E}{kT'}} dT'\right]$$

$$(b = 1) \qquad (5)$$

$$I(T) = n_0 s \exp(-E/kT)$$

$$\times \left[1 + (b-1)(s/\beta) \int_{T_0}^{T} e^{-\frac{E}{kT'}} dT'\right]^{b/(1-b)} \quad (b \neq 1), \quad (6)$$

where n_0 is initial trapped charge. It reduces to Randall and Wilkins equation in the limit b tending to 1[13] (first-order kinetics, which is valid in the case where recombination is the most likely relaxation process in space charge detrapping). In the case of $b = 2$, this equation reduces to Garlick and Gibson equation[13] (second-order kinetics, which is valid in the case where retrapping is the prevailing relaxation mechanism). Parameter b has no obvious physical meaning, but the equation allows the description of a wide variety of kinetic phenomena and b can be interpreted as balance between the two extreme cases (1 or 2) considered. The activation energy calculated using this model is very close to its true value.

The characteristic parameters can be obtained by fitting the resulting depolarization current based on the eqs. (3), (5), and (6). The fitting software was developed in our laboratory. One example of the curve fitting procedure is plotted in Figure 3. It shows a good agreement between calculated data and theoretical spectra coming from deducting the interference of spontaneous current. Theoretical TSDC spectra for polyamide 610 films are shown in Figure 4. There is only slight difference in the amplitude and the temperature for α peak with the increase of X_c. For ρ peaks, there are evident differences on the intensity and the temperature with the increase of X_c. The temperatures of ρ peak shift to high temperature with increasing the degree of crystallinity.
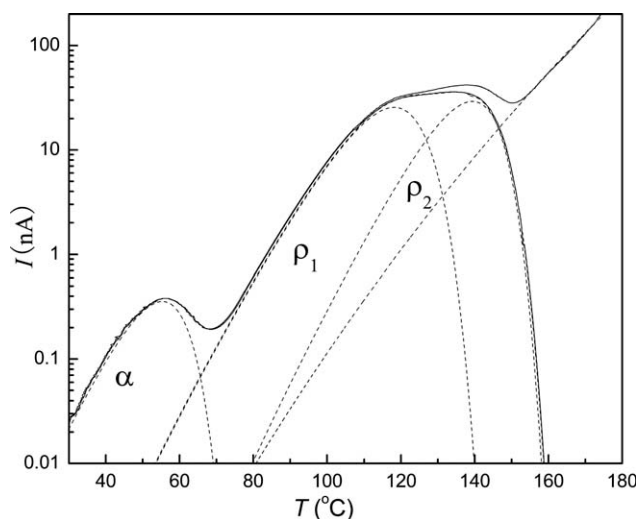
Figure 3 The curve fitting procedure of TSDC spectra of polyamide 610 annealing at 140 °C.

The obtained parameters of α peak (the initial polarization P_0 and the activation energy E_α) are shown in Figure 5. The initial polarization of α relaxation is 0.174 μC for S1 and decreases to 0.127 μC for S4. The temperature of α peak increases from 50.2 to 56.5°C and E_α increases from 1.15 to 1.24 eV. The increase of X_c increases the relaxation activation energy of frozen-in dipole and restrains the chain segment movement. So, intensity of α peak becomes weak and activation energy increases with the degree of crystallinity.

The complicated segment motion and supermolecular structure of polymer in condensed state lead to various localized state distributions. The factors influencing localized state distributions include three aspects. The first aspect is impurity, disordered molecular conformation, and freedom volume physics disfigurement in amorphous phase. The second is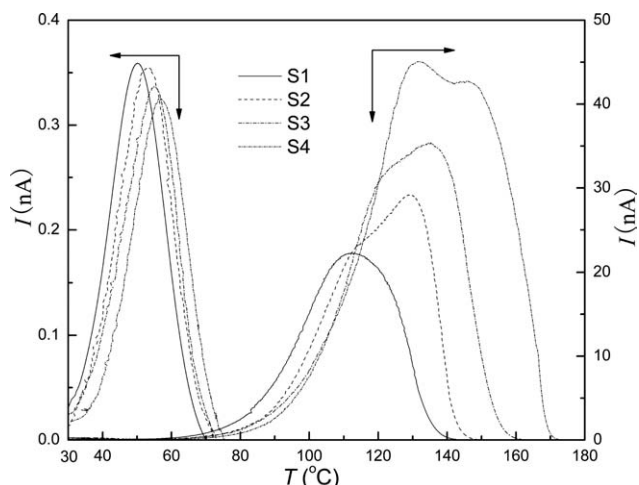 interphase state between crystalline and amorphous phases. The third one is crystal disfigurement in crystalline phase.[32]

With polarization of polyamide 610, the formation of crystalline structure is not perfect that makes interphase space less. So, on one hand, the chain segments of amorphous phase including the movement of protons in amide groups have sufficient time for diffusion to the interface of crystalline phase, and on the other hand, the thermal stimulation have enough time to adjust the distribution of localized states of amorphous phase, change the depth of trap energy level, and make the energy difference between shallow trap and deep trap energy decrescent. The captured carriers' mobility becomes larger, and detrapping of carriers in amorphous phase is simultaneous with detrapping of carriers in interphase. So, there are two space charge peaks (ρ_1 and ρ_2 peaks) reflected in the thermally stimulated current spectra and the single middle peak corresponding to detrapping of carriers in interphase does not appear.[18,19]

Because the glass transition in the amorphous phase of polyamide 610 is around 50°C and ρ_1 peak follows temperature range of the glass transition and the thermorelaxation mechanism of frozen-in dipole of segments, the detrapping of charge carriers trapped in the amorphous phase and interphase can release. With the increase of X_c, the temperature of ρ_1 increases from 113.4 to 131.4°C, the temperature of ρ_2 increases from 131.6 to 148.2°C. The increasing magnitude for ρ_1 peak (18°C) is more than that for ρ_2 (16.6°C). So, the rate of increase of ρ_1 is faster than that of ρ_2. The intensity, shape and temperature of ρ peak are markedly dependent on X_c. With the increase of X_c, the intensity of ρ peak increases because more structure defects come into being in polyamide 610 films. With increase of X_c, the temperature of ρ_1 and ρ_2 peaks increases because crystalline

Figure 4 Theoretical TSDC spectra for polyamide 610 above room temperature.
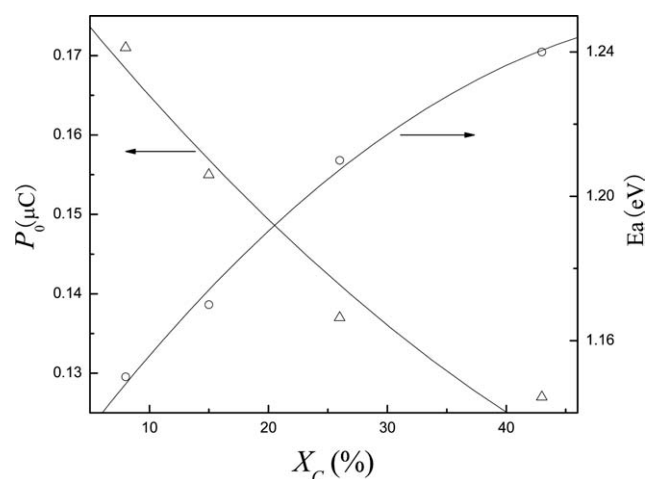

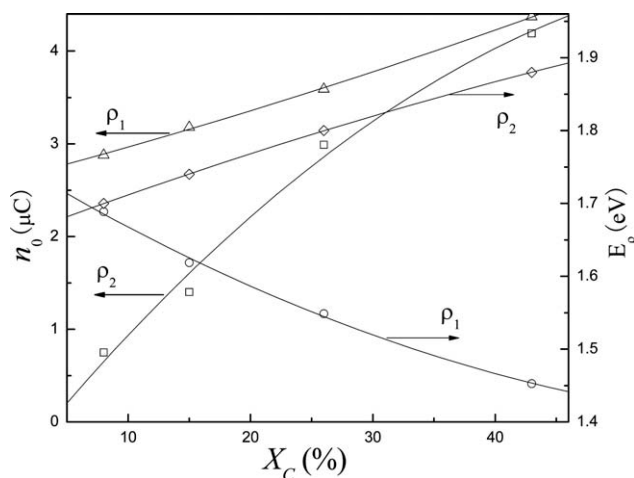**Figure 5** The initial polarization and the activation energy of α peak.

Figure 6 The initial trapped charge and the trap depth of ρ peak.

phase decreases the chain segment mobility. The ρ_2 peak temperature is close to the melting temperature. So, the ρ_2 peak is brought about by the detrapping of space charge that trapped in crystalline phase.

The fitted parameters

The fitted parameters (the initial trapped charge n_0 and the trapping depth E_ρ) are shown in Figure 6. The kinetic order has a value between 1.88 and 1.92, which is near to 2 for space charge detrapping. In space charge detrapping processes, the retrapping process is predominant in polyamide 610.

The initial trapped charge for ρ_1 peak is 2.88 μC for S1 and increases to 4.37 μC for S4. The initial trapped charge for ρ_2 peak is 0.75 μC for S1 and increases to 4.19 μC for S4. It is found that annealing promotes the creation of structural defects in polyamide 610. The initial trapped charge n_0 of two ρ peaks increase with increasing the structural defects. The trap depth for ρ_1 peak is 1.68 eV for S1 and decreases to 1.45 eV for S4 and the trap depth for ρ_1 peak becomes shallower with the increase of X_c. The decrease of amorphous regions would result in the shallower traps in the amorphous phase and interphase. The trap depth for ρ_2 peak is 1.70 eV for S1 and increases to 1.88 eV for S4 and the trap depth for ρ_2 peak becomes deeper with the increase of X_c. The higher the crystallinity, the more the crystalline regions that would result in the deeper traps in the crystalline regions. So, the increase of X_c decreases the stability of trapped charge in the amorphous phase and interphase but enhances the stability of trapped charge in crystalline phase.

CONCLUSIONS

The chain segment motion and charge detrapping in polyamide 610 films were investigated by TSDC

technique. It is found that the increase of X_c induces the decrease of chain segment mobility and promotes the creation of traps in polyamide 610. Annealing decreases the stability of charge trapped in amorphous phase and the interphase, and increases the stability of charge trapped in crystalline phase. In space charge detrapping processes, retrapping process is the predominance in polyamide 610.

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