

TSC STUDIES ON SUB- T_g STORAGE OF POLYETHYLENE TEREPHTHALATE

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ABSTRACT

The Thermally Stimulated Current (TSC) spectra of a series of Sub- T_g annealed polyethylene terephthalate (PET) specimens have been measured. It is found that there is only one peak at 80°C above room temperature, which related to the thermo-relaxation of frozen-in dipoles. The activation energy of such dipole motion has been calculated. The relation between the maximum current and the storage time can be explained by the free volume theory and agrees with the results from the excess thermodynamic properties. Compared with Differential Scanning Calorimeter (DSC) and tensile stress-strain method, TSC is a simpler and more sensitive method in studying Sub- T_g annealed polymers.

INTRODUCTION

Significant changes have been observed in mechanical and physical properties of glassy polymers as a result of storage at temperature below its T_g (Sub- T_g annealing). The study on the mechanism of Sub- T_g storage is the current topic for the purpose of engineering plastic application [1-5]. To date, it is a general consensus that the changes in the properties of glassy polymers on Sub- T_g annealing are the result of relaxation phenomena associated with the non-equilibrium nature of the glassy state and the molecular mobility as well.

It is recognized that the decrease of the free volume during Sub- T_g storage reduces the number of molecular segments having enough space to move. The electrical and mechanical properties caused by the segmental motion, should be affected by Sub- T_g storage in a similar way.

Recently the Differential Scanning Calorimeter (DSC) is widely accepted as a main method for Sub- T_g storage research, but it has less sensitivity. Thermally Stimulated Current (TSC) is widely used for understanding the dipole reorientation, charge-trapping and charge transport process as well as the molecular mobility of polymer electrets [6-10]. Despite the sensitivity of TSC technique, only a few papers concerning Sub- T_g storage have been published so far [6,8]. In comparison with DSC, we suggested that the TSC technique might be a most sensitive one. In the present paper, our experimental results from PET showed that the TSC was a potential method for the investigation of Sub- T_g storage effect of glassy polymers, revealing the nature of segmental mobility, while having a good correlation with mechanical properties.

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EXPERIMENTAL

Samples

Samples of PET film were provided by Changzhou Insulation Materials Manufactory. The amorphous PET film had the crystallinity (ρ) less than 3% revealed by density measurement, the glass transition temperature (T_g) = 78°C and the thickness (h) = 400 μ m. Al electrodes were evaporated onto both sides of each specimen under 10^{-5} Torr. All specimens were annealed at $T_g + 15^\circ\text{C}$ for 15 min before Sub- T_g storage annealing schedule in order to erase the prior thermal history. The Sub- T_g annealing temperature is 65°C.

TSC measurements

TSC measurements were carried out by using a Thermal Electrical Analyzer produced by Toyo-Seiki Corporation, the sensitivity of current measurement is 10^{-12} Amp. The experimental conditions of poling and TSC measurement are $T_p = 65^\circ\text{C}$, $E_p = 56(\text{kV}/\text{cm})$, $t_p = 20(\text{min.})$ and $\beta = 2^\circ\text{C}/\text{min.}$, where T_p is the poling temperature, E_p is the poling strength, t_p is the poling time and β is the heating rate respectively. Details of TSC measurement set-up have been published in the previous paper^[2].

Density measurement

Density measurements were done by means of density gradient column which consists of dimethyl benzene and tetrachloro-methane. Stress-strain behavior and DSC thermogram of PET specimens were taken by using Instron-1122 and Pekin-Elmer DSC-2 respectively.

RESULTS AND DISCUSSION

Effect of Sub- T_g annealing on TSC thermogram of PET specimens is shown in Fig.1 and the corresponding data are given in Table 1 as well. It shows a strong dependence of the TSC peak upon the Sub- T_g annealing time. The TSC peaks appear in a narrow temperature interval and its

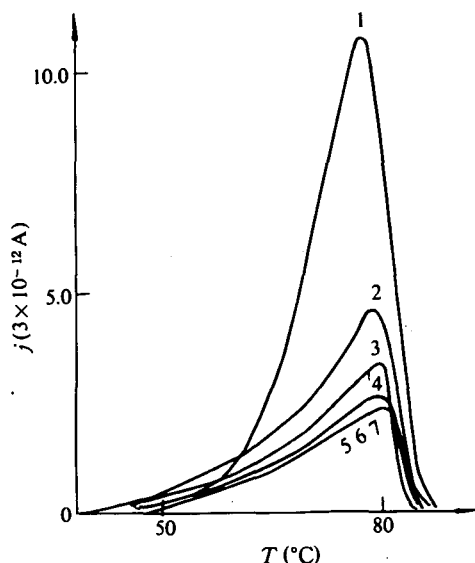


Fig.1 TSC thermogram of PET specimens stored at 65°C for different times.

shape and position are unaffected by changes in the poling conditions. Such a behavior is typical for TSC of dipoles relaxation with single relaxation time.

Table 1 The TSC data for aged and unaged PET specimen

Specimen No.	1	2	3	4	5	6	7
<i>t</i> (h)	0	10	20	30	50	70	120
<i>j</i> _{max} × 10 ¹² (A)	32.0	12.9	9.0	7.5	6.6	6.6	6.6
<i>T</i> _{max} (°C)	77	79	79	80	81	81	81
<i>Q</i> × 10 ¹⁰ (C)	27.0	10.8	7.38	6.30	5.67	5.67	5.67

where *t* is the annealing time, *T*_{max} is the TSC peak temperature, *Q* is the total released charge.

According to dipole disorientation theory when poling time *t_p* >> *τ*₀ (*τ*₀ is the relaxation time), the thermally stimulated current (*j*(*T*)) in term of Δ*E*, *T_p* and β can be expressed as^[3]:

$$j(T) = -\frac{N\mu^2 E_p}{2kT_p \tau_0} \exp \left[-\frac{\Delta E}{kT} - \frac{1}{\tau_0 \beta} \int_{T_0}^T \exp \left(-\frac{\Delta E}{kT} \right) dT \right], \tag{1}$$

Where *N* is the number of dipoles in unit volume, μ is the dipole moment of specimen, *k* is Boltzmann constant, Δ*E* is the activation energy and the *E_p* and β have been defined before.

The TSC peak area is proportional to the total released charge (*Q*) which can be obtained by integrating equation(1).

$$Q = \int_0^\infty j(T) dt = N\mu^2 E_p / 3kT_p \tag{2}$$

Equation (2) shows a linear relationship between the peak area *Q* and the poling strength *E_p*. Fig.2 shows the good linear relationships of aged and unaged PET specimens. From our experimental results, we may conclude that the TSC peaks (near 80°C) of PET specimens can be attributed to the dipole relaxation mechanism.

When *T* << *T*_{max}, the integral of equation (1) can be approximated in the following way:

$$j(T) = -\frac{N\mu^2 E_p}{3kT_p \tau_0} \exp \left(-\frac{\Delta E}{kT} \right) \tag{3}$$

From equation(3) the activation energy Δ*E* can be calculated. The calculated values of Δ*E* vs. annealing time are listed in Table 2. Values of Δ*E* are rather small, about 0.8—0.9(eV), and they seem to be independent of the annealing time. This result shows that the molecular motion units of the relaxation are much smaller than that of *T_g* relaxation of PET.

Table 2 the Δ*E* value calculated for different annealing time(*t*)

<i>t</i> (h)	0	10	20	30	50	70	120
Δ <i>E</i> (eV)	1.05	0.84	0.87	0.81	0.78	0.88	0.88

Mininni et al. ^[14] reported that the free volume in glassy polymers decreased during the Sub-

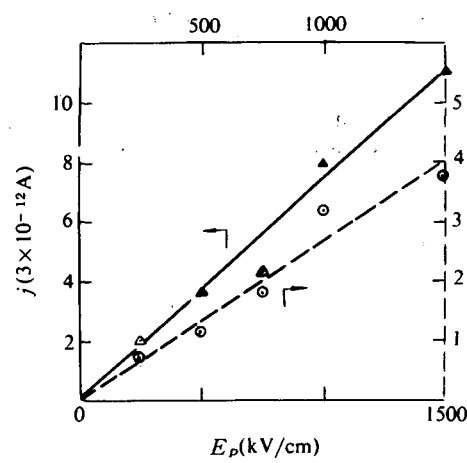


Fig. 2 The relationship of the $j_{\max}$ to the poling voltage. — for unaged specimen; ---- for aged specimen.

T_g annealing proceeding. In the case of TSC measurement, we found that the depolarization current $j_{\max}$ is markedly influenced by the annealing time(t) as shown in Table 1 and Fig.3 respectively. The peak value of the depolarization current decreases with the increase the storage time, while the peak temperature remained almost unchanged. It is quite natural that since the decreasing of the free volume reduces the number of molecular segments having enough space to move, which is proportional to the number of dipoly orientation, the depolarization current will decrease as mentioned before.

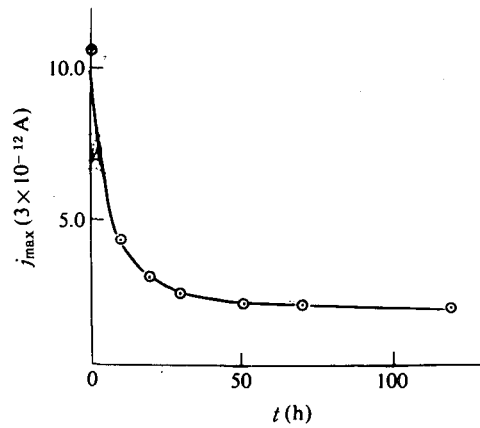


Fig. 3 The relationship of the $j_{\max}$ to the stored time

The transition of the mechanical behavior from ductile to brittle fracture of amorphous PET after annealing at 65°C for different duration times is demonstrated by the tensile stress-strain curves shown in Fig. 4. It is interesting to note that this transition in the mechanical behavior happened after 50 hour storage, just the same range of $j_{\max}$ transition in the TSC measurements as shown in Fig.1 and Table 1 respectively. These results indicate the good coincidence of TSC with the mechanical behavior.

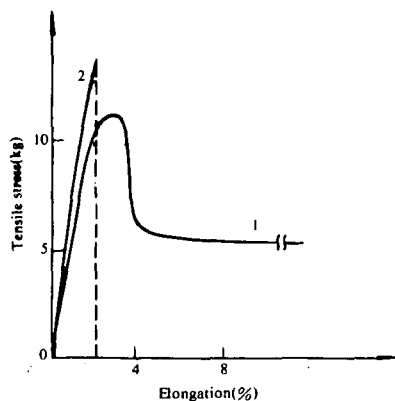


Fig. 4 The tensile stress-elongation curves of PET specimen
Annealing time: 1—unaged; 2—after 50h.

A slightly monotonic increment of the density with storage time is shown in Fig. 5. Since the unchanged structure of molecular chains and crystallinity of amorphous PET specimens after annealing treatment at 65°C were confirmed by means of IR spectroscopy, intrinsic viscosity and X-ray measurements, so, the increment of the density can only be attributed to the increment of the packing density in the amorphous region of the PET specimens.

The plot of $\Delta j_{\max}$ against the storage time is shown in Fig. 6, where $\Delta j_{\max} = j_{\max} - j_{\max(\infty)}$ and $j_{\max(\infty)}$ is the $j_{\max}$ where $t \rightarrow \infty$, and the linear relationship between $\ln \Delta j_{\max}$ and t means that the initial activation energy of the Sub- T_g storage process can be determined.

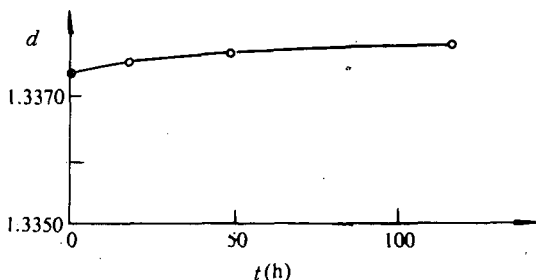


Fig. 5 The density of PET specimen during Sub- T_g annealing process.

Fig.7 shows the DSC curves of PET specimens which correspond with the specimens of Fig.1. Excess enthalpy relaxation endothermal peaks at glass transition temperature for aged specimens are shown in Fig.7, which is a characteristic of Sub- T_g annealing or physical aging. On the other hand, the unaged or quenched specimen shows no such endothermal peak. This is because of the kinetic nature of glass transition. So, in the conventional DSC technique for physical aging study, the second scan serves as a reference DSC trace of a quenched specimen. Therefore, the excess enthalpy measurements were made by superimposing the first and second scans for each sample. By comparing the results of DSC with the TSC, it can be seen that the sensibility of TSC is much higher than that of DSC. Furthermore the results from TSC technique show a good correlation with the mechanical behavior.

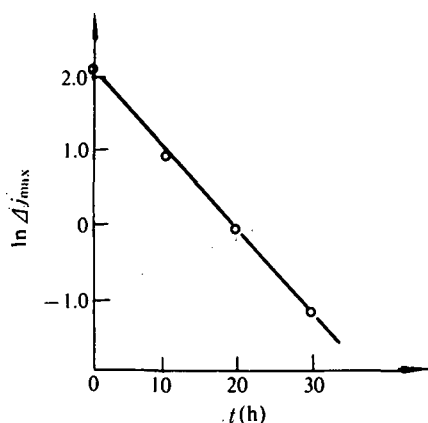


Fig. 6 The relationship of $\ln \Delta j_{\max}$ to annealing time.

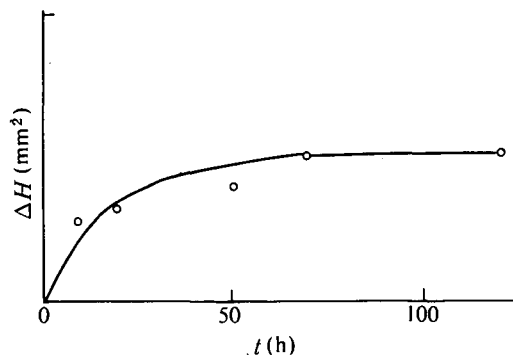


Fig. 7 The effect of Sub- T_g annealing on the excess enthalpy relaxation endothermal peaks of aged PET specimens.

In summary, TSC technique based on measurement of $j_{\max}$, Q , and ΔE could be used as one of the methods in physical aging studies. A correlation between the aging time and the TSC parameters is thus demonstrated. Results of this work inferred that TSC technique might be useful in physical aging studies of polymers.

Keywords:

Polyethylene terephthalate; Sub- T_g Storage; TSC Studies.

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