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EFFECT OF CATALYSTS ON THERMALLY STIMULATED CURRENT IN POLY(ETHYLENE TEREPHTHALATE)

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Abstract

The effect of catalysts on relaxation phenomena in poly(ethylene terephthalate) (PET) was studied by thermally stimulated current (TSC). Resins Sb-PET and Ge-PET were produced by the antimony and germanium main catalyst systems, respectively. Spontaneous, global and thermal sampling of TSC were compared in both PETs. The lower TSC peaks are observed in Ge-PET than those in Sb-PET for equivalent treatment. The compensation parameters were determined from the variation polarization temperatures (T_p) data. These parameters were used to calculate degree of disorder (DOD). The DOD of Sb-PET and Ge-PET were 36.14 and 66.23, respectively. The relaxation time at the maximum current and the dipolar relaxation strength in the Sb-PET has the higher values and wider distribution than that in Ge-PET. Furthermore, Sb-PET exhibited electrically softer. These results are attributed to the stiffening amorphous parts by the entanglement network in Ge-PET.

Keywords: catalyst, dipolar relaxation strength, PET, relaxation time

Introduction

Processing of poly(ethylene terephthalate) (PET) has been extensively studied during these five decades, since PET is a suitable material in order to obtain the products having a desired specification. Characteristic properties are attained by molecular orientation and the products can be molded in various shapes, such as fibers, films and bottles through processing. Orientation of PET is induced by stretching in the rubbery region, i.e. between the glass transition temperature (T_g) and the temperature at which the onset of rapid thermal crystallization occurs. Special attention has been paid to the structural reorganization in the above temperature region, since characteristic features of the final products are affected by the processing conditions.

Germanium and antimony catalyst systems are often used as the main catalysts in the production of PET resin. Catalyst remnant affects the final product through the melt polymerization. For example, bottle blow molding grade is usually germanium catalyst

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PET (Ge-PET), and the film grade is antimony catalyst PET (Sb-PET). It should be noted that resin Ge-PET is not always replaceable by resin Sb-PET, besides a large difference in their prices. This indicates that some characteristic difference in both PETs should exist. However, the any known reference is the difference in the crystallization.

After the polymerization process, a part remain of antimony catalyst still mixed in PET [1, 2]. This catalyst remnant affects the chemical reaction at high temperatures during processing. Esterification and transesterification take place during solid state polycondensation in PET [3]. The polycondensation rate in the solid state depends on both chemical and physical processes. Various parameters, such as: temperature and time, crystallinity, end-group content, initial molecular mass, and the catalyst system used for its preparation influence polycondensation [4–7]. Although it has been extensively studied whether very small quantities (in the order of ppm) of several metals such as Ge and Sb in polymer exist or not [8, 9], attention has only been paid to the investigation of the effects on the mechanism of thermal decomposition.

The aim of the study is to gain insight concerning on the different relaxation behavior in both commercial PETs polymerizied using Sb and Ge catalyst systems above their T_g. Since PET is a polar polymer, thermally stimulated current (TSC) measurement is a suitable technique. This present work provides further experimental data which show the different effect of Ge and Sb catalyst systems on the TSC in both PETs. The evolution of relaxation times and the mobility of the molecular chain are discussed. This will be of value from a scientific viewpoint, and that of processing application.

Experimental

Materials

Two kinds of commerical grade PET resins polymerized using a main catalyst system either Sb(OAc) or GeO_2, were obtained from Mitsui Chemical Co., Japan. In this study, the former PET was designated as (Sb-PET) and the latter as (Ge-PET). Intrinsic viscosity, [η], of both PETs was 0.83 dL g^{-1} at 30°C in tetrachloroethane/phenol (50/50 mass/mass). According to the manufacturer's report, the molecular mass distribution of both samples was the same. Unstretched sheet with a thickness about 200 μm was prepared using a single-screw extruder at 280°C. The take-up reel was kept at room temperature and the take-up speed was kept at the same speed as the extruder sheets. The unstretched sheet was biaxially stretched with the speed of 5 cm s^{-1} after annealing at 90°C for 5 min. The thickness of stretched sheet thus obtained was 20 μm. Details of sample preparation were described elsewhere [10].

Methods

The TSC measurements were performed at the heating rate of 4°C min^{-1}. Current intensity was measured by means of a Keithley-617 electrometer. Three TSC methods were used in this experiment, i.e. (1) spontaneous, (2) global and (3) thermal sampling (TS). (1) Spontaneous TSC experiments were performed by measuring the current during constant heating rate without polarization before. (2) For global-polarization experiments, the sample was polarized by a static electric field (E_p) over a temperature range from polarization temperature (T_p) down to $T_0 << T_p$ in order to freeze dipolar orientation where T_0 is lower than room temperature. The electric field was then turned off and the depolarization current was recorded when the temperature was increased at the constant rate. (3) For thermal sampling (TS) TSC, the E_p about 250 kV cm^{-1} was applied to a very narrow temperature range. The electric field was turned off when the temperature became T_p–0.2°C. The sample was depolarized at the depolarization temperature $T_d = T_p - 1$°C for 5 min. The fractional dipolar orientation was then frozen-in by quenching the sample down to $T_0 << T_p$. The depolarization was subsequently recorded in the same way as for the global experiment. The details of experimental procedure were essentially the same as those in our previous study [11].

Results and discussion

Spontaneous TSC curves of Ge-PET and Sb-PET unstretched films are shown in Fig. 1. The peak of Sb-PET is higher than that of Ge-PET. Those peaks are associated with α relaxation process correspond to the main glass transition of the material. Molecular relaxation of the PET chains associates with motion of the dipoles along these chains. Current is consequently created by this motion of dipoles in the sample thickness direction. A smaller peak of Ge-PET related to the smaller dipole motion, which may be attributed to stiffening of amorphous regions and or the more rigid molecular chain in the Ge-PET. The low negative peak associated to ρ relaxation process corresponds to a constraint state. The smaller peak area in Ge-PET curve correlates with a smaller depolarization. It might correspond to the higher orientation in the plane of Ge-PET film, since it is known that a higher ordered chain prevents dipole relaxation in the thickness direction [11].

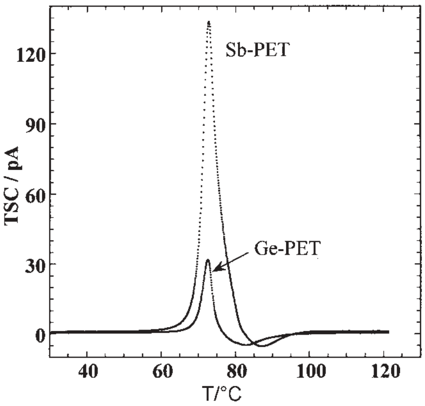

Fig. 1 Spontaneous TSC curves of unstretched PET films. Heating rate of 4°C min^{-1}

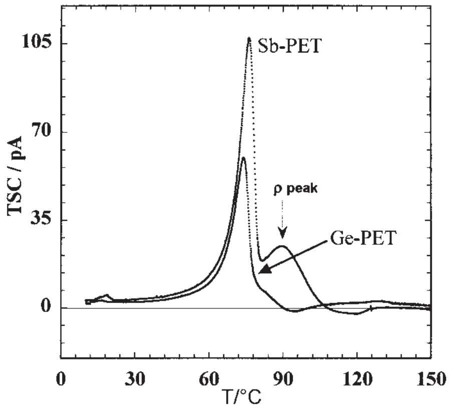

Fig. 2 TSC curves of unstretched PET films after global polarization. T_p=100–30°C, E_p=48 kV cm^{-1} for 3 min

The global polarization TSC of unstretched films is shown in Fig. 2. The ρ peak becomes positive in the Sb-PET. This ρ peak is attributed to the second T_g. The second T_g is related to dipolar behavior attributing to a constraint state [10, 11]. The curves in Fig. 2 can be considered as a sum of elementary peaks. In this experiment, an elementary peak was isolated assuming that ΔT_p=0.2°C is sufficiently small. The elementary peak can be analyzed using the Bucci–Fieschi–Guidi (BFG) analysis [12]:

$$\tau(t)=\int_t^{\infty} J(t')\mathrm{d}(t')/J(t) \tag{1}$$

where $\tau(t)$ is the relaxation time at the time t, $J(t)$ being the current density of elementary TSC spectrum at the same time t.

In our experiment, time and temperature are related by a linear relationship. On this account, the relaxation time is temperature dependent and it can be written as $\tau(T)$. The temperature evolution of the relaxation time usually can be approximated by the Arrhenius equation:

$$\tau(T)=\tau_o\exp(E/kT) \tag{2}$$

where τ_o is a pre-exponential factor, k is the Boltzmann's constant, and E is the apparent activation energy for the process.

Arrhenius plots can be found from each elementary spectrum of thermal sampling TSC. These plots have revealed that the elementary relaxation times isolated in the complex relaxation mode associated with the glass transition of polymers which obey a compensation law. The Arrhenius lines converge into a single point, this point is called a compensation point. The compensation line is defined in frequency–temperature space by two phenomenological parameters: the compensation temperature (T_c) and the relaxation time (τ_c).

$$\tau_o=\tau_c\exp(-E/kT_c) \tag{3}$$

Substituting Eq. (3) into the Arrhenius Eq. (2), one finds:

$$\tau(T)=\tau_c\exp\{E/k\,(1/T-1/T_c)\} \tag{4}$$

This equation suggests that at the compensation temperature ($T=T_c$), relaxation occurs with a single relaxation time τ_c. The Arrhenius lines all converge into a single point at T_c. A plot of logarithm of relaxation time as a function of inverse temperature is called BFG plot. BFG plots for the unstretched Ge-PET and Sb-PET is shown in Fig. 3. The slope and intercept of this plot gives activation energy and τ_o. These values are given in Table 1. Since these two parameters are the characteristic of the materials, the Ge-PET and Sb-PET are having different characteristics.

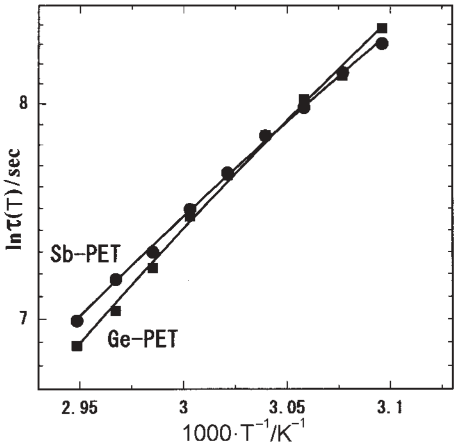

Fig. 3 BFG plots in the unstretched Ge-PET and Sb-PET. T_p=70°C, E_p=70 kV cm^{-1} for 4 min

It is thought that physical aging may occur during polarization. Physical aging is found mainly in amorphous polymers. When the crystallinity is developed in polymers such as PET, physical aging is markedly reduced [13], even if crystallinity is moderate. Fiore *et al.* [2] also showed the effect of antimony catalyst remnants on the cystallization of PET. The PET without removal catalyst remnant showed the higher crystallinity after annealing. The effect of Sb_2O_3, which is used as the main catalyst in the production of PET by melt polymerization, was also studied by Kokkalas and co-workers [3]. They observed that the catalyst works efficiently even in the solid state. The molecular-number average molecular mass of the PET after annealing increased as much as 122% in the PET with Sb_2O_3 catalyzed. When the catalyst was absent, the molecular mass of the same PET under the same conditions increased around 23%. From the aforementioned reports, it is obvious that catalyst in PET affects crystallization and/or changes the molecular weight after annealing. The above factors have markedly effect on the molecular relaxation. Since all the experiments for thermal sampling were carried out in the same thermal histories, it is thought that the different relaxation time distribution shown in Fig. 3 can be attributed to the different catalyst system. The details on the distribution relaxation time will be discussed later.

Table 1 Pre-exponential factor and activation energy of unstretched PET, calculated from BFG plots

Sample	T_p/°C	T_m/°C	τ_o/s	E/eV
Ge-PET	70	75.7	7.6E–11	0.88
Sb-PET	70	75.4	3.5E–9	0.77

Figure 4 shows the elementary spectra isolated in stretched Ge-PET by thermal sampling experiments. T_p=90–120°C in steps of 5°C. A different specimen was used for each spectrum and the same E_p=250 kV cm^{-1} was applied. Each elementary spectrum can be considered as a single Debye peak. In solid polymers, relaxation processes are in most cases distributed, thus we applied the thermal sampling technique to analyze the TSC spectra due to the distributed processes. The relaxation behavior was compared for Ge-PET and Sb-PET. Sb-PETs show the higher TSC peaks than that of Ge-PETs for the equivalent treatment. As stated in the experimental section, the molecular masses and molecular mass distribution in both PETs are the same. On this account, it is supposed that number of end dangling chains is the same. It has been reported that a same molecular origin can be considered as responsible for the mechanical and dielectric relaxations in accordance with the compensation law analysis [14]. Based on the above facts, TSC peaks height shown in Fig. 4 is considered to reflect the different dielectric relaxation process coming from their difference microstructures.

The T_p dependence of the activation energies in the stretched PET obtained from thermal experiments is shown in Fig. 5. There are various methods suggested for use in determining the activation energy [15–18]. These methods use the lower, upper and both half width temperatures of TSC peaks. Absolute value of the activation energies calculated by using those methods can be different. However, taking one method of them to calculate the activation energy would be sufficient for our aim. The data presented in Fig. 5 are calculated from Eq. (15) in reference [18].

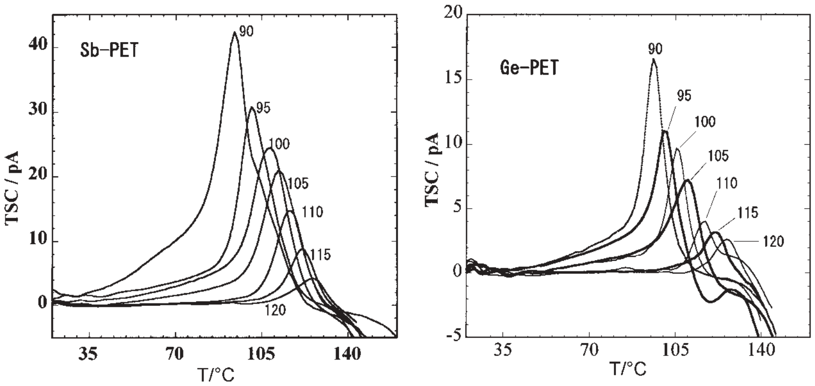

Fig. 4 TSC curves from TS experiment of stretched Sb-PET and Ge-PET films. E_p=250 kV cm^{-1}, T_p is shown in the figure

$$E=\{(ST_m)\}/\{8881(T_m-S)\}-(T_m/9439) \tag{5}$$

where S is the temperature in which the TSC curve has the value of 1/4 peak height at the high-temperature side of the curve, giving the value of E in eV.

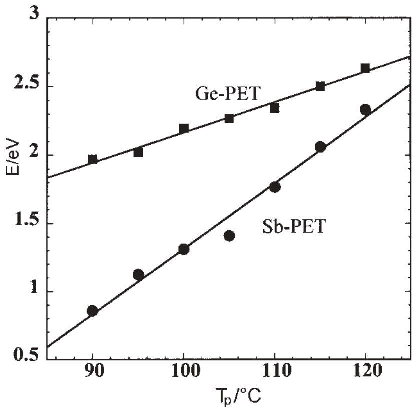

Fig. 5 Plot of activation energy (E) as a function of polarization temperature (T_p) in the stretched PET films. Thermal sampling was done with E_p=250 kV cm^{-1} for 3 min

The relative value of activation energy in Ge-PET is higher than that in Sb-PET. Clear difference of activation energy observed in both stretched PET comes from their difference TSC curves. The difference TSC curves is expected coming from the differencen in their microstructures, since all the experimental conditions were same.

Using TSC maximum at the temperature T_m, the relaxation time τ_m can be derived as:

$$\tau_m=\tau(T_m)=\tau_o\exp(E/kT_m)=kT_m^2/\beta E_a \tag{6}$$

where β is the heating rate.

The broadness of the distribution of relaxation time in the current maximum of TSC, τ_m, calculated from Eq. (6) is shown in Fig. 6. Almost constant τ_m values are observed at around 90 s for Ge-PETs, in contrast, τ_m values of Sb-PET decrease with increasing T_p. These data may be correlated with annealing effect during the polarization, where Ge-PET is thermally more stable than Sb-PET. The relatively constant value of τ_m as a function of T_p in Ge-PET suggests that molecular motion occurs homogeneously.

Figure 7 shows the plot of logτ_o *vs.* activation energy from logarithm Eq. (3). The good linearity seen in this plot indicates that the relaxation is governed by a compensation rule. A compensation line can be used to see whether a set of Arrhenius lines obtained at various T_p values converge to T_c. Two segments in logτ_o *vs.* E plot indicate that the respective relaxation obeys the different compensation laws. The coordinates of the compensation point can be calculated from the slope and intercept of the compensation line. The coordinates of the compensation are important because they transcribe the coupling characteristics between the different mode of relaxation observed as individual activated processes in the set of Arrhenius lines. These coordinates can be used to describe

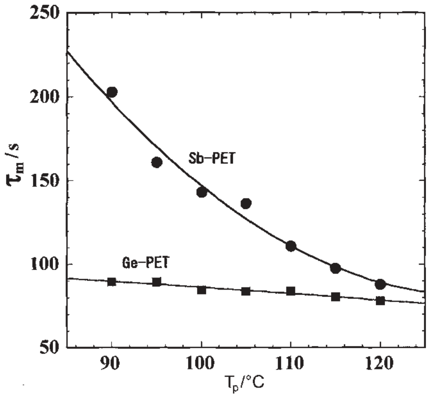

Fig. 6 Dependence of relaxation time at peak current on polarization temperature (T_p) for stretched PET films

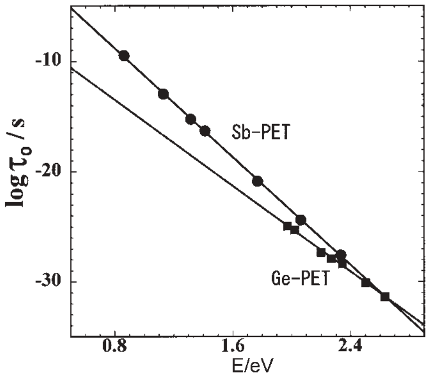

Fig. 7 Plots of pre-exponential factor *vs.* activation energy in the stretched PET films

the fundamental properties of the state of the polymer as influences by the environment of the bonds and polar groups [19]. If the environment structure is 'loose' the contrary of 'ordered' i.e. when molecular mobility is less hindered by the interactive intra-intermolecular surrounding, the entropy of activation is larger. One can calculate degree of disorder (*DOD*) (in unit of cal deg^{-1}) from the compensation point coordinates T_c and τ_c, when T_p is varied [19–21].

$$DOD=100-2[\ln(T_c\tau_c)+23.76] \tag{7}$$

The number 100 is arbitrarily added in order to shift all values to the positive side. Ge-PET has T_c=243°C, τ_c=2.0*E*–6 s and *DOD*=66.23 while Sb-PET has T_c=138°C, τ_c=8.6 s and *DOD*=36.14. *DOD* values can vary from low around 30 and high around 70 for amorphous material [19].

The dipolar relaxation strength ($\Delta\varepsilon$) can be calculated as:

$$\Delta\varepsilon = \sigma/E_p\varepsilon_o \tag{8}$$

where σ is the charge density and ε_o is the permittivity of vacuum.

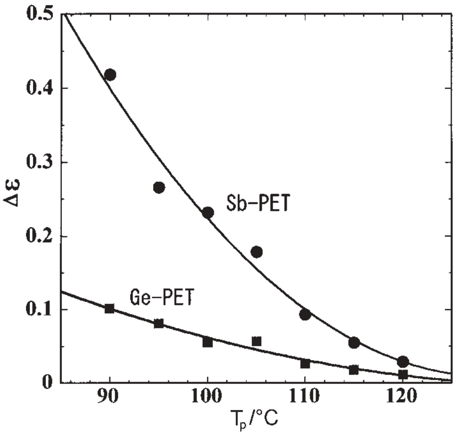

Fig. 8 The change of dipolar relaxation strength (Δε) values as a function of polarization temperature (T_p) in the stretched PET films

Figure 8 shows dipolar relaxation strength values in Ge-PET and Sb-PET as a function of the polarization temperature. In Sb-PET, the values are high and the change of Δε is more significant. For the copolymers, this high value is mainly due to the presence of ρ peak [22]. As can be seen in Fig. 2, the ρ peak appears in Sb-PET, and almost not observable in Ge-PET. Qualitatively, Fig. 8 means that Ge-PET is more stable against the temperature. It is interesting to note that both values decreased by increasing T_p. One could invoke the possibility of annealing effect during thermal sampling polarization. The values in Ge-PET are relatively smaller and the smaller change with T_p. This means that the dipole may be polarized more in the Sb-PET segments, in other words, the molecular segments in Sb-PET are electrically and thermally softer than that in Ge-PET.

Conclusions

The different behavior of Ge-PET and Sb-PET is clearly shown from the TSC data. The real effect introduced by electric field and temperature might modify the fine structure of the material. The decrease in the mobility of chains in the polymer prevents the dipole polarization, leaving a smaller peak in the TSC measurements. It is concluded from the TSC data that the Sb-PET exhibits the higher segmental relaxation. Since the Ge-PET and Sb-PET can be regarded as materially identical, these results are tentatively attributed to the different entanglement network in the both PETs.

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