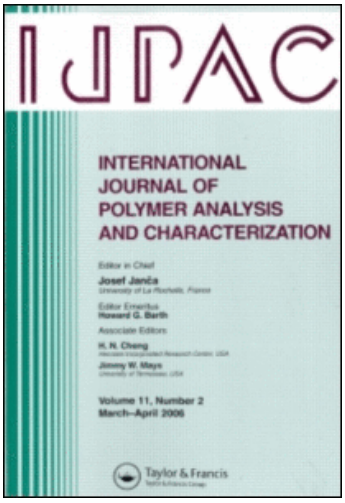

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SHORT COMMUNICATION

Study of the Influence of the Speed of Cooling on the α-Relaxation in Polymers by the Thermostimulated Current Method

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Abstract: Thermostimulated current technique (TSC) was used to investigate the influence of the cooling rate on the α-relaxation in the glass transition range of poly(vinyl-acetate) and poly (ethylene) phase in ethyl-vinyl-acetate (EVA) copolymer. High resolution of TSC allowed the detection of the α-relaxation processes in polyethylene phase. The obtained spectra revealed two peaks, always at the same temperatures, but their maximum intensities are decreasing with the cooling rate. An empirical formula describing the maximum intensity evolution is proposed.

Keywords: Cooling rate; α-Relaxation; TSC (thermostimulated current)

INTRODUCTION

The thermostimulated current (TSC) method, introduced four decades ago to investigate the dielectric properties of doped alkali halides,[1,2] is used as a basic tool to study the dipole reorientation processes.

The TSC measurements have already been used to study crystalline and amorphous insulators, biomedical materials, and organic substances,[3–5] and

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the relaxation properties of dielectric materials in solid state, mainly because TSC allows working in a range of very low equivalent frequencies (10^{-3}–10^{-4} Hz) as well as resolving the transitions that cannot be detected by other techniques.[6]

There are an important number of articles describing the influence of the experimental conditions on the α-relaxation by means of the TSC technique, such as, for example, a study of the dependence of the TSC spectrum on heating rate[7] and a study of the effect of the short-circuiting time and gaseous charge environment.[8]

In this study, our attention was concentrated on the effect of the cooling rate on the α-relaxation process in EVA copolymer.

PRINCIPLE OF TSC TECHNIQUE

The studied sample is exposed to an electrical field E_P, during a polarization time Δt_P, at a polarization temperature T_P to allow the mobile entities to orient themselves to field direction.[6,9–10] The temperature is then decreased (maintaining the field) to reduce the internal motion, thus trapping the polarized dipoles within the material. The electrical field is then switched off, and the sample reheated, allowing the thermal energy to release the "trapped" molecular motion. Consequently, a small current is observed corresponding to one or more types of relaxations.

EXPERIMENTAL SECTION

Measurements were carried out on the commercial ethyl-vinyl-acetate (EVA) block copolymer film standards supplied by Dupont De Nemours, in the form of square sheets (1.2 cm^2), 0.5 mm thick.

Before each experiment, the sample was placed in a measuring cell, which was short-circuited, and degassed in primary vacuum. The cell was then filled with dry helium under a pressure of approximately 0.5 kPa. The current was measured with sensitive electrometer (Keithley 610 C) and recorded by using an X-Y plotter. A platinum temperature sensor PT 100, mounted in the sample holder and adjacent to the film, allows the temperature measurement with a precision of 0.5°C. A heating rate of 7°C/min was applied.

All complex spectra were obtained by exposing the sample to a constant electrical field $E_P = 4.10^5$ V/m during 2 min at a polarization temperature of $T_P = 40$°C. The sample was then cooled with different cooling rates to very low temperature by applying the field E_p.

The field was then switched off at the temperature of approximately −80°C, and the electrodes were short-circuited for 10 mn. Thereafter, the

sample was heated at 7°C/mn to 60°C. In order to check the credibility of the results, all measurements were repeated.

RESULTS AND DISCUSSION

Figure 1 shows the complex spectra obtained by using different values of cooling rate (from quenching to slow cooling). These spectra reveal two quite distinct peaks at around $T_{M1} = -26°C$ and $T_{M2} = 24°C$. The first peak (α_1), which appears at T_{M1}, is attributed to the α-relaxation of polyethylene phase. The second peak (α_2), located at T_{M2}, is attributed to the α-relaxation of the poly(vinyl-acetate) phase.[11–12]

The α_1 and α_2 relaxations are attributed to glass transitions of polyethylene and poly (vinyl-acetate) phases respectively in EVA copolymer.[11–13]

Significant atom movements of the homopolymers main chain (polyethylene and poly vinyl acetate) are associated with these transitions.[6,11–14] The values of maximum current I_{max} corresponding to the two peaks α_1 and α_2 for different values of cooling rate are given in Table I.

The layout of the curve representing I_{max} versus the cooling rate reveals the same evolution for the two peaks (see Figure 2). The maximum

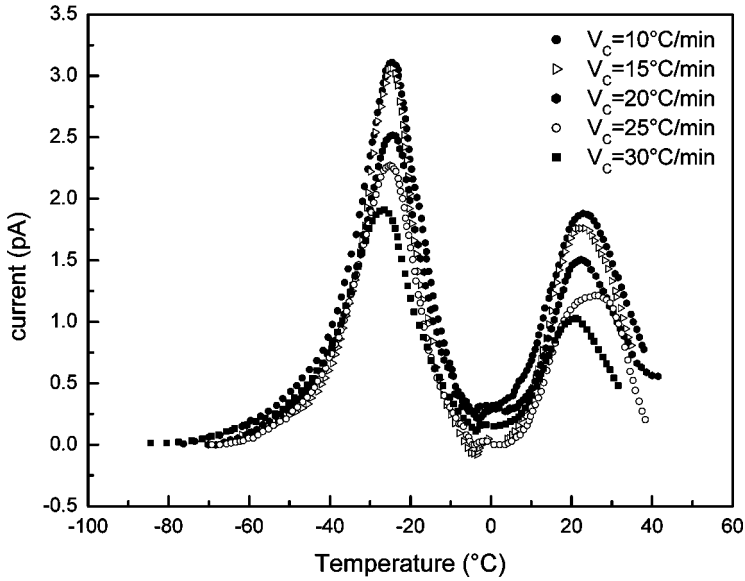

Figure 1. TSC spectra of EVA film for different cooling rates (10–30°C/min), heating rate 7°C/min, polarization temperature 40°C.

Table I. Values of the maximum intensities I_{max} of the two peaks α_1 and α_2 for different values of V_C

	V_C (°C/min)				
	10	15	20	25	30
I_{max}(pA) α_1	3.12	3.00	2.43	2.24	1.80
I_{max}(pA) α_2	1.80	1.75	1.36	1.16	0.88

intensity of the obtained peaks decreased as the cooling rate increased. In contrast, the temperatures corresponding to these maximum intensities remain unchanged. This behavior can be explained by the fact that the faster the cooling rate, the shorter the time necessary for the polarizable entities to be aligned with the electrical field direction. The latter fact brings about a decrease in TSC spectra maximum intensities.

The evolution of the maximum current I_{max} versus the cooling rate V_C is the same for the two peaks. These results allowed establishing an empirical formula describing such evolution:

$$I_{max} = a_2 - \frac{a_1 - a_2}{1 + \left(\frac{V_C}{V_{C0}}\right)^P}$$

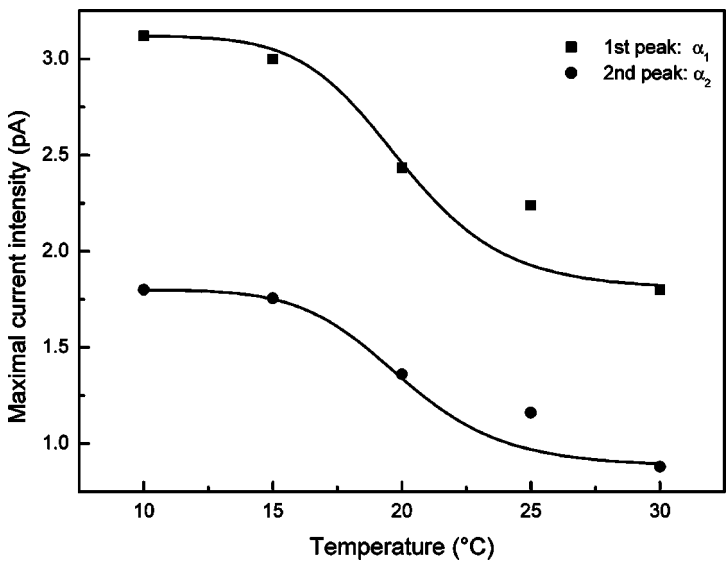

Figure 2. Cooling rate dependence of the maximum current intensity of the TSC peaks.

where a_1 and a_2 represent the maximum currents for the rapid and slow rate, respectively, and V_{C0} and P are empirical values (V_{C0} and P in the case of polyethylene and poly (vinyl-acetate) are equal, respectively, to 20°C/min and 10).

CONCLUSIONS

- Measurements of TSC spectra carried out with the copolymer films EVA revealed two distinct peaks around glass-rubber transitions of polyethylene and poly(vinyl-acetate).
- The intensity of the obtained peaks decreased as the cooling rate increased. On the other hand, no influence with regard to the maximum temperatures has been observed.
- Finally, the empirical formula that describes the peaks' maximum evolution has been established.

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