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# THERMOACTIVATIONAL SPECTROSCOPY OF THE HIGH IMPACT POLYSTYRENE BASED COMPOSITE FILMS

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The relaxation processes in the high impact polystyrene (HIPS) films filled with 2, 4, 6 vol.% of titanium dioxide ($TiO_2$) of the rutile modification have been studied using the thermally stimulated depolarization current (TSDC) technique. Three relaxation processes were observed in the composite HIPS films. The first one (α-relaxation peak) appeared at about 93 °C and represented the glass transition. The second peak ρ was a high-temperature part of the first one and overlapped it. The ρ peak was caused by the release and subsequent motion of excess charges deposited during the electret preparation or the polarization process. The third peak appeared at about 150 °C and occurred only in the spectra of the composite films. The overlapping peaks were separated by the thermal cleaning technique. The subsequent application of the numerical methods (the Tikhonov regularization technique) allowed to determine the activation energy of the second process and to compare the obtained value with the corresponding data on the dielectric relaxation.

**Keywords:** thermoactivational spectroscopy, high impact polystyrene, titanium dioxide

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# ТЕРМОАКТИВАЦИОННАЯ СПЕКТРОСКОПИЯ КОМПОЗИТНЫХ ПОЛИМЕРНЫХ ПЛЕНОК НА ОСНОВЕ УДАРОПРОЧНОГО ПОЛИСТИРОЛА

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С помощью метода токов термостимулированной деполяризации (ТСД) исследованы релаксационные процессы в пленках ударопрочного полистирола (УПС) без наполнителя и с различным содержанием диоксида титана $TiO_2$ (2, 4, 6 об.%). На кривых тока ТСД, полученных для композитных пленок, обнаружено три пика. Первый (α-релаксация) возникает при температуре около 93 °С и соответствует переходу вещества из стеклообразного состояния в высокоэластическое. Второй (ρ-пик) появляется как высокотемпературное плечо α-пика и соответствует процессу высвобождения и

движения избыточных носителей заряда. Наличие третьего пика при температуре около 150 °С характерно только для композитных пленок УПС. Разделение перекрывающихся α- и ρ-пиков проведено методом частичной термоочистки. Последующее применение регуляризующих алгоритмов Тихонова позволило определить энергию активации второго процесса и сравнить полученное значение с результатом, полученным методом диэлектрической спектроскопии.

**Ключевые слова:** термоактивационная спектроскопия, ударопрочный полистирол, диоксид титана

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## Introduction

The thermally stimulated depolarisation current (TSDC) technique is commonly used for the investigation of charge carrier relaxation in dielectrics. It is widely applied as a complement to the frequency domain and the time domain dielectric spectroscopy.

The basic experiment includes two main steps:

the first one is that sample material is polarised in a D.C. field $E_p$ for a time $t_p$ at a high temperature $T_p$. At this temperature particular dipolar units or charge carriers are free to move, the former orient in the field and the latter drive towards the electrodes or internal boundaries in heterogeneous materials forming a space charge;

the second one is that the sample is shorted at a low temperature. Under this condition the relaxation times of the species of interest are much longer than the measuring time, and finally it is linearly heated, while the depolarisation current is recorded. During the heating, oriented dipolar units turn back to their equilibrium position and accumulated charge carriers return to a uniform distribution. Due to thermal stimulation, the polarisation decay is more and more accelerated [1 – 3].

A TSDC measurement corresponds to a loss-versus-temperature measurement at a very low equivalent frequency of $10^{-2}$ to $10^{-3}$ Hz [4]. Here, an attempt is made for a more detailed description of the relaxation processes in the composite high-impact polystyrene films by means of the thermally stimulated depolarization currents (TSDC) method.

## Experimental details

High impact polystyrene (HIPS-0801, GOST (Russian State Standard) 28250-89E) without filler as well as composite HIPS films were used in the present study. HIPS contains 4 to 6 % butadiene rubber, the butadiene rubber particles form agglomerates from 0.1 to 1 μm in size, and they are embedded in the polystyrene matrix [5].

Titanium dioxide ($TiO_2$) powder of the rutile modification (R-01, GOST 9808-65, specific surface area is 15 $m^2/g$, particle size is from 0.1 to 0.8 μm) was used as a filler. Mixing of HIPS and $TiO_2$ was performed using a laboratory rolling mill under heating at (175 ± 5) °C for 3 min. Films of pure HIPS as well as HIPS with $TiO_2$ contents of 2, 4, 6 vol.% were manufactured by melt pressing according to GOST 12019-66 at (170 ± 5) °C for 5 min. The films with thicknesses ranging from 350 to 450 μm were investigated.

For electrical measurements, circular aluminum electrodes (12 mm in diameter, about 50 nm thick) were evaporated onto both sides of the films.

Thermally stimulated depolarization currents (TSDC) were recorded with a Keithley model 5617 electrometer and the Novocontrol QUATRO cryosystem. TSDC measurements (heating rate was 2.8 K/min) were performed after poling with the field $E_p = 0.67 \cdot 10^6$ V/m at $T_p$ = 110 °C for $t_p = 10$ min, subsequent rapid cooling to room temperature and short-circuiting.

## Experimental results

TSDC thermograms of unfilled HIPS and HIPS with 2 and 4 vol.% $TiO_2$ are shown in Fig. 1. Three peaks could be observed for composite HIPS films. The α peak appears at about 93 °C and denotes the glass transition [6, 7]. The second ρ peak is caused by the release and subsequent motion of excess charges deposited during the electret preparation or the polarization process [3]. It is a high-temperature

part of the α peak and overlaps it. The third peak appeared at about 150 °C occurs only in the composite films.

In order to separate the α and ρ peaks the peak-cleaning technique was applied according to the following procedure: after passing the first peak the heating was interrupted. Then, the sample was quickly cooled down followed by a second heating where only the response of the second process was expected [6].

The results of the peak-cleaning technique applied to the pure HIPS samples with an attempt to separate the α relaxation (related to the glass transition) and the higher-temperature relaxation process is shown in Fig. 2 (blue curves). Fig. 3 represents the results for composite HIPS films with 4 vol.% of $TiO_2$.

After the ρ peak was separated from the α peak, the activation energy $E_a$ for the ρ peak was determined using the Tikhonov regularization technique [8, 9]. For this purpose, the TSDC measurement was performed for two different heating rates under identical conditions for composite HIPS films with 4 vol.% of $TiO_2$ (Fig. 4).

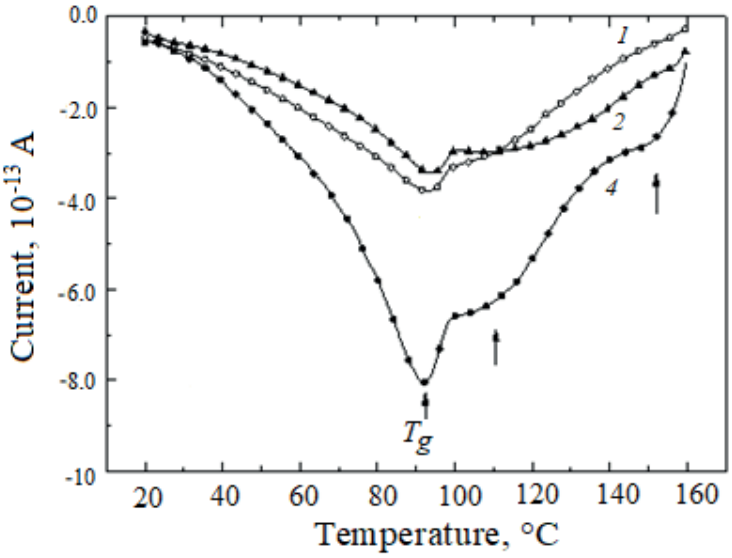


Fig. 1. Thermally stimulated depolarization current (TSDC) spectra of pure HIPS (*1*) as well as of the HIPS with 2 (*2*) and 4 (*4*) vol.% of $TiO_2$ (heating rate β = 3 K/min); $T_g$ is the glass transition temperature

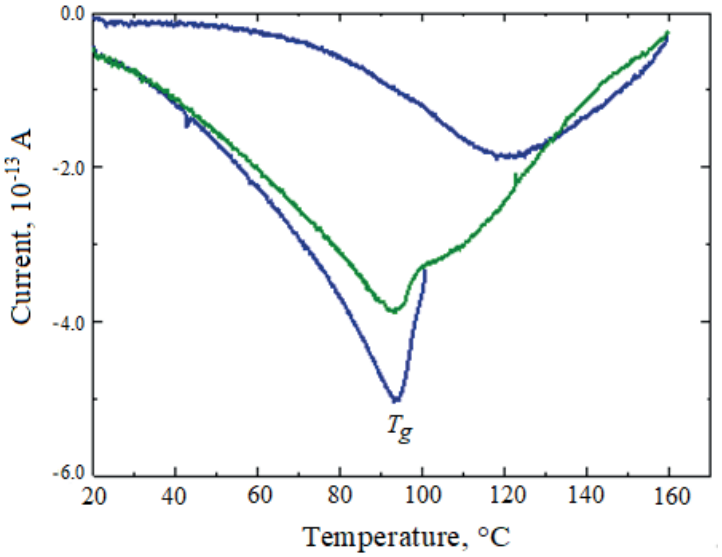


Fig. 2. The peak cleaning technique (blue curves) applied to the pure HIPS samples (heating rate β = 3 K/min) and shown together with the initial TSDC spectrum (a green curve)

This method allows one to obtain information about values of the activation energy $E_a$ and the effective frequency factor $\omega_e$. The energy distribution $G(E)$ was calculated from the current density $J(T)$. The determination of the distribution function $G(E)$ using the experimental TSDC curves represents the ill-posed problem and could be solved by means of numerical calculations (here the Tikhonov regularization technique was used) [8, 9].

The effective frequency factor $\omega_e$ was varied until the peak positions of the energy distribution functions $G(E)$ coincide. This procedure was the criterion for the correct choice of the effective frequency factor $\omega_e$. The calculated activation energy value yields $E_a = 1.10 \pm 0.05$ eV for the composite HIPS films with 4, 6 vol.% (Figs. 5 and 6). This value was in a good agreement with the activation energy calculated by means of the dielectric relaxation spectroscopy (DRS). At temperatures from 105 to 130 °C the activation energy of 1.1 eV was found [6, 10].

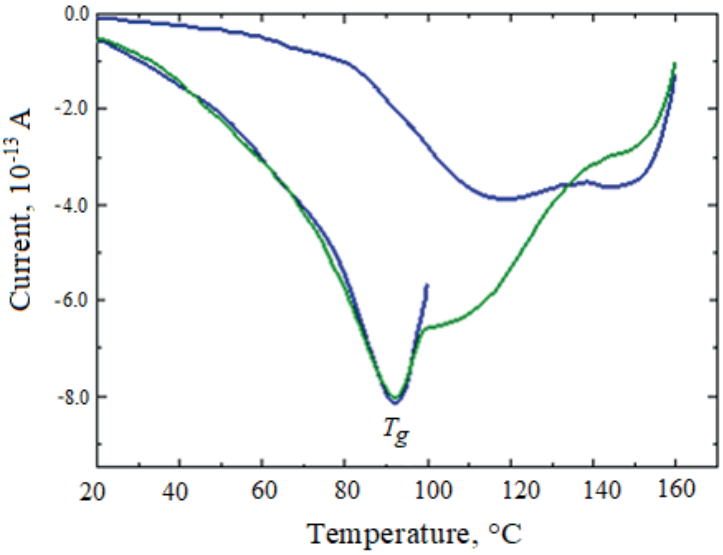


Fig. 3. The peak cleaning technique (blue curves) applied to the HIPS samples with 4 vol.% of $TiO_2$ (heating rate $\beta = 3$ K/min) and shown together with the initial TSDC spectra (a green curve)

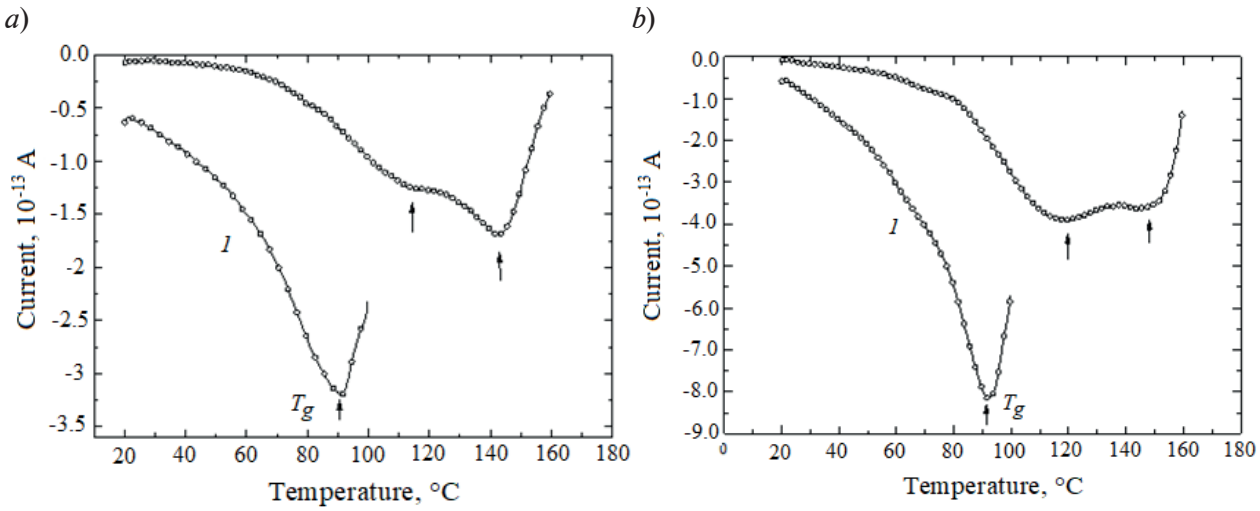


Fig. 4. Thermally stimulated depolarization current (TSDC) spectra (both curves) of the HIPS with 4 vol.% of $TiO_2$ for two different heating rates β: 1 K/min (*a*) and 3 K/min (*b*); curves *1* show the α peaks obtained before (see explanation in the text)

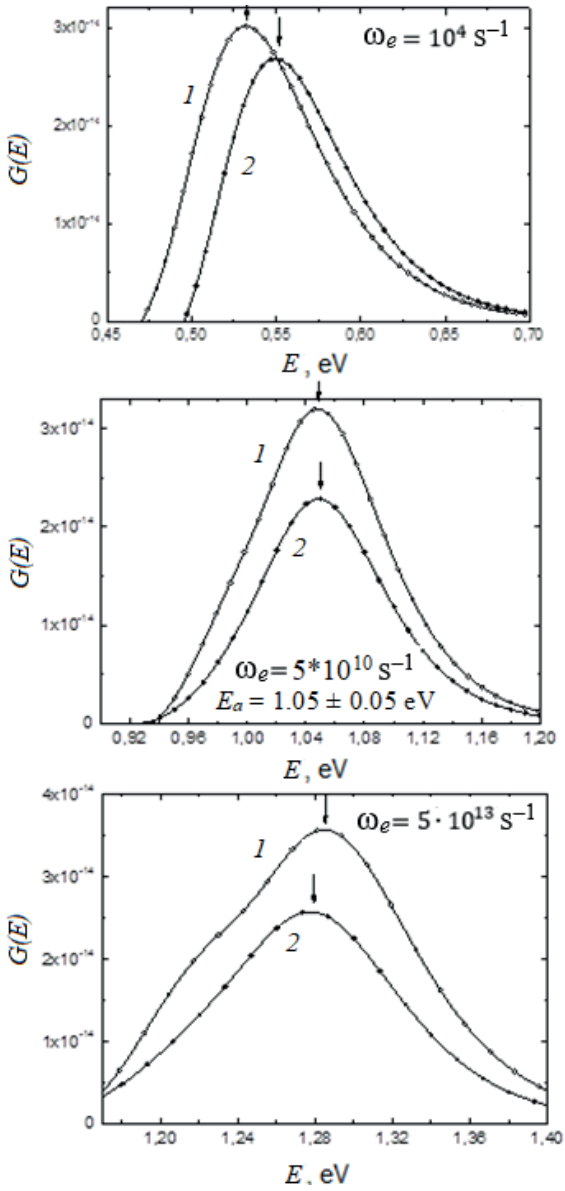


Fig. 5. Determination of the activation energy by means of the Tikhonov regularization technique for HIPS with 4 vol.% of $TiO_2$ using TSDC curves for 2 heating rates β, K/min: 1.0 (*1*) and 2.8 (*2*); $\omega_e$ is the obtained effective frequency factor; $E_a$ = 1.05 ± 0.05 eV

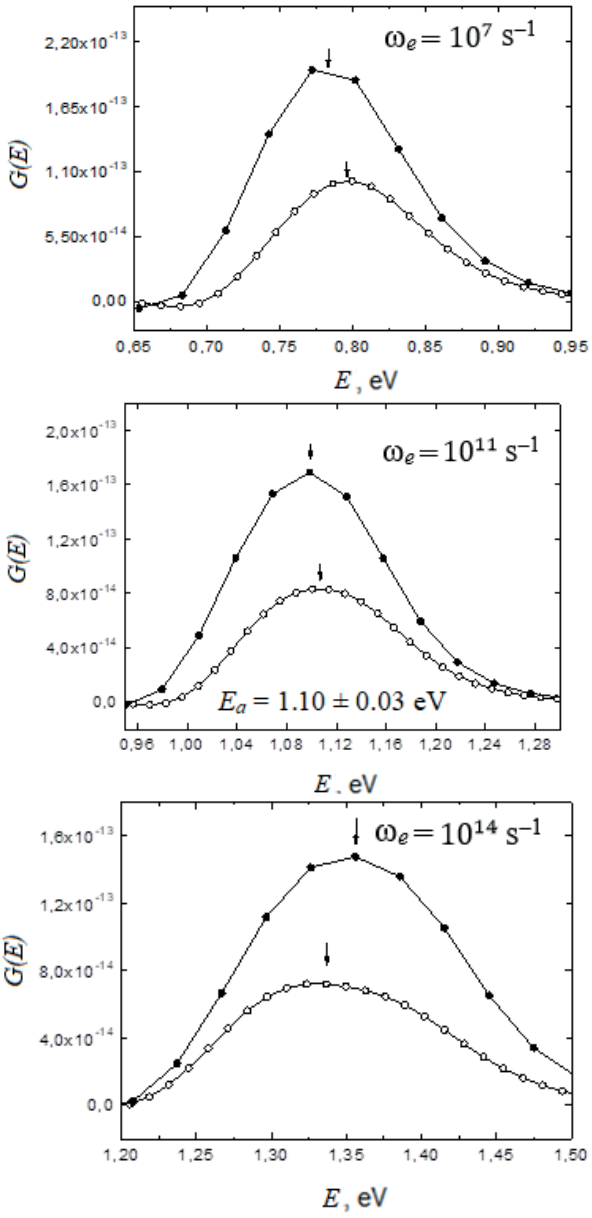


Fig. 6. The data similar to those shown in Fig. 5 but for HIPS with 6 vol.% of $TiO_2$; $E_a$ = 1.10 ± 0.03 eV


## Summary

Three relaxation peak processes have been observed in composite HIPS films with $TiO_2$ inclusions using the TSDC method:

(*i*) the α peak at about 93 °C which denotes the glass transition;

(*ii*) the ρ peak appears as the high-temperature side of the α peak;

(*iii*) the peak at about 150 °C for composite HIPS films.

The peak-cleaning technique allowed separating the two (α and ρ) superimposed peaks. The Tikhonov regularization technique was applied in order to determine the activation energy for the ρ peak:

$$E_a = 1.10 \pm 0.05 \text{ eV}$$

for HIPS films with 4 and 6 vol.% of $TiO_2$.

The process with the same activation energy of 1.1 eV has been determined by means of the dielectric relaxation spectroscopy (DRS).

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