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DIELECTRIC RELAXATION SPECTROSCOPY IN THE HIGH-IMPACT POLYSTYRENE/TITANIUM-DIOXIDE COMPOSITE FILMS

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The relaxation processes in high-impact polystyrene (HIPS) films filled with titanium dioxide (TiO_2) of the rutile modification have been investigated by means of dielectric relaxation spectroscopy (DRS) supplemented by differential scanning calorimetry (DSC). Films with 2, 4, 6 and 8 vol.% TiO_2 were compared to each other and to unfilled samples. Above the glass transition one relaxation became visible for unfilled HIPS. It could be identified as the α relaxation, related to the onset of micro-Brownian motions at the glass transition. The low-frequency (LF) process (which superimposed with α relaxation near T_g) was observed in all TiO_2 containing films. The LF process for composite films was not uniform and showed Arrhenius behavior. At lower temperatures (up to about 130 °C) an activation energy of 1.1 eV was found, whereas in the limit of high temperatures, and particularly for higher TiO_2 content the activation energy was 2.4 eV.

Keywords: dielectric spectroscopy, high-impact polystyrene, titanium dioxide, composite film

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ДИЭЛЕКТРИЧЕСКАЯ РЕЛАКСАЦИЯ В КОМПОЗИТНЫХ ПЛЕНКАХ НА ОСНОВЕ УДАРОПРОЧНОГО ПОЛИСТИРОЛА С ВКЛЮЧЕНИЯМИ ДИОКСИДА ТИТАНА

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Методом диэлектрической спектроскопии проведено исследование релаксационных процессов в композитных пленках на основе ударопрочного полистирола (УПС) с диоксидом титана TiO_2 в качестве наполнителя. Сравнивалось поведение пленок УПС без наполнителя и композитных пленок с разным содержанием TiO_2 (2, 4, 6 и 8 об.%). Для пленок УПС без наполнителя установлено наличие одного релаксационного процесса (α-релаксация). Для композитных пленок обнаружен неоднородный низкочастотный релаксационный процесс, подчиняющийся закону Аррениуса. Значения энергии активации, рассчитанные для низких (до 130 °С) и высоких (свыше 130 °С) температур, составили 1,1 и 2,4 эВ, соответственно.

Ключевые слова: диэлектрическая релаксация, ударопрочный полистирол, диоксид титана, композитная пленка

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Introduction

Titanium dioxide (TiO_2) used as a filler in the present study serves as an additive for different polymeric materials in order to modify their crystallinity and morphology, change their elastic modulus, and increase their permittivity or conductivity, to improve their thermal stability.

Titanium dioxide exhibits a high dielectric constant as well as very low conductivity. Therefore, composite materials of an insulating polymer with TiO_2 fine particles are considered as dielectric materials with adjustable permittivity and conductivity for electrical and electronic applications [1–6].

Scientific interest has mostly been focused on structural investigations and mechanical properties of the polystyrene (PS) composites as it is an important engineering material. High-impact polystyrene (HIPS) is a rubber-modified version of PS in which higher toughness is achieved by incorporation of micron-sized polybutadiene-rubber particles. [7, 8].

Here, an attempt was made for a more detailed investigation of the relaxation processes in the pure and composite HIPS films.

Experimental details

High-impact polystyrene (HIPS-0801, GOST (Russian State Standard) 28250-89E) contains from 4 to 6 % of a butadiene rubber. 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 between 0.1 and 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 and 8 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 as received.

Dielectric spectra were recorded in the temperature range between 20 and 160 °C and in the frequency range from 0.1 Hz to 1 MHz with a Novocontrol ALPHA high-resolution dielectric analyzer and a Novocontrol QUATRO cryosystem, where the sample holder was immersed in a dry nitrogen-gas stream. The data was acquired as a function of frequency through a series of ascending temperatures (usually 5 K steps, with an accuracy of ±0.1 K).

For differential scanning calorimetry (DSC), a PerkinElmer Pyris Diamond differential scanning calorimeter was employed. For electrical measurements, circular aluminum electrodes (of diameter 12 mm and thickness about 50 nm) were evaporated onto both sides of the films.

Experimental results

The temperature dependence of the dissipation factor tan δ of pure HIPS and HIPS with different content of TiO_2 is shown in Fig. 1.

Two relaxation regions can be observed. The α relaxation at about 120 °C is present in all samples and marks the onset of micro-Brownian motions at the glass transition. The temperature dependence of this lower-temperature (LT) process confirms its relation to the glass transition. The high-temperature (HT) relaxation at about 150 °C (Fig. 1) exists only for composite HIPS films [9].

The frequency dependence of the dielectric loss of pure HIPS is plotted in Fig. 2. The peak is shifted to higher frequency with increasing temperature.

The plot of the loss-peak frequency f_{max} versus the inverse temperature bends towards the glass transition according to the Vogel – Fulcher – Tammann (VFT) law (Fig.3)

$$\tau_{max}(T) = \tau_{max,0} \exp \frac{E_a}{k(T - T_V)},$$

where the inverse frequency factor $\tau_{max,0}$, the activation energy E_a and the Vogel temperature T_V are fit parameters.

The thermal glass transition appears at a temperature where the relaxation time is approximately 100 s [10]. This circumstance is taken here as the criterion for the determination of T_g in Fig. 4: the extrapolation of the VFT line to τ = 100 s gives T_g = 92.8 °C.

By means of differential scanning calorimetry (DSC) T_g values between 97.1 and 99.4 °C were obtained for HIPS, no correlation with filler content was visible (Table 1).

For unfilled HIPS the glass transition

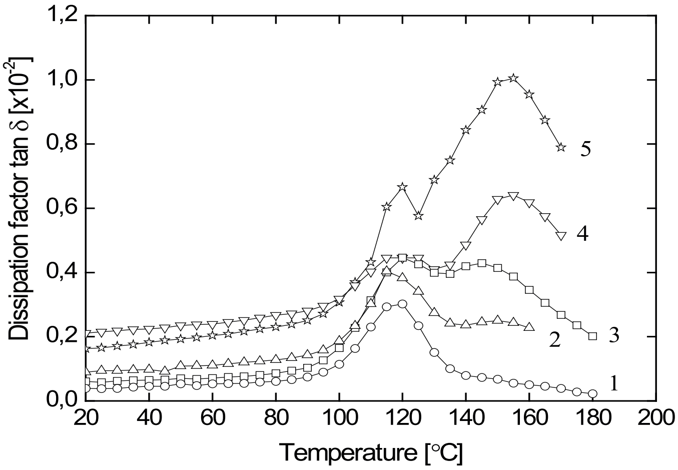

Fig. 1. Temperature dependence of the dissipation factor tan δ at 1 kHz for pure HIPS and HIPS with TiO_2 contents (*1* – pure HIPS, *2* – 2 vol.%, *3* – 4 vol.%, *4* – 6 vol.%, *5* – 8 vol.%). The data points are connected only for guiding the eyes

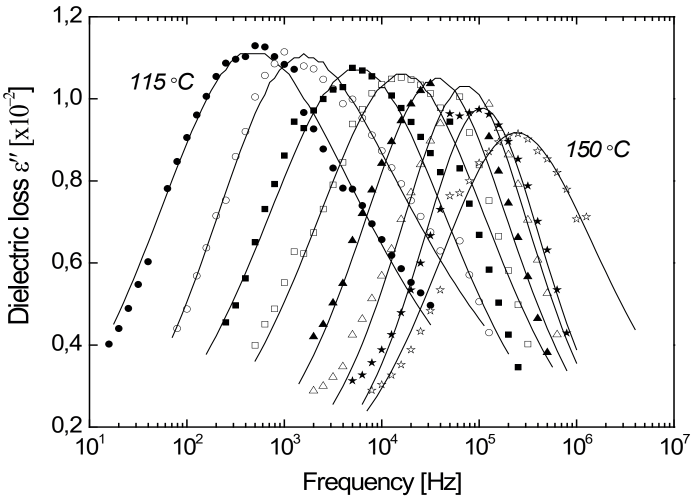

Fig. 2. Frequency dependences of the dielectric loss of pure HIPS at selected temperatures (5 K step) as indicated. The data are fitted with the Havriliak – Negami (HN) function (solid lines)

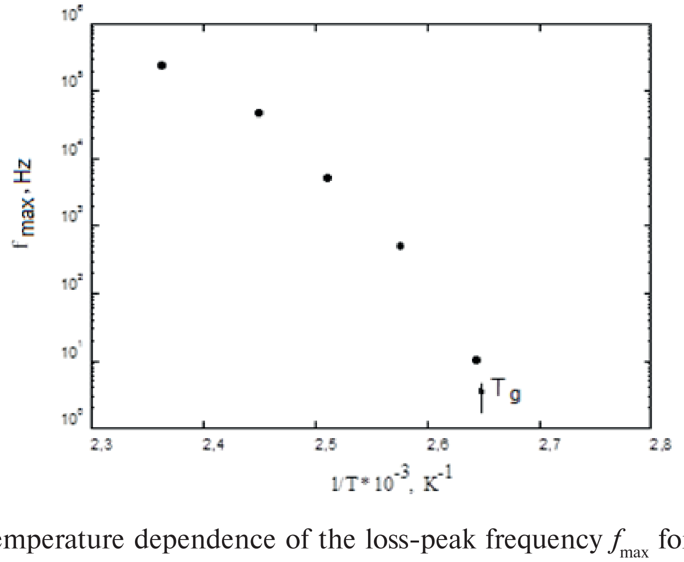

Fig. 3. Temperature dependence of the loss-peak frequency f_{max} for pure HIPS

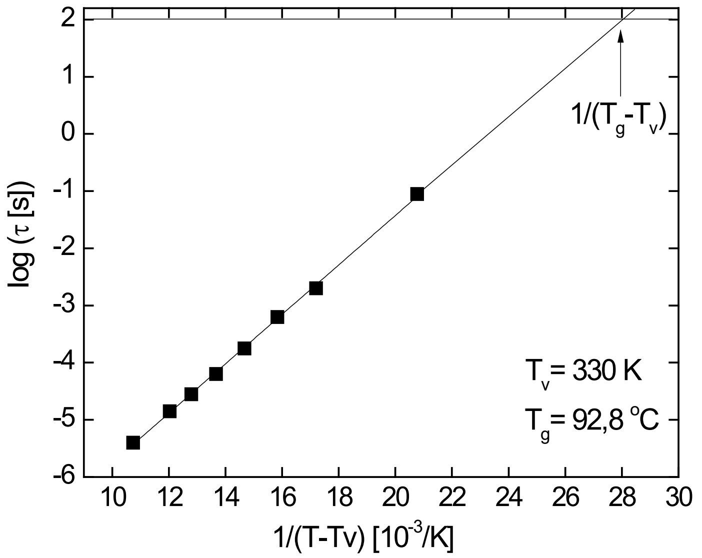

Fig. 4. VFT plot of the parameter τ obtained from the HN fits of Fig. 2

Table 1

DSC results for unfilled HIPS and HIPS with different TiO_2 contents

Filler content, vol. %	Glass transition temperature T_g, ±0.1 °C
0	98.7
2	97.1
4	99.0
6	99.4
8	97.9

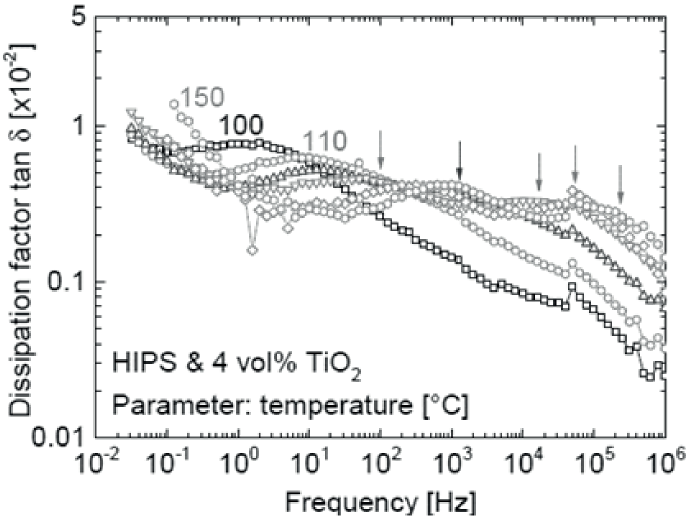

Fig. 5. Frequency dependence of the dissipation factor of HIPS with 4 vol.% TiO_2 at selected temperatures as indicated (10 K steps). The arrows mark the positions of the α relaxation peaks on unfilled HIPS [6]

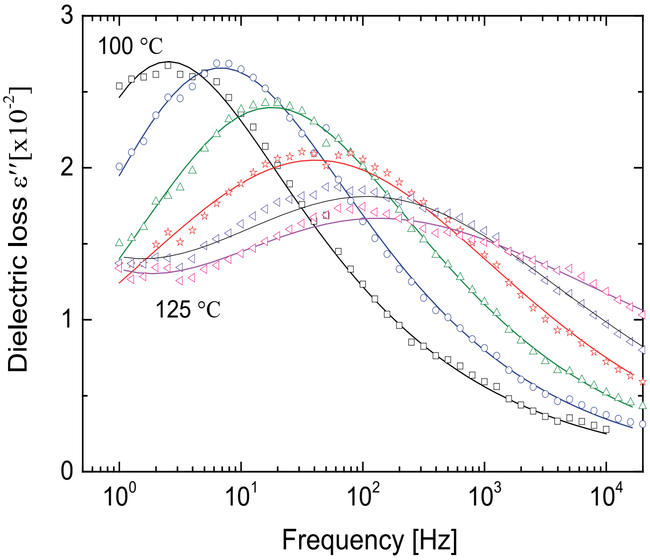

Fig.6. Frequency dependence of the dielectric losses ε" of HIPS with 4 vol.% TiO_2 at selected temperatures

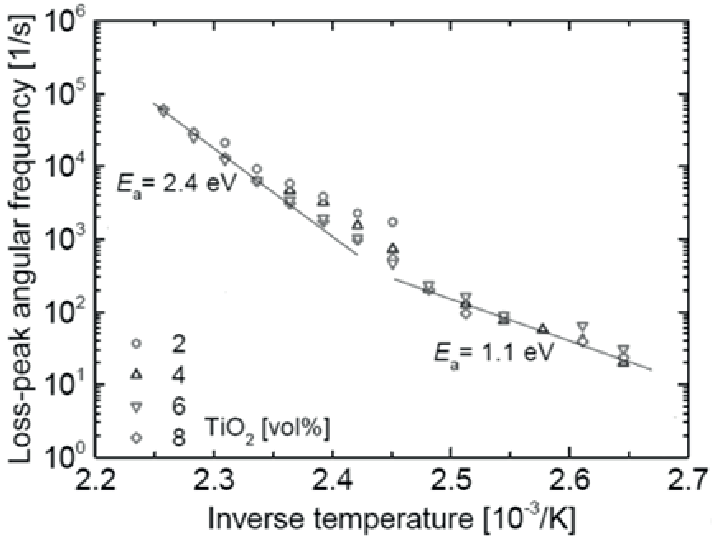

Fig. 7. Arrhenius diagram showing the peak angular frequency of the visible loss peak in HIPS with different TiO_2 contents

temperature T_g is 98.7 °C [6]. Both slight increase and slight decrease of T_g have been reported by other authors [11]. The value of T_g depends on interfacial grafting between the butadiene-rubber inclusions and the polystyrene matrix [12] and on the molar mass of the polystyrene component.

Fig. 5 shows the spectrum of the dissipation factor tan δ of HIPS with 4 vol.% TiO_2.

Another relaxation process appears at lower frequencies (LF). This process superimposes on the α relaxation at temperatures near the glass transition and is observed for all TiO_2 containing HIPS films. The LF process manifests as a strong high-temperature loss-factor peak at about 150 °C (Fig.1), increasing with filler content, whereas the α relaxation loss-factor peak appears at about 120 °C.

In order to separate the LF process from the α relaxation, the temperature dependence of its loss-peak angular frequency has been determined by fitting the empirical Havriliak – Negami (HN) function to the measured loss (Fig. 6). One broad loss peak is visible, which constitutes the superposition of the LF process and the α process.

Arrhenius diagram (Fig.7) shows the peak angular frequency of the visible loss peak in HIPS with different TiO_2. For 4, 6 and 8 vol.% TiO_2-containing films, the LF process shows Arrhenius behavior, but the process is not uniform.

At low temperatures (up to about 130 °C) an activation energy of 1.1 eV is found [6], whereas the activation energy is 2.4 eV in the limit of high temperatures.

Summary

Thus, by means of dielectric relaxation spectroscopy, one relaxation process was found for unfilled HIPS films. This process could be identified as the α relaxation, related to the onset of micro-Brownian motions at the glass transition.

By means of differential scanning calorimetry (DSC), the T_g values between 97.1 and 99.4 °C were obtained for HIPS, no correlation with filler content was visible. The Arrhenius plot of the α relaxation bends towards the glass transition temperature, the best fit is obtained with a Vogel temperature of 330 K which yields T_g = 92.8 °C closely related to the T_g values obtained by DSC.

For composite HIPS films, except α relaxation, another nonuniform relaxation process appeared at lower frequencies. At low temperatures (up to about 130 °C) an activation energy of 1.1 eV was found, whereas the activation energy is 2.4 eV in the limit of high temperatures. The appearance of two different activation energies needs to be further investigated.

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