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.

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 °C) и высоких (свыше 130 °C) температур, составили 1,1 и 2,4 эВ, соответственно.

Introduction

Titanium dioxide (TiO_2) used as a filler is a well-known white pigment for paper and plastics. Moreover, it serves as an additive for different polymeric materials, elastomers, ferroelectric polymers 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 − 5].

Polystyrene (PS) 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. However, scientific interest has mostly been focused on structural investigations and mechanical properties of the composites. Here, an attempt has been made for a more detailed investigation of the relaxation processes in the pure and composite HIPS films [6, 7].

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.

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. 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 were acquired as a function of frequency through a series of ascending temperatures (usually 5 K steps, with an accuracy of ±0.1 K).

Experimental results

Fig. 1 shows DSC results of unfilled and filled composite films. The thermograms for various TiO_2 contents look very similar. The transition at about 100 °C is the glass − rubber transition of the polystyrene component. For unfilled HIPS the glass-transition temperature T_g is 98.7°C. The value of T_g depends on interfacial grafting between the butadiene-rubber inclusions and the polystyrene matrix [8] and on the molar mass of the polystyrene component. Rieger [9] found $T_g = (98 \pm 1)$°C (midpoint) in the limit of infinite molar mass. No significant correlation with filler content is visible here, though both slight increase and slight decrease of T_g have been reported by other authors [10]. The broad exothermal peaks which are always observed in the first heating run around 230°C may refer to the formation of lower-ordered structures in the polystyrene matrix. The absence of a melting region indicates that the PS is present in an amorphous atactic configuration (isotactic PS and syndiotactic PS have melting temperatures of about 240 and 270°C, respectively).

The frequency dependence of the dissipation factor tan δ of unfilled HIPS is shown in Fig. 2. Below the glass transition the dissipation factor is very small (tan $\delta \leq 10^{-3}$), and there is no significant dependence on frequency (not shown here), because the dipolar motion is frozen and the conductivity is very low.

Above the glass transition one relaxation becomes visible which can be identified as the α relaxation, related to the onset of micro-Brownian motions at the glass transition [11]. This is shown by determining the temperature dependence of the inverse loss-peak angular frequencies (or time constants) $\tau_{max}(T)$ via Havriliak − Negami (HN) fits to the measured losses
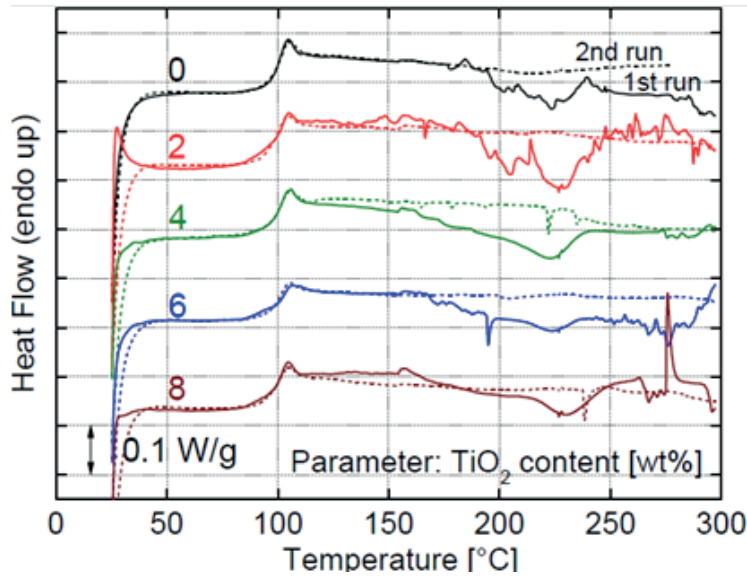
Fig. 1. DSC thermograms of unfilled HIPS (0 wt.%) and HIPS with different TiO_2 contents
$(2 - 8$ wt.%) as indicated.
The heating and cooling rates were always 20 K/min
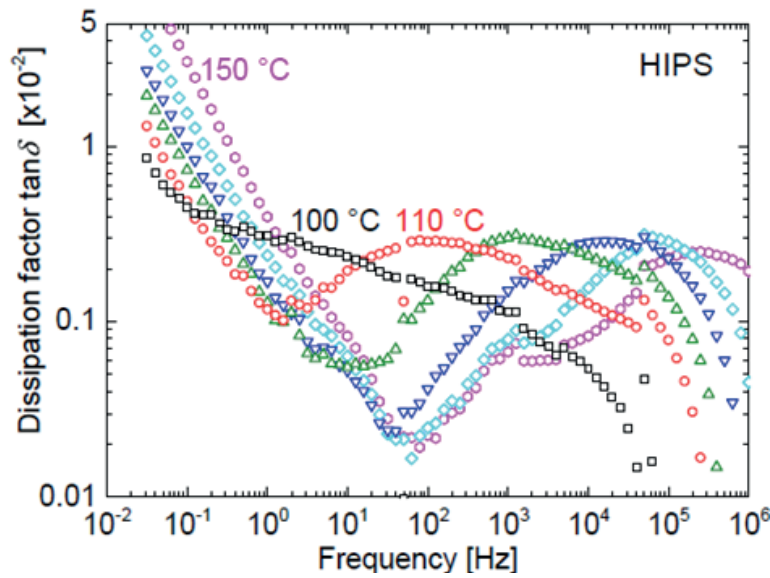

Fig. 2. Frequency dependence of the dissipation factor of unfilled HIPS at selected temperatures
as indicated

(Fig. 3) and then fitting $\tau_{max}(T)$ with the Vogel − Fulcher − Tammann equation:

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

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

The Arrhenius plot of the α relaxation bends towards the glass-transition temperature T_g. It is usually defined as the temperature at which the frequency $1/(2\pi\tau_{max})$ reaches 10^{-2} Hz [12].

Here, the best fit is obtained with a Vogel temperature of 330 K which yields $T_g = 95.3°C$, closely related to the T_g values obtained by DSC. The linearized VFT plot is shown in the inset of Fig. 3. The continuous increase of tan δ towards low frequencies (see Fig. 2) is supposed to be caused by relaxation and/or transport of the charge carriers, which may stem from the dissociation of impurities, e. g. residues of catalysts used in polymer synthesis or from contact charging during film preparation.

Fig. 4 shows the spectrum of the dissipation factor tan δ of HIPS with 4 vol.% TiO_2 with
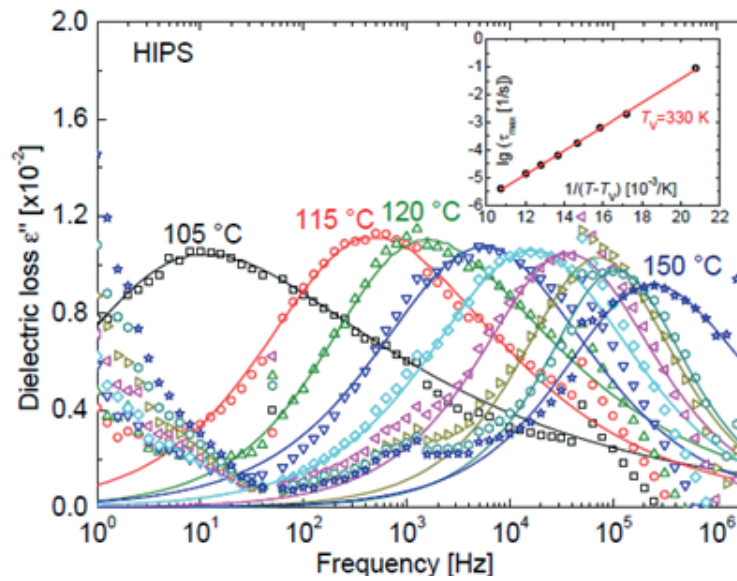
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Fig. 3. Dielectric loss of the α relaxation associated with the glass transition; experimental curves (symbols) at 105 K and then from 115 to 150 K (with 5 K steps) of unfilled HIPS and corresponding Havriliak − Negami fits to the loss-peak data (solid lines). The inset shows the VFT plot of the inverse peak angular frequencies τ_{max}
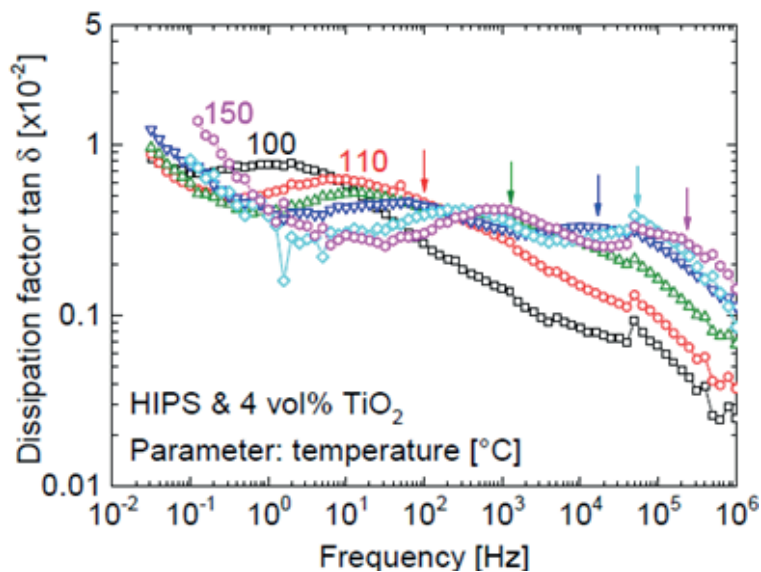

Fig. 4. Frequency dependence of the dissipation factor of HIPS with 4 vol.% TiO_2 at selected temperatures as indicated (10 K steps). The arrows mark the positions of the α relaxation peaks on unfilled HIPS in Fig. 2. Symbols and scaling are similar to those given in Fig. 2. The data stem from two measurements (up to 130 °C and above 130 °C)

a scaling similar to that given in Fig. 2. It is clearly visible that another relaxation process appears at lower frequencies. It superimposes with the α relaxation at temperatures near the glass transition. The positions of the α relaxation loss-factor peaks of unfilled HIPS from Fig. 2 are indicated by arrows for better visualization and comparison. The low-frequency (LF) process is observed in all TiO_2 containing films.

Fig. 5 shows the dependence of the loss factor tan δ on temperature at 1 kHz with the TiO_2 content as the parameter. At this frequency the LF process manifests as a strong high-temperature loss-factor peak at about 150°C, 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. In general, the loss is small (of the order of 10^{-2}) and only one broad loss peak is visible, which constitutes the superposition of the LF process and the α process. However, there is no sufficient and reliable information about the relaxation strength and the shape of the LF loss peak.

Furthermore, a third process at very low frequencies (VLF process) would have to be taken into account in order to describe the continuous increase of loss towards low frequencies which superimposes the observed loss peak.

Fits with two HN functions (each one with 4 parameters) and a two-parameter conductivity term proved to be not unambiguous because of the high number of uncertain fit parameters. Therefore, only a single HN function has been used in order to determine the peak angular frequency of the visible loss peak. An example of curve fitting is given in Fig. 6 for 4 vol.%
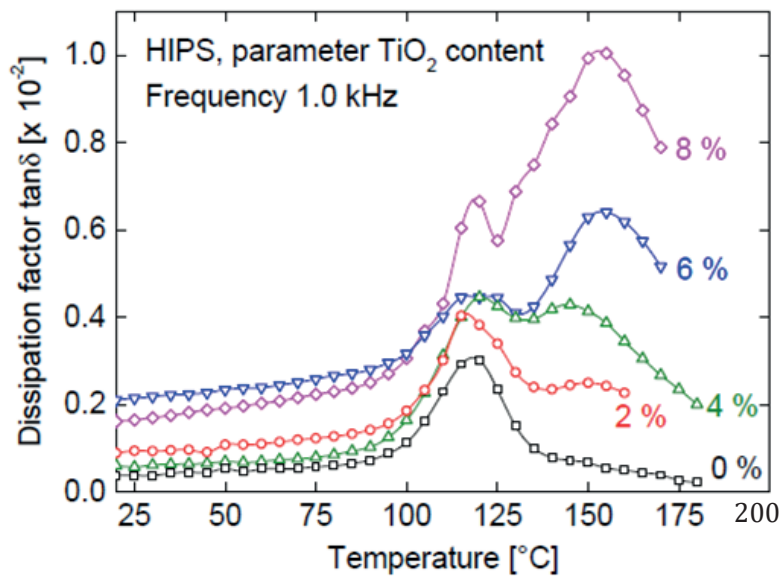
Fig. 5. Temperature dependence of the dissipation factor at 1 kHz of HIPS with the TiO_2 content as the parameter
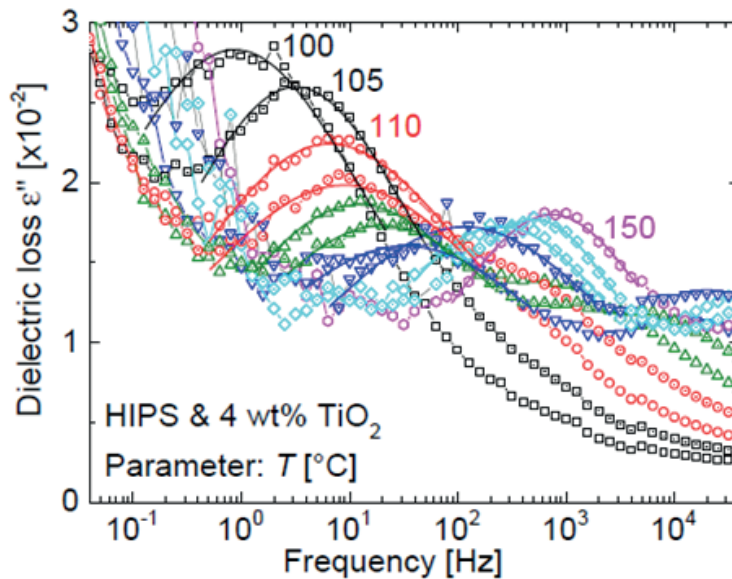
Fig. 6. Frequency dependence of the dielectric loss of HIPS with 4 vol.% TiO_2 at selected temperatures as indicated (5 K steps) together with single HN fits. The data stem from two measurements (up to 130 °C and above 130 °C)
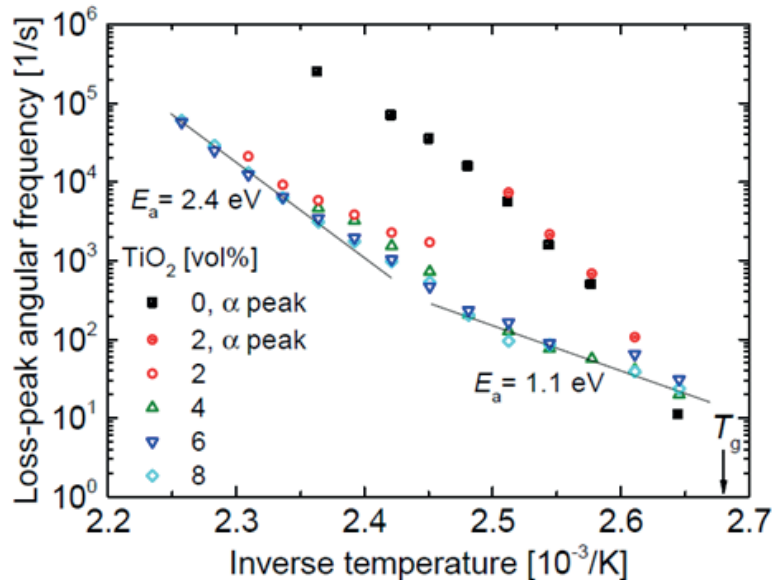
Fig. 7. Arrhenius diagram showing the peak angular frequency of the visible loss peak in HIPS with different TiO_2 contents, together with the data of unfilled HIPS as presented in the inset of Fig. 3. The data was obtained by fitting a single HN function to the experimental loss curves in the vicinity of the loss peak, as presented in Fig. 6, for example

TiO_2. Finally, the loss-peak angular frequencies $\omega_{max}(T)$ are plotted in an Arrhenius diagram (see Fig. 7).

The position of the log ω_{max}-versus-$1/T$ plot of the α relaxation agrees with related measurements by Roland on polystyrene [13], though the molecular mass of the polystyrene component in our samples is not known. For the TiO_2 containing films, the loss-peak angular frequencies obviously cannot be assigned to the α relaxation, except for 2 vol.% TiO_2 below 125°C where the peak position still follows the temperature dependence of the α peak of unfilled HIPS, but above this temperature approaches the loss-peak positions of the other TiO_2-containing films (4, 6 and 8 vol.% TiO_2). For these films, the LF process determines the position of the visible loss peak in the whole temperature range above T_g. It 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, whereas in the limit of high temperatures, and particularly for higher TiO_2 content the activation energy is 2.4 eV.

In heterogeneous materials, a relaxation processes above the glass transition is commonly attributed to an interface polarization. Here, it is supposed that interface polarization is caused by accumulation of unipolar charges at polymer-filler interfaces. However, the appearance of two different activation energies needs to be investigated.

Summary

Thus, 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. One relaxation process was found for unfilled HIPS films which could be identified as the α relaxation, related to the onset of micro-Brownian motions at the glass transition. 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 = 95.3 °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 in the limit of high temperatures the activation energy was 2.4 eV. The appearance of two different activation energies needs to be further investigated.

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