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Polarization spectra analysis for the investigation of space charge in dielectric nanocomposites

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The aim of the study was to examine the influence of the dimension of matrix–filler interface on properties of epoxy nanocomposites. Using traditional investigation methods: dielectric spectroscopy, transient currents and thermally stimulated depolarization, as well as measurements of space charge distribution by the electroacoustic method, it was possible to evaluate the types of polarization and capability of accumulation and decay of space charge. The measurements performed made it possible to compare properties of a nanocomposite, microcomposite and pure resin. It was confirmed that the size of interface area plays a crucial role in the phenomena occurring in composites under the influence of electric fields.

Key words: *nanocomposite; interface; dielectric spectroscopy; thermally stimulated depolarization; TSD; pulse electroacoustic analysis; PEA*

1. Introduction

Dielectric composites made of polymers with inorganic fillers have been successfully used in electrical engineering for many years. The advantage of such materials, compared to pure resins, is the improvement of their mechanical and thermomechanical properties, lower shrinkage, and – not less important – reduction of their price. Using different fillers one can control the composite properties, e.g. conductivity, electric permittivity, thermal conductivity, etc. However, the use of traditional fillers of macro- or micro-sizes, such as SiO_2 in epoxy resins leads to a worsening (to an acceptable degree though) of dielectric properties, such as resistivity, dielectric strength or tanδ [1]. It should be indicated, however, that in spite of many years of research our knowledge of mechanisms responsible for these changes is still insufficient. In par-

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ticular, very few works deal with the influence of composite microstructure on phenomena occurring in an electric field.

Introduction of a granular filler into resin matrix results in creation of interface boundaries influencing the composite properties. The influence of interface in macro scale is well known and utilised in the so called multilayer insulation, used in manufacturing of transformers, cables or capacitors. In an insulation containing components with different electric conductivities, ions can be adsorbed on boundary surfaces, thus creating dipoles. This process continues until the flow of current is settled. In this way a new distribution of electric field is established, and in consequence the electric permittivity ε, loss tangent tanδ and resistivity ρ are changed as well. Binding of free carriers within material structure, from the point of view of dielectric properties, should be regarded as a positive effect, because, particularly in weak fields, it should lead to a decrease of conductivity and hence to lower dielectric losses. However, when local limiting values of the electric field at a phase boundary are exceeded, the collected charges can be released with all consequences, and thus they can enable easy discharging, decrease of electric strength, increase of loss tangent, etc. That is why new experimental methods have been sought which would make it possible to evaluate the distribution of space charge in a dielectric, changes of this distribution under the influence of electric field or temperature. Similarly to numerous previous works [2–5], also in this paper the use is made of the possibilities presented by measurements of dielectric spectroscopy in wide frequency range, measurements of thermo-stimulated depolarization (TSD), distribution of space charge using pulse electroacoustic (PEA) method, as well as measurements of absorption and resorption transient currents. In order to describe the samples with different contents of matrix-filler interface, standard tests of mechanical and electric properties were performed. The authors are aware of the shortcomings of the methods used, it is, however, essential to check their usefulness for evaluation of the influence of nanofillers on the phenomena occurring in nanocomposites in electric fields.

2. Experimental

2.1. Samples

The experiments were performed on samples made of epoxy composition without any filler, and composition filled with quartz meal of average grain size from 4 μm to 20 μm and silica gel of grain size from 7 nm to 40 nm. Quartz meal of 20 μm grain is the most popular filler in epoxy composites used for manufacturing of high and medium voltage insulators. 60 wt. % content of the meal in a composite is considered the optimum [1]. The maximum content of silica gel in a nanocomposite amounts to ca. 3.4 wt. %. This limitation results from the need to preserve the viscosity required in the process of casting (250 mPa at 343 K). In the samples used in the experiments described in this paper, the composite matrix was the dian epoxy resin Epidian 5, with epoxy content 4.7–5.4 Eq/kg, cross-linked with anhydride hardener Ciba HY 905, with addition of amine accelerator K-54. The mass proportion used was 100 parts of resin, 90 parts of the hardener and 0.2 part of the accelerator. A half of the filler was added to the liquid epoxy resin at 343 K. Both components were mixed for 15 min, with a "Cowel" stirrer of 25 mm diameter, at 10 000 rpm. In the same way, the second part of the composition was prepared, and then both parts were mixed together for another 15 min and degassed in vacuum. The samples were cast and hardened in vertical open moulds. The process of hardening proceeded in two stages. In the first stage, the samples were hardened at 343 K for 5 h. The second stage consisted in afterbaking at 403 K for 12 h.

Measurements of electric properties were performed using samples with dimensions 100×100×1 mm^3, using a three-electrode set with a protective ring. The measuring electrode had a diameter of 50 mm, and the diameter of the voltage electrode was 75 mm. The electrodes were made of vacuum-evaporated silver. Measurements of mechanical properties were done on samples with dimensions 120×10×4 mm^3. The interface areas contained in 1 cm^3 of the composites, in function of the filler share and grain diameter, are given in Table 1.

Table 1. Surface of interface matrix-filler in 1cm^3 of the composite

Composite	Filler	Weight share of the filler [%]	Average size of the filler grain [nm]	Interface area matrix–filler [m^2/cm^3]
1	Aerosil 380	3.4	7	18.6
2	Aerosil 200	3.4	12	8.2
3	Aerosil 0X50	3.4	40	2,1
4	SF 500	44	4000	1.1
5	W-12	60	20000	1.0

Table 2 presents the specific surface area of fillers used for fabricating the composites.

Table 2. Specific surface areas of nanofillers

Nanofiller	Specific surface area [m^2/g]
Aerosil 380	380
Aerosil 200	200
Aerosil 0X50	50
SF 500	3.9
W-12	0.9

The specific surface areas were calculated from the equation

$$S_{\mathrm{int}} = \gamma A S_w \tag{1}$$

where S_{int} is the interface area in 1 cm^3 of the composite, A – weight share of the filler, γ – mass of 1cm^3 of the composite, and S_w – specific surface area of the filler [m^2/g].

Scanning microscope (SEM) was used to visualise plane surfaces of fractures of the epoxy composite samples 2–4 (Figs. 1–3).

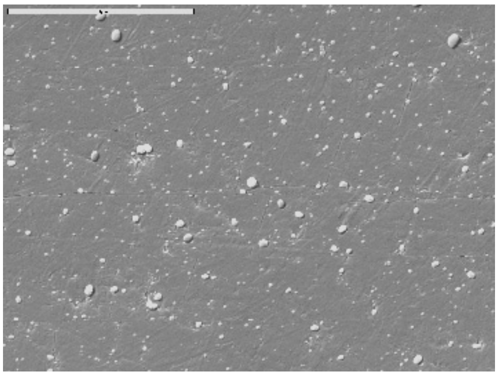

Fig. 1. Scanning photograph of the fracture surface of the epoxy nanocomposite with silica gel of 12 nm grains

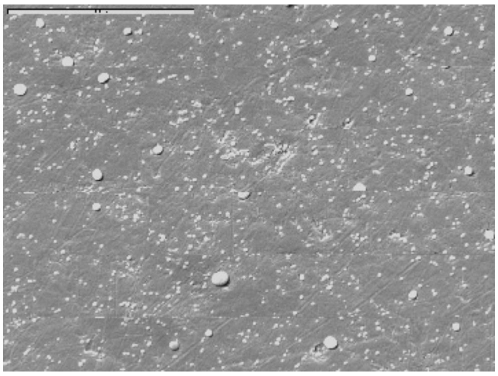

Fig. 2. Scanning photograph of the fracture surface of the epoxy nanocomposite with silica gel of 40 nm grains

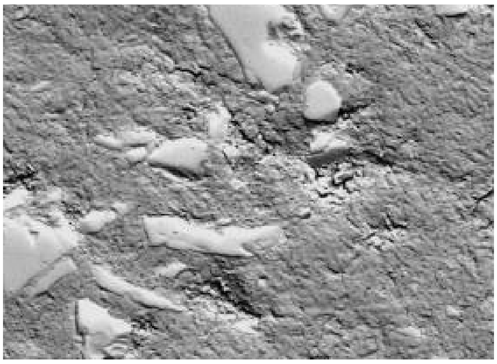

Fig. 3. Scanning photograph of the fracture surface of the epoxy microcomposite with quartz meal of 4 μm grains

Quartz meal SF-500 and W-12 produced by Quartzwerke used in the composites is a ground quartz sand with irregular grain shapes (Fig. 3). Nanosilica gels Aerosil 380, Aerosil 200 and Aerosil OX50, produced by Degussa with use of the flame method have ball-shaped grains. The contents of SiO_2 amounted to over 99% in quartz meals, and above 99.8% in silica gels.

During preparation of the samples much attention was paid to a proper dispergation of filler grains in epoxy matrix. The results of this treatment are shown in Figs. 1–3 as scanning electron microscope pictures of plane surfaces of fractures of the epoxy composite samples. Beside grains of diameters of 20 nm there are agglomerates of diameters from 100 to 500 nm.

Based on these microscopic photographs, it can be concluded that the smaller the grains of a filler, the easier the agglomerates are created and the more difficult is their dispergation.

2.2. Measuring equipment

In order to establish the influence of the size of the interface area on the properties of epoxy composite, basic standard measurements of mechanical properties (impact resistance, flexural strength) as well as of electric properties (volume resistivity, electric strength and permittivity ε and loss tangent tanδ at the frequency 50 Hz) were performed.

The measurements of $\varepsilon''(f,T)$, measurements of currents of thermally stimulated depolarization (TSD), transient currents and distributions of space charges using pulse electroacoustic analysis (PEA) were applied to investigate the space charge. The measurements of ε'' in the range from 10^{-4} Hz to 10^2 Hz were performed using a General Electric IDA 200 analyzer. The measurements were taken at ambient temperature and at 373 K. For the frequencies from 10^2 Hz to 2×10^5 Hz, the measurements were made in the temperature range from 293 K to 373 K with use of an HP 4284 A impedance analyzer.

The activation energy was calculated from the $\varepsilon''(f,T)$ characteristics (Eq. (2)) [6]. For the TSD measurements an 6517 A (Keithley) electrometer was used. After evaporation of silver electrodes, the samples were polarized with constant voltages of 100 V and 200 V at 403 K. The TSD measurements were made at a constant heating rate equal to 5.5 K/min.

The measurements of isothermal transient currents (absorption and resorption) were made at 293 K and 373 K.

The measurements of space charge with use of pulse electroacoustic analysis (PEA) were made as described in [7–9].

3. Results and discussion

3.1. The influence of interface area on nanocomposite properties

Solid dielectrics designed for manufacturing of electric insulators have to possess good mechanical properties. In nanocomposites with a thermoplastic matrix, these properties depend considerably on the size of the interface area [10, 11]. The results obtained in our research for an epoxy resin matrix are shown in Fig. 4 as a dependence of flexural strength on the interface area. Figure 5 shows this dependence for the impact resistance.

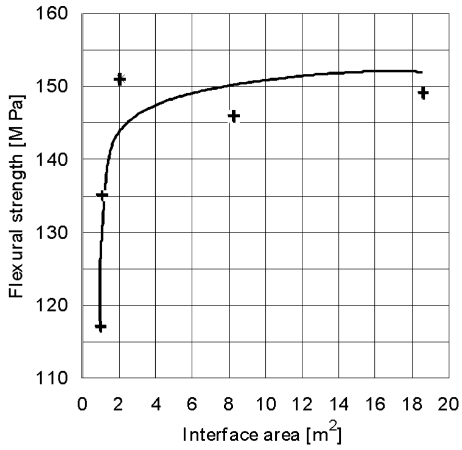

Fig. 4. Interface area dependence of the flexural strength in the epoxy composites 1–5

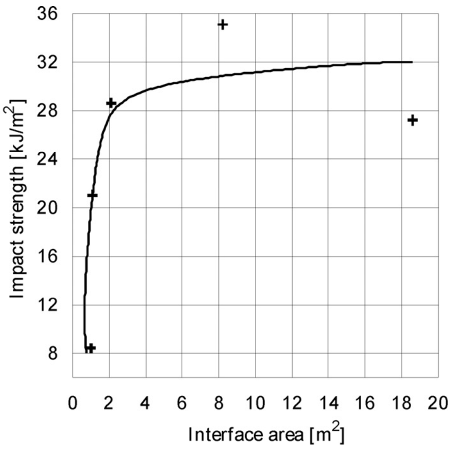

Fig. 5. Interface area dependence of the impact strength in the epoxy composites 1–5

Upon increase of the interface area from zero to ca. 2 m^2, the flexural strength and impact resistance grow considerably from ca. 120 MPa to 150 MPa and from ca. 10 kJ/m^2 to 30 kJ/m^2, respectively. These values are much higher than those for microcomposites and pure resins. It should be stressed that we obtained these very good mechanical properties with practically unchanged specific weight related to pure resin. Electrical properties – resistivity ρ, loss tangent $\tan\delta$, permittivity ε and electric strength E_s are essential features characteristic of electroinsulating materials. These properties in function of the interface area are shown in Figs. 6–9.

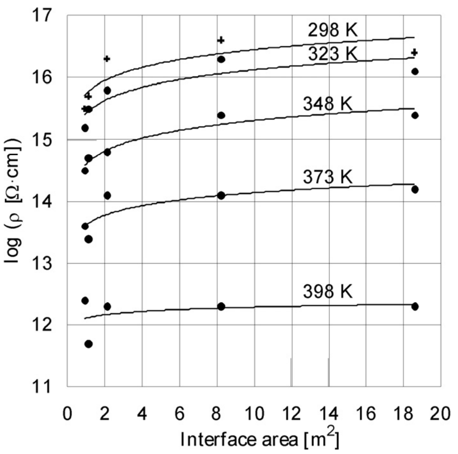

Fig. 6. Interface area dependence of the volume resistivity ρ in the epoxy composites 1–5

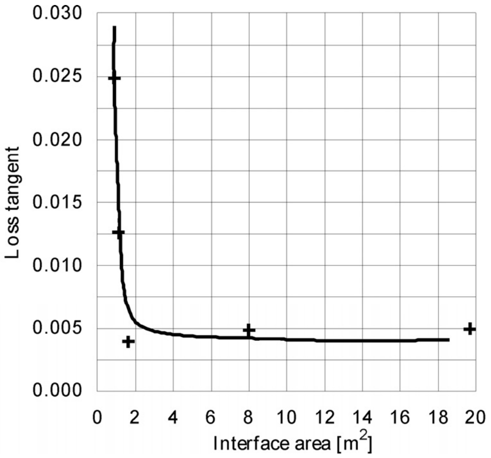

Fig. 7. Interface area dependence of the dielectric loss tangent $\tan\delta$ in the epoxy composites 1–5; temperature 296 K, voltage 1000 V, 50 Hz

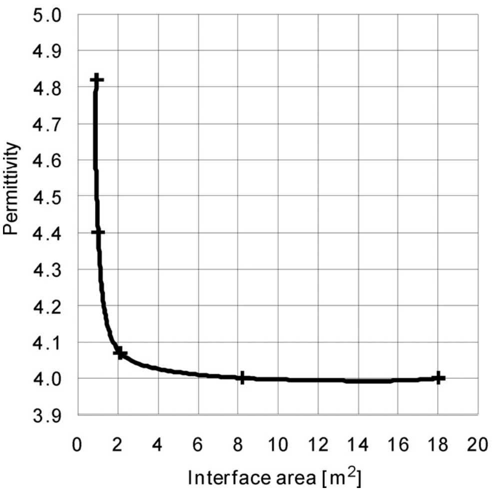

Fig. 8. Interface area dependence of the permittivity ε of the epoxy composites 1–5. Temperature 296 K, voltage 1000 V, 50 Hz

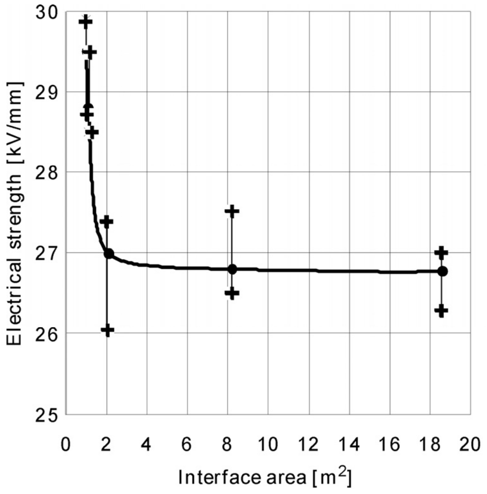

Fig. 9. Interface area dependence of the electric strength of the epoxy composites 1–5. Temperature 296 K, alternative voltage 50 Hz

The volume resistivity increases with the increase of the interface area, particularly for measurements performed at temperatures lower than 373 K (Fig. 6). A stronger influence of the interface is visible in the case of loss tangent and dielectric permittivity (Figs. 7 and 8). Introduction of nanofiller and increase of interfacial area lead to a lowering of the electric strength (Fig. 9).

Essential information about the space charge in a dielectric can be obtained from measurements of absorption and resorption transient currents. The lack of a mirror reflection of both time-dependent curves is an evidence that space charge is accumulated in the material [12]. Such a situation was also noted in our investigation.

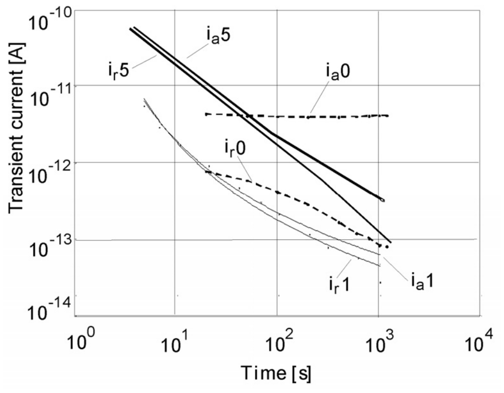

Fig. 10. Time dependences of transient currents of absorption i_a and resorption i_r of epoxy composites 0, 1, 5

Figures 11 and 12 show dispersional curves of the imaginary part of permittivity ε'' determined at 293 K and 373 K, in the frequency range from 10^{-4} Hz to 2×10^5 Hz.

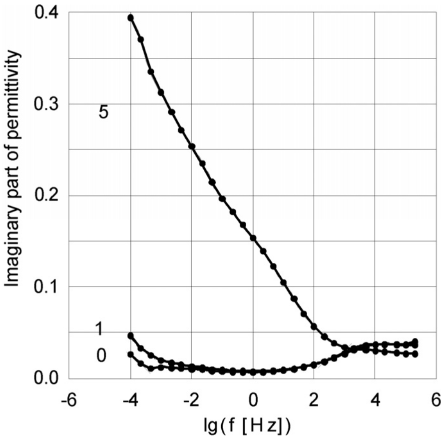

Fig. 11. Dependence of the imaginary part of permittivity ε on the frequency *f* in epoxy composites 0, 1, 5. Measurements at 296 K

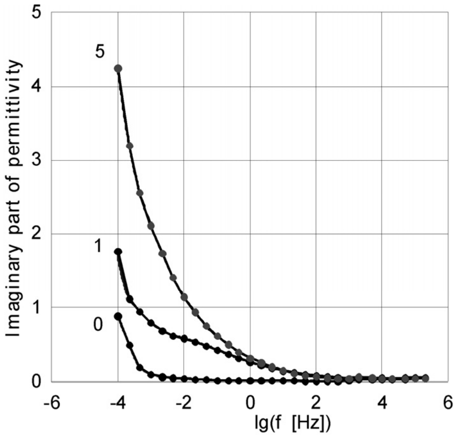

Fig. 12. Dependence of the imaginary part of permittivity ε on the frequency *f* in epoxy composites 0, 1, 5. Measurements at 373 K

At ambient temperature, the highest values of ε'' were obtained for the frequency 10^{-4} Hz for the composite 5 with microfiller of interfacial area 1 m^2, whereas pure resin and the resin with nanofiller (18.6 m^2) had similar, visibly lower values, slightly changing with frequency. At 373 K, the curves visibly vary, again the highest values obtained for the composite 5 and the lowest ones with the pure resin. When the temperature is raised, the values of ε'' are by one order of magnitude higher than those at ambient temperature. From the characteristics $\varepsilon''(f,T)$, activation energies were determined using the equation [6]:

$$\Delta W = \frac{0.198}{\Delta\left(\frac{T}{1000}\right)} \quad [\mathrm{eV}] \tag{2}$$

where: $\Delta(T/1000)$ is an increment $T/1000$ for one frequency decade. The results are presented in Table 3.

Table 3. Activation energy ΔW of epoxy composites 0, 1, 5 [eV]

Composite	$T < 403$ K	$403 < T < 413$ K	$T > 413$ K
0	3.30	3.30	2.44
1	3.80	3.04	2.34
5	2.87	2.87	2.55

At the investigated temperature ranges, three polarization processes are visible with three different activation energies. Below 403 K a process of group polarization γ takes place, at temperature range 403–413 K group polarization β, and above 413 K, a process of segmented polarization α is likely to occur [13, 14]. Taking into account that for each composite tested the same epoxy matrix7 was used, the reasons for different values of activation energies can be attributed to different resisting forces during charge relocation. The smallest activation energy is characteristic of composite 5, with micro-size quartz meal, and the highest one of composite 1. These differences disappear at higher temperatures. Dipole polarization processes induced by space charges can be determined from the TSD current curves which are shown in Figs. 13–16.

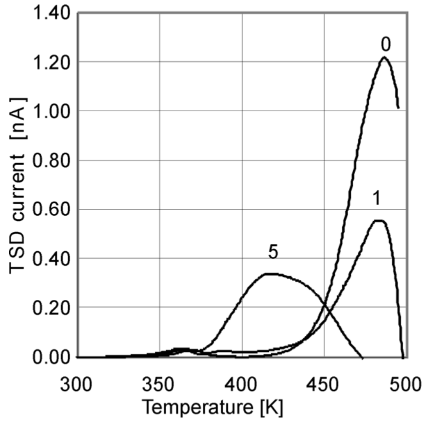

Fig. 13. Temperature dependences of the TSD currents in composites 0, 1, 5. Polarization in the electric field 100 kV/m, temperature 403 K

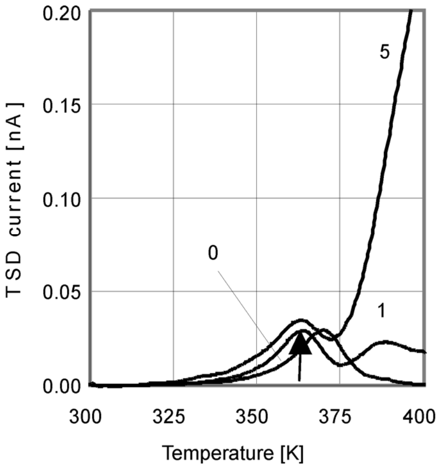

Fig. 14. Temperature dependences of the TSD currents in composites 0, 1, 5. Polarization in the electric field 100 kV/m, temperature 403 K.
A detail from Fig. 13

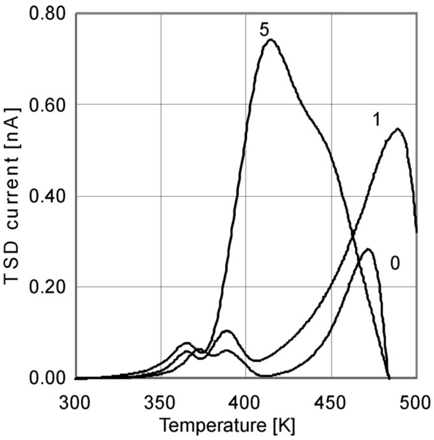

Fig. 15. Temperature dependences of the TSD currents in composites 0, 1, 5. Polarization in the electric field 200 kV/m, temperature 403 K

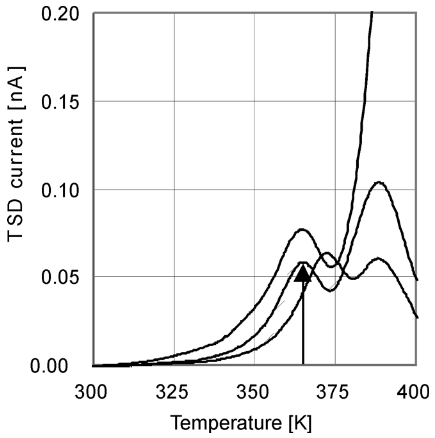

Fig. 16. Temperature dependences of the TSD currents in composites 0, 1, 5. Polarization in the electric field 200 kV/m, temperature 403 K
A detail from Fig. 15

The dipole feature of the local maximum is confirmed by a change of TSD current value, proportional to the polarizing voltage, at a given temperature [15, 16]. For instance, for composite 0, the dipolar character of the peak at temperature 370 K is confirmed by the doubled increase of this value for a doubled polarizing voltage (cf. Figs. 14 and 16). A complete analysis of the presented TSD spectra requires additional measurements with other parameters of sample polarization.

The investigation of the role of interface area in accumulation and decay of the space charge in the tested epoxy composites 0, 1, 5 was performed using the pulse electroacoustic analysis (PEA). The results are shown in Figs. 17–22.

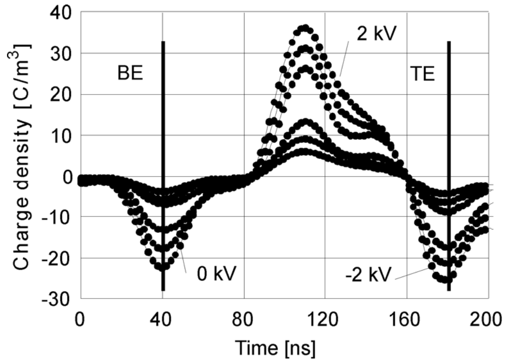

Fig. 17. Charge density distribution in composite 0 obtained with PEA. Polarizing voltage from – 2 kV to 2 kV. BE – lower electrode, TE – upper electrode

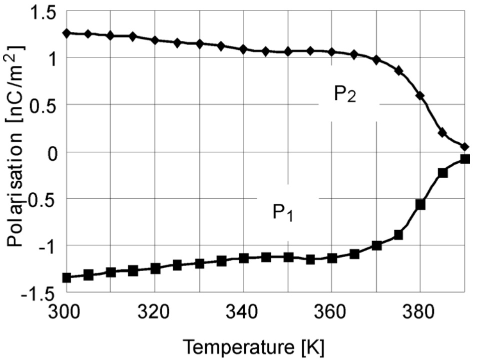

Fig. 18. Charge decay in composite 0 measured with PEA

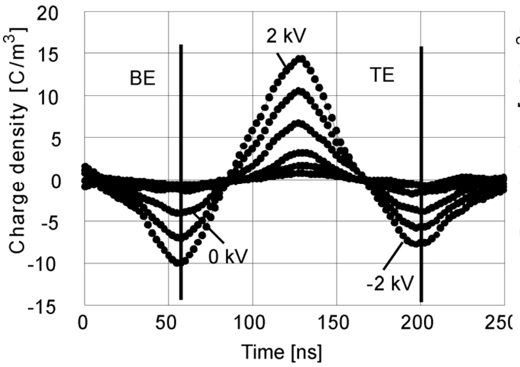

Fig. 19. Charge density distribution in nanocomposite 1 obtained with PEA. Polarizing voltage from –2 kV to 2 kV; BE – lower electrode, TE – upper electrode

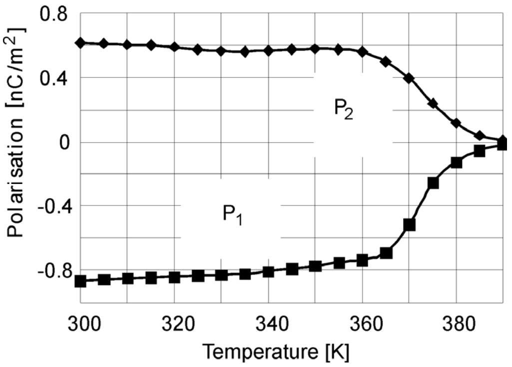

Fig. 20. Charge decay in nanocomposite 1 measured with PEA

The results of measurements point to an essential role of interface in the accumulation and distribution of the space charge in the tested composites, affecting new distribution of electric field. Free charge is adsorbed on the interface. Free charge on electrodes is compensated by polarization charges. The highest amount of charge is gathered in composite 0 (without filler), twice lower amount in nanocomposite 1 (interfacial area 18.6 m^2), and six-fold lower in composite 5 with micro-filler with interfacial area 1 m^2, (Figs. 17, 19 and 21).

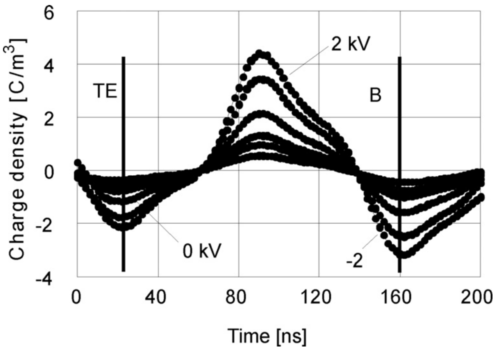

Fig. 21. Charge density distribution in microcomposite 5 obtained with PEA. Polarizing voltage from –2 kV to 2 kV; BE – lower electrode, TE – upper electrode

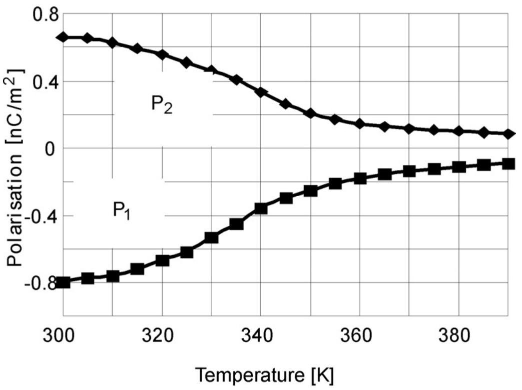

Fig. 22. Charge decay in microcomposite 5 measured with PEA

On increasing temperature, the charges on the interface disappear, what is confirmed by the polarization curves P_1 and P_2 (Figs. 18, 20 i 22). In composite 0, a visible dropout of the polarization begins at the highest temperature (ca. 375 K) and is the fastest one (Fig. 18). In sample 1 with the nanofiller, the dropout begins at ca. 365 K and proceeds somewhat slower (Fig. 20). At the lowest temperature (ca. 325 K) the polarization begins to vanish in composite 5 with a micro-filler (Fig. 22).

4. Conclusions

In the process of nanocomposite production a particular attention should be paid to a proper dispergation of nanoparticles in a polymer matrix, so as to avoid creation of agglomerates.

The investigation of mechanical properties showed a visible increase of impact and flexural strength in comparison to micro-composites. This means that the insulators made of such material will be lighter and much stronger.

With the increase of the interfacial area, the dielectric properties are improved, as are resistivity, loss tangent and permittivity. Only a slight worsening of electric strength could be observed. This effect could result from an increase of a local electric field caused by gathering of charges near the interface boundary.

The measurements of transient currents show that a space charge gathers in the tested material what is confirmed by the lack of a mirror reflection in the curves of absorption and resorption currents.

The role of interface is also visible in the measurements of the imaginary part of the permittivity (ε'') in function of frequency. A microcomposite is characterized by a much higher imaginary permittivity, particularly at lower frequencies, in comparison to a pure resin, and the introduction of a nanofiller practically makes dielectric losses independent of the frequency at room temperature, forcing them to remain at a level characteristic of a pure resin. Similarly, at higher temperatures the nanocomposite loss is visibly lower than that of a micro-composite. This considerable increase of dielectric loss in a micro-filled composite can be explained by the occurrence of the Maxwell–Wagner polarization on micro-grains absent in nanocomposites. This was confirmed by the observations described in [17].

The activation energy calculated for the pure resin (composite 0), microcomposite (5) and nanocomposite (1) based on measurements of ε'' in function of frequency and temperature (Eq. (2)), at temperature ranges slightly higher than glass transition temperature was found to be the lowest for a microcomposite. At higher temperatures (above 413 K), the activation energies of the tested samples are very similar. This finding is essentially different from the results reported in [2] where TiO_2 was used as a filler.

The comparison of TSD current curves for three investigated materials (composites 0, 1 and 5) showed that in the pure resin and in composite 1 both the dipole polarization and the polarization due to the space charge are present. For microcomposite 5, however, the size of the TSD current peak varies proportionally to the change of the polarization voltage what suggests that it is related to dipole polarization only. Asymmetrical shape of this peak (Fig. 15) may be an effect of overlapping with a component due to the space charge.

PEA tests showed that the ability to collect the charge generated by corona discharge is the highest for pure resin, twice lower for a nanocomposite and six time lower for a microcomposite. Charge decay for pure resin begins at the highest temperature 375 K and its duration is the shortest. Introduction of a micro-filler lowers this temperature to ca. 325 K and visibly prolongs the time. A nanocomposite compared to a microcomposite is characterized by a higher loss temperature and shorter loss time.

Constantly growing number of papers concerning this issue indicates that introducing nanofillers into a polymer matrix essentially influences the properties of nanocomposites due to the increase of a boundary surface area filler–matrix. The mechanism of this phenomenon has not been fully clarified, nonetheless in the investigation of dielectrics, dielectric spectroscopy, measurements of transient currents, TSD currents and analysis of charge distribution with acoustic methods are commonly used. The weakness of these methods consists in the fact that the results obtained are usually quantities averaged from local signals, generated in numerous electrically active weak places which decide about electric strength, partial discharges or dielectric losses. It should also be stressed that the investigation methods mentioned above are applied at different voltages and different local field intensities and therefore the results obtained cannot be directly compared. Thus it is necessary to investigate and develop new methods and measurement techniques. Nonetheless, making use of the classical tests permits a better evaluation of application potentials of new materials and can be useful in drawing conclusions on the mechanisms of phenomena occurring in dielectrics exposed to electric fields.

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