

Investigation of the processes of accumulation and relaxation charge in composite films of polypropylene

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Abstract. The work is devoted to the investigation of relaxation processes in composite films of polypropylene with aerosil. The investigation shows that relaxation of electret state is determined by the bulk conductivity. Two volume percentage of aerosil is optimal volume for electret stability of samples. The investigation of the sample by means of the method of thermostimulated depolarization reveals that particles of aerosil in composite samples play the role of macrodipoles.

1. Introduction

Range of application of polymeric electret materials is very wide: from household appliances to special equipment and medicine. This causes the need for a polymer with a high and stable electret characteristics. One of the most simple and accessible ways of creation similar material is added to the polymer matrix various dispersed fillers. However, despite the strong interest to the creation and use of composite materials, there are almost no models that explain the processes responsible for changing the electret properties of polymers after the introduction of these fillers. Therefore investigation of the influence of dispersed fillers on the electret properties of polymers and explain of relaxation processes in composite materials is an urgent problem of polymer physics.

2. Experimental results

The objects of study are films of polypropylene (PP), a thickness of 300 microns. The filler is aerosil (brand A-175) with a particle size of about 12 nm.

Time and temperature stability of the electrets state for polypropylene were done using isothermal and thermoactivated relaxation of the surface potential. For the study of the time stability of the electrets state the samples were charged at a temperature of 70°C to 1 kV surface potential by corona discharge and the dependence of the surface potential of the time was obtained at a temperature of polarization. For the study of the temperature stability of the electrets state, the samples were charged at a temperature of 20°C and the temperature dependence of the surface potential in a linear heating mode was investigated. The experimental results (figure 1, 2) showed that the addition of aerosil leads to the increase of the time and temperature stability of the electrets state in polypropylene. Optimal content of aerosil to the stability of the electrets state is a number of 2 vol.% of aerosil.

The relaxation time (time of decreasing of the surface potential in e times) of electrets state was calculated (table 1).



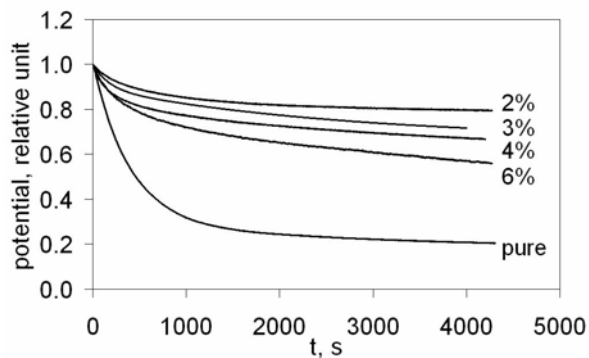


Figure 1. The time dependence of the surface potential for the samples charged in the negative corona discharge. $T = 100^\circ\text{C}$. 1 – pure PP; 2 – PP + 2 vol.%; 3 – PP + 3 vol.%; 4 – PP + 4 vol.%; 5 – PP + 6 vol.% of aerosil.

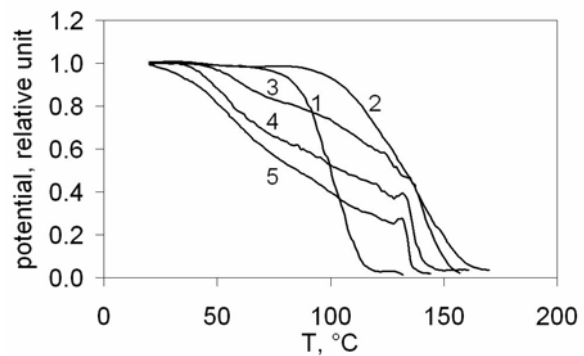


Figure 2. The temperature dependence of the surface potential for the samples charged in the negative corona discharge. Heating rate $5^\circ\text{C}/\text{min}$. 1 – pure PP; 2 – PP + 2 vol.%; 3 – PP + 3 vol.%; 4 – PP + 4 vol.%; 5 – PP + 6 vol.% of aerosil.

Table 1. Relaxation time of electret state and bulk conductivity of composite samples

Volume percentage of aerosil, %	Relaxation time ($T = 100^\circ\text{C}$), s	Bulk conductivity ($T = 140^\circ\text{C}$), $10^{-15} (\text{Om}\cdot\text{m})^{-1}$
0	1994	192,5
2	13915	7,5
3	10000	12,2
4	8280	16,9
6	6050	53,7

Electrical conductivity of materials was studied using a method of thermostimulated polarization. The sample was heated from 20°C to 150°C in the applied electric field intensity of 500 V/mm and cooled in the same temperature range (without turning off the electric field) with the same speed. Cycles «heating-cooling» was held until the heating curve of the cycle does not coincide with the curve of the heating of the previous cycle. The results of measurements showed that the introduction of 2% vol. aerosil reduces the conductivity of polypropylene. During the increase of the percentage of filler conductivity is growing, but is still significantly less than the conductivity of the original polymer. Conductivity of the samples was calculated and the results for the temperature of 140°C given in table 1.

Comparison of the obtained values of the relaxation time and conductivity (figure 3) allows to make a conclusion that the relaxation of the electret state in the studied material is due to the conductivity.

This result can be explained by the interaction of particles of aerosil and water molecules in the polymer. There are hydroxyl groups in a polymer. The groups are formed from the molecules of water available in the volume of the polymer. The hydroxyl groups are attached to the surface atoms of silicon particles of aerosil. Arising out of the active centres of the surface absorb water, resulting in the characteristic shell, consisting of hydroxyl groups and of the adsorbed water, forms around of aerosil particles [1-4]. The presence on the surface of aerosol particles of hydroxyl groups attached to the silicon atoms, also confirmed by the existence of the IR spectra of composite polypropylene strip 3680 cm^{-1} (figure 4). Bands in this area of the spectrum are traditionally considered to be OH-fluctuations in the SiOH-groups [2, 5-7].

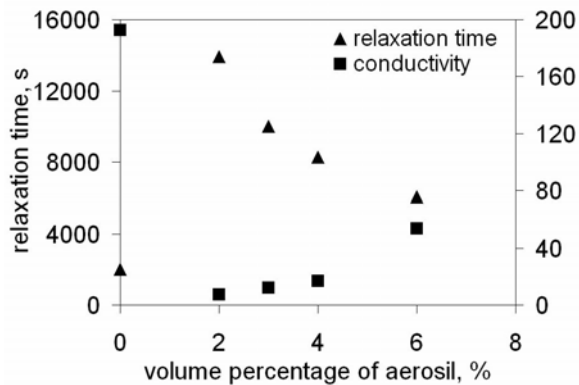


Figure 3. The dependence of the relaxation time and the conductivity from the volume percentage of aerosil.

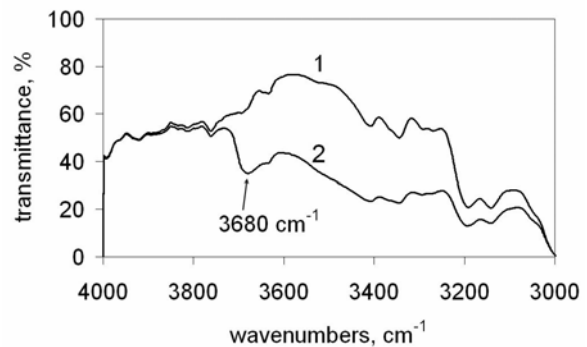


Figure 4. IR-spectra of pure polypropylene (1) and polypropylene with 6 vol.% aerosil (2).

According to the model of conductivity, developed by the authors [8-10], the water molecules are the catalyst for the conductivity. Therefore, decrease of their number in the volume of polymer leads to a decrease of conductivity of the material. This fact was observed in the curves of thermally stimulated polarization. However, the dependence of the conductivity of composite samples from the volume percentage of aerosil is not monotonous. Adding more than 2 vol.% of the filler leads to increase of conductivity of the material. To explain this fact were studied the composite samples by the method of small-angle X-ray scattering.

The experimental scattering intensity for composite films at different volume concentrations of aerosil and the experimental intensity of scattering for a pure polypropylene shows in figure 5a. The scattering indicatrix for the composite samples differ only a shift in the axis of ordinates (figure 5a). Moreover, normalized by the concentration curves coincide in the framework of the inaccuracy (figure 5b). This means that significant interference effects don't occur with increasing concentration of aerosil and, consequently, of aerosil particles don't form aggregates.

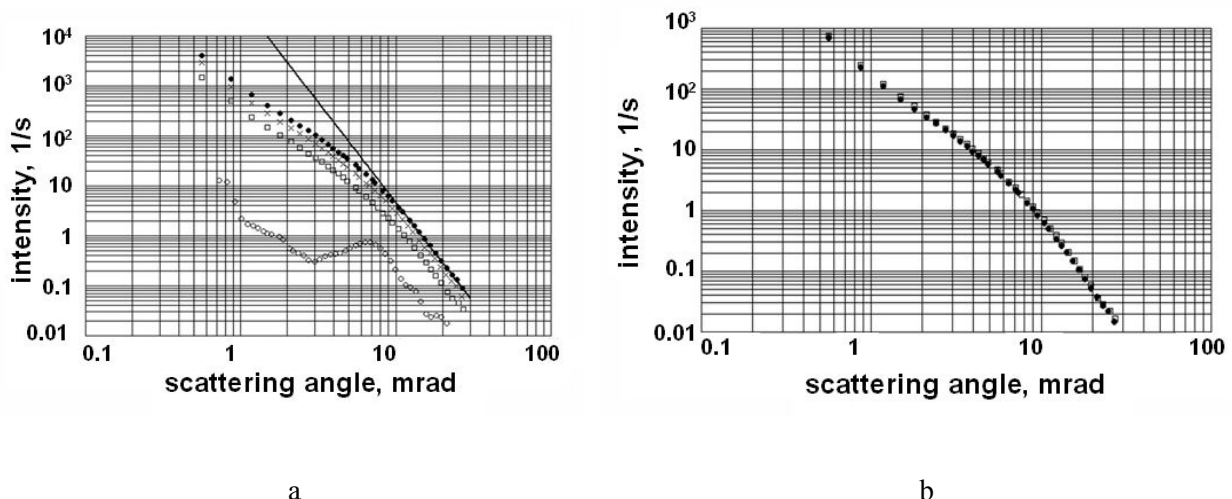


Figure 5. Results of the experimental scattering intensity for composite films: a) pure polypropylene ($\circ\circ\circ$), polypropylene with 2 vol.% ($\square\square\square$), 3 vol.% ($\times\times\times$), 6 vol.% ($\bullet\bullet\bullet$) of aerosil; b) dependence normalized to the concentration for polypropylene with 2 vol.% ($\square\square\square$), 6 vol.% ($\bullet\bullet\bullet$). — line with $\alpha = 4$.

All of the indicatrix of the scattering in the range of large angles have linear dependence with the slope $\alpha = 4$. According to the theory of X-ray small-angle scattering, extended linear dependence of the logarithm of the intensity of logarithm of the scattering angle indicates the fractal structure of the surface of the scattering object. The fractal dimension D_s of the surface can be calculated by the formula $D_s = 6 - \alpha$ [11]. Fractal dimension from the experimental curves is $D_s = 2$. According to the theory, the value of D_s for the fractal surface can vary from $D_s = 2$ (completely smooth) to $D_s = 3$ (full rough). Thus it can be argued that the surface of the aerosil particles is sufficiently smooth, based on the experimental data.

We can make the following conclusion from the results. Increase the volume of filler leads to a increase its free surface in the volume sample and, as a consequence, to increase numbers of OH-groups and adsorbed on them water molecules. The increase in the number of aerosil over 2 vol.%, apparently, leads to the emergence of conduction of the surface of the particles. The total conductivity of composite samples increases, as it is observed on the dependence of the conductance on the volume fraction of filler.

We investigated the role of the filler particles in processes of the relaxation of charge by thermally stimulated depolarization (TSD). The temperature dependence of the depolarization currents shows in figure 6. The position and shape of the peaks in the polypropylene and composites on its base are different. There is a new wide peak at a lower temperature on the spectra of composite materials. The position of the peak is independent of numbers of the filler (figure 6), and its height is proportional to the share of filler in the composite material (figure 7). The latter fact leads to the assumption that properties of the filler or to the properties of the phase boundary of polymer-filler responsible for formation the peak. The process observed in the pure polypropylene, are also present. It shows by the presence of a large current in the composites at 140-150°C. Investigation the dependence of the peak positions from the temperature polarization samples also showed differences in the spectra obtained for pure polypropylene and polypropylene with particles of aerosil. The position of maximum of the depolarization current of pure polypropylene is independent on the temperature of the polarization, but position of peak of the composite materials shifts to the region of high temperatures (table 2).

Table 2. The dependence of position of peak from temperature of polarization

$T_{\text{polar}}, ^\circ\text{C}$	$T_{\text{max}}, ^\circ\text{C}$ pure PP	$T_{\text{max}}, ^\circ\text{C}$ composite polymer
50	144	62
80		98
100	147	116
140	147	

These differences in the position and shape of the peaks, their behavior depending on the temperature of the polarization suggest the different nature of the processes taking place in composite and initial polymers. The process of the dipole relaxation appears in composite samples. The dipole moment induced in the particles in the applied of the electric field.

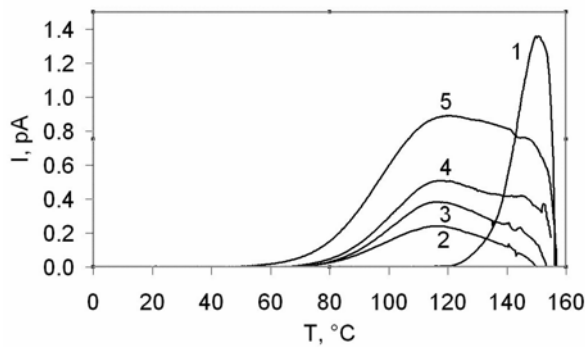


Figure 6. Currents of thermally stimulated depolarization. $T_{\text{polar}} = 100^\circ\text{C}$, heating rate $5^\circ\text{C}/\text{min}$. 1 – PP; 2 – PP + 2 vol.%; 3 – PP + 3 vol.%; 4 – PP + 4 vol.%; 5 – PP + 6 vol.% of aerosil.

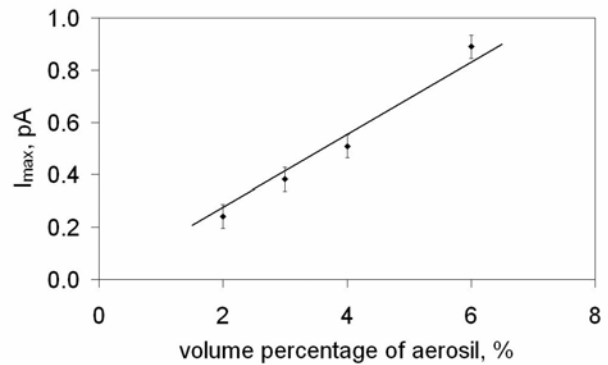


Figure 7. The dependence of maximum depolarization current from volume percentage of aerosil.

The mechanism of formation of the dipole moment can be explained by using the information about the structure of aerosil particles and polyelectrolyte model [2, 3, 8-10]. As mentioned above, there are hydroxyl groups on the surface of aerosil. If the group loses a proton, it becomes negatively charged $[\text{O}]^-$, and addition of a proton leads to the formation of a positively charged group $[\text{OH}_2]^+$. These groups move on the surface of the particle, when the particle is placed in an electric field. As a result of the particle becomes macrodipole.

The shift of the peak of depolarization current in the range of high temperatures with increasing temperature of the polarization means the presence of a dipole mechanism of relaxation (table 2). Dipoles that polarized at higher temperatures are better oriented along the field, and therefore require more energy for disordering.

The literature describes another way to distinguish the dipole peaks from the peak of the spatial charge: the dependence of the height of the peak from intensity of electric field is non-linear for the peak of the space charge [12]. Investigation of the composite polypropylene observed linear dependence of height of the peak from the intensity of the polarizing field (figure 8).

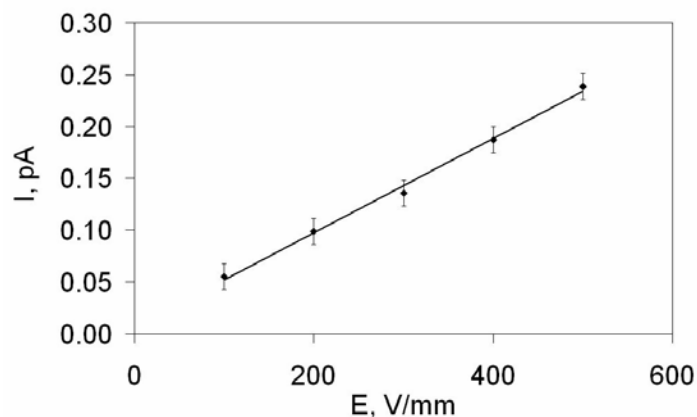


Figure 8. The dependence of maximum depolarization current from electrical field (PP + 2 vol.% of aerosil).

3. Conclusions

Thus, the main results of the work:

- relaxation of electret state in composite materials with aerosil is determined by the bulk conductivity;
- the addition of aerosil in the polypropylene leads to the increase of temperature and time stability of the electret state;
- optimal content of aerosil to the stability of the electrets state is a number of 2 vol. % of aerosil;
- particles of aerosil in the composite material play the role of macrodipoles.

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