

Study of Dielectric Properties of Polymer Systems Containing Nanosized Soot and Aluminum Particles

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Abstract – The main idea of this work was to obtain and study polymer composites based on synthetic isoprene elastomer and low density polyethylene, which contain soot and aluminum nanoparticles in various quantities. The composites were saturated with nanosized particles of aluminum and DG-100 soot with specific adsorption surface of 100 m²/g and an average particle size of 20-30 nm.

Keywords – synthetic isoprene rubber; polyethylene; dielectric constant; resistivity.

I. INTRODUCTION

The study of the dielectric properties of polymer systems (composites, mixtures) containing nanoparticles in small quantities is an important task of physics of high-molecular compounds and physics of dielectrics. One of the main objectives of this study is to investigate the impact of concentration of soot and aluminum nanoparticles on the process of dielectric polarization and electrical conductivity of polymer composites based on isoprene synthetic rubber (SIR-3) and low density polyethylene (LDPE).

It is known that the behavior of dielectric constant for microsystems is usually considered according to the effect of Maxwell-Wagner polarization. In the work [1], an approximate solution was offered regarding common and important practical problem of dielectric with the inclusions of electrically conductive impurities. The values of conductivity and dielectric

constants should be known for the additives. However, for the practical purposes there is an interesting case with the metallic or similar conductive inclusions without known values of the effective dielectric constant.

II. METHODS AND MATERIALS

The composites were saturated with nanoparticles of aluminum and DG-100 soot with the specific adsorption surface of 100 m²/g and an average particle size of 20-30 nm. The distribution of soot and aluminum nanoparticles by size is presented in Fig. 1 and 2.

From Fig. 1 it can be seen that aluminum nanoparticles are rather small and most of them are 20-30 nm (Fig. 1).

Unlike inert aluminum, soot is very active and the nanoparticles form agglomerates with sizes ranging from 100 nm to 10 μm (Fig. 2).

The amount of soot and aluminum was calculated using the following equation:

$$c = 0,1e^n, \quad (1)$$

where, c is the content of the filler, in wt %,

n is the integers from 0 to 4 inclusive,

e is the basis of natural logarithms equal to about 2.71.

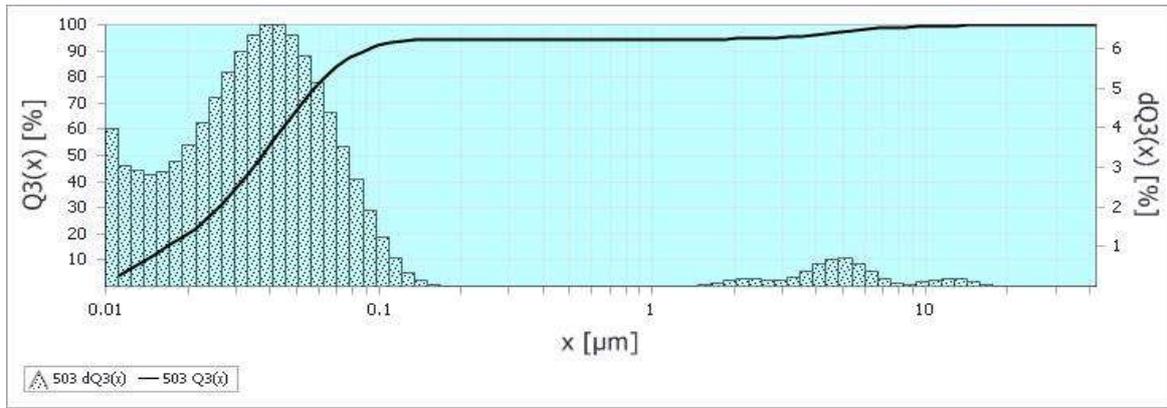


Fig. 1. Size distribution of aluminum nanoparticles

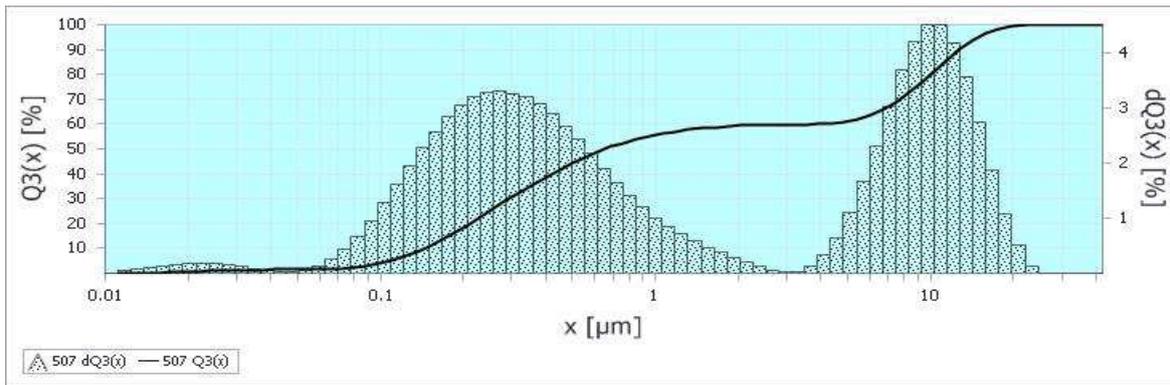


Fig. 2. Distribution of DG-100 soot particles by size

The exponential approach allows better control the area of small additives, which is eliminated with the linear distribution of nanofillers with small additives.

In this case, changing the concentration of nanofillers (conductors), it is easy to change the resistance of the investigated composites over a wide range.

The electrophysical parameter measurements were carried out according to standard methods. It should be noted that the effective dielectric constant is a complex value

$$\varepsilon = \varepsilon' + j' \varepsilon'' \quad (2)$$

The real part of dielectric constant was determined as the ratio of capacitances

$$\varepsilon' = \frac{C_x}{C_0}, \quad (3)$$

where, C_0 is the capacity of an empty cell (air filling); C_x is the capacity of a composite sample. The imaginary part of dielectric constant is defined as

$$\varepsilon'' = tg \delta \cdot \varepsilon' = \frac{1}{Q} \cdot \varepsilon', \quad (4)$$

where Q is the quality factor of the capacitor.

The quality factor of the capacitor was determined for diagram of parallel connection of the capacitor and the resistance by standard method. The measurements of capacitance and quality factor were made at a frequency of 1 kHz.

III. RESULTS

The main results of experimental studies of the electrical properties of composites 80% of SIR-3+20% of LDPE containing aluminum nanoparticles and soot in various quantities are presented in Fig. 3-7.

Fig. 3 (curve 2) and 4 show that the dielectric constant of the composite with an increase in the content of *Al* nanoparticles to 0.73 wt % goes down by almost 2 units, then with a further increase in the *Al* content to 5.37 wt % the value of the real part of the dielectric constant increases and reaches values amounting to $\varepsilon' = 4.10$, which is slightly higher than ε' of the initial (pure) composite.

Fig. 4 shows that with an increase in the content of *Al* nanoparticles to 0.73 wt % the insulativity ρ'_v decreases by an order of magnitude and the electrical conductivity of the composite increases 10 times. With further increase in the content of *Al* nanoparticles the dependence $\rho_v(c)$ leads to saturation.

Fig. 1 (curve 1) shows that in the composite under study 80% of SIR-3+20% of LDPE with 0.1% soot content the value of dielectric constant decreases by 1.5 units. Then with further increase of soot nano-additives it reaches the value of $\varepsilon' = 3.8$. If we compare the dependences $\varepsilon' = \varepsilon'(C)$ for composites containing soot nanoparticles (Fig. 1, curve 1) and *Al* (Fig. 3, curve 2), we may see that they differ significantly. In the first composite the decrease in ε' is observed only in the range of additives of 0.1%, and then the sharp increase in ε' begins, and in the second fall ε' is observed with the *Al* concentration of 0.73%, and then a gradual increase in ε' to 4 units.

The data comparison of dependences $\rho_v = \rho_v(C)$ for composite 80% of SIR-3+20% of LDPE containing soot nanoparticles (Fig. 5) and *Al* (Fig. 4) shows that the course of these curves also varies greatly. If for the composite containing *Al* nanoparticles 0.1%, 0.27% and 0.73%, as described above, the ρ_v value decreases by 1.5 orders of magnitude and then comes to saturation, then for the same composite containing soot nanoparticles, at such concentrations, the value of ρ_v increases almost by 2 orders of magnitude, then with a further increase in the content of soot, the values of ρ_v approach the values of ρ_v of pure composite.

Usually, when considering a polymer dielectric containing electrically conducting impurities (particles), the theory and model of the Maxwell-Wigner polarization is used. This results in the following relations:

$$\varepsilon' = \varepsilon'_\infty \left(1 + \frac{k}{1 + \omega^2 \tau^2} \right) \quad (1)$$

$$\varepsilon'' = \frac{\varepsilon'_\infty k \omega \tau}{1 + \omega^2 \tau^2} \quad (2)$$

$$\varepsilon'_\infty = \varepsilon'_1 \left[1 + \frac{3C(\varepsilon'_2 - \varepsilon'_1)}{2\varepsilon'_1 + \varepsilon'_2} \right] \quad (3)$$

$$k = \frac{9C(\varepsilon'_2 - \varepsilon'_1)}{2\varepsilon'_1 + \varepsilon'_2} \quad (4)$$

$$\tau = \frac{\varepsilon'_\infty(2\varepsilon'_1 - \varepsilon'_2)}{\sigma_2} = \varepsilon'_\infty(2\varepsilon'_1 + \varepsilon'_2)\rho^2 \quad (5)$$

where, ε'_1 , ε'_2 is the real part of dielectric constant of composite and inclusion, σ_1 and σ_2 is a specific conductivity of composite and inclusion. ρ – is the electrical resistivity, ε'_∞ is the dielectric constant at high frequencies, τ is relaxation time, ω is frequency.

Based on (5) it can be stated that the relaxation time is inversely proportional to the conductivity of inclusions, and the ε' and ε'' of the composite and the inclusions depend on the relaxation time \mathcal{T} .

Fig. 6 and 7 show the logarithmic dependence of the dielectric constant on the specific volume resistance of composite 80% of SIR-3+20% of LDPE containing *Al* nanoparticles and soot. This shows that the concentration dependence $\varepsilon' = f(\log \rho_v)$ is very complex.

Up to the concentration of 0.27 wt % *Al*, ρ_v drops by one and a half of the order and the dielectric constant remains almost unchanged. With the content of 0.73 wt % in the composite ε' is reduced by almost 2 units.

With the further increase in the *Al* content the values of ρ_v and ε' take average statistical values corresponding to the composite under study containing inclusions in the form of aluminum nanoparticles.

Such a paradoxical drop or growth of various physical parameters of the composite under study with small additions of *Al* and soot nanoparticles can be called the nanoeffect and is observed in the study of mechanical strength of composite when studying the density of composite and the amount of aluminum particles and soot on the surface of composite.

Based on the foregoing, the obtained concentration dependences $\rho_v(C)$ and $\varepsilon'(C)$ and the function for the composite under study cannot be explained in terms of the model of Maxwell – Wagner polarization.

In the work [2], an attempt was made to determine analytically the real part of the dielectric constant ε' for polymer composites containing metallic inclusions by the method of contact groups, where groups are groups of conductive impurities that are introduced into the dielectric high-resistance matrix; in our case into the composite.

$$\varepsilon' = \varepsilon'_1 \frac{1 + \frac{8\pi}{3} \sum_{a=1}^s C_a \alpha_a}{1 - \frac{4\pi}{3} \sum_{a=1}^s C_a \alpha_a} \quad (6)$$

where, ε'_1 is the real part of dielectric constant of composite based on rubber and polyethylene, C_a is the volume concentration of *a* - component, α_a is the effective polarization of *a* - component.

If we assume that the dispersed particles are homogeneous ellipsoids with dielectric constant ε'_a and specific volume V_a , then

$$\alpha_a = \frac{3}{4\pi} V_a \frac{\varepsilon'_a - \varepsilon'_0}{2\varepsilon'_0 - \varepsilon'_a} \quad (7)$$

Based on [3] the contact group method (equations (6) and (7)) was used to calculate the values of ε' for paraffin+aluminum and paraffin+iron system. The main particle size of conductive iron impurities “r” is 6×10^{-6} m; of aluminum “r” is 10-5m. Satisfactory agreement was obtained between the calculated and experimental $\varepsilon' = \varepsilon'(C)$ curves for the paraffin+*Al* system and for the paraffin+*Fe* system curves were obtained that had nothing to do with the experimental dependence of dielectric constant ε' on the concentration of iron particles. The authors of the work [3] explain a similar situation with the possibility of formation of conducting chains inside a fractal in the composite under study. It is known that aluminum powder consisting of micron-sized particles has a surface layer of Al_2O_3 , which is a good insulator with dielectric constant $\varepsilon' = 10$ and specific volume resistance $\rho_v = 1,5 \times 10^9 \text{ Ohm} \times \text{m}$.

This oxide film prevents the formation of conductive circuits reducing the conductivity of systems. In contrast to

aluminum iron is capable of forming conductive chains and drastically reducing the conductivity of systems.

Using the method of contact groups according to the equations (6) and (7), based on the values of electrophysical parameters of conductive inclusions of *Al* particles of micron sizes given in [3] we calculated the dependence of the real part of dielectric constant of composite $\epsilon'=\epsilon'(C)$ on the concentration of *Al* nanoparticles. They are presented in Fig. 3 (curve 3). This shows that the experimentally detected minimum in the dependence $\epsilon'=\epsilon'(C)$ at low concentrations ($C = 0.73$ wt %) is absent on the calculated curve. For the studied composite containing *Al* nanoparticles with the concentration of 1.99 wt % and above there is a good agreement between the experimental and calculated values of ϵ' . A significant discrepancy between the results of calculation of ϵ' by the contact group method and experimental data in the field

of small additions of *Al* nanoparticles to the composite can apparently be attributed: firstly, the fact that our electrically conductive additives of *Al* particles have nano-dimensions of the order of 20-30 nm (Fig. 1); secondly, equations (6) and (7) are constructed for micron-sized particles having an ellipsoidal shape and *Al* nanoparticles are not as such; thirdly, when deriving equations (6) and (7), it was assumed that the concentration of the conducting component (*Al* particles) is proportional to the conductivity of composite. This assumption is hardly true and difficult to verify for our conducting additives of *Al* nanoparticles.

For the composite under study, which contains conducting additives of soot in various concentrations it was not possible to obtain ϵ' values by the contact group method commensurate with the experimental data (Fig. 3, curve 1)

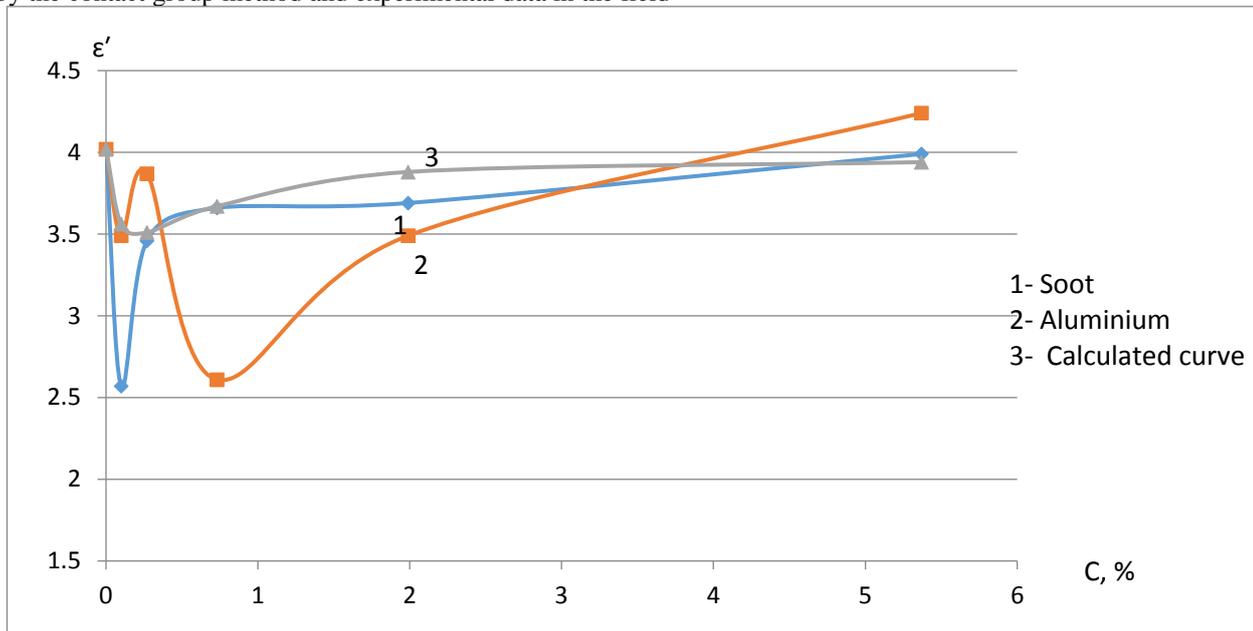


Fig. 3. Concentration dependences of real part of dielectric capacitance: 1 - 80% of SIR-3+20% of LDPE+soot; 2 - 80% of SIR-3 + 20% of LDPE+Al; 3 - calculated curve using the method of contact groups for composite of 80% of SIR-3+20% of LDPE+Al

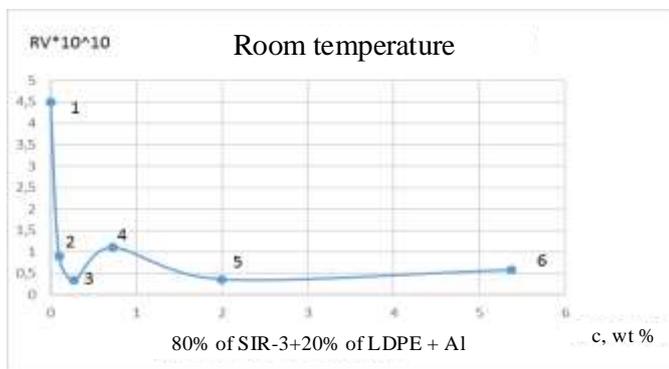


Fig. 4. Concentration dependences of specific resistance for composite of 80% of SIR-3+20% of LDPE + Al

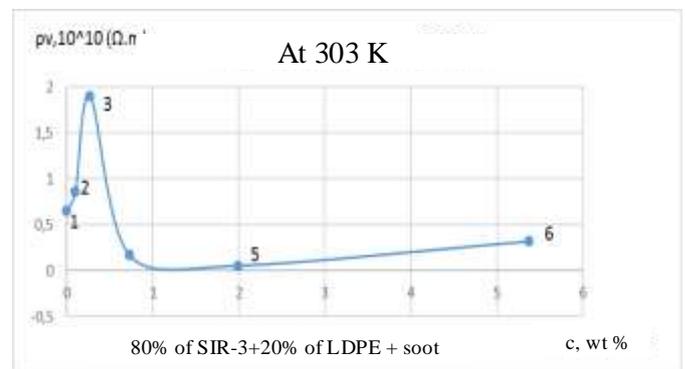


Fig. 5. Concentration dependences of specific volume of electrical resistance for composite of 80% of SIR-3+20% of LDPE+soot

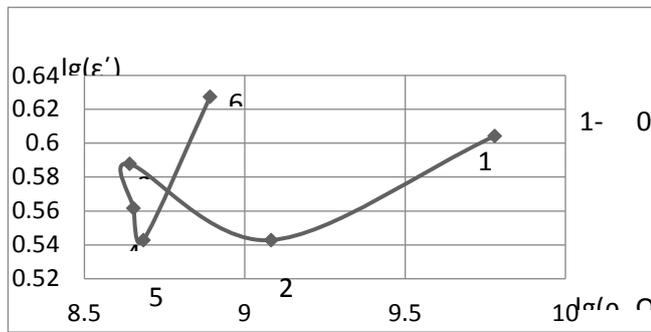


Fig. 6. Logarithmic dependence of dielectric constant on specific volume resistance of composite of 80% of SIR-3+20% of LDPE+Al at a temperature of 300 K

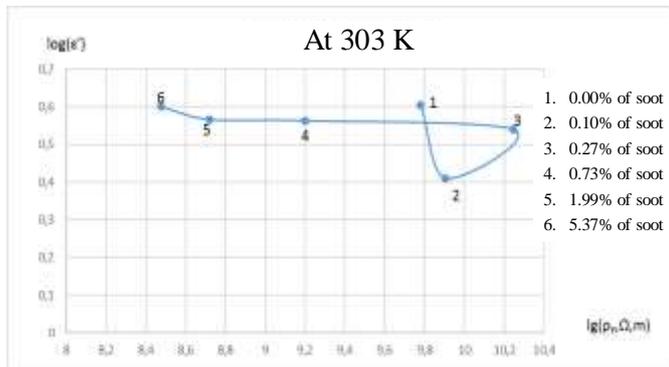


Fig. 7. Logarithmic dependence of dielectric constant on specific insulation resistance for composite of 80% of SIR-3+20% of LDPE+soot

Fig. 3–7 show that the dependences $\varepsilon' = \varepsilon'(C)$, $\rho_v = \rho_v(C)$, $\lg \varepsilon' - f(\lg \rho_v)$ undergo significant changes in the region of small additions of Al and soot nanoparticles in the SIR-3 composite 80 wt % + 20 wt % of LDPE, and the nature of nanoparticles (Al or soot) determines, sometimes at the same concentrations, a diametrically opposite change in some of the electrical parameters of the composite under study.

As noted above, these results cannot be explained neither with the Maxwell – Wagner polarization of dielectrics with conducting inclusions, nor by the Khokhlov – Grosberg reptational model [1].

In order to explain the experimental data obtained, the dielectric parameters and the specific electrical conductivity, we studied the structure and morphology, the change of density of composite SIR-380%+20% of LDPE, with Al nano additives and soot additives using electron microscopy, electron shadow microscope and hydrostatic weighing. These data are presented in Fig.8 and 9, respectively.

The elemental surface scanning data obtained with the help of an electron microscope shows (Fig. 8a) that aluminum particles (small concentration) are evenly distributed in the composite matrix. However, with an increase in the aluminum content up to 5.37 wt %, a certain part of nanoparticles line up in the 2nd order lines, possibly settling at the boundaries or delineating the forms of supramolecular formations in the composite.

Such an arrangement of Al nanoparticles in the composite, apparently, is due to the fact that they occupy the most energetically favorable positions when mixing the ingredients of the composite in the melt [11].

The authors of the work [5] observed a similar distribution of soot particles for some heterogeneous polymer blends, which led to superadditive electrical resistance.

In the work [6] it was shown that such redistribution of filler particles is due to thermodynamic advantage of this process, and in most cases the filler (above 5 wt %) is localized at the phase interface.

Unlike inert aluminum (due to the fact that the particles have an oxide film (Al₂O₃) soot is quite active and its nanoparticles form agglomerates with the sizes from 100 nm to 10 microns. (Fig.9).

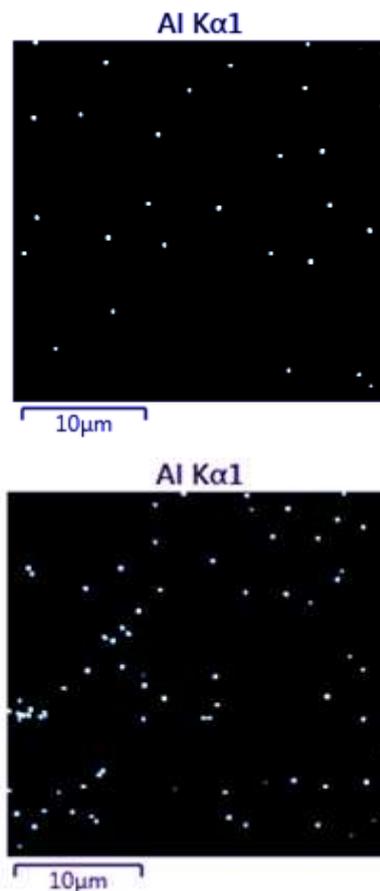


Fig. 8. Distribution of aluminum on the surface of SIR-3, containing: a) 0.1 wt %; b) 5.37 wt % of filler particles

However, in the process of preparing the composite, the soot associates are destroyed to nanometers [7]. The authors of this work have shown that soot agglomerates are crushed into parts under the action of stresses that occur during mixing.

Another approach is that these agglomerates experience “corrosion” during which small pieces break out of their surfaces [8].

The authors of the work [8] showed that both mechanisms work sequentially. The agglomerates are destroyed at the first stages followed by “corrosion”.

Fig. 10 shows the experimental dependences of the density (ρ) of the composite of 80 wt % of SIR-3+20% wt % of LDPE on the concentration of soot and aluminum nanoparticles.

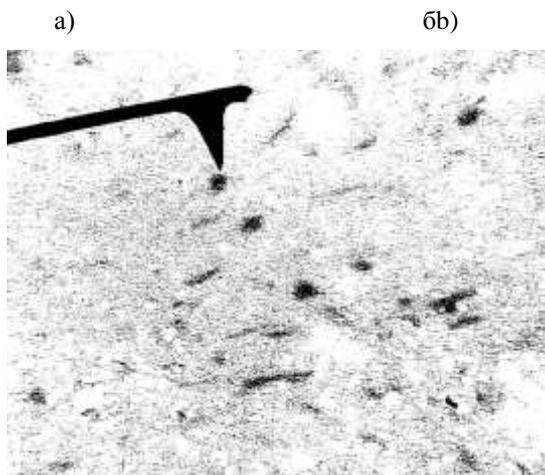


Fig. 9. Image obtained with an electron shadow microscope for the composite of 80 wt % of SIR-3+20 wt % of LDPE+0.1 wt % of soot

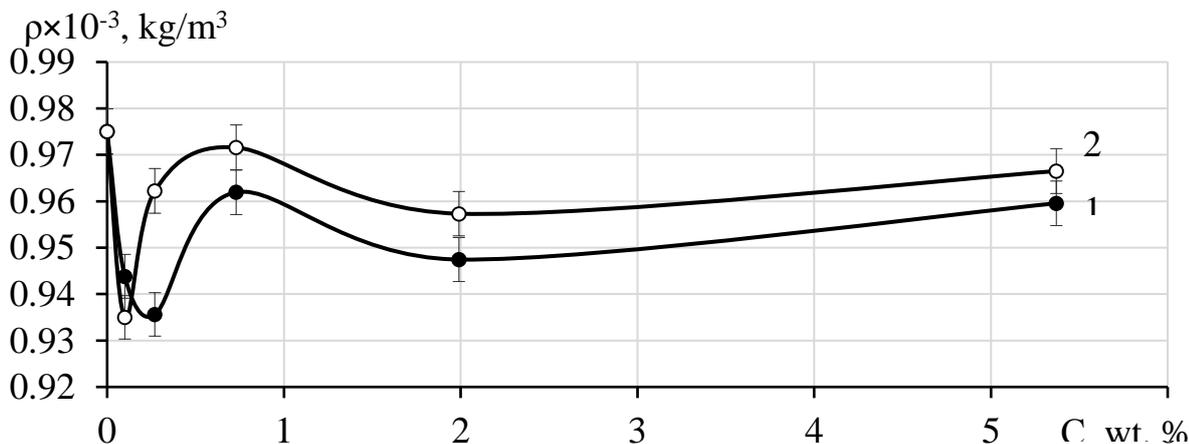


Fig. 10. Density (ρ) as a function of concentration: 1 - soot and 2 - aluminum in mixture of 80 wt % of SIR -3 +20 wt % of LDPE

Thus, the presence of *Al* nanoparticles in the composite under study above 2.0 wt % does not have a significant effect on the formation of macroscopic physical properties and structure of this composite.

The experimental data presented in Fig. 3 (curve 1), Fig. 5 and Fig. 7 for the dependencies $\varepsilon'=\varepsilon'(C)$, $\rho_v=\rho_v(C)$ and $lg \varepsilon'=(log \rho_v)$ do not fit in the framework of known models and can not be explained by structural studies. However, we can assume the existence of special effect, i.e. fractal polarization for composite of 80% of SIR-3+20% of LDPE+soot. In the

Hence, it can be seen that the extremum on the curves $\rho'=\rho(C)$ as for the curves $\varepsilon'=\varepsilon'(C)$, $\rho_v=\rho_v(C)$ are observed in the region of small additions of *Al* and soot nanoparticles.

Based on the experimental data presented in Fig. 8 and 10 for a composite of 80% of SIR-3+20% of LDPE containing *Al* nanoparticles, the path of curves $\varepsilon'=\varepsilon'(C)$, $\rho_v=\rho_v(C)$ presented in Fig.3 and 4, respectively, can be associated with loosening (amorphization) of the structure of this composite with the content of 0.1% to 0.73% of *Al* nanoparticles, which is confirmed by a decrease in the density of composite at such concentrations of *Al* nanoparticles (Fig. 10) and their uniform distribution in the volume (Fig. 8). Under such conditions the process of orientational polarization in the composite is facilitated, the magnitude of ε' decreases by 1.5 units, the values of ρ_v fall by an order of magnitude, and the electrical conductivity improves.

The implementation of these processes of dipole orientation consumes a significant part of the energy of an external electric field, which is confirmed by an increase in the values of the dielectric loss factor (Table 1) in this concentration region several times.

A further increase in the concentration of *Al* nanoparticles in the composite leads to their redistribution at the boundaries of morphological formations in composite: the dependence $\rho'=\rho(C)$, $\varepsilon'=\varepsilon'(C)$ appear almost on the plateau and the dependences $\rho_v = \rho_v(C)$ are saturated.

Fig. 11a and b present the structure of fractal conducting structures assumed by us in a composite of 80% of SIR-3+20% of LDPE+soot.

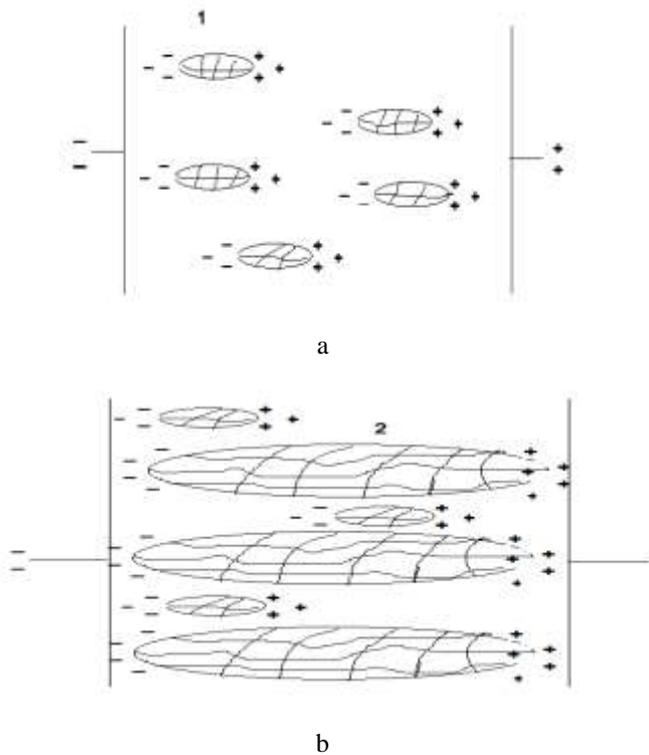


Fig. 11. Estimated schematic structure of fractal conductive formations in composite of 80% of SIR-3+20% of LDPE+soot

- The percolation threshold was not reached; it contains only inclusions of type 1.
- The percolation threshold was reached; the inclusions of type (2) appear; however, the inclusions of type (1) still remain.

The schematic structure presented in Fig. 10 is a sample of the composite-dielectric under study, which contains fractal clusters-conducting inclusions of soot nanoparticles.

It is known that when introducing the concept of dielectric constant, the concept of isotropy of a substance [11] and possible small deviations is mentioned. However, when considering composites, especially those containing conductive inclusions, the isotropy conditions are substantially violated. In fact, there are pronounced anisotropic properties in conductivity, thermal conductivity and other macroscopic properties in the composite. Moreover, it is impossible to take this anisotropy into account, for example, in crystals, because of the chaotic arrangement of fractal structures that can form different phases.

The path of the dependence curve $\rho_v = \rho_v(C)$ for a composite containing soot nanoparticles with the concentration of 0.1% wt % (1), 0.27 wt% (2) and 0.73% wt% (3) can be explained by the implementation of hypothetical fractal arrangement clusters in the composite shown in Fig. 11 (a). The percolation threshold has not been reached yet. The conductivity in the composite is

low. When an external field is applied, the orientation of the polar molecules of dielectric changes with respect to the initial one; however, such displacements in the composite are insignificant. Such reasoning is confirmed by an increase in the value of ρ_v by 1.0–2.0 orders of magnitude in the region of small additions of soot nanoparticles and by the highest values of the dielectric loss factor.

With an increase in the content of soot nanoparticles in the composite of more than 2 wt % the hypothetical scheme presented in Fig. 11 (b) is implemented.

The percolation threshold occurred in the composite and the conductivity was improved, while apart from the inclusion of type 1 the inclusions of type 2 appear, which close both electrodes. However, the electrical connection between electrodes is far from the ideal as in the mathematical models of percolation.

TABLE I. THE VALUES OF THE DIELECTRIC LOSS FACTOR ϵ'' CAUSED BY THE ELECTRICAL CONDUCTIVITY OF COMPOSITE ARE 80% OF SIR-3+20% OF LDPE CONTAINING AL NANOPARTICLES AND SOOT.

No.	Al, wt %	$\epsilon'' \cdot 10^3$	Soot, wt %	$\epsilon'' \cdot 10^3$
1	0	2.74	0	2.74
2	0.10	13.84	0.10	2.25
3	0.27	4.50	0.27	1.00
4	0.73	1.12	0.73	9.00
5	1.99	4.50	1.99	18.00
6	5.37	3.60	5.37	3.00

The complex nature of the resistance between individual clusters is preserved. This means that at alternating voltage on the electrodes of the capacitor, the percolation cluster recharges through significant active and capacitive resistances. The process of recharging the percolation cluster contributes to the change in both parts of the dielectric constant. The described mechanism is confirmed by the curve $\epsilon' = \epsilon'(C)$, $\rho_v = \rho_v(C)$ and Fig. 3 and 5, i.e. high values of the loss factor ϵ'' (Table 1) for the composite containing soot nanoparticles of more than 2 wt %.

IV. CONCLUSION

1. The dependences of dielectric constant and specific volume resistivity of composite of 80 wt % of SIR-3+20% wt % of LDPE on the concentration of nanoparticles of aluminum fillers and soot were experimentally investigated. The features of these curves were considered.

2. It was shown that at a low content of Al and soot nanoparticles in the composite, significant changes are observed: extremes on the curves $\epsilon' = \epsilon'(C)$, $\rho_v = \rho_v(C)$, which do not fit into the Maxwell-Wagner polarization model.

3. Using a set of modern methods for studying macroscopic properties and electron microscopy to study the structure and morphology of supermolecular formations of composite, models were developed and possible physical mechanisms leading to extreme changes in ϵ' and ρ'_v in the region of low concentrations of nanoparticles were presented.

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