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THE ROLE OF THE INTERFACIAL LAYER IN TIME-TEMPERATURE DEPENDENCE OF THE ELECTRICAL RESISTANCE OF HIGH DENSITY POLYETHYLENE/CARBON BLACK COMPOSITES[*]

N.N. Komova@

Moscow Technological University (Institute of Fine Chemical Technologies),
Moscow, 119571 Russia
@*Corresponding author e-mail*: komova_@mail.ru

To explain the time-temperature dependence of the electrical resistance of HDPE filled with carbon black proposed a model in which the important role plays interfacial layer between the solid phase filler and polymer matrix. Changing the properties of the layer during the electric conductivity estimated using fractal concepts. The fractal dimension increases with decreasing particle size of the filler, and is accompanied by a decrease in electrical resistance. During isothermal annealing treatment of the samples the fractal dimension of the interfacial layer is changed from 2.3 to 3. Presents the correlations observed parameters. Calculate the energy of activation of increasing resistance in the initial period of treatments of sample. It is shown that the electrostatic field restrains an increase of fractal dimension of the interfacial layer and the resistance change of filled systems.

Keywords: *high density polyethylene, carbon black, the activation energy of electrical conductivity changes, the relative resistance, interfacial layer, fractal dimension.*

Introduction

Polymers, as a rule, are insulating materials. However, their mechanical characteristics are very attractive for the creation of conductive materials based on them. One of methods for increasing the electric conductivity of materials based on polymers is the addition of conducting fillers such as metal powders or fibers, graphite, carbon black and carbon fibers [1–4]. The electric behavior of such composite systems is successfully described by the theory of percolation [5–8].

The conductivity of polymeric composites is explained by several theories, by means of which it is possible to describe the observed regularities in a varying degree. One of the theories considers the ionic mechanism of conductivity in amorphous polymers [9]. According to the second theory applicable for the filled systems on the basis of partially crystalline low-conductivity polymers, conductivity is determined by the emission of electrons, most likely, by the tunneling transfer between particles, the distance between which is less than 5 nanometers [10].

In case of high conductivity it is assumed that contacts between filler particles are ohmic. When such conductivity is realized, continuous conducting chains are formed. In this theory the main attention is paid to the geometrical factor connecting the value of conductivity with a random set of conducting chains. The theory determines the ratio of conductivities of a composite σ and a

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conductive component σ_c as the product of the ratio of the fraction of conducting and non-conducting elements, the probability of the formation of a chain (p) and a geometrical factor – the cross-sectional area of the conducting element (C): $\sigma/\sigma_c = f_\upsilon \cdot p \cdot C^2$ (f_υ is the volume fraction of the filler) [10]. Such approach to the analysis of conductivity of composite materials is similar to the description of systems from the view point of fractal physics [11].

A specific feature of conductive polymeric composites is the change of their electric properties while in service. Works [12–17] describe studies on the change of samples resistance in isothermal conditions in the course of time. In [13] it is noted that the specific resistance of samples increases by a factor of 1.5 within the first minutes of keeping high-density polyethylene (HDPE) filled with carbon black at 60°C. The fact of initial increase of resistance is explained as the result of heat transfer in the sample, i.e., the result of attaining thermal balance in the bulk of the whole sample. Further keeping of the sample in isothermal conditions results in an exponential reduction of resistance, the latter approaching asymptotically a constant value. This process is described in [17] by the equation of the following form:

$$\rho=\rho_o + \Delta\rho \exp(-t/\tau),$$

where $\rho_o + \Delta\rho$ is the value of initial maximal resistance, ρ_o is the limit value of specific resistance, τ is the characteristic time of resistance reduction.

In works [13, 14] an estimation of the results of differential scanning calorimetry (DSC) of polyethylene samples filled with carbon black was performed. It was concluded that reduction of resistance upon keeping the samples at elevated temperatures is determined by dynamic reorganization of the conductive network of the filler, and such structural changes are not regulated by linear viscoelasticity. In this case the conductivity mechanism based on conducting chains of the filler particles is implemented. The effect of temperature causes rearrangements in the conductive chain of the filler particles in the polymeric matrix. This results in the phenomenon of segregation of soot particles in the amorphous regions. In [13, 18] it is pointed out that rearrangements of the filler become more and more noticeable upon reduction of the surface of the soot particles. Such behavior is explained by the fact that well-structured particles of the filler restrain the local mobility of the polymeric chain and, therefore, reduce the possibility of intensive rearrangements. However, these works considered neither the influence of the electric field applied upon the measurements nor the influence of the properties of the interfacial layer arising around the filler particles in the polymeric matrix.

An important condition of creating composite materials based on polymers and disperse fillers is the considerable size of adhesive forces between the polymer macromolecules and the solid surfaces of the filler particles [19]. Such forces act in areas where there is interaction between the filler and polymer (on interface boundaries) [20]. Interaction of segments of macromolecules with the filler particles changes the packing density [21] and the ways of the arrangement of sites of macromolecules at the particles surface. As a result, an interfacial layer is formed. It has characteristics other than the properties of the polymeric matrix situated far from the filler.

Adhesive forces, quite obviously, will influence the formation of conductive channels of the filler particles. Therefore, the properties and supramolecular structure of the interfacial layer in composite materials have essential impact on the conductive properties of materials.

Works in the field of solid state physics showed the core role of surface energy, which is shown in adhesion interaction, as well as in the formation of the structure and properties of composite materials [22]. Important information on the structural state of a substance is born by the fractal dimension, a fundamental concept of fractal physics [23]. The topological dimension of a volume is considered to be equal to 3, and that of a surface, equal to 2. Transition from volume structures to surface ones is characterized by a change of the fractal dimension of the polymeric chain. This dimension, generally, is a fractional value between two and three units [24]. According to the theory of adhesion [25], as the value of fractal dimension decreases, the substance fills the three-dimensional space. Transition from the volume part of the material object to its surface results in the release of energy. The latter can be found as the surface energy of the condensed phase [26]. In [24] it is suggested to estimate the value of surface energy by the difference of the fractal dimensions in the volume and in the interfacial layer. Such method allows comparing adhesion and cohesion energies and giving an estimation of the durability of the filled polymeric system.

As shown in works [11–13], the structural features of nanocomposites substantially influence the conductivity of such materials. When the filler content exceeds a certain critical value (the so-called percolation threshold), conductive particles form a continuous network throughout the whole system [13]. Therefore, in the range of concentrations above the percolation threshold resistance sharply decreases by some orders of magnitude. The ability to form a conducting system in composite materials depends on many factors: on the physical and geometrical characteristics of the filler particles; on the properties of the polymeric matrix (in particular, the degree of crystallinity of the polymer); on the filler/polymer ratio etc. In case of composites containing carbon black as a filler the material conductivity substantially depends on the microstructure of the filler particles [27–30].

As shown in a number of works [12–16, 31, 32], in the course of isothermal heating the change of resistance of the high density polyethylene / carbon black (HDPE/CB) system has a complex extremal character. Considerable changes of electric resistance are characterized by both positive and negative temperature coefficients [1, 13–16, 33]. In the low-temperature ranges (225–275 K) an exponential fall of electric resistance is observed, which is typical of semi-conductor materials [34]. This is caused by the growth of the number of conducting channels at the expense of an increase in the contribution of tunnel conductivity [35].

At higher temperatures growth of electric resistance is usually observed. This is generally associated with the thermal expansion of the polymeric matrix and, as a result, the increase of the distance between the filler particles and the destruction of conductive channels [36–39].

The specific resistance of conductive composite materials based on crystalline polymers increases as temperature grows. Their specific resistance is determined by a positive temperature coefficient [36, 40–43]. This phenomenon is attributed usually to the difference in the temperature expansion coefficients of the polymeric matrix and the filler particles. At temperatures above the melting point of the polymeric matrix the system resistance decreases as temperature increases. This tendency, as a rule, is determined by a negative temperature coefficient [40, 41, 43–49]. In general, the question of the reasons of the sharp increase and fall of electric resistance remains open [50] because of the complex structure of such composite materials.

The influence of the surface area of technical carbon black particles, the density of the particles and their content in the polymeric matrix on conductivity and the value of the percolation threshold in HDPE/CB system in the course of isothermal heating is studied in detail in [13]. It is noted that the percolation barrier decreases as the surface of CB particles increases, and the time dependence of resistance at isothermal heating of samples has an extremal character passing through a maximum. The result of the analysis of experimental data in this work showed that rearrangement of the conductive network of carbon particles in the polymeric matrix occurs in the course of isothermal heating, which reduces specific resistance. It is noted also that the decrease in specific resistance is influenced by the surface area of the filler particles. The experimental data obtained in [13] unambiguously indicate the influence of the structure of the particles and their interactions with the polymeric matrix on the electric resistance of the composite material.

Literature data analysis gives ground to conclude that the change of electric resistance of HDPE/CB system in the course of isothermal heating is determined not only by the temperature expansion of the polymeric matrix, but also by processes occurring on the surface of the filler particles, as well as by the rearrangement of the interfacial layer.

This work presents a semi-quantitative model of changes of HDPE/CB system resistance. The model is based on the core role of the interfacial layer, the structural change of which can be characterized within the fractal conception. The obtained experimental data on the change of resistance in the course of isothermal heating of HDPE/CB system in an electrostatic field are analyzed within this model.

Physical Ground

Article [13] presents data on the quantitative dependence of percolation threshold (Φ_c) on parameters characterizing the interaction of the filler particles surface with the polymeric matrix on the basis of experimental works on the resistance of HDPE filled with CB. These parameters are: CB particles density (d_p) and OAN (the amount of oil adsorbed on the surface of the particles). The latter parameter characterizes the complexity of the filler particles structure and of their aggregates

$$\Phi_c = (1 + 4\ d_p\ OAN)^{-1} \tag{1}$$

This dependence was obtained within the Kirkpatrick model of conductivity [51]:

$$\rho = \rho_o(\Phi - \Phi_c)^{-t}, \tag{2}$$

where ρ is the specific resistance of the filled system at CB concentration above the percolation threshold; ρ_o is the specific resistance of the filled system depending on the filler nature; Φ is the volume content of the filler.

In order to determine the dependence of Φ_c on the arrangement of segments of macromolecules on the filler surface it is expedient to redetermine dependence (1) using the value of the average specific surface area of the filler particles, S_u. The dependence of S_u on OAN determined with the use of the experimental data for HDPE/CB system provided in work [13] is linear (Figure 1).

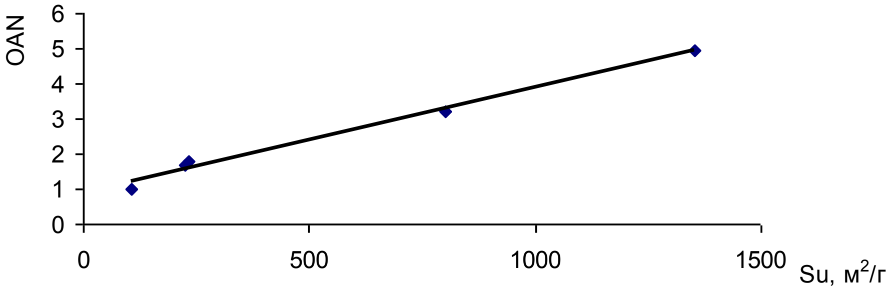


Figure 1. Dependence of OAN on S_u for HDPE/CB system determined at room temperature.

This dependence is described by the following formula:

$$OAN = 0.003\ S_u + 0.9. \tag{3}$$

According to [52, 53] the specific surface of filler particles can be estimated by means of the following formula:

$$S_u = 420\ (R_p\ )^{dn-d}, \tag{4}$$

where d_n is the dimensionality of the particles surface, d is the dimension of the Euclidean space (d = 3).

The dimensionality of the particles surface in essence is the fractal dimension of d_n: $D= d_n$. So,

$$S_u = 420 \, (R_p)^{D-3} \tag{5}$$

The filler particle size considerably influences the physical properties of the filled material by means of the influence on the degree of crystallinity and on the structure of the interfacial layer. This determines the influence of the filler particle size on the electric conductivity of the composite material and has an impact on the change of the percolation barrier upon the introduction of particles of various diameters into the polymer.

Using the concept of a particle as a spherical object and the phenomenological association of the average specific surface area of the particles S_u with the average diameter of these particles of D_p [54] it is possible to obtain the following formula:

$$S_u = 6/\, d_p D_p, \tag{6}$$

where d_p is the density of the filler material.

The experimental data obtained in [13] enable obtaining the values of the effective radiuses of the filler particles and to determine the dependence of the percolation threshold of HDPE/CB system (Φ_c) on the CB particle size (Figure 2). The dependence can be approximated by a fractional order curve, from which it follows that

$$R = 300\Phi_c^{1.42}, \tag{7}$$

where R is the average effective radius of the filler particles.

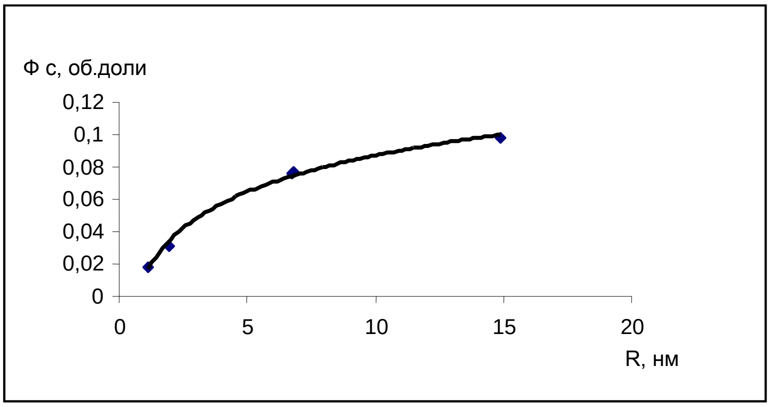


Figure 2. Dependence of the percolation threshold at room temperature on the filler particle size for HDPE/CB system.
[об. доли means volume fractions: нм means nm]

After substitution of the corresponding expressions in formula (1) we obtain

$$1/\Phi_c = 1 + 4\, d_p[1.26(300\, \Phi_c^{\,1.42})^{D-3} + 0.9] \tag{8}$$

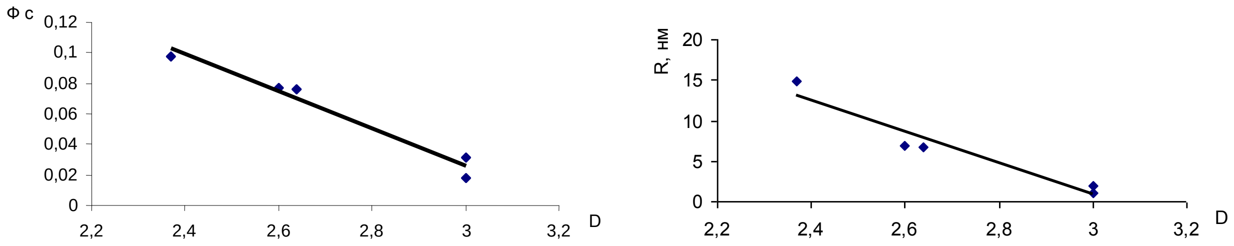
Formula (8) enables calculating fractal dimension D, and then the thickness of the interfacial (adsorptive) layer (δ) using the formula suggested in [55]:

$$\delta = l_{st}(R/l_{st})^{2(d-D)/d} \ , \qquad (9)$$

where *d* is the dimensionality of the Euclidean space, in which the fractal object is considered; l_{st} is the lower linear scale of fractal behavior. In case of polymers l_{st} is taken to be equal to the length of a statistical segment [56].

For polyethylene the length of the statistical segment representing the length of a structural element of the polymeric chain is equal to 2.08 nm [57].

Calculations carried out with the use of the experimental data of [13] showed that the value of the fractal dimensionality of the studied samples changes from 2.37 to 3, and the interfacial layer thickness, from 22.53 to 0.6 nm. Figure 3 shows the dependences of the percolation threshold (Φ_c) on the fractal dimensionality (Figure 3a) and the dependence of the particles radiuses on the fractal dimensionality when the percolation threshold is attained (Figure 3b). Both dependences are linear and show that, as the fractal dimension increases, the percolation threshold and particles sizes, at which the resistance drop in the considered system is realized, decrease.



a b

Figure 3. Dependence of the percolation threshold (a) and particle radius (b) on fractal dimensionality for HDPE/CB system.

Analysis of fractal dimensionality change upon interaction of polymeric macromolecules with the surface of a solid filler [58] shows that the increase of the fractal dimensionality of the filler particles reflects the increase of its roughness. At the same time the surface area of the particles increases, and the reinforcing effect of the nanofillers in the polymer grows. It is proved in [25] that the maximum level of adhesion is realized at identical fractal dimensionalities of the interfacial layer and the three-dimensional polymeric matrix. Therefore, the formation of an interfacial layer with the fractal dimension typical of the polymeric matrix is energetically favorable. On the other hand, if the particle size is equal to the size of the elementary structural repeating unit of the macromolecule, which is equal to the length of the statistical segment of the polymer, arranging such segments completely on a solid surface becomes difficult, and the interaction of the segments of the macromolecules with the particles does not occur on the whole surface, but only in points of contact. Therefore, the fractal dimensionality of the part of the macromolecules entering the interfacial layer changes as well.

The authors of [59] showed that measurement of the fractal dimensionality of the surface d_{sp} by the adsorption of "molecules" with finite sizes gives an extreme dependence of d^a_{sp} on the real dimensionality d_{sp}. Namely, the following formula was obtained in the system of the three-dimensional Euclidean space at $d_{sp} > 2.5$:

$$d^a_{sp} = 5 - d_{sp}. \tag{10}$$

This means that the segments cannot follow the particles surface roughness and, as d_{sp} grows, they perceive it as a smother and smoother one. (When $d_{sp} = 3$, according to equation (10) $d^a_{sp} = 2$.) Therefore, dimensionality of d_{sp} should be replaced with d^a_{sp}.

According to this conception correct estimation of the particles size and of the percolation threshold value takes place at fractal dimensionality not higher than 3. Under different conditions it is necessary to adjust the value of fractal dimensionality.

According to equation (8) D attains the value of 3 at $\Phi = 0.053$ volume units, which corresponds to particle size $R = 4.63$ nm, and the interfacial layer thickness under these conditions is $\delta = l_{st}$. Thus, when the greatest conductivity is realized in case of particle size comparable to the size of the elementary base unit of the polymeric chain, fractal dimension is not less than 3, and the radius of such particles does not exceed 4.63 nm.

It can be seen from Figure 4 that the value of the percolation threshold decreases with increasing fractal dimension of the interfacial layer. This dependence has two areas. According to the above consideration, fractal dimension cannot exceed 3. Thus, the value of fractal dimension becomes maximum possible having reached the value of percolation threshold 53% vol. In the course of further reduction of the percolation threshold value it should be calculated with the use of equation (10). The value of the percolation threshold decreases with decreasing thickness of the interfacial layer (Figure 5), and the thickness of the interfacial layer increases in proportion to the filler particles size (Figure 6).

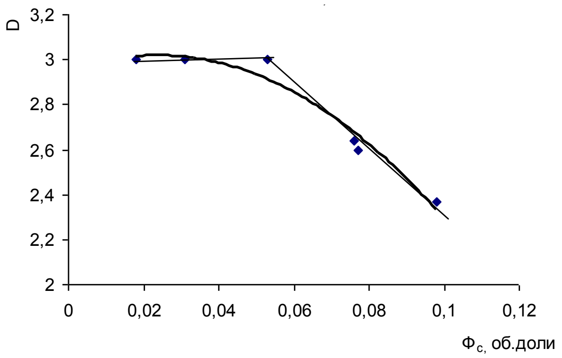


Figure 4. Dependence of fractal dimensionality on the percolation threshold value for HDPE/CB system.

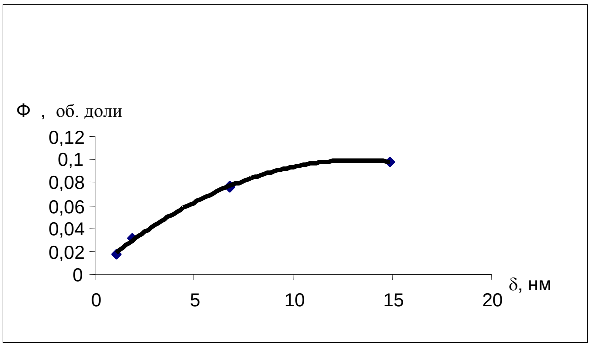


Figure 5. Dependence of the percolation threshold value on the thickness of the interfacial layer.

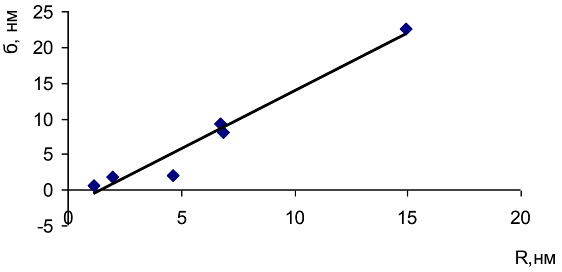


Figure 6. Dependence of the interfacial layer thickness on the CB particles radius at the attainment of the percolation threshold.

Analyzing the obtained results, it is possible to conclude that the dependence of HDPE/CB system resistance on the filler concentration is a mediated value. The resistance (or conductivity) of such system will depend considerably on the thickness of the interfacial layer and on the way of its organization (fractal dimensionality). This follows from the conception of conductivity arising upon the formation of a continuous conductive grid of fillers or upon the realization of tunneling effect. These processes depend both on the distance between the particles and on the way of arrangement of segments of macromolecules between these particles, which depends on the properties of the interfacial layer. As a result, one should expect strict dependence of resistance on fractal dimensionality and the interfacial layer thickness. Experimental data enabling to estimate such dependences for HDPE/CB system (Figures 7 and 8) are provided in [13].

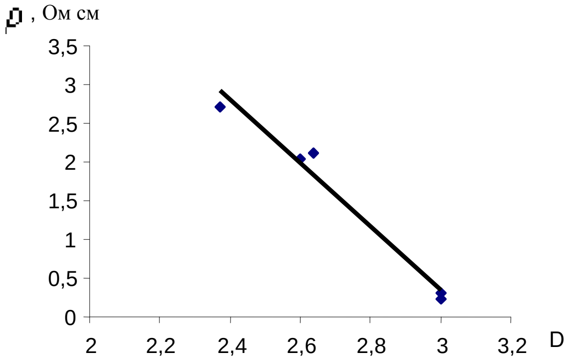


Figure 7. Dependence of the specific resistance of HDPE/CB system that attained the percolation threshold at room temperature on the fractal dimensionality of the interfacial layer. [Ом·см means Om·cm]

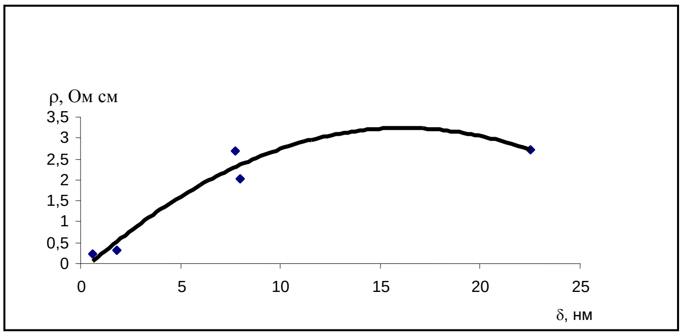


Figure 8. Dependence of the specific resistance of HDPE/CB system that attained the percolation threshold at room temperature on the interfacial layer thickness.

While the dependence of resistance on fractal dimensionality is linear (resistance decreases with increasing dimensionality of the interphase layer), the dependence of resistance upon the attainment of the percolation threshold at room temperature is best approximated by a quadratic function. The quadratic dependence of resistance on the layer thickness is explained by an analogous dependence of fractal dimensionality on the layer thickness (Figure 9).

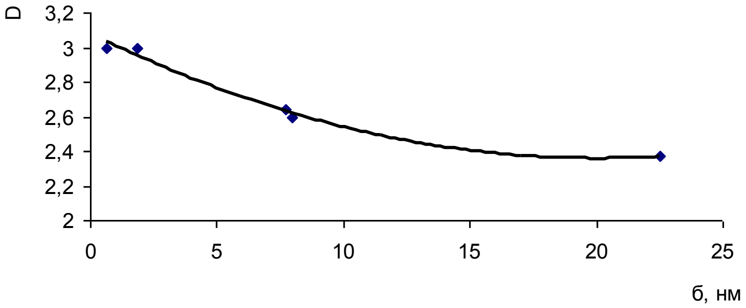


Figure 9. Dependence of the fractal dimensionality of the interfacial layer of HDPE/CB system upon realization of the percolation threshold at room temperature on the thickness of this layer.

Thus, the reduction of the interfacial layer thickness upon the reduction of the particle size results in an increase of the fractal dimensionality of the area between the polymer and the filler particles, which reduces the percolation threshold of the filled system and reduces resistance upon the attainment of this threshold.

It should be noted that in case of the considered HDPE/CB system the process of realization of conductivity will be affected not only by the structure and size of the interfacial layer, but also by the degree of crystallinity of the polymeric matrix [13, 60]. Moreover, these processes will determine each other when forming the general structure of the filled system. Besides, according to the presented features of the arrangement of the molecules with respect to the filler particles it is more correct to characterize the properties of the interfacial layer with the use of values of the change in the fractal dimensionalities of this layer.

A method for estimating the energy of adhesive interaction for the compositions of an aromatic polyamide filled with carbon fibers is suggested in [25]. The method is based on the statement that decreasing the value of the dimensionality of filling a three-dimensional space with a substance upon transition from the three-dimensional part of the material object to its surface results in energy release, which is experimentally found as superficial energy of the condensed phase. The value of surface energy is estimated by the difference of fractal dimensionalities in the polymeric matrix and on the filler surface [61].

The work also shows that the reduction of the fractal dimension value in the interfacial layer or the increase of the difference of the fractal dimensionalities in the matrix and in the interfacial layer results in the growth of the interfacial layer durability. In order to estimate this phenomenon, the density of energy contained in the interfacial layer [62] was used. The dependence of energy on the difference of the fractal dimensionalities is linear. The conclusion is drawn that the reduction of the dimensionality of the distribution of the interfacial layer substance in the three-dimensional space results in energy release, which should be compensated by "injection" of mechanical energy for the destruction of the interfacial layer.

Thus, the less is fractal the dimensionality of the interfacial layer, the more difficult it is to destroy, because strong interactions between the filler and the polymeric matrix on the interface tend to reduce molecular mobility near the filler surface as compared to the polymeric matrix.

It is possible to conclude within the considered conceptions that the reduction of resistance and of the percolation threshold value in HDPE/CB system with growing fractal dimensionality, other things being equal, is due to the reduction of the interfacial layer size and to the increase of molecular mobility in the bulk of this layer.

Figure 10 shows the dependence of the specific resistance of HDPE/CB system on the difference between the fractal dimensionalities in the polymeric matrix and in the interfacial layer.

The dependence is linear and indicates that the reduction of resistance (the growth of conductivity) corresponds to the reduction of the energy accumulated in the interfacial layer. This means that if the values of the fractal dimensionality in the polymeric matrix and in the interfacial layer coincide, the destruction of this layer will require minimal energy, and, accordingly, the formation of a conductive chain of the filler particles will require minimal power consumption. In order to estimate this process it is possible to use the dependence of the relative resistance of HDPE/CB system containing a filler above the percolation threshold at room temperature on the relative difference of the fractal dimensionalities. This dependence is linear (Figure 11):

$$R/R_{min} = 18(3.14 - D) \qquad \text{or} \qquad R/R_{min} = 18(\pi - D) \qquad (11)$$

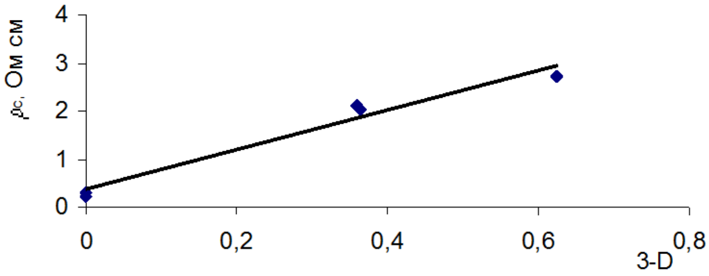


Figure 10. Dependence of the specific resistance of HDPE/CB system on the difference of the fractal dimensionalities in the polymeric matrix and in the interfacial layer at room temperature upon realization of the percolation threshold.

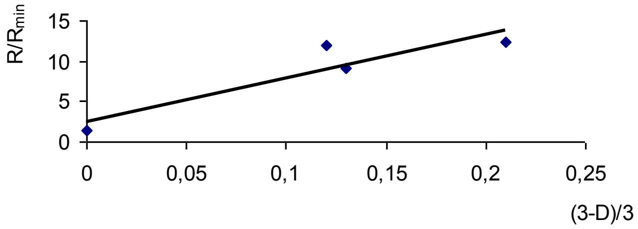


Figure 11. Dependence of the relative resistance of HDPE/CB system at room temperature upon realization of the percolation threshold on the relative difference of the fractal dimensionalities.

Experimental

OBJECTS AND RESEARCH METHODS

Objects of the research were compositions based on thermoplastic polymers: Eltex A4009 high-density polyethylene (HDPE) produced by BP Solvay, Belgium (melt flow rate 0.8 g / 10 min at 190°C, density 0.958 g/cm^3) and electroconductive carbon P 366-E (specific external surface 110–130 m^2/g, specific adsorptive surface 170–190 m^2/g, specific volume resistance $6 \cdot 10^{-3}$ Ohm·m at 0.5 g/cm^3. The introduced amount of the filler was calculated so that its value was not less than the percolation threshold of this system, HDPE/CB: 10% mass [63, 64].

Compositions were prepared in a closed Brabender rotor mixer with the work chamber volume 30 ml with liquid heating within 10 min at the rotation speed of the rotors 50 rpm. Mixing temperature for HDPE was 160°C. Test samples were produced with the use of a hydraulic press at 200°C. Disc-shaped samples about 1 mm thick with a diameter of 50 mm were located between electrodes in a thermostat, where temperature was set within the accuracy of 0.1°C. Constant tension of 100 or 10 V was applied to the electrodes. The samples resistance was measured by E6-13A teraohmmeter in two modes:

1) with electric field switched-off in the course of heating the sample to a preset temperature;

2) with constant field in the course of heating.

Results and Discussion

Kinetic curves describing the change of the resistance of HDPE/CB system in 100 V electric field at different temperatures have different shapes (Figure 12). Warming up the system in electric field for more than 2 min changes the temperature dependence of resistance radically. When temperature is 30°C, resistance increases and reaches the maximum value within 5 min. This value does not change in the course of all the subsequent time of holding the material in isothermal conditions (60 min). In contrast, the change of resistance at higher temperatures (40–70°C) has an extremal character. The rate of resistance fall for samples at long influence of electric field is proportional to the samples temperature. This effect was also observed in [32].

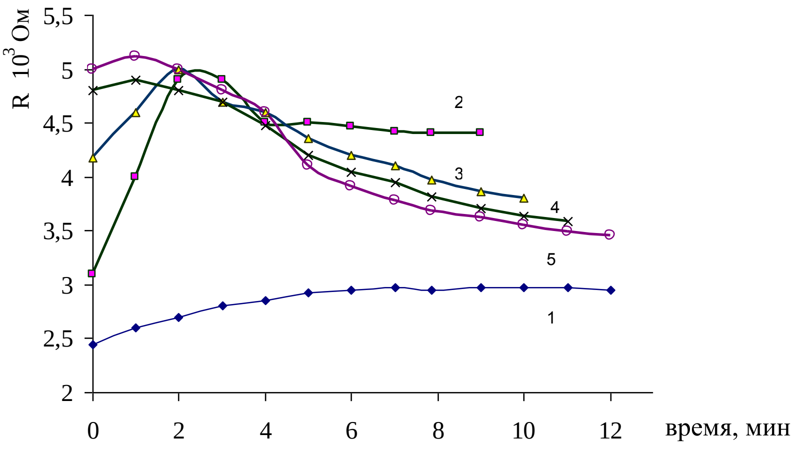


Figure 12. Kinetic curves of changes in the resistance of HDPE filled with 10% mass of carbon black (CB) obtained at warming up in a constant field (voltage applied to the electrodes: 100 V) and temperature: 1 – 30°C; 2 – 40°C; 3 – 50°C; 4 – 60°C; 5 – 70°C. [Ом means Om; время, мин means time, min]

Observing the change of the resistance of HDPE/CB system without voltage on the electrode plates between measurements gives a similar dependence of resistance on the time of holding the samples at different temperatures (Figure 13).

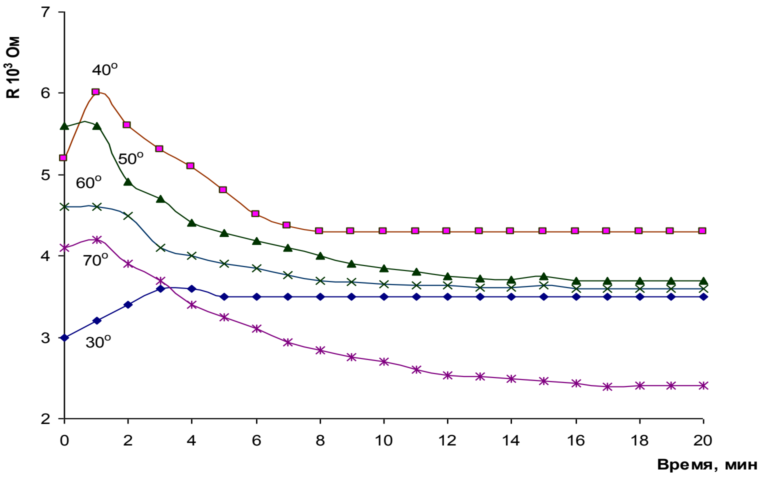


Figure 13. Kinetics of change of the relative resistance of the composite material HDPE containing 10% mass of CB at 100 V in the course of resistance measurement:
1 – 30°C; 2 – 40°C; 3 – 50°C; 4 – 60°C; 5 – 70°C.
[Ом means Om; время, мин means time, min]

Similar dependences were found for a weaker field obtained by applying a voltage of 10 V to the electrodes [18]. (The corresponding graphs are not presented here.)

On the basis of the model describing the influence of interfacial layers on the resistance of the composite material presented in the theoretical part it is possible to assume that the change of resistance within the first 5 min of the samples examination is due to, in addition to other factors, restructuring in the interfacial layer, which should have an effect on the change of fractal dimensionality of this layer. An estimation of the change of fractal dimensionality upon warming up HDPE containing 10% mass of CB in a constant field and in a field switched in only when measuring resistance showed that the change of fractal dimensionality according to formula (11) is determined by the following dependence:

$$\Delta D = (R/R_o - 2.5)/18 \qquad (12)$$

The corresponding dependences are given in Figure 14. In all the cases the change of fractal dimensionality is negative, which indicates the reduction of dimensionality in the course of examining the samples. The maximal change of fractal dimensionality occurs at 60 and 70°C. At of these temperatures the values of dimensionality change do not depend on whether the sample is in a constant field or this field is switched on only in the course of carrying out the resistance measurements. However, at lower temperatures the minimal change of fractal dimensionality occurs in case of a constant field. This is as if the electrostatic field exercised a stabilizing effect, because the change of fractal dimensionality reflects the restructuring in the interfacial layer. The maximal stabilizing effect of the field on fractal dimensionality, and, therefore, also on the interfacial layer size is observed at 30–40°C and a stronger field (100 V, Figure 14, curve 1).

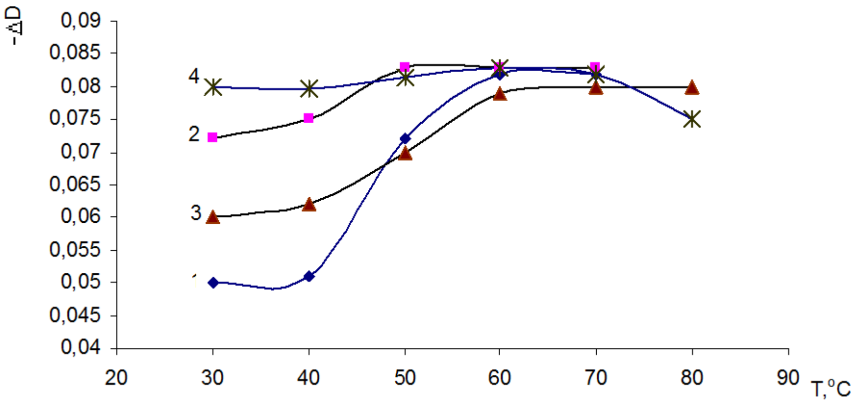


Figure 14. Effect of temperature on the change of the fractal dimensionality of the interfacial layer in HDPE containing 10% of CB upon warming up in a constant field of 100 V (1) and 10 V (3). Change of fractal dimensionality at shutdown of the field in the course of warming up:
2 – 100 V; 4 – for 10 V.

The stabilizing effect of constant electric field on the structure of the filled system is evidenced also by the fact that the time of attaining the maximal value of resistance in the initial phase of examining the samples with other things being equal is maximal upon the action of a constant field (Figure 15).

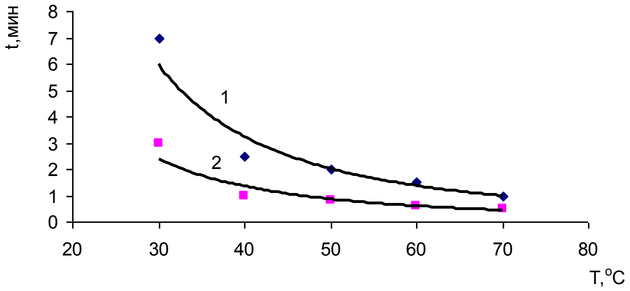


Figure 15. Dependence of the time of attaining the maximal resistance of HDPE samples containing 10% mass of CB in the initial stage of isothermal study on temperature:
1 – in a constant field at a voltage of 100 V on the electrodes; 2 – in a field at a voltage of 100 V on the electrodes switched on for measuring resistance.

It can be seen from Figure 15 that, when the samples are in a constant field, the time of attaining the maximum resistance increases. While the initial growth of resistance, as follows from the suggested model, is associated with rearrangement of the system, constant field delays this rearrangement. The time of restructuring before the increase of the conductive channels (reduction of resistance) decreases with increasing temperature, which is generally explained by the energy factor. Warming up the samples in a constant field increases the time of attaining the maximum resistance. Perhaps this is due to the influence of electric field on the thermofluctuation processes. The field suppresses structural rearrangements when heating the samples and acts as a conserver of the conducting channels (the conductive grid consisting of a chain of the filler particles).

In [13] the increase of electric resistance at the initial stage of measurement is associated with the heat transfer in the sample. However, in this work measurements were taken after warming up samples in a thermostat in isothermal conditions, under which the nature of the kinetic dependences did not change.

Heating systems containing a polymeric matrix is followed by relaxation processes with consecutive "defrosting" of various forms of molecular mobility. One can distinguish alpha transitions due to the increase in the mobility of large sites of segments-molecules cooperated with the motion of adjacent molecules, and beta transitions determining the increase of the mobility of separate, rather small sites of polymer macromolecules. The beginning of these processes is associated with a certain value of the system temperatures: T_α and T_β, respectively. T_α is referred to as "glass transition temperature", because transition from the vitreous state to the rubbery one occurs at this temperature. Both transitions characterized for a concrete system by certain temperatures or by temperature ranges occur due to local fluctuations of energy that promote overcoming of energy barriers in elementary acts of transitions. The value of such barriers is the effective activation energy of relaxation processes. Knowing the value of activation energy and the parameters affecting it enables to characterizing the elementary acts of the process quantitatively.

Because the restructuring is of relaxation nature, it should be estimated with the use of a certain characteristic time, the meaning of which is similar to relaxation time (τ). Using the obtained experimental data (Figure 15) it is possible to estimate the activation energy of the structural transformations of the filled system in the course of resistance measurement.

Transition of the system from one state to another occurs due to local fluctuations of energy provided that the energy of fluctuation $E_f \geq U$, where U is transition barrier. The average response time of local fluctuation of energy $E_f(\tau)$ depends on temperature and is described by a fundamental expression [65] confirmed by the method of computer simulation in solid bodies [66].

On the basis of the fact that the times of local fluctuations of repeating units of the macromolecules determine the time of the system transition from one energy state to another [7] it is possible to estimate the activation energy of this process using the parameters of equation (13).

Figure 16 shows the dependence of the logarithm of the ratios of times of attaining the maximum resistance for HDPE filled with 10% mass of CB on the difference of the inverse values of the corresponding temperatures. The dependence is linear and is determined by the following formula:

$$\mathrm{Ln}(t/t_x) = 0.683 + 3036\,(1/T - 1/T_x), \tag{14}$$

where t is the time of attaining the maximum at basic temperature T; t_x is the time of attaining the maximum at temperature T_x; $\mathrm{Ln}(t/t_x) = 0.1699$ is the ratio of vibrations of repeating units of the macromolecules in the corresponding states; and $U/R = 3036$. From these values it is possible to obtain the activation energy of resistance change $U \cong 25.23$ kJ/mol, which coincides with the activation energy of destruction of the polymeric grid (or of grid nodes: gamma transition), and it is very close to the activation energy of beta-transition for HDPE [67].

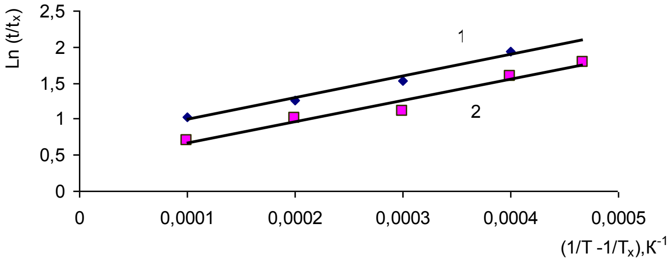


Figure 16. Dependence of the relative time of attaining the maximum resistance for HDPE filled with 10% mass of CB on the difference of the inverse values of the corresponding temperatures: 1 – in a constant field of 100 V; 2 – in a constant field of 10 V. (t is the time of attaining the maximum resistance at basic temperature T (T = 343 K); T_x is the temperature of warming up the samples; t_x is the time of attaining the maximum resistance at temperature T_x).

The value of the activation energy of the corresponding process upon warming up the samples in a constant electric field of 10 V (Figure 16, curve 2) is 24.6 kJ/mol.

Calculation of the activation energy of transient processes of the filled system at periodically applied fields showed that their values are less than those for constant fields (see the table).

$$\tau = \tau_o \exp(U/kT), \tag{13}$$

where τ_o is the vibration period of atoms in condensed bodies (10^{-13}–10^{-12} s).

The activation energies of relaxation processes for HDPE containing 10% mass of CB

Voltage on the electrodes, V	U at constant field, kJ/mol	U in the absence of constant field, kJ/mol	ΔU, kJ/mol
100	25.23	19.8	5.6
10	24.6	22.6	2.0

It can be seen from the table that the transition of the system from one state with an initial resistance to a state with the maximum resistance at continuous action of the field requires more energy consumption than in the absence of constant electric field. Moreover, the more intensive is the field (more than the voltage at the electrodes), the higher is activation energy. The difference of activation energies in the presence and in the absence of an electrostatic field shows the effect of action of this field on the process of changing the system state. Increasing the field by a factor of 10 increases this effect increases more than twice.

Conclusions

Thus, analyzing the literature data and the obtained experimental results it is possible to conclude that, when the state of conductivity in the filled system based on HDPE and CB is realized, another model is applicable with high probability in addition to the models suggested in the literature. An important role in this model is played by the interfacial layer and by the influence of the applied voltage upon it.

The properties of the interfacial layer can be characterized with the use of fractal conceptions. On the basis of such conceptions it is shown that, as the fractal dimensionality of the interfacial layer increases (the filler particle size decreases), the interfacial layer size decreases, which is followed by reduction of the resistance of the filled system. This fact indicates the difference of the structures of the interfacial layer. The action of constant electric field stabilizes the structure of the interfacial layer preventing from its change. Therefore, fractal dimensionality changes to a lesser extent at the action of electric field.

The activation energy of the corresponding transition, which is of relaxation nature, also depends on the action of the field. As the field intensity grows, the activation energy of the process increases.

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