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PHYSICAL PRINCIPLES OF THE CONDUCTIVITY OF ELECTRICAL CONDUCTING POLYMER COMPOSITES (REVIEW)

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Abstract. The role of the structural peculiarities of electrical conducting polymer composites (ECPC) has been considered. Different conception on the nature of the conductivity, the mechanisms of charge transfer in heterogeneous structures are presented in this review. Experimental results obtained by different scientists are only partially in concordance with existing theoretical models. It is suggested that missing of various physical and chemical factors influencing the processes of electrical current formation in polymer composites is one of the main reasons of the mentioned divergence between theory and experimental results among which the rate of the values of inter- and intra-phase interactions in composites may be considered as a very important factor. The peculiarities of dependence of the conductivity of systems with binary conducting fillers are considered in this work as well.

Keywords: polymer composite, structure, electroconductivity, filler content, electrical conducting polymers, interphase interactions.

1. Introduction

Investigations of molecular and super-molecular structure effects on physical and physico-chemical properties revealed in heterogeneous polymer systems show that the formation of the structure is one of the main processes in formation of electrically conducting properties of ECPC [1-6]. In its turn, the structure significantly depends on various recipes and technological factors at production of these composites [7-9].

2. Dependence of ECPC on the Content of Filler

Growth of ECPC conductivity with the increase of conducting filler content is a rule without exclusions [1–4, 10]. A typical dependence of specific volume electric resistance r of organic or inorganic binders based composites on the content of conducting filler is shown in Fig. 1. The specific feature of this dependence is a jump-like increase of conductivity γ or, which is the same, a decrease of r at a definite (for a particular composite) threshold filler concentration, induced by an insulator-conductor transition. This transition conforms to the so-called threshold of proceeding, or percolation. In this case a γ value jump, which may reach several decimal degrees, is stipulated by the formation of a continuous chain of filler particles in the polymer matrix – the infinite cluster [11, 12].

Structural insulator-conductor percolation transition may be presented by a scheme (Fig. 2). Resulting from the increase of filler content the probability of occurrence of associates of these particles in the composition, or the so-called isolated clusters, grows (see Fig. 2a). Further increase of the filler content promotes the juncture of isolated clusters into greater associates up to occurrence of an infinite cluster, i.e. a continuous electrically conducting channel in ECPC macro-system. However, in this case not all associates are included into the infinite cluster (Fig. 2b). Continuous growth of the filler concentration may induce a situation when all isolated clusters are included into an infinite cluster (Fig. 2c).

In accordance with the considered scheme of the infinite cluster formation, the jump-like change of r in Fig. 1 may belong to such a concentration of the filler when necessary conditions for occurrence of the cluster presence appear. Further growth of the filler concentration leads to a monotonous decrease of r, followed by its gradual decrease.

As it can be seen below, the transition of insulator-conductor type is sensitive to the filler content and many other factors effectively affecting the location of the filler particles.

At present the problem of the conductivity mechanism of ECPC is still to be discussed. As to the opinion of some investigators [13, 14] the charge transfer is conducted by chains, consisting of filler particles having direct electric contact. In the opinion of other authors [15, 16] conductivity of ECPC is caused by thermal emission of electrons through spaces between particles. They also speak out that current exists in ECPC with air gaps or polymer films between filler particles. In this case electrons which have energy below the potential barrier value may tunnel through it, if their own wave-length is comparable with space width of insulating film [17-19].

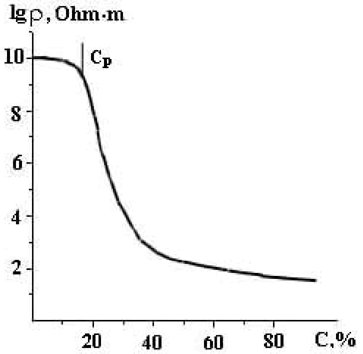

Fig. 1. Typical dependence of specific volumetric electrical resistance ρ of composites on the concentration of conducting filler. C_p is the percolation threshold

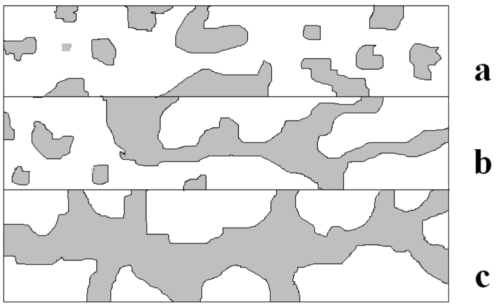

Fig. 2. Scheme of infinite cluster formation from conducting particles in anisotropic polymer matrix

Let us consider the most wide-spread models of the charge-carrier transfer in ECPC, connected to the composition and structural features of composites.

The formulas for calculation of electric resistance of composite were suggested on the basis of the formula presented below [20-22]. These formulas were suggested based on the ideas of two-phase composite structures as a polymeric matrix, in which chains composed by conducting filler are arranged according to one rule or another. In this case, it is also assumed that all conducting particles participate in formation of the electrical conductivity

$$R_c = R' + R'' \qquad (1)$$

where R' and R'' are electric resistance of filler particles and the sum of contact resistances between them, respectively. As total number of chains in a sample with a specific volume is

$$N = 6V_f/(\pi d^2)$$

where V_f and d are volumetric part and diameter of filler particles, respectively, the sum (1) could be presented as follows:

$$R = r_f/V_f + R_c n/N$$

Here r_f is the specific volumetric resistance of a filler; $R_c = r/2r$, where r is the specific volumetric resistance of the material; r is the radius of the contact point; $n = 1/d$ is the number of filler particles with diameter d.

Density packed system possesses $r = R_c d$ [23].

Electric conductivity of the two-phase system matrix (simple cubic lattice in points of which similarly sized filler particles locate) is expressed as follows [24]:

$$\gamma = \gamma_p \left[1 + \frac{V_f}{(1-V_f)/3 + V_p/(V_f - V_p)} \right] \qquad (2)$$

and electric conductivity of a statistic system (chaotic distribution of filler particles) is presented as follows:

$$\gamma = \frac{(3V_p - 1)\gamma_p + (3V_f - 1)\gamma_f}{4} + \sqrt{\frac{[(3V_p - 1)\gamma_p + (3V_f - 1)\gamma_f]^2}{16} + \frac{\gamma_f \gamma_p}{2}} \qquad (3)$$

where g_p and g_f are electric conductivities of polymer and filler, respectively; V_p and V_f are their volumetric amounts, respectively.

Based on the developed model of two-phase system conductivity the authors of the work [25] suggested a formula for generalized conductivity:

$$\lambda = \lambda_1 \left[c^2 + \nu(1-c)^2 + 2\nu c(1-c)(\nu c + 1 - c)^{-1} \right] \qquad (4)$$

where l is the system conductivity corresponding to transfer phenomenon (heat conductivity, electric conductivity, *etc.*); l_1 and l_2 are conductivities of components at $l_1 < l_2$; c is a parameter corresponding to a volumetric part of the conducting component by the expression $V^2 = 2c^3 - 3c^2 + 1$; $\nu = l_1/l_2$

Some of authors suppose that the average distance between filler particles is a deterministic index for estimating electric conductivity of the composite [26, 27]. For example, in the case of spherical carbon particles, which form a cubic lattice in a polymer, the filler concentration will be the following [27]:

$$C = \frac{1/6 \cdot \pi D^3 d_f \cdot 100}{\left[(D+S)^3 - 1/6 \cdot \pi D^3\right] d_p} \qquad (5)$$

Here C is the filler concentration; S is the distance between particles; D is the diameter of particles; d_p is the polymer density; d_f is the filler density. The formula (5) makes it possible to calculate the average distance S between filler particles. Similar estimation of this parameter is shown in [28].

Experimental and theoretical studies of composite conductivity were conducted in superfine gaps between graphite particles [28, 29]. In this case a significant meaning was devoted to the polymer molecule state in the gap, if filler particles were of a hypothetic form of a truncated cone. Based on the quantum-mechanical ideas about the nature of conductivity through gaps between filler particles the following equation was deduced [30]:

$$\rho = \frac{Ah^2 S}{a^2 e^2 \cdot 2m\varphi} \times \left(1+\beta S\varphi^2\right) exp\left(\beta S + \frac{\beta^2 S^2 \sigma^2}{2}\right) \qquad (6)$$

Here A is the parameter depending on structure of conducting particles in the system; h is the Plank constant; S is the average gap width between particles; a is the particle cross-section square; e and m are the charge and mass of electron, respectively; j is the parameter depending on the work function of the charge yielding filler particles; b = $= 8pmj/n$ is the parameter depending on the dispersion degree.

The following formula is suggested for calculating r [31]:

$$\lg r = -a \lg S + b \lg h + d_f \qquad (7)$$

Here $\lg a = n - mc$; $\lg b = p - qc$; $\lg d = r - tc$, where n, m, q, r, p and t are constants; c is the mass part of the filler; S is the specific filler surface, h is hydrogen content in the filler.

According to [27]:

$$lg\left(\rho/\rho^*\right) = \frac{lg\left(\rho^k/\rho^*\right)}{1+exp\left[\left(c - C_0/DC\right]\right.} \qquad (8)$$

where r^k is a specific resistance of rubber; $r*$ is the minimum of r; C_0 and ΔC are the equation parameters depending on the filler type.

The authors of the work [32] suggest another formula:

$$r = k/c^3 \qquad (9)$$

where k is the parameter depending on the type of rubber; c is the filler concentration.

The paper [33] presents one more formula:

$$r = \exp(a/c)^p \qquad (10)$$

where a and p are constants for particular types of fillers.

In the works [34-36] the model of effective medium was used for calculation of the conductivity of ECPC possessing statistic (chaotic) distribution of conducting filler particles. This model is an analytical method of the calculation, based on the principle of self-coordination. The method is based on the calculation of electric field inside a composite element of the "effective" medium, whose conductivity is the same as the desired effective conductivity of the composite. Taking the average value of the internal field in the whole sample, it is equalized to the assigned macroscopic field. This gives the equation for determination of the effective electric conductivity [36]:

$$V_c \frac{\gamma_c - \gamma}{2\gamma + \gamma_c} + (1 - V_c)\frac{\gamma_m - \gamma}{2\gamma + \gamma_m} = 0$$

where V_c is the volumetric part of the filler; g_c and g_m are conductivities of the filler and the matrix, respectively.

At present the percolation theory is widely used for calculations of γ for conducting composites (with both organic and inorganic binders) [11, 37]. According to this theory the expression for γ of composites consisted of non-interacting phases, may be written as follows:

$$\gamma = \begin{cases} \gamma_1\left(c_p - c\right)^{-q} \; at\; c < c_p \\ \gamma_2\left(\gamma_1/\gamma_2\right)^s \; at\; c = c_p \\ \gamma_2\left(c - c_p\right)^t \; at\; c > c_p \end{cases} \qquad (11)$$

Here g_1 and g_2 are specific volumetric conductivities of the components; q, s and t are empiric constants (it is assumed that $q = \frac{t}{1/s - 1}$); c and c_p are concentration of the filler and its threshold value, respectively.

It was computed that c_p dramatically depends on the model dimension. For example, $c_p = 0.45$ for a two-dimensional sample, and 0.15 for a three-dimensional one. Another critical index t also depends on the space dimension: $t_2 = 1.3$ and $t_3 = 1.8$ [37]. However, the conditions required by the percolation theory for most of ECPC (the absence of interactions between components, first of all) are rarely fulfilled, which significantly decreases the possibilities of the theory application.

Recently the works [38-42] were published, in which the attempts were made to calculate the interactions between composite components. The models considered were based on the most energetically profitable states of the polymer-filler system [38]. In this case, the percolation threshold is determined, whose value is different from that predicted by the percolation theory and effective medium model. The model suggested in the works [39, 40] is based on the determination of the total interphase free energy of the polymer-filler mixture. It was shown that there are other parameters which effectively affect the formation of chain structure. They are polymer melt viscosity and diameter of filler particles. The fact is that the probability of the formation of chain structure grows with the decrease of the filler particle size. The final equation for calculation of the percolation threshold is the following:

$$\frac{1\text{-}V_p}{V_p} = \frac{3}{gd}\left[\left(\pi_f + \pi_m - 2\sqrt{\pi_f \pi_m}\right) \times \right.$$
$$\left. \times \left(1 - exp\left(-\frac{ct}{r} + K_0\, exp\left(-\frac{ct}{r}\right)\right)\right)\right]$$

where g is the total interphase free energy of the mixture (polymer + filler); p_f and p_m is the surface tension of filler particles and the matrix, respectively; r is viscosity of the polymer matrix under the conditions of the composite preparation; d is the diameter of the filler particles; t is the time of mixing of two components; K_0 is the interphase free energy at the beginning of mixing (its value is determined experimentally); c is the constant of g change rate, which is also experimentally determined.

The Wessling model [41, 42] considers formation of chains as the process based on the non-equilibrium thermodynamics. It was shown that the minimal amount of filler, which gives a possibility to obtain conducting chains, is given by the following formula:

$$C_p = 0.64(1-C)K\left[\frac{X}{\left(\sqrt{\pi_f}+\sqrt{\pi_m}\right)^2}+Y\right]$$

where $(1-C)$ is the volumetric part of the amorphous fragment in the polymer matrix at room temperature; X is the constant depending on the molecular mass of the polymer; Y is the constant; K is the coefficient which allows for the presence of adsorbed polymer layers on particle surfaces.

The following formula was suggested in [43] for calculations of the γ values of ECPC:

$$\gamma = \frac{\gamma_c}{d\left(\frac{3}{2V_c d}-\frac{1}{2}\right)}$$

where d is the filler density in the density-packed state; g_C is the conductivity of the density-packed cubic lattice filler particles. Values of g calculated by this formula correlate well with experimentally obtained ones at high filling degree only (*e.g.*, for a composite of natural rubber (caoutchouc) with PME-100V carbon black).

A model of a composite structure, according to which filler particles are distributed between polymer granules (globules), allows one to calculate the filler concentrations required for complete covering of globules by filler particles (V_{f1}) and formation of infinite chains in the interglobular space (V_{f2}), as well [43]:

$$V_{f1} = \frac{1}{2}P_f V_{f2} = \frac{1}{2}P_f\left(1+F\,\frac{r_m}{4r_f}\right)^{-1}$$

$$V_{f2} = \left(1+F\,\frac{r_m}{4r_f}\right)^{-1}$$

where I_m and I_f are the radii of polymer and filler particles, respectively; Φ is the factor depending on the type of filler particle packing and possessing the following values for different plate lattices: $\Phi = 1.110$ for hexagonal, $\Phi = 1.27$ for quadratic, and $\Phi = 1.375$ for trigonal lattice.

Nilsen *et al.* suggested a model of ECPC conductivity based on polymers and metal powders [44]. In this case the calculation of γ requires data about the coordination number of filler particles in the composite:

$$\gamma = \gamma_m \frac{1+ABV_f}{1-B\varphi V_f}$$

Here:

$$B = \frac{\gamma/\gamma_m - 1}{\gamma/\gamma_m + A},\quad \varphi = 1+\left(\frac{1-P_f}{P_f^2}\right),$$

where P_f is the coordination number of filler particles; A is the parameter depending on the particle length/diameter ratio (l/d) and the type of filler particle packing.

The works [45-49] show theoretical dependences of γ of composites with the chaotically distributed fiber filler on its concentration. It was shown that γ grows with the length/diameter ratio of the fibers. For example, the percolation threshold for fibers with l/d = 110 equals to 0.03, instead of 0.17 for spherical particles [50].

Recently, some papers appeared which mentioned that conductivity may also appear in the case when polymer interlayers between conducting filler particles are much greater (by 3–5 decimal degrees) than at the current-carrier tunneling [51, 52]. It was shown that the charge transfer in ECPC is also possible at 1 nm gap between filler particles, if so-called polarons or superpolarons are formed in the polymer based on thermodynamic profit of their formation in a polymer matrix [53, 54]. However, such systems possess non-stable electric conductivity that raises some doubts about that model of conductivity.

The model suggested in [55] determines conductivity of a composite by thickness of the polymer layer between filler particles according to the formula followed by other defined parameters of the system (work function, electron affinity to polymer, energetic structure of polymer with surface states and levels of volumetric defects in the prohibited zone, concentration and mobility of carriers, *etc.*):

$$a = d\left[\left(\frac{\pi(1+\varphi)}{6\varphi}\right)^{1/3} - 1\right] \qquad (12)$$

where φ is the volumetric part of a carbon black in the polymer; d is the diameter of carbon black particles.

The calculation conducted according to the Eq. (12) shows that d = 35 nm, if φ = 0.08, *i.e.* it possesses a size degree similar to the filler particles.

The model of conductivity is shown in Fig. 3. A double electric layer occurs on the border of the polymer-carbon black contact. Thickness of the charged sphere is l. At low l values (see Fig. 3a) curves of the charge density decrease on neighbor particles overlap, and a continuous concentration of injected charge appears. This charge is able to form electric current in electric field. At high values of l (see Fig. 3b) the composite possesses a sphere without injected charges. This part of the composite forms a barrier for current conduction because of its low self-conductivity (see Fig. 3b).

The concentration distribution of carriers in the interlayer is the following:

$$n = n_k\left(\frac{l}{l+x}\right)^2 \qquad (13)$$

$$l = \left(\frac{\varepsilon kT}{2\pi n_k e^2}\right)^{1/2} \qquad (14)$$

where n_k is the concentration of charges at the polymer-carbon black contact; e is the electron charge; x is the current coordinate; k is the Boltzman constant; T is the absolute temperature; ε is the dielectric permeability of the medium; l is the characteristic length.

Such distribution of charges in the depth is usual for the case, when there are no charged traps in the prohibited zone. The criterion of ECPC conductivity is the condition $a \leq$ l. Substituting Eqs. (12) and (13) into Eq. (14), we obtain the following equation:

$$\varphi \geq \left\{ \frac{6}{\pi} \left[\left(\frac{\varepsilon kT}{2\pi n_k e^2 d^2} \right)^{1/2} + 1 \right]^3 - 1 \right\}^{-1} \qquad (15)$$

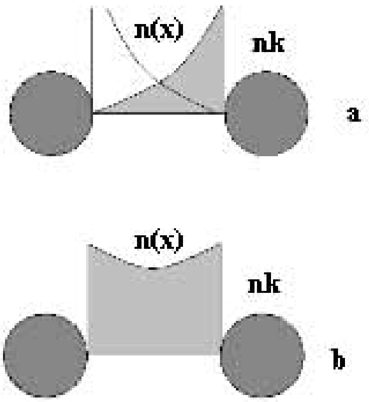

Fig. 3. The model of conductivity [55]

The analysis of works on the investigations of electrically conducting properties of ECPC induces one general conclusion: despite a variety of the above considered models of electrically conducting ECPC, unfortunately none could provide versatility. Each model includes one or several approximations and suppositions, which affect the correctness of estimations of ECPC conducting properties. That is why the comparison of theoretically calculated data with the experimental results usually gives deviations, reaching several degrees in some cases. The coincidence is rarely reached at definite concentrations of conducting filler and specific conditions of the composite production. For example, the deviation between the experimental data and those calculated by formulas (1)–(3) for ECPC, based on some thermoplastics and carbon-graphite materials, reaches two decimal degrees [56]. This is apparently stipulated by an approximation of participation of all filler particles in an infinite cluster. Usually, ECPC possess γ values of separate components (of a polymer-insulator and filler-conductor, in particular), which differ by many indexes, that is why Eq. (4) displays $v \approx 0$, and then $l = l_1 c^2$. That is equal to its transformation into a divergent function, that a high filler concentration causes significant deviations of l values from experimental data. Similar conclusion could be made regarding Eq. (9) at high concentration of conducting filler. Great differences between computed and experimental data were also observed at the application of Eq. (5). Apparently, it is stipulated by a limit simplification of the composite model (cubic lattice, spherical filler particles, matrix system model). Practical application of Eq. (6) is complicated by a significant dispersion of S and σ parameters. The necessity of experimental determination of a great number of coefficients in Eq. (7) essentially decreases the degree of its generalization. Application of Eq. (1) for r of real composites is complicated by a wide dispersion of r values, which depend on the carbon black structurization and difficulties in estimation of the interlayer thickness without preliminary selection of a mechanism for the charge transfer.

Some experimental data are satisfactorily described by Eq. (11) [57-60]. In other cases application of this equation is correct only for rough approximations. Structural analysis and estimation of interactions between components of various electrically conducting composites show that the correctness of Eq. (11) in relation to ECPC significantly depends on the values of interactions between the components, *i.e.* the weaker they are, the higher is the accuracy of the description of conductivity dependence on concentration, made with the help of the present equation [61-64]. It is known that the r values of ECPC, based on various polymers with different degree of interactions with the same electrically conducting filler at equal concentration, differ by a degree or more [65-67]. For example, r of chlorinated PVC and fluoroplast-based composites, filled by P357E and ATG-70 carbon blacks 35 mass parts content, was found 0.25 Ohm·m and 0.036 Ohm·m, respectively [65]. In this case, it was found that comparing with PVC fluoroplast, characterized by lower interaction with the filler; values of r of ethylene-propylene triple copolymer and Vulcan XC-72 carbon black composite were found a decimal degree lower than that of PP-based composites with the same filler [66]. In the case of composites based on siloxane elastomer SCTV-1, r was found three degrees lower than for similar material with natural rubber as the polymer binder [67].

Differences in values of electric conductivity, computed according to the percolation model of conductivity and the one obtained in experiments, is frequently observed due to structural features of the filler particles. For example, experimentally measured electric conductivity of polyethylene composites, filled by acetylene carbon black, differs from the theoretical one by a decimal degree [68]. This is explained by the presence of agglomerates (associates) of particles and their statistic distribution in the matrix volume. Generally speaking, the ability of filler particles to aggregate is a significant reason of the above mentioned deviation. Difference between theoretical and experimental data on conductivity is also observed for composites which contain a binder possessing different interaction effects with carbon black during plasticization, which is connected to free radical occurrence in this process [69]. These free radicals make their own contribution into the interaction between components. One more reason of the difficulties in the theoretical forecast of *r* value of ECPC is the existence of polar groups in macromolecules. For example, *r* of carbon black-filled composites increases in the sequence of polymers as follows: cellulose acetopropyonate < cellulose acetobutyrate < cellulose triacetate [70]. These polymers differ by hydroxyl group concentration in them, the amount of which increases in the mentioned sequence.

Comparison of different ECPC based on different thermoplastics, obtained under similar conditions, shows that the composites with crystallizing polymeric binders are characterrized by lower values of *r*, than those with amorphous binders. For example, it was shown that *r* of amorphous *cis*-1.4-polybutadiene, filled by "Vulkan" carbon black (in 35 mass parts concentration) equals 10^3 Ohm·m [71]. At the same time, crystallizing ***trans***-1,4-polybutadiene possesses $r = 1$ Ohm·m. According to [72] *r* of the composites decreases with the growth of polyolefin crystallinity degree.

Introduction of some mineral filler (kaolin, whiting) into the composite induces growth of structural heterogeneity. This is the reason of differences in the *r* of materials with the same content of insulator (polymer + mineral filler) and conducting part [73]. Based on the data of the structural analysis, the authors of the works [72, 73] found out that the decrease of electric conductivity in composites in the cases of both crystallizing polymers and mineral fillers is stipulated by dislocation of conducting filler particles near the surfaces of crystallites or kaolin and other mineral fillers and consequently leads to more dense packing of current-conducting channels in amorphous (lower dense) phase of the polymer. However, some authors with groundlessly ascribe this experimental result to high conductivity of crystalline forms in polymer [71, 74].

Taking into account interactions between phases and in phases of ECPC we obtain satisfactory results by using formulas (16) for ECPC with completely amorphous binder [56]:

$$\begin{aligned} \rho &= \rho_0 \, exp\left(\frac{C_p - C}{C_p}\right)^a & at\, C > C_p \\ \rho &= \rho_0 & at\, C \le C_p \end{aligned} \qquad (16)$$

where r_0 is the specific volumetric electrical conductivity of pure polymer, equal to *r* of the composites containing a conducting filler in concentrations below the percolation threshold mass part ($C \angle C_p$); ***a*** is the constant proportional to the expression: $a \sim \frac{e_2 \times e_3}{e_1^2}$, and depending on the energies of interactions of polymer-polymer (e_1), polymer-filler (e_2) and filler-filler (e_3) types.

Analysis of the ideas suggested in [10, 56] on the influence of the ratio of interaction energies between components brings about a conclusion that the situation when e_2 and e_3 are close by values and e_1 reaches its minimum. In this case, *r* also obtains its minimum, whereas growth of any of e_2 and e_3 induces the increase of *r* [10]. If $e_2 > e_3$, the probability of stable bond formation between filler particles decreases, *i.e.* the system loses its conductivity. But if $e_2 < e_3$, the probability of agglomerate formation from conducting particles grows, which leads to a decrease of branching of conducting channels (pathways). In both cases we obtain the growth of *r*.

It is evident that preliminary estimation of energetic parameters e_1, e_2 and e_3 is very difficult (estimation of the affinity between components by adhesive parameters), but some experiments allow to estimate the parameter ***a*** for the components of the present composite, which significantly simplifies calculation of *r* for different concentrations of conducting filler in the same ECPC by Eq. (16). Application of this equation to polymeric composite whose polymer phase contains crystalline spheres is also possible in the case when the mass part of the binder includes only the amorphous part of the polymer in which filler particles are localized.

To verify the correctness of Eq. (16) application in the *r* calculation and to compare it with the experimental data, the tests of electrically conducting rubbers based on organosilicon elastomers of type SCTV (polydimethylmethylvinilsiloxan) and three types of carbon black P803, P357E and ATG-70 were conducted [56]. All samples were obtained by the additive vulcanization technique with ADE-3 (diethyl-aminomethyl-triethoxisilan) as a hardener (curing agent). The main difference between these types of carbon blacks is in values of specific geometrical surface *S* and *r* (the *r* values for these carbon blacks were found $14{\cdot}10^{-4}$, $25{\cdot}10^{-4}$ and $1.6{\cdot}10^{-4}$ Ohm·m, respectively; *S* values were 106, 56 and 46 m^2/g, respectively). Materials possessing different *r* values were obtained by introduction of different amounts of the mentioned carbon blacks into composites. Fig. 4 shows that the character of the *r* dependence on the filler concentration significantly depends on the filler type. For example, to obtain rubbers containing P357E and P803 carbon blacks and possessing equal *r* values, significantly greater amounts of P803 should be introduced comparing with P357E.

The result obtained correlates well with the data from [75], which show that a sufficient effect on ECPC conductivity is induced by the carbon black dispersion and the ratio of carbon black particle square to its mass (*S*/*m*). The value of γ of ECPC containing carbon blacks with different *S*/*m* values increases proportionally to this ratio with the concentration.

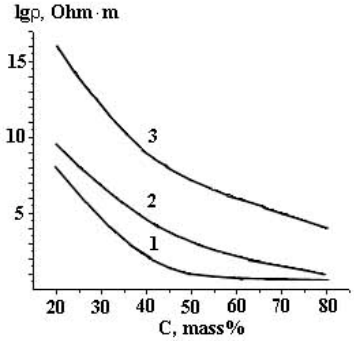

Fig. 4. The dependence of r values of SCTV-based composites on filler concentration. The fillers are P357E (1), ATG-70 (2) and P803 (3)

Table 1 shows experimental data and the results of the r value calculations by Eq. (16) for SCTV-based composites with various filler contents, and the filler concentration C_p corresponding to the insulator-conductor transition for the same materials. To estimate the generality degree of the formula (16) r and C_p were also calculated for non-organosilicon conducting rubbers and compared with experimental data on those materials, obtained by different authors.

The data shown in Table 1 display that deviation between experimental and calculated data does not exceed 20 %. In this case we can state that Eq. (16) may be used for calculations of concentrational dependences of r in ECPC with amorphous polymeric matrix.

Table 1

Experimental and calculated data on r and C_p for electrically conducting rubbers

Composite	r_{exp}, Ohm·m	r_{calc}, Ohm·m	C_p (exp.)	C_p (calc.)	Ref.
SCTV + P357E (40)*	0.058	0.045	12	10	56
SCTV +ATG-70 (50)	0.04	0.03	16	13	56
SCTV +P803 (60)	0.19	0.16	40	48	56
BSC + Vulcan-3 (50)	25.3	22.4	30	35	69
NC + ATG-70 (50)	18.7	19.6	28	33	61
SCN + PM-100 (60)	11.6	13.8	25	30	3

Notes: * – numbers in brackets mark mass parts of the filler per 100 mass parts of elastomer; C_p is measured in the same units.

3. Structure Models of ECPC

Conductivity of polymers filled by electrically conducting fillers depends, first of all, on the current-conducting channel density in a polymer matrix which, in its turn, seriously depends on capability of filler particles for forming an infinite cluster. It was mentioned above that formation of a current-conducting system in polymer sufficiently depends on the ratio of interaction energies between the composite components. If we take into account that highly structured carbon blacks P357E and ATG-70 possess comparatively high energies of interactions between their own particles with polymer, and that intermolecular interaction in organosilicon elastomers is weaker than in other polymers, it becomes clear why composites based on highly structural carbon blacks and SCTV possess the conductivity higher than of the composite based on SCTV and lower structural carbon black P803.

Physics and chemistry of the surface of filler particles are the decisive measures in the filler-polymer and filler-filler interactions which, in turn, play the leading role in formation of the structure and electrically conducting properties of ECPC [2, 10].

The structure of carbon black and graphite seriously affects the electric conductivity of composites. In some cases, the increase of the structure degree becomes more effective than the increase of specific surface square. For example, rubbers filled by higher structured carbon black (PM-90) possess higher conductivity than those filled by lower structured but higher dispersed carbon black (PM-100) [76]. A similar result was obtained for the comparison of the conductivity of conducting rubbers filled by highly structured acetylene carbon black ATG-70 and lower structured PM-100 [77]. However, the situation often occurs, when the effectiveness of carbon blacks is compared with other intercompensating properties (structure degree, dispersion, porosity, roughness, *etc*.), which complicate estimation of one factor or another. It is known that dispersion [78] and porosity significantly affect conductivity of filled rubbers and plastics. The analysis of effects of structural indexes of carbon blacks on electric conductivity of composites is presented in [79].

Chemical composition of carbon black particle surfaces is very important for the analysis of the carbon black type effects on the conductivity of ECPC. Substances adsorbed or chemically bonded to surfaces of carbon blacks may prevent formation of contacts between particles or promote formation of bonds between polymer and fillers.

Chemical properties of the surface are defined by the existence of functional groups, consisted of oxygen, hydrogen, and sulfur. Amounts of oxygen and hydrogen in carbon blacks reach 5 % of carbon mass. Oxygen exists in the basic composition of carboxylic, phenolic, quinoid, and lactic groups. Many data support the idea about free-radical origin of carbon blacks [80, 81]. Destruction of carbon black structure is an additional source of free radicals, which significantly affect further filler interactions with the polymer [82]. The effect of functional carbon black groups on affinity to the polymer depends on the polymer nature. For example, its adhesion to butylcaoutchouc increases at carbon black oxidation, and adhesion to BSC and polybutadiene decreases [3].

Preliminary thermal treatment of a carbon black in inert atmosphere at high temperatures (over 1000 K) effectively affects conductivity of composites. Experiments showed that in most cases conductivity of ECPC containing heat-treated carbon blacks increases (in some cases by 6 decimal degrees) [83].

The chemical groups of carbon black surface significantly influence the polymer-filler interactions, because it may cause an activation of different types of interactions. High energy of the polymer-filler interaction may promote the ECPC structure degradation. Oxidation of carbon black particle surfaces always increases r, and elimination of volatile substances and chemical groups at thermal treatment without oxygen induces r decrease in ECPC [84].

Influence of conducting filler type on the percolation threshold is well seen in the investigation of electrically conducting properties of polyester epoxy-based composites, dissolved in styrene with carbon-graphite fillers [85]. Hydroperoxide of isopropyl benzene oxide (hyperysis) is the hardener of that composite, and cobalt naphthenate is the accelerator of the process. Mixtures were prepared according to two techniques: by mixing ingredients in a vessel with a mixer (high-ohmic samples) and cold pressing of previously rolled masses in press-forms under 15 MPa pressure (low-ohmic samples). The choice of preparation technique depends on viscosity of mixtures, which, in its turn, depends on the filler concentration. Low concentration of the filler and, consequently, low viscosity of the mixture, induces a possibility of mixture preparation in a usual mixer with mechanical mixing machine. Increased filler concentration and viscosity require significant mechanical forces and application of rollers.

The compositions produced in accordance with the mentioned technique differ by an intensive increase of conductivity at comparatively low filler concentrations. The data from [3] suggest that similar transition in different composites occurs at relatively high filler concentrations. For example, this fact is explained in the work [19] by an irregular distribution of the filler in the polymer matrix. Microstructure of the composite represents electrically conducting spatial network, consisted of the filler particles, and disposed between dielectric blocks (domains). These blocks may be formed by macromolecules with definite order in the distribution of ones or crystal areas (Fig. 5). Polymer blocks (domains) may be formed as a result of macromolecular aggregation via interactions under the effect of Van der Waals forces and electrostatic forces of polar groups (some authors named such blocks “the minor elements of supramolecular structures” (NENS) [86]. Particles of electrically conducting filler form a conducting structure, concentrated in the inter-block space. This structure appears denser than it would be in the case of the block structure absence. Thus, morphological features of the considered composition are the deterministic factors of the conducting channel formation with relatively low threshold concentration of the filler [87]. In this case, the effect of the filler structure degree correlates with the experimental data in conductivity dependence on the carbon black type [18].

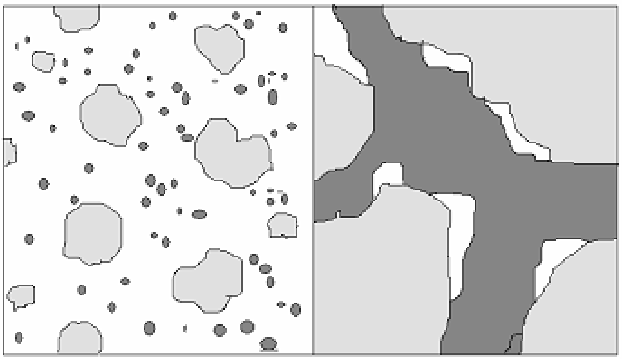
a b

Fig. 5. The scheme of current-conducting system (in accordance with an electron microscopic picture) formation on the basis of polymers and electric conducting particles: initial state (a) before formation of infinite clusters in ECPC (dark spots – conducting particles, light spots – polymer domains, white area - amorphous polymer) and ECPC (b) after formation of the infinite cluster (dark area) among polymer domains (light area) and free volume (white area)

Application of two different types of electrically conducting fillers in a single composite induces an extremal character (with a minimum) of r in accordance with the ratio of the fillers. The works [85, 88] show the curves of r dependence on concentrations of two conducting fillers – graphite and carbon black at various concentrations, and suggest the following equation for calculation:

$$\rho = \frac{ac_2^2}{(c_1 + c_2)^m} - \frac{bc_2}{(c_1 + c_2)^n} - \frac{K}{c_1^3} \qquad (17)$$

where c_1 and c_2 are concentrations of ATG-70 and graphite, respectively; a, b, K, m and n are coefficients depending on the type of elastomer. At $c_2 = 0$ Eq. (17) transforms into (9). Although the authors of [87, 89] succeeded in the application of Eq. (17) for ρ calculation for various combinations of binary filler components at different total filling of SCI-3-based rubber, that equation displays no invariance to binary filler components. Moreover, it was mentioned above that the consideration of related Eq. (9) displays incorrectness of Eq. (17) at transition from specific volumetric resistance to specific volumetric electric conductivity of the material.

To clear up the functional dependence of r of ECPC on concentration of the binary filler, polyester varnish-based composites with carbon-graphite filler were produced [84] (C-1 graphite and P357E, ATG-70, and P803 carbon blacks). The composites with P803 and graphite (total concentration was 40 mass parts) displayed the change of r expressed by a curve with a minimum, which corresponded to P803 carbon black concentration of 25 mass parts and graphite of 15 mass parts (Fig. 6). It is known [10] that carbon black is capable of creating a secondary structure owing to the existence of an active surface as associates of particles or clusters, which leads to the formation of a three-dimensional conducting system. Possessing relatively high conductivity, graphite displays no such capability. That is why composites containing carbon black as filler are characterized by much higher conductivity, than the composites based on the same polymer filled by the same graphite amount. Fig. 6 shows curves reflecting one of the dependences of the so-called synergic effect. This effect results in inhomogeneous distribution display at the increase or weakening of another reactions and properties of material at introducing two or more active components into it. Synergism of binary fillers is connected with the features of the composite morphology. In particular, this phenomenon is explained by the type of interdisposition of two types of filler particles in the polymer matrix. For example, microstructure of a composite which contains carbon black and graphite may be schematically presented as a conglomerate of particles of the fillers, "injected" into the polymer matrix (Fig. 7). Carbon black particles possessing lower electric conductivity form a secondary structure, looking like bridges between conducting particles of graphite, including them into the general conductive system. If it is presented as an electrical scheme of parallel-consequent connected resistant elements, it becomes possible to explain the reason of a significant improvement of electrically conducting properties of the composite.

The experimental data on electric conductivity of ECPC with binary electrically conducting filler at different values of total filler concentration and simultaneous application of mathematical planning of the experiment [90] allow us to deduce a regularity for the r-c dependence, described by the following formula:

$$r = -A\cdot(r_1 c_1 \ln c_2 + r_2 c_2 \ln c_1) \qquad (18)$$

where r_1 and r_2 are specific volumetric resistances of pure fillers (carbon black and graphite), respectively; c_1 and c_2 are concentrations of these fillers in mass parts; A is the constant depending on the material type.

Calculations by Eq. (18) should be easier conducted for one concentration, *i.e.* expressing the second filler concentration via the first one, taking into account that $c_1+c_2 = 1$:

$$r = -A\cdot[r_1 c_1 \ln(1-c_1) + r_2\cdot(1-c_1)\ln c_1] \qquad (19)$$

Experiments showed that the data on the determination of the r dependence on composition of the binary filler (carbon black 1 + carbon black 2, graphite + carbon black) satisfactorily correlate with those calculated by Eq. (19).

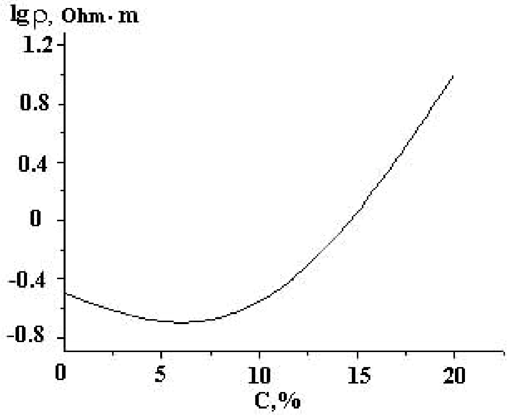

Fig. 6. The dependence of r of polyester epoxy-based composites on the ratio of binary filler (graphite + P803) components at the sum content of fillers 20 %. On the x-axis – the content of graphite in fillers blend

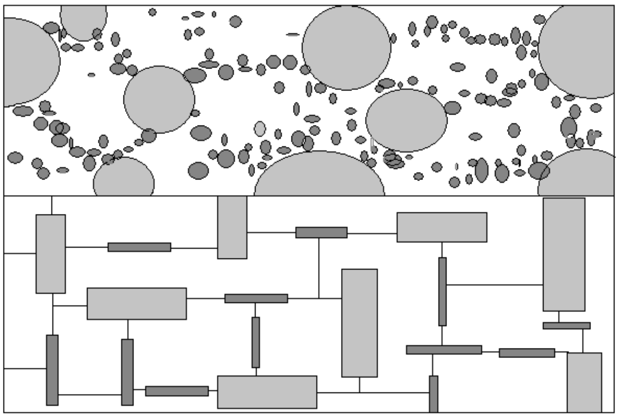

Fig. 7. Two-dimensional model of the composition based on polymers with a binary filler (graphite + carbon black) (top) and equivalent direct current scheme (bottom). Big circles — graphite particles; small circles – carbon black particles; big rectangles – resistance of graphite particles; small rectangles – resistance of carbon black particles

Influence of the composition on electrically conducting properties of ECPC was shown on the example of the systems consisting of the two types of organosilicon elastomers SCTVF-803 and SCTVF-2103 and carbon black fillers – P803, P324, and ATG-70 [91]. Some of the composites contained A-300 aerosil. Concentrations of the fillers were varied from 20 to 80 mass parts per 100 mass parts of elastomer. Dicumyl peroxide in 3 mass parts concentrations was used as a vulcanizing agent. Rubber mixtures were prepared on laboratory rolls. Vulcanization was performed by the well-known technique of peroxide vulcanization [92]. Electrodes were introduced into the rubber mass before the vulcanization start.

It should be mentioned that in most cases investigators measure electric resistance of materials by the four-electrode technique [3].

Table 3 shows characteristics obtained in tests of electroconducting and physical-mechanical properties of vulcanizates [56].

According to the data shown in Table 2, SCTVF-803-based composites possess higher conductivity than SCTVF-2103-based rubbers at equal concentration of the filler. For example, r of SCTVF-803-based rubber, which contains 60 mass parts of P324 carbon black, is one decimal degree lower, than that of SCTVF-2103-based one containing the same filler in the same concentration. This may be explained by two phenomena: (i) filler dispersion during rubber mixture rolling and (ii) distribution of filler particles in elastomer matrix.

Growth of the filler concentration, induced by the dispersion increase, promotes simultaneous growth of the number of conducting channels and, consequently, the decrease of r, only in the case if electrically conducting particles form branched spatial network in the matrix. This becomes possible at a definite ratio of intensities of two types of interactions: the filler-filler and the elastomer-filler interaction. Predomination of the first type of interaction ambiguously induces the increase of the rubber conductivity, because in this case the formation of associates (lumps) is intensified. These lumps induce increase of homogeneity in the filler particle distribution that might cause the r growth and decrease of physical and mechanical parameters starting from a definite (for the particular composite) filler concentration. That is why the existence of the elastomer-filler interaction is also required for the formation of highly developed conducting system in the rubber. This interaction prevents the process of the lump formation. Consequently, one may suppose that high conductivity is obtained by composites at a definite ratio of the mentioned interactions.

Taking into account the supposition and technical indexes, shown in Table 2, the ratio of the interactions mentioned in the first of the compared composites (among No. 3 and No. 16 composites) should be optimal comparing with the second one (r of the first composite is lower than that of the second one). The spin probe technique was used for obtaining results on the homogeneity degree. It was found that the homogeneity degree of the filler distribution in the matrix of No. 3 rubber is lower than that in the composite No. 16. This correlates well with the known character of the filler particle distribution in composites with high compatibility of the components [93].

Table 3

Physical and mechanical indexes of electroconducting rubbers, based on SCTVF-803 and SCTVF-2103 elastomers

Group	N	Composite	r, Ohm·m	σ, MPa	ε, %	θ, %
I	1	SCTVF-803 + P324 (30)*	50	3.3	200	0
	2	SCTVF-803 + P324 (50)	11	6.2	260	8
	3	SCTVF-803+ P324 (60)	0.42	3.8	200	16
	4	SCTVF-803+ P324 (80)	0.37	2.2	120	26
II	5	SCTVF-803 + P803 (40)	10^9	2.0	160	0
	6	SCTVF-803 + P803 (50)	21	3.0	140	0
	7	SCTVF-803 + P803 (60)	2.4	4.1	140	0
	8	SCTVF-803 + P803 (80)	0.7	4.6	100	0
III	9	SCTVF-803 + P324 (20) + A300(20)	300	7.7	350	4
	10	SCTVF-803 + P324 (30)	48	6.3	220	3
	11	SCTVF-803 + P324 (40)	17	6.1	220	8
IV	12	SCTVF-803 + ATG70(20) +A300 (20)	37	6.4	270	4
	13	SCTVF-803 +ATG70(25)	1.2	6.5	250	4
	14	SCTVF-803 +ATG70(30)	0.25	6.5	230	8
V	15	SCTVF-2103 + P803(60)	9.9	4.0	100	0
	16	SCTVF-2103 + P324(60)	7.3	4.9	265	15
	17	SCTVF-2103+ATG70(25) +A300(20)	0.7	6.6	280	4
	18	SCTVF-2103+ATG70(25) +A300(40)	1.8	8.4	175	4

* Numbers in brackets correspond to filler concentrations in mass parts per 100 mass parts of the elastomer

The effect of the filler type on the properties of composites are well seen on the example of two groups of rubbers, based on SCTVF-803 elastomer with two types of carbon black (P324 and P803). Carbon black P324 possesses higher conductivity than P803. That is why these composites possess different *r* values. However, it should be taken into account that the difference in properties of the composites of the groups I and II is stipulated by the properties of carbon blacks separately, and by their behavior in the polymer matrix. This affects, in particular, the physical and mechanical indexes of the composites. For example, if the maximum of resistance of the group I rubbers is displayed at 50 mass parts concentration of the carbon black P324, the rubbers of the group II possess the maximum (according to the tendency of resistance growth) at higher filler concentrations. Moreover, difference in the properties of the groups of composites compared is also expressed by the value of residual elongation: all composites of the group II are characterized by its absence.

The reason of the mentioned differences in the properties of those groups of rubbers should be searched in the character of interactions between the composite components. On the one hand, stronger polymer-filler and filler-filler interactions in the rubbers of the group I, comparing with the group II, induce higher conductivity, and on the other hand, they promote formation of a composite with the maximum resistance at relatively low filler concentrations. Zero values of the residual elongation of the group II rubbers evidently point out fast relaxation processes in the macromolecular system, which proceed in the composites after the sample rupture, caused by a weak polymer-filler interaction.

Dielectric filler aerosil is known as a good intensifier of rubber mixture [7]. That is why in the obtained three-component systems aerosil A-300 acts as an intensifier of organosilicon rubbers (groups III and IV). However in the case of the present filler, optimal concentrations also exist, which give high physical and mechanical properties to rubbers. For example, the sample with lower concentration of the binary filler aerosil + carbon black is characterized by higher resistivity (sample 9), than the sample with higher carbon black concentration. The improvement of electrically conducting and resistive properties of composites is observed at ATG-70 carbon black application, combined with aerosil (samples from the groups IV and V) at optimal ratio of the fillers. Thus, variation of the filler concentration may improve some properties at simultaneous decrease of the other. For example, the increase of aerosil concentration induces the decrease of electric conductivity of the composites with binary fillers, but resistance simultaneously increases (samples 17 and 18). Aerosil effect is evident and requires no additional explanations. In its turn, decrease of the conductivity of rubbers at aerosil concentration growth may depend on two factors: the decrease of the total part of conducting filler in the composite and destruction of the current-conducting system by aerosil particles.

4. Conclusions

The experimental data confirm that most important factors effectively influencing the conductivity of ECPC are the following: concentration, average size and type of filler particles, and values of three types of interactions: macromolecule-macromolecule, macromolecule-filler, and filler-filler.

Searching for the *r* dependence on the filler concentration in ECPC should probably induce a logic conclusion that a composition with the highest conductivity may be obtained at the maximal filling degree. However, it is also known that due to the deterioration of physical and mechanical properties of the composites at high filling degree the technologists are forced to introduce some limits in the selection of the optimum concentration of conducting fillers.

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ФІЗИЧНІ ОСНОВИ ПРОВІДНОСТІ ЕЛЕКТРОПРОВІДНИХ ПОЛІМЕРНИХ КОМПОЗИТІВ (ОГЛЯД)

Анотація. *Розглянута роль структурних особливостей електропровідних полімерних композиційних матеріалів. В роботі приведені різні концепції стосовно характеру провідності, механізму переносу заряду в гетерогенних структурах. Експериментальні результати, отримані різними вченими, знаходяться у відповідності з існуючими теоретичними моделями лише частково. Показано, що відсутність різних фізичних і хімічних чинників, що впливають на процеси формування електричного струму в полімерних композитах, є однією з основних причин зазначеної розбіжності між теорією та експериментальними результатами, серед яких швидкість між- і внутрішньофазової взаємодії в композиціях можна розглядати як дуже важливий фактор. Приведені особливості залежності провідності системи з бінарним провідними наповнювачами.*

Ключові слова: *полімерний композит, структура, електропровідність, вміст наповнювача, електропровідні полімери, міжфазна взаємодія.*