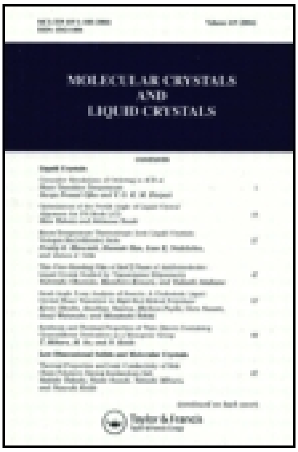

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Physical Principles of the Conductivity of Electrically Conductive Polymer Composites (Review)

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Physical Principles of the Conductivity of Electrically Conductive Polymer Composites (Review)

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The role of the structural peculiarities of electrically conductive polymer composites is considered in this review. Different conceptions of the nature of the conductivity and the mechanisms of charge transfer in heterogeneous structures are presented. Experimental results obtained by different scientists are only partially in accord with existing theoretical models. It is suggested that lack of information on various physical and chemical factors influencing the processes of electrical current formation in polymer composites is one of the main reasons for the divergence between theory and experimental results, among which the rate of the inter- and intra-phase interactions in composites may be considered very important. The conductivity of systems with binary conducting fillers is also considered.

Keywords Electro-conductivity; electrically conductive polymers; filler content; interphase interactions; polymer composite; structure

Introduction

Investigations into effects of the molecular and supermolecular structure on the physical and physico-chemical properties of heterogeneous polymer systems show that the formation of the structure is one of the main processes responsible for the properties of electrically conductive polymer composites (ECPC) [1–6]. In turn, the structure depends significantly on various formulations and technological factors in the production of these composites [7–9].

Dependence of Ecpc on the Filler Content

The growth of ECPC conductivity with an increase in the conductive filler content is a rule without exclusions [1–4,10]. A typical dependence of the specific volume of electrical resistance, ρ, of organic or inorganic binder-based composites on the content of conductive filler is shown in Fig. 1. The particular feature of this dependence is a jump-like increase in

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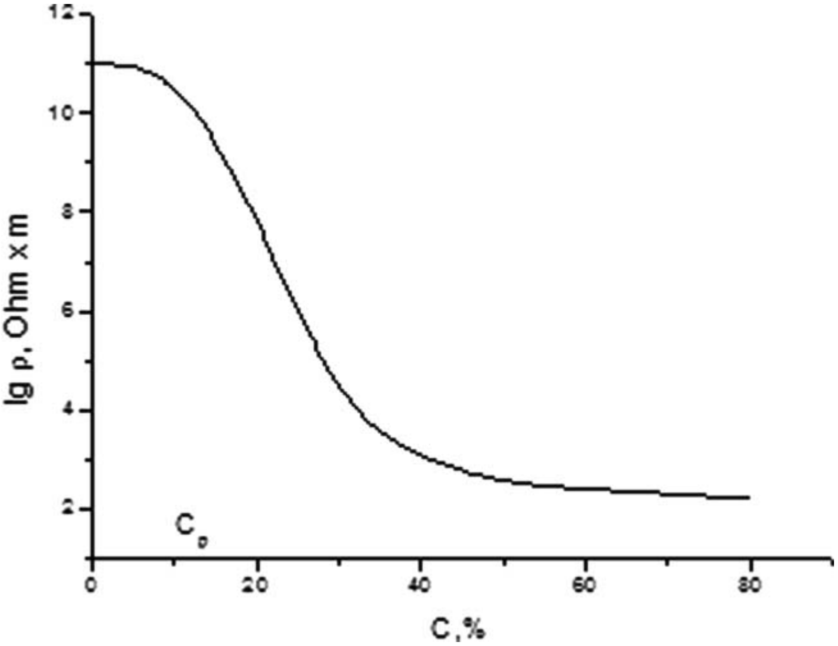

Figure 1. Typical dependence of the specific volumetric electrical resistance ρ of composites on the concentration of conductive filler. C_p is the percolation threshold.

conductivity, γ, or (which is the same thing), a decrease in ρ 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 brought about 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 represented as a scheme (Fig. 2). An increase in filler content raises the probability of the formation of agglomerates of these particles in the composition, or so-called "isolated clusters" (see Fig. 2a). A further increase in the filler content promotes the joining of these isolated clusters into larger agglomerates, agglomerate up to the occurrence of an "infinite cluster", i.e. a continuous

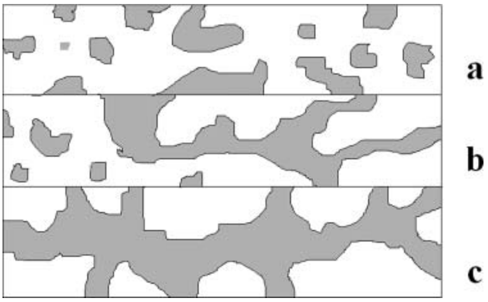

Figure 2. Scheme of infinite cluster formation from conductive particles in an anisotropic polymer matrix.

electrically conducting channel in an ECPC macro-system. However, in this case not all the agglomerates are included in the infinite cluster (Fig. 2b). A continuous increase in the filler concentration may induce a situation in which all isolated clusters are included in an infinite cluster (Fig. 2c).

In accordance with this scheme of the infinite cluster formation, the jump-like change of ρ in Fig. 1 may result from such a filler concentration when the necessary conditions for occurrence of a cluster appear. Further growth of the filler concentration leads to further increase in ρ, followed by its gradual decrease.

As is discussed below, the insulator-conductor type transition is sensitive to the filler content and many other factors that affect the location of the filler particles.

At present the conductivity mechanism of ECPC is still in need of elucidation. In the opinion of some investigators [13,14], the charge transfer is conducted by chains consisting of filler particles having direct electrical contact. Other authors [15,16] are of the opinion that the conductivity of ECPC is caused by the thermal emission of electrons through spaces between particles. They also speak of current existing in ECPC with air gaps or polymer films between filler particles. In this case electrons that have energy below the potential barrier value may tunnel through it, if their own wavelength is comparable with the gap width of the insulating film [17–19].

Models of Charge Transfer in Ecpc

Let us consider the most widespread models of charge-carrier transfer in ECPC that take into account the composition and structural features of composites.

The formulas for calculating the electrical resistance of composites were suggested [20–22] on the basis of the formula presented below. These formulas were based on the idea of a two-phase composite structure 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 the formation of the electrical conductivity:

$$\mathrm{R_c} = \mathrm{R}' + \mathrm{R}'' \tag{1}$$

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

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

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

$$R = \rho_f/V_f + R_c n/N$$

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

A densely packed system possesses $\rho = R_c d$ [23].

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

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

and the electrical conductivity of a statistical system (chaotic distribution of filler particles) is presented as follows:

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

where γ_p and γ_f are the electrical conductivities of polymer and filler, respectively; and V_p and V_f are their volumetric amounts, respectively.

Based on the developed model of two-phase system conductivity, Dulnev and Novikov [25] suggested a formula for generalised conductivity:

$$\lambda = \lambda_1 \lfloor \mathrm{c}^2 + \nu(1 - \mathrm{c})^2 + 2\nu \mathrm{c}(1 - \mathrm{c})(\nu \mathrm{c} + 1 - \mathrm{c})^{-1} \rfloor \tag{4}$$

where λ is the system conductivity corresponding to the transfer phenomenon (heat conductivity, electrical conductivity, etc.); λ_1 and λ_2 are the conductivities of components at $\lambda_1 < \lambda_2$; and c is a parameter corresponding to a volumetric part of the conducting component from the expression $V^2 = 2c^3 - 3c^2 + 1$; $\nu = \lambda_1/\lambda_2$

Some authors [26,27] propose that the average distance between filler particles is a deterministic index for estimating the electrical conductivity of the composite. 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]:

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

Here C is the filler concentration; S is the distance between particles; D is the diameter of particles; d_p is the polymer density; and d_f is the filler density. Eq. (5) makes it possible to calculate the average distance, S, between filler particles. A similar estimation of this parameter was made by Enikolopyan et al. [28].

Experimental and theoretical studies of composite conductivity were conducted in superfine gaps between graphite particles [28,29]. In this case significance was attached to the state of the polymer molecules in the gap, with the filler particles having the hypothetical 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]:

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

Here A is a parameter that depends on the structure of the conducting particles in the system; h is the Plank constant; S is the average gap width between particles; a is the particle cross-section squared; e and m are the charge and mass of the electrons, respectively; φ is a parameter that depends on the work function of the charge-yielding filler particles; and $\beta = 8\pi m\varphi/n$ is a parameter that depends on the degree of dispersion.

Pushkova et al. [31] suggest the following formula for calculating ρ [31]:

$$\lg\rho = -a\lg S + b\lg h + d_f \tag{7}$$

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

According to Abdel-Bary et al. [27]:

$$\lg(\rho/\rho^*) = \frac{\lg(\rho^k/\rho^*)}{1 + \exp[(c - C_0/\Delta C]} \tag{8}$$

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

Pushkova et al. [32] suggest another formula:

$$\rho = k/c^3 \tag{9}$$

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

Boonstra [33] presents one more formula:

$$\rho = \exp(a/c)^p \tag{10}$$

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

In references [34–36], the model of an effective medium was used to calculate the conductivity of ECPCs possessing a statistical (chaotic) distribution of conducting filler particles. This model is an analytical method of calculation, based on the principle of self-coordination. The method is based on the calculation of the electrical field inside a composite element of the "effective" medium, whose conductivity is the same as that of the desired effective conductivity of the composite. The average value of the internal field in the whole sample is equalised to the assigned macroscopic field. This gives an equation for determination of the effective electrical 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; and γ_c and γ_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 consisting of non-interacting phases may be written as follows:

$$\gamma = \begin{cases} \gamma_1(c_p - c)^{-q} & \text{at c} < c_p \\ \gamma_2(\gamma_1/\gamma_2)^s & \text{at c} = c_p \\ \gamma_2(c - c_p)^t & \text{at c} > c_p \end{cases} \tag{11}$$

Here γ_1 and γ_2 are specific volumetric conductivities of the components; q, s and t are empirical constants (it is assumed that $q = \frac{t}{1/s-1}$); and c and c_p are the concentration of the filler and its threshold value, respectively.

It was computed that c_p depends greatly on the model's dimensions, e.g. $c_p = 0.45$ 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 possibility of applying the theory.

Lux [38], MiYasaka et al. [39], Watanabe et al. [40], and Weessling [41,42] attempted 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 by MiYasaka et al. [39] and Watanabe et al. [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 that effectively influence the formation of the chain structure. They are the polymer melt viscosity and the diameter of the filler particles. The fact is that the probability of the formation of a chain structure grows with a decrease in the size of the filler particle. The final equation for calculation of the percolation threshold is:

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

where g is the total interphase free energy of the mixture (polymer + filler); π_f and π_m is the surface tension of the filler particles and the matrix, respectively; r is viscosity of the polymer matrix under the conditions of 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); and c is the constant of g change rate, which is also experimentally determined.

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

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

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

The following formula was suggested by Malliamis and Turner [43] for calculations of the γ values of ECPC:

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

where d is the filler density in the density-packed state; and γ_C is the conductivity of the density-packed cubic lattice filler particles. Values of γ calculated from this formula correlate well with experimentally obtained ones, but only at a high degree of filling (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_{fl}),as well as the formation of infinite chains in the interglobular space (V_{f2}) [43]:

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

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

where I_m and I_f are the radii of polymer and filler particles, respectively; and Φ is a 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.

Nilsen et al. [44] suggested a model of ECPC conductivity based on polymers and metal powders. 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: $B = \frac{\gamma/\gamma_m - 1}{\gamma/\gamma_m + A}$, $\varphi = 1 + (\frac{1-P_f}{P_f^2})$, where P_f is the coordination number of filler particles; and A is a parameter depending on the particle length:diameter ratio (l:d) and the type of filler particle packing.

Pike and Seager [45], Yamaki et al. [46,47], Musamoto et al. [48] and Cherleux et al. [49] showed the theoretical dependences of γ of composites with the chaotically distributed fibre filler on its concentration. It was shown that γ grows with the length:diameter ratio of the fibres. For example, the percolation threshold for fibres with l:$d = 110$ equals 0.03, instead of 0.17 for spherical particles [50].

Bridge et al. [51,52] 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 tunnelling. Grigorov and co-workers [53,54] showed that charge transfer in ECPC is also possible at a 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. However, such systems possess non-stable electrical conductivity, which raises some doubts about this model of conductivity.

The model suggested by Losoto et al. [55] determines the conductivity of a composite by the 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.):

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

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

The calculation done according to the Eq. (12) shows that $d = 35$ nm, if $\varphi = 0.08$, i.e. it possesses a size degree similar to that of 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. The thickness of the charged sphere is l. At

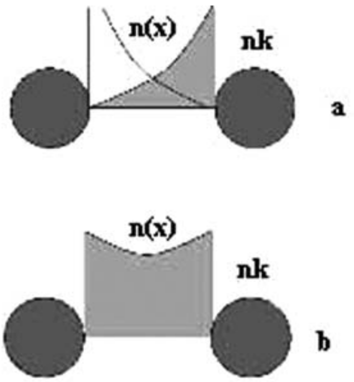

Figure 3. The model of conductivity suggested by Losoto et al. [55].

low l values (see Fig. 3a) the curves of the charge density decrease when neighbouring particles overlap, and a continuous concentration of injected charge appears. This charge is able to form an electrical current in an electrical field. At high values of l (see Fig. 3b) the composite is a sphere without injected charges. This part of the composite forms a barrier to current conduction because of its low self-conductivity (see Fig. 3b).

The concentration distribution of carriers in the interlayer is as follows:

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

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

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; and l is the characteristic length.

Such distribution of charges in the depth is usual when there are no charged traps in the prohibited zone. The criterion of ECPC conductivity is the condition $a \leq 1$. Substituting Eqs. (12) and (13) into Eq. (14), we obtain the following equation:

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

Conclusion with Regard to Models Discussed

Analysis of the reports and papers on investigations into the electrically conductive properties of ECPC considered above leads to one general conclusion: despite the variety of models of electrically conductive ECPC, unfortunately none of them provides sufficient versatility. Each model includes one or several approximations and suppositions, which affect the correctness of estimations of ECPC's conductive properties. That is why comparison of theoretically calculated data with the experimental results usually shows deviations, reaching several degrees in some cases. Coincidence is rarely reached at definite concentrations of conductive filler and specific conditions of composite production. For example, the deviation between the experimental data and those calculated by Eqs (1) to (3) for ECPC, based on some thermoplastics and carbon-graphite materials, reaches two decimal degrees [56]. This is apparently the result of the assumption of participation by 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, and that is why Eq. (4) displays $\nu \approx 0$, and then $\lambda = \lambda_1 c^2$. This is equivalent to its transformation into a divergent function, i.e. a high filler concentration causes significant deviations of λ values from the experimental data. A similar conclusion could be drawn regarding Eq. (9) at a high concentration of conducting filler. Large differences between the computed and experimental data were also observed in the application of Eq. (5). Apparently, this results from 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 the S and σ parameters. The necessity for experimental determination of a great number of coefficients in Eq. (7) essentially decreases the extent to which it could be generalised. Application of Eq. (1) for the ρ of real composites is complicated by a wide dispersion of r values, which depend on the structure of the carbon black, and by difficulties in estimating 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 the components of various electrically conductive composites show that the correctness of Eq. (11) in relation to ECPC depends significantly on the nature 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 this equation [61–64]. It is known that the ρ values of ECPC, based on various polymers with different degrees of interaction with the same electrically conductive filler at equal concentration, differ by a degree or more [65–67]. For example, the ρ of chlorinated PVC and fluoroplast-based composites, filled with P357E and ATG-70 carbon blacks (35 mass parts content), was found to be 0.25 Ωm and 0.036 Ωm, respectively [65]. In this case, it was found that compared with PVC fluoroplast, which is characterised by lower interaction with the filler, the values of ρ of ethylene-propylene triple copolymer and Vulcan XC-72 carbon black composite were a decimal degree lower than those of PP-based composites with the same filler [66]. In the case of composites based on siloxane elastomer SCTV-1, ρ was found to be three degrees lower than for similar material with natural rubber as the polymer binder [67].

Differences in the values of electrical conductivity, between those computed according to the percolation model of conductivity and those obtained in experiments, are frequently observed due to structural features of the filler particles. For example, the experimentally measured electrical conductivity of polyethylene composites, filled with acetylene carbon black, differs from the theoretical conductivity by a decimal degree [68]. This is explained by the presence of particle agglomerates and their statistical distribution in the matrix volume. Generally, the ability of filler particles to aggregate is a significant reason for such deviation. A difference between the theoretical and experimental conductivity data is also observed for composites that contain a binder possessing different interaction effects with carbon black during plasticisation, which is connected to free radical occurrence in this process [69]. These free radicals make their own contribution to the interaction between components. A further reason for the difficulty in forecasting theoretically the ρ value of ECPC is the existence of polar groups in macromolecules. For example, the ρ of carbon black-filled composites increases in the sequence of polymers as follows: cellulose acetopropyonate < cellulose acetobutyrate < cellulose triacetate [70]. These polymers differ according to the hydroxyl group concentration in them, the amount of which increases in the above sequence.

A comparison of different ECPCs based on different thermoplastics, obtained under similar conditions, shows that the composites with crystallising polymeric binders are characterised by lower values of ρ than those with amorphous binders. For example, it was shown that the ρ of amorphous cis-1.4-polybutadiene, filled with "Vulkan" carbon black (in 35 mass parts concentration) equals $10^3 \cdot \Omega$m [71]. At the same time, crystallising *trans*-1,4-polybutadiene possesses $\rho = 1 \cdot \Omega$m. According to Gilg [72], the ρ value of the composites decreases with the growth of polyolefin crystallinity degree.

The introduction of some type of mineral filler (kaolin, whiting) into the composite induces the growth of structural heterogeneity. This is the reason for the differences in the ρ of materials with the same content of insulator (polymer + mineral filler) and the same conductive part [73]. On the basis of the structural analysis data, Gilg [72] and Gul' [73] found that in the cases of both crystallising polymers and mineral fillers, the decrease in electric conductivity in composites is caused by the dislocation of conductive filler particles near the surfaces of the crystallites or kaolin and other mineral fillers, and consequently leads to more dense packing of current-conducting channels in the amorphous (less dense) phase of the polymer. However, some authors (groundlessly) ascribe this experimental result to the high conductivity of crystalline forms in polymer [71,74].

Taking into account the interactions between phases and within phases of ECPC, we obtained satisfactory results by using Eq. (16) for ECPC with a completely amorphous binder [56]:

$$\begin{aligned} \rho &= \rho_0 \exp\left(\frac{C_p - C}{C_p}\right)^a && \text{at } C > C_{\mathrm{p}} \\ \rho &= \rho_0 && \text{at } C \leq C_p \end{aligned} \tag{16}$$

where ρ_0 is the specific volumetric electrical conductivity of pure polymer, equal to the ρ of composites containing a conductive filler in concentrations below the percolation threshold mass part ($C \angle C_p$); and a is a constant proportional to the expression: $a \sim \frac{e_2 \times e_3}{e_1^2}$, and depends on the energies of interaction of polymer-polymer (e_1), polymer-filler (e_2) and filler-filler (e_3) types.

From an analysis of the ideas suggested by Pechkovskaya [10] and Aneli [56] on the influence of the ratio of interaction energies between components, it can be concluded that when the values of e_2 and e_3 are close and e_1 reaches its minimum, ρ also reaches its minimum, whereas an increase in the values of either e_2 or e_3 causes an increase in ρ [10]. If $e_2 > e_3$, then the probability of stable bond formation between filler particles decreases, i.e. the system loses its conductivity. But if $e_2 < e_3$, then the probability of agglomerate formation from conducting particles increases, which leads to a decrease in branching of conducting channels (pathways). In both cases the result is that ρ increases.

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

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

The results obtained correlate well with the data from Yakubovich and Narkis [75], which show that a sufficient effect on the conductivity of ECPC is induced by the dispersion of carbon black and the ratio of carbon black particle Ω to its mass (S:m). The value of γ of ECPC containing carbon blacks with different S:m ratios increases proportionately to this ratio with the concentration.

Table 1 shows experimental data and the results of the ρ value calculations by Eq. (16) for SCTV-based composites with various filler contents, and the filler concentration, C_p,

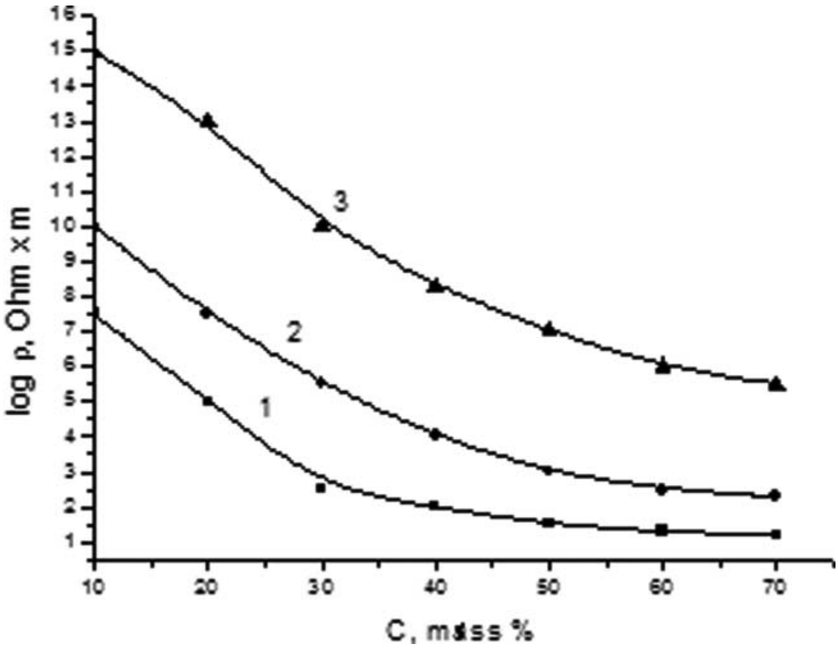

Figure 4. Dependence of ρ values of SCTV-based composites on filler concentration. The fillers are P357E (1), ATG-70 (2) and P803 (3).

Table 1. Experimental and calculated data on ρ and C_p for electrically conductive rubbers

Composite	ρ_{exp}, Ohm·m	ρ_{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 denote mass parts of the filler per 100 mass parts of elastomer; C_p is measured in the same units.

corresponding to the insulator-conductor transition for the same materials. To estimate the extent to which Eq. (16) could be generalised, ρ 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 in Table 1 show that the deviation between the experimental and calculated data does not exceed 20%.We can therefore state that Eq. (16) may be used to calculate the concentration dependences of ρ in ECPC with an amorphous polymeric matrix.

Structural Models of ECPC

The conductivity of polymers containing electrically conductive fillers depends, firstly, on the density of current-conducting channels in a polymer matrix which, in turn, depends very much on the ability of filler particles to form an infinite cluster. It was mentioned above that the formation of a current-conducting system in a polymer depends on the ratio of interaction energies between the components of the composite. If we take into account that the highly structured carbon blacks P357E and ATG-70 possess comparatively high interaction energies between their own particles and those of the polymer, and that intermolecular interaction in organosilicon elastomers is weaker than in other polymers, it becomes clear why composites based on highly structured carbon blacks and SCTV possess a higher conductivity than a composite based on SCTV and the less highly structured carbon black P803.

The physical and chemical properties of the surface of filler particles are the decisive features in the filler-polymer and filler-filler interactions which, in turn, play the leading role in the formation of the structure and the electrically conductive properties of ECPC [2,10].

The structure of carbon black and graphite seriously affects the electrical conductivity of composites. In some cases, an increase in the extent of structure becomes more important than an increase in the specific surface square. For example, rubbers filled with more highly structured carbon black (PM-90) possess higher conductivity than those filled with less structured but more highly dispersed carbon black (PM-100) [76]. A similar result was obtained when the conductivity of conducting rubbers filled with highly structured acetylene carbon black (ATG-70) was compared with that of less structured PM-100 [77]. However, this situation often occurs when the effectiveness of carbon blacks is compared with that of other intercompensating properties (structural degree, dispersion, porosity, roughness, etc.), which complicates the estimation of the effect of one factor or another.

It is known that dispersion [78] and porosity significantly affect the conductivity of filled rubbers and plastics. Verhelst et al. [79] analysed the effects of the structural indexes of carbon blacks on the electrical conductivity of composites.

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

The chemical properties of the surface are defined by the existence of functional groups, consisting of oxygen, hydrogen, and sulphur. The 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 the free-radical origin of carbon blacks [80,81]. The 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 nature of the polymer. 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 an inert atmosphere at high temperatures (over 1,000 K) affects the conductivity of composites. Experiments reported by Perepelkin et al. [83] showed that in most cases the conductivity of ECPC containing heat-treated carbon blacks is increased (in some cases by 6 decimal degrees).

The chemical groups of the carbon black surface significantly influence the polymer-filler interactions, promoting different types of interaction. High energy of a polymer-filler interaction may promote the structural degradation of ECPC. Oxidation of carbon black particle surfaces always increases ρ, and elimination of volatile substances and chemical groups at thermal treatment without oxygen causes a decrease in ρ in ECPC [84].

The influence of conducting filler type on the percolation threshold is clear from the investigation by Aneli et al. [85] into the electrically conductive properties of polyester epoxy-based composites, dissolved in styrene with carbon-graphite fillers. Hydroperoxide of isopropyl benzene oxide (hyperysis) was the hardener in this composite, and cobalt naphthenate was 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 by cold pressing of previously rolled masses in press forms under 15 MPa pressure (low-ohmic samples). The choice of preparation technique depends on the viscosity of the mixtures, which, in turn, depends on the filler concentration. A low concentration of filler and, consequently, low viscosity of the mixture allows mixtures to be prepared in the usual mechanical mixer. Increased filler concentration and viscosity require significant mechanical forces and the application of rollers.

The compositions produced in accordance with this technique differ in that there is a considerable increase in conductivity at comparatively low filler concentrations. The data from Gul' and Shenfil [3] suggest that a similar transition occurs in different composites at relatively high filler concentrations. For example, Bridge et al. [19] explain this fact as an irregular distribution of the filler in the polymer matrix. The microstructure of the composite represents an electrically conductive spatial network, consisting of the filler particles, and disposed between dielectric blocks (domains). These blocks may be formed by macromolecules with definite order in the distribution of single molecules or crystal areas (Fig. 5). Polymer blocks (domains) may be formed as a result of macromolecular aggregation via interactions resulting from the effect of Van der Waals forces and electrostatic forces of

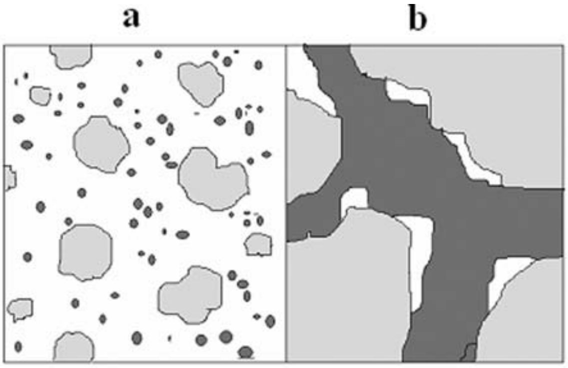

Figure 5. Scheme of the formation of a current-conducting system (in accordance with an electron microscope photo) based on polymers and electrically conductive particles: (a) initial state before the formation of infinite clusters in ECPC (dark spots—conductive particles, light spots—polymer domains, white area—amorphous polymer). (b) ECPC after the formation of the infinite cluster (dark area) among polymer domains (light area) and free volume (white area).

polar groups (the current authors have previously termed 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 if the block structure were absent. Thus, the morphological features of the composition being considered determine the formation of the conducting channel when there is a relatively low threshold concentration of the filler [87]. In this case, the degree of filler structure correlates with the experimental data with regard to conductivity dependence on the type of carbon black [18].

The application of two different types of electrically conductive filler in a single composite results in an extreme value of p (with a minimum) in accordance with the ratio of the fillers. Aneli et al. [85] and Lukyanova et al. [88] give curves of ρ dependence on concentrations of two conductive fillers—graphite and carbon black—at various concentrations, and suggest the following equation for calculation:

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

where c_1 and c_2 are concentrations of ATG-70 and graphite, respectively; and a, b, K, m and n are coefficients depending on the type of elastomer. At $c_2 = 0$, Eq. (17) transforms into Eq. (9). Although Vinogradov and Sarychev [87] and Os'kin et al. [89] succeeded in applying Eq. (17) for the calculation of ρ for various combinations of binary filler components at different total fillings of SCI-3-based rubber, this equation displays no invariance to binary filler components. Moreover, as mentioned above, application of the related Eq. (9) implies that Eq. (17) is not correct at the transition from the specific volumetric resistance to the specific volumetric electrical conductivity of the material.

To elucidate the functional dependence of the ρ of ECPC on the 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 of 40 mass parts) showed a change of ρ expressed by a curve with a minimum, which corresponded to a P803 carbon black concentration of

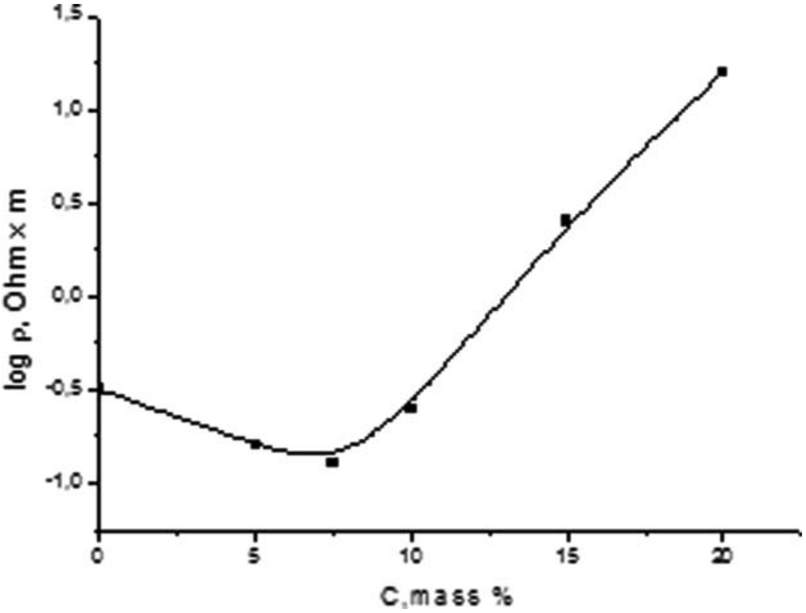

Figure 6. Dependence of the ρ of polyester epoxy-based composites on the ratio of binary filler (graphite + P803) components with 20% filler content. x-axis—content of graphite in the filler blend.

25 mass parts and a graphite concentration 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 in the form of agglomerates 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 characterised by much higher conductivity than those based on the same polymer filled by the same amount of graphite.

Figure 6 shows curves reflecting one of the dependences of the so-called “synergistic effect”. This effect results in inhomogeneous distribution when other reactions weaken or strengthen and when the properties of the material change as a result of the introduction of two or more active components. The synergism of binary fillers is related to the morphology of the composite. In particular, this phenomenon is explained by the type of interdisposition of the two types of filler particle in the polymer matrix. For example, the 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 electrical conductivity form a secondary structure, which resembles bridges between conducting particles of graphite and which then includes them in the general conductive system. If this phenomenon is presented as an electrical scheme of parallel-consequent connected resistance elements, it becomes possible to explain the reason for the significant improvement in the electrically conductive properties of the composite.

The experimental data on the electrical conductivity of ECPC with binary electrically conductive filler at different values of total filler concentration, and the simultaneous application of mathematical planning of the experiment [90] allowed us to deduce a regularity

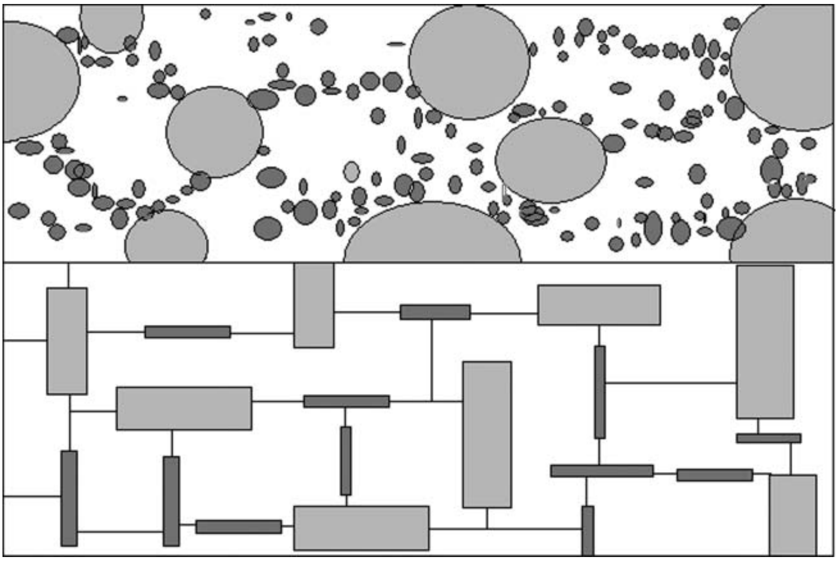

Figure 7. Two-dimensional model of the composition based on polymers with a binary filler (graphite + carbon black) (top) and an equivalent direct current scheme (bottom). Large circles – graphite particles; small circles – carbon black particles; large rectangles – resistance of graphite particles;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

for the ρ-c dependence, described by the following formula:

$$\rho = -A \cdot (\rho_1 c_1 \ln c_2 + \rho_2 c_2 \ln c_1) \tag{18}$$

where ρ_1 and ρ_2 are the specific volumetric resistances of pure fillers (carbon black and graphite), respectively; c_1 and c_2 are concentrations of these fillers in mass parts; and A is a constant, depending on the material type.

It should be easier to do calculations for one concentration using Eq. (18), i.e. to express the second filler concentration via the first one, taking into account that $c_1+c_2 = 1$:

$$\rho = -A \cdot [\rho_1 c_1 \ln(1 - c_1) + \rho_2 \cdot (1 - c_1) \ln c_1] \tag{19}$$

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

Aneli et al. [91] investigated the influence of the composition on the electrically conductive properties of ECPC using as an example systems consisting of two types of organosilicon elastomer, SCTVF-803 and SCTVF-2103, and the carbon black fillers P803, P324, and ATG-70 [91]. Some of the composites contained Aerosil® A-300. The concentrations of the fillers were varied from 20 to 80 mass parts per 100 mass parts of elastomer. Dicumyl peroxide in three mass parts concentration was used as a vulcanising agent. Rubber mixtures were prepared on laboratory rollers. Vulcanisation was performed by the well-known technique of peroxide vulcanisation [92]. Electrodes were introduced into the rubber mass before the start of vulcanisation.

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

Table 2. Physical and mechanical indexes of electro-conductive rubbers, based on SCTVF-803 and SCTVF-2103 elastomers

Group	N	Composite	ρ, 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 denote filler concentrations in mass parts per 100 mass parts of the elastomer.

Table 2 shows the characteristics obtained in tests of the electroconductive and physical-mechanical properties of vulcanisates [56].

According to the data shown in Table 2, SCTVF-803-based composites possess higher conductivity than SCTVF-2103-based rubbers at equal concentrations of the filler. For example, the ρ 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 rubber containing the same filler concentration. This may be explained by two phenomena: (i) filler dispersion during rubber mixture rolling; and (ii) the distribution of filler particles in the elastomer matrix.

The growth of the filler concentration induced by the increase in dispersion promotes simultaneous growth of the number of conducting channels and, consequently, the decrease of ρ, but only if the electrically conductive particles form a branched spatial network in the matrix. This becomes possible at a definite ratio of intensities of two types of interaction, namely the filler-filler and the elastomer-filler interactions. Predomination of the first type of interaction apparently increases the rubber conductivity by intensifying the formation of agglomerates (clumps). These clumps increase homogeneity in the filler particle distribution, which may cause the growth of ρ and the decrease of physical and mechanical parameters, starting from a definite (for the particular composite) filler concentration. That is why the elastomer-filler interaction is also required for the formation of a highly developed conducting system in the rubber. This interaction prevents the process of clump formation. Consequently, one may suppose that composites attain high conductivity at a definite ratio of the mentioned interactions.

Taking into account the suppositions and technical indexes shown in Table 2, the ratio of the interactions shown for the first pair of compared composites (Nos 3 and

16 – based on SCTVF-803) should be optimal compared with that of the second pair, based on SCTVF-2103 (ρ of the first composite is lower than that of the second one). The spin probe technique was used to obtain results on the degree of homogeneity. It was found that the degree of homogeneity of the filler distribution in the matrix of No. 3 rubber is lower than that in No. 16 rubber. This correlates well with the known nature of filler particle distribution in composites with high compatibility of the components [93].

The effect of the filler type on the properties of composites is clear from 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 ρ values. However, it should be taken into account that the difference in properties of the composites of groups I and II is determined by the properties of the carbon blacks separately, and by their behaviour in the polymer matrix. This affects, in particular, the physical and mechanical indexes of the composites. For example, if the maximum of resistance of group I rubbers is displayed at 50 mass parts concentration of the carbon black P324, then the rubbers of group II possess the maximum resistance (according to the tendency of resistance growth) at higher filler concentrations. Moreover, the difference in the properties of the groups of composites compared is also expressed by the value of residual elongation: all composites of group II are characterised by its absence.

It should be possible to find the reason for the differences in the properties of these groups of rubbers in the nature of the interactions between the composite components. On the one hand, stronger polymer-filler and filler-filler interactions in the rubbers of group I, compared with group II, induce higher conductivity. On the other hand, these interactions promote the formation of a composite with maximum resistance at relatively low filler concentrations. Zero values of the residual elongation of group II rubbers evidently indicate fast relaxation processes in the macromolecular system, which proceed in the composites after sample rupture caused by a weak polymer-filler interaction.

The dielectric filler Aerosil® is known as a good intensifier of rubber mixtures [7]. That is why in the three-component systems obtained Aerosil® A-300 acts as an intensifier of organosilicon rubbers (groups III and IV). However in the case of the present filler, there are also optimal concentrations that give rubbers excellent physical and mechanical properties. For example, the sample with the lower concentration of the binary filler Aerosil® + carbon black (No. 9) is characterised by higher resistivity, than the sample with higher carbon black concentration. Improvement in the electrically conductive and resistive properties of composites is observed with the application of ATG-70 carbon black combined with Aerosil® (samples from groups IV and V) at optimal ratio of the fillers. Thus, variations in the filler concentration may improve some properties and simultaneously decrease others. For example, an increase in the Aerosil® concentration induces a decrease in the electrical conductivity of the composites with binary fillers, but simultaneously increases the resistance (Nos 17 and 18). The effect of Aerosil® is clear and requires no additional explanation. In turn, a decrease in the conductivity of rubbers at higher Aerosil® concentrations may depend on two factors: the decrease in the total content of conductive filler in the composite, and the destruction of the current-conducting system by Aerosil® particles.

Conclusions

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

In the search for the dependence of the specific volume of electrical resistance, ρ, on the filler concentration in ECPC, it is logical to conclude that a composition with the highest conductivity may be obtained at the maximum degree of filling. However, it is also known that due to the deterioration of the physical and mechanical properties of composites at high degrees of filling, technologists are forced to introduce some limits on the selection of the optimum concentration of conductive fillers.

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