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Transport Processes in Electrically Conducting Dispersely Filled Polymeric Composites

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The mechanisms of electrical conduction in polymeric composites with electrically conducting fillers are examined on the basis of effective medium, fluctuation tunnelling, and percolation models. The properties of the conducting fillers—metals, graphite, and technical carbon—are analysed. Factors influencing the electrical conductivity of the composites, in particular the methods of preparation of the filler and of the material, are discussed. The prospects for the utilisation of composites of this type are indicated.
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I. INTRODUCTION

In connection with the increasing demands imposed by the technology and economic factors, many branches of industry have been faced in recent years with the increasingly acute problem of the manufacture of materials with a set of new properties. This applies particularly to materials which should combine the properties characteristic of semiconductors and metals and also polymeric materials. In principle, these requirements can be satisfied in two ways—either by synthesising polymers with a new chemical structure, for example, polymers with a conjugation system, and doping them or by introducing an electrically conducting filler (powders, metals, graphite, carbon black, etc.) into polymeric dielectrics. Both these procedures are well known from the literature. The creation of materials of this type naturally requires the knowledge of the structure and mechanism of the generation and transport of [current] carriers in the materials. Because of their chemical structure, an extensive literature has been devoted to polymeric materials with semiconducting properties[1,2], while electrically conducting polymeric composites have been studied to a much lesser extent at the present stage of development[3-6]. This review deals mainly with transport processes in electrically conducting polymeric composites.

The range of applications of such materials is fairly broad and the study of the existing and the creation of new electrically conducting materials therefore constitutes an extremely urgent task[7].

II. ELECTRICALLY CONDUCTING FILLERS

Various metals, graphite, and technical carbon (carbon black) can be used as electrically conducting fillers. Fig.1 presents typical relations between the resistivities ρ_v of the compositions and the concentration of the electrically conducting filler. At low concentrations ρ_v is close to the resistivity of the polymer, its value decreasing sharply subsequently and approaching ρ_v for the filler at higher concentrations. Fig.1 shows that organic fillers are usually more effective as electrically conducting additives than metallic powders. We shall consider the properties of various types of fillers.

1. Metallic Fillers

When metals (Cu, Al, Ni, Zn, Au, Ag) are introduced into a polymer, a fairly high conductivity is reached only at their high concentrations[3], because the surfaces of the particles of many of the available metals are in most cases coated by an oxide film, which hinders the transport of carriers between the filler particles. Furthermore, the density of the metal greatly exceeds that of the polymer, which results in a considerable increase of the weight of the composite. All these factors resulted in the use of metals only in certain instances: in compositions with various ceramics (the so-called cermets) in order to obtain high-resistance resistors[8] and also in electrically conducting adhesives used in the electronic industry in order to avoid the welding of components. In the latter case expensive colloidal silver must be used at fairly high concentrations (up to 70 wt.%) in order to obtain the required conductivities and this naturally limits the applications of such adhesives[9].

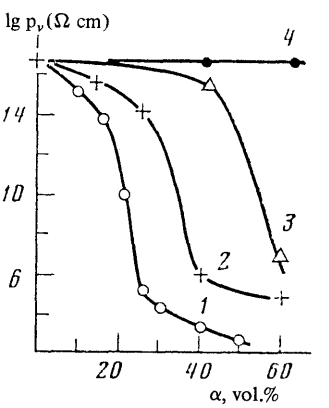


Figure 1. Dependence of the specific bulk-phase resistivity ρ_v of the composition based on low-density polyethylene on the concentration of electrically conducting fillers[3]: *1*) acetylenic carbon black; *2*) ZKA graphite; *3*) PAK-3 aluminium powder; *4*) zinc dust.

The use of special mixing procedures or the application of metallic particles of an unusual shape (in the form of scale, metallic leaf, dendrites, etc.) makes it possible to reduce their concentration necessary for the attainment of specific levels of conductivity[10,11].

The theoretical principles of the preparation of colloidal metals and composites based on them were developed approximately ten years ago[12,13]. Polymeric composites with highly dispersed metallic fillers have been obtained by electrolytic[13] and thermal[13,14] methods.

2. Graphite

It is known[15,16] that the crystal lattice of graphite consists of a set of planes in each of which the carbon atoms form a network of regular hexagons with a side of 0.418 Å.[17] The distance between the planes of the conjugated π-bonds is much greater (3.35 Å) and the planes are therefore weakly bound to one another and graphite can be readily cleaved. The conductivity of graphite in the plane of the layers σ_a is metallic and reaches $10^4\ \Omega^{-1}\ cm^{-1}$ at a concentration of carriers $n \cong 10^{19}\ cm^{-3}$ and their mobility $\mu \cong 10^4\ cm^2\ V^{-1}\ s^{-1}$.[16] The conductivity at right angles to the layers σ_c depends greatly on the perfection of the structure of the single crystal, the presence of impurities, and many other factors. For this reason graphites are classified as semimetals. The anisotropy of the electrical conductivity (σ_a/σ_c) varies within fairly wide limits: from 250 to 10^4. The natural graphite used as the conducting filler has a polycrystalline structure with a high content of amorphous carbon and the conductivity of such graphites is therefore low. Furthermore, the graphite particles are unable to form chain structures and the increase of the conductivity of the composites is therefore achieved by introducing high concentrations of the filler, which impairs the physicomechanical properties of the material[3]. For these reasons, natural graphite was not considered previously as a promising electrically conducting filler. However, data obtained recently concerning new methods of filling[18–20] may modify this view.

It has been observed recently that the introduction into graphite of powerful electron acceptors (SbF_5 and AsF_5), which form the so-called intercalated or layer graphite compounds, increases the conductivity of graphite to values exceeding that of the best conductor—copper. The employment of such compounds as conducting fillers appears to be extremely interesting in some cases[21].

3. Technical Carbon (Carbon Black)

The most widely used electrically conducting filler is carbon black (technical carbon). At the present time more than 90% of technical carbon manufactured and consumed consists of pitch carbon black but special varieties of acetylenic carbon black are most frequently employed as fillers[22]. X-Ray diffraction studies of the carbon black particles have shown that they consist of individual small crystalline cells of the graphite type. The disposition of carbon atoms in the layer is the same as in graphite crystals but the distance between layers is greater. The sites where the end faces of the parallel layers emerge on the surfaces of the particles have an increased energy and hence an increased adsorption capacity. This is in fact the reason for the ability of carbon black particles to form chains and network structures—the property referred to as "degree of structure" of the carbon black[5]. The active sections on its surface can also adsorb extraneous components (for example, oxygen) and the presence of the latter impairs the "degree of structure" of the carbon black. For this reason, the conductivity of the carbon black usually increases with decrease of the concentration of volatile substances[23]. Another factor which determines the conductivity of the carbon black is the specific surface which depends on the size and porosity of the particles.

Thus technical carbon (carbon black) which is effective as an electrically conducting filler must have the following characteristics: a large specific adsorption surface, a high porosity, a small particle size, a low content of volatile admixtures, and a high degree of structure[24]. It will be shown below that the conductivity of the composite is determined not only by the characteristics of the filler but also by the method of mixing of the components.

III. THE MECHANISMS OF ELECTRICAL CONDUCTION IN POLYMERIC COMPOSITES

Electrically conducting composites lack long-range order in the distribution of filler particles and such materials are therefore classified as typical disordered systems. The results obtained for disordered semiconductors and other systems can be used in the study of transport phenomena in the composites under consideration[25].

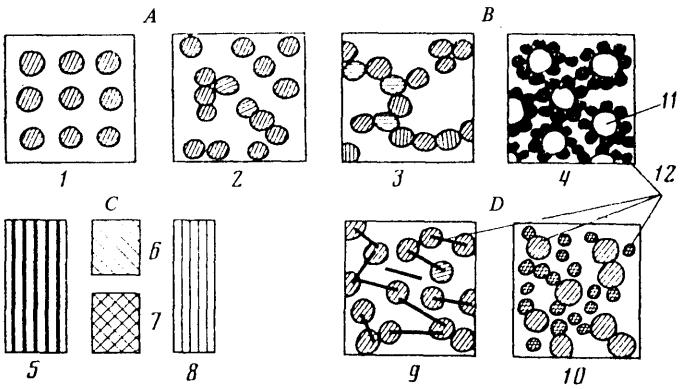


Figure 2. Different types of distribution of fillers in a polymer matrix: *A*) disperse systems [*1*) matrix mixture; *2*) statistical mixture]; *B*) structured disperse systems [*3*) two-component system; *4*) three-component system]; *C*) filler in the form of fibres, fabrics, and strips [*5*) layer structure; *7*) biaxially oriented structure; *6*) and *8*) monoaxially oriented structure]; *D*) mixed filler [*9*) fibre–sphere; *10*) two spheres]; *11*) dielectric; *12*) various forms of conducting fillers.

To a first approximation, it is possible to distinguish matrix systems, statistical mixtures, and structured compositions in terms of the nature of the distribution of the components[4]. In matrix systems one phase is continuous and at any concentration. In statistical mixtures the components are distributed at random and do not form regular structures. Systems whose components form chain, planar, or bulk-phase structures are classified as structured composites. Fig. 2 presents typical structures of composites and the distribution of the filler in the matrix.

In a number of studies theoretical calculations have been made to establish a relation between the properties of the components, on the one hand, and those of the composite, on the other. The early investigations of transport phenomena date back to 1892 when Rayleigh examined the conductivity of a matrix with a cubic packing of conducting spheres[26]. In the same year Maxwell proposed a mathematical analysis of systems containing spheres distributed at random in a continuous matrix[27]. Odelevskii proposed in 1951 a method for the calculation of the generalised conductivity of heterogeneous composites[28]. His relations can be used to calculate the electrical and thermal conductivities, magnetic permeabilities, and dielectric constants of composites. Such generalisation is possible because the equations describing the scalar and vector fields of these quantities are formally identical. The electrical conductivity of a matrix system (polymer matrix) is described by the equation

$$\sigma = \sigma_p\left(1+\frac{\alpha_f}{\frac{1+\alpha_f}{3}+\frac{\sigma_p}{\sigma_f+\sigma_p}}\right)$$

For a statistical mixture, we have

$$\sigma = \frac{(3\alpha_p-1)\sigma_p+(3\alpha_f-1)\sigma_f}{4}+\left[\frac{[(3\alpha_p-1)\sigma_p+(3\alpha_f-1)\sigma_f]^2}{16}+\frac{\sigma_f\sigma_p}{2}\right]^{1/2},$$

where α_p, α_f, σ_p, and σ_f are the concentrations and conductivities of the polymer and filler respectively.

The Lorentz–Lorenz and Lichtenecker formulae are also available for the calculation of the conductivities of mixtures[4,8,29,30].

It is noteworthy that none of the expressions enumerated above employ any specific mechanism of the transport of carriers in the composites but are based on the "effective medium" model. Reliable results are therefore obtained with the aid of the above computational formulae only in cases where σ_p and σ_f do not differ by a factor greater than 10^2. In many composites with a polymer matrix, this condition is not observed: the conductivity of polymers [polyethylene, polystyrene, and poly(vinyl chloride)] is 10^{-12}–10^{-16} Ω^{-1} cm^{-1},[4] while that of carbon black is 10 Ω^{-1} cm^{-1} [22] and that of graphite is up to 10^4 Ω^{-1} cm^{-1}.[16] Thus new approaches are necessary for the description of the properties of electrically conducting polymeric composites.

There is so far no unanimous view concerning the mechanism of electrical conduction in filled polymers. The following views are the most common: (a) charge transfer is based on the direct contact between the particles of the electrically conducting filler distributed in the specimen in the form of chains[31,32]; (b) charge transfer takes place not only on direct contact between the conducting particles, but also as a result of electron tunnelling through the dielectric layers of the polymer[33]. The level of the experimental technique does not so far permit an unambiguous answer to the question whether the sharp increase of conductivity with increase of the concentration of the filler is associated with the direct contact of the filler particles with one another or whether a mutual approach of the conducting particles to within distances necessary for the achievement of the tunnel effect is sufficient.

In order to estimate the dominant type of contact, analysis of the dependence of the current on the potential is frequently employed[4]. To a first approximation, this dependence is described by an equation of the type

$$i = cu^n,$$

where c and n are constants. The direct proportionality between the current and the potential ($n = 1$; Ohm's law) indicates the dominance of carbon black–carbon black contacts. A deviation from Ohm's law shows that the carbon black particles are separated by layers of the polymer.

In the presence of the tunnel effect, the dependence of the current on the potential is described by another expression:

$$i = Au^{n_1}e^{B/u},$$

where A, B, and n_1 are constants. It has been established experimentally that, with increase of the potential, this formula is suitable for the description of certain real systems starting from a critical potential[34]. However, one should note that the resistance may be Ohmic also in the presence of the tunnel effect. The characteristics of contacts of different types have been examined[35,36].

1. The Fluctuation Tunnelling Model

The fluctuation tunnelling model is apparently closest to reality[37]. According to this model, the conductivity of polymers filled with carbon black is determined by two factors. The ability of the carbon black to combine into chain structures (clusters) is responsible for charge transfer between the particles within the cluster directly via contacts. For certain relatively high degrees of filling, the distance between the clusters becomes much smaller than the dimensions of the latter and the conductivity is determined by the tunnelling of electrons between the clusters at the point of the maximum approach of the latter. Tunnelling is promoted by the thermal energy fluctuations (kT), which modulate the energy barrier; the decrease of the height of the energy barrier induced by the fluctuations can be fairly large. Furthermore, the presence of fluctuations leads to the appearance of a temperature dependence of the conductivity.

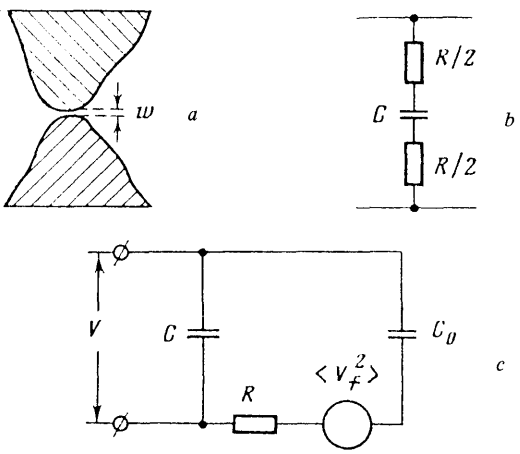


Figure 3. Equivalent circuit of the tunnel transition in the fluctuation tunnelling model[37]: *a*) type of contact; *b*) circuit; *c*) equivalent circuit (C_0 is the total capacitance between two particles).

Such a barrier can be represented approximately by a series-connected resistance R and a capacitance $C = S/4\pi w$ (where S is the area and w the distance between the clusters in the region of their maximum approach) and also by an equivalent circuit (Fig. 3). The fluctuations of the potential are described by the familiar Nyquist formula $\langle V_f \rangle^2 = 4kTRdf$, where df is the frequency range. Averaging with respect to the frequency and taking into account the equivalent circuit

yields the thermal fluctuations of the potential drop across the barrier $\langle V_T \rangle^2 = kT/C$.

Calculations yield the following temperature dependence of the resistivity of the composites:

$$\rho = \rho_0 \exp\left[\frac{T_1}{T + T_0}\right],$$

where T_1 is the temperature corresponding to the energy necessary for the electron jump across the gap between the clusters and T_0 is the temperature below which ρ is independent of temperature.

Experimental results have shown that composites based on poly(vinyl chloride) (PVC), filled with various types of carbon black, have conductivities whose temperature variation is described by the above formula[38]. This indicates the fluctuation mechanism of the conduction in the systems considered (Fig.4).

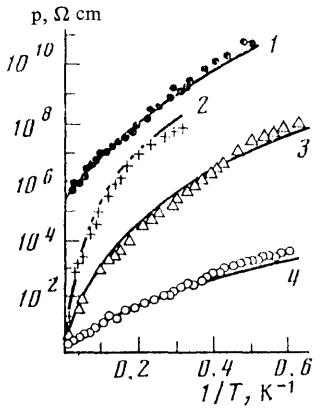


Figure 4. Temperature variation of ρ for carbon black-filled PVC compositions[38]: *1*) Mogul-L carbon black (45 wt.%); *2*) Columbia SA40-220 carbon black (15 wt.%); *3*) Columbia SA40-220 carbon black (20 wt.%); *4*) Ketjenblack EC carbon black (16 wt.%).

A characteristic feature of polymeric composites of this kind is that electrical breakdown occurs for comparatively low electric field strengths $E < 10^2$ V cm^{-1}. The low breakdown potentials are due to the fact that the potential drop occurs mainly in the gap between the conducting clusters and the gaps w are much smaller than the size of the cluster W. The field strength in the gap therefore reaches EW/w, which is sufficient for thermal breakdown[38].

2. The Degree of Linkage in Polymeric Composites

In order to estimate the degree of linkage between the particles of the electrically conducting filler in composites, one can apparently employ the approach developed for the determination of a measure of the degree of linkage of graphite[39]. The ratio of the electrical conductivity of the test specimen σ_m to the electrical conductivity of pore-free volumes σ_0, i.e. $K = \sigma_m/\sigma_0$, is used as a quantitative characteristic of the macrostructure of graphite. The quantity K varies from $K \cong 0$ for graphite powder to $K = 1$ for the single crystal. The conductivity σ_0 is determined from the concentration of the charge carriers n_0 and their mobility μ_0 by means of the formula $\sigma = en_0/\mu_0$. The quantity n_0 is usually close in magnitude to the concentration of carriers in the single crystal ($n_0 = 1.1 \times 10^{19}$ cm^{-3} at 300 K). This quantity can be determined by ESR. The following formula is used to determine μ_0:

$$\mu_0 = \frac{1}{H}\left[\frac{\rho(H) - \rho(0)}{\rho(0)}\right]^{1/4},$$

where H is the magnetic field and $\rho(H)$ the resistivity in the magnetic field.

We may note that K for different graphite specimens is linearly correlated with Young's modulus E, which in certain cases is determined solely by the degree of linkage in the specimen (Fig.5). The application of a similar approach to electrically conducting polymeric composites can yield information about the aggregation of the filler particles and the formation of conducting chain structures.

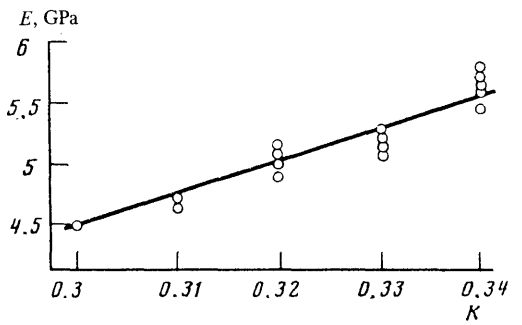


Figure 5. Dependence of Young's modulus E on the degree of linkage $K = \sigma_m/\sigma_0$ for graphite specimens[39].

3. The Percolation Theory

The most general approach to the description of the conductivity of non-ordered structures is apparently one involving the percolation theory[40,41]. Diffusion is usually regarded as the random movement of particles in an ordered medium; on the other hand, percolation is represented as directed movement in a non-ordered system. An example may be provided by the flow of water through porous minerals. Percolation in a regular lattice or in a continuous medium may be considered.

For a lattice made up of regularly distributed sites, where the neighbouring sites are connected by bonds, there is a possibility of, for example, flow of a current, a liquid, etc. between the sites. Disorder is introduced in two ways into such a system: (a) in a random fashion with a probability $1 - c$ by blocking (rupturing) the bonds in the system (the bond problem); (b) in a random fashion with a probability of $1 - c$ by blocking the sites (the site problem).

A macroscopically large (infinite) system is said to be permeable if the flow of a liquid (current, heat, etc.) through it via non-ruptured bonds (in case a) or similarly via bonds passing through non-blocked sites (in case b) is possible. The problem consists in the determination of the minimum value of c ($c = c^*$) down to which the infinite system remains permeable. The flow threshhold constitutes the threshhold of the formation of an infinite cluster of bonds "hooked" onto one another.

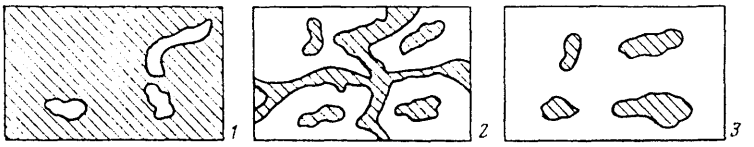


Figure 6. Dependence of the degree of linkage in a composite on the concentration of the conducting filler (shaded region) (c^* = percolation threshhold): *1*) $c < c^*$; *2*) $c = c^*$; *3*) $c > 1 - c^*$.

If the distribution of conductivity in the material defined by $\sigma = 0$ with a probability $1 - c$ and $\sigma = \sigma_0$ with a probability c obtains, then, according to the percolation theory, the conducting parts of the material under conditions where $c < c^*$ are insulated from one another and the overall conductivity is zero. When $c \geq c^*$, a continuous conducting pathway appears through the entire specimen and the conductivity increases further with increase of c. Finally, when $c > 1 - c^*$, the non-conducting parts of the material are insulated from one another. Thus in the vicinity of the percolation threshhold c^*, there is an insulator–conductor transition, as shown in Fig.6.

More accurate results have also been obtained for binary continuous media[42], for which the local conductivity σ is equal to σ_0 with a probability c and to σ_1 with a probability $1 - c$, while $x = \sigma_1/\sigma_0 \ll 1$. The following relations have been obtained:

$$\sigma \sim \sigma_0 (c - c^*)^{\beta} \quad \text{when } c \gg c^*,$$
$$\sigma \sim \sigma_1 (c^* - c)^{-1} \quad \text{when } c \ll c^*,$$
$$\sigma \sim \sigma_0 x^{\delta} \quad \text{when } c \to c^*,$$

and $\delta = \beta/(\alpha + \beta)$. These relations are illustrated schematically in Fig.7.[42] The parameters for different problems of the percolation theory are presented below[42]:

	c^*	β	δ
Three-dimensional bond problem	0.25	1.6	0.67
Two-dimensional bond problem	0.48	1.1	0.51
Three-dimensional problem of percolation in a continuous medium	0.145	1.4	0.65
Three-dimensional model of a continuous (additive) medium	0.33	1	0.5

The model of an electrically conducting composite in which the filler particles are distributed at the sites of a regular three-dimensional lattice (cubic, diamond-like, etc.) has been examined[43]. It was assumed that the particles located at neighbouring sites are in contact. With increase of the filler concentration, the dimensions of the cluster consisting of particles in contact increase until a continuous chain passing from one edge to another is formed (i.e. the percolation threshhold is attained). In contrast to the traditional approaches of the percolation theory[40,41], this problem is solved by analogy with the problem of random motion in a three-dimensional lattice and resembles the model employed by Flory in the analysis of the conformations of polymeric chain molecules[44]. As a result, relations were obtained for different types of lattice between the average length of the continuous chain and the conductivity, on the one hand, and the filler concentration, on the other. The average percolation threshhold obtained[43] for six types of lattice was 0.095, which the author believes to be close to the value of 0.145 obtained by other methods[42].

An interesting example of a system of practical importance in which there is a dielectric–conductor transition of the percolation type is provided by the so-called granulated metals or cermets, which are composites consisting of a non-conducting matrix (SiO_2, Al_2O_3) in which fine grains of a metal (Ni, Pt, Au, etc.) are dispersed[8,45]. Such systems are used to prepare thick-film resistors.

The study of the dependence of the conductivities of such systems on the content of the metal c_M indicates the presence of three regions[45]. When $c_M < 0.4$, the system consists of insulated unconnected particles of the metal distributed in the dielectric matrix. In this case conductivity is due to the thermally activated tunnelling of charge carriers between the metallic particles. The transport of charge carriers takes place via electron "jumps" from one neutral grain to another; this results in the formation of a pair consisting of positively and negatively charged grains, which requires a definite consumption of energy. A characteristic temperature variation of the conductivity of the form $\sigma \propto e^{-A/\sqrt{T}}$ arises as a consequence[45].

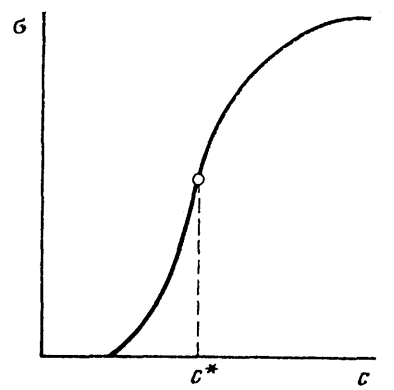


Figure 7. Dependence of the electrical conductivity σ on the concentration c_M of the conducting filler near the percolation threshhold for a two-component random medium.

In the region $0.4 < c_M < 0.5$ the percolation threshhold occurs; conducting chains permeating the entire specimen begin to be formed. When $c_M > 0.5$, the metal forms a continuous phase in which particles of the dielectric are distributed.

The high concentration of the metal corresponding to the percolation threshhold (50% of the filler instead of the theoretical value of 15%) is explained by the fact that, during the preparation of the cermets, layers of oxides preventing the transfer of electrons are formed on the surface of the metallic grains even when the particles are in contact. This shows that phenomena at the interface play an important role in the mechanism of conduction in composites. Indeed, when

$c_M > 0.5$ the resistivity varies in the following manner with the contact force between the particles:

$$\rho_c = 0.8\rho_M\left(\frac{E}{p}\right)^{1/3},$$

where ρ_M is the resistivity of the conducting phase, E the modulus of elasticity, and p the pressure in the system, equal to the ratio of the contact force to the area of contact[8].

Thus, in order to ensure electrical conduction, a simple contact between the particles of the conducting phase is insufficient—conditions ensuring an obstacle-free electron transfer between the particles are necessary.

4. Structured Composites

The so-called structured composites merit separate consideration. An example is provided by systems obtained by pressing mixtures of polyethylene or polypropylene and metal powders[10,11]. In this case the specimen is pressed at a temperature below the melting point of the polymer and the polymer particles do not therefore fuse and are merely deformed, while the metallic particles are distributed on the surface of polymer grains, forming a separate continuous two-dimensional phase. Such a structure is illustrated in Fig. 2*B* (see structure 4). The dependence of the resistivity ρ_v on the content of the metal is illustrated schematically in Fig. 8. Evidently, up to a concentration c_A, the conductivity varies little—a continuous filler phase is not formed. From the instant of the formation of the continuous phase, the resistivity falls sharply but, at a concentration in excess of c_B, the decrease slows down.

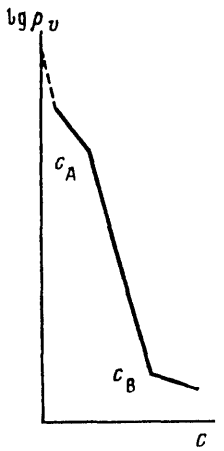


Figure 8. Schematic illustration of the dependence of ρ_v for the polyethylene–nickel composite on the nickel concentration[10].

The degree of filling c_B corresponds to the case where a close-packed layer of metallic particles is formed on the surface of each grain, i.e. N_p polymer spheres with a radius R_p are coated by N_M metallic spheres with a radius R_M:

$$N_p \times 4\pi R_p^2 = N_M\, \pi R_M^2 \Phi\,,$$

where Φ is a coefficient which depends on the type of packing.

When $c > c_A$, the layers of filler particles are built up and the conductivity increases slightly, approaching the conductivity of the filler. The quantity c_B is calculated from the formula

$$c_B = \frac{\frac{4}{3}\pi N_M R_M^3}{\frac{4}{3}\pi N_M R_M^3 + \frac{4}{3}\pi N_p R_p^3} = \frac{1}{1 + \frac{\Phi}{4}\cdot\frac{R_p}{R_M}}\,.$$

When $c_A = \frac{1}{2}(P_c c_B)$, the two-dimensional metallic phase is a monolayer (P_c is the packing coefficient).

The packing coefficients Φ and P_c for different types of lattice are as follows in the case of a structured composite:

	Hexagonal lattice	Cubic lattice	Trigonal lattice
Φ	1.11	1.27	1.375
P_c	1/3	1/2	2/3

It is noteworthy that the transition c_A for structured composites corresponds to much lower degrees of filling than for a statistical mixture. Comparison of the experimental and theoretical results for the dependence of the percolation threshholds c_A on the ratio of the particle radii R_P/R_M for a structured composite is indicated below:

R_P/R_M	30	16	12	10	7.5
c_A (theor.)	2.9	5.1	6.5	7.5	9
c_A (exp.)	6	6	11	13	14

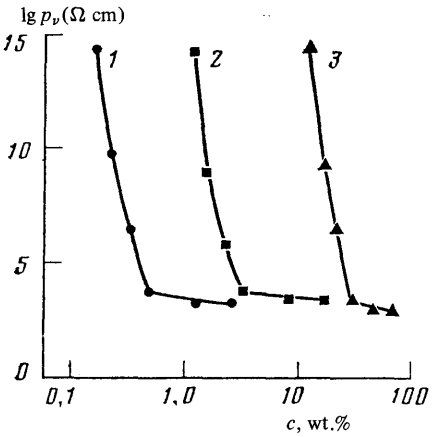


Figure 9. Dependence of ρ_v on the concentration c of the Ketjenblack EC carbon black for different methods of preparation of polymeric composites based on polystyrene[46] (see text).

IV. METHODS FOR THE PREPARATION OF COMPOSITES AND THEIR ELECTRICAL CONDUCTIVITIES

The examples quoted above show that the method of preparation of the composites is important for the attainment of a specific electrical conductivity. Shear forces, which should be maximum in the stage where the composite is prepared and minimum in the stage involving the formation of articles from it, play an important role here. The temperature and mixing time of the components, the order in which they are introduced, the presence of substances altering the viscosity of the mixture, etc. have a significant influence on the conductivities of composites[3,10].

This can be illustrated by several further examples. The dependence of ρ_V for the polystyrene–Ketjenblack EC carbon black composites on the carbon black concentration has been investigated[46] for different methods of preparation of the composite. Three mixing procedures were used: (1) pressing of a mixture of carbon black with the powdered polymer; (2) mixing of the carbon black with a solution of the polymer in toluene in a ball mill followed by the casting of a film with slow evaporation of the solvent, comminution of the film, and pressing; (3) calendering of a mixture of carbon black and the polymer between heated rollers, grinding of the product, and pressing. Fig. 9 shows that the critical concentration of the carbon black c_B for the first method is only 0.5%; evidently this case is close to the model described above with $R_P/R_M \gg 1$. For the third method, c_B increases to 25%. In this procedure it is apparently more difficult to retain the conducting carbon black structure.

Certain carbon black-filled compositions are used to prepare articles by extrusion. Thus the RCA Company (USA) uses the propylene–vinyl chloride copolymer–Ketjenblack EC carbon black composition to manufacture video discs for the recording of television programmes[47]. Fig. 10 illustrates the dependence of ρ_V for such a composition (measured using d.c. and a.c.) on the number of extrusions n. Evidently the optimum conducting structure is formed when $n = 2$; after a larger number of extrusions, the structure breaks down.

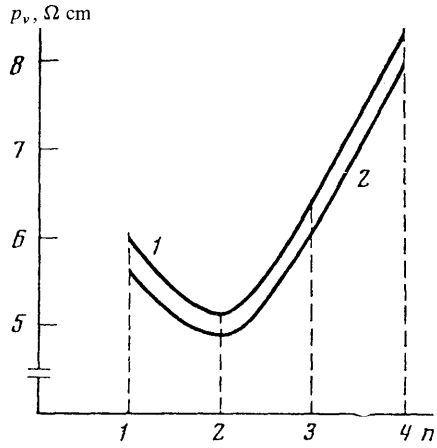


Figure 10. Dependence of ρ_V for the composition comprising the propylene–vinyl chloride copolymer and the Ketjenblack EC carbon black on the number of extrusions[47]: *1*) $f = 0$; *2*) $f = 9.5$ MHz.

Surfactants are used to improve the dispersion of the carbon black in polymers. Binary fillers are also employed. Thus, when 110 parts of kaolin are added to the ED-16 epoxide resin containing 10 parts of graphite per 100 parts of the resin, the ρ_V of the composition diminishes by six orders of magnitude (from 10^9 to 10^3 Ω m). In the absence of kaolin, the same value of ρ_V can be obtained only after the introduction of 50 parts of graphite. The effect of kaolin is explained by the fact that it promotes a rigid fixation of the electrically conducting structures which determine the stability of the electrical properties of the filled material[48,49].

In the preparation of electrically conducting films from pyrolysed polymers on the surfaces of inert fillers (kaolin, talc, etc.), there is a possibility of obtaining compositions based on these fillers and polyethylene and with a low content of the conducting component for which ρ_V is smaller by 5–11 orders of magnitude than the value for the initial polymer. The content of the conducting component (pyrolysed polyacrylonitrile) is then only 1–3%.[50]

A new method for the preparation of filled polymeric materials—the method of polymerisation filling—has been developed recently[18,19,41]. In this procedure the catalyst is deposited on the surface of the filler where polymerisation takes place. The resulting material can then be converted into articles by the usual methods. Polypropylene–graphite compositions have been obtained by this procedure; for comparison, the same compositions were prepared by extrusion[20] and it was found that the films of the polymerisation filled polymers have a much smaller resistivity ρ_V (by 2–8 orders of magnitude) than the extruded films with the same graphite content. A specific instance of the interaction of the filler and polymer apparently occurs here, which leads to the cleavage of the graphite along its planes and its more effective dispersion in the polymer. The details of this process are in the research stage, but many results support this hypothesis.

In conclusion one should mention organic polymers which are as it were "intrinsic" composites. Their electrical, optical, and certain other characteristics indicate the presence of conducting regions in a non-conducting matrix of the same composition. Among such systems, mention may be made of pyrolysed polymers (polyacrylonitrile, polyimides[38]) as well as doped polyacetylene[51,52].

V. APPLICATIONS OF CONDUCTING COMPOSITES

The range of applications of conducting composites is extremely wide. New possibilities for their employment are nowadays discussed in the literature, in particular in meeting the requirements of radioelectronics for the creation of low-noise and high-frequency cables and shields over a wide frequency range, in components of radioelectronic apparatus, in highly efficient solar batteries, and in other fields[7,53,54].

The employment of capacitive transducers for the decoding of information from video discs require the creation of compositions with a high degree of homogeneity in the distribution of the filler in the matrix and with reproducible properties. The Ketjenblack EC composition[47] mentioned above satisfies such requirements.

Among other potential applications of such composites are those in the chemical industry and non-ferrous metallurgy where there is a need to replace the scarce lead and leaded steel employed in the manufacture of electrofilters[55,56]. Composites with a level of conductivity not less than 10^{-6} Ω^{-1} cm^{-1} are widely used as antistatic materials[3].

A tendency has arisen in recent years to employ highly filled composites incorporating carbon fibre fabrics in electrical engineering for the manufacture of collectors and contact rings in electrical machines[57,58]. The comparatively small-scale application of conducting composites in the preparation of tensotransducers, necessary both in the modelling and employment of constructional equipment, is no less important[59].

As already stated, the creation of highly conducting polymeric adhesives constitutes an urgent task, since hitherto they have been made from scarce noble metals (Au, Ag, etc.)[9].

Vigorous studies are being prosecuted nowadays in order to prepare conducting composites with the aid of new methods—polymerisation filling[20,60], electrochemical deposition of metals from salt solutions into a polymer solution[12,57], and high-speed thermal decomposition of solutions of the metal carbonyls, formates, and oxalates in polymers[14]. This factor gives rise to the hope for the creation of new composites with a set of new valuable properties[61,62].

* * *

One of the main difficulties in the study of the electrical conductivities of organic, including polymeric, materials is that they cannot be treated within the framework of classical ideas, for example, within the framework of the band model. A criterion of the applicability of this model is a current carrier mobility $\mu > 1$ cm^2 V^{-1} s^{-1}. For the majority of the electrically conducting polymers in composites, this condition is [not?] fulfilled: thus $\mu \cong 10^{-4}$ cm^2 V^{-1} s^{-1} for carbon black-filled raw rubbers[34]. Another factor which hinders the understanding of the mechanism of electrical conduction in composites (for example, those based on polyolefins) is that the concentration of the intrinsic current carriers in polymers of this class is negligible. Thus the conducting properties of such composites are determined, firstly, by the material of the filler and secondly, by the properties of the filler–polymer interface. Since the electrical conductivity is ensured by carriers injected from the filler, it is necessary to create interphase injecting contacts (ohmic contacts are suitable in some cases).

Thus, in order to understand the mechanism of the electrical conduction in polymeric composites, it is necessary to take into account the influence of a number of factors, which include the properties of the filler and the polymer, the distribution of the filler in the matrix, and the type of contacts between the polymer and the filler particles. None of the models existing at the present time takes into account all these factors and reflect only one of the characteristic aspects of the phenomenon. In view of the increasing use of such composites, it is therefore necessary to carry out combined theoretical and experimental studies on the lines discussed above.

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