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Review
Models proposed to explain the electrical conductivity of mixtures made of conductive and insulating materials

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The electrical conductivity of mixtures of conductive and insulating materials is reviewed. In general, the conductivity of such mixtures increases drastically at a certain concentration of the conductive component, the so-called percolation concentration. Among the parameters influencing the percolation concentration, the filler distribution, filler shape, filler/matrix interactions and the processing technique are the most important ones. On the basis of these parameters, different models have been proposed aimed at the prediction of the conductivity or the percolation concentration. It will be shown here that statistical, geometric or thermodynamic models explain the conductivity behaviour of specific mixtures on the basis of insufficient assumptions. However, the conductivity seems to be predictable with the help of structure-oriented models.

1. Introduction

Although every engineering material has a field of application in its pure form, many examples exist in which pure components are mixed to give new materials with tailored properties. One class of those materials is constituted of mixtures of either electrical conducting and insulating particles or electrical conductive particles incorporated in an insulating matrix. These mixtures have gained a large area of application, e.g. for electromagnetic shielding and antistatic purposes.

The main question concerning these mixtures, is how the conductivity changes with the content of the conductive filler. Fig. 1 shows the general course of the conductivity as a function of the filler content. The conductivity is plotted on a logarithmic scale in Fig. 1 to emphasize the drastic increase in the conductivity at a certain filler concentration.

The usual explanation for such conductivity/filler concentration curves is as follows. In the region of low filler concentrations the filler, incorporated in the form of small particles with a different shape, is distributed homogeneously in the volume of the insulating host. There are no contacts between adjacent filler particles. With rising filler concentration, agglomerates of the filler particles begin to form. In these agglomerates the filler particles are in contact with each other. At a certain filler content, the growing agglomerates reach a size which makes it possible for them to touch each other; a compact one-, two- or three-dimensional network of the conducting phase within the insulating one is formed. As a consequence of the first appearence of the network, the conductivity of the mixture shows a drastic increase to the high value of the conductive network. After the first conductive network is formed, the conductivity of the mixtures again shows a slow increase with growing filler content. This can be rationalized with a slightly improved quality of the conductive network.

More important for the production of optimized conductive mixtures, i.e. compounds showing the jump in the conductivity at the smallest amount of the conductive filler possible for a certain mixture, are the physical and chemical factors determining the appearence of the conductive networks.

To understand the network formation on a scientific level, many so-called percolation models and equations have appeared in the literature. This review will present some of these models, with emphasis on the more prominent ones. In summary, there are still many open questions in connection with every proposed model or equation. The most promising models, from the engineer's point of view, are the structure-oriented ones which try to explain the conductivity on the basis of factors determined from the micro-level structure of the as-produced mixtures.

2. Statistical percolation models

Statistical percolation models [1–13] have occupied the majority of the literature about the electrical percolation phenomenon, although the classical percolation theory was not concerned with the electrical conductivity in binary mixtures. On the contrary, the classical theory dealt with the problem of the penetration of porous media by liquids [1]. In the meantime

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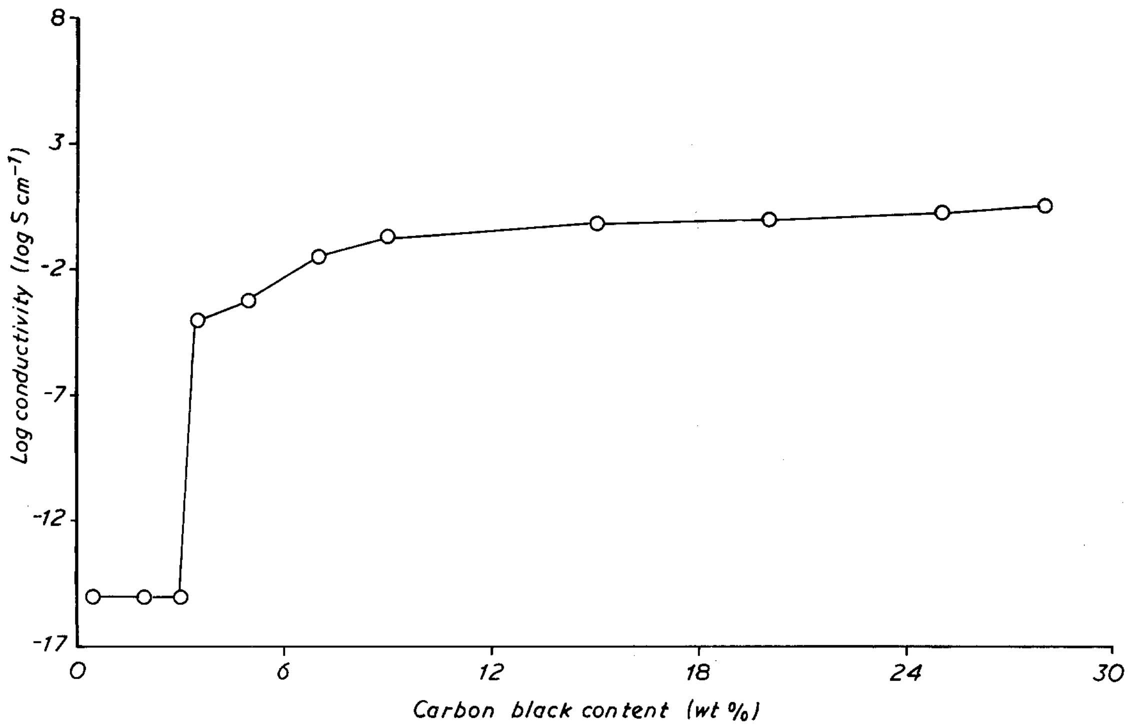


Figure 1 Conductivity of a binary mixture, made of an insulating matrix (polyethylene) and a conductive filler (carbon black); dependence of the conductivity of the mixture on the filler content.

TABLE I Fields of application for the ideas of the percolation theory after Zallen [1]

Phenomenon or system	Transition
Flow of liquid in a porous medium	Local/extended wetting
Spread of disease in a population	Containment/epidemic
Communication or resistor networks	Disconnected/connected
Conductor insulator composite materials	Insulator/metal
Composite superconductor–metal materials	Normal/superconducting
Discontinuous metal films	Insulator/metal
Stochastic star formation in spiral galaxies	Nonpropagation/propagation
Quarks in nuclear matter	Confinement/nonconfinement
Thin helium films on surfaces	Normal/superfluid
Metal–atom dispersion in insulators	Insulator/metal
Dilute magnets	Para/ferromagnetic
Polymer gelation, vulcanization	Liquid/gel
Glass transition	Liquid/glass
Mobility edge in amorphous semiconductors	Localized/extended states
Variable-range hopping in amorphous semiconductors	Resistor–network analogue

these basic percolation considerations were used to explain many other physical and chemical problems (see Table I).

The breakthrough of the statistical percolation considerations in the area of conductive binary mixtures was made in the early 1970s, especially stimulated by the work of Kirkpatrick and Zallen [1, 2].

2.1. The classical statistical percolation models

2.1.1. The model of Kirkpatrick and Zallen

To obtain an estimate of the percolation concentrations, according to the considerations of Kirkpatrick and Zallen, it is usual to start with finite regular arrays of points and bonds (between the points). Typical examples for such arrays are the simple cubic lattice (s c), the face-centred cubic lattice (f c c) and the body-centred cubic lattice (b c c). Then, by computer simulation, it is possible to determine the fraction of existing points or bonds according to various statistical laws. The next step is to determine the part of existing points or bonds, incorporated in a big cluster (within the array of points or bonds). The points or bonds in this cluster are in contact with each other. It is easy to realize that the percolation point (which depends on the considered dimensionality) in these models is reached when the cluster first spans the relevant boundaries of the underlying array.

However, the calculated percolation concentrations of points p_c^{site} or bonds, p_c^{bond} are not equal to the volumetric percolation concentrations normally found in experimental studies. Furthermore, to obtain equations for the conductivity/filler concentration curves, it is necessary to correlate the values of p_c^{site} or p_c^{bond} with the specific electrical properties of the points or bonds.

It is far beyond the scope of this work to show the exact way to reach these aims, therefore only the results of the considerations are given. Equation 1 correlates the conductivity of real mixtures with the volume fraction of the conductive filler.

$$\sigma = \sigma_0(V - V_c)^s \qquad (1)$$

where σ is the conductivity of the mixture, σ_0 the conductivity of the filler particles, V the volume fraction of the filler, $V_c = p_c^{\text{site}}\text{v}$ the volume percolation concentration, s a quantity determining the power of the conductivity increase above V_c, and v the filling factor of the unit cell of a specific point arrangement.

According to the literature [1, 2], the values of V_c and s should be dimensional invariants, i.e. they only depend on the dimensions of the lattice (one- or two-dimensional, etc.). Table II gives values of the volume percolation concentration for different dimensions (last column). Kirkpatrick gave the following values for the exponent s:

s (bond percolation model) $= 1.6 \pm 0.1$
s (point percolation model) $= 1.5 \pm 0.1$.

Studies supporting Equation 1 and the underlying theoretical assumptions span a wide range of materials, including inorganic conductive mixtures [6], metal/polymer mixtures [7, 8] and, most of all, mixtures made of polymers and carbon black (CB) or intrinsically conductive polymers (ICP) [14–21].

2.1.2. The model of Janzen, Aharoni and Gurland

Janzen [3] derived his percolation equation on the basis of considerations, made by Aharoni [10] and Gurland [11]. The latter authors stressed the importance of the so-called "medium number of contacts ($\bar{m}$)" of adjacent particles. If this number takes the value $\bar{m} = 2$ in a real mixture, a one-dimensional (worm-like) conductive network should appear. Unfortunately, the experimental results of Aharoni and Gurland did not support their assumptions.

Bearing in mind the ideas of Aharoni and Gurland, and using the results of the percolation calculations of Kirkpatrick and Zallen (p_c^{bond} and the coordination number z; see Table II) Janzen emphasized the meaning of $\bar{m} = 1.5$ (three-dimensional; column 7, Table II) for the percolation process. Using this, his final percolation equation takes the form

$$V_c = \frac{1}{1 + 0.67\, z \rho \varepsilon} \qquad (2)$$

where V_c is the volume percolation concentration, z the coordination number (number of nearest neighbours) in a specific lattice, ρ the density of the filler particles, and ε the specific pore volume of the filler particles.

Janzen found the calculated percolation concentrations in agreement with experimental values for a number of metal/polymer and CB/polymer mixtures.

2.2. The model of Scarsbrick

Scarsbrick [12] proposed a statistical percolation model with no relation to the previous models. This model explains the conductivity of the mixtures, σ, on the basis of four factors:

(a) the specific conductivity of the filler particles, σ_c;

(b) the volume fraction of the conductive phase, V_f;

(c) the probability, p_n, of the development of an at least one-dimensional conductive network; this

TABLE II Percolation theory and the problem of the electrical conductivity in binary mixtures after Zallen [1]; percolation concentrations p_c^{bond}, p_c^{site}, $m = z^* p_c^{\text{bond}}$ and $V_c = \text{v}^* p_c^{\text{site}}$ for different dimensionalities of the underlying point array

Dimensionality d	Lattice or structure	p_c^{bond}	p_c^{site}	Coordination z	Filling factor v	zp_c^{bond}	$vp_c^{\text{site}} = V_c$
1	Chain	1	1	2	1	2	1
2	Triangular	0.3473	0.5000	6	0.9069	2.08	0.45
2	Square	0.5000	0.593	4	0.7854	2.00	0.47
2	Kagome	0.45	0.6527	4	0.6802	1.80	0.44
2	Honeycomb	0.6527	0.698	3	0.6046	1.96	0.42
						2.0 ± 0.2	0.45 ± 0.03
3	fcc	0.119	0.198	12	0.7405	1.43	0.147
3	bcc	0.179	0.245	8	0.6802	1.43	0.167
3	sc	0.247	0.311	6	0.5236	1.48	0.163
3	Diamond	0.388	0.428	4	0.3401	1.55	1.146
3	rcp		[0.27]^b		0.637 [0.6]^b		[0.16]^b
						1.5 ± 0.1	0.16 ± 0.02
4	sc	0.160	0.197	8	0.3084	1.3	0.061
4	fcc		0.098	24	0.6169		0.060
5	sc	0.118	0.141	10	0.1645	1.2	0.023
5	fcc		0.054	40	0.4653		0.025
6	sc	0.094	0.107	12	0.0807	1.1	0.009

quantity is given by Equation 3

$$p_n = V_f \, 1/V_f^{2/3} \tag{3}$$

and

(d) the surface fraction of the conductive phase at the sample electrode boundary, C^2.

The resulting equation has the form

$$\sigma = \sigma_c p_n C^2 \tag{4}$$

Fig. 2, taken from the work of Scarsbrick, shows a comparison of Equation 4 with experimental conductivity values for a silver paint system. It is evident from this figure, that the assumptions of Scarsbrick can account only for the conductivity behaviour above the percolation point. Therefore, it cannot be used to predict the volume percolation concentration.

2.3. The model of Bueche

Bueche [13] tried to explain the S-shaped conductivity curves of binary mixtures on the basis of the concept of polymer gelation, as proposed by Flory. The transfer of Flory's assumptions to conductive binary mixtures resulted in an equation for the resistivity of the mixtures.

$$\frac{\rho}{\rho_m} = \frac{\rho_f}{(1 - V_f)\,\rho_f + V_f\,\omega_g\,\rho_m} \tag{5}$$

where ρ is the resistivity of the mixture, ρ_m the resistivity of the insulating material, ρ_f the resistivity of the conductive material, V_f the volume fraction of the conductive phase in the mixture, ω_g the fraction of the conductive phase being incorporated in an infinite cluster; its value is determined by the subfactors f and α (in a rather complicated manner), α is the probability for the appearance of a contact between neighbouring particles, and f is the maximum number of contacts a particle can make with its neighbours.

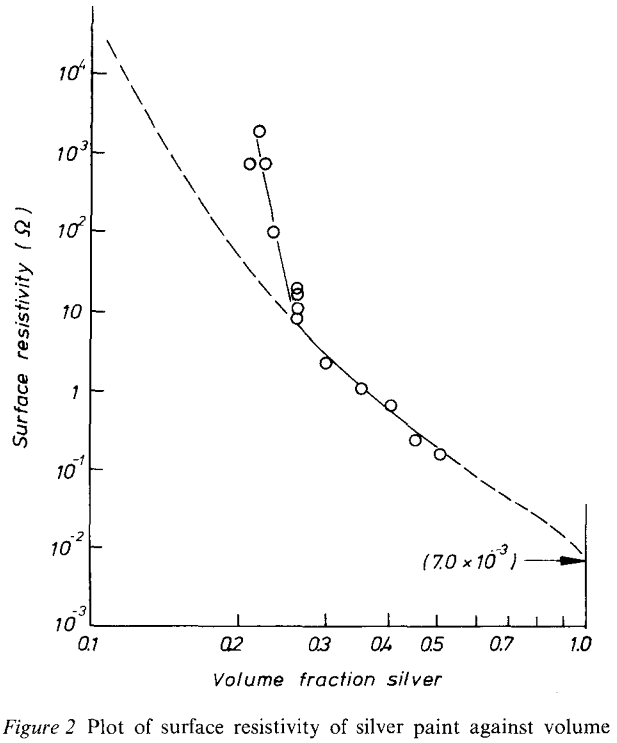


Figure 2 Plot of surface resistivity of silver paint against volume fraction of silver: (– – –) theoretical curve for random distribution according to the theory of Scarsbrick [12], (———) observed values.

Fig. 3 shows the course of the normalized specific resistivity of a hypothetical mixture as a function of the filler content and the maximum number of contacts. Obviously, Bueche's equation can account for different drastic jumps in the conductivity, if the right number f is choosen.

The comparison of the main parameters of Bueche's equation with the most important ones, according to the model of Kirkpatrick and Zallen, suggests some parallels between the two models. Indeed, as discussed by Zallen [1] in some detail, the theory of Flory is a rough estimate of the polymer gelation, being considered as a classical statistical percolation problem. Therefore, the parallels between both models are not surprising.

3. Thermodynamic percolation models

Sumita and co-workers [22–25] and Wessling and co-workers [26–36] proposed thermodynamic percolation models for CB/polymer and ICP/polymer mixtures, because of the serious disagreements between the predictions of the statistical percolation models and the experimentally found percolation concentrations. Both models emphasize the importance of the interfacial interactions at the boundary between the individual filler particles and the polymeric host for the network formation. As a consequence, these models interpret the percolation phenomenon as a phase separation process.

3.1. The model of Sumita and co-workers

The model of Sumita and co-workers [22–25] relies on the principles of chemical thermodynamics. The main assumption of these authors is concerned with the overall interfacial free energies in the mixtures. It is assumed that the network formation begins at a certain mixture-independent overall interfacial free energy, g^*. This concept was adopted from the theory of the glass transition in polymers; the glass transition occurs at a universal polymer-independent value of the free volume within the polymer.

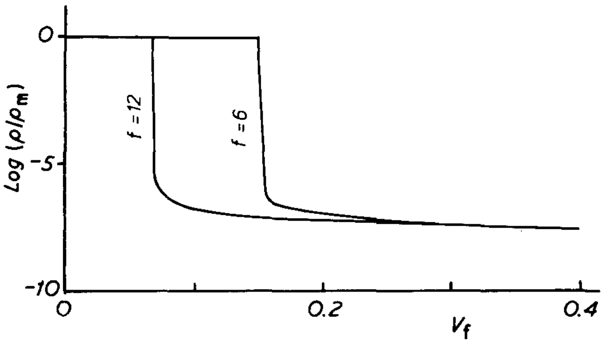


Figure 3 Relation between the normalized resistivity and the volume fraction of the conductive particles according to the theory of Bueche [13]; the resistivity drops at a critical volume fraction.

Bearing in mind the g^*-concept, it is possible to explain the different volume percolation concentrations with different specific values of the interfacial free energies (Fig. 4). If the specific interfacial free energy has a low value, the volume percolation concentration (or the point, characteristic for the onset of the phase separation of the two phases) will be high. On the other hand, a greater value of specific free energy is accompanied by a lower volume percolation concentration.

Other parameters important to the percolation process are the viscosity of the polymer melt and the diameter of the CB particles. According to the results of their experimental studies Sumita and co-workers say that the percolation process is easier to accomplish with smaller CB particles. The viscosity of the polymers has an inhibiting influence on the "equilibrium" phase separation process: the higher the value of the melt viscosity, the longer it will take until the mixtures reach their equilibrium structures. Therefore, it might be that the experimental investigations on a special mixture yield a higher volume percolation concentration than the "true" equilibrium value.

The final equation of Sumita and co-workers has the form

$$\frac{1 - V_c}{V_c} = \frac{3}{g^* R}\{[(\gamma_c + \gamma_p - 2(\gamma_p \gamma_c)^{\frac{1}{2}}] \times (1 - e^{-ct/\eta}) + K_0 e^{-ct/\eta}\} \qquad (6)$$

where V_c is the volume percolation concentration, γ_c the surface tension of the CB particles, γ_p the surface tension of the polymer, g^* the universal interfacial free energy, responsible for the onset of the network formation, K_0 the interfacial free energy at time $t = 0$ (start of the mixing process), its value has to be determined experimentally, c a constant of speed for the evolution of the universal interfacial free energy, its value has to be determined experimentally, t the time of mixing the two components, η the viscosity of the polymer matrix during the mixing process, and R the diameter of the CB particles. The experimental results of Sumita and co-workers are in agreement with Equation 6.

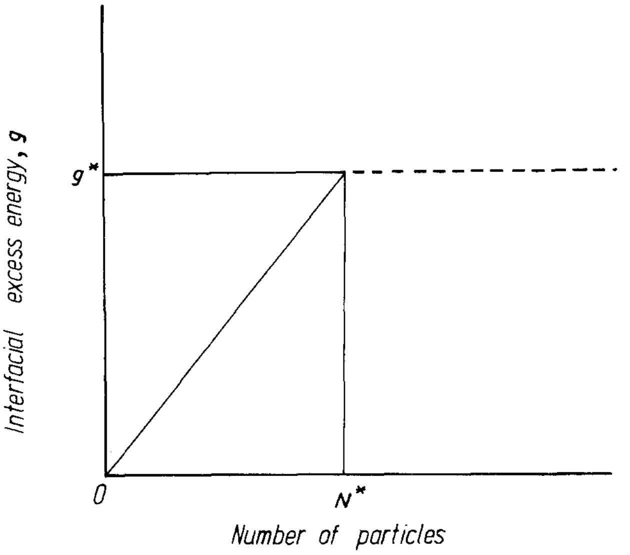


Figure 4 Schematic representation of the assumed relation between the interfacial excess energy and the number of carbon black particles after Miyasaka *et al.* [25]; for $N \ll N^*$ the slope is constant depending on the exact interaction parameters, and it becomes zero for $N \gg N^*$, because the phase separation process takes place in the system.

3.2. The model of Wessling and co-workers

The model of Wessling and co-workers [26–36] is called "the dynamic boundary model". Basically, this thermodynamic percolation model is identical to that of Sumita and co-workers. However, as Wessling stated [29], his model involves two important hypotheses, not considered in any other percolation model. First, his model explains the percolation process on the basis of the non-equilibrium thermodynamics. Secondly, the assumptions being involved, offer the opportunity to explain the percolation process vividly.

To understand the model of Wessling it is helpful to know the main assumptions of it:

(a) the CB particles are spherical;

(b) below the percolation concentration all individual CB particles are fully covered by the surrounding polymer host;

(c) the distribution of the CB particles in the polymer matrices is non-homogeneous, i.e. the particles are somewhat concentrated in flat agglomerates;

(d) each CB particles has a thin layer of adsorbed polymer; the thickness of the layer is determined by the kind of polymer. The structural and energetic properties of the CB particle surfaces have no influence on this thickness;

(e) the kinetics of the adsorption process (the formation of the adsorption layers) are equal to those appearing in the adsorption processes with low-viscosity fluids;

(f) the adsorbed layers have unusual properties. The interactions between the CB particle surfaces and the polymeric hosts are so strong that it is impossible to destroy the layers during any processing step. Although the original polymer is in the liquid state, the polymer consumed in the layers is solid. The physical properties of the layers differ from the properties of the original polymer, i.e. a layer consists of a glassy, brittle material, having a low flexibility and being nearly incompressible.

Using these assumptions, Wessling explains the percolation process as follows (see Fig. 5). Just below the percolation point, all CB particles, including their adsorption layers, are distributed in the remaining polymer volume. They are arranged in flat agglomerates. The agglomerates are distributed unevenly in the polymeric host. If one now mixes more CB particles into the liquid polymer, the spaces of the flat agglomerates will become overfilled with CB particles. Therefore, as a consequence of compression forces, the adsorption layers of some of the CB particles have to be destroyed partially. These particles migrate towards each other until they are in electrical contact. This stage is reached, when the distance between the particle surfaces is equal or less than 10 nm [37]. The polymer of the destroyed regions of the adsorption

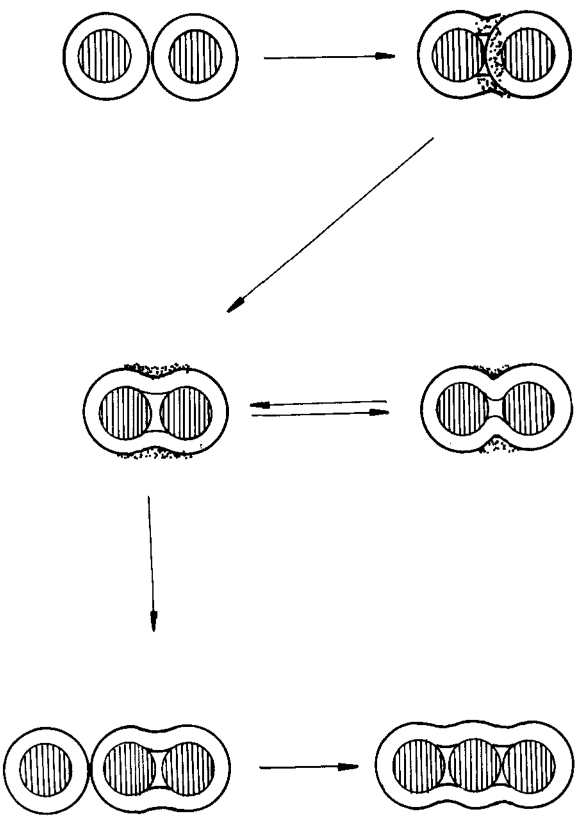


Figure 5 Formation of a conductive network in polymer/carbon black polymer/ICP mixtures according to the assumptions of Wessling [30].

layers is transferred into non-layer polymer. CB particles, with an intact adsorption layer, and about to contact the "conductive particle arrangements" have to approach such agglomerates from the outer sides for energetic reasons.

After many of the original CB particles migrated towards each other, the flat agglomerates are transformed into two-dimensional conductive islands.

The generation of a three-dimensional conductive network should proceed as follows. First, the two-dimensional conductive islands are still separated from each other. They also wear adsorption layers. But the interfacial energies at the CB particles and adsorption polymer/polymer boundaries cause a phase separation process. This separation process leads to the three-dimensional network.

The percolation equation, resulting from the considerations of Wessling and co-workers, aims at the calculation of the volume percolation concentration and has the form

$$V_c = \frac{0.64(1-c)\phi_0}{\phi_e}\left[\frac{x}{(\gamma_c^{1/2}+\gamma_p^{1/2})^2}+y\right] \quad (7)$$

where V_c is the volume percolation concentration, γ_c the surface tension of the CB and ICP particles, respectively, γ_p the surface tension of the polymer, $1 - C$ the amorphous part (by volume) of the polymer matrix at room temperature, x (medium value $\bar{x} = 0.451$) a quantity, dependent on the molecular weight of the polymer; as Wessling discussed in a further paper [29], this quantity bears the non-equilibrium character of his theory, y a quantity with an unknown basis (until now), and ϕ, ϕ_0 the volume factor to recognize the appearence of the adsorption layers on each CB or ICP particle, respectively; $1 \leq \phi_e/\phi_0 \leq \infty$.

With the aid of Equation 7, using surface tensions γ_c and γ_p, estimated at room temperature, Wessling calculated the volume percolation concentrations for mixture, produced at temperatures > 100 °C and under drastic shear conditions. Under these conditions, Wessling could predict the experimentally found percolation concentrations exactly.

4. Geometrical percolation models

This class of percolation model was proposed to explain the percolation phenomenon in different dry-premixed and subsequently sintered mixtures of conductive and insulating powders. Slightly different models were proposed by Slupkowski [38], Rajagopal and Satyam [39], Malliaris and Turner [40] and Bhattacharya and Chaklader [41]. All these models assume that during the sintering process the insulating powder particles are deformed into more or less regular cubic particles and the conductive powder particles are arranged in a more or less regular manner on the surfaces of these superparticles. The quantitative considerations involve, as the main parameters, either the particle diameters of the non-sintered powder particles or the edge length of the sintered insulating superparticles and the diameter of the conductive particles.

4.1. The model of Slupkowski

The considerations of Slupkowski [38] were based on the dry-premixed mixtures and included the diameters of the insulating and conducting particles as the main influence factors. Fig. 6 shows the arrangement of the conductive particles on the surfaces of the insulating ones according to the assumptions of Slupkowski.

Slupkowski's considerations resulted in the equation

$$\sigma = 2\pi\sigma_f \frac{d([x]+P)}{D\ln\{1+1/(([x]+1)\alpha)\}} \quad (8)$$

where σ is the conductivity of the mixture, σ_f the conductivity of the conductive powder, D the diameter

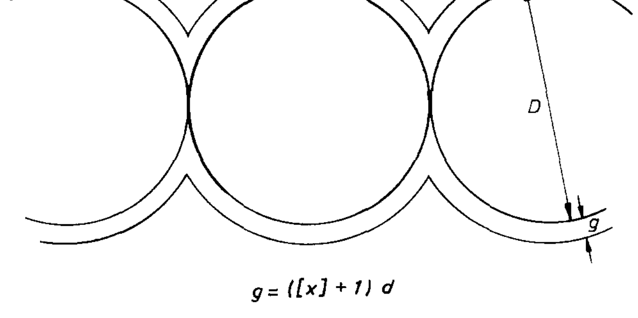


Figure 6 Model of adjoining insulating particles surrounded by a conducting layer according to Slupkowski [38].

of the insulating powder particles, d the diameter of the conductive particles, P the probability for the occurrence of a network, only consisting of conductive particles; its value depends on the statistical laws, used for the determination

$$[x] = \left[\left(\frac{1}{1-V_f}\right)^{1/3} - 1\right]\frac{D}{2d} \tag{9}$$

which is the number of totally filled sublayers of conductive particles, and V_f is the volume fraction of the conductive powder.

Fig. 7 shows that Slupkowski's equation can, in principle, account for the variation of the percolation concentration if the ratio of the particle diameters is changed.

4.2. The model of Rajagopal and Satyam

The considerations of Rajagopal and Satyam [39] are valid for a wax/graphite system. For the derivation of their conductivity equation they substituted the real material structure with a hypothetical one. In this model structure, the wax particles consist of cubic grains of edge length D. The graphite particles, being slightly deformed, cover the surfaces of the wax particles and have the diameter d. Fig. 8 shows the elemental cell of the hypothetical structure.

The final equation of Rajagopal and Satyam has the form

$$\sigma = \sigma_f \frac{2r(V_f 3D - 4d)(3D - 2d)}{D^2 d} \tag{10}$$

where σ is the conductivity of the mixture, σ_f the conductivity of the conductive particles, D and d, are already defined in the text, V_f the volume fraction of the conductive powder, and r the radius of the contact area between adjacent conductive particles.

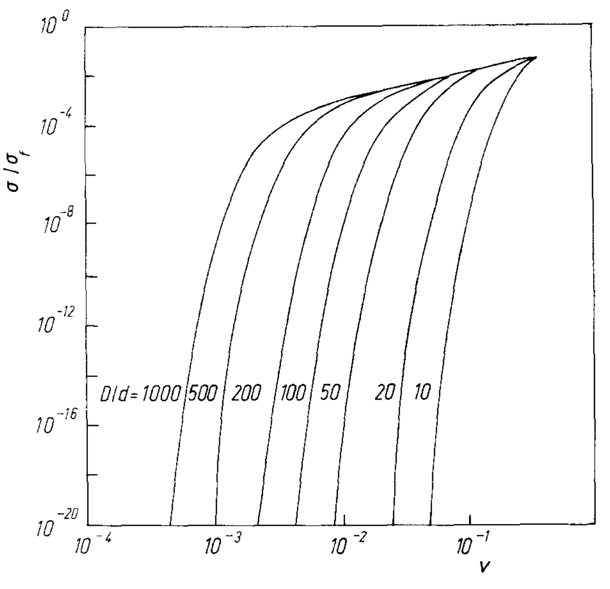


Figure 7 Dependence of the relative specific conductance on the volume fraction, v, of the conducting component for various ratios of insulating and conducting particle diameters according to Slupkowski [38].

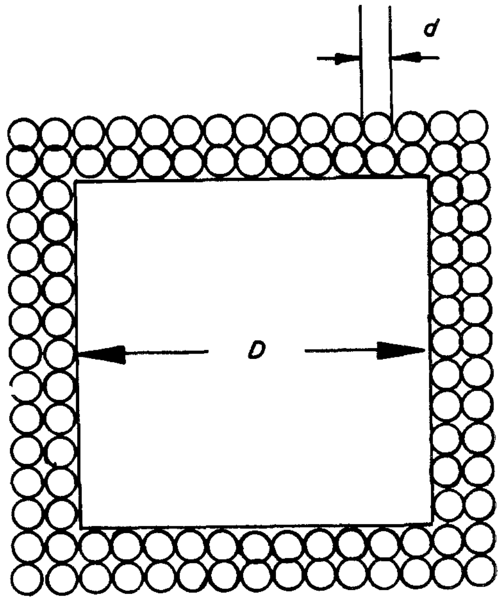


Figure 8 Cross-section of the elemental cell of a composite material according to Rajagopal and Satyam [39].

4.3. The model of Malliaris and Turner

The model of Malliaris and Turner [40] is the most prominent geometrical percolation model. As in the foregoing model of Slupkowski and the following one of Bhattacharya and Chaklader, the considerations of these authors are based on the dry-premixed, non-sintered structures of the mixtures. Malliaris and Turner derived two equations for the volume percolation concentration. The first one applies to the volume concentration, V_A, characteristic of the onset of the network formation. The second equation allows the calculation of the volume concentration, V_B, characteristic of the end of the drastic increase of the conductivity.

$$V_B = 100\left[\frac{1}{1+\left(\frac{\theta D}{4 d}\right)}\right] \tag{11a}$$

$$V_A = 0.5\, p_c V_B \tag{11b}$$

where V_A, and V_B are defined in the text, θ is a quantity to estimate the arrangement of the conductive particles on the surfaces of the insulating ones; the following values are given: hexagonal arrangement $\theta = 1.11$; cubic arrangement $\theta = 1.27$; triangular arrangement $\theta = 1.375$, D is the diameter of the insulating powder particles, d the diameter of the conductive powder particles, and P_c the first non-zero probability for the occurrence of infinitely long bands of conductive particles on the surfaces of the insulating particles, the following values are given: hexagonal array: $P_c = 1/3$; cubic array: $P_c = 1/2$; triangular array $P_c = 2/3$.

Comparison of experimentally determined percolation values with predicted ones, according to Equation 11a and b, showed Malliaris and Turner that their assumptions were insufficient to predict the percolation concentrations in conductive binary mixtures.

4.4. The model of Bhattacharya and Chaklader

Bhattacharya and Chaklader stated [41] that their percolation considerations are an optimization of the model proposed by Malliaris, Turner and their co-workers earlier. Therefore, the equations of Bhattacharya and Chaklader also deal with the volume percolation concentrations V_A and V_B.

$$V_B = \frac{2.99\, d/D}{1 + (2.99\, d/D)} \qquad (12a)$$

$$V_A = 0.5 V_B \qquad (12b)$$

where the parameters have the same meanings as those in Equation 11a and b. Although the predictions for the percolation concentrations according to Equation 12a and b gave better estimates than Equation 11a and b, the disagreement is still typically ± 15%–20% (with respect to the experimental value).

5. Structure-oriented percolation models

In different scientific groups around the world, it is fully accepted that a certain reproducible percolation concentration can only be found when the conductive mixtures are prepared via the compression moulding route. This preparation technique is one (of a few) ensuring the lack of any inhomogeneity in the distribution of the conductive phase. Furthermore, in the case of a certain processing method, differences in the exact route of preparing the mixtures give rise to different percolation concentrations or conductivities [29, 42].

Recognizing these problems, Yoshida [43], Nielsen [44], McCullough [45, 46] and Ondracek and co-workers [47–51] proposed conductivity models on the basis of parameters, which have to be determined from the micro-level structure of the mixtures after the final processing step. It is obvious that a detailed substitution of the real material structure by a theoretical model structure is needed for the determination of such parameters. Furthermore, it is a fact that the build up of a theoretical substitution structure requires a large computer and a structure-analysis plant.

5.1. The model of Yoshida

Yoshida [43] considered the percolation process of mixtures, equal to those discussed in Section 4. A further precondition of his work is that the mixtures have to be homogeneous. The structures of such mixtures can be substituted by two effective spherical elements. The one consists of a conductive core with an insulating shell, the other has a reverse structure (Fig. 9).

The details of these two substitution elements are very freely eligible. The only parameters to be determined exactly, are the core volume fractions, $\gamma_{A,B}$, of the two elements. These volume fractions depend on two so-called structural cross-over concentrations, α_1 and α_2. The values of α_1 and α_2 are always found in the range [0, 1] and α_1 is always smaller than α_2 [43].

With the aid of:

(a) the structural crossover concentrations $\alpha_{1,2}$;

(b) the core volume of the substitution elements $\gamma_{A,B}$;

(c) the volume fractions of the insulating and conductive powders $f_{a,b}$;

(d) the volume fractions of the substitution elements $F_{A,B}$; and

(e) the specific conductivities of the two powders $\sigma_{A,B}$; the conductivity of the mixture can be assessed using Equation 13a

$$\frac{1}{3\sigma} = \left[\frac{\sigma_A + 2\sigma_B + \gamma_A(\sigma_B - \sigma_A)}{(2\sigma + \sigma_B)(\sigma_A + 2\sigma_B) + 2\gamma_A(\sigma_B - \sigma)(\sigma_A - \sigma_B)}\right] F_A + \left[\frac{\sigma_B + 2\sigma_A + \gamma_B(\sigma_A - \sigma_B)}{(2\sigma + \sigma_A)(\sigma_B + 2\sigma_A) + 2\gamma_B(\sigma_A - \sigma)(\sigma_B - \sigma_A)}\right] F_B \qquad (13a)$$

with

$$F_A = \frac{\gamma_B - f_B}{\gamma_A + \gamma_B - 1} \qquad (13b)$$

and

$$F_B = \frac{\gamma_A - f_A}{\gamma_A + \gamma_B - 1} \qquad (13c)$$

The determination of $\gamma_{A,B}$ as a function of the parameters $\alpha_{1,2}$ and the determination of $\alpha_{1,2}$ themselves, is described by Yoshida [43].

A comparison between experimental results and the predictions, according to Equation 13a, gives a good correlation as is seen in Fig. 10.

5.2. The models of Nielsen, McCullough and Ondracek

Nielsen [52], McCullough [45, 46] and Ondracek [47–51] made a proposal to explain the electrical conductivity in binary mixtures in the context of the general transport properties in materials. The general class of transport properties includes the electrical conductivity, the thermal conductivity, the dielectric and magnetic properties and the permeablity properties.

5.2.1. The model of Nielsen

Nielsen proposed a model for the conductivity of metal/polymer mixtures [52]. The most important parameters for calculating the conductivity of such mixtures are the length-to-diameter ratio of the conductive filler and the coordination number of the filler in the mixture. The final equation of Nielsen's consid-

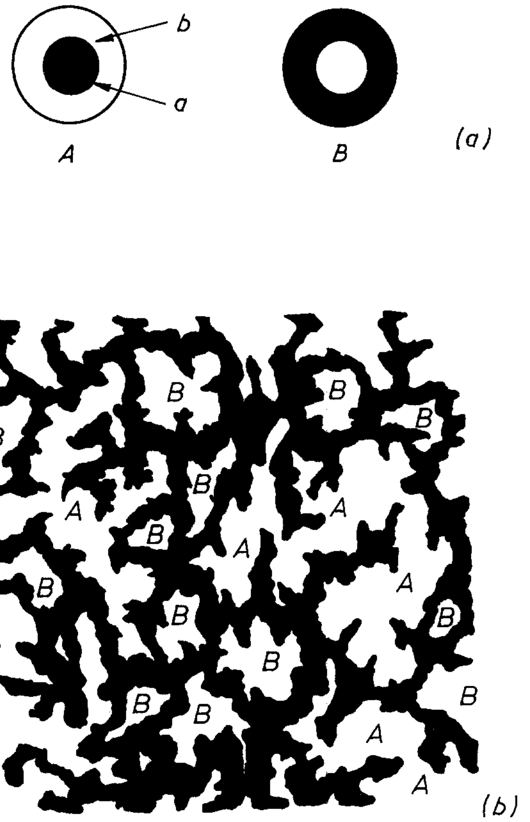


Figure 9 Substitution elements for the real materials structure according to the conductivity theory of Yoshida [43]. (a) Complex cells of Types A and B as structural elements. (b) Specification of the cells on the percolation cluster (black).

erations has the form

$$\sigma_c = \sigma_{poly} \frac{1 + AB\phi_f}{1 - B\psi\phi_f} \tag{14a}$$

with

$$B = \frac{\sigma_f/(\sigma_{poly} - 1)}{\sigma_f/(\sigma_{poly} + A)} \tag{14b}$$

$$\psi \approx 1 + \left(\frac{1 - P_f}{P_f^2}\right) P_f \tag{14c}$$

$$A = f(L/D;\ \text{packing of the conducting particles}) \tag{14d}$$

σ_c is the conductivity of the mixture, σ_{poly} the conductivity of the polymer, σ_f the conductivity of the metal, ϕ_f the volume fraction of the filler, P_f the coordination number of the metal within the polymer, L the length (medium value) of an individual filler particle, and D the diameter (medium value) of an individual filler particle.

It is worth mentioning that Nielsen proposed Equation 14 also to explain the modulus of metal/polymer mixtures [53].

Bradbury and Bigg [54] and Berger and McCullough [46] examined the applicability of Equation 14 in the case of aluminium/polymer composites. Their results contradict the applicability of Equation 14 for the explanation of the electrical conductivity behaviour of binary mixtures.

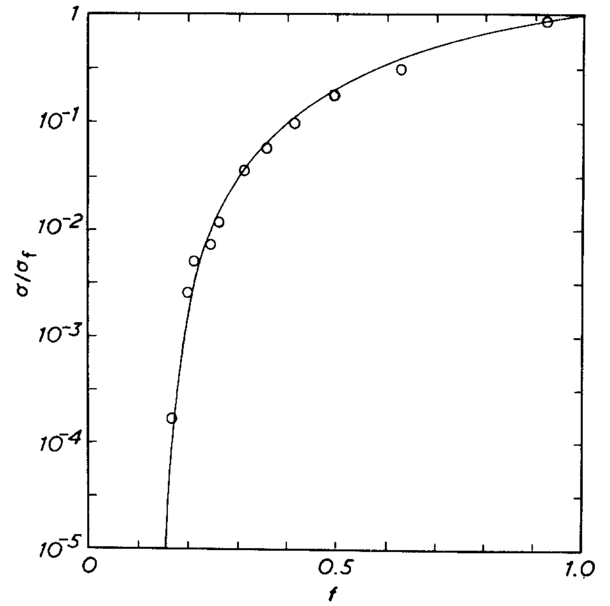


Figure 10 Plot of semi-logarithmic plotting of the normalized conductivity, σ (with respect to the intrinsic conductivity of the conductive filler, σ_f) against the volume fraction f, of the conductive filler according to Yoshida [43].

5.2.2. The model of McCullough

McCullough [45] proposed the use of a transport equation, once derived for the transport properties in homogeneous materials, for the explanation of the transport properties of binary mixtures with polymers. To adjust the equation to the growing conductive networks in the mixtures, McCullough defined a so-called chain length factor, λ_i. The subscript i can adopt the values $i = 1, 2, 3$ and describes the directions of a cartesian coordination system. The λ_i values have to be determined by quantitative analysis of the structure of the mixtures. The exact procedure for doing this is described in the work of Berger and McCullough [46].

With the aid of the three λ_i values, McCullough developed an equation for the conductivity of the mixtures, suitable to account for the anisotropy of the conductivity of the mixtures. The equation has the form

$$\sigma_i = v_{poly}\sigma_{poly} + v_f\sigma_f - \frac{\lambda_i v_{poly} v_f (\sigma_f - \sigma_{poly})^2}{V_{poly,i}\sigma_{poly} + V_{f,i}\sigma_f} \tag{15a}$$

where σ_i is the conductivity of the mixture in direction i, σ_{poly} the conductivity of the pure polymer, σ_f the conductivity of the filler particles, v_{poly} the volume fraction of the polymer, v_f the volume fraction of the filler particles,

$$V_{poly,i} = (1 - \lambda_i) \cdot v_{poly} + \lambda_i \cdot v_f \tag{15b}$$

$$V_{f,i} = \lambda_i \cdot v_{poly} + (1 - \lambda_i) \cdot v_f \tag{15c}$$

and

$$V_{poly,i} + V_{f,i} = 1 \tag{15d}$$

For the case of a homogeneous mixture (compression moulded plates), Equation 15a can be reduced to Equation 16a.

$$\frac{1}{\sigma} = \frac{1}{\sigma_{\text{poly}}}\left\{\frac{v_{\text{poly}}^2(1 - [\lambda])}{V_{\text{poly}}}\right\} + \frac{1}{\sigma_f}\left\{\frac{v_{\text{poly}}^2 + [\lambda]\, v_{\text{poly}}(1 + V_{\text{poly}})}{V_{\text{poly}}}\right\} v_f \quad (16a)$$

where $[\lambda]$ is the spatial medium value of the λ_i values and

$$v_{\text{poly}} = v_{\text{poly}}(1 - [\lambda]) + [\lambda] v_f \quad (16b)$$

Berger and McCullough [46] found their predictions "in qualitatively good agreement with the experiment" for a polyester/aluminium system (see Fig. 11).

5.2.3. The model of Ondracek

The considerations of Ondracek and co-workers [47–51] are only valid for mixtures having a statistical structure and reaching their equilibrium states. If those preconditions are fulfilled, it is possible to understand the conductivity of the mixtures as a superposition of the conductivities of the pure components. To reach singular equations for interpenetrating structures and for mixtures with an embedded structure, respectively, it is necessary to substitute the real structures with model structures. The model structures involve the conductive phase in the shape of elliptical eggs. Then, the characteristic parameters of the eggs, i.e. a shape factor, F_f, and an orientation factor, $\cos \alpha_f$, allow the calculation of the conductivity of the mixtures.

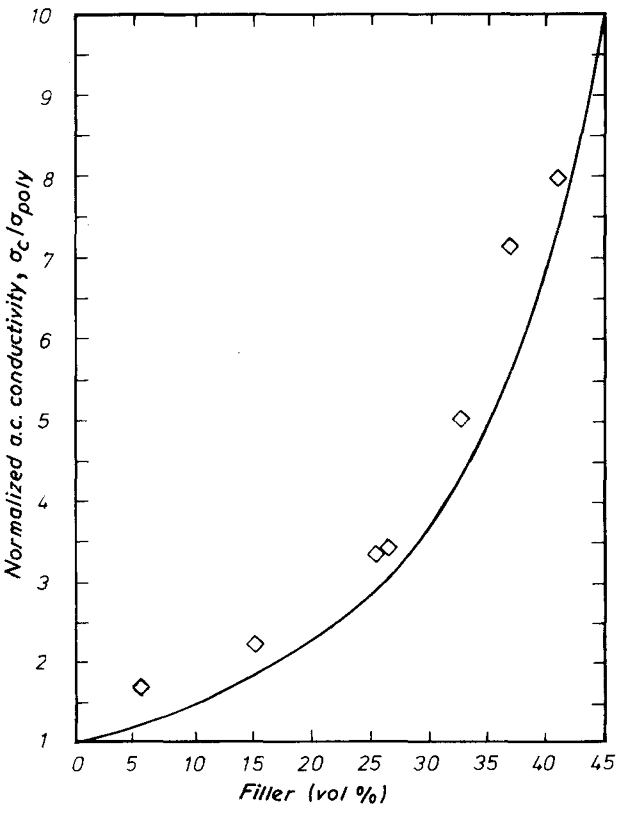


Figure 11 Comparison between the measured a.c. conductivity in a polyester/aluminium powder mixture at 20 °C and 10 kHz and the predictions of McCullough [46].

Mixtures, having an embedded structure

$$1 - c_f = \left(\frac{\sigma_{\text{in}}}{\sigma}\right)^m \cdot \frac{\sigma_f - \sigma}{\sigma_f - \sigma_{\text{in}}} \cdot \left(\frac{\sigma + n \cdot \sigma_f}{\sigma_{\text{in}} - n \cdot \sigma_f}\right)^9 \quad (17a)$$

where σ is the conductivity of the mixture, σ_{in} the conductivity of the insulating phase, σ_f the conductivity of the conductive phase, c_{in} the volume fraction of the insulating phase $= 1 - c_f$, c_f the volume fraction of the conducting phase,

$$m = \frac{F_f(1 - 2F_f)}{1 - (1 - F_f)\cos^2\alpha_f - 2F_f(1 - \cos^2\alpha_f)} \quad (17b)$$

$$n = \frac{1 - (1 - F_f)\cos^2\alpha_f - 2F_f(1 - \cos^2\alpha_f)}{2F_f(1 - \cos^2\alpha_f) + (1 - F_f)\cos^2\alpha_f} \quad (17c)$$

and

$$q = m + \frac{(1 - F_f)2F_f}{2F_f(1 - \cos^2\alpha_f) + (1 - F_f)\cos^2\alpha_f} - 1 \quad (17d)$$

Mixtures, having an interpenetrated structure

$$c_f(\sigma_f - \sigma)\left[\frac{2(1 - \cos^2\alpha_f)}{\sigma_f + \sigma} + \frac{\cos^2\alpha_f}{\sigma}\right] = -c_{\text{in}}(\sigma_{\text{in}} - \sigma)\left[\frac{2(1 - \cos^2\alpha_f)}{\sigma_{\text{in}} + \sigma} + \frac{\cos^2\alpha_f}{\sigma}\right] \quad (18)$$

The parameters in Equation 18 have already been explained in context with Equations 17a–d.

The procedure to obtain reliable values for the shape and the orientation factors is described by Ondracek and co-workers [47, 50].

A comparison of experimental conductivity curves in binary mixtures with the predictions of Equations 17 and 18 shows that a good correlation is found in most systems, but there are also examples which seem to contradict the conductivity equations of Ondracek (see, for example, Figs 12 and 13).

6. Limitations of the models

Having summarized the models available for the prediction of the conductivity or the percolation concentration of filled systems, their applicability and limitations will be discussed. Before doing this it should be emphasized that the above mentioned models represent only a small number of the wide variety of models proposed for the explanation of the conductivity behaviour of binary mixtures. This is especially true for the groups of the geometrical and structure-oriented models. For information in this connection the reader is referred to the works of Bhattacharya and Chaklader [41], Berger and McCullough [46], Ondracek [49] and Yoshida [43]. Furthermore, it should be stressed that some of the different models have been described in some detail to enable the reader to understand the general way of thinking when deriving equations for the conductivity or the percolation concentration on the basis of a special set of assumptions.

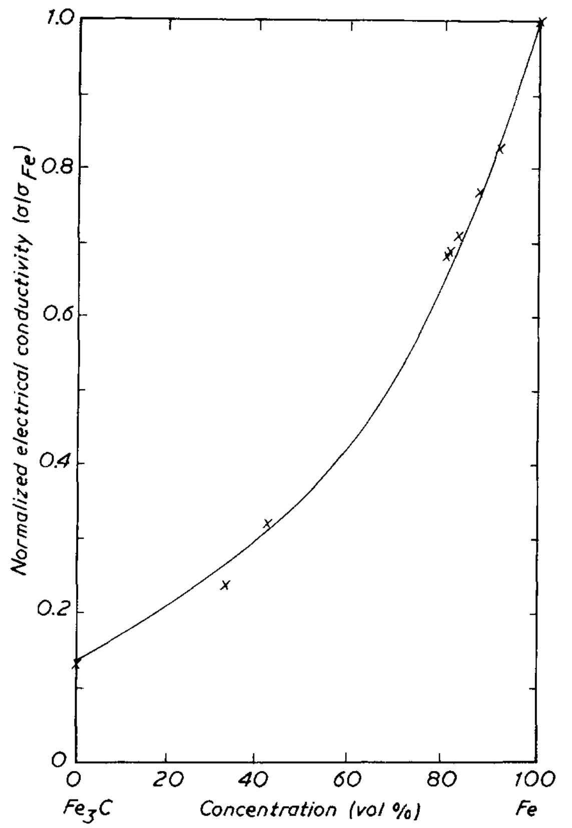


Figure 12 Comparison of the experimentally found conductivities in Fe/Fe_3C mixtures with the predictions of the conductivity model of Ondracek [51].

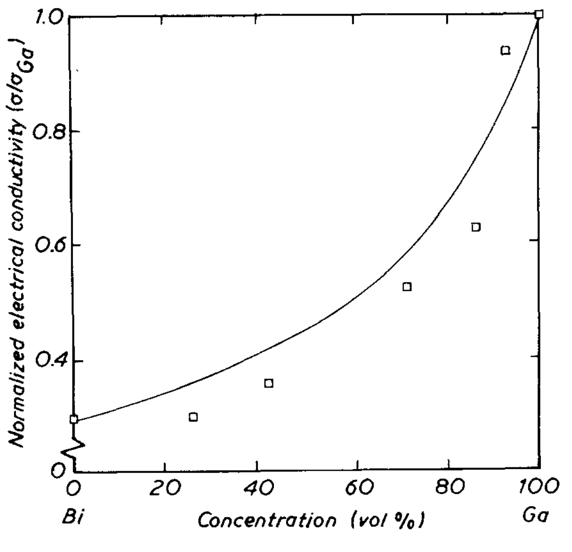


Figure 13 Comparison of the experimentally found conductivities in Bi/Ga mixtures with the predictions of the conductivity model of Ondracek [51].

Although the above summary of the different models shows that they are derived for rather different mixtures, it is easy to deduce that, independent of the special case, the following parameters are most important for the derivation of the individual equations:

(a) the size and the geometry of the conductive particles;

(b) the amount and the distribution of the conductive particles in the insulating matrices;

(c) interactions between the conductive and insulating components; and

(d) the preparation method of the mixtures.

The correct-mixture-dependent choice of these four parameters is crucial for the quality of any estimate about the conductivity or the percolation concentration. Consequently, the following discussion deals with the adequacy of the assumed parameters a–d in the different percolation models and the question: is it possible to explain all experimental results with the aid of only one model.

It is seen in the description of the percolation and conductivity models that most of the authors assume a spherical geometry for the individual conductive particles. However, it is well known that the more important conductive fillers, like metal fibres, metallized glass fibres, metal flakes and, in particular, CB and ICP particles, have a rod-, disc- or grape-like geometry. Figs 14 and 16 show the morphology of polyaniline particles (polyaniline is a prominent ICP) and CB aggregates, respectively.

The discrepancy between the assumed filler particle geometry and the real appearance of the conductive particles is a serious restriction for the applicability of the concerned models. It gives rise to the question what conductivities or percolation concentrations would result from the quantitative considerations, if a non-spherical geometry of the filler particles is assumed? Pike and Seager [4, 5] and Yamaki *et al.* [9] focused their work on this question for the case of the statistical percolation model of Kirkpatrick and Zallen. Both groups showed that the obtained percolation concentration depends strongly on the shape of the filler particles; the more irregular the shape of the conductive particles, the lower the percolation concentration. With respect to the other models, assuming a spherical geometry of the conductive particles, no investigations concerning the effect of the particle geometry have appeared in the literature until now. Nevertheless, it can be speculated on the basis of the original papers of the geometric and thermodynamic models that a more complicated structure of the conductive particle would make it impossible to obtain

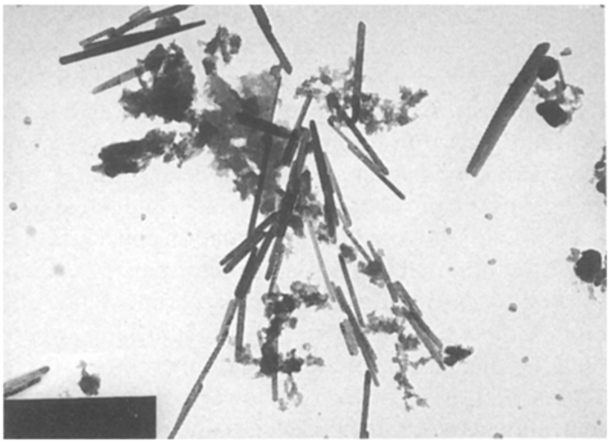


Figure 14 Transmission electron micrograph of polyaniline particles, resulting from the well-known HCl-preparation route [82]; × 15 600; Lux [83]; both the needles and the grape-like aggregates are typical of this intrinsically conductive polymer.

a reliable estimate for the conductivity or the percolation concentration of the mixtures.

The true structure of the conductive particles is also the basis for speculations about the experimentally determined percolation concentrations in CB- and ICP-filled polymers [42]. The grape-like structure of these conductive fillers is accompanied by the appearance of closed and non-closed holes in the CB and ICP aggregates. The closed holes in the aggregates are empty or include a gas or a fluid, typical for the specific synthesis conditions. However, the calculation of the volume concentration of the conductive phase in these cases assumes a structure of the conductive phase in which no closed holes appear. So, the experimental error in the calculation of the true volume concentration of the conductive phase might be one reason for the difference between the theoretical and the experimentally found percolation concentrations.

A similar argument is true for uncertainties in the measured conductivities. Normally, the description of the measurement cell for the conductivity determination is not included in an article dealing with conductive binary mixtures. On the contrary, it is usual to find inexact statements like "the conductivity was estimated using the standard four-point technique" [19, 55]. Such statements are not beneficial to allow a comparison between the results of different groups. Everybody, who has ever tried to measure the conductivity of filled systems over a typical range of ten decades of the conductivity, knows the serious problems in measuring very small and very high conductivities with one measurement circuit (avoidance of antenna and EMI effects and other problems). For this reason, the experimental error in the measurement of the conductivity must not be underestimated. A value of ± 50% of the quoted (measured) value might be the usual error.

The effect of the absolute size of the conductive particles on the conductivities or the percolation concentrations of binary mixtures somewhat interferes with those of the particle geometry and the interactions between the conductive and insulating components. For the case of fibre-like fillers (the fibre dimensions are in the upper micrometre range) the assumption of a certain aspect ratio of the fibres is equivalent to a minimum size of the fibres. The correlation between the aspect ratio and the size of the fibre results from the synthesis route of the fibres; as the synthesis route determines the fibre diameter, a given aspect ratio can be correlated with the size of the conductive particle. From the correlation of size and geometry in the case of fibre-like conductive particles it follows that a lower percolation concentration might be obtainable with larger filler particles. Contrary to the last statement are the experimental results on CB-filled polymers [56–58]. In these cases, where the filler dimensions are in the sub-micrometre range ($\ll 500$ nm), it is shown that lower percolation concentrations are obtained, if the diameter of the primary CB particles is reduced. It should be mentioned that the diameter of the primary CB particles is not identical with the size of the CB aggregates appearing as the conductive particles, but means the diameter of an individual grape of the grape-like aggregate. Assuming a given overall size of the CB aggregates, it follows that a lower percolation concentration results from an increase in the surface area of the filler particles and, consequently, from an increase in the interactions between the filler particles and the insulating host. The different behaviour of mixtures, containing CB particles or conductive fibres, with respect to variations in the "particle" size, therefore seem to contradict the idea of a universal, particle-shape independent percolation model.

The problem of a reasonable explanation for the unusual and extremely non-linear dependence of the conductivity on the amount of the conductive phase has been the origin of the whole scientific work on the conductivity of binary mixtures. The central problem might be described as follows: Is it possible to explain the conductivity behaviour with a mathematical concept that is independent of a special mixture, *or* could only a detailed description of the distribution of the conductive phase, as it results from the preparation method and the interactions between the conductive and insulating phases, account for the conductivity behaviour of different mixtures?

Kirkpatrick and Zallen have shown that it might be possible to explain certain conductivity/filler concentration curves with the aid of a mixture-independent mathematical concept. However, their derivation is speculative rather than precise with respect to mixtures with an irregular structure.

It emerges from Table II and the description of the way in which Kirkpatrick and Zallen obtained their universal percolation concentration, V_c, that they assumed a regular array for the conductive particles. On this basis they deduce V_c by multiplying p_c^{site} with the filling factor of the elemental cell of the assumed particle array. Furthermore, Table II suggested that Kirkpatrick and Zallen obtained the V_c value for the case of an irregular arrangement of the conducting particles in the same way. However, this is not true. On the contrary, these authors obtained the V_c value for the irregular arrangement by postulating that the V_c value of the regular case is also valid for the irregular arrangement, simply because all regular arrangements give the same V_c value. Assuming this, Kirkpatrick and Zallen obtained the p_c^{site} value for the irregular array of the conducting particles from the quotient $V_c/v = 16\ \mathrm{vol}\%/0.6$. Obviously this way of obtaining V_c value for the irregular array of the conductive particles has no scientific root and is therefore not acceptable.

Further discussions concerning the model of Kirkpatrick and Zallen deal with the choise of the p_c^{site} values for the calculation of V_c instead of the p_c^{bond} values or a combination of a site and bond percolation. This problem was investigated by Pike and Seager [4, 5] and by Janzen [3]. It leads the latter author to the derivation of his own percolation concept on the basis of the p_c^{bond} values.

Aside from these uncertainties of the "classical" percolation considerations of Kirkpatrick and Zallen, many experimental investigations have appeared in the literature, manifesting that many interactions between the insulating and conductive particles might appear in real binary mixtures and that the mixing process of the constitutents of a mixture, as well as any post-mixing step, have a serious influence on the conductivity and the percolation concentration of a mixture [22–29, 38–40, 43, 56–77]. For example, the following results are quoted: Bigg [59] examined the influence of the CB structure, the morphology of the polymeric matrices and the processing parameters on the conductivity of CB-filled polymers. He found a strong influence on the polymeric host and stated: "Segregation processes leading to an uneven distribution of the filler particles are beneficial for lower volume percolation concentrations. One such process is the crystallization of the polymeric host". Harbour and Walzak [60, 75] probed CB/polymer mixtures with the aid of the electron spin resonance (e.s.r.) method. They found that the mixing process of the two materials resulted in an electrical charging of the CB particle surfaces. Such permanent surface charges might stimulate interactions between the CB particles and the polymeric host. Boluk and Schreiber [66] focused their work on the influence of reactive surface groups on the conductive particles. They found that attractive forces between the conductive particles and the matrices facilitate the mixing process of the two materials. Therefore, surface groups might hinder the formation of a "pure" network of the conductive particles. Medalia [56], Miyasaka *et al.* [22–25] and Gilg and Bode [57, 58] studied the percolation process in CB/polymer mixtures systematically. They deduce that the following factors are important for the formation of conductive networks:

(a) the rheology (viscosity) of the polymer during the mixing process and in post-processing steps;

(b) the wettability of the CB particles for the polymers;

(c) the crystallinity in thermoplastic polymers;

(d) the details of the solidification process after the mixing process and in post-processing steps;

(e) the thermodynamic miscibility of the CB particles with different polymers in polymer blends, e.g. in acrylic–butatiene–styrene (ABS); and

(f) the parameters of the mixing process and of post-processing steps.

Noguchi *et al.* [77] described a new technique for dispersing metallic particles into a polymer. The characterization of the resulting composites comprised dynamic-mechanical investigations (DMA) and showed that a new phase appeared in the composite (probably at the metal/polymer boundary). The experimental studies of Wessling [27–29] on CB/polymer and ICP/polymer mixtures also give indications for interactions of the constitutents of the mixtures, because

(i) the density of the mixtures does not rise proportionally with rising filler content, and

(ii) the gas permeability of the mixtures rises drastically in the region of the network formation.

Bayer *et al.* [69–71] investigated the effect of the injection moulding technique on the distribution of carbon black in high-density polyethylene. It becomes evident that this processing technique results in a totally irregular arrangement of the carbon black particles in the polyethylene matrix; the particles are arranged in axial channels and are (at least partly) separated from the polyethylene matrix. The anisotropic distribution of the CB particles is accompanied by a higher conductivity and a lower percolation concentration (in the direction of preferred orientation) when compared with compression moulded parts.

Fig. 15 is taken from the work of Malliaris and Turner [40]. It shows the geometry and arrangement of the conducting and insulating particles before and after the sintering process. Apparently, sintering the dry-premixed powders leads to a strong change in the geometry of the insulating particles. Furthermore, the arrangement of the conducting particles at the boundaries of the insulating ones is somewhat changed.

The above description of some of the different interactions between the constitutents of a binary mixture and the obvious influence of mixing and post-mixing processes strongly contradict a mixture-independent mathematical explanation of the conductivity and is the basis for the thermodynamical and structure-oriented models. Moreover, it seems speculative to

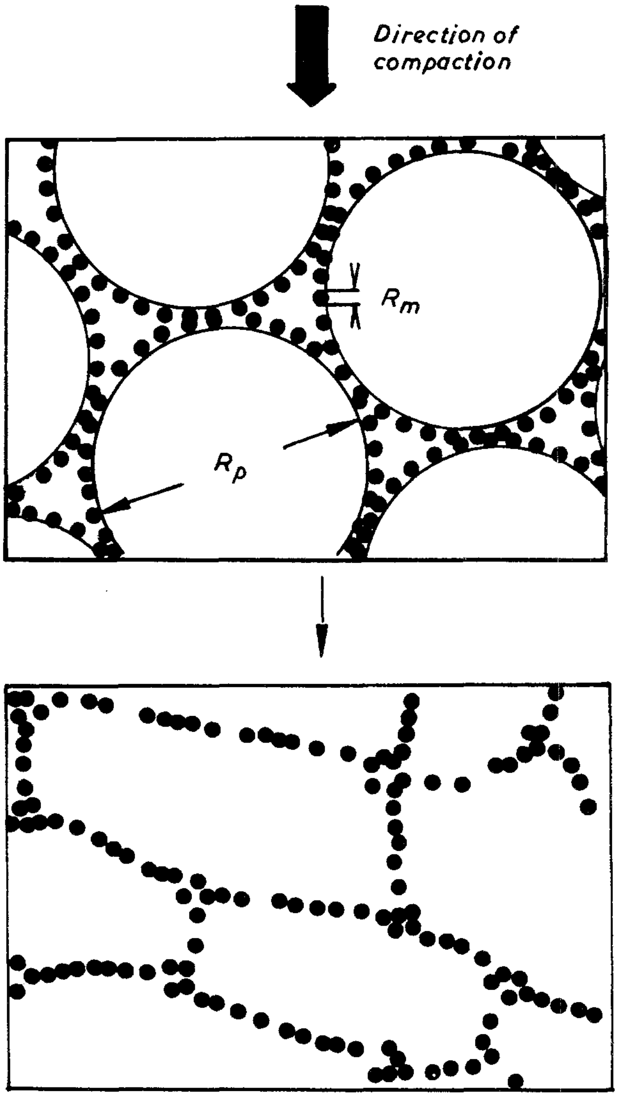


Figure 15 Schematic representation of the compaction process in mixtures made of polymeric particles and smaller particles of metal according to the assumptions of Malliaris and Turner [40].

explain the conductivity of a sintered mixture on the basis of the diameters R_p and R_m of the insulating and conducting particles, respectively, as proposed by Malliaris and Turner, Slupkowski, and Battacharya and Chaklader.

The thermodynamical percolation model of Sumita and co-workers [22–25] was the first attempt to account for interactions between the constitutents of CB/polymer mixtures. So, it is no wonder that the derivation of the final percolation equation includes some assumptions which are too rough for a general thermodynamical explanation of the percolation phenomenon. It has been already mentioned that CB particles have a grape-like appearance and the distribution of the particles depends on the parameters of the mixing and post-mixing process. Nevertheless, Sumita and co-workers assumed the CB particles to be spherical and concentrated their considerations on compression moulded materials. Possible interactions, not considered in the work of Sumita and co-workers, are the crystallization of the insulating phase during cooling the mixture from the processing temperature to room temperature, the different miscibility of the conducting particles with the polymeric constitutents of polymer blends, and the appearence of an interphase at the insulating matrix/conductive particles boundary. To obtain an estimate for the percolation concentration in mixtures with normally semi-crystalline polymers, Sumita and co-workers suppressed the crystallization by rapid cooling of the mixtures in ice–water.

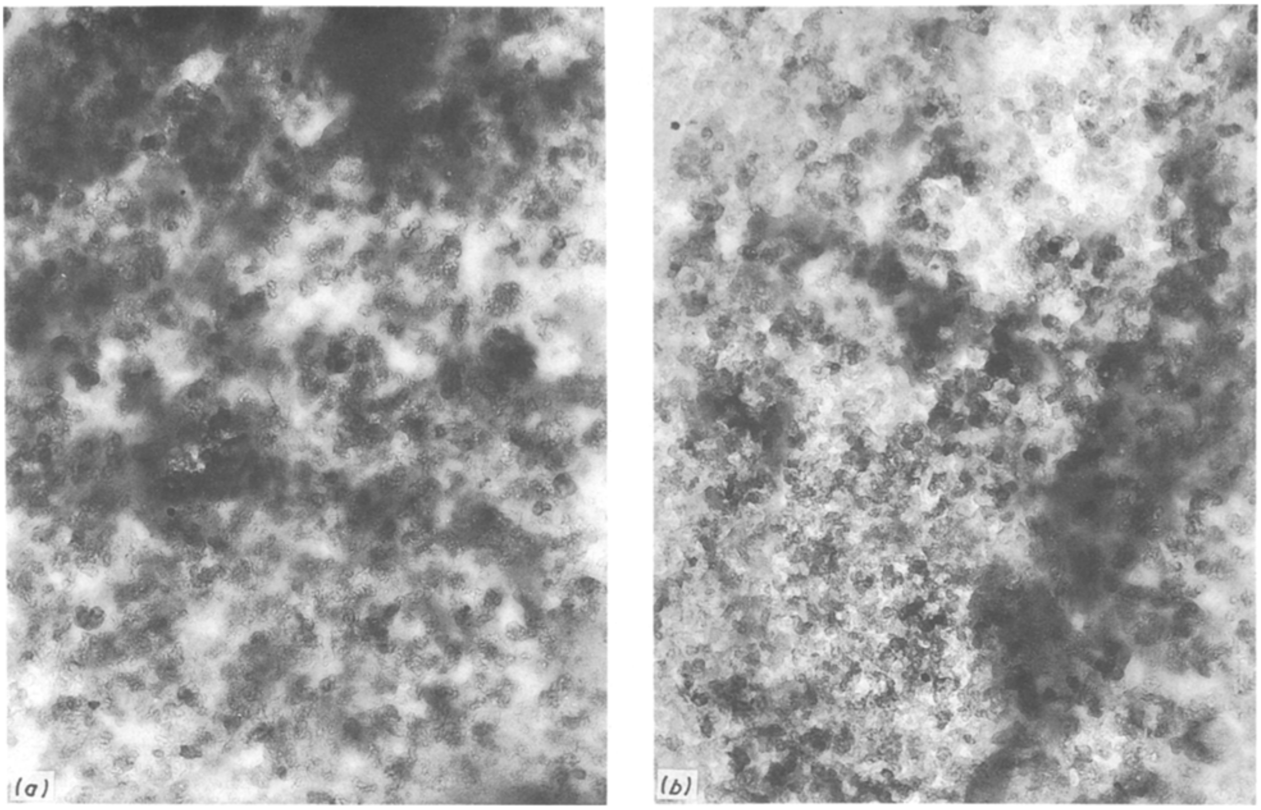
A large experimental error in the considerations of Sumita and co-workers might be caused by the way in which they calculate the specific interfacial excess energy. To obtain an estimate for this parameter, the authors used Equation 19

$$K = \gamma_c + \gamma_p - 2(\gamma_c \gamma_p)^{1/2} \qquad (19)$$

where K is the specific excess energy, γ_c the surface tension of the conductive particles, and γ_p the surface tension of the polymer matrix. Equation 19 was originally proposed by Fowkes [44] and is valid, in a strict sense, only for non-polar polymers, i.e. hydrocarbon polymers, like polyethelene and polypropylene. However, Sumita and co-workers used it also for the calculation of the percolation concentration in CB/polymer mixtures with more polar polymer matrices (PMMA and nylon).

Wessling and co-workers [26–36] proposed a percolation model which is able to account for the existence of an interlayer at the CB/polymer boundary, with the properties of the layer being different from the properties of the remaining polymer. Unfortunately, most of his other assumptions, concerning different parameters and the propagation of the percolation process, seem very speculative. First, Wessling assumed the CB and ICP particles to be spherical. As is shown in Figs 14 and 16 this is not true for these conductive fillers. Furthermore, if it was possible for Wessling to account for a different geometry of the conductive particles, his assumption of an interlayer around each conductive particles is still not true. Fig. 16b shows in the middle of the lower half, a region of the CB/polymer mixture, in which the CB particles appear isolated from the rest of the mixture. Such regions with pure conductive filler result from the mixing procedure and are due to the problem of effectively destroying the CB agglomerates (a CB agglomerate is constituted of several hundred to thousand CB aggregates) in the shear stress field of the mixing unit. Second, Wessling used the same equation as Sumita and co-workers for the calculation of the free energy of the filler/polymer interactions; the values of the surface tensions were measured at room temperature. Therefore, it is hard to believe that the equation and the values of the surface tensions could account for the interactions between the filler particles and the polymer during mixing at temperatures $\gg 100^\circ$ C and under drastic shear conditions. Third, Wessling postulated that the individual filler particles are totally separated from each other before percolation takes place. It has already been shown that this assumption interferes with the problem of effectively distributing the CB or ICP agglomerates during the mixing process. Fourth, Wessling's assumption of a solid interphase of polymer at temperatures somewhat above the melting temperatures of the respective polymers is not acceptable. If this interphase is amorphous, as assumed by Wessling, it should soften before melting of the polymer crystals takes place. Fifth, Wessling used the factor "1–C", i.e. the amorphous part of a semi-crystalline polymer, for estimating the influence of different crystallization processes in the polymer matrix. However, as the amorphous part of a semi-crystalline polymer has no relation to different nucleation and growth mechanisms, it is unsuitable to account for the effect of the crystallization on the percolation concentration. Sixth, Wessling claimed that the density/filler concentration curves, measured by himself, are in accordance with his theory. However, he has not derived the theoretical density/filler curves on the basis of his model until now. The latter work was done by Lux [78]. Fig. 17 compares the experimental results of Wessling with the theoretical density curves for a CB/polyethylene system. It is seen in this figure that the theory of Wessling cannot account for the experimental density curve.

Another way to account for the influence of different interactions between the constitutents of conductive binary mixtures is offered by the structure-oriented conductivity models. All models of this group evaluate the interactions in an integrated manner, i.e. by means of an analysis of the micro-level structure of the as-processed mixtures. It follows immediately from the concept of such models that they do not include preconditions for a certain shape and size of conductive filler. This is an important advantage of these models. However, some of the models are based on assumptions which are not fulfilled in any case. The best examples of this are the models of Yoshida [43] and Ondracek [47–51]. Both authors assumed a homogeneous structure of the mixtures. Furthermore, Ondracek demanded the thermodynamic equilibrium state and the existence of only two phases in the mixtures for his considerations. Material structures, having these features, might result from sintering and



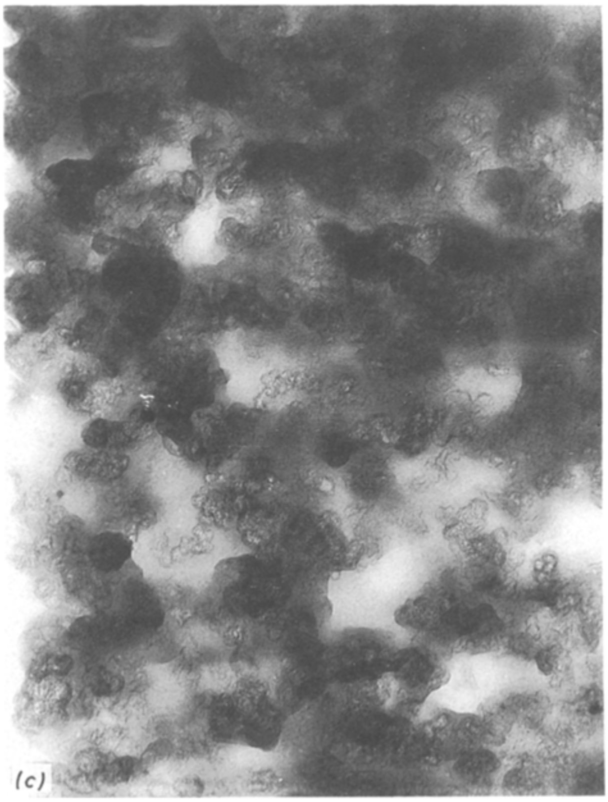


Figure 16(a, b) Transmission electron micrographs of a carbon black/polystyrene mixture just above the percolation point (about 11 wt % carbon black); ×26 500; Pohl and Lux [81]. (c) See (a) ×65 120.

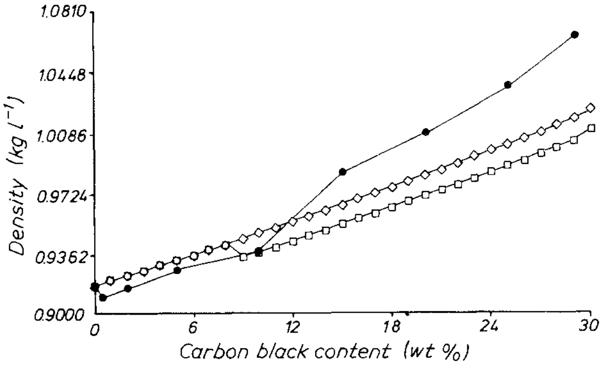


Figure 17 Calculated and measured density/filler concentration curves for mixtures of polyethylene and a carbon black according to the results of Lux [78] and Wessling [29]; (□) diameter of the CB particles 50 nm, lower density bound; (◇) diameter of the CB particles 50 nm, upper density bound; (●) density/filler curve measured by Wessling.

compression moulding processes but not from extrusion or injection moulding processes. Moreover, the absence of interlayers at the boundaries between the conductive filler particles and the insulating matrices in the model of Ondracek gives a further serious restriction to his model. It has already been mentioned [60, 66, 75, 77] that different chemical surface groups and physico-chemical processes during the preparation of the mixtures might give rise to the appearance of interlayers, i.e. a third phase in the mixtures.

The absence of specific interaction parameters in the semi-empirical conductivity models is responsible for their non-applicability in predicting the behaviour of a mixture when changing one or the other parameter. So, the structure-oriented models are not able to explain the propagation of the percolation process on the ground of physical and chemical laws.

The greatest difficulty for all structure-oriented models arises from the necessity of a quantitative analysis of the micro-level structure. Independent of the system under investigation, such an analysis demands a sophisticated plant for preparing the samples and a large computer, able to account for all the different *grey-spots* in a picture of a sample. Fig. 16, showing the micro-level structure of a CB/polystyrene (PS) mixture just above the "percolation point", has been included in this review to demonstrate the problem. It is seen in this figure that the analytical separation of the conductive network from the insulating matrix is a very difficult task [79]. Another problem, emanating from Fig. 16a and b, is the choice of a representative picture of the structure. In fact, both figures show the same mixture at the same magnification. Nevertheless, the features of both pictures are quite different. Fig 16a shows the CB particles quite well distributed in the PS matrix, whereas Fig. 16b shows the CB particles in a pure agglomerate surrounded by a filled PS matrix. The choice of the "correct" picture is further complicated by the pronounced influence of the preparation method of the samples on the resulting images. It is well known that an inadequate preparation method of the samples might lead to totally wrong evaluations of the micro-level structure of a material [80].

The choice of the adequate conduction mechanism is also a problem for some of the structure-oriented conductivity models. As is shown by Bradbury and Bigg [54] for Nielsen's model, this model failed in predicting the electrical conductivity of the mixtures, because the author assumed the thermal conduction mechanism to be also applicable for the electrical conduction.

The model of McCullough [45] has the advantage of not including a prerequisite for the morphology of the mixtures. So, it might be applicable for the theoretical evaluation of the conductivity after rather different processing steps (especially those leading to anisotropic material structures). Unfortunately, McCullough has not tried to use his equation in a general way, but restricted the considerations to mixtures with a homogeneous structure. As is seen in Fig. 11, the latter case of application of Equation 16a needs further optimization to allow a quantitative aggreement with the experimentally observed behaviour.

7. Conclusion

In conclusion, it follows from the discussion of the various statistical, geometric and thermodynamic percolation and conductivity models that currently no model exists which is able to explain all the different results of experimental studies. Furthermore, no model is able to account for the extensive influence of different processing methods on the percolation process. A good correlation between experimental results and a special percolation model does not necessarily give significant evidence for the validity of this model, but seems to be a consequence of a favourable superposition of different serious mistakes appearing:

(a) in the derivation of the percolation equation;

(b) when choosing the values of the respective influence factors for the theoretical calculation of the percolation concentration or conductivity, and

(c) in the experimental determination of the conductivity or the percolation concentration.

In view of the serious deficiencies of individual models, the disputatious discussion between the scientific groups, having proposed the different percolation or conductivity equations, concerning the question "which model fits best the experimental results", seem really obstinate. It is not beneficial to the aim of finding a generally applicable percolation concept (if such a concept exists at all). For the derivation of a general percolation concept, a combined activity of the involved scientist would be desirable. Such an activity might include the mathematically or statistically motivated scientists to propose reasonable concepts for the influence of particular interaction parameters. The work of finding all the different parameters of influence might be transferred to the manufacturers of conductive mixtures and the scientist, emphasizing thermodynamic percolation concepts.

On the basis of today's understanding of the conductivity behaviour of binary mixtures, the conductivity/filler concentration curves are best described by structure-oriented conductivity equations. However, the applicability of such concepts is closely linked to the availability of a sophisticated plant for quantitatively analysing the micro-level strucure of the mixtures. A further complication is the fact that *one* quantitative analysis of the structure only gives *one* conductivity/filler concentration value. So, to obtain the whole conductivity/filler concentration curve much analysis work would have to be performed. Obviously, having the choice between a time-consuming analysis of the micro-level structure to obtain a conductivity value and the possibility of simply measuring the conductivity in an adequate cell, one would choose the second option immediately.

The structure-oriented conductivity models are useless in predicting the effect of certain interaction parameters on the resulting conductivity or the percolation concentration. Therefore, they do not contribute to a general understanding of the percolation process.

The derivation of structure-oriented equations for the conductivity of binary mixtures demands the acceptance of the right conduction mechanism and often results, as a consequence of the problem of adequately describing the micro-level structures theoretically, in boundary equations for the conductivity [47–51].

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