

Influence of pressure on the electrical conductivity of metal powders used as fillers in polymer composites

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Received 1 August 2002; accepted 25 November 2003

Abstract

In this work, the influence of pressure on the electrical conductivity of metal powders (copper, nickel, and iron), used as fillers in conductive polymer composites, was investigated. It was found that the conductivity of the powders as a function of the applied pressure, P , is described by the equation: $\sigma = k(P - P_0)^n$. In this equation, P_0 is the minimal pressure necessary for the appearance of conductivity and it is affected by the presence of oxidized layers on the surface of the metal particles. Exponent n depends on the kind of the powder and the particle size. It is also affected by the properties of the oxidized layers on the surface of the particles. Coefficient k depends only on the kind of the powder. It was shown that the conductivity of copper powder increases exponentially with increasing particle size. The value of the packing factor, F , increases with the applied pressure, due to the deformation of the particles. It is affected by the hardness of the powder particles. The conductivity of powders with small and big copper particles was compared with the conductivity of polymer composites, based on epoxy resin with the same powders as fillers.

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Keywords: Metal powders; Pressure; Electrical conductivity; Particle size; Packing factor; Polymer composites

1. Introduction

The conductivity of polymer composites that contain dispersed conductive fillers, depends on many factors such as the size and shape of the filler particles, their spatial distribution within a polymer matrix, the interactions between the filler surface and the polymer matrix, and the contact resistance between adjacent particles [1–5]. All these factors determine the conditions of charge transport from one particle to another, i.e., the conductivity of the filler phase. Clarifying the role of all these factors enable us to choose the suitable processing method for obtaining the composites and to improve the electrical characteristics of these systems. Contact resistance between particles is important in the case that the filler volume concentration, φ , exceeds the percolation threshold, φ_c , and charge transport through the filler phase takes place via direct contact

between the particles. In this case, conductivity can be defined as “metallic conductivity”. On the contrary, when a thin, insulating polymer layer separates the filler particles, conductivity is dominated by charge transport via tunneling effect [6].

During curing of the thermoset matrix or cooling of the thermoplastic matrix in polymer composites, internal stresses appear. Many works study the influence of these stresses on the contact resistance between filler particles [5,7]. These stresses increase the pressure between adjacent particles, give the contact pressure and decrease the contact resistance. The higher the internal stresses are, the lower the contact resistance is. Internal stresses in a cured epoxy resin can achieve 35–40 kg/cm² [7]. On the other hand, the behaviour of metal fillers under pressure in a polymer matrix is not sufficiently studied. Such information can be obtained by investigating the influence of pressure on “dry” metal powders (without polymer matrix).

In this work, the dependence of conductivity of metal powders (copper, nickel, and iron), used as dispersed conductive fillers in polymer composite materials, on the applied pressure is studied. Copper powder had various particle-size fractions. This enabled us to study the influence

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of the particle size on the conductivity of the powders. Obtained data were compared with the conductivity of composites based on epoxy resin with the same metal powders as fillers.

2. Experimental

The following metal powders were studied:

- copper powder (Cu) (produced by an electrolytic method, Russian standard GOST 4960-75), with size fractions 0/20, 20/45, 45/70, 70/90 and 90/120 μm . These fractions were obtained by sieving the powder through sieves with holes of the corresponding diameters;
- nickel powder (Ni) (produced by a carbonyl method, GOST 9722-79) with average particle size 10 μm and
- iron powder (Fe) (type R-10, GOST 13610-79) with average particle size 3.5 μm .

The composites based on epoxy resin (Ep) were prepared by mixing the copper powder (size fractions 20/45 and 90/120 μm) with the resin (bisphenol A diglycidyl ether) and the hardener (diethylene triamine). After mixing, the composites were cast into a pan and cured for 2 h at 120 °C. To prevent filler sedimentation and to ensure random spatial distribution within the polymer matrix, the pans were rotated with a frequency of 1 s^{-1} until the specimens were cured.

Measurements of the powder conductivity, under variable pressure, were performed with the equipment shown in Fig. 1. The pressure was varied in the range 0–25 kg/cm^2 . The electrodes were made of copper. The electrical resistance of the metal powders was measured by a dc bridge,

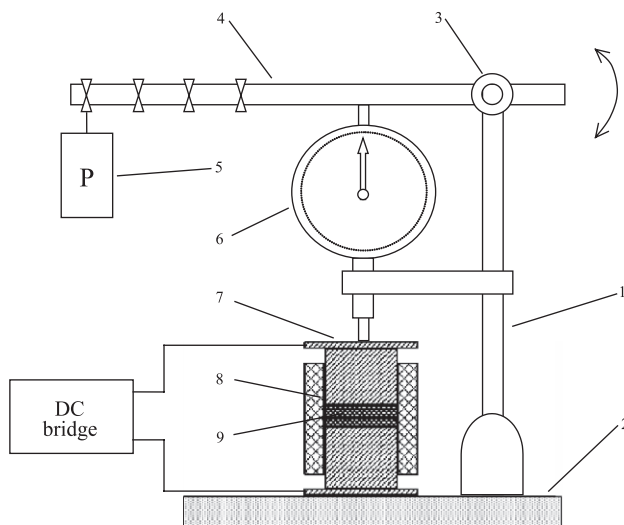


Fig. 1. Schematic representation of the experimental device used for measurement of electrical conductivity of metal powders: (1) rod, (2) stand, (3) hinge, (4) arm, (5) weight, (6) displacement gauge, (7) electrode, (8) insulating cylinder, (9) metal powder.

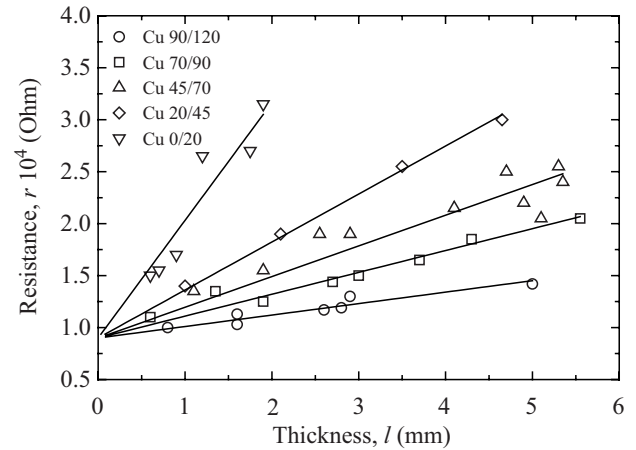


Fig. 2. Measured resistance, r , as a function of the powder thickness, l , for various copper size fractions, indicated on the plot.

type P 4833. The specific electrical conductivity of the metal powders, σ , was calculated by the equation:

$$\sigma = \frac{1}{r - r_c} \cdot \frac{1}{S_{el}} \quad (1)$$

where r is the resistance measured by the dc bridge, r_c is the electrode–powder contact resistance plus the circuit resistance, l is the thickness of the powder in the cell under pressure, S_{el} is the electrode area.

3. Results and discussion

The electrical resistance, r , measured with the equipment shown in Fig. 1, is equal to: $r = r_p + r_c$. It consists of two parts: r_p is the resistance of the metal powder and r_c is the resistance on the electrode–powder boundary surface plus the resistance of the circuit wires. For the separation of these two parts, the electrical resistance, r , with variable thickness of the metal powder, l , at a given pressure, P , is measured. The dependence of the electrical resistance on the powder thickness for all size fractions of the copper powder is presented in Fig. 2. It is seen that this dependence is linear. Extrapolation of these straight lines to the value $l=0$ (this corresponds to measurement without powder) gives the value of $r_c = 0.9 \cdot 10^{-4} \Omega$, which is the same for all size fractions. From the slope of these plots, the powder resistivity, or conductivity, can be calculated. We observe that, for the same value of l , the measured resistance of the copper particles having smaller size fraction is higher than that of the bigger ones. Because in both cases r_c is the same, we conclude that the powder resistance of the smaller copper particles is higher than that of the bigger ones. Thus, for the bigger copper particles, r_c contributes by a more essential part in the total measured resistance, r .

When pressure, P , is applied on a metal powder, the particles are deformed and the contact points become a

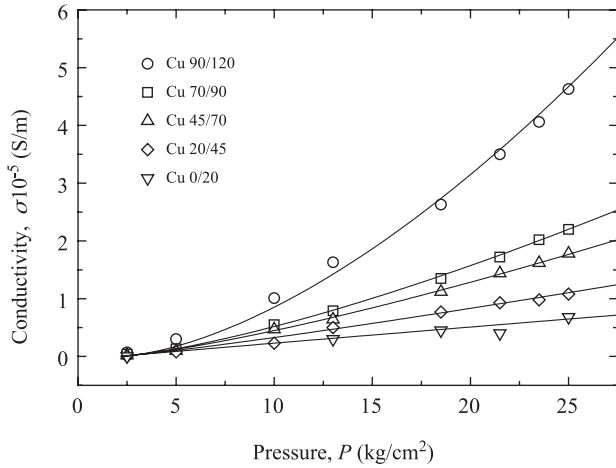


Fig. 3. The dependence of electrical conductivity of copper powder with various size fractions on applied pressure, P . The lines are the best fittings of Eq. (6) to the experimental data.

contact area. In this case, the resistance of the contact area is defined by the transient resistance [8]:

$$R_{tr} = \frac{\rho}{2a} \quad (2)$$

where ρ is the specific volume resistivity of a metal particle and a is the radius of the contact area.

Practically, the surface of the metal particles is not perfectly clean, but it is covered by a thin insulating layer (oxidized or polymer one). Thus, the resistance due to this layer is:

$$R_l = \frac{R_1}{\pi a^2} \quad (3)$$

where R_1 is the resistance on the unit of the layer surface.

The total contact resistance is the sum of these two quantities [7]:

$$R_c = \frac{\rho}{2a} + \frac{R_1}{\pi a^2} \quad (4)$$

With increasing pressure on a metal powder, electrical conductivity increases, due to the increase of the contact area and distortion of the insulating layers on the particles

surface. According to Ref. [8], electrical conductivity of a metal powder is:

$$\sigma = K \left(\frac{P}{H} \right)^n + C \quad (5)$$

where P is the applied pressure, K is a constant, C is a very small quantity depending on the applied pressure and H is the hardness of the particles. In this equation, the value of the exponent n varies in the range: $0.5 < n < 1$. If transient resistance R_{tr} exists only, then $n=0.5$.

When the insulating layer is thick enough (more than 10 nm, [7]), powder conductivity does not appear under pressure lower than P_0 , which is the limit for the layer distortion. In this case, charge transport through this layer cannot be realized by tunneling effect, which is possible only through thin layer (several nm). Then, the influence of the applied pressure on the powder conductivity can be expressed by the equation:

$$\sigma = k(P - P_0)^n \quad (6)$$

where k is a constant including the hardness H .

In Fig. 3, the dependence of electrical conductivity of copper powder with various size fractions on the applied pressure is presented. At a given pressure, conductivity increases with increasing particle size, to be discussed later. Eq. (6) was used to fit experimental data. For all size fractions, the same value, $P_0=2.0 \text{ kg/cm}^2$, was found. The values of the exponent n were calculated in the range: $0.98 < n < 1.61$. The higher values of n were calculated for the bigger copper particles. This exceeds the values predicted by Eq. (5). Coefficient k takes the same value for all size fractions studied. The calculated values of the parameters k , P_0 and n are given in Table 1.

The influence of the particle size fraction on the exponent n is shown in Fig. 4. It is seen that exponent n increases linearly with increasing the average particle size. Therefore, conductivity rise is higher for the bigger particles (see also Fig. 3). This effect may be a result of the higher contribution of the oxidized layers to the total contact resistance for the bigger particles, as it can be seen from Eq. (4).

The pressure dependence of electrical conductivity for nickel and iron powders is presented in Fig. 5. Experi-

Table 1
Properties of the metal powders studied

Powder	Average particle size (μm)	P_0 (kg/cm^2)	k ($\text{S}\cdot\text{cm/kg}$)	n	F	ΔF (%)	$H \cdot 10^{-2}$ (MPa)
Ni	10	0.5	4	0.9	0.510	9.9	16
Fe	3.5	1.0	0.003	1.9	0.490	10.2	14
Cu 0/20	10	2.0	30	0.98	-	-	6
Cu 20/45	32.5			1.15	0.240	33.8	
Cu 45/70	57.5			1.30	0.266	28.6	
Cu 70/90	80			1.37	0.286	24.0	
Cu 90/120	105			1.61	0.312	22.2	

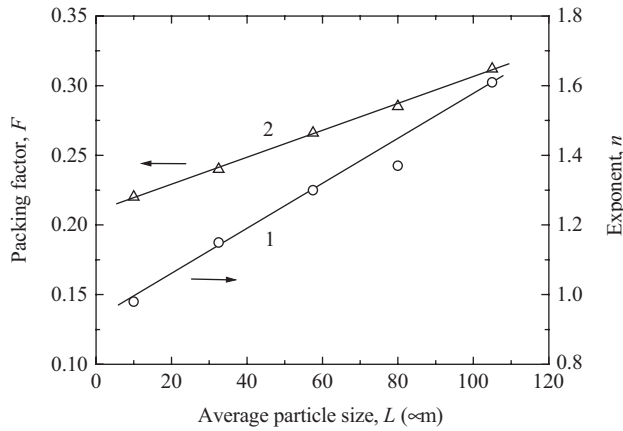


Fig. 4. Influence of copper particles size, L , on exponent, n , of Eq. (6) (right axis, line 1) and on packing factor, F , (left axis, line 2).

mental data were fitted with Eq. (6). As it is seen, this dependence is different for nickel and iron, giving values $n < 1$ and $n > 1$, respectively. The calculated values of the parameters P_0 , k and n for these metal powders are also given in Table 1.

Analysis of data in Table 1 allows us to assume that P_0 is probably related to the solidity of the insulating layer, while n shows the contribution of the resistance of this layer to the total contact resistance, R_c . Copper particles have the most solid oxidized layer (higher value of P_0), while the oxidized layer with the higher influence on conductivity is that of iron powder (higher value of n). For nickel powder, values of P_0 and n are the lowest ones, so the oxidized layer in this case is less solid and thick.

One of the most important characteristics of fillers is the packing factor, F , which is defined as [9]:

$$F = \frac{V_p}{V_p + V_s} \quad (7)$$

where V_p is the volume occupied by the filler particles at the most dense packing and V_s is the volume of the free space among particles. For statistically packed monodispersed spherical particles of any size, F is equal to 0.64 [9]. In the case of deviation of the particle shape from the spherical one, or of aggregation of the particles and formation of a skeleton structure, the value of the packing factor decreases, due to the increase of V_s . The use of polydispersed powder particles results in an increase of F . Authors of Ref. [10], which proposed a new model to predict the packing behaviour of irregularly shaped particles, have obtained value of F about 0.78 for bimodal dispersed fillers. In Ref. [11], it was found that $F=0.95$ for a system which includes four fractions of metal spherical particles. As a rule, real dispersed fillers have values of the packing factor lower than 0.64 [9], due to the irregular shape of the particles and aggregation. Thus, the value of the packing factor characterizes the filler topology taking into account the shape, the fractional size and the spatial

distribution of the particles. Packing factor, F , is a limit of filling the composites and has great influence on the rheological properties of polymer composites filled with dispersed fillers [10,12].

The values of the packing factor, F , were calculated by the equation:

$$F = \frac{W}{d \cdot S_{el} \cdot l} \quad (8)$$

where W is the weight of the powder portion in the cell and d is the true density of the powder particles. The values of F for all metal powders studied, at $P=0 \text{ kg/cm}^2$, are given in Table 1. As it is seen, the value of the packing factor for the copper particles is significantly lower than that for nickel and iron powders. It can be explained by the irregular dendritic shape of the copper particles, whereas the shape of nickel and iron particles is close to spherical. For the copper powder, packing factor decreases with decreasing particle size because small particles have more irregular shape than the big ones. The influence of the copper particle size on the packing factor is shown in Fig. 4. This dependence is linear.

Fig. 6 presents the dependence of the packing factor, F , on the applied pressure, P , for copper, nickel and iron powders. With increasing the pressure from 0 up to 25 kg/cm^2 , packing factor, F , increases. The percentage increase, ΔF , is also given in Table 1. As it is seen, ΔF decreases with increasing copper particle size; that is, small copper particles deform more than the big ones. Probably the reason for this effect is the more irregular shape of the small copper particles. For nickel and iron powders, ΔF is significantly lower, due to the more regular shape of these particles and the higher hardness of these metal powders (see Table 1).

It is also interesting to note that the higher deformation of the copper particles with smaller size fraction should lead to an increase of the contact area and, consequently, to higher

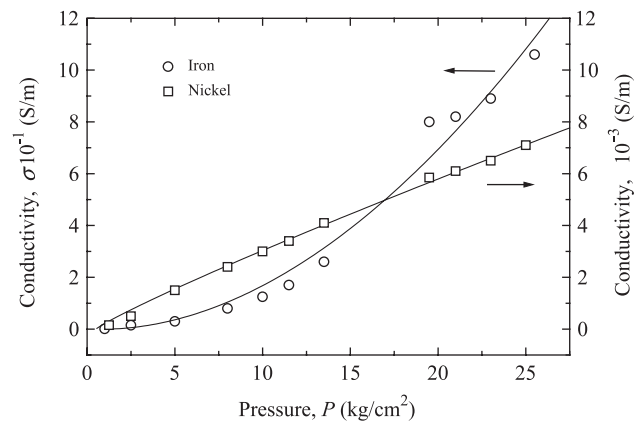


Fig. 5. The dependence of electrical conductivity of nickel and iron powders on applied pressure, P . The lines are the best fittings of Eq. (6) to the experimental data.

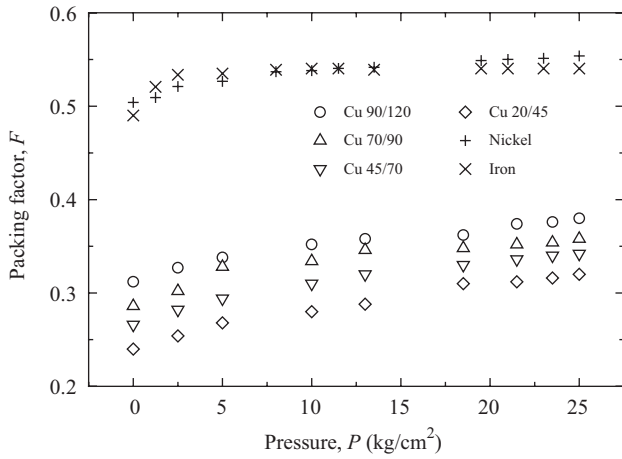


Fig. 6. Packing factor, F , as a function of pressure, P , for all metal powders studied.

rise of conductivity with increasing pressure. Our experimental results show the contrary effect (see Fig. 3) because the value of the exponent n in Eq. (6) is lower for the small copper size fractions. A possible reason for this effect is the linear dependence of the exponent n on the particle size L , i.e., $n \sim L$ (see Fig. 4). According to our assumptions mentioned above, the formation of contact areas under pressure, due to the breakdown of the oxidized layers, is more intense for the big copper particles.

In Fig. 7, the dependence of electrical conductivity on the size fraction of copper particles (under constant pressure 25 kg/cm²) is presented. Strumpler and Glatz-Reichenbach [5] consider strong dependence of the contact resistance on the plastic deformation of the powder particles, due to the increase of the contact spot radius, a [see Eqs. (2)–(4)]. Because the value of the radius, a , depends on the particle diameter [8], they predict a decreasing contact resistance with increasing particle size. It is also necessary to take into account the influence of

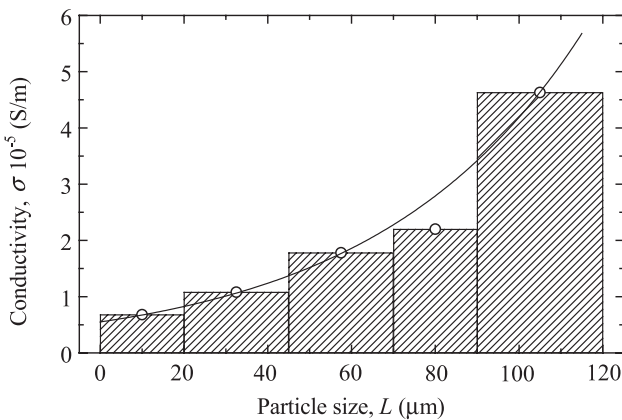


Fig. 7. Influence of copper particles size fraction on its conductivity, at $P = 25 \text{ kg/cm}^2$. The curve was calculated according to Eq. (9).

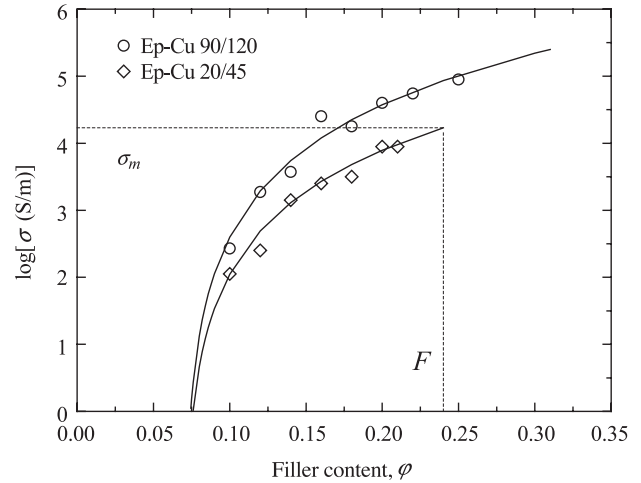


Fig. 8. Electrical conductivity, σ , of Ep–Cu composites as a function of the filler volume content, ϕ , for two different copper size fractions, 20/45 and 90/120 μm . Eq. (11) was used to fit experimental data (solid lines), while dashed lines show the values of the parameters σ_m and F for Ep–Cu (20/45) system.

the particle size on the powder conductivity, as a result of the breakdown of the oxidized layers. Considering strong dependence of electrical conductivity of the copper powder on the particle size, L , we fit the experimental data by the equation:

$$\sigma = \sigma_0 \cdot e^{CL} \tag{9}$$

where σ_0 is the minimum conductivity at $L=0$. It is seen that, conductivity increases with increasing particle size; that is, powder with smaller particle size has lower conductivity value, compared to the powder with bigger particle size. Our experimental data are in good agreement with a curve calculated according to Eq. (9) with the parameters σ_0 and C taking the values $0.55 \cdot 10^5 \text{ S/m}$ and $0.0203 \mu\text{m}^{-1}$, respectively.

The influence of the particle size on the electrical conductivity of filled polymer systems was investigated in composites consisting of epoxy resin (Ep) and dispersed copper particles having two different size fractions, 20/45 and 90/120 μm . Fig. 8 shows the dependence of the composites conductivity, σ , on the filler volume content, ϕ , for Ep–Cu (20/45) and Ep–Cu (90/120) composites. It is seen that this dependence shows percolation behaviour; that is, conductivity increases sharply when the filler concentration exceeds a critical value, the so-called percolation threshold, ϕ_c .

According to the percolation theory, electrical conductivity in the region above the percolation threshold ($\phi > \phi_c$) is connected to the conductive phase content with the relation [13]:

$$\sigma \propto (\phi - \phi_c)^t \tag{10}$$

Table 2
Parameters of Eq. (11) for polymer composites based on epoxy resin and copper powders

Composites	φ_c	F	t	σ_c (S/m)	σ_m (S/m)
Ep–Cu (90/120)	0.07	0.31	3.1	3.2×10^{-13}	2.5×10^5
Ep–Cu (20/45)	0.07	0.24	2.9	3.2×10^{-13}	1.7×10^4

where t is a critical index equal to 1.6–1.9. Eq. (10) may be written in a normalized form as [2]:

$$\frac{\sigma - \sigma_c}{\sigma_m - \sigma_c} = \left(\frac{\varphi - \varphi_c}{F - \varphi_c} \right)^t \text{ or}$$

$$\sigma = \sigma_c + (\sigma_m - \sigma_c) \cdot \left(\frac{\varphi - \varphi_c}{F - \varphi_c} \right)^t \quad (11)$$

In this equation, σ_c is the conductivity at the percolation threshold ($\varphi = \varphi_c$) and σ_m is the maximal conductivity of the composites at $\varphi = F$ (the values of σ_m and F for Ep–Cu (20/45) system are shown in Fig. 8). Eq. (11) was used to fit the concentration dependence of conductivity for each composite and the values of the parameters of this equation are given in Table 2. The values of the critical exponent t are higher than those predicted by the percolation theory. This effect may be related to the complex structure of the percolation cluster [14–16]. As it is seen, the value of φ_c is the same for both composites, whereas the values of σ_m are differed by one order of magnitude. The difference on the conductivity values between copper powders with size fractions 20/45 and 90/120 μm is less than that between σ_m of the composites filled with these powders. Apparently, epoxy resin changes the conditions of particle contact within the polymer matrix, compared to the “dry” powder. However, powder with smaller particle size, both “dry” as well as dispersed within a polymer matrix, has lower conductivity value, compared to the powder with bigger particle size. On the other hand, strong decrease of the particle size results in an increase of conductivity, due to the particle aggregation and formation of conductive paths between adjacent aggregates within a polymer matrix [17].

4. Conclusions

In this work, the influence of pressure on the electrical conductivity of metal powders, used as fillers in polymer composites, was studied. Our experimental results allow us to ascertain that the dependence of conductivity of metal powders, σ , on applied pressure, P , is described by the equation:

$$\sigma = k(P - P_0)^n$$

In this equation, P_0 is the minimal pressure necessary for the appearance of conductivity and it is affected by the presence of oxidized layers on the surface of the metal

particles. The value of P_0 is higher for the copper powder and lower for the nickel powder. It is determined by the properties of the oxidized layer, which is thinner on the nickel surface and significantly thicker on the copper surface. The value of the exponent n depends on the particle size, L , ($n \sim L$ for the copper powder) and the kind of the powder. It is also affected by the properties of the oxidized layers on the particle surface. The value of k does not depend on the particle size, but only on the kind of the powder. For the copper powder, the dependence of electrical conductivity, σ , on particle size, L , is given by the equation:

$$\sigma = \sigma_0 \cdot e^{cL}$$

As it is seen, powder with small particle size fraction has lower conductivity value than the powder with big particles.

Packing factor, F , takes the lowest value for the copper powder, due to the irregular dendritic shape of the copper particles. For the copper powder, packing factor increases with increasing particle size because small particles have more irregular shape than the big ones. Packing factor increases with increasing the applied pressure, due to the deformation of the particles, and this change of F is affected by the hardness and the size of the metal particles. Small copper particles deform more than the big ones.

The dependence of electrical conductivity of polymer composites, consisting of epoxy resin and two different size fractions of copper powder (20/45 and 90/120 μm), on the concentration of the metal filler is described by the equations of percolation theory. The percolation threshold is the same for both composites. Powder with small particle size, both “dry” as well as dispersed within a polymer matrix, has lower conductivity value, compared to the powder with big particles. The difference on the conductivity values between small and big copper size fractions is higher in polymer composites than in “dry” powders.

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