

ELECTRICAL CONDUCTIVITY IN THE QUANTUM-SIZE EFFECTS OF COMPOSITE MATERIALS CONTAINING NANOPARTICLES OF METALS

Boymuratov Fakhridin Tog'aymuradovich
Tashkent Institute of Textile and Light Industry,
Tashkent, Uzbekistan

Abdurakhmanov Umarbek
National University of Uzbekistan,
Tashkent, Uzbekistan

Isayev Xamid
Tashkent Institute of Textile and Light Industry,
Tashkent, Uzbekistan

Urazaliyev Roziqjon Turanovich
Tashkent Institute of Textile and Light Industry,
Tashkent, Uzbekistan

ABSTRACT

The interest in nanoobjects can be explained by the fact that reducing materials to nanometer sizes leads to the manifestation of so-called “quantum-size effects” in them, when the sizes of the objects under study are comparable to the de Broglie wavelength of electrons, phonons and excitons. It is found that the percolation-like behaviour of σ and ε , which is observed when the Ni particles are the sizes of 1-3 μm (micro-dispersed particles), gave way to another behaviour characterized by an additional contribution to σ and ε below the percolation threshold when the Ni particles are the sizes of ≤ 30 nm (nanoparticles). This peculiarity of the behaviour of σ and ε of the composites can be explained in the frame of the network hierarchy model of composites, which was proposed recently by Balberg et al.

Keywords: Quantum-size effects, metal-polymer composites; Nanoparticles; Conductivity;

INTRODUCTION

Conductive polymer composites have significant potential for applications, which is stimulating to study the mechanisms of their conductivity [1]. In our previous paper [2] we obtained that, for composites comprising the nickel particles of sizes ≤ 30 nm dispersed in insulating polymer matrix of polyarylate, below the percolation threshold, the measured conductivity differs from that calculated in the frame of the classical percolation theory. In other hand, the electrically conductive polymer composites, for which the dependence of conductivity on the fractional content of filler is in agreement with that predicted by this theory, are known (e. g., the carbon black-polymer composite). In [3], the percolation-like behaviour of the conductivity of the carbon black-polymer composite has been explained by the fact that, in this composite, the radius of the filler particles is greatly superior to the tunnelling range parameter, and only the tunnelling

between nearest-neighbours contribute to the conductivity. In the same work, it is shown that, in the case that the radius of the filler particles are close to the tunnelling range parameter, the conductivity behaviour is bound to be different from that predicted by the classic percolation theory, and, in support of this inference, the dependence of the conductivity on the fractional content of filler for the Ni-SiO₂ cermets has been presented there. The dependence of the conductivity behaviour on the size of the filler content, like that predicted by the conductivity model proposed in [3], has been directly demonstrated by us [4] for composites comprising the Ni particles dispersed in ceramic matrix by measuring the conductivity on samples with the identical composition, but with the different sizes of the Ni particles. In [4], it has also been obtained that the curves of the dependence of conductivity and static permittivity on the fractional content of Ni particles are similar. In this paper we present results of study of the filler particle size influence on the conductivity and permittivity of metal-polymer composites comprising the Ni particles dispersed in the polymer matrix of phenilon.

EXPERIMENTAL

Two types of composites were used for the investigation. One is a metal-polymer composite containing the nanoscale nickel particles. The other is a metal-polymer composite containing the micro-dispersed nickel particles. In both cases the phenilon is used as the polymer matrix. The composite with the nickel nanoparticles was prepared by thermal decomposition of the nickel formiate in the phenilon. The following procedure was used. The powder of the nickel formiate was added to the liquid phenilon prepared by its dissolving in dimetilformamid in the proportion 4 gram of the phenilon to 100 gram of the solvent. After the thorough mixing, the resulting mixture was subjected to heating in order to evaporate the solvent. During the evaporation, applying a powder disperser (UZDN-1, Moscow, Russia), the treatment of the mixture by ultrasound with a frequency of 22 kHz and power of 0.3 w. was used to prevent the aggregation of particles of the nickel formiate powder. The powder formed in consequence of evaporation of the solvent was placed in vacuum and held at a temperature of 373 K to remove a remainder of the solvent. Thereafter the temperature was raised to 573 K, and the powder was held at this temperature over a period of time, which is sufficient for full decomposition of the nickel formiate. In this composite, the sizes of the nickel particles did not exceed 30 nm as this was found by the X-ray diffraction at a glancing angle of incidence using the X-ray camera (KRM-1, Russia)

The composite with the micro-dispersed nickel particles was prepared by mixing the nickel powder with the phenilon in an agate ball mill within 7 h. The nickel powder used was prepared by thermal decomposition of the nickel formiate under vacuum at a temperature of 573 K for 7 h. To determine the sizes of the micro-dispersed particles of the nickel powder, an electron microscope (BS242E, Tesla, Prague, Czech Republic) was used. It was found that the sizes of these particles fell in the range from 1 to 3 μm (Fig. 1).

In both cases called values of the fractional Ni content V in the composites were obtained by the calculation of the source materials used. In order for the electric measurements to be made, samples of composites in form of tablets 15 mm in diameter and 2 mm in thickness were prepared by hot forming.

The conductivity σ was determined by measuring the resistance of the samples. To do this, metal electrodes with a diameter of 13 mm were prepared by vacuum evaporation of aluminium on the flat surfaces of the samples under study. Two meters were used: an ohmmeter for the resistance measurements in the range of 10^1 – 10^{13} Ω (E6-13A, Russia), and an ohmmeter for the resistance measurements in the range of 10^9 – 10^{17} Ω (B7-30, Russia). The obtained values of conductivity exhibited an error of 1%–7%.

The permittivity ε of the composites was determined in the frequency range from 20 to 10^3 Hz by measuring the capacitance of the samples and calculating ε with the formula:

$$\varepsilon(\omega) = \frac{c(\omega)h}{\varepsilon_0 S} \tag{1}$$

where $\varepsilon(\omega)$ is the permittivity at a given frequency ω , $c(\omega)$ is the capacitance of sample at this frequency, h is the thickness of sample, S is the area of the above-mentioned electrodes placed on the flat surfaces of the samples, and ε_0 is the permittivity constant. The capacitance measurements were performed by means of a bridge of capacitors (E8-2, Moscow, Russia) using a sine-wave generator (G3-33, Russia) and a balance indicator (F510, Russia). The obtained values of the permittivity exhibited an error of 2%.

RESULTS AND DISCUSSION

Figure 2 shows the experimental dependences of conductivity σ on the fractional Ni content V for both metal-polymer composites under study. In this figure, the dependences σ on V calculated in the frame of the percolation theory using the formulas cited below are also shown. According to the percolation theory [5,6], the conductivity σ of systems containing metal particles randomly distributed in a dielectric matrix is described by the following formulas:

$$\sigma(V) = \sigma_m (V - V_c)^t \quad \text{for } V > V_c \tag{2}$$

and

$$\sigma(V) = \sigma_d (V_c - V)^{-q} \quad \text{for } V < V_c \tag{3}$$

where σ_m is the conductivity of the metal particles, σ_d is the conductivity of the dielectric matrix, V_c is the critical fractional volume of the metal particles that initiated a first infinite metallic cluster; the parameters t and q are named as critical indexes.

Using boundary conditions ($V=0$ and $V=1$), formulas 2 and 3 can be written in the following form:

$$\sigma(V) = \sigma_m \left(\frac{V - V_c}{1 - V_c} \right)^t \quad \text{for } V > V_c \tag{4}$$

and

$$\sigma(V) = \sigma_d \left(\frac{V_c - V}{V_c} \right)^{-q} \quad \text{for } V < V_c. \tag{5}$$

The theoretical V -dependences presented in Fig. 2 were obtained using formulas 4 and 5. Values of parameters contained in these formulas were found using the following procedures.

Values of V_c were found by differentiation of the experimental $\lg\sigma$ with respect to V (see the insert in Fig. 2). To determine the critical indexes t , the experimental data were presented as an $\lg\sigma\text{-}\lg[(V-V_c)/(1-V_c)]$ plot which is the linear according to formula 4. The value of t is the degree of inclination of this plot. The critical index q for the composite with the micro-dispersed nickel particles was found by the same method starting from the formula 5 (presenting experimental data as an $\lg\sigma\text{-}\lg[(V-V_c)/V_c]$ plot). For the composite with the nanoscale nickel particles, the $\lg\sigma\text{-}\lg[(V_c-V)/V_c]$ plot is nonlinear, and the critical index q is undeterminable using this formula. The values of σ_d and σ_m were obtained by extrapolation of the experimental dependences σ on V to $V=0$ and $V=1$, respectively. Besides, the value of σ_d was determined by electrical measurement [7].

It was found that, for the composite with the micro-dispersed nickel particles, $\sigma_m = 3.2 \cdot 10^2 \text{ OM}^{-1} \cdot \text{M}^{-1}$; $V_c = 0.210$; $t = 1.78$; $q = 1.02$, and, for the composite with the nanoscale nickel particles, $\sigma_m = 4.3 \cdot 10^2 \text{ OM}^{-1} \cdot \text{M}^{-1}$; $V_c = 0.105$; $t = 2.2$. In both cases, the values of σ_d obtained by extrapolation procedure are equal to $1.2 \cdot 10^{-12} \text{ OM}^{-1} \cdot \text{M}^{-1}$ and are in good agreement with the value determined by measurement. The critical index q for the composite with the nanoscale nickel particles was taken to be equal to 1.0, which is true for three-dimensional systems [8,9].

The filler particle conductivity obtained by extrapolation procedure is one order of magnitude less than that for a nickel or for an ideal single-phase material, which is formed from the nickel particles. This is attributable to the distinction of real composite from its model in the percolation theory. In real composite, the filler particles are heterogeneity. They consist from core represent the nickel particles and sheath from the oxide layers (The presence of the latter layer has been observed, for example, in a metal-polymer composite by scanning electron microscopy [1]). To apply the formula 4 to the real composites, the filler particles must be taken as an effective medium with an effective conductivity σ_{meff} . Thus the above values of conductivity obtained by extrapolation procedure are the values σ_{meff} of the filler particles in the composites studied.

As can be seen from Fig. 2, for both types of the metal-polymer composites under study, the agreement between the theoretical and experimental dependences is observed when $V > V_c$. In the case of $V < V_c$, the agreement between the theoretical and experimental dependences is observed for the metal-polymer composite with the micro-dispersed nickel particles only. For the metal-polymer composite with the nanoscale nickel particles, there is an additional contribution to σ in the range below V_c . These results, in the same manner as for the nickel-containing ceramic composites [4], can be understood in terms of the model of the electrical conductivity proposed by Balberg et al. [3,10,11].

According to this model, all metal particles in composites, in which the metal particles randomly distributed in a dielectric matrix, are electrically connected, and the conductivity of these composites is dictated both by the nearest-neighbours tunnelling and by the non-nearest-neighbour tunnelling. The percolation-like behaviour is observed when the contribution of the tunnelling between non-nearest neighbours to the macroscopic conductivity is negligible. It takes place when the radius b of the particles is greatly superior to the tunnelling range (or tunnelling decay) parameter d . In the case where $b \approx d$, the tunnelling between non-nearest neighbours makes a contribution to the macroscopic conductivity along with the nearest-

neighbours tunnelling, and the dependence of the macroscopic conductivity on the fractional content of metal particles is different from that dictated by the classical percolation theory. One can see that the above-described behaviour of the conductivity of the metal-polymer composite under study is consistent with these model predictions.

As is followed from this model, in composites for which a contribution to σ from the non-nearest-neighbours tunnelling takes place, there are two percolation thresholds. One of them observed at high values of V , and it is the above-defined percolation threshold V_c . Another (the additional percolation threshold V_{cd}) was observed at low values of V , and it is a critical fractional volume of metal particles, which initiates a first infinite cluster of tunnelling-connected conductors. Fitting the part (for $V < V_c$) of the experimental curve 1 (Fig. 2) for the metal-polymer polymer composite with the nickel nanoparticles to the functional dependence of Eq. (4) (denoting, in this equation, the percolation threshold as V_{cd} and the critical index as t'), we found that $V_{cd} = 0.05$ and $t' = 3.4$.

In Figure 3, for the metal-polymer composites containing micro-dispersed nickel particles, the frequency dependences of the permittivity $\varepsilon(\omega)$ obtained experimentally in the frequency range between 20 and 1000 Hz is shown. One can see that, with the increase of frequency, $\varepsilon(\omega)$ decreases appreciably at first and slowly thereupon. Such behaviour of $\varepsilon(\omega)$ is explained by the Maxwell-Vagner capacitor model [6,12]. When a constant potential is applied to the metal-polymer composite, there is an accumulation of the free charge at the boundary between the polymer and the filler because their conductivities are different. As a result an additional capacitance arises. If the applied potential is alternating, the charge is accumulated less than in the case of the constant current (the charge has no time to accumulate to the utmost since the current periodically reverse its direction). Therefore, in this case, the additional capacitance and consequently $\varepsilon(\omega)$ is less than in the case of the constant current and it decrease with increase of the frequency.

According to the percolation theory [5, 13] the static dielectric permittivity $\varepsilon(\omega=0)$ of systems containing metal particles randomly distributed in a dielectric matrix is described by the following formulas:

$$\varepsilon(V, \omega = 0) = \frac{\varepsilon_d}{|V - V_c|^q} \tag{6}$$

where ε_d is the static permittivity of the dielectric matrix.

Using boundary conditions ($V=0$ and $V=1$), formula (6) can be written in the following form:

$$\varepsilon(V, \omega = 0) = \varepsilon_d \left(\frac{V_c - V}{V_c} \right)^{-q} \tag{7}$$

In Figure 4, for the metal-polymer composite with the micro-dispersed nickel particles, are shown V -dependences of the static permittivity $\varepsilon(\omega=0)$. These dependences were obtained by calculation with the formula (7) and by extrapolation of the experimental frequency dependences $\varepsilon(\omega)$ (Fig. 3) to the zero frequency. The calculation was performed using the value of V_c obtained from the experimental V -dependence of σ . The static permittivity of phenilon ε_d was taken equal to 3,5.

As is seen from Fig. 4, there is the agreement between the dependences presented in this figure. This fact permits to conclude that V -dependence of the static permittivity of the metal-polymer composite with the micro-dispersed nickel particles on V is described by the percolation theory. This agreement is also the cause to consider the above extrapolation as allowable.

In Figure 5, for the metal-polymer composite with the micro-dispersed nickel particles, are shown the experimental V -dependences of the permittivity $\varepsilon(\omega)$ for two frequency (20 and 1000 Hz). In this figure, are also shown the V -dependences of the static permittivity $\varepsilon(\omega=0)$ obtained by extrapolation of the experimental frequency dependences of $\varepsilon(\omega)$ to the zero frequency and by calculation with the formula (7).

As is seen from Fig. 5, the experimental V -dependences of the static permittivity does not agree with that calculated in the frame of the percolation theory. The experimental dependences show an additional contribution to $\varepsilon(\omega=0)$, like the additional contribution to σ . The fact that there is correlation between the dependences presented in Fig. 5 allows one to conclude that the additional contribution to the static permittivity not is the result of the applied extrapolation procedure. As for the metal-ceramic composites containing the nanoparticles of Ni, the additional contribution to the static permittivity of the metal-polymer composites containing the nanoparticles of Ni can be interpreted as follows [4, 14].

In the metal-polymer composites under study, as V increases, the nickel particles form metallic clusters, which are separated by dielectric material of the matrix. Each pair of the clusters represents a capacitor. In the case of the metal-polymer composite with relatively large nickel particles (micro-dispersed particles), the contribution of non-nearest-cluster-included capacitors to the macroscopic capacitance is negligible, and V -dependence of ε is percolation like [15]. This form of dependence resulted from the fact that the capacitance of the capacitors increases with V (as a result of the decrease in the clusters' separation and an increase of their effective surface) and tends to infinity near the percolation threshold (as a result of formation in continuous metallic network). In the case of the metal-polymer composite with relatively small nickel particles (nanoparticles), the presence of the characteristic feature of V -dependence of ε at the additional percolation threshold V_{cd} considered above allows one to conclude that the non-nearest-cluster-included capacitors contribute to the macroscopic capacitance along with the nearest-cluster-included capacitors [16]. The change of run of curve of dependence of ε on V for this composite in the range of V_{cd} may be attributed to the process of formation of the continuous network of tunnelling-connected conductors.

CONCLUSION

The behaviour of conductivity σ and permittivity ε of metal-polymer composites comprising Ni particles dispersed in the phenilon was studied. It is found that the percolation-like behaviour of σ and ε , which is observed when the Ni particles are the sizes of 1-3 μm (micro-dispersed particles), gave way to another behaviour characterized by an additional contribution to σ and ε below the percolation threshold when the Ni particles are the sizes of ≤ 30 nm (nanoparticles). It is shown that this peculiarity of the behaviour of σ and ε of the composites is in agreement with the network hierarchy model of composites, which was proposed by Balberg et al.

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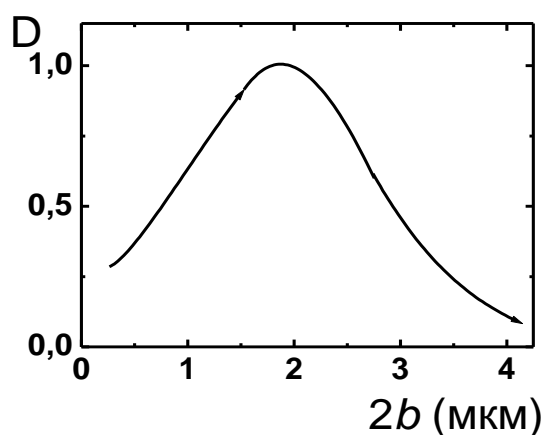


Fig. 1. Size distribution of the micro-dispersed nickel particles in the metal-polymer composites.

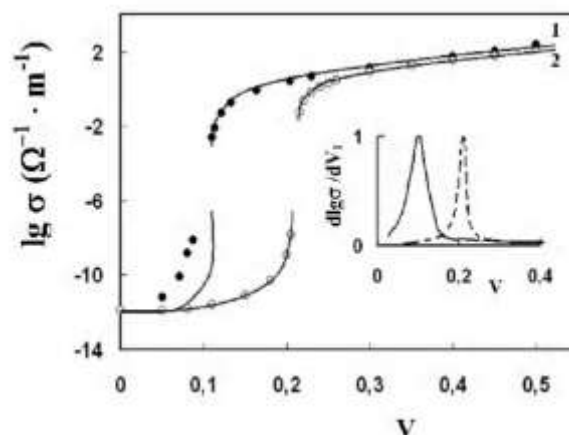


Fig. 2. Comparison of the measured (points) and calculated (solid curves) dependences of the conductivity σ on the fractional Ni content V for the metal-polymer composites containing nanoscale Ni particles (full points, curve 1) and micro-dispersed Ni particles (empty points, curve 2). In the insert are shown plots of the dependence of $d \lg \sigma / dV$ on V (the solid line is for the composite containing nanoparticles, the dashed line is for the composite containing micro-dispersed particles).

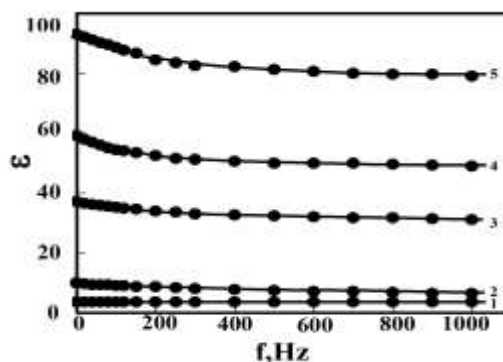


Fig. 3. The experimental frequency dependences of the permittivity $\varepsilon(\omega)$ of the metal-polymer composites containing nanoscale Ni particles 1- фенилон.

Объемная доля наночастицы Ni в композициях: 2 = 0,05; 3 = 0,07;

4 = 0,08; 5 = 0,1

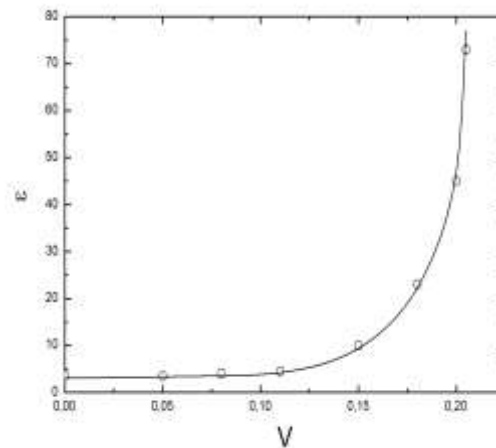


Fig. 4. V-dependences of the static permittivity $\epsilon(\omega=0)$ for the metal-polymer composites containing micro-dispersed Ni particles. V-dependences are obtained by calculations in the frame of the percolation theory (solid curve) and by extrapolation measured data of the frequency dependences of ϵ to the zero frequency (points).

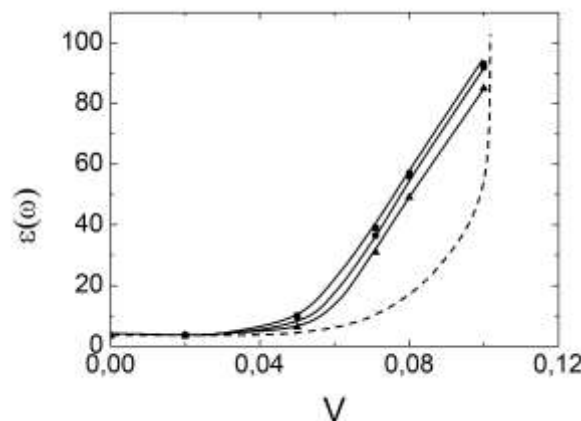


Fig. 5. V-dependences of the permittivity $\epsilon(\omega)$ for the metal-polymer composites containing nanoscale Ni particles. V-dependences are obtained by measurements at frequency 1000 Hz (●) and 20 Hz (▲), by extrapolation measured data of the frequency dependences of ϵ to the zero frequency (○), and by calculations in the frame of the percolation theory (the dashed line).