Macromol. Symp. **2003**, *198*, 461-472

Structure and Dielectric Properties of a Thermoplastic Blend Containing Dispersed Metal

Haralampos Zois,[1] Yevgen P. Mamunya,[2] Lazaros Apekis[1]*

[1]National Technical University of Athens, Department of Physics, Zografou Campus, 157 80 Athens, Greece
[2]Institute of Macromolecular Chemistry, National Academy of Sciences of Ukraine, Kharkovskoe shausse 48, Kiev 02160, Ukraine

Summary: In the present work broadband dielectric relaxation spectroscopy measurements were employed to investigate the dielectric properties of polymer composites. A polyethylene/polyoxymethylene (PE/POM) thermoplastic blend was used as a matrix, while the inclusions were iron (Fe) particles. For comparison, the two pure polymers- PE and POM- were used as a matrix, too. In the PE/POM-Fe composites, the polymer matrix is two-phase and the filler particles are localized only in the POM phase, resulting in an ordered distribution of the dispersed filler particles within the blend. In PE-Fe and POM-Fe composites, the filler spatial distribution is random. The behaviour of all the composites studied is described in terms of the percolation theory. The PE/POM-Fe composites, based on the PE/POM blend, demonstrate different electrical behaviour compared to that of POM-Fe and PE-Fe systems. The percolation threshold value of the PE/POM-Fe composites was found much lower than that of the other two systems. The results were related to the microstructure of the composites. A schematic model for the morphology of the composites studied has been proposed. This model explains the peculiar behaviour of the PE/POM-Fe composites by taking into account the ordered distribution of the filler particles in a binary polymer matrix. Optical microscopy photographs confirm this model.

Keywords: composite materials, dielectric properties, morphology, percolation

Introduction

Composite materials, consisting of a polymer matrix and dispersed conductive inclusions, is a relatively new, interesting class of materials. The electrical characteristics of such composites are close to the properties of the filler, whereas their mechanical properties and processing methods are typical for plastics.[1] These composites have several advantages over the conventional conductive materials.[2] The electrical and dielectric properties of polymer composites have been the subject of both theoretical and experimental studies over the last decades, due to their wide range of industrial applications.[1-3] At the same time, these materials hold interest from fundamental point of view. They can be considered as typical disordered systems, consisting of randomly distributed inclusions within a polymer matrix.

DOI: 10.1002/masy.200350839

Metal-filled polymer composites have been the subject of extensive research.[1-3] Considerable effort has been expended in the investigation of the structure-properties relationship,[4-7] at molecular and morphological level, which is necessary for designing new materials with desirable properties for specific technological applications.[8-11]

In this work our experimental results on the dependence of the dielectric characteristics on the filler volume fraction and the frequency are reported. A thermoplastic polymer blend (PE/POM) was used as a matrix, while the dispersed filler was iron (Fe) particles. For comparison, the two pure polymers- PE and POM- were used as a matrix, too. Broadband dielectric relaxation spectroscopy measurements were carried out. The behaviour of such systems is described on the basis of the percolation theory.[12-14] The main objective of this work is to study the effect of the polymer matrix on the dielectric properties of the composites. The results were related to the microstructure of the systems and a schematic model was proposed. This model is in good agreement with results of optical microscopy investigations.

Fundamental Aspects

Polymers filled with metal additives have very interesting properties and behaviour. When the filler volume fraction is low, the samples behave as insulators or semiconductors, while for higher metal concentration these materials exhibit conducting behaviour. In order to achieve conduction in such filled polymer systems, conductive pathways of metal particles throughout the polymer matrix are required. This situation is very well known as percolation.[12-14] The electrical percolation phenomenon has been thoroughly studied during the last years. Although many experimental works study this phenomenon, no general theory exists, that can satisfactorilly describe all experimental results. Several theoretical models and mixing rules have been proposed to describe the percolation phenomenon in binary mixtures. They include statistical percolation, thermodynamic, geometrical and structure-oriented percolation models. A detailed discussion on these models can be found in the review paper published by Lux.[15]

By gradually increasing the filler content in a metal-polymer composite, the most significant changes on the electrical and dielectric properties occur in a certain, relative narrow critical region of the filler volume fraction; the so-called percolation threshold, P_C. Percolation theory[12-14] predicts that the dielectric characteristics fulfill, in the critical region near the threshold, the following universal power-laws:

$$\varepsilon' \propto \left(P_C - P\right)^{-s} \qquad \text{for } P<P_C \qquad (1)$$

$$\text{and} \qquad tan\,\delta \propto (P_C - P)^{-r} \qquad \text{for } P<P_C \qquad (2)$$

where s, r are the dielectric permittivity and dielectric loss tangent critical exponents, P is the filler volume concentration and P_C is the percolation threshold.

The values of the critical exponents, s and r, depend only on the lattice dimensionality and not on its geometrical characteristics.[14] In particular, for three-dimensional structures, values of s=0.7-0.9 have been reported.[12, 13] Divergence of the critical exponents values from the theoretical ones can be attributed to the non-random (ordered) distribution of the filler particles within the host matrix.[16] On the other hand, percolation threshold value depends on many factors, such as the size, the shape and the spatial distribution (topology) of the filler particles within the polymer matrix, the adhesion and the interactions between the two phases and the processing method.[5, 17-20] The influence of these factors on the percolation threshold values has been discussed in details elsewhere.[1, 5, 11, 17-20]

Experimental

Composite materials, consisting of polyethylene/polyoxymethylene (PE/POM) polymer blend as a matrix and dispersed iron (Fe) particles as inclusions, were studied. For comparison, the two pure polymers- PE and POM- were used as a matrix, too. The iron particles were of R-10 type with an average size of 3.5 μm and shape close to spherical. The filler volume fraction varying in a wide range (0-40 % vol. Fe). PE/POM-Fe composites were prepared in a two-step procedure. First, a master batch of the less viscous polymer (POM) with iron particles was prepared. The filler content in the master batch was 32 % vol. Fe. Then the grinded master of POM-Fe was mixed with the other polymer (PE) at the necessary ratio and extruded. The samples were obtained by hot pressing of the grinded extrudates. PE-Fe and POM-Fe composites were prepared by extrusion of the mechanical mixture of the thermoplastic polymer and the iron powder. The samples were disc-shaped with diameter of 30 mm and thickness of about 1.5 mm.

Broadband dielectric relaxation spectroscopy measurements[21] of the complex dielectric permittivity: $\varepsilon^* = \varepsilon' - i \cdot \varepsilon''$ in the frequency range 10^{-2}-10^{6} Hz were carried out at room temperature using a Frequency Response Analyzer (Schlumberger, FRA 1260) supplemented by a buffer amplifier of variable gain (Chelsea Dielectric Interface). A two-terminal parallel-plate capacitor dielectric cell with gold-coated metal electrodes (Novocontrol) was used.[22]

Optical microscopy investigations of the composites were carried out by means of a BIOLAR microscope via light transmission through thin sections of the samples, which were cut with thickness above 10-20 μm.

Results and Discussion

Figure 1 presents the dependence of the dielectric permittivity, ε′, at the constant frequency of 1 kHz on the filler concentration, P, measured at room temperature for all the composites studied. The sharp increase of the ε′ values when the filler content reaches the critical P_C value is clearly observed. This behaviour is similar for the concentration dependence of the dielectric loss tangent, too (not presented here). This increase is characteristic for the existence of percolation phenomenon in composite materials.

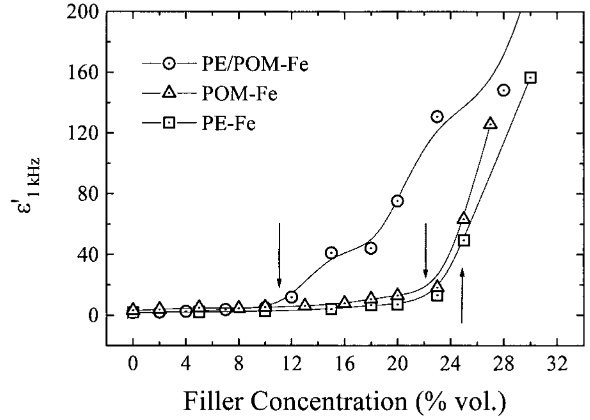


Fig. 1. Dielectric permittivity, ε′, obtained at a constant frequency equal to 1 kHz and at room temperature as a function of the filler concentration, P, for all the composites studied. The arrows indicate the percolation threshold values. The lines are to guide the eye.

Another interesting point, which is worth mentioning, is that, for filler concentration higher than 10 % vol., the PE/POM-Fe composites have higher values of the dielectric permittivity, compared to that of PE-Fe and POM-Fe composites. This means that, in the PE/POM-Fe composites, direct contacts between adjacent metal particles exist at lower filler concentration and at lower conductivity values, than in the other two composites.

Eqs. (1) and (2) suggest that plots of logε′ (or logtanδ) as a function of the logarithm of the reduced filler concentration, $\log[(P_C\text{-}P)/P]$, should be straight lines with slopes equal to the critical exponents s and r, respectively. These linear relations are shown in Figure 2. For the PE/POM-Fe composites, least-square best fitting lines give: P_C=11 % vol. Fe, s=0.75 and r=5.1. The results for the other two systems (PE-Fe and POM-Fe) are listed in Table 1 below. The most striking result is that, the percolation threshold values, for PE-Fe and POM-Fe composites, were calculated equal to 22 and 25 % vol. Fe, respectively, which are much higher compared to that of the PE/POM-Fe system. This will be discussed in details later.

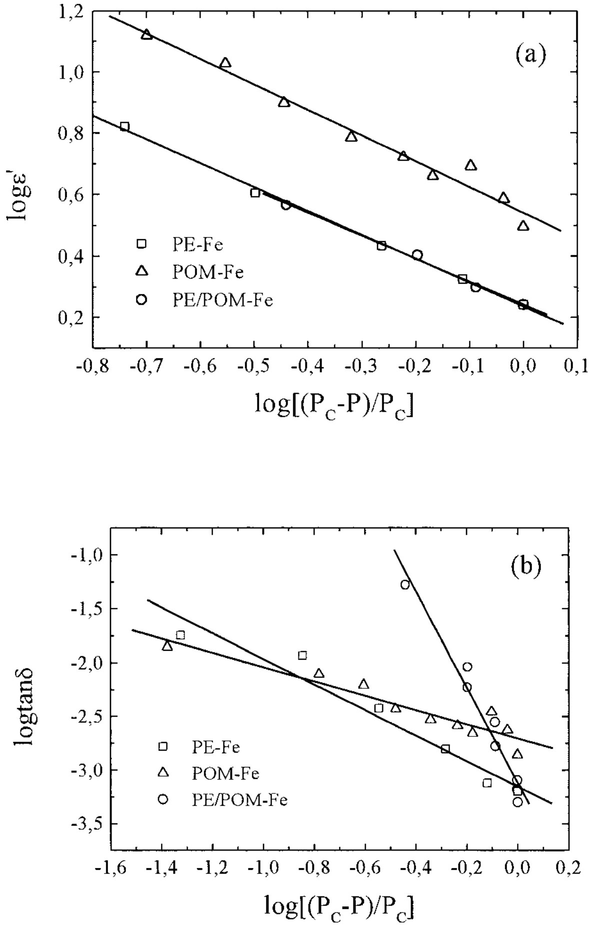


Fig. 2. Linear plots of logε′ (a) and logtanδ (b) as a function of $\log[(P_C-P)/P_C]$ for all the composites studied. The slopes of these lines give the values of the critical exponents s and r, respectively.

For all the composites studied, the values of the critical exponent s (0.75-0.84) were estimated in good agreement with those predicted by the theory ($s_{theor} \cong 0.8$)[12, 13] for systems having random filler distribution, as well as with other experimental values reported for metal-filled polymer systems.[23, 24]

The values of the critical exponent r, for the composites studied, differ each other, but they are in good agreement with the values obtained by dc conductivity measurements.[25] The peculiar micromorphology and the complex structure of the created infinite conductive cluster of the composites based on the PE/POM blend may be responsible for this effect, to be discussed later.

Table 1. Dielectric parameters for all the composites studied.

Composite System	P_C (% vol. Fe)	s	r
PE-Fe	22	0.77	1.6
POM-Fe	25	0.84	0.8
PE/POM-Fe	11	0.75	5.1

The filler volume concentration dependence of the dielectric permittivity, ε′, for PE-Fe and PE/POM-Fe composites at several frequencies is presented in Figure 3. At a given frequency and for filler contents below the percolation threshold, only moderate changes to the dielectric permittivity values occur. A sudden increase to the dielectric permittivity values over 2-3 orders of magnitude is clearly observed, when the iron concentration aproaches the percolation threshold, P_C. This increase is more intense for the lower frequencies, indicating the strong contribution of the metal particles (and the created conductive networks) to the dielectric permittivity of the composites.[24]

At a given filler content below the percolation threshold ($P<P_C$), dielectric permittivity practically does not depend on frequency (ε′ is almost constant for all the frequencies shown). Near the percolation threshold, only negligible changes to the dielectric permittivity values, at the various frequencies studied, are observed. Finally, above the percolation threshold ($P>P_C$), great differences to the dielectric permittivity values, at the various frequencies, are observed. The lower the frequency is, the higher are the dielectric permittivity values. This behaviour is also similar for the POM-Fe composites and the same holds for the dependence of the dielectric loss tangent on the filler volume fraction (not presented here).

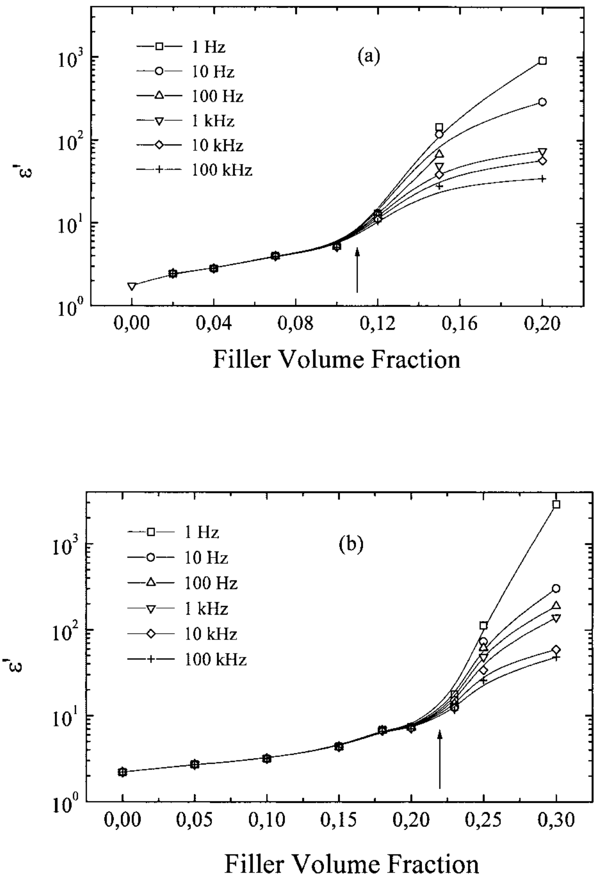


Fig. 3. Dielectric permittivity, ε', as a function of the filler volume fraction for PE/POM-Fe (a) and PE-Fe (b) composites at several frequencies indicated on the plots. The arrows show the percolation threshold values. The lines are guides to the eye.

We also observe that, for the PE/POM-Fe composites, a specific value of the dielectric permittivity is achieved at lower filler volume fraction, compared to that of PE-Fe and POM-Fe systems. Moreover, thermal conductivy studies in these composites showed that the PE/POM-Fe composites possess better conditions for heat transport through its volume, as compared to the other two composites of the same filler.[25] This result is interesting from the point of view of applications of these materials, since PE/POM-Fe composites can be used for absorption of electromagnetic radiation.

It is well known that, the appearance of conductivity in metal-filled polymer systems is determined by the structural features of the composites. One of the most important factors affecting the percolation threshold value is the interactions between the polymer and the metal inclusions.[17] In general, the stronger the interaction is, the slower becomes the creation of the conductive network and, consequently, the higher is the percolation threshold value. This is a possible reason for the different percolation threshold value of PE-Fe and POM-Fe composites. The percolation threshold value is also affected by the spatial distribution (topology) of the metal particles within the host polymer matrix. The percolation threshold value for composites having ordered filler distribution is lower compared to that of systems having random filler distribution.

It follows, from the results listed in the Table, that the percolation threshold value for the PE/POM-Fe composites, which have the PE/POM blend as a matrix, is much lower (P_C=11 % vol. Fe) compared to that of the PE-Fe and POM-Fe systems. The differences observed can be attributed to the peculiar morphology of the PE/POM-Fe composites.

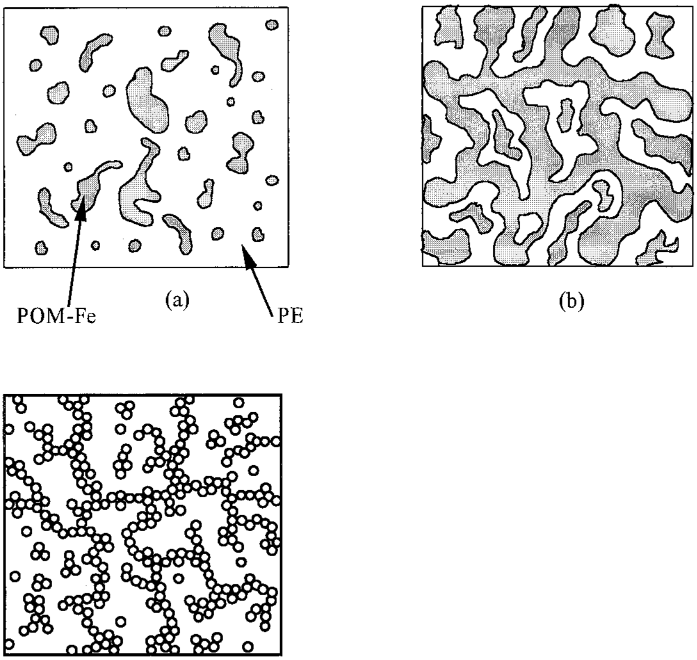
As mentioned above, PE/POM-Fe composites have been prepared in a two-step procedure. First, the metal particles were introduced into one polymer (POM) and then this mixture was diluted by pure PE. Since POM is less viscous than PE, iron particles are localized only in POM and, consequently, they are not randomly distributed within the whole volume of the blend matrix. In that case, PE forms a separate, non-conductive phase, which does not contain iron particles and the filler distribution is now ordered. As a result, the two distinct phases (POM-Fe and PE) create an interpenetrating structure, at comparable concentrations, and the filler distribution is now ordered. Similar morphology with non-random distribution of the filler particles (carbon black) and unusual electrical characteristics have also been observed in composites based on various polymer blends.[20, 26-29]

During the preparation of PE/POM-Fe composites, the iron concentration within the POM phase was always kept constant (32 % vol. Fe), which is higher than the percolation threshold of POM-Fe system (25 % vol. Fe). So, for low filler concentration within the PE/POM blend ($P<P_C$), the dispersed phase is the POM-Fe, creating isolated conductive aggregates within the non-conductive PE phase. For high filler content ($P>P_C$), the conductive POM-Fe clusters come in physical contact each other, creating a continuous conductive network.

In the case of composites having ordered filler distribution, two different filler concentrations can be specified; a local and an average one. In our case, the local filler concentration in the

POM phase is high, so that POM-Fe phase becomes conductive, even if the average filler content within the PE/POM blend matrix may be low.

In order for conductivity to exist in the PE/POM-Fe composites, it is necessary that two conditions are fulfilled: existence of a conductive network of dispersed iron particles into the POM phase and second, continuity of the conductive POM-Fe network within the PE/POM matrix. Sumita and coworkers[28] first proposed the term ''double percolation'' for such an effect in composites with a two-phase polymer matrix. Since, in our case, the POM-Fe phase is conductive, the percolation threshold value of the PE/POM-Fe composites will be defined only by the continuity of the conductive POM-Fe phase.



(a)

(b)

(c)

Fig. 4. The proposed model for the morphology of the composites having ordered (PE/POM-Fe) (a, b) and random filler distribution (PE-Fe or POM-Fe) (c). The filler volume fraction is: $P<P_C$ (a) and $P>P_C$ (b, c).

A schematic model, based on the above-mentioned considerations, has been proposed[25] for the microstructure of the composites studied. The proposed structural model compares the morphologies of the composites having ordered (PE/POM-Fe) and random filler distribution (all the other systems) and is schematically shown in Figure 4. This model explains the much lower percolation threshold value of the PE/POM-Fe composites. As it is seen, in the range $P<P_C$, the filler particles are incorporated in small aggregates located in the volume of one polymer (POM) and these capsules of iron-filled POM are distributed randomly in the PE phase (Figure 4a). When the filler content takes values higher than the percolation threshold ($P>P_C$), the conductive clusters of POM-Fe merge together and a branched structure is created (Figure 4b). On the other hand, PE-Fe and POM-Fe composites have distinctly different structures. For these systems, the filler particles are randomly distributed within the volume of the polymer matrix, both below and above the percolation threshold (Figure 4c).

This structural model is in good agreement with results of optical microscopy investigations, shown in Figure 5. For the PE/POM-Fe composites and at low filler content ($P<P_C$), these composites have ''island'' structure, since the iron particles are localized only in the POM phase (Figure 5a). At higher filler concentration, the conductive POM-Fe clusters merge in a branched continuous structure (Figure 5b) and the PE/POM-Fe composites become now conductive ($P>P_C$). On the contrary, for the PE-Fe composites, the iron particles are situated separately, or in small aggregates, both at low and high filler concentrations (Figure 5c). In both cases, the composites are non-conductive, since these filler contents are below the value of the percolation threshold. This behaviour is similar for the POM-Fe composites having random filler distribution, too. These pictures justify the microstructures proposed by the model.

Percolation theory predicts the values of the percolation threshold, P_C, and the critical exponents for composites with statistical distribution of the conductive particles. The proposed model explains the low values of the percolation threshold by assuming ordered distribution and high local concentration of the conductive filler particles within one of the polymer components.

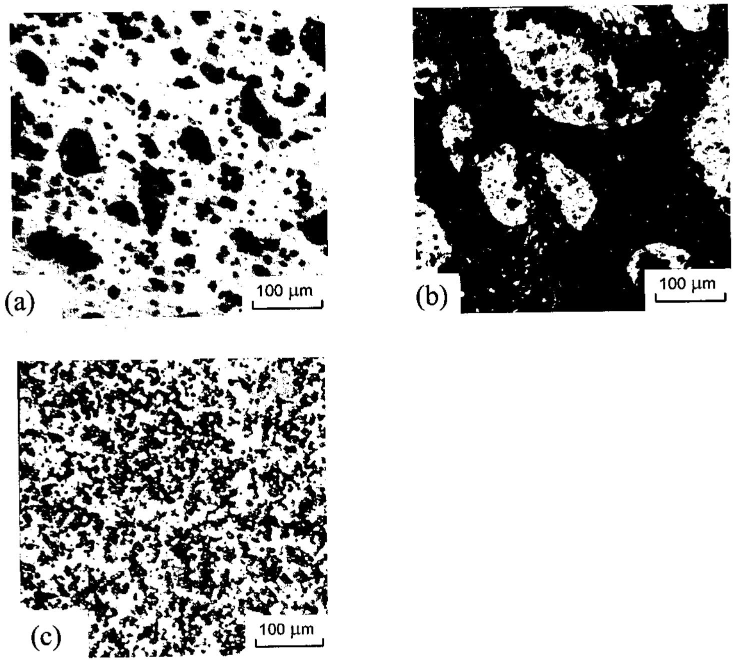


Fig. 5. Optical microscopy photographs of the PE/POM-Fe (a, b) and PE-Fe (c) composites. The filler volume concentration is below (a) and above (b, c) the percolation threshold. These photographs are in agreement with the schematic model presented in Figure 4.

Conclusions

The dielectric properties and the microstructure of various composite materials based on a thermoplastic polymer blend (PE/POM) as a matrix, and iron (Fe) particles as inclusions were investigated in this work. For comparison, the two pure polymers- PE and POM- were used as a matrix, too. In PE-Fe and POM-Fe composites the filler particles are randomly distributed within the polymer matrix, while in the PE/POM-Fe system the filler spatial distribution is ordered. For all the systems studied, the values of the dielectric permittivity critical exponent, s, are in good agreement with the values predicted by the general power-laws of the percolation theory. On the other hand, the percolation threshold value depends on the type of the polymer matrix (PE, POM or PE/POM). This fact is a result of the polymer-filler interaction. For the composites based on the PE/POM polymer blend, the percolation threshold value is much lower, as a result of the peculiar structure of these composites. For such a system, the polymer matrix is two-phase and the dispersed filler particles are localized within one (POM) of the two polymer components. The two distinct phases (the conductive POM-Fe and the nonconductive pure PE) create an interpenetrating network and double percolation phenomenon exists. The local iron concentration within the POM phase is high, whereas the average metal content, on account of the whole volume of the blend matrix, may be low. So, the percolation threshold value is determined by the continuity of the POM-Fe network within the PE/POM blend. A schematic model, proposed for the morphology of the composites studied, explains the different behaviour of the PE/POM-Fe composites. The proposed model is in good agreement with results of optical microscopy investigations.

[1] S.K. Bhattacharya (Ed.), ''*Metal-Filled Polymers, Properties and Applications*'', Marcel Dekker, New York, 1986.
[2] R.H. Norman, ''*Conductive rubbers and plastics*'', Elsevier, New York, 1970.
[3] J. Delmonte, ''*Metal/Polymer Composites*'', Van Nostrant Reinhold, New York, 1990.
[4] R. Pelster, U. Simon, *Colloid Polym. Sci.* **1999**, *277*, 2.
[5] E.P. Mamunya, V.V. Davidenko, E.V. Lebedev, *Polym. Compos.* **1995**, *16*, 319.
[6] H.S. Gokturk, T.J. Fishke, D.M. Kalyon, *IEEE Trans. Magn.* **1993**, *29*, 4170.
[7] J. Yacubowicz, M. Narkis, S. Kenig, *Polym. Eng. Sci.* **1990**, *30*, 469.
[8] G. Boiteux, J. Fournier, D. Issotier, G. Seytre, G. Marichy, *Synth. Met.* **1999**, *102*, 1234.
[9] R. Strumpler, *J. Appl. Phys.* **1996**, *80*, 6091.
[10] R.A. Crossman, *Polym. Eng. Sci.* **1985**, *25*, 507.
[11] D.M. Bigg, D.E. Stutz, *Polym. Compos.* **1983**, *4*, 40.
[12] S. Kirkpatrick, *Rev. Mod. Phys.* **1973**, *45*, 574.
[13] D. Stauffer, ''*Introduction to Percolation Theory*'', Taylor and Francis, London 1985.
[14] R. Zallen, ''*The Physics of Amorphous Solids*'', Wiley, New York, 1973.
[15] F. Lux, *J. Mater. Sci.* **1995**, *28*, 285.
[16] Ye.P. Mamunya, V.V. Davidenko, H. Zois, L. Apekis, A.A. Snarskii, K.V. Slipchenko, *Polym. and Polym. Compos.* **2002**, *10*, 219.
[17] E.P. Mamunya, V.V. Davidenko, E.V. Lebedev, *Compos. Interf.* **1997**, *4*, 169.
[18] Ye.P. Mamunya, *Macromol. Symp.* **2001**, *170*, 257.
[19] Ye.P. Mamunya, Yu.V. Muzychenko, P. Pissis, E.V. Lebedev, M.I. Shut, *J. Macrom. Sci.-Phys.* **2001**, *B40*, 591.
[20] Ye.P. Mamunya, *J. Macrom. Sci.-Phys.* **1999**, *B38*, 615.
[21] J.P. Runt, J.J. Fitzgerald (Eds.), ''*Dielectric Spectroscopy of Polymeric Materials, Fundamentals and Applications*'', American Chemical Society: Washington DC, 1997.
[22] H. Zois, L. Apekis, M. Omastová, *Macromol. Symp.* **2001**, *170*, 249.
[23] In-Gann Chen, W.B. Johnson, *J. Mater. Sci.* **1991**, *26*, 1565.
[24] Y. Baziard, S. Breton, S. Toutain, A. Gourdenne, *Eur. Polym. J.* **1988**, *24*, 633.
[25] Ye.P. Mamunya, Yu.V. Muzychenko, P. Pissis, E.V. Lebedev, M.I. Shut, *Polym. Eng. Sci.* **2002**, *42*, 90.
[26] R. Tchoudakov, O. Breuer, M. Narkis, A. Siegmann, *Polym. Eng. Sci.* **1996**, *36*, 1336.
[27] O. Breuer, R. Tchoudakov, M. Narkis, A. Siegmann, *J. Appl. Polym. Sci.* **1999**, *73*, 1655.
[28] M. Sumita, K. Sakata, Y. Hayakawa, S. Asai, K. Miyasaka, M. Tanemura, *Colloid Polym. Sci.* **1992**, *270*, 134.
[29] F. Gubbels, S. Blacher, E. Vanlathem, R. Jerome, R. Deltour, F. Brouers, Ph. Tessyie, *Macromolecules* **1995**, *28*, 1559.