

Dielectric Properties and Morphology of Polymer Composites Filled with Dispersed Iron

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ABSTRACT: The dielectric properties and the structure of various metal–polymer composites, based on a polymer matrix of polyamide (PA), polyethylene (PE), polyoxymethylene (POM), or blend PE/POM filled with dispersed iron (Fe) particles, have been investigated in this work. In PE–Fe, PA–Fe, and POM–Fe composites the filler spatial distribution is random. 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. The concentration and frequency dependence of the dielectric permittivity, ϵ' , and the dielectric loss tangent, $\tan\delta$, are described in terms of the percolation theory. The experimental values of the critical exponents (namely, s , r , and y) are in good agreement with those predicted by the theory for the composites with

random filler distribution. The PE/POM–Fe composites demonstrate low value of the percolation threshold, P_C , and high values of the critical exponents r and y . This is attributed to the specific structure of these composites. A schematic model for the morphology of the composites studied has been proposed. This model explains the peculiar behavior of the PE/POM–Fe composites by assuming ordered distribution of the filler particles in a binary polymer matrix. The proposed model is in good agreement with the results of optical microscopy. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 3013–3020, 2003

Key words: composites; percolation; dielectric properties; morphology; structure–property relations

INTRODUCTION

Composite materials, consisting of a polymer matrix and dispersed conductive inclusions (such as metal particles, carbon black, graphite, or conducting fibers), are an interesting, relatively new class of materials with many applications. 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, including processability, flexibility, light weight, ability to absorb mechanical shock.² The electrical and dielectric properties of composite materials have been the subject of both theoretical and experimental studies over the last decades due to their wide range of industrial applications.^{1–3} These composites can be used as antistatic materials and in applications such as switching devices and devices for surge protection and for electromagnetic

interference shielding of electronic equipment. At the same time, these materials hold our interest from a fundamental point of view. They can be considered as typical disordered systems, consisting of randomly distributed inclusions within a polymer matrix.

Metal–polymer composites have been the subject of extensive research.^{1–3} Considerable effort has been expended in the investigation of the structure–property relationship,^{4–9} at molecular and morphological level, which is necessary for designing new materials with desirable properties for specific technological applications.^{10–14}

In order to achieve conduction in filled polymer systems, conductive pathways of metal particles throughout the polymer matrix are required. The percolation theory^{15–17} is usually used for explaining the behavior of composite materials, although sometimes the experimental results do not agree with the theoretical predictions. 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, relatively narrow critical region of the filler concentration: the so-called percolation threshold, P_C . It is well known that the percolation threshold value depends on many factors, such as the size, the shape, and the spatial distribution of the filler particles within the host polymer matrix, the adhesion and the interactions between the two

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phases, and the processing method.^{18,19} On the other hand, the critical exponents of the equations of the percolation theory depend on the lattice dimensionality.¹⁷

In this work, the dielectric properties of composite materials were studied. Several thermoplastic polymers were used as a matrix, while the filler was iron particles. The dependence of the dielectric characteristics of these polymer composites on the filler volume content and on the frequency was investigated. The main purpose of this work was to study the influence of the polymer matrix and the spatial distribution of the filler particles on the electrical properties of metal-filled polymer composites. The results were related to the microstructure of the composites and a schematic model was proposed. Optical microscopy photographs are compared with this model.

EXPERIMENTAL

Several composite materials, consisting of a polymer matrix and dispersed iron (Fe) particles as inclusions, were prepared. Various thermoplastic polymers, such as high-density polyethylene (PE), polyamide-12 (PA), and polyoxymethylene (POM), were used as a matrix. Melt flow indexes (MFI) were 1.6, 11.7, and 10.9 g/10 min, respectively. Blend PE/POM was also used as a matrix. The dispersed iron was of R-10 type with an average particle size of 3.5 μm and particle shape close to spherical. The filler volume concentration was varied in a wide range (0–40 vol % Fe). PE–Fe, PA–Fe, and POM–Fe composites were prepared by extrusion of the mechanical mixture of the thermoplastic polymer and the iron powder. PE/POM–Fe composites, based on the polymer blend, were prepared in a two-step procedure. First, a master batch of the polymer having the higher MFI (POM) with the iron particles was prepared as mentioned above. The filler concentration in the master batch was 32 vol % Fe. Then the ground master batch of POM–Fe was mixed with the polymer with higher viscosity (PE) at the necessary ratio and extruded. The samples were obtained by hot pressing of the ground extrudates. The specimens were disks 30 mm in diameter and about 1.5 mm thick.

Broadband dielectric relaxation spectroscopy (DRS) measurements²⁰ of the complex dielectric permittivity, $\varepsilon^* = \varepsilon' - i\varepsilon''$ in the frequency range 10^{-1} – 10^6 Hz, were carried out at room temperature using a Schlumberger Frequency Response Analyzer (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.²¹

Dielectric measurements at the constant frequency of 1 kHz and at room temperature were also performed with the ac bridge E8-4 according to Russian standard GOST 22372-77. The dielectric cell was sim-

ilar to the one described above, but with brass electrodes.

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

Dielectric properties

The dielectric behavior, as a function of the filler volume fraction, is similar for all the composites studied. When the filler content is low, the samples behave as insulators or semiconductors, while for higher filler concentration the samples exhibit conducting behavior. The onset of the electrical conductivity is believed to occur as a result of the formation of conductive pathways due to the intimate contact between adjacent filler particles. This situation is very well known as percolation.^{15,16} Although many experimental works study this phenomenon, no general theory exists that can satisfactorily describe all experimental results. Several models have been introduced to explain the percolation phenomenon in binary mixtures. These include statistical percolation,^{15,17,22} thermodynamic,^{23,24} geometrical,^{25,26} and structure-oriented percolation²⁷ models. A review and discussion on these models can be found elsewhere.²⁸

The critical filler volume concentration, at which the conductive network is formed (percolation threshold, P_C), is characterized by a sharp increase of the dielectric permittivity (ε'), the dielectric loss tangent ($\tan\delta$), and the direct current conductivity (σ_{dc}) values. According to Efros and Shklovskii,²⁹ the transition from the nonconductive to the conductive state in a two-phase insulator–conductor system occurs within a narrow volume concentration region of the conductive phase, the so-called smearing region, which coincides with the percolation threshold, P_C . In this region, the theory predicts that the dielectric permittivity takes very high finite (but not infinite) values and that the conductivity of the composites increases over many orders of magnitude.

Figure 1 presents the dependence of the dielectric permittivity, ε' , on the filler volume concentration, P , obtained at the constant frequency of 1 kHz and at room temperature. In the vicinity of the percolation threshold, a sharp increase of the dielectric permittivity values is clearly observed for all the composites studied. Dielectric permittivity increases from $\varepsilon'_p = 2$ –3 for the unfilled polymers up to $\varepsilon' > 100$ for the highly filled ones. This increase is characteristic for two-phase metal–polymer systems. It is related to the existence of conductive clusters, which merge into an infinite conductive cluster during the transition of the system from a nonconductive to a conductive state.

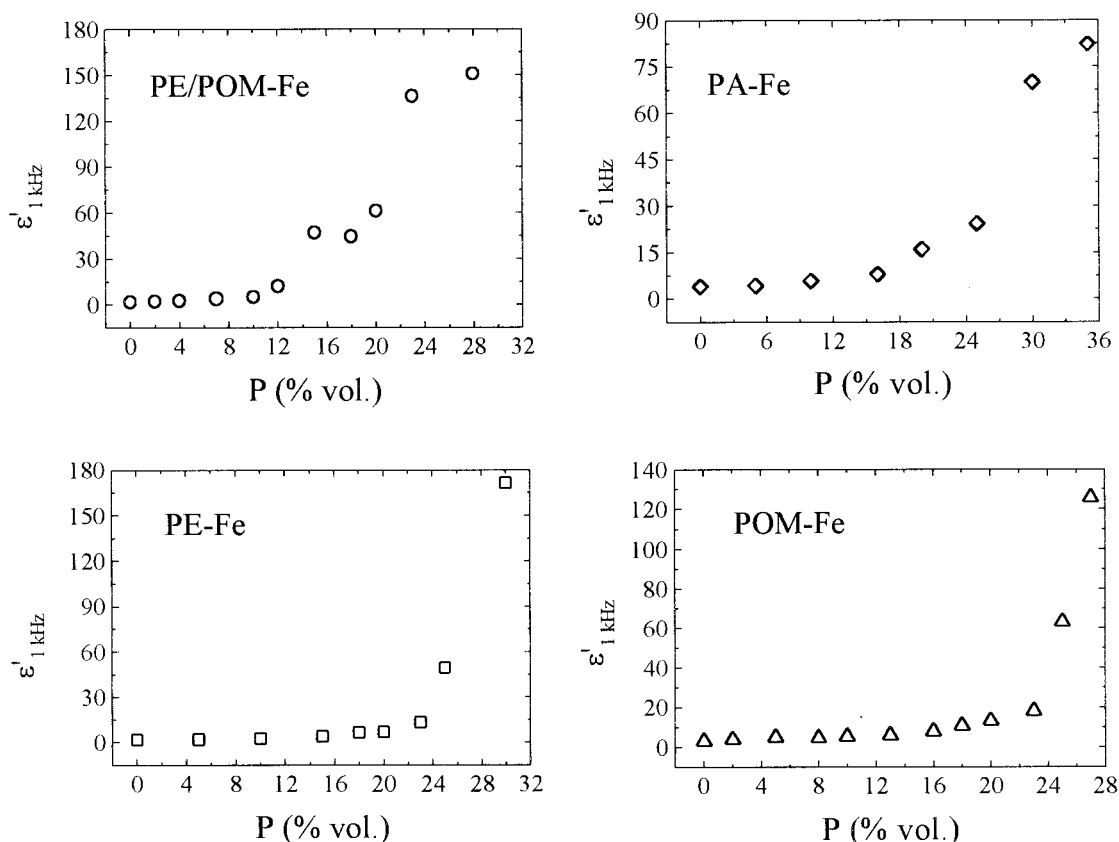


Figure 1 Dielectric permittivity, ϵ' , obtained at the constant frequency of 1 kHz and at room temperature as a function of the filler volume concentration, P .

Percolation theory predicts that ϵ' , $\tan\delta$, and σ_{dc} should fulfill, in the critical region near the threshold, the following universal power laws^{15-17,29}:

$$\epsilon' \propto (P_c - P)^{-s}, \text{ for } P < P_c \quad (1)$$

$$\tan\delta \propto (P_c - P)^{-r}, \text{ for } P < P_c \quad (2)$$

$$\sigma_{dc} \propto (P - P_c)^t, \text{ for } P > P_c \quad (3)$$

where s , r , and t are the dielectric permittivity, the dielectric loss tangent, and the direct current conductivity critical exponents, respectively.

The critical exponents of the equations of the percolation theory depend only on the lattice dimensionality.¹⁷ Percolation theory predicts, in the case of a three-dimensional lattice, values of s and t equal to 0.7–0.8 and 1.6–1.9, respectively.^{15,16} These values do not depend on the details of the lattice geometry.¹⁷ Divergence of the critical exponent values from the theoretical ones can be attributed to the nonrandom (ordered) distribution of the filler particles within the polymer matrix.³⁰ Moreover, according to Chen and Johnson,³¹ these critical exponents are interconnected by the scaling law: $r = t - 2s$.

The percolation threshold, P_c , takes different values for the various composites. It depends on several factors, such as the size, the shape, and the spatial distribution of the filler particles within the host polymer matrix, the adhesion and the interactions between the two phases, and the processing method. The influence of these factors on the percolation threshold values can be summarized as follows.^{1,5,14,18,32} One, the more the shape of the filler particles deviates from the spherical one, the lower is the percolation threshold. Two, as the size of the filler particles decreases, the surface area available for conductive contacts increases relative to the particle volume, thus causing the formation of conductive pathways at lower volume fractions. Three, the stronger the metal–polymer interactions are, the better the polymer wets the filler particles and the higher becomes the percolation threshold. Four, the spatial filler distribution depends on the polymer–filler interactions, the viscosity of the polymer melt, and the method of obtaining the composites. By increasing the degree of segregation, the critical volume fraction is reduced. Consequently, the state of agglomeration of the filler particles affects the percolation threshold value. Five, processing methods have also great influence on the percolation threshold

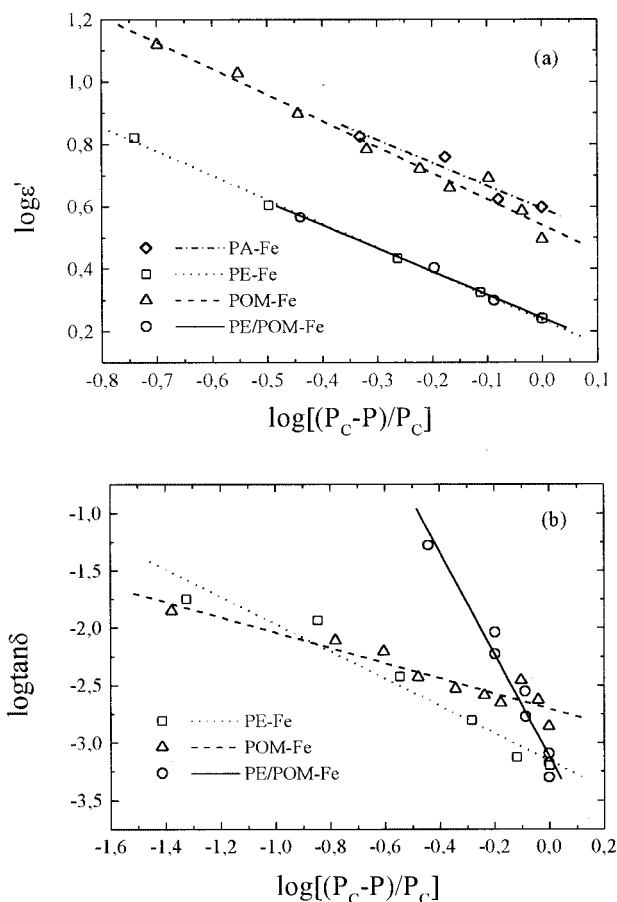


Figure 2 Plots of $\log \varepsilon'$ (a) and $\log(\tan \delta)$ (b) as a function of $\log[(P_C - P)/P_C]$ for the composites studied. The lines are the best fittings according to eqs. (1) and (2). The slopes of these lines are the critical exponents s and r , respectively.

value, since some methods regulate effectively the filler topology (spatial distribution) and, in some cases, ordered filler distribution with low percolation threshold values is formed.

For the composites studied in this work, the percolation threshold values were calculated between 22 and 30 vol % Fe for PE-Fe, POM-Fe, and PA-Fe systems and much lower ($P_C = 11$ vol % Fe) for the PE/POM-Fe composites, to be discussed later.

The relationship between the dielectric permittivity, ε' , and the metal volume fraction, P , near the percolation threshold obeys the power law dependence on the distance from threshold, $P_C - P$, shown in eq. (1).

To determine the value of the critical exponent s , $\log \varepsilon'$ is plotted as a function of the reduced filler concentration, $\log[(P_C - P)/P_C]$ and s is the slope of this linear dependence. These linear relations are shown in Figure 2(a) and the results are listed in Table I. The calculated values of this exponent ($s = 0.74$ – 0.84) are in good agreement with those predicted by the theory ($s_{th} \approx 0.75$).^{15,16,29} Values of $s = 0.6$ – 0.9 have been reported for metal-polymer composites^{31,33} and graphite-filled systems³⁴ as well.

The dependence of direct current conductivity on the filler concentration is given by eq. (3). The values of the critical exponent, t , for these composites have been calculated previously elsewhere.³⁵ The experimental values of t are given in Table I, too. The value of t for PA-Fe, POM-Fe, and PE-Fe composites is almost the same ($t \approx 3.0$) and it is higher than the theoretical value of 1.7, while for the PE/POM-Fe system it is significantly higher ($t = 8.0$). The peculiar micromorphology and the complex structure of the infinite conductive cluster of the composites based on the PE/POM blend may be responsible for this effect.

The concentration dependence of $\tan \delta$ for all the composites studied is described by eq. (2). In the vicinity of the percolation threshold, $\tan \delta$ increases sharply over 2–3 orders of magnitude. The values of the critical exponent, r , are given by the slope of the least-squares fitting line in plots of $\log(\tan \delta)$ vs. $\log[(P_C - P)/P_C]$. These plots are presented in Figure 2(b). The experimental values of r are close to those calculated from the relationship $r_{calc} = t - 2s$ for all the composites studied. The experimental and the calculated values of the critical exponent r are also given in Table I. Similar to the exponent t , r is much higher for the PE/POM-Fe composites than that for the other systems. It means that the energy dissipation, with increasing filler concentration, is higher in the PE/POM-Fe composite system compared to that of the other composites.

Figure 3 presents the frequency dependence of the dielectric permittivity, ε' , in the frequency range $f = 10^{-1}$ – 10^6 Hz for PE-Fe and PE/POM-Fe composites. This dependence is similar for the other systems studied (not presented here). All the composites studied demonstrate a critical behavior near the percolation threshold, P_C . Dielectric permittivity, ε' , of the pure polymer matrix practically does not depend on

TABLE I
Dielectric Characteristics of Polymer Composites Containing Dispersed Iron Particles

Composite	P_C (vol %)	ε'_p	$\tan \delta_p$	s	t^a	r	r_{calc}	y
PE/POM-Fe	11	2.1	4.9×10^{-4}	0.75	8.0	5.1	6.5	0.74
PE-Fe	22	2.1	4.9×10^{-4}	0.77	2.9	1.6	1.4	0.30
POM-Fe	25	3.2	14×10^{-4}	0.84	3.0	0.8	1.3	0.34
PA-Fe	30	3.8	736×10^{-4}	0.74	3.0	1.1	1.5	0.23

^a Values of t are taken from Mamunya et al.³⁵

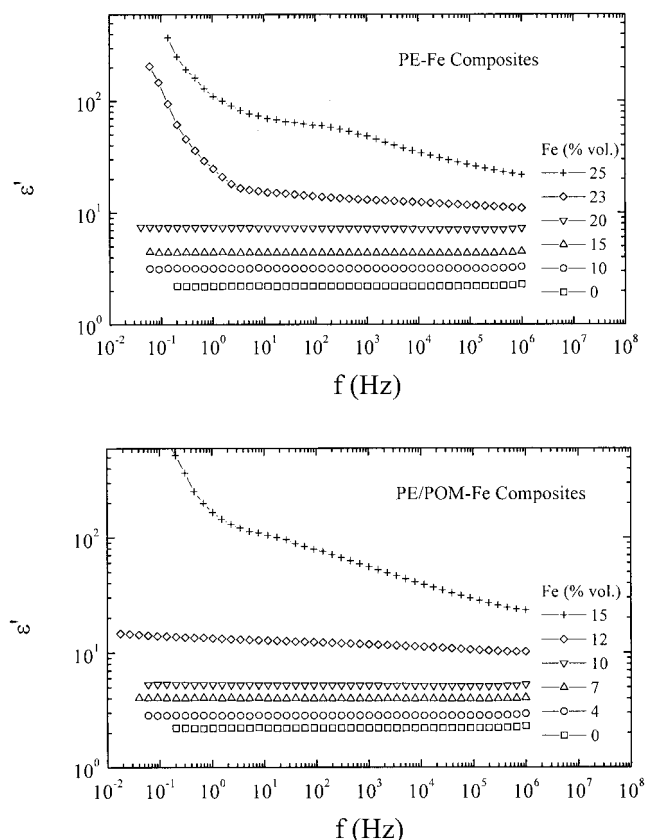


Figure 3 The frequency dependence of the dielectric permittivity, ϵ' , for PE–Fe and PE/POM–Fe composites. The filler concentration is shown on the plots.

frequency in the whole frequency range. The addition of a small quantity of filler does not change significantly the nature of this dependence. Near the percolation threshold, a sharp increase of the dielectric permittivity values is observed, especially in the low frequency region.

Strong frequency dependence of the dielectric permittivity, in the low frequency region, has also been observed,^{30,31,33,34} which has been explained by the possibility of total surface charge reorientation occurring on metallic fillers at low frequencies.⁶ The frequency dependence of the dielectric permittivity is given by^{29,36}

$$\epsilon'(\omega) \propto \omega^{-y} \quad (4)$$

where y is a critical exponent. The theoretically predicted value of the exponent y , for randomly distributed filler particles, is $y = 0.27$.³⁶

The critical exponent y has been calculated, for all the composites, in the low frequency region and for filler concentration equal or slightly higher than the percolation threshold ($P \approx P_C$). The experimental values of the exponent y for PE–Fe, PA–Fe, and POM–Fe composites are equal to $y = 0.23$ – 0.34 , which are close

to the theoretical ones for systems with random filler distribution. These values are given in Table I, too. It is interesting to note that, for the PE/POM–Fe composites, $y = 0.74$, much higher than that for the other systems. This fact is attributed to the peculiar morphology of this system.

Structure–property relationship

It follows from the results listed in Table I that the percolation threshold, P_C , and the critical exponents s , t , r , and y take different values for the various composites studied. In general, the appearance of conductivity in metal-filled polymer systems is determined by the structural features of the composites. So these differences can be attributed to the spatial distribution (topology) of the filler particles and the morphology of the systems under investigation.

As mentioned before, the interactions between the polymer matrix and the metal inclusions affect the percolation threshold value. The stronger the interaction is, the slower is the creation of the conductive network and, consequently, the higher becomes the percolation threshold value. In our case, for the PA–Fe system, higher percolation threshold value ($P_C = 30$ vol % Fe), compared to that of the other composites, has been observed. This can be ascribed to the fact that PA matrix exhibits higher adhesion with the iron particles compared to that of POM and PE. Similar behavior of carbon black-filled polymer composites has also been reported.^{18,32,37,38} In these works, various polymers were used as a matrix and the value of the percolation threshold, P_C , was found to increase in the order of PP, PE, POM, PMMA, and PA.

Another factor affecting the percolation threshold value is the spatial distribution of the metal particles within the polymer matrix. In PA–Fe, PE–Fe, and POM–Fe composites, the filler distribution is random. In the PE/POM–Fe system, where the matrix is the PE/POM blend, the percolation threshold value is much lower compared to that of the other composites. This is due to the peculiar morphology of this system. The PE/POM–Fe composites have been prepared by a two-step procedure. First, the metal particles were introduced into one polymer (POM) and then this mixture was diluted by pure PE. Melt viscosities of PE and POM are significantly different from each other (melt flow indexes are 1.6 and 10.9 g/10 min, respectively). So iron particles remain in the less viscous polymer (POM) and, consequently, they are not randomly distributed within the volume of the sample. The filler distribution is now ordered, since PE forms a separate, nonconductive phase, which does not contain iron particles. As a result, the two distinct phases (POM–Fe and PE) create an interpenetrating structure at comparable concentrations. Similar morphology with nonrandom distribution of the filler particles

(carbon black) and unusual electrical characteristics have also been observed in composites based on various polymer blends.^{32,38–41}

During the preparation of the PE/POM–Fe composites, the iron concentration within the POM phase was kept higher than the percolation threshold of the POM–Fe system. Since the filler particles are localized only in the POM phase, the local filler concentration in this phase is necessarily high for the appearance of conductivity in the POM–Fe phase. Then POM–Fe was mixed with PE and, consequently, the average metal concentration, taking into account the whole volume of the POM/PE blend matrix, may be low. This means that, as a consequence of the preparation procedure, the composites having high iron concentration have also high concentration of POM and low concentration of PE.

For low filler concentration in the PE/POM–Fe composites ($P < P_C$), POM–Fe phase creates small conductive aggregates within the nonconductive PE phase. Consequently, the composites are nonconductive. For high iron content ($P > P_C$) in the PE/POM matrix, the conductive POM–Fe clusters come into physical contact with each other, creating a continuous conductive network.

For the appearance of conductivity in the PE/POM–Fe composites, it is necessary that two conditions are fulfilled: existence of a conductive network of dispersed iron particles in the POM phase, and continuity of the conductive POM–Fe network in the PE/POM blend matrix. The term “double percolation” has been proposed by Sumita et al.⁴⁰ for such an effect in composites with a two-phase polymer matrix. For the systems studied in the present work, the local filler concentration within the POM phase was kept constant (equal to $P = 32$ vol % Fe), which is higher than the percolation threshold of the POM–Fe system ($P_C = 25$ vol % Fe). So the first conductivity condition is always satisfied ($P > P_C$) and, consequently, the percolation threshold value of the PE/POM–Fe composites is determined by the second percolation condition, i.e., continuity of the conductive POM–Fe network within the blend matrix.

A schematic model, based on the above-mentioned considerations, has been proposed³⁵ for the microstructure of these composites. This model could explain the much lower percolation threshold value for the PE/POM–Fe composites. 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 presented in Figure 4. For PE–Fe, POM–Fe, and PA–Fe composites, the filler particles are randomly distributed within the volume of the polymer matrix, both below and above the percolation threshold [Fig. 4(a) and (b)]. On the other hand, PE/POM–Fe composites have distinctly different structure. In the range $P < P_C$,

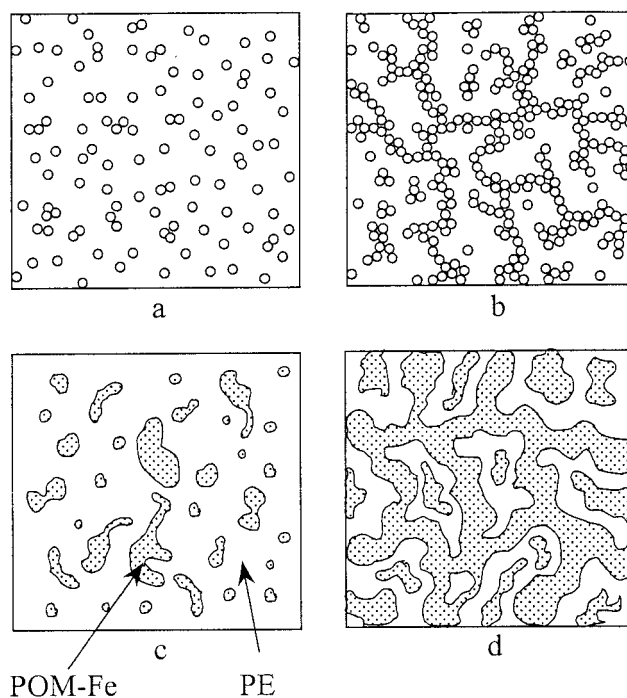


Figure 4 Schematic model for the microstructure of the composites having random [PA–Fe, POM–Fe, and PE–Fe (a,b)] and ordered filler distribution [PE/POM–Fe (c,d)]. The filler concentration is $P < P_C$ (a,c) and $P > P_C$ (b,d).

the filler particles are incorporated in aggregates located in the volume of the one polymer (POM) and these capsules of iron-filled POM are distributed within the volume of PE [Fig. 4(c)]. When the iron concentration becomes higher than the percolation threshold ($P > P_C$) and hence the PE content is low, the conductive clusters of metal-filled POM merge together and a branched structure is created [Fig. 4(d)].

This model is in good agreement with the results of optical microscopy investigations presented in Figure 5. For the PE–Fe composites, the iron particles are situated separately, or in small aggregates, both at low ($P = 5$ vol % Fe) and high ($P = 15$ vol % Fe) filler contents [Fig. 5(a) and (b)]. In both cases, the composites are nonconductive, since these filler concentrations are below the percolation threshold value. This behavior is similar for the other composites having random filler distribution. On the other hand, for the PE/POM–Fe composites and at low filler concentration ($P = 5$ vol % Fe), these composites have the “island” structure, since the iron particles are localized only in the POM phase [$P < P_C$, Fig. 5(c)]. At higher filler content ($P = 15$ vol % Fe), the conductive POM–Fe clusters merge in a branched continuous structure [Fig. 5(d)] and the PE/POM–Fe composites become now conductive ($P > P_C$).

Percolation theory predicts the values of the percolation threshold and the critical exponents for systems

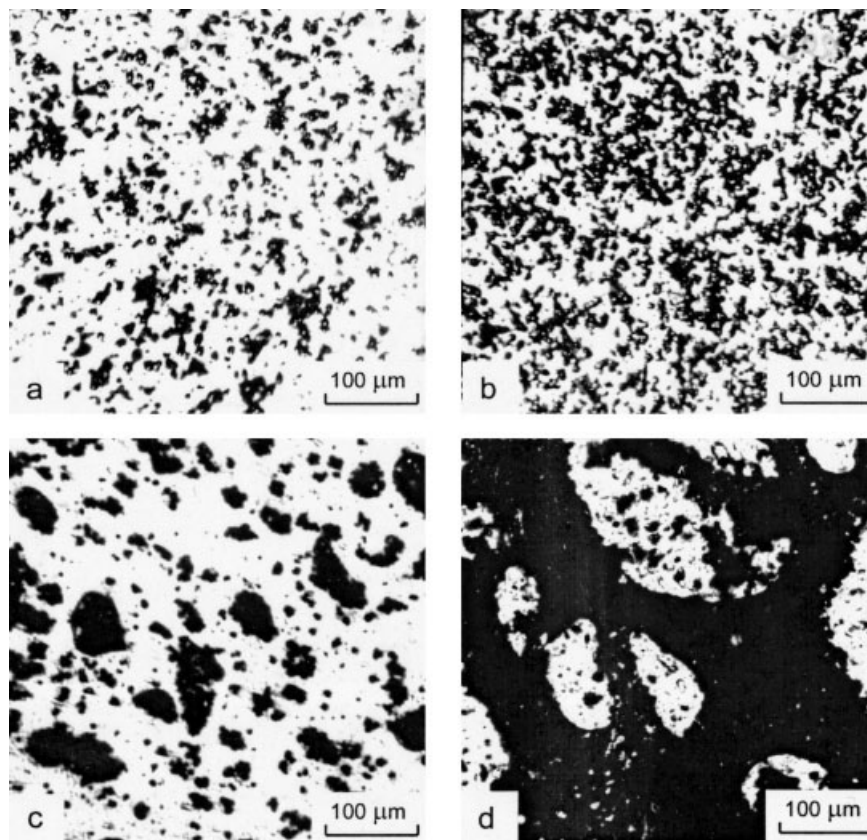


Figure 5 Optical microscopy photographs for the morphology of PE-Fe (a,b) and PE/POM-Fe (c,d) composites at filler concentrations of $P = 5$ vol % Fe (a,c) and $P = 15$ vol % Fe (b,d).

with statistical distribution of the conductive particles. The proposed model explains the low value of the percolation threshold, P_C , and the high values of the critical exponents t , r , and y by assuming ordered distribution and high local concentration of the conductive filler particles within one of the polymer components.

CONCLUSIONS

In this work, the dielectric properties and the morphology of various composite materials based on a thermoplastic polymer (PA, PE, POM, or blend PE/POM) filled with dispersed iron particles were investigated. In PE-Fe, PA-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. The concentration and frequency dependence of the dielectric characteristics are described in terms of the percolation theory. The values of the percolation threshold, P_C , depend on the polymer matrix and increase in the order of PE/POM, PE, POM, PA. The critical exponents of the equations of the percolation theory are close to the theoretical ones for the composites having random filler distribution. On the other hand, PE/POM-Fe

composites, based on the polymer blend PE/POM, demonstrate low values of the percolation threshold and high values of the critical exponents t , r , and y . This is attributed to the peculiar morphology 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. In this case, the two distinct phases (the conductive POM-Fe and the nonconductive pure PE) create an interpenetrating network. The local iron concentration in the POM phase is high, whereas the average metal content, within the whole volume of the blend matrix, may be low. So, the percolation threshold 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 behavior of the PE/POM-Fe composites. The proposed model is in good agreement with results of optical microscopy investigations.

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