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Structure-Electrical Properties Relationships of Polymer Composites Filled with Fe-Powder

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Summary: Structure-properties relationships of composite materials, consisting of a polymer matrix and metal inclusions, is very important for designing new materials with desirable properties. In the present work the electrical and dielectric properties of several composites, consisting of a polymer matrix and iron (Fe) particles as filler, were investigated. Broadband dielectric relaxation spectroscopy measurements were carried out. The electrical behaviour of the composites is described in terms of the percolation theory. Percolation threshold values were calculated and the values of the dielectric permittivity critical exponent were found in good agreement with the theoretical ones. The influence of using different polymer matrices on the physical properties of the composites was also of particular interest. The results were related to the microstructure of the composites and a schematic model was proposed.

Introduction

The electrical and dielectric properties of composite materials based on metal, or other conductive, additives dispersed within an insulating matrix have been the subject of both theoretical and experimental studies, over the last decades, due to their wide range of industrial applications.[1-3] They can be used, as insulating materials with special properties (electrical, mechanical, thermal, etc.), in applications like capacitor films or electronic package materials, etc. As electrically conductive materials, they can be used as a replacement of metals or for electromagnetic radiation shielding. 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. Metal particles[1, 2, 4-6], carbon black[3, 7-12], graphite particles[13, 14] and conducting fibers[15, 16] are some of the fillers, which are widely used in practical applications.

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Metal-polymer composites have been the subject of extensive research.[1-2] These materials are typical representatives of percolative composite systems. The addition of suitable types and concentrations of metal particles results in compounds with conductivities varied in a wide range. Detailed investigations in this field contribute to a better understanding of the structure-properties relationships[8, 16-18] at morphological level, and, thus, for designing new materials with desirable properties for specific technological applications.[19, 20]

In this work our experimental results on the dependence of the dielectric permittivity on the filler content are reported. Several thermoplastic polymers were used as a matrix, while the dispersed filler was iron (Fe) particles. Broadband dielectric relaxation spectroscopy measurements were carried out. The most general theoretical approach which describes the behaviour of such systems is provided by the percolation theory.[21, 22] The electrical conductivity of these materials depends on the filler content, with existence of the percolation threshold. It is well known that the percolation threshold value depends on many factors, such as the spatial distribution of filler particles within the host polymer matrix and the interactions between the two phases, etc.[17, 23] The main objective of this work is to study the effect of the above mentioned factors on the dielectric properties of the composites. The influence of using different polymer matrices on the physical properties of the composites was also studied. The results were related to the microstructure of the systems and a schematic model was proposed.

Experimental

Several composite materials, consisting of a polymer matrix and iron (Fe) particles as inclusions, were studied. As matrix various thermoplastic polymers, polyethylene (PE), polyamide 12 (PA), poly(oxymethylene) (POM) or PE/POM blend, were considered. The iron particles were of R-10 type with an average size of 3.5 μm and volume fraction varying in a wide range (0-40 % vol.). PE-Fe, PA-Fe and POM-Fe composites were prepared by mechanical mixing the two powder components followed by an extrusion. Composites PE/POM-Fe, based on the polymer blend as a matrix, were prepared in two stages. First, a master batch of POM with iron particles was prepared as mentioned above (the filler content in the master batch was 32 % vol.). Then the grinded master batch was mixed with PE powder in the necessary ratio and extruded. The samples were obtained by hot pressing of the grinded extrudates. The samples were disc-shaped with diameter of 30 mm and thickness of about 1.5 mm.

Broadband Dielectric Relaxation Spectroscopy (DRS) measurements[24] of the complex dielectric permittivity: $\varepsilon^*=\varepsilon'-i\cdot\varepsilon''$ were carried out at room temperature in the frequency range 10^{-2}-10^{6} Hz. A Schlumberger Frequency Response Analyzer (FRA 1260) supplemented by a buffer amplifier of variable range (Chelsea Dielectric Interface) and a Hewlett-Packard precision LCR meter, HP 4284A, were used. A two-terminal parallel-plate capacitor dielectric cell with gold-coated metal electrodes (Novocontrol) was used combined with a cryostat and the Quatro Cryosystem (Novocontrol).[7]

Results and discussion

The dielectric behaviour, as a function of frequency and filler concentration, is similar for all the systems studied. As the filler content is low, the samples behave as insulators or semiconductors, while for higher filler concentration the samples exhibit conducting behavior. In the last case, to provide a conductive path throughout the samples, a three-dimensional network of filler particles is required. This situation is very well known as percolation.[21, 22] 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 models have been introduced to explain the percolation phenomenon in binary mixtures. They include statistical percolation[21, 25, 26], thermodynamics[9, 27, 28], geometrical[29, 30], and structure-oriented percolation[31] models. A detailed discussion on these models can be found in the review paper published by Lux.[32]

The critical volume filler concentration, at which a continuous conductive network of macroscopic length is formed (percolation threshold, P_C), is characterized by a sharp increase of many orders of magnitude of the values of the dielectric permittivity, ε'. Percolation theory[21, 22] predicts that the dielectric permittivity fulfills, near the percolation threshold, the following universal power law:

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

where s is the dielectric permittivity critical exponent, P is the filler concentration and P_C is the percolation threshold. The critical exponent, s, depends only on the dimensionality of the system and not on its geometrical characteristics.[21, 22] In particular, for three-dimensional structures, values of s=0.7-0.9 have been reported.[33] Percolation threshold value depends on many factors, such as the size, the shape, and the spatial distribution (topology) of the filler particles within the host polymer matrix, the adhesion and the interactions between the two phases and, finally, the processing method.[14, 23]

Figure 1 gives the dependence of the dielectric permittivity, ε′, at the constant frequency of 1 kHz on the filler concentration, P, measured at room temperature. The sharp increase of the ε′ values, when the filler content reaches the critical P_C value, is clearly observed. This increase is characteristic for the existence of percolation phenomenon in composite materials.

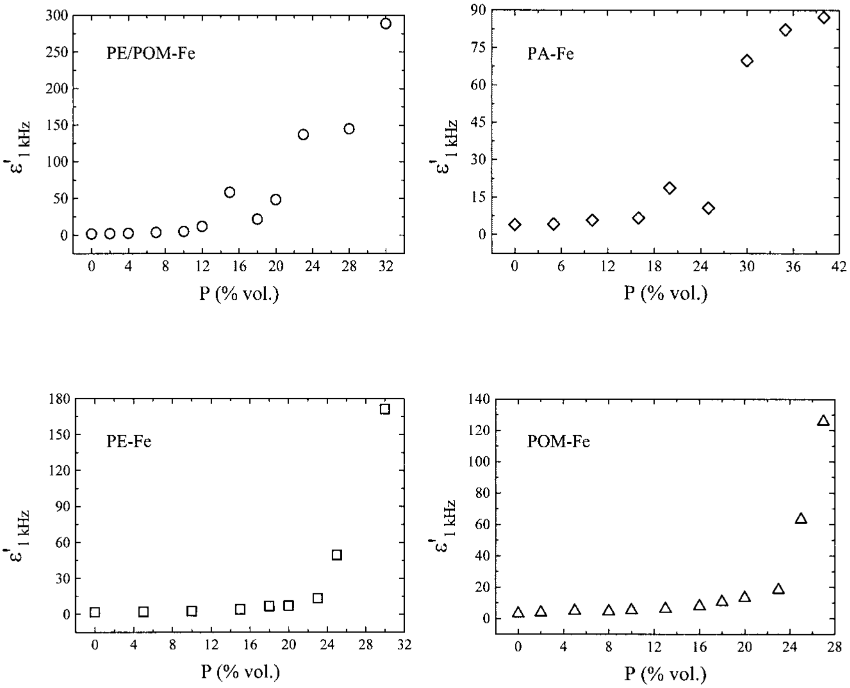

Figure 1. Dielectric permittivity, ε', obtained at constant frequency equal to 1 kHz and at room temperature as a function of the filler volume concentration, P, for all the composites studied.

The values of the percolation threshold, P_C, and the critical exponent, s, have been determined, according to Eq. (1), by the slope of the least-squares fitting line in plots of logε′ vs. log[(P_C-P)/P]. These linear relations are shown in Figure 2 and the results are listed in Table 1 below. The calculated values of the critical exponent (s≅0.74-0.84) were estimated in good agreement with those predicted by the theory ($s_{theor}\cong 0.8$)[21, 22, 33], as well as with other experimental values reported for metal-filled polymer systems.[4-6] The percolation threshold values were calculated between 22-30 % vol. for PE-Fe, PA-Fe and POM-Fe composites and much lower (11 % vol.) for the PE/POM-Fe system.

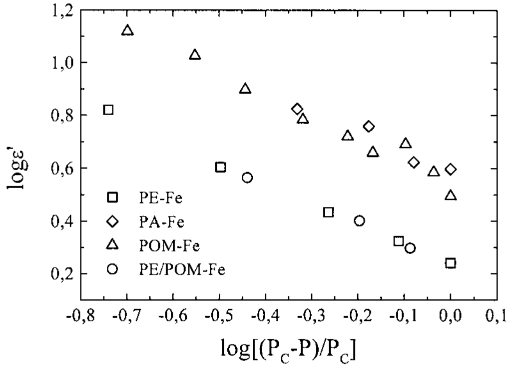

Figure 2. Linear plots of logε′ vs. log[(P_C-P)/P_C] for all the systems studied.

Table 1. Dielectric parameters for all the composites studied.

Composite System	P_C % vol.	s
PE-Fe	22	0.774
POM-Fe	25	0.836
PA-Fe	30	0.737
PE/POM-Fe	11	0.746

The interactions between the polymer matrix and the inclusions affect the percolation threshold value.[23] The stronger the interaction is, the slower is the creation of the required conductive network and, consequently, the higher becomes the percolation threshold value. In our case, for PA-Fe system, higher threshold value (P_C=30 % vol.), compared to that of the other systems, has been calculated. This is attributed to the fact that PA exhibits high adhesion with the iron particles, in contrary with the POM and PE matrices. Similar behaviour has also been reported for carbon black-filled composites. In these composites, the value of the percolation threshold, P_C, has been found to increase in the order of PP-PE-POM-PMMA-PA as the polymer matrix.[9-11, 23]

Another factor affecting the value of the percolation threshold is the different spatial distribution (topology) of the metal particles within the polymer matrix. For PA-Fe, PE-Fe and POM-Fe composites random filler distribution is ensured. It is interesting to note that, for PE/POM-Fe composites, which have the PE/POM blend as a matrix, the percolation threshold value is much lower (P_C=11 % vol.) compared to that of the other systems. This is due to the peculiar morphology of these composites, to be discussed later.

As a result of the processing method, the iron particles are localized only in the POM phase and they are not randomly distributed within the whole volume of the samples. In that case, the filler distribution is ordered, since PE, which is part of the blend, forms a separate, non-conductive phase that contains no filler particles. Hence, the two distinct phases (POM-Fe and PE) create an interpenetrating structure at comparable concentrations. Similar effects have also been observed for various polymer blends filled with carbon black.[10-12, 34]

For low filler concentration in the PE/POM matrix ($P<P_C$), the dispersed phase is the POM-Fe, creating isolated conductive aggregates within the non-conductive PE phase. For high filler content ($P>P_C$), POM-Fe clusters come in physical contact each other, creating a continuous conductive network. Two different filler concentrations can be specified; a local and an average one. The local filler concentration in the POM phase may be high, so that POM-Fe phase becomes conductive, even if the average filler content in the PE/POM matrix is low.

The percolation threshold value depends on two factors: existence of a conductive network of dispersed metal particles into POM phase and second, continuity of the conductive POM-Fe network in the PE/POM matrix. Authors[12] first proposed the term ''double percolation'' for such an effect. During the preparation of PE/POM-Fe composites, the local filler concentration within the POM phase was always constant (32 % vol.), which is higher than the percolation threshold (25 % vol.) of POM-Fe system. Consequently, the percolation threshold value of PE/POM-Fe composites is defined by the continuity of the conductive POM-Fe phase.

A schematic model based on the above-mentioned considerations has been proposed for the microstructure of PE/POM-Fe composites. This model explains the much lower percolation threshold value of these composites and is shown in Figure 3. It is seen that, 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 3a). 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 3b).

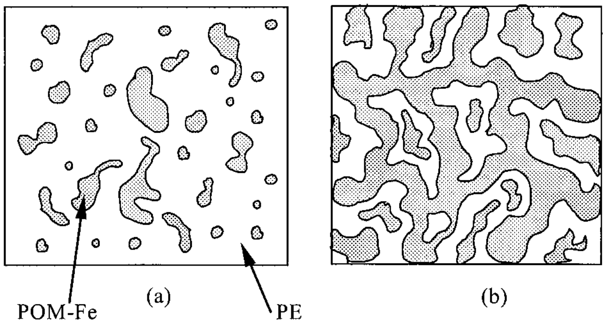

Figure 3. The proposed model for the microstructure of the PE/POM-Fe composites. Filler concentration in the blend matrix is: $P<P_C$ (a) and $P>P_C$ (b).

This structural model is in good agreement results of optical microscopy investigations. These pictures justify the microstructures proposed by this model. More detailed analysis on the electrical properties of these composites and micrographs showing their morphologies will be published soon in another paper being in preparation.[35]

Conclusion

In this work the electrical and dielectric properties of various composite materials, based on a thermoplastic polymer matrix (PA, PE, POM or PE/POM blend) and iron (Fe) particles as inclusions, were investigated. For PA-Fe, PE-Fe and POM-Fe composites, filler particles are randomly distributed within the polymer matrix, while for PE/POM-Fe composites, the filler distribution is ordered. For all the systems studied, the values of the dielectric permittivity critical exponent, s, are in good agreement with those predicted by the general power laws of the percolation theory. On the other hand, the percolation threshold value depends on the polymer matrix and increases in the order PE-POM-PA. This fact is a result of the polymer-filler interaction; the stronger the interaction is, the less completed is the conductive network and, consequently, the higher is the percolation threshold. For composites based on the polymer blend PE/POM, the percolation threshold value is much lower, as a result of the peculiar micromorphology of these composites. The structure of PE/POM-Fe composites is interpenetrating, consisting of a conductive network of POM-Fe and a nonconductive pure network of PE. For such a system, double percolation phenomenon exists and the value of the percolation threshold is defined by the existence of continuity of the POM-Fe phase, because, due to the processing conditions, continuity of the filler particles into POM phase holds for all PE/POM-Fe composites.

Acknowledgements

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