Effect of the Matrix Crystallinity on the Percolation Threshold and Dielectric Behavior in Percolative Composites

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ABSTRACT: Through the use of polyethylenes with different crystallinities as matrices, the effects of the matrix crystallinity on the percolation threshold and dielectric behavior of percolative composites have been investigated. The results suggest that the percolation threshold is negatively related to the matrix crystallinity, whereas the enhancement of the dielectric constant is positively related to the matrix crystallinity. A two-dimensional diagram is proposed to illustrate such relationships. In addition, it has been found that the insulator–conductor transition is much flatter in low-crystallinity-matrix-based composites, and this may be favorable for preparing threshold composites with a high dielectric constant and a low loss tangent. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3359–3365, 2007

Key words: blending; composites; conducting polymers; dielectric properties, matrix

INTRODUCTION

Electrically percolative composites have attracted much attention because they can possess a high dielectric constant at a critical concentration of fillers and thus can have potential applications as electroactive polymers, gate dielectrics, dielectrics for energy-storage capacitors, and so forth.[1,2] Therefore, the development goals for percolative composites are essentially enhancing their dielectric constant while reducing their percolation thresholds to retain good processing of the polymer matrix and low cost. To this end, many investigations have been conducted with different fillers such as metallic fillers,[3] carbon black,[4] conductive polymeric particles,[1] semiconductor particles,[5] and carbon nanotubes.[6] Further research has shown that the microstructure,[5] size distribution,[7] and other physical properties[8] of fillers also have a strong effect on the dielectric behavior of percolative composites. In addition, the dimensions of the fillers may play an important role in the percolation threshold, as evidenced by some recent research.[9] Very recently, a percolative low-loss composite with self-passivated aluminum fillers has also been fabricated, and this makes percolative composites much more practical.[10] However, there is still an interesting phenomenon incompletely investigated: the percolation threshold and dielectric behavior of some percolative composites are fairly different even when their fillers are the same materials of similar sizes.[8,11] Therefore, the effect of matrix materials on the dielectric behavior of percolative composites may have been neglected.

In this article, by employing high-density polyethylene (HDPE) and low-density polyethylene (LDPE) as polymer matrices and iron (Fe) powder as a filler, we disclose the effect of the polymer matrix crystallinity on the percolation threshold and dielectric behavior in percolative composites.

EXPERIMENTAL

Materials

LDPE (112A) from Yanshan Petrochemical Co., Ltd. (Beijing, China), with a melt index of 2.0 g/10 min, and HDPE (6098) from Qilu Petrochemical Co., Ltd. (Zibo, China), with a melt index of 0.1 g/10 min, were used as matrix materials in this study. Reduced Fe powder from Beifang Tianyi Co. (Tianjin, China), with an average diameter of 70 μm (mainly between 50 and 100 μm), was employed as a filler.

Preparation of the composites

Fe/HDPE and Fe/LDPE composites with various Fe concentrations were prepared with physical-blending and hot-pressing procedures. The preweighed Fe powder was mixed with a certain amount of HDPE or LDPE on a Haake 90 rheometer (Vreden, Germany) at 130 and 105°C with a rotor speed of 60 rpm. The mixtures were then molded by hot pressing at 170 and 140°C for the Fe/HDPE and Fe/LDPE composites, respectively, under 10 MPa. The hot molding temperature of both composites was a little bit higher than the melting points of the corresponding polymer matrices to avoid gas cavities in the composites. The final samples were disks with a diameter of 23 mm and a thickness of about 1.5 mm.

Differential scanning calorimetry (DSC) and dielectric characterization

For the dielectric measurements, gold electrodes were sputtered on both sides of each sample. The dielectric behavior of the composites was measured with an Agilent 4294A (Palo Alto, CA) impedance analyzer with a frequency range of 50 Hz to 50 MHz at room temperature (ca. 30°C). The crystallinity of the pure HDPE and LDPE was measured with a Mettler–Toledo (Greifensee, Switzerland) DSC 822^e differential scanning calorimeter at a heating rate of 10°C/min. The DSC measurements were conducted with the ASTM D 3418 standard method, and the samples used for DSC measurements were blended and hot-pressed as all other samples were to eliminate the influence of the preparation procedures on the crystallinity of the polymers.

RESULTS AND DISCUSSION

Crystallinity of the matrices

A polymer is composed of both crystalline regions in which molecules are arranged in regular order and amorphous regions in which molecules are arranged in a random, disorganized state. Polymer crystallinity is the key property of all polymers and indicates the amount of the crystalline region in a polymer with respect to the amorphous content. To determine the crystallinity of a polymer, the measured melting enthalpy (ΔH_f) is compared with the value of a 100% crystalline sample ($\Delta H_{f100\%}$). The crystallinity (α) is given by[12]

$$\alpha = \frac{\Delta H_f}{\Delta H_{f100\%}} \times 100\% \qquad (1)$$

ΔH_f for pure HDPE and LDPE is the integral of the closed region of the corresponding DSC data and, as
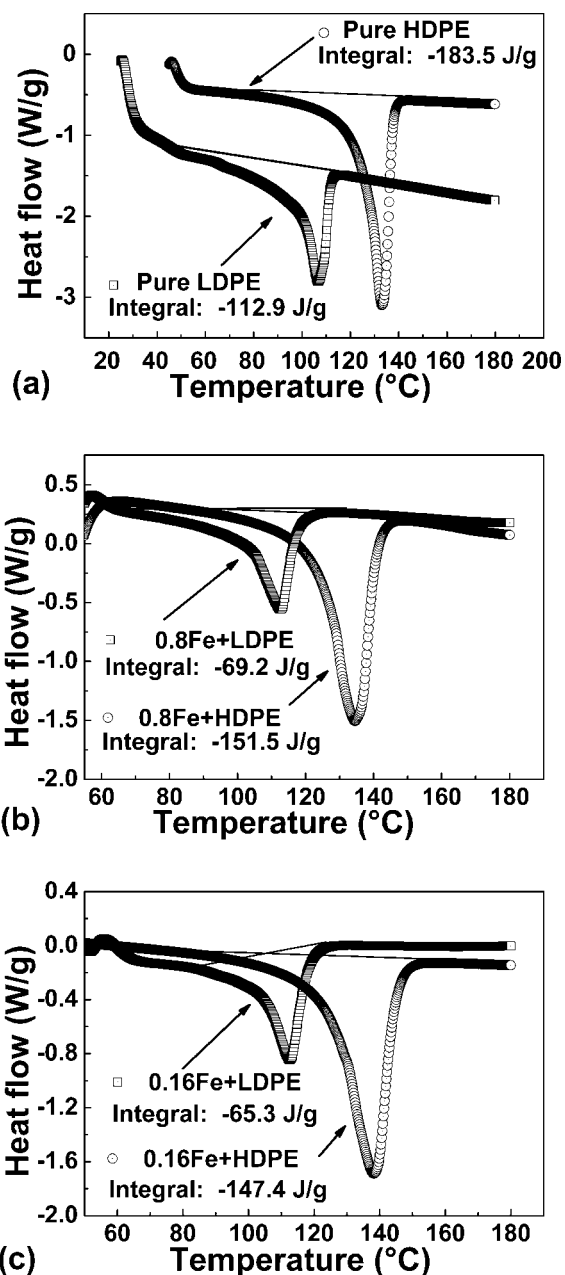

Figure 1 DSC results for (a) pure HDPE and LDPE, (b) Fe/HDPE and Fe/LDPE composites with an Fe concentration of 8 vol %, and (c) Fe/HDPE and Fe/LDPE composites with an Fe concentration of 16 vol %.

shown in Figure 1(a), is 183.5 and 112.9 J/g for HDPE and LDPE, respectively. $\Delta H_{f100\%}$ for both HDPE and LDPE is 293 J/g.[12] Therefore, the crystallinity values of the pure HDPE and LDPE used in this study are 62.6 and 38.5%, respectively, according to eq. (1).

To study the effect of the matrix crystallinity on the percolation threshold and dielectric behavior in percolative composites, the influence of the metallic filler on the matrix crystallinity must first be inves-

tigated to ensure that the relationship between the crystallinity values of the two matrices still remains when dielectric divergence is observed. Therefore, the crystallinity of composites with a low filler fraction (8 vol %) and a high filler fraction (16 vol %, which is close to the percolation threshold) is measured. Figure 1(b) shows the DSC curves of Fe/LDPE and Fe/HDPE composites with an 8 vol % filler fraction, and the calculated crystallinity values are 23.6% and 51.7%, respectively. Although both values decline compared with that of the pure matrix, the relationship between the crystallinity values of the two matrices is still the same; that is, the crystallinity of HDPE is still much higher than that of LDPE. Similarly, the crystallinity values of the two composites with an Fe concentration of 16 vol %, calculated with the DSC data shown in Figure 1(c) according to eq. (1), are 22.3 and 50.3% for the Fe/LDPE and Fe/HDPE composites, respectively. The relationship remains. In addition, the crystallinity of the matrix goes down as the filler concentration increases because the presence of the fillers may impede the crystallization process of the polymers.[13]

Conductivity and percolation threshold

The percolative composites exhibit an insulator–conductor transition at a certain concentration of their conductive fillers (i.e., the percolation threshold). A large enhancement in the conductivity of several orders of magnitude is usually observed near the percolation threshold, indicating the formation of a continuous conductive network in a composite. When the filler concentration is higher than the critical value, the conduction is dominated by percolation and can be characterized by the power law of the percolation theory as follows:[9]

$$\sigma_{eff} \propto (f - f_c)^t \quad \text{for } f > f_c \quad (2)$$

where σ_{eff} is the effective conductivity of the composite, f is the volume fraction of the metallic phase, f_c is the percolation threshold, and t is the corresponding critical exponent.

Figure 2(a) shows the conductivity of the Fe/LDPE and Fe/HDPE composites as a function of the volume fraction of Fe fillers. The insulator–conductor transition can be clearly observed at Fe filler volume fractions of 0.14–0.15 and 0.12–0.20 for the Fe/HDPE and Fe/LDPE composites, respectively. The range of the insulator–conductor transition in the Fe/LDPE composites is much wider that that of the Fe/HDPE composites, and this may indicate that the abruptness of the insulator–conductor transition is in direct
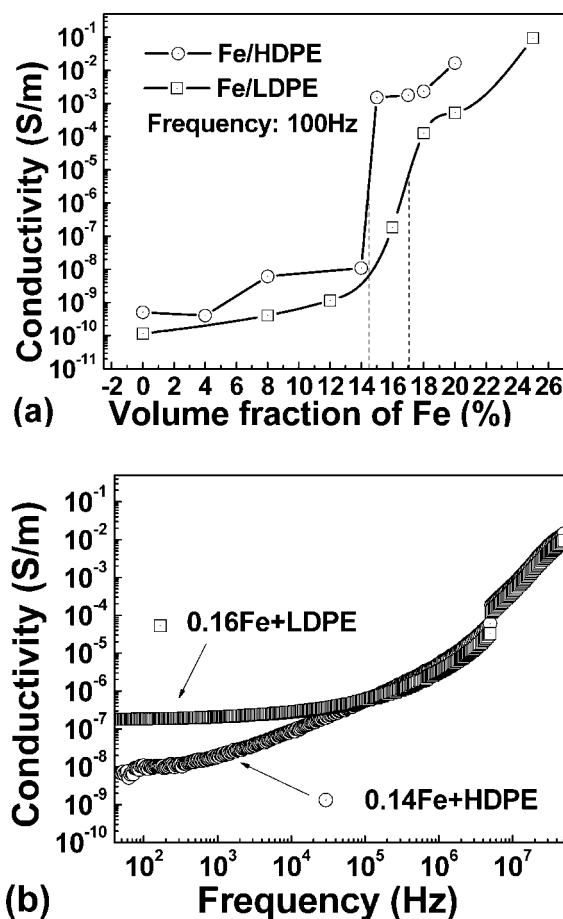

Figure 2 Effective conductivity of Fe/HDPE and Fe/LDPE composites plotted against (a) the Fe volume fraction (measured at 100 Hz and room temperature) and (b) the frequency at room temperature.

proportion to the matrix crystallinity. Such differences in the abruptness of the insulator–conductor transition are quite often observed but have not been noted [e.g. 0.09–0.1[9] and 0.16–0.18[14] for high-crystallinity poly(vinylidene fluoride)-based composites and 0.1–0.2[8] and 0.2–0.3[15] for low-crystallinity-LDPE-based composites]. The abruptness of the insulator–conductor transition is fairly important for applications of the percolative composites because the composites are often fabricated with a filler concentration very close to but lower than the percolation threshold to obtain a high dielectric constant while avoiding a large enhancement of the loss tangent.[6] However, in high-crystallinity-matrix-based composites; such fabrication is hard because the insulator–conductor transition often takes place when the filler concentration varies less than 0.01. In addition, as previously pointed out, it is also risky to prepare such threshold dielectrics because of the intense variations of the dielectric constant near the percolation threshold.[16] Selecting a low-crystallinity polymer as

a matrix for a composite may address these insufficiencies of percolative composites.

The best fits of the conductivity data to the log–log plots of the power laws give f_{c1} = 0.144 ± 0.001 and f_{c2} = 0.170 ± 0.002 for the Fe/HDPE and Fe/LDPE composites, respectively. The results suggest that the percolation threshold of the percolative composites is in inverse proportion to the crystallinity of the matrix. Such a characteristic may be well understood because of the structural features of the polymers. The structure of the crystalline region is highly compact, whereas that of the amorphous region is quite loose; therefore, the conductive fillers can be dispersed only in the amorphous regions, as shown in Figure 3(a). The higher the matrix crystallinity is, the greater the crystalline region is, and the fillers are restrained into a smaller space; this leads to the low percolation threshold in the HDPE matrix composites. Such a process can be quantitatively and schematically illustrated by a two-dimensional diagram, as shown in Figure 3(b,c). The formation of the percolation cluster is much easier when the matrix crystallinity is higher. Despite the differences, the percolation thresholds of both composites are close to the universal value of f_c, 0.16, which is commonly observed in the metal–polymer 0–3 connected composites.[9,14] Therefore, the properties of the fillers play an important role in dominating the percolation threshold of the composites; the crystallinity of the matrix may also have a dramatic effect on the percolation threshold.

Figure 2(b) shows the frequency dependence of the conductivity of the two composites with filler concentrations (14 and 16 vol % for the HDPE- and LDPE-based composites, respectively) close to but lower than the percolation threshold. Commonly, the measured alternating-current conductivity consists of two components, that is, the volume conductivity (direct-current conductivity, which is frequency-independent) and the conductivity contributed by the polarization (frequency-dependent). When the filler fraction of the composites is lower than the percolation threshold, the direct-current conductivity is quite low because of the absence of a continuous conductive network. Therefore, the polarization should be the main conducting factor for both composites. Commonly, the conductivity of a capacitor containing only one insulating component (i.e., pure capacitive) is almost in direct proportion to the frequency, whereas it can be seen in Figure 2(b) that the conductivity of both composites exhibits obvious nonlinearity toward a low frequency. This phenomenon suggests that there should be Maxwell–Wagner–Sillars (MWS) polarization (interfacial polarization) induced by the accumulation of a space charge on the interface between the filler and matrix, which commonly take places in heterogeneous materials composed of com-
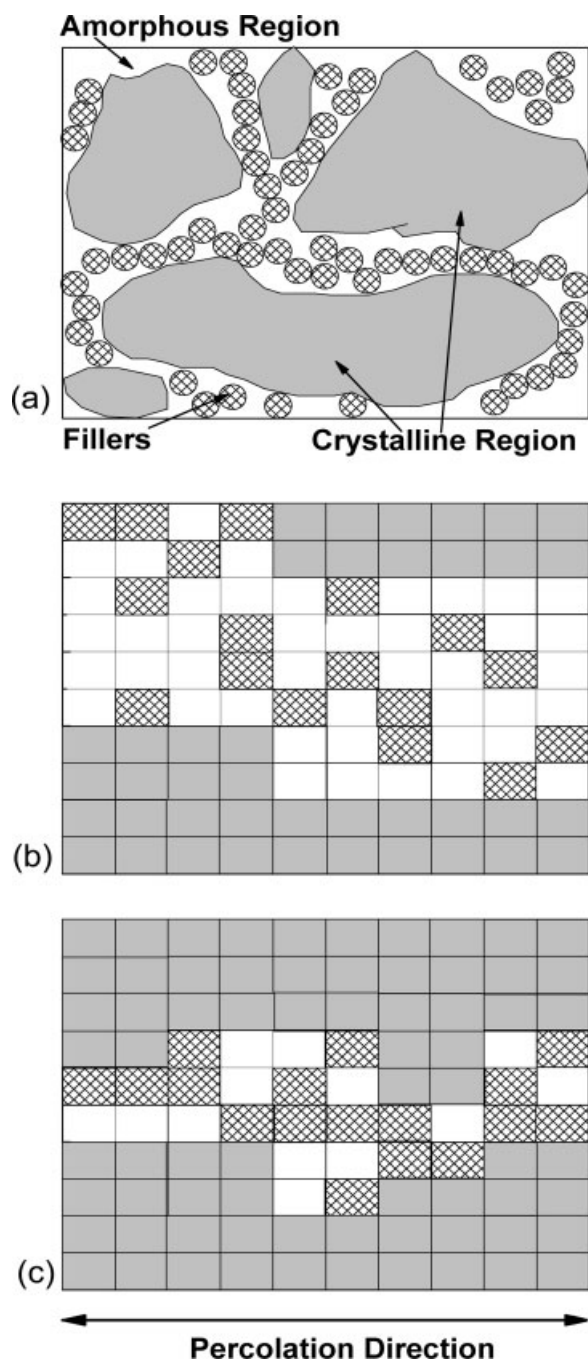

Figure 3 (a) Schematic illustration of the dispersion of the fillers in the polymeric matrix, (b) quantitative scheme of the matrix crystallinity effect on the percolation threshold (assuming the crystallinity is 40% and the filler concentration is 17 vol %), and (c) quantitative scheme of the matrix crystallinity effect on the percolation threshold (assuming that the crystallinity is 70% and the filler concentration is 17 vol %). The gray parts represent the crystalline regions, the white parts represent the amorphous regions, and the reticulate-patterned parts represent the conductive fillers dispersed in the amorphous regions.

ponents with different conductivities. MWS polarization is known to taken place in the frequency range of 10^{-3}–10^3 Hz, which is in good accordance with the data of Figure 2(b). However, neither a trough nor a peak reflecting the setup of the MWS polarization can be observed, and this may indicate that MWS polarization is not the dominating factor for the nonlinearity. Therefore, we propose that, despite the effect of the MWS polarization on the conductivity of the composites, the formation of a network of tunnel junctions based on MWS polarization may be responsible for the nonlinearity in Figure 2(b). It is unique in the composites with metallic fillers. MWS polarization makes two adjacent fillers in the direction of the electric field accumulate different types of charges on their opposite surfaces and form a tiny capacitor, and when the distance between the two fillers is small enough (the content of the filler is large enough), the tunneling effect will occur. Therefore, we propose that MWS polarization is the main conducting mechanism for inorganic (nonmetal)/organic composites toward a low frequency; the MWS-polarization-induced tunneling may be responsible for the conductance in metal/organic composites.

Dielectric constant

The dielectric constant is a key parameter for determining the energy-storage capacity of dielectric materials. It is desirable for us to enhance the dielectric constant of percolative composites to attain better performance from them. A large enhancement in the dielectric constant near the percolation threshold is also considered an important feature of percolative composites. The power characteristic of the dielectric constant of percolative composites is given by the power law of the percolation threshold as follows:[9]

$$\varepsilon_{eff} \propto (f_c - f)^{-s} \quad \text{for } f < f_c \quad (3)$$

where ε_{eff} is the effective dielectric constant and s is the corresponding critical exponent. Figure 4(a) shows the dielectric constant of the Fe/HDPE and Fe/LDPE composites as a function of the volume fraction of the Fe fillers. A large enhancement of the dielectric constant in both composites near the percolation threshold can also be observed as predicted. The dielectric constant increases rapidly near the percolation threshold and up to about 166 and 46 when the Fe volume fractions are 0.17 and 0.20, which are 66 and 25 times larger than that of the pure matrix, respectively, for the Fe/HDPE and Fe/LDPE composites. The dielectric constant of the composites can reach a large value at a lower filler concentration when the matrix crystallinity is higher because of the reduced percolation threshold. The
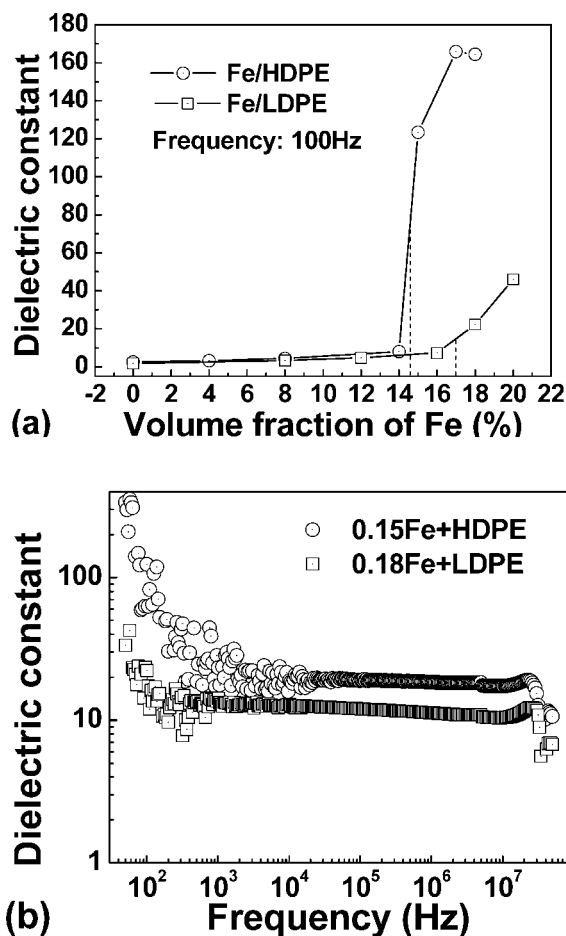

Figure 4 Dependence of the effective dielectric constant of Fe/HDPE and Fe/LDPE composites on (a) the Fe volume fraction (measured at 100 Hz and room temperature) and (b) the frequency at room temperature.

dielectric constants of the Fe/LDPE composites have a lower value near the percolation threshold than many other percolative composites reported (e.g., $\sim$ 300 at 100 Hz,[6] $\sim$ 200 at 100 Hz,[9] and $\sim$ 400 at 100 Hz,[14]), whereas it is quite close to that of carbon-fiber-filled LDPE composites ($\sim$ 45).[15] A similarly low dielectric constant has also been reported for copper-particle-filled LDPE composites.[8]

The dielectric constants of pure HDPE and LDPE are quite close, that is, 2.52 and 1.82, respectively. However, the enhancement of the dielectric constant in the two composites is quite different, and this suggest that the crystallinity may play an important role in the enhancement of the dielectric constant of percolative composites; that is, the enhancement of the dielectric constant of composites with a low-crystallinity matrix may be correspondingly low. Such a divergence can be understood from the origin of the enhancement of the dielectric constant pointed out by Bergman and Imry.[17] In the 0–3 percolative

composites, the fillers form conducting clusters in the matrix, and many clusters will form conducting paths across the whole system when the composites reach the percolation threshold. Each of the conducting paths contributes an extremely large capacitance, and all of them are connected in parallel. The total capacitance of the parallel-connected capacitors is simply the sum of each capacitance, so the total capacitance will be larger when more capacitors are connected. Therefore, the origin of the difference in the enhancement of the dielectric constant can be understood as follows. As can be seen in Figure 3, the distribution of clusters in the high-crystallinity matrix is quite compact, whereas in the low-crystallinity matrix, it is quite loose. Thus, when the composites reach their percolation threshold, the number of conducting paths in the HDPE-based composite may be larger than the number in the LDPE-based composite. The total capacitance of the HDPE-based composite will be higher than the total capacitance of the LDPE-based composite, and this means that the macroscopic dielectric constant of the HDPE-based composite will be correspondingly higher than that of the LDPE-based composite. The percolation thresholds of the composites according to the best fits of the dielectric constant data to log–log plots of eq. (3) are 0.144 ± 0.001 and 0.180 ± 0.002 for the Fe/HDPE and Fe/LDPE composites, respectively. The value for the LDPE-based composites is a little higher than that obtained from the conductivity data, and this may also be a result of the flat insulator–conductor transition.

Figure 4(b) shows the dependence of the dielectric constant of the Fe/HDPE and Fe/LDPE composites with filler concentrations near the percolation threshold on the frequency. The two plots possess nearly the same characteristics, that is, rapidly dropping at a low frequency (50–300 Hz), remaining nearly invariable at an intermediate frequency (300 Hz to 20 MHz), and again rapidly dropping at a high frequency (20–50 MHz). The dielectric constants of the Fe/HDPE and Fe/LDPE composites dropped from about 336 and 33 at 50 Hz to around 43 and 14 at 300 Hz, respectively. Such a rapid drop in the dielectric constant toward a low frequency has been observed previously, and it has been attributed to the large leakage of current resulting from the high conductivity of the composites.[9] However, such a rapid drop may originate from the inherent property of the conducting fillers: the observed dielectric constant of polymer-based composites is usually no more than 1000 at a low frequency (ca. 100 Hz), whereas the dielectric constant of a metallic filler is infinite at a frequency of 0 Hz. Therefore, the drop at a low frequency should be very abrupt. The matrix crystallinity has no obvious effect on the frequency dependence of the dielectric constant of percolative composites.

Loss tangent

Under an alternating electric field, dielectric materials experience energy loss resulting from both conductance and periodic relaxation polarization. When an alternating voltage is applied to a composite, the current contains both an active component and a reactive component, as schematically illustrated in the inset of Figure 5. To describe the energy loss, the loss tangent is introduced; it is defined as the ratio of the active component of the current (I_R) to the reactive component of the current [i.e., the capacitive current (I_C)] in the dielectric, that is, I_R/I_C. Therefore, the loss tangent is mainly dominated by I_R at a low frequency, at which I_C varies little. As mentioned previously, a percolative composite undergoes an insulator–metal transition characterized by an abrupt enhancement of the conductivity at a certain content of the fillers. Such a conductivity enhancement will certainly result in a large exaltation of I_R and thus raise the loss tangent of the composite. Therefore, the loss tangent of the composite should be similar to its conductivity, and the matrix crystallinity should have the same effect on the loss tangent of the composite.

Figure 5 shows the loss tangent of Fe/HDPE and Fe/LDPE composites versus the volume fraction of Fe. Both plots clearly exhibit the same rule with the conductivity measured in Figure 2(a). The insulator–metal transition appears at Fe filler volume fractions of 0.14–0.15 and 0.12–0.20 for the Fe/HDPE and Fe/LDPE composites, respectively, accompanied by enhancements of 4 orders of magnitude in the loss tangent. Such large enhancements in the loss tangent have also been reported for a carbon-nanotube-filled
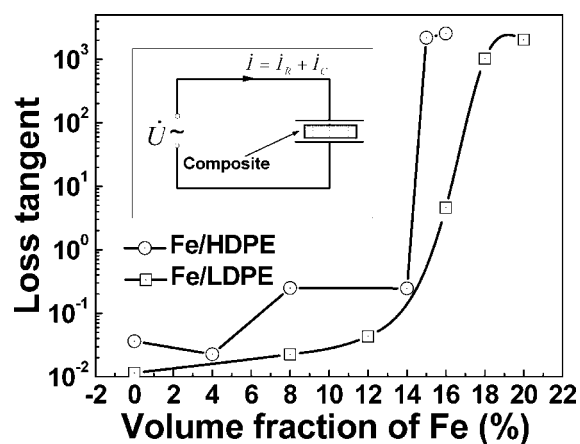

Figure 5 Loss tangent of the Fe/HDPE and Fe/LDPE composites as a function of the Fe volume fraction (measured at 100 Hz and room temperature). The inset is a schematic illustration of the voltage and current in the composites.

composite[6,18] and a magnetite (Fe_3O_4) powder/talc–wax system.[4] The high loss tangent is unfavorable for the application of the composites. To address the problem, much work has been done. Xu and Wong[10] prepared self-passivated aluminum-filled composites,[10] Qi et al.[17] prepared silver/epoxy nanocomposites, and Wang and Dang[6] fabricated threshold composites with filler concentrations very close to but lower than the percolation threshold; all these approaches rendered composites with a high dielectric constant and a low loss tangent.

CONCLUSIONS

We have found that polymer matrices with different crystallinities can have remarkable effects on the percolation threshold and dielectric behavior of their percolative composites. It is proposed that the percolation threshold is in inverse proportion to the matrix crystallinity, whereas an enhancement of the dielectric constant is in direct proportion to the matrix crystallinity. In addition, the insulator–conductor transition is much flatter in low-crystallinity-matrix-based composites, and this may be favorable for preparing threshold composites.

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