Dielectric behavior of a metal-polymer composite with low percolation threshold

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Stainless steel fiber (SSF)/poly(vinylidene fluoride) composite is prepared via simple blending and hot pressing route. The dependence of the dielectric properties of the composite on both volume fraction of the fillers and frequency is investigated. The percolation threshold of the composite, 9.4 vol % (0.094 volume fraction), is much lower than that of the common two phase metal particle-polymer composite. A dielectric constant of 427 is observed at 50 Hz with 10 vol % of SSF.

Large enhancements of the ac conductivity and loss tangent are also observed near the percolation threshold. The dielectric properties are explained by percolation theory while the dielectric anomalies are attributed to the high slenderness ratio of the SSF fillers. © 2006 American Institute of Physics.[DOI: 10.1063/1.2337157]

Electroactive polymers, such as poly(vinylidene fluoride) (PVDF) and its copolymer poly[(vinylidene fluoride)-co-trifluoroethylene] (P(VDF-TrFE)), have become the subject of many intensive investigations recently for their broad applications in electromechanical systems. Traditional approach of enhancing their dielectric constants is to disperse high-dielectric-constant ceramic powder into the polymer matrix randomly. However, the applications of such composites are seriously limited due to their disadvantages such as flexibility loss, low dielectric constant, containlead, etc., giving rise to the focus on the metal-polymer composite. The metal-polymer composite could possess a high dielectric constant at a low filler concentration and thus make it possible to preserve the flexibility of the polymer matrix. Dang et al. reported a Ni-PVDF composite with a dielectric constant of about 400.7 Rao and Wong observed a high dielectric constant of about 2000 in a Ag-flake/epoxy composite.8 Similar composites with different metallic fillers, e.g., Fe, W, Zn, and Cu, are also reported with percolative features.9,10 Qi et al. synthesized a Ag-epoxy composite with Ag fillers of 40 nm in diameter, the composite has a high dielectric constant (>300) while keeping it nonpercolative, which maintains its loss tangent a low value (<0.05).11 In an Al-epoxy composite, a high dielectric constant (~110) and low loss tangent (0.02) were also observed, which could be attributed to tunneling network composed of the self-passivated Al particles with outside thick Al2O3 shells.12 However, the dielectric behavior of the composite with metal fibers as fillers has not been studied.

In this letter, we report a percolative metal-fiber/polymer composite with high dielectric constant at low percolation threshold. Our composite is PVDF based, with cheap and stable stainless steel fiber (SSF) selected as fillers. The SSF, as shown in Fig. 1(a), is mostly rodlike with circular, triangular, or elliptical cross section. The average length and diameter of the SSF are 500 and 30 μm, respectively. The PVDF and SSF are blended together on a Haake 90 rheometer at 170 °C for 10 min. Then the mixtures are molded by hot pressing at 200 °C under 7 MPa. The final samples are disks with a diameter of 25 mm and thickness of about 1.5 mm. Figure 1(b) shows the micrograph of a thick film cut from the final sample, confirming a randomly homogeneous dispersion of the SSF. Gold is sputtered on both sides of the samples as electrodes for the electrical measurement. The dielectric properties are measured using a NOVOControl broadband dielectric spectrometer with an Alpha-A high performance frequency analyzer in the frequency range of 50 Hz–10 MHz at room temperature. The morphology of the SSF and composite is examined by Olympus BX15M optical microscopy.

It is well known that the metal-polymer composite undergoes a metal-insulator transition at a certain concentration of its metallic phase (i.e., the percolation threshold). The transition is often characterized by an abrupt change of conductivity and a divergence of the real part of the dielectric constant. When the concentration of the metallic phase is high enough to form a continuous conductive network, the conductivity of the composite, \( \sigma_{\text{eff}} \), yields to the power law of the classical percolation theory:1,15

\[
\sigma_{\text{eff}} \propto (f - f_c)^t \quad \text{for } f > f_c, \tag{1}
\]

where \( f \) is the volume fraction of the metallic phase, \( f_c \) is the percolation threshold, and \( t \) is the corresponding critical exponent. Figure 2 shows the alternating current (ac) conductivity (hereinafter, the conductivity) of the SSF/PVDF composite as a function of the volume fraction of the SSF (fSSH). An obvious metal-insulator transition was observed at \( f_{\text{SSF}} \approx 0.09–0.1 \). The best fits of the conductivity data to the log-log plots of the power laws give \( f_c = 0.094 \) and \( t = 2.02 \) according to Eq. (1) [see inset (a) in Fig. 2]. The percolation threshold of SSF/PVDF composite, \( f_c = 0.094 \), is much smaller than the value \( f_c \approx 0.16 \) that is commonly obtained in

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the metal/polymer composite with microsized granular fillers. The dimensional singularity (one dimension) and the high slenderness ratio of the SSF compared with the traditional granular fillers (three dimensions) may be responsible for the low percolation threshold of our composite. The critical exponent, $\tau = 2.02$, is in excellent agreement with the universal ones $\tau = 2.0$. When the concentration of the metallic phase is lower than the percolation threshold $f_{c, \text{SSF}}$, a considerable finite enhancement in the conductivity is also observed, which could be explained by the interparticle tunneling. Such tunneling occurs when the effective tunneling range of two fillers overlaps, as schematically illustrated by inset (b) of Fig. 2, which shows the best fits of the conductivity to Eq. (1). (b) Schematic illustration of the interparticle tunneling (Ref. 14).

The frequency dependence of the dielectric constant, which made the composite invalid for applications as well. The power law expresses the enhancement of the dielectric constant near the percolation threshold as follows:

$$\varepsilon_{\text{eff}} \approx (f_c - f)^{-s}$$ for $f < f_c$,  \hspace{1cm} (2)

where $\varepsilon_{\text{eff}}$ is the effective dielectric constant and $s$ is the corresponding critical exponent. The dielectric constant as a function of the volume fraction of SSF exhibits clearly power characteristic as described by the power law. From the inset of Fig. 3 we can get the value $f_c = 0.094$ and $s = 0.36$ according to Eq. (2). The critical exponent here, $s = 0.36$, is lower than the universal ones ($s \sim 1.0$). The low $s$ value in our composites was also observed in a similar percolative system with one-dimension conducting carbon nanotubes. It suggests that the low $s$ value may be caused by the dimensional effect of the SSF, and maybe it is the universal one for the percolative composite with one-dimension fillers.

Figure 4 shows the dependence of dielectric behavior of the SSF/PVDF composite on the frequency at room temperature. The conductivity of the composite in the regime of $f_{\text{SSF}} < f_c$ exhibits a strong frequency dependence while exhibits a rarely weaker dependence in the regime of $f_{\text{SSF}} > f_c$. The characteristics of the conductivity, i.e., low percolation threshold, high conductivity in the regime of $f_{\text{SSF}} > f_c$, and its weak frequency dependence, make the

![FIG. 1. (Color online) Optical micrographs of (a) stainless steel fibers and (b) SSF/PVDF composite with a SSF volume fraction of 0.09.](#)

![FIG. 2. Effective conductivity of the SSF/PVDF composite as a function of the SSF volume fraction, measured at 50 Hz and room temperature. Inset (a) shows the best fits of the conductivity to Eq. (1). (b) Schematic illustration of the interparticle tunneling (Ref. 14).](#)

![FIG. 3. Effective dielectric constant of the SSF/PVDF composite as a function of the SSF volume fraction, measured at 50 Hz and room temperature. The inset shows the best fits of the dielectric constant to Eq. (2).](#)

![FIG. 4. The dependence of dielectric behavior of the SSF/PVDF composite on the frequency at room temperature. The inset shows the best fits of the dielectric constant to Eq. (2).](#)
SSF/PVDF composite excellent antistatic media and shielding for electromagnetic or radio-frequency interference of electronic devices. The power law of the percolation theory gives \[ \sigma_{eff}(\omega, f_c) \propto \omega^n \] as \( f_{SSFs} \to f_c \),

where \( \omega = \frac{2\pi}{\tau} \), \( \tau \) is the frequency and \( n \) is the corresponding critical exponent. The linear fit of the conductivity versus frequency plots at a SSF volume fraction of 0.09 gives \( n=1.04 \), which is inconsistent with the universal ones (\( n=0.70 \)). The dimensional singularity of the SSF and the deviation of 0.004 between \( f_{SSFs}=0.09 \) and percolation threshold \( f_c=0.094 \) may account for this variance. Theoretically, the \( n \) is related to \( s \) and \( t \) by the equation \( u=t/(t+s)^{1.7} \) and according to the equation, the calculated \( u \) value is about 0.85 for our composite. The \( u \) value is close to that of a similar composite with one-dimension nanotube (0.809).\(^1\)

Compared with the universal ones (0.70), a little large \( u \) value in Fig. 4(a) mainly origins from the dimensional singularity of SSF. And the deviation of 0.004 between \( f_{SSFs}=0.09 \) and percolation threshold \( f_c=0.094 \) is also in charge of the large \( u \) value. The frequency dependence of the dielectric constant becomes gradually stronger as the content of the SSF increases. In addition, a rapid drop of dielectric constant of the composites with filler concentrations of 0.10 and 0.11 is observed at 50–100 Hz. From 50 to 100 Hz, the dielectric constant value of both the samples drops from about 400 to around 200, and from 100 Hz towards high frequency (~10 MHz) maintains a slow and steady drop. The rapid drop in dielectric constant may be attributed to the large leakage current resulted from the high conductivity of the composites. When \( f_{SSFs}>f_c \), the loss tangent of the composite undergoes a sharp increase at low frequency as reported by Wang and Dang,\(^1\) while maintains a value under 1 at high frequency (>500 kHz). Such increase of the loss tangent is the inevitable consequence of the significantly raised conductivity in the composite and could be considered as one important feature of the percolative composite. Therefore, the very high loss tangent (~1000) near 100 Hz may also be considered as the evidence of the large leakage current in the composites. For the composite of \( f_{SSFs}<f_c \), the loss tangent is less than 0.3, irrespective of the frequency.

In conclusion, the dielectric behaviors of SSF/PVDF composite were investigated as a function of frequency and volume fraction of the SSF, respectively. The composite possesses a low percolation threshold of 9.4 vol %, which can be attributed to the high slenderness ratio of the SSF. The conductivity and dielectric constant increase rapidly when the content of SSF is more than 9 vol %, accompanied with a significantly enhanced loss tangent. Such percolative composite could be employed as both high-dielectric-constant material and conductive polymer.

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