

# High Dielectric Constant and Superparamagnetic Polymer-Based Nanocomposites Induced by Percolation Effect

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**ABSTRACT:** To obtain the high dielectric constant and superparamagnetic composites for application in dielectric energy storage capacitors and other electromagnetic devices, the Fe<sub>3</sub>O<sub>4</sub> nanoparticles have been embedded into polyvinylidene fluoride (PVDF) polymer. As expectation, a distinct percolation effect has been found in these composites, because of the good conductivity of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The composites exhibit great increase of the dielectric constants and conductivities near the percolation threshold. The maximum of dielectric constant is up to

5240 at 100 Hz, which is the highest value reported to date among the PVDF based percolative composites. Meanwhile, the dielectric loss is controlled in the range of 0–2.2. These composites also exhibit superparamagnetic with the presence of Fe<sub>3</sub>O<sub>4</sub> nanoparticles. The maximum of saturation magnetization is 30.8 emu/g. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 2711–2715, 2012

**Key words:** dielectric; superparamagnetic; nanoparticles; composites

## INTRODUCTION

There is a growing demand for the new composites to meet the requirements of miniaturization and multifunctionality.<sup>1,2</sup> The polymer based composites with excellent dielectric and magnetic properties are promising for advanced applications in electronic devices.<sup>3–8</sup> The efforts to improve the overall dielectric performance of these materials are devoted to maximize the dielectric constant and suppress the loss. To achieve the high dielectric constant polymer composites, different conductive particles (metal particles, carbon tubes, and conductive polymers) have been filled into polymers for percolation.<sup>9–12</sup> With the increasing volume percent of conductive particles,

the composites exhibit a percolative behavior, attributed to a phase transition from insulator to conductor.<sup>13–16</sup> Then, the high dielectric constant can be obtained when the volume fraction of the conductive filler is very close to but does not exceed the percolation threshold.

In the past few years, the Fe<sub>3</sub>O<sub>4</sub> nanoparticle and its composites have been widely used as multifunctional materials in magnetofluid, sensors, and biological medicine, etc.<sup>6,17–23</sup> However, many works mainly pay attention to the magnetic performance of Fe<sub>3</sub>O<sub>4</sub> particles. It is well known that Fe<sub>3</sub>O<sub>4</sub> has excellent electrical performance, which can be used as the conductive filler in the percolative dielectric composites. Here the Fe<sub>3</sub>O<sub>4</sub> nanoparticles have been chosen as the candidate filler in the polyvinylidene fluoride (PVDF) polymer matrix, which is an excellent ferroelectric polymer. It is expected to achieve a multifunctional polymer-based composite with high dielectric constant and superparamagnetic. It has been proved the critical size Fe<sub>3</sub>O<sub>4</sub> nanoparticles with strong superparamagnetic is about 20 nm,<sup>24,25</sup> and the dielectric constant of composites can be enhanced greatly when the size of conductive filler is in the nanometer scale.<sup>16</sup> Therefore, here the Fe<sub>3</sub>O<sub>4</sub> nanoparticles have been prepared by hydrothermal synthesis with the controlled diameter about 10 nm. A distinct percolation effect has been found in Fe<sub>3</sub>O<sub>4</sub>/PVDF composites, accompanying with high dielectric constant (5240 at 100 Hz) and low-loss (2.2

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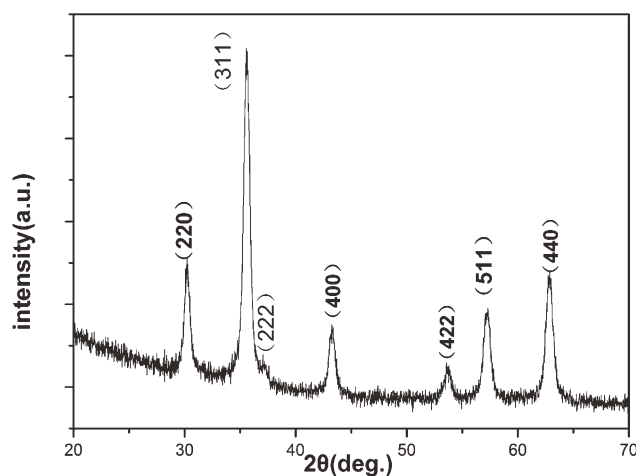
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**Figure 1** The XRD spectrum of Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

at 100 Hz). Simultaneously, the Fe<sub>3</sub>O<sub>4</sub>/PVDF composites also exhibit a good superparamagnetic performance, because of the presence of Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

## EXPERIMENTAL

The synthesis of Fe<sub>3</sub>O<sub>4</sub> nanoparticles is prepared by hydrothermal synthesis procedure. 0.5 mol L<sup>-1</sup> FeCl<sub>3</sub> and 0.25 mol L<sup>-1</sup> FeSO<sub>4</sub>·7H<sub>2</sub>O were dissolved in 100 mL deionized water in a three-neck flask, followed by adding 2 mol L<sup>-1</sup> NH<sub>3</sub>·H<sub>2</sub>O solution with agitation at 55°C under the N<sub>2</sub> atmosphere. The NH<sub>3</sub>·H<sub>2</sub>O was progressively added to adjust the aqueous dispersion pH to 11.0–12.0. Then, the system was further mixed for 2 h at 65°C. After cooling to room temperature, black precipitation of magnetite nanoparticles were separated by centrifugation in an ultracentrifuge and collected by filtration. And then, these nanoparticles were carefully washed with deionized water and ethanol, finally dried in the vacuum drying oven.

The Fe<sub>3</sub>O<sub>4</sub>/PVDF composites with the volume fraction of Fe<sub>3</sub>O<sub>4</sub> in the range of 0–28% are prepared as following process. The Fe<sub>3</sub>O<sub>4</sub> particles were first thoroughly mixed with the PVDF powder by grinding for 2 h. The mixture was then molded by hot-pressing at about 200°C under 10 MPa. The final samples were about 11 mm in diameter and 1 mm in thickness.

For the structural information, the X-ray diffractometer (XRD) of Fe<sub>3</sub>O<sub>4</sub> nanoparticles was recorded by step scan in an XRD (D8-Advance, Bruker Axs) with CuKα radiation at 40 kV. For electric measurements, the samples of composites were painted on both sides using silver paste, and then the dielectric properties and conductivity of the samples were measured at room temperature by using a precision impedance analyzer (Agilent 4294A, United States of America) with a fixture of 16451B. The microstructure of the Fe<sub>3</sub>O<sub>4</sub> nanoparticles and the fractured

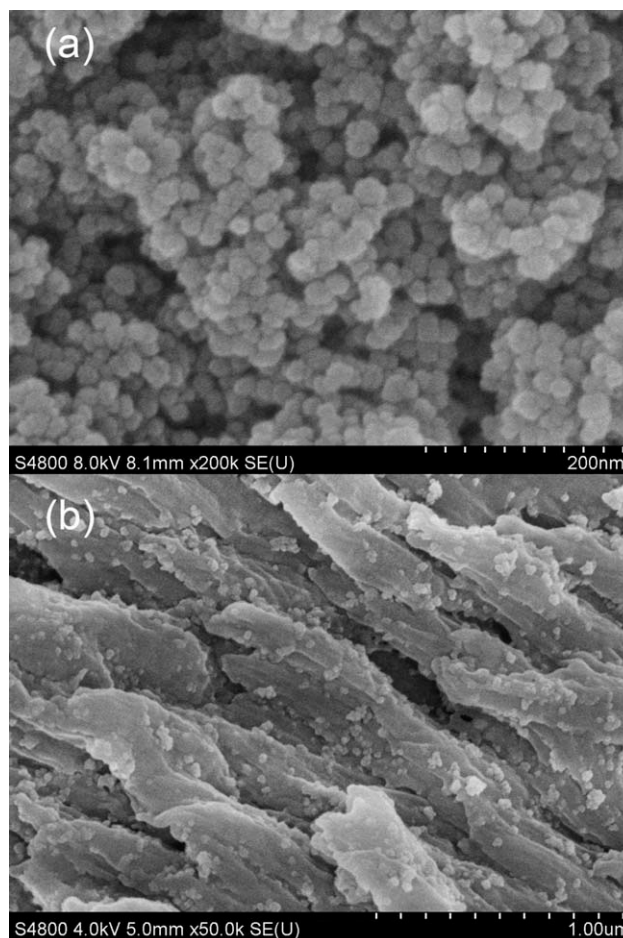
cross-sections of the composites were examined by a scanning electron microscopy (SEM) (SEM, S-4800, Hitachi).

## RESULTS AND DISCUSSION

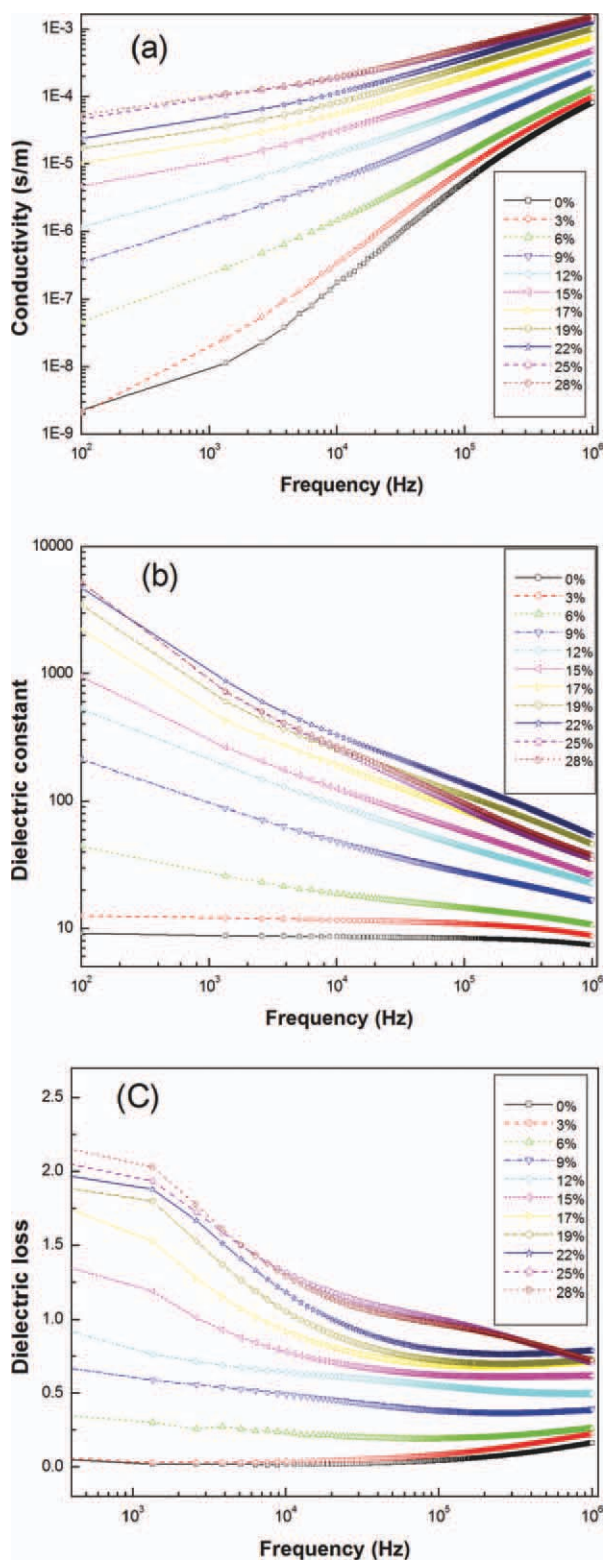
The XRD pattern of the synthesized Fe<sub>3</sub>O<sub>4</sub> is shown in Figure 1. All the diffraction peaks are well in agreement with the standard spectra of spinel magnetic. According to the standard XRD data (Joint Committee on Powder Diffraction Standards (JCPDS) card, file No. 19-0629), the major diffraction peaks at 2θ = 30, 36, 43.5, 57.5, and 63.4 can be indexed to (220), (311), (400), (511), and (440) planes of Fe<sub>3</sub>O<sub>4</sub> magnetite, respectively. It indicates that the Fe<sub>3</sub>O<sub>4</sub> nanoparticles have a cubic spinel structure.<sup>22–23</sup> In addition, the size of the synthesized Fe<sub>3</sub>O<sub>4</sub> can be calculated out about 13 nm by using Debye-Scherrer equation,<sup>26</sup>

$$d_{\text{domain}} = k\lambda / (\beta \cos \theta)$$

where 2θ is the diffraction angle, *K* is a constant of value 0.9, β is the full width at half-maximum of the reflection peak (*hkl*), and λ is the X-ray wavelength.



**Figure 2** The scanning electron microscopy images of the Fe<sub>3</sub>O<sub>4</sub> particles and the Fe<sub>3</sub>O<sub>4</sub>/PVDF composites.

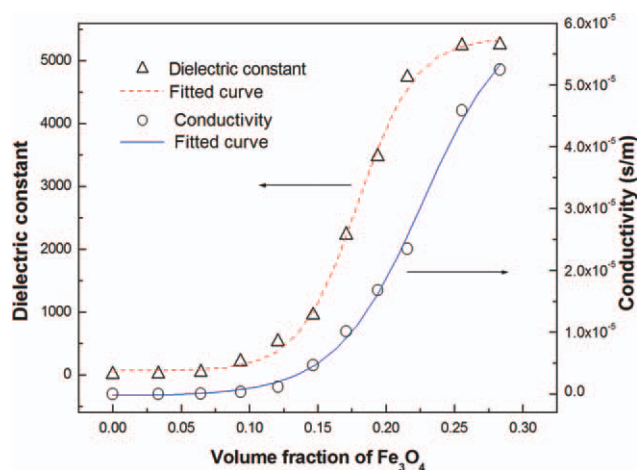


**Figure 3** Dependence of conductivity, (a) dielectric constant, (b) dielectric loss, and (c) of the  $\text{Fe}_3\text{O}_4$ /PVDF composites on the frequency. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).].

To further make clear the size and morphology of the  $\text{Fe}_3\text{O}_4$  particles and their composites, the SEM images of the  $\text{Fe}_3\text{O}_4$  nanoparticles and the  $\text{Fe}_3\text{O}_4$ /

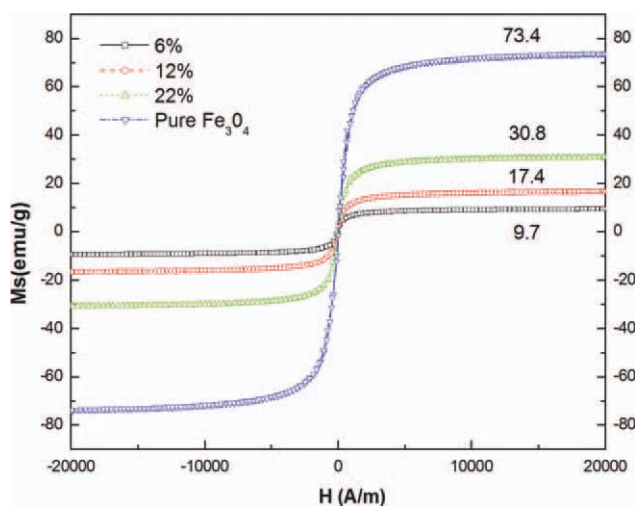
PVDF composites are presented in Figure 2. From Figure 2(a), it can be seen that the  $\text{Fe}_3\text{O}_4$  particles are in spherical shape with size range from 6 to 20 nm and the dominant population is at 8–13 nm. Figure 2(b) shows the micrograph of the cross-section of the  $\text{Fe}_3\text{O}_4$ /PVDF composite. Although, the aggregation of the  $\text{Fe}_3\text{O}_4$  nanoparticles in the PVDF matrix is not prohibited because of the aggregation interaction, these  $\text{Fe}_3\text{O}_4$  nanoparticles or clusters are dispersed uniformly in PVDF matrix, exhibiting a porous sponge like structure with nanoparticles appearing clearly on the surface and inside the pores, as shown in Bhatt's study.<sup>23</sup>

The dependency of the conductivity ( $\sigma$ ), dielectric constant ( $\epsilon$ ), and dielectric loss ( $\tan\theta$ ) of the  $\text{Fe}_3\text{O}_4$ /PVDF composites on the frequency are shown in Figure 3, respectively. It can be seen that the  $\epsilon$  decrease and the  $\sigma$  increase with the frequency. With the increasing volume fraction of  $\text{Fe}_3\text{O}_4$ , the  $\sigma$  of the  $\text{Fe}_3\text{O}_4$ /PVDF composites increase by orders of magnitude, which is the typical character in the conductor-insulator percolative system. The maximum of  $\sigma$  is up to  $5.25 \times 10^{-5}$  s/m. Meanwhile, the  $\epsilon$  increased slowly with the increase of  $\text{Fe}_3\text{O}_4$  content and increased dramatically when the  $\text{Fe}_3\text{O}_4$  content is above 15%. Specially, in the low-frequency range, the  $\epsilon$  grows up to 5240 at 100 Hz when the  $\text{Fe}_3\text{O}_4$  content is 25%, which is 520 times of the value of PVDF matrix and about 2.5 times of that in Maheswar Panda's result (2050 at 100 Hz).<sup>16</sup> It is obvious that the nanoparticles of  $\text{Fe}_3\text{O}_4$  (about 10 nm) may play an important role on the dielectric properties of  $\text{Fe}_3\text{O}_4$ /PVDF composites, in accordance with the microns powder/PVDF composites reported previously.<sup>14,17</sup> It is thought to be caused by the increasing interfacial space-charge polarization between the polymer matrix and the filler. It is also observed the



**Figure 4** Dependence of conductivity and dielectric constant of the  $\text{Fe}_3\text{O}_4$ /PVDF composites on the volume fraction of  $\text{Fe}_3\text{O}_4$  at 100 Hz. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).].





**Figure 5** The magnetization curves of  $\text{Fe}_3\text{O}_4/\text{PVDF}$  composites. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

$\tan \theta$  increases with the volume fraction of the filler increasing, which is mainly attributed to the large leakage current due to the formation of a conducting filler network. Here the loss can be controlled in the low-value, and the maximum is 2.2.

Figure 4 shows the dependence of the  $\sigma$  and  $\epsilon$  on the volume fraction of  $\text{Fe}_3\text{O}_4$  ( $f_{\text{Fe}_3\text{O}_4}$ ) at  $10^2\text{Hz}$ . Being compared with theoretical values, the experimental results are in good agreement with the power law of percolation theory as follow,<sup>27</sup>

$$\sigma \propto (f_c - f_{\text{Fe}_3\text{O}_4})^{-q}, \text{ for } f_{\text{Fe}_3\text{O}_4} < f_c$$

$$\epsilon \propto (f_c - f_{\text{Fe}_3\text{O}_4})^{-s}, \text{ for } f_{\text{Fe}_3\text{O}_4} < f_c$$

where  $f_c$  is the percolation threshold,  $f_{\text{Fe}_3\text{O}_4}$  is the volume fraction of  $\text{Fe}_3\text{O}_4$ ,  $s$  and  $q$  are the critical exponents in the insulating region. Here the experimental values of  $\sigma$  and  $\epsilon$  agree with above equations very well, with  $f_c = 0.17$ ,  $q = 2.38$ , and  $s = 3.99$ . The percolation threshold is close to the value commonly obtained in two-phase random media ( $f_c = 0.16 - 0.18$ ) for spherical inclusions,<sup>27</sup> while the critical exponents ( $s, q$ ) are not in agreement with that in transitional percolation theory of three-dimensional percolative system, where the critical exponents  $q \approx 0.8 - 1$ ,  $s \approx 2$ .<sup>27</sup> It interprets the present percolative behavior is not in the same universality class with transitional percolation.

The magnetization curves of  $\text{Fe}_3\text{O}_4$  nanoparticles and composites at room temperature are presented in Figure 5. It can be seen that coercive force and residual magnetization in all curves are all equal to zero, which is the characteristic of superparamagnetism. The saturation magnetization of  $\text{Fe}_3\text{O}_4$  nanoparticles is 73.4 emu/g, which is approximate to the

value in bulk material and in agreement with the Bhatt's results.<sup>23</sup> For these  $\text{Fe}_3\text{O}_4/\text{PVDF}$  composites, the saturation magnetization ( $M_s$ ) increase with content of  $\text{Fe}_3\text{O}_4$ , on account of the ferromagnetism of filled  $\text{Fe}_3\text{O}_4$ . The maximum of  $M_s$  can be up to 30.8 emu/g, when  $f_{\text{Fe}_3\text{O}_4}$  is 22%. So the prepared  $\text{Fe}_3\text{O}_4/\text{PVDF}$  composites can be further exploited for electromagnetic applications.

## CONCLUSIONS

The superparamagnetic  $\text{Fe}_3\text{O}_4$  nanoparticles with the diameter of about 10 nm has been prepared by hydrothermal method and embedded into the PVDF matrix to achieve the multifunctional composites. For these  $\text{Fe}_3\text{O}_4/\text{PVDF}$  composites, very high values of dielectric constant and low-dielectric loss at percolation threshold of 17% have been observed. The maximum of dielectric constant is 5240 at 100 Hz and the dielectric loss is controlled in the range 0–2.2. Although, the results are explained on the basis of conventional percolation theory, further study is still needed in order to a better understanding of the mechanism, for the critical exponents are not in agreement with transitional percolation theory of three-dimensional percolative system.

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