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Ferroelectric polymer/silver nanocomposites with high dielectric constant and high thermal conductivity

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Ferroelectric polymer nanocomposites with silver (Ag) nanoparticles as inclusions were prepared and the dielectric properties and thermal conductivity were studied. The results showed that the nanocomposites have high dielectric constant and high thermal conductivity. When the loading level of Ag nanoparticles is 20.0 vol %, the dielectric constant and thermal conductivity of the nanocomposites were 120 at 10^3 Hz and 6.5 W/mK, respectively. Our results also showed that there is no percolation in the nanocomposites when Ag loading range is within 20.0%. © 2009 American Institute of Physics. [doi:10.1063/1.3273368]

Polymer composites with high dielectric constant and high thermal conductivity are highly desirable for use in various branches of application, such as electric stress control,¹ electromagnetic shielding,² and higher storage capability of the electric energy.³ The processability and the other physicochemical properties of the polymer matrix are more advantageous for practical applications compared to ceramic materials.⁴ The common approach to increase the dielectric constant of a polymer is known to adopt high-dielectric-constant ceramics as fillers.⁵ For the polymer/ceramic composites, high filler loadings are usually needed in order to realize the values of dielectric constant high enough for the purposed industrial applications. However, such a high filler loading is sure to deteriorate the mechanical and other electrical properties. Recently, polymer composites filled with metal nanoparticles have invoked much interest due to their high dielectric constant.⁶ It should be noted that, although several polymer/metal nanocomposites with very high dielectric constant have been prepared, few papers have dealt with the systematic investigation on the thermal conductivity of the nanocomposites up to now.

Cooling is one of the most important technical challenges facing microelectronics and high-voltage industries.⁷ An important method to increase cooling rates is to use materials with high thermal conductivity. Therefore, the thermal conductivity of the nanocomposites can be regarded to be of a great importance from the viewpoint of their practical applications.⁸ Our interest is to grasp how to prepare the polymer composites not only with the expectable high dielectric constant but also with high thermal conductivity. Actually, since the nanosized metal particles generally have high specific surface and surface tension, most of them are known to be easily passivated in air, which can cause high interface thermal resistance and has been understood as one of the main reasons why high values of thermal conductivity could not be easily obtained in polymer/metal nanocomposites.

In this letter, we report a strategy to resolve aforementioned problems by fabricating the ferroelectric polymer/

silver nanocomposites. Our nanocomposites show high dielectric constant and high thermal conductivity at relatively low nanoparticle loading levels.

The silver (Ag) nanoparticles with an average diameter 100 nm were supplied by Hongwu Nanomaterials Co. (Hubei, China). Poly(vinylidene fluoride) (PVDF) powder was purchased from 3F Co. (Shanghai, China). The solution method was adopted to prepare the PVDF/Ag nanocomposites. First, Ag nanoparticles were added to N,N-Dimethylformamide (DMF), and were dispersed by applying the ultrasonic wave for 10 min at room temperature. At the same time, PVDF was dissolved in DMF at 333 K. Then, the suspension of Ag/DMF was added to a solution of PVDF/DMF, and the resulting mixture was stirred with an electric stirrer at 333 K. After 30 min, the mixture was dried on a hot plate at 393 K. Finally, the dried mixture was compressed into films with a thickness of around 420 ± 30 μm at 200 °C under a pressure of about 10 MPa. For the sake of comparison, the composites were denoted using the following notation: PVDF-silver volume fraction, thus PVDF-2.0 indicates the nanocomposite sample with 2.0 vol % nanoparticles.

FE-SEM (field emission scanning electron microscopy, JEOL 7401F, Tokyo, Japan) was used to observe the nanoparticle dispersion in the composite samples. The dielectric properties were measured using an impedance analyzer (Agilent 4294A, USA) with 16451B dielectric test fixture in the frequency range of 40 to 10 MHz. Laser flash method is used for thermal diffusivity measurement. Thermal conductivity (λ , $\text{Wm}^{-1} \text{K}^{-1}$) of the composites at 25 °C was given by the product of thermal diffusivity (δ , mm^2/s), specific heat (C , J/g K), and bulk density (ρ , g/cm^3). In this paper, thermal diffusivity (δ) and specific heat (C) were measured on disk samples (ϕ 12.6×0.5 mm^3) by the laser flash method (NETZSCH LFA447, Germany). Furthermore, bulk density (ρ) of specimen was measured by water displacement. For each measurement, three samples were tested three times. After that, thermal conductivity (λ) was calculated by

$$\lambda = \delta \times C \times \rho. \quad (1)$$

Figure 1 displays the dependence of the dielectric constant ϵ on the loading level of the Ag nanoparticles for our nanocomposites. We can see that the addition of Ag nanoparticles

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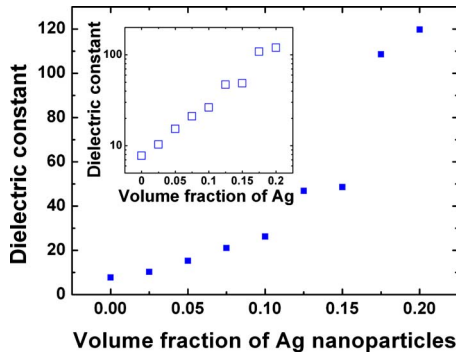


FIG. 1. (Color online) Effective dielectric constant of the nanocomposites as a function of Ag volume fraction at 10^3 Hz and room temperature. Inset: Shows the $\log \epsilon$ against Ag volume fraction.

results in much higher ϵ value and that the increase in ϵ value becomes more apparent at the relatively high loading levels. Of interest is that the dielectric constant of the nanocomposites increases notably when the Ag loading level is above 17.5 vol %. PVDF-17.5 shows a dielectric constant value of 110, which is 15 times of pure PVDF. The increase in effective dielectric constant in the silver/PVDF nanocomposites could be understood according to the “boundary layer capacitor effect.”⁶ At high Ag loading levels, the nanocomposites can be simulated by means of a large number of equivalent elementary capacitors where the single Ag particles or clusters are isolated by thin dielectric insulating layers and can act as electrodes when an external electric field is applied on the composites, which give rise to high dielectric constant.⁶ Another interesting finding is that there is no percolation in the Ag fraction range of 0% to 20.0%. According to percolation theory,⁹ the percolation threshold of composites can be deduced from the following power laws:

$$\epsilon \propto (p_c - p)^{-s} \quad \text{for } p < p_c, \quad (2)$$

where ϵ is the effective dielectric constant of the composites; p_c is the percolation threshold and p is the volume fraction of the conducting particles inside the insulating matrix; and s is a scaling constant. According to Eq. (2), there is an abrupt increase in $\log \epsilon$ if the volume fraction of the conducting phase reaches the percolation threshold. However, $\log \epsilon$ of our nanocomposites shows a linear increase with the loading level of the Ag nanofiller, indicating no percolation behavior in the Ag fraction range of 0% to 20.0%.

Figure 2 shows the frequency dependence of effective dielectric constant and conductivity of the silver/PVDF nanocomposites, respectively. It can be seen that the dielectric constants of the nanocomposites with relatively high fraction of Ag fillers show clear dispersion. This observation may be attributed to the enhanced tunneling current resulting from higher conductivity of the nanocomposites due to decrease in interparticle distance with increase in nanoparticle loading. According to the tunneling model,¹⁰ the interparticle tunneling conductivity σ_{tun} is given by

$$\sigma_{\text{tun}} \propto \exp\left(-\frac{l-2b}{d}\right), \quad (3)$$

where l is the distance between the centers of the particles, b and d are the radius of the particles and the typical tunneling range, respectively. The average interparticle l can be expressed approximately as $l = r[(4\pi/3p)^{1/3} - 2]$, where r is the radius of the Ag particles. According to Eq. (3), the values of

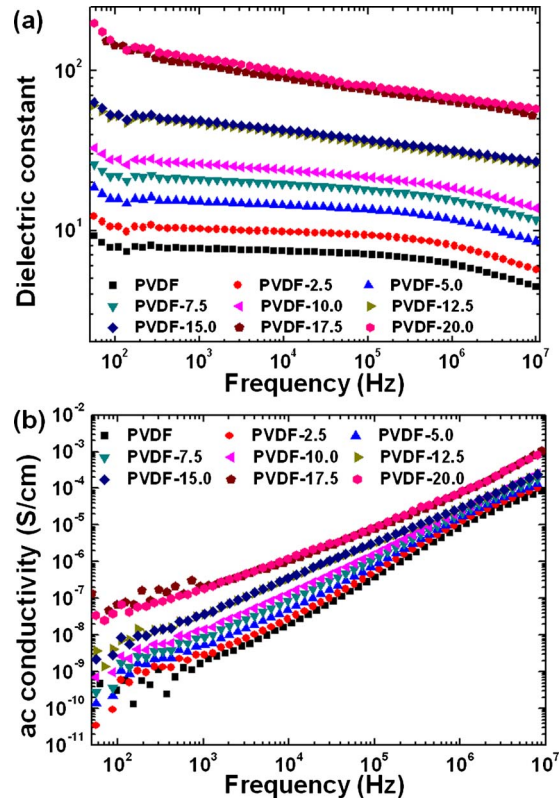


FIG. 2. (Color online) Effective dielectric constant (a) and conductivity (b) of the nanocomposites as a function of Ag volume fraction.

l decrease exponentially as the Ag loading increases from a purely geometric consideration, and hence the conductivity of the nanocomposites rapidly increases when the loading levels near the percolation threshold. Interestingly, although the rapid increase in conductivity at relatively high Ag loading levels has been observed, the conductivity data for all the nanocomposites show strong frequency dependence and there is no percolation over the whole loading range. In view of a forementioned observation, a reasonable explanation for the absence of percolation in our nanocomposites is that the adsorption of the polymer chains onto the nanoparticle surface occurs. The absorbed polymer chains can act as the dielectric barrier governing the tunneling conduction between the neighboring Ag clusters; on the other hand, the absorbed polymer chains make it impossible for the complete contacts to be realized between the nanoparticle clusters.

The experimental determined thermal conductivities, displayed as a function of volume fraction are shown in Fig. 3. It can be seen that the addition of Ag nanoparticles is very effective in improving thermal conductivity of PVDF. The thermal conductivity of the nanocomposites increases notably when the loading level is higher than 15.0% and achieves 6.5 W/mK when the loading level reaches 20.0%, which is nearly 27 times of pure PVDF. An effective medium model for the effective thermal conductivity κ of a dilute suspension of randomly spherical and perfect interface (interfacial resistance=0) was developed by Nan¹¹

$$\kappa = \frac{\kappa_p + 2\kappa_m + 2f(\kappa_p - \kappa_m)}{\kappa_p + 2\kappa_m - f(\kappa_p - \kappa_m)}, \quad (4)$$

where κ_p and κ_m are the thermal conductivity of the fillers and matrix, respectively.

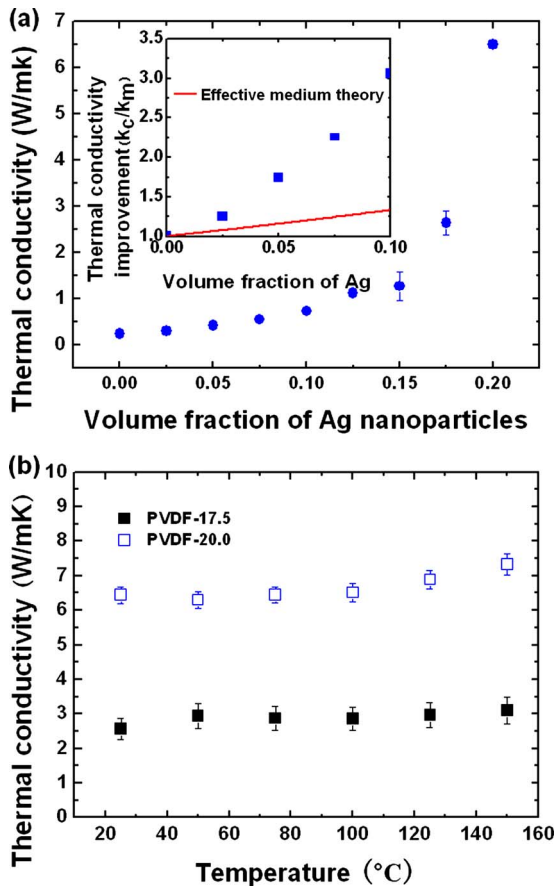


FIG. 3. (Color online) Thermal conductivity as a function of Ag volume fraction. Inset: Shows the comparison between the experimental results of the thermal conductivity of the nanocomposites and the calculated values by the effective medium theory.

As indicated in Fig. 3, the model of Nan's predication terribly underestimated the thermal conductivity enhancement even though the interfacial thermal resistance is not considered. As shown in Fig. 4, this result is associated with the complex shape factor of the Ag nanoparticle clusters.^{8,12} At the nanoscale, London–van der Waals forces are inversely proportional to the sixth power of the particle radius.¹³ Therefore, this force becomes very significant for nanoparticles and aggregation is commonly observed. The natural tendency for nanoparticles to aggregate makes it likely to form clusters with complex shape factor, which can

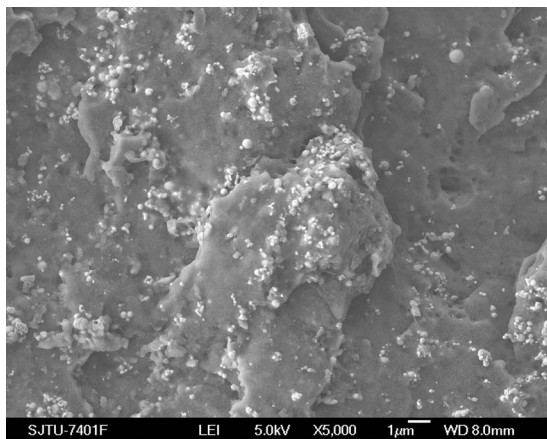


FIG. 4. FE-SEM image of a composite sample containing 17.5% Ag nanoparticles.

significantly enhance the thermal conductivity of the nanocomposites when compared with the spherical particles. Such a conclusion is reasonable because the Ag nanofillers used in this work are oxide-free nanoparticles.¹⁴ Figure 3(b) shows that the thermal conductivity of the nanocomposites slightly increases with the temperature, which is consistent with the general trend of dielectric materials.

In view of the forementioned content, it is rather surprising that there is apparently no agreement with the classical insulator-conductor systems on the universal value (16.0 vol %) of the critical point of percolation,¹⁵ which could be attributed to the process conditions and physicochemical characteristics of the nanoparticles. Panda *et al.*⁶ reported that the PVDF/Ni nanocomposites show a value of percolation threshold of 28.0 vol %. Huang *et al.*¹ showed that the percolation threshold of polyethylene/aluminum nanocomposites is strongly affected by the surface modification of the aluminum nanoparticles. These results indicate that the properties of polymer nanocomposites are not only determined by the raw materials but also should be ascribed to the process conditions and physicochemical characteristics of the nanoparticles. The understanding of these relationships guides us to choose proper process conditions and modification approaches of the raw materials to gain desired properties.

In summary, the dielectric properties and thermal conductivity of PVDF/Ag nanocomposites were investigated. The nanocomposites show high dielectric constant and high thermal conductivity and do not display percolation behavior in the loading range of 0–20.0 vol %. The high dielectric constant as well as the high thermal conductivity makes the PVDF/Ag nanocomposites a good candidate for microelectronics and high-voltage industries.

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