

# Novel Dielectric Behaviors in PVDF-Based Semiconductor Composites

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**ABSTRACT:** Composites of polyvinylidene fluoride (PVDF) filled with different conductive fillers as carbon black (CB), nickel (Ni), zinc (Zn), and tungsten (W), respectively, were prepared at same processing condition. The temperature dependence of dielectric behaviors of composites was studied at wide filler concentration and wide frequency ranges. Results show that there are giant dielectric constants as the concentration of filler is near the percolation threshold. The dielectric constants of all studied composites decrease slowly with increasing of frequency and rise gradually with increasing filler contents in the compo-

sites. Two relaxation peak regions of dielectric constant are observed from  $-30$  to  $40^{\circ}\text{C}$  and from  $100$  to  $150^{\circ}\text{C}$ , which can be attributed to the contribution of polar effect of PVDF. The CB filled PVDF (CB/PVDF) composites present a lower percolation threshold than other metallic-filler filled PVDF composites. The maximal dielectric constant was found in the Ni filled PVDF (Ni/PVDF) composite. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 3466–3473, 2011

**Key words:** polymer–matrix composites; dielectric property; thermal properties

## INTRODUCTION

There is an ever-increasing interest in flexible polymer materials with good piezoelectric and pyroelectric responses, such as polyvinylidene fluoride (PVDF) due to the wide range of important technological applications.<sup>1–4</sup> The incorporation of other fillers into polymer matrix provides available opportunities for attaining composites with special physical property applied in electronic industry areas, such as static-charge dissipation, radio-frequency shielding and capacitor.<sup>5–8</sup> For such applications, it is fairly essential for us to enhance the dielectric constant.<sup>9,10</sup> Traditional way of enhancing the dielectric constant is to disperse the high dielectric constant ceramic powders into the polymer.<sup>9,11,12</sup> However, the disadvantages of flexibility loss, low dielectric constant badly limit the potential progress, giving

rise to the focus on the conductive filler filled polymer composite. Conductive fillers, such as carbon black (CB), metal particles, carbon fibers (CF), and carbon nanotube (CNT), have attracted extensive attention for their superior electric conductivity. The conductive filler filled polymer composite can possess a high dielectric constant at a low filler concentration and thus make it possible to preserve the flexibility of the polymer matrix.<sup>13–15</sup> Therefore, an understanding for the dielectric behavior of the polymer matrix semiconductor composites is very important in engineering application of new materials. The dielectric property of semiconductor composites depends on the volume fraction, size, and shape of conducting fillers, also depends on other factors such as preparation method, interface and interaction between the fillers and the polymer.

The extensive researches and applications in these semiconductor polymer composites are based on the discovery of the percolation phenomenon, which makes significant increase in electrical or dielectric properties when the filler content is in the neighborhood of critical concentration referred as the “percolation threshold.”<sup>7,8,16</sup> According to the percolation theory, the effective dielectric constant of semiconductor polymer composites can be improved dramatically as the concentration of filler reaches the percolation threshold.<sup>17,18</sup> It is interesting to acquire some expectable semiconductor polymer composites, which should have high dielectric constant when the filler content is below to the percolation threshold.

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Although many studies on semiconductor composites have been carried out, the dielectric properties of semiconductor composites with different conductive fillers at different temperatures and frequencies have not been fully studied. In this article, our semiconductor composites are PVDF-based loaded with different conductive fillers as CB, nickel (Ni), zinc (Zn), and tungsten (W), because PVDF has relative high dielectric constant value ( $\sim 10$ )<sup>1</sup> and the four mentioned conductive fillers are all cheap particles and with different conductivity. The CB/PVDF, Ni/PVDF, Zn/PVDF, and W/PVDF composites were prepared at the same processing conditions. Dielectric behavior of the PVDF-based semiconductor composites was studied over a broad range of volume fraction of fillers, frequencies and temperature. The objective of this study is to find out the influencing law of conductive filler on percolation threshold and dielectric property of semiconductor composites. Especially, the composites with the filler content slightly below the percolation threshold were chosen to study the frequency and temperature dependences of dielectric constant.

## EXPERIMENTAL

### Raw materials

PVDF (FR903) powder was supplied by Shanghai 3F New Materials Ltd. Conductive filler acetylene CB was obtained in beaded form from Beijing Calcium Carbide Manufactory. The metal powders Ni, Zn, W were purchased from VAS Lab Supplies of China. Before doping into the PVDF, the surface of conductive fillers was embellished, respectively, by a  $\gamma$ -aminopropyl triethoxysilane coupling agent (KH550) at 1.0 wt % to improve the dispersion of conductive fillers in the PVDF host.

### Preparation of the PVDF-based semiconductor composites

The PVDF-based semiconductor composites were prepared by solution method. The PVDF was firstly dissolved in an organic solvent [N, N-dimethylformamide (DMF)], then mixed with the treated fillers in a ball mill to achieve a reasonably uniform dispersion. The mixture films were obtained by vaporizing the solvent. In this study, the volume fraction of fillers ( $f_{\text{filler}}$ ) in the composites was selected near the percolation threshold with  $f_{\text{CB}}$  ranging from 0.02 to 0.08,  $f_{\text{Ni}}$  from 0.08 to 0.20,  $f_{\text{Zn}}$  from 0.10 to 0.32, and  $f_{\text{W}}$  from 0.06 to 0.23, respectively. The samples with diameter of 12 mm and thickness of 1 mm were molded by a hot press at about 200°C and 18 MPa for 10 min and slowly cooled to room temperature under pressure.

### Dielectric measurement and characterization of the PVDF-based semiconductor composites

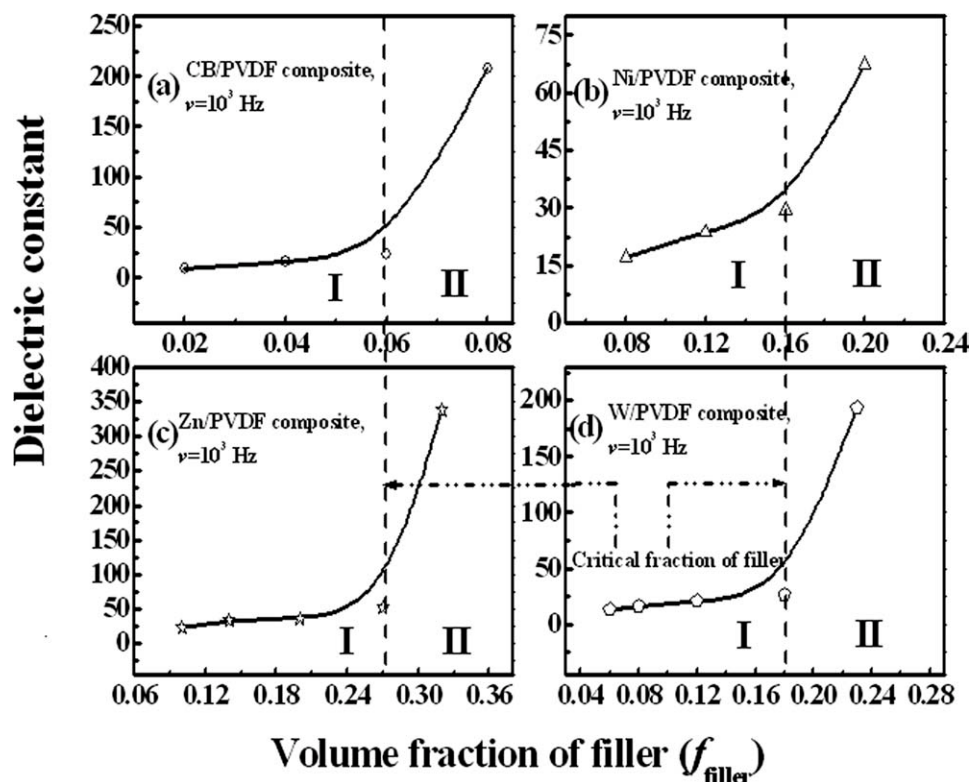
The surface of specimens was coated with thin silver pastes to ensure good contact with electrodes of the conduction tester. The dielectric properties of the samples were measured by an impedance analyzer (Agilent 4294A) in frequency ranges of 10<sup>2</sup> Hz to 10<sup>6</sup> Hz and temperature ranges of -50 to 150°C. The morphologies of composites were observed by a scanning electron microscope (SEM, HITACHI S-4800). The samples were fractured in liquid nitrogen and the surfaces were deposited with a thin gold layer before SEM observations.

## RESULTS AND DISCUSSION

### Dielectric percolation behavior of PVDF-based semiconductor composites with different conductive fillers

Dielectric properties of the functional materials are an important factor in practice applications. Therefore, the dielectric behaviors of the four system composites are investigated as a function of volume fraction of fillers and frequency, respectively. Figure 1 shows the effect of filler volume fraction on dielectric constant of composites at frequency 10<sup>3</sup> Hz. The dependences of dielectric constant on filler content of the four systems all can be divided into two stages I and II. First, the dielectric constant rises gradually with increasing filler contents in the composites, as shown in Figure 1(I). Subsequently, the percolation threshold ( $f_c$ ) is visible, at a critical volume concentration  $f_{\text{CB}} = 0.08$ ,  $f_{\text{Ni}} = 0.20$ ,  $f_{\text{Zn}} = 0.32$ , and  $f_{\text{W}} = 0.23$ , respectively, where the dielectric constant abruptly increases, as shown in Figure 1(II). At this stage, the dielectric constant of CB/PVDF, Ni/PVDF, Zn/PVDF, and W/PVDF composites reaches as high as 208, 67, 337, and 194 at 10<sup>3</sup> Hz, which is more than 20, 6, 33, and 19 times larger than that of pure PVDF about 10, respectively. According to the percolation theory, the percolation threshold of the two-phase random composite should be about  $f_c = 0.16$  if the conducting fillers are sphere particles. In our composites, the CB filler with good conductivity results in a relatively lower percolation threshold than  $f_c = 0.16$ . In comparison with the CB/PVDF composite, the percolation threshold values of the metallic-filler/PVDF composites are higher probably due to the metal particles easily to be oxidized, so it is hard for the metallic volume fraction to reach the percolation when the same content of CB and metallic-filler are dispersed into the polymer. The maximal dielectric constant was found in Ni/PVDF composite.

The dielectric constant of a material is proportional to the quantity of charge stored on either



**Figure 1** Dependence of dielectric constant of (a) CB/PVDF, (b) Ni/PVDF, (c) Zn/PVDF, and (d) W/PVDF composites on the filler volume fraction at  $10^3$  Hz, respectively.

surface of the sample under an applied electric field. The quantity of the accumulated charge of filler/PVDF semiconductor composites is more than the pure PVDF because the polarization of the filler/PVDF interfaces makes an additional contribution to the charge quantity when an electric field is applied on the samples. Thus, a great deal of charge is formed due to the polarization of the filler/PVDF interfaces. In addition, the conduction behavior of the composites is also controlled by the concentration of the conducting fillers. Therefore, the higher dielectric constant appears in the composites with a higher volume fraction of fillers.

The giant dielectric constant of conductive polymer composite would be attributed to conductivity of fillers. The selected fillers as CB, Ni, Zn, and W have high conductivity and may induce the effect of electron tunnel. Percolation theory also allows one to describe the effective conductivity and dielectric constant of conductive polymer composites near the conductor-insulator transition using laws of power<sup>19–21</sup>

$$\sigma_{\text{eff}} \propto (f_c - f_{\text{filler}})^{-s'} \quad \text{for } f_{\text{filler}} < f_c \quad (1)$$

$$\varepsilon_{\text{eff}} \propto (f_c - f_{\text{filler}})^{-s} \quad \text{for } f_{\text{filler}} < f_c \quad (2)$$

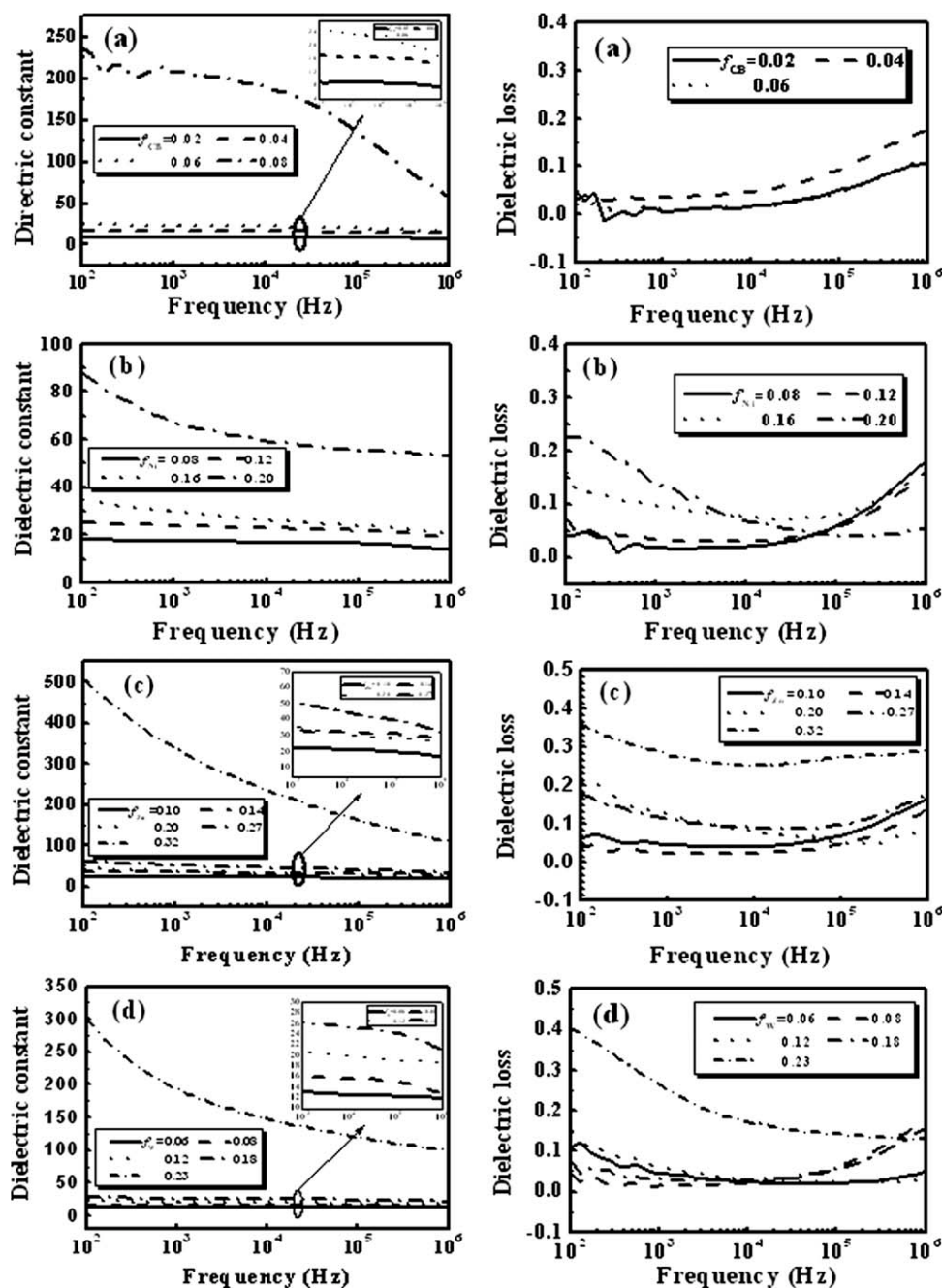
where  $\sigma_{\text{eff}}$  and  $\varepsilon_{\text{eff}}$  are the effective conductivity and effective dielectric constant of composites,  $f_c$  is the

percolation threshold,  $f_{\text{filler}}$  is the volume fraction of conductive fillers,  $s'$  and  $s$  are the critical exponents in the insulating region. The universality of the percolation theory suggests that the effective dielectric constant should exhibit the same power-law dependence on the volume fraction as the conductivity below  $f_c$ , i.e.,  $s' \approx s \sim 1$ . The dielectric constant as a function of the volume fraction of fillers exhibits clearly power characteristic as described by the power law. Such result has been experimentally discovered.<sup>22–24</sup>

#### Dependences of dielectric properties on frequency at room temperature of PVDF-based semiconductor composites

Figure 2 shows the dependences of dielectric constant and dielectric loss of CB/PVDF [see Fig. 2(a)], Ni/PVDF [see Fig. 2(b)], Zn/PVDF [see Fig. 2(c)], and W/PVDF [see Fig. 2(d)] composites on frequency at different concentration of fillers, respectively.

With increasing frequency from  $10^2$  Hz toward  $10^6$  Hz, the dielectric constant of four system samples displays a slight drop at the lower filler loading. And with  $f \rightarrow f_c$ , the dielectric constant reduces more rapidly with increasing frequency. For example, the dielectric constants of CB/PVDF composites tardily decrease from 23 to 20 when the frequency increases

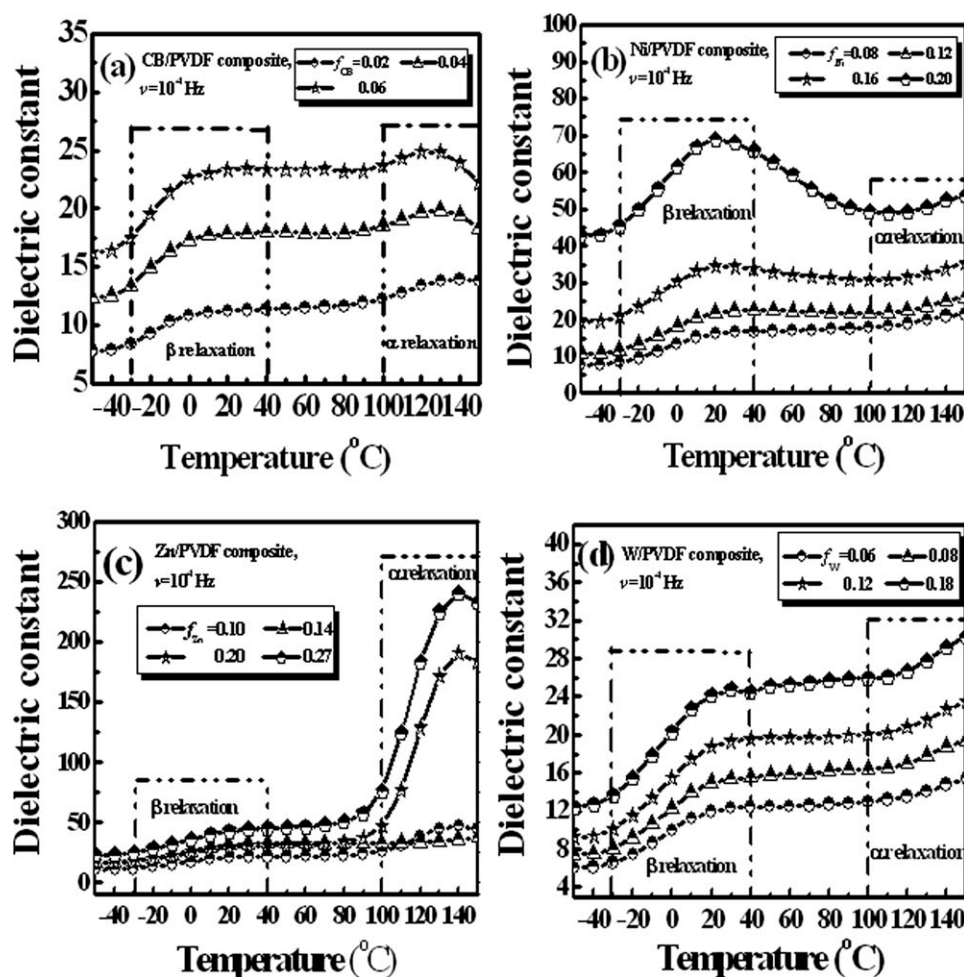


**Figure 2** Frequency dependences of dielectric constant and dielectric loss on frequency ranging from  $10^2$  Hz to  $10^6$  Hz at room temperature of (a) CB/PVDF, (b) Ni/PVDF, (c) Zn/PVDF, and (d) W/PVDF composites, respectively, with different concentration of fillers. The insets in (a), (c), and (d) show the dependence of dielectric constant on frequency at room temperature of CB/PVDF, Zn/PVDF, and W/PVDF composites, respectively, at various concentration of filler as indicated.

from  $10^3$  Hz to  $10^5$  Hz at  $f_{CB} = 0.06$ . While the dielectric constants of the composites at  $f_{CB} = 0.08$  remarkably decrease from 208 to 134 at the same frequency range. The similar results can be seen in Ni/PVDF, Zn/PVDF, and W/PVDF composites. The rapid drop in dielectric constant at percolative stage may be attributed to the large leakage current resulted from the high conductivity of the composites.<sup>25</sup> The dielectric loss of the semiconductor composites still keeps

the low value less than 0.2 over a wide range of frequency. When  $f \rightarrow f_c$ , the loss tangent of the composite undergoes a sharp increase at low frequency. Such increase of the loss tangent is the inevitable consequence of the significantly raised conductivity in the composites and can be considered as one important feature of the percolative composite.

In summary, the dielectric properties of PVDF-based semiconductor composites loaded with



**Figure 3** Temperature dependence of the dielectric constant of (a) CB/PVDF, (b) Ni/PVDF, (c) Zn/PVDF, and (d) W/PVDF composites, respectively, with different concentration of filler at  $10^4$  Hz on temperature ranging from  $-50$  to  $150^\circ\text{C}$ .

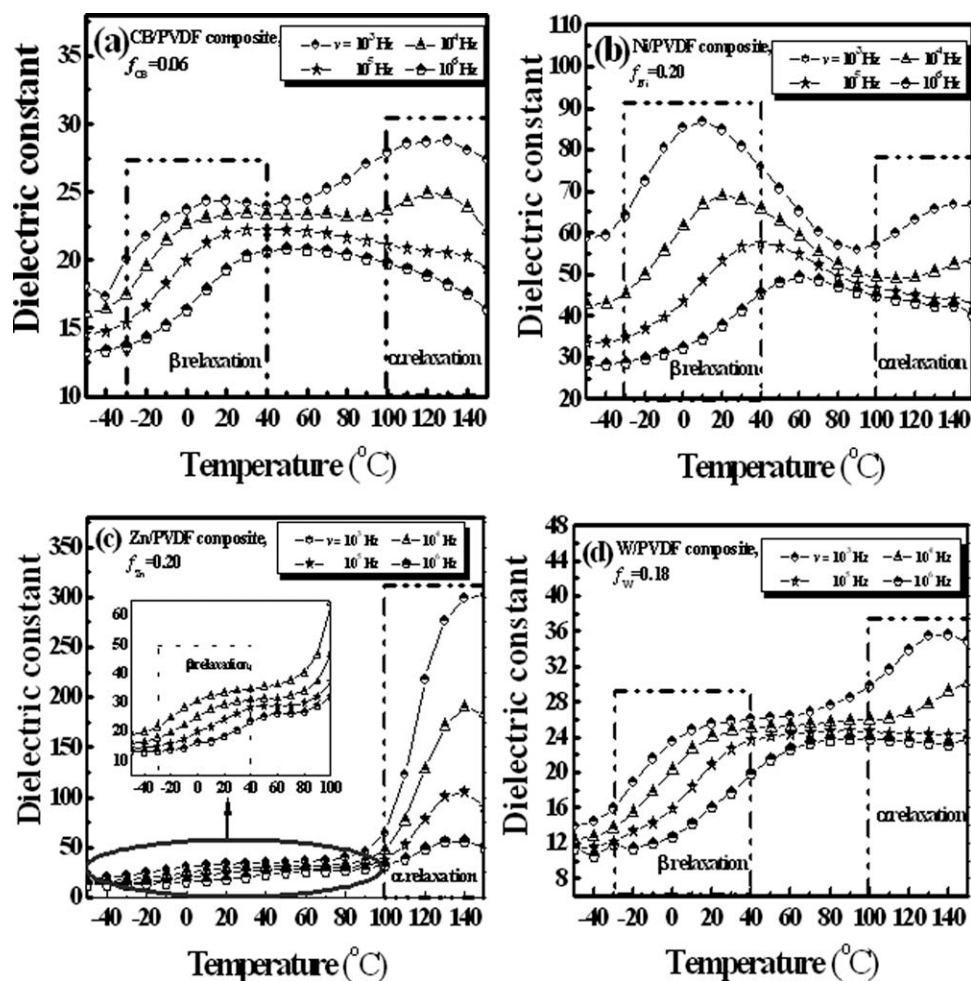
different fillers are enhanced with increasing of filler content. The frequency dependence of dielectric constant becomes gradually stronger when  $f < f_c$ . For the composites with filler content is up to the percolation threshold, we observed intense fluctuations in the frequency dependence of dielectric constant, accompanied with a significantly enhanced loss tangent, which made the composite invalid for applications as well.

#### Temperature dependence of dielectric constant of PVDF-based semiconductor composites

Figure 3 shows the dependences of dielectric constant of the CB/PVDF, Ni/PVDF, Zn/PVDF, and W/PVDF composites with various filler contents on the temperature from  $-50$  to  $150^\circ\text{C}$  at frequency of  $10^4$  Hz, respectively. It is interesting to note that the dielectric constants of all composites increase steadily when the temperature changes from  $-30$  to  $20^\circ\text{C}$ , while the dielectric constants exhibit a clear peak at about  $20^\circ\text{C}$ . Then the dielectric constant presents

good thermal stability from  $40$  to  $100^\circ\text{C}$ , subsequently, they increase again and up to another peak at about  $140^\circ\text{C}$ . It can also be seen that the marked change of dielectric constants near the two peaks is considerably clearer at higher filler contents in comparison with those of lower filler contents. These results can be attributed to a complicated polarization of pure PVDF host.

It is well known that the dielectric constant of a material is related to the polarization. When an alternating current is applied to the dielectric material, the complicated polarization can be initiated. The two relaxation peak regions from  $-30$  to  $40^\circ\text{C}$  and from  $100$  to  $150^\circ\text{C}$  in PVDF-based composites are corresponding to the  $\beta$  and  $\alpha$  relaxations of PVDF, respectively.<sup>26</sup> The low-temperature constant peak corresponding to  $\beta$  relaxation is probably associated with the glass transition of PVDF. It has been suggested that this process is due to rotational motions of dipolar groups in the amorphous regions of the PVDF polymer. But these rotational motions of dipolar groups are often frozen so that they can not catch



**Figure 4** Temperature dependences of dielectric constant of (a) CB/PVDF, (b) Ni/PVDF, (c) Zn/PVDF, and (d) W/PVDF composites, respectively, at a selected filler concentration and at various frequencies as indicated with temperature ranging from  $-50$  to  $150^{\circ}\text{C}$ . The inset in Figure 4(c) shows the dependence of dielectric constant of Zn/PVDF composites on temperature between  $-50$  and  $100^{\circ}\text{C}$ .

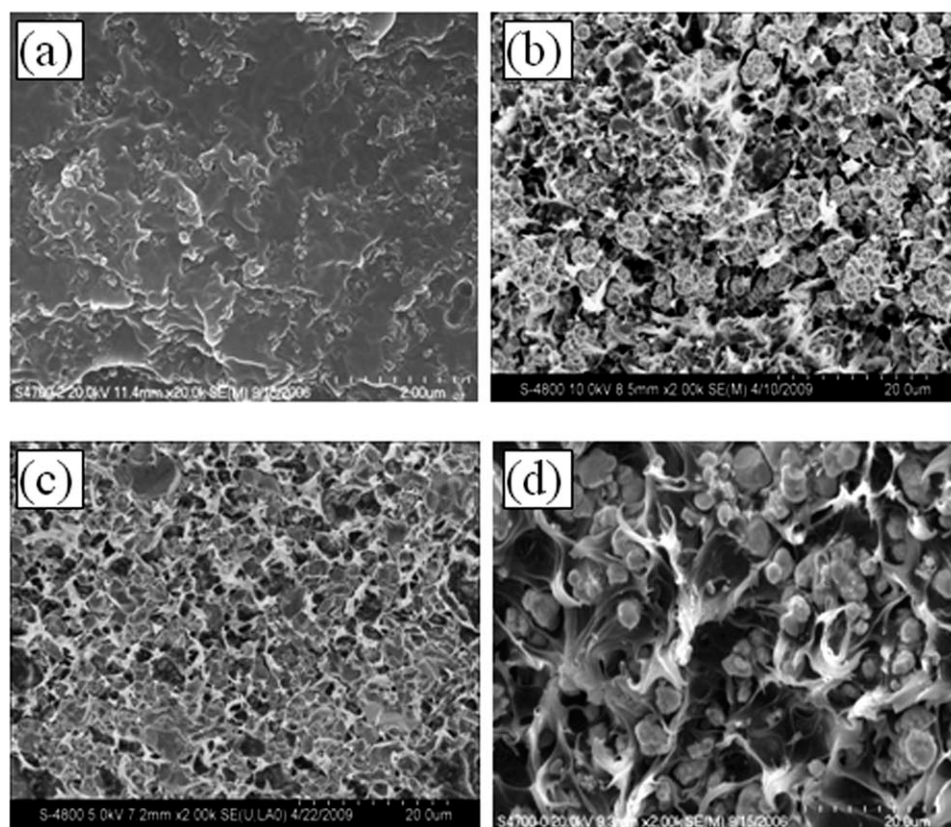
up with the frequency change of the electric field. This is changeable with the low dielectric constant at the  $\beta$  relaxation process. The high-temperature peak corresponding to  $\alpha$  relaxation is probably associated with the annealing process in the crystalline regions, which is due to molecular motions that alter the dipole direction only along the applied electrical field because the dipolar units are unfrozen at high temperature, and they can move smoothly. Therefore, we always find that the dielectric constant at high temperature is larger than at low one. The four system composites can further confirm the contribution of PVDF. The peak of constant represents more outstanding with increasing the filler content can be explained that the interface polarization influenced the dielectric constant of the composites, as a significant amount of two-phase interfaces are formed between the fillers and PVDF host.

Figure 4 shows the temperature dependences of dielectric constants of CB/PVDF, Ni/PVDF, Zn/PVDF, and W/PVDF composites at given filler con-

centration, measured at several different frequencies between  $10^3$  and  $10^6$  Hz, respectively. The distinctive feature is the peak points of dielectric constant in the temperature of  $-30$  to  $40^{\circ}\text{C}$  shifting toward higher temperature with the increasing of frequency. The behavior is related to a freezing of dipolar motion in the amorphous region. With increasing frequency, the temperature at the dissipation peak shifts to a higher temperature range, which is also a hint of the thermally excited relaxation process. The difference in dielectric constants as a function of temperature between the four system composites is attributed to the complicated two-phase interface polarization between the fillers and PVDF host.

#### SEM images of CB/PVDF and Ni/PVDF composites

The fractured surface morphology of CB/PVDF composite containing CB volume fraction of 0.08, as shown in Figure 5(a), indicates that CB particles are randomly dispersed in the matrix without serious



**Figure 5** SEM images illustrating the morphology of a section of (a) CB/PVDF composite with  $f_{CB} = 0.08$ , (b) Ni/PVDF composite with  $f_{Ni} = 0.20$ , (c) Zn/PVDF composite with  $f_{Zn} = 0.32$ , and (d) W/PVDF composite with  $f_W = 0.23$ , respectively.

aggregation, and the CB particles are self-connected into a continuous phase. The Ni/PVDF composite containing Ni volume fraction of 0.20, as shown in Figure 5(b), shows that Ni particles consisting of large agglomerations in PVDF host. There is no distinct interface between Ni particles and polymer because the magnetism of Ni particles acts as a good consistent agent for Ni in PVDF host. The morphology of Zn/PVDF composite with Zn volume fraction of 0.32, as shown in Figure 5(c), displays the bigger size and nonsphere particles of Zn filler in PVDF host. The large size and polygonal structure of Zn particles might be the main reason to cause the higher percolation threshold of Zn/PVDF composite than other systems because it needs more particles to form the continuous conductive chains. From the micrograph of W/PVDF composite with W volume fraction of 0.23, as shown in Figure 4(d), it can be observed that W particles are much smaller aggregations and are randomly dispersed in PVDF host because the tremendous difference in density of W and PVDF might decrease the interfacial excess energy. It is coincident that the percolation threshold of CB/PVDF composite is much lower than metallic-filler/PVDF composites. Therefore, the mechanical property of CB/PVDF composite could be better

than other composite. In fact, when the volume fraction of conducting filler is near the critical value, i.e., percolation threshold, the conducting filler could connect with each other and form a continuous random cluster or partial agglomeration grain clusters. The obvious separation of the conducting fillers each other in the semiconductor composites is not effective on forming the percolation.

## CONCLUSIONS

The semiconductor composites prepared by mixing PVDF and various conductive fillers were investigated with regard to the dielectric constant as a function of frequency, temperature and the concentration of fillers. It could be suggested that the percolation threshold, the dielectric behavior of conductive filler/PVDF composites are dominated by the kind of fillers but the effective contribution of each aspect was difficult to quantify. The dielectric constants of all studied composites decrease with increasing of frequency and the dielectric constants increase with increasing of the filler concentration. Two relaxation peak regions of dielectric constant are observed from  $-30$  to  $40^\circ\text{C}$  and from 100 to

150°C, which can be attributed to the contribution of polar effect of PVDF. The difference in dielectric constants as a function of frequency, temperature, and the concentration of filler between the four system composites is attributed to the complicated two-phase interface polarization between the fillers and PVDF host. The CB/PVDF composite reveals obviously lower percolation threshold value than the metallic-filler/composites. The maximal dielectric constant is found in the Ni/PVDF composite. The morphologies indicate that the CB particles are randomly dispersed in the matrix without serious aggregation, whereas the Ni particles consisting of large agglomerations in the PVDF host. So the kind of fillers is an important factor in fabrication of semiconductor polymer-based composite. Such PVDF-based semiconductor composites can be employed as high dielectric constant material.

## References

1. Zhang, Q. M.; Li, H. F.; Poh, M.; Feng, X.; Cheng, Z. Y.; Xu, H. S.; Huang, C. *Nature* 2002, 419, 284.
2. Shawna, M. L.; Nitin, K.; Gareth, H. M. *Nature* 2007, 6, 76.
3. Levi, N.; Czerw, R.; Xing, S. Y. *Nano Lett* 2004, 4, 1267.
4. Zhu, B. K.; Xie, S. H.; Xu, Z. K.; Xu, Y. Y. *Comp Sci Technol* 2006, 66, 548.
5. Neese, B.; Chu, B. J.; Lu, S. G.; Wang, Y.; Furman, E.; Zhang, Q. M. *Science* 2008, 321, 821.
6. Xu, H. P.; Dang, Z. M.; Jiang, M. J.; Yao, S. H.; Bai, J. B. *J Mater Chem* 2008, 18, 229.
7. Li, S. P.; Qin, Y. J.; Shi, J. H.; Guo, Z. X.; Li, Y. F.; Zhu, D. B. *Chem Mater* 2005, 17, 130.
8. Yang, S.; Yue, Z. X.; Li, M.; Nan, C. W. *Adv Funct Mater* 2005, 15, 1100.
9. Krzysztow, K.; Juan, V.; Anna, M.; Marcelo, M.; Philip, C.; Michae, S.; Alan, W. *Science* 2007, 318, 1892.
10. Jung, H. M.; Kang, J. H.; Yang, S. Y.; Won J. C.; Kim, Y. S. *Chem Mater* 2010, 22, 450.
11. Milind, A.; Shan, X. B. *Adv Mater* 2007, 19, 1369.
12. Kobayashi, Y.; Tanase, T. *J Eur Ceram Soc* 2008, 28, 117.
13. Wang, Y.; Wang, J. W.; Wang, F.; Li, S. Q.; Xiao, J. *Polym Bull* 2008, 60, 439.
14. Koerner, H.; Price, G.; Pearce, N. A.; Alexander, M.; Vaia, R. A. *Nature Mater* 2004, 3, 115.
15. Xu, H. P.; Dang, Z. M.; Yao, S. H.; Jiang, M. J.; Wang, D. Y. *Appl Phys Lett* 2007, 90, 152912.
16. Taipalus, R.; Harmia, T. *Comp Sci Technol* 2001, 61, 801.
17. Hong, C. Y.; You, Y. Z.; Wu, D. C.; Liu, Y.; Pan, C. Y. *Macromolecules* 2005, 38, 2606.
18. Xu, H. P.; Dang, Z. M.; Shi, D. H.; Bai, J. B. *J Mater Chem* 2008, 18, 2685.
19. Chiteme, C.; McLachlan, D. S. *Phys B* 2000, 69, 279.
20. Nan, C. W. *Prog Mater Sci* 1993, 37, 1.
21. Chiteme, C.; McLachlan, D. S. *Phys Rev B* 2003, 67, 024206.
22. Zhang, Y. H.; Lu, S. G.; Li, Y. Q.; Dang, Z. M.; Xin, J. H.; Fu, S. Y.; Li, G. T.; Guo, R. R.; Li, L. F. *Adv Mater* 2005, 17, 1056.
23. Psarras, G. C.; Manolakaki, E.; Tsangarris, G. M. *Compos A* 2001, 33, 375.
24. Li, Y. J.; Xu, M.; Feng, J. Q.; Cao, X. L.; Yu, Y. F.; Dang, Z. M. *J Appl Polym Sci* 2007, 106, 3359.
25. Pecharroman, C.; Fatima, E. B.; Moya, J. S. *Adv Mater* 2001, 13, 1541.
26. Winsor, D. L.; Scheinbeim, J. I.; Newma, B. A. *Polym Sci: Part B* 1996, 34, 2967.