Role of polymer matrix in large enhancement of dielectric constant in polymer-metal composites

Maheswar Panda, V. Srinivas, and A. K. Thakur

Articles you may be interested in

The influence of self-assembly behavior of nanoparticles on the dielectric polymer composites
AIP Advances **3**, 112106 (2013); 10.1063/1.4830279

Percolative conductor/polymer composite films with significant dielectric properties
Appl. Phys. Lett. **91**, 022912 (2007); 10.1063/1.2757131

Dielectric behavior of a metal-polymer composite with low percolation threshold
Appl. Phys. Lett. **89**, 072902 (2006); 10.1063/1.2337157

Dielectric enhancement in polymer-nanoparticle composites through interphase polarizability
J. Appl. Phys. **98**, 054304 (2005); 10.1063/1.2034654

Carbon nanotube composites with high dielectric constant at low percolation threshold
Appl. Phys. Lett. **87**, 042903 (2005); 10.1063/1.1996842

Role of polymer matrix in large enhancement of dielectric constant in polymer-metal composites

Maheswar Panda,[1,2] V. Srinivas,[1,3,a] and A. K. Thakur[1,4]

[1]*Department of Physics and Meteorology, Indian Institute of Technology Kharagpur, Kharagpur 721302, India*
[2]*Centre for Applied Physics, Central University of Jharkhand, Brambe, Ranchi-835205, India*
[3]*Department of Physics, Indian Institute of Technology Madras, Chennai 600036, India*
[4]*Department of Physics, Indian Institute of Technology Patna, Patna 800013, India*

Dielectric behavior of polymer (polar/nonpolar)-metal nanocomposites (PMCs) prepared under identical processing conditions have been compared. A high effective dielectric constant ($\varepsilon_{\text{eff}} > 2500$) with a moderate loss and a lower ε_{eff} (74) with low loss was observed, respectively, for polar and nonpolar PMC at their respective percolation thresholds (f_c). The results have been explained with the help of percolation theory and dipolar polarization. Similar value of f_c observed in both the PMC is attributed to the same order of conductivity of polymer matrices. The dipolar polarization present in the polymer plays a major role in the enhancement of ε_{eff}. © *2011 American Institute of Physics*. [doi:10.1063/1.3600345]

Insulating polymer-conductor composites (PCCs) have attracted the recent interest because of their very high effective dielectric constant (ε_{eff}) along with better mechanical flexibility that makes the materials suitable for a number of applications, such as, high charge storage capacitors,[1–14] embedded capacitor applications,[3] printed circuit boards,[15] etc. These PCC undergo an insulator–metal transition (IMT) at a critical volume fraction of the conductor (f_{con}) called percolation threshold (f_c) which is characterized by an abnormal increase in ac conductivity (σ_{eff}) and divergence in the real part of ε_{eff} in accordance with the percolation theory.[16,17] A variety of conducting fillers (such as, metals, alloys, carbon black/fiber, carbon nanotubes, conducting polymers, etc.) have been used for preparing PCC.[2–15,18–22] Among various PCC the polymer-metal composites (PMC) have attracted attention because of their high ε_{eff} and easier processing as compared to other PCC.[2–7] Several PCC have been investigated for higher ε_{eff}, such as, epoxy/silver composites,[2] ferroelectric polymer [polyvinyledene fluoride (PVDF)]/conductor composites have spanned recently.[4–15] These investigations show scattered values of ε_{eff} and f_c. The effects of nature of filler, along with their particle size, shape, and process conditions on ε_{eff} and f_c have been investigated in various PCC.[4–15,18–22] However, few studies are oriented towards investigation of (i) what is the role of polymer matrix in increasing the ε_{eff} at f_c? (ii) whether the extent of enhancement of ε_{eff} at f_c depend on the polymer matrix in case of PMC. We believe that polymer matrix also contributes in the extent of enhancement of ε_{eff} at f_c in the case of PCC/PMC. Therefore, in the present work two series of PMC with well characterized nanocrystalline nickel (n-Ni) have been prepared. Two types of polymers, such as, polar/ferroelectric (PVDF) and a nonpolar [low density polyethylene (LDPE)] polymers are used to prepare the composites under identical processing conditions and the dielectric behaviour has been investigated to compare the effect of polymer matrices.

Powders of PVDF/n-Ni and LDPE/n-Ni have been blended with the help of mortar and pestle for 2 h and the mixed powders have been hot molded under a temperature of 200 °C and 130 °C, respectively, (above the melting temperature of the polymers) at 10 MPa pressure. Several samples of diameter 13 mm and thickness ∼1.6 mm have been prepared to approach the value of f_c as closely as possible. Details of synthesis and electrical characterization method have been discussed elsewhere.[4,5]

The optical micrographs of the percolating PMC show that distribution of the bright metal clusters in their corresponding background polymer matrices (Fig. 1). The insets show the corresponding optical micrographs of the pure polymer matrices i.e., PVDF [inset, Fig. 1(a)] and LDPE [inset, Fig. 1(b)]. The distribution of metal clusters and the extent of connectivity of the fillers in both the matrices appear to be identical because of the same volume fraction of conductor (f_{con}) and same processing conditions suggesting that connectivity mainly originates from the process conditions although the adhesiveness for the two different polymers is different.

As shown in the Fig. 2(a) in the case of LDPE/n-Ni composites, the ε_{eff} rises from 19 to 36 at 1 kHz when f_{con} increases from 0.05 to 0.06. But in case of PVDF/n-Ni composites, the ε_{eff} rises from 90 to 2000 at 1 kHz when f_{con} increases from 0.06 to 0.07. Thus with the use of nonpolar polymer matrix a very low value of ε_{eff} is achieved although the f_c value remain same due to the identical process condition and same order of conductivity of both the polymer matrices. The ε_{eff} as a function of f_{con} for both the series of samples shows a sharp rise in its value and follows the power law Eq. (1),[16,17] given by

$$\varepsilon_{\text{eff}} \propto (f_c - f_{con})^{-s} \text{ for } f_{con} < f_c. \quad (1)$$

For PVDF/n-Ni and LDPE/n-Ni composites, the value found for f_c are 0.07 and 0.06, respectively, and the value of "s" are 0.75 ± 0.10 and 1.11 ± 0.12 [inset, Fig. 2(a)]. The critical

a)Author to whom correspondence should be addressed. Electronic mail: veeturi@phy.iitkgp.ernet.in. FAX: +91-3222-255303. Tel.: +913222283848.
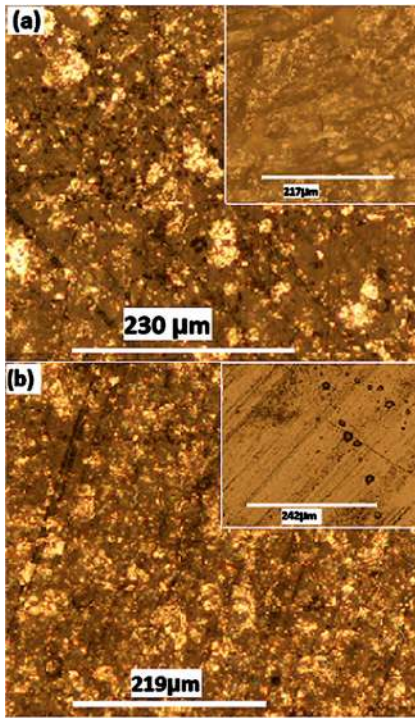
FIG. 1. (Color online) The optical micrographs of percolative samples corresponding to two different series of samples (a) PVDF based, inset: pure PVDF. (b) LDPE based, inset: pure LDPE.

FIG. 2. (Color online) The variation (a) σ_{eff} and (b) ε_{eff} as a function of f_{con} at 1 kHz for both the series of PMC. The solid (–■–) and open ($-\oplus-$) symbols represent PVDF and LDPE matrix, respectively. Inset: (a) least square fit to Eq. (1), upper: PMC based on PVDF, lower: PMC based on LDPE. (b) fit to Eq. (2), upper: PVDF, lower: LDPE based PMCs.

exponent $s = 0.75$ for PVDF/n-Ni composites is in agreement with the universal value of "s" (s_{un}) predicted for a 0–3 composite i.e., $s_{\text{un}} = 0.8 - 1$,[16,17] while $s = 1.11$ for LDPE/n-Ni composites does not agree with "s_{un}." This may be attributed to the difference in adhesive property of polymer matrices giving rise to different extent of interaction between the components although the connectivity remains same in both the PMC (Fig. 1). Similarly as shown in the Fig. 2(b) the value of σ_{eff} in case of both series of composites clearly demonstrates an IMT in the vicinity of $f_{con} = 0.07$ and 0.06, respectively. The σ_{eff} as a function of f_{con} increases abruptly near the critical concentration $f_c \sim 0.06$ indicating the formation of the continuous conductive network in the composite. The best fit of the conductivity data of PVDF/n-Ni and LDPE/n-Ni composites to Eq. (2),[16,17]

$$\sigma_{\text{eff}} \propto (f_c - f_{con})^{-s'} \text{ for } f_{con} < f_c \qquad (2)$$

yields $f_c = 0.07$ and 0.06, $s' = 1.16\pm0.4$ and 1.71 ± 0.66, respectively [inset, Fig. 2(b)]. The exponent value "s'" in both the cases is greater than the universal value ($s'_{\text{un}} = 0.8 - 1$) (Refs. 16 and 17) and explained on the basis of swiss-cheese model.[16,17] However the extent of connectivity in both the cases appears to be same (Fig. 1), higher value of $s' = 1.71\pm0.66$ for LDPE/n-Ni is observed as compared to $s' = 1.16\pm0.4$ in case of PVDF/n-Ni composites. It is attributed to the different extent of interaction between the two components in the respective PMC due to their difference of adhesiveness of the polymers. We note that both "s and s'" increase at the same rate for both the PMC. It is interesting to point out that the value of f_c is consistent with the values obtained from dielectric and conductivity data, sepa-
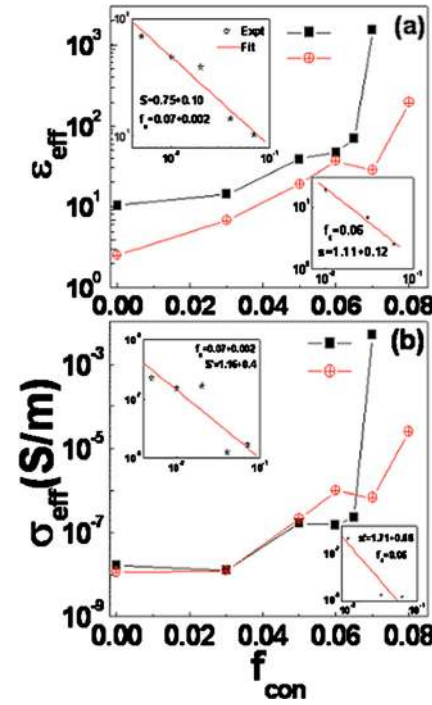
rately for both the PMC. Although the value of f_C of LDPE/n-Ni (0.06) and PVDF/n-Ni (0.07) composites is essentially same, but this f_c value neither coincides with the universal value of 0.16[16,17] nor with other experimental reports[4,5] which is attributed to the process conditions and particle size. Hence it may be suggested that as long as matrices used are of same order of conductivity, the value of f_c will not change much for a particular processing conditions.

The variation in σ_{eff}, ε_{eff}, and tan δ of the PMC based on PVDF and LDPE matrix as a function of frequency at 300 K is shown in Fig. 3. As shown in the Fig. 3(a), the static ε_{eff} value (at 100 Hz and room temperature) for the two pure polymers LDPE and PVDF are 2 and 10, respectively. The higher value of ε_{eff} in case of PVDF is due to the presence of additional dipolar polarization (presence of permanent dipoles) in case of PVDF as compared to LDPE. With increase in f_{con} in both the polymer matrices we observe that the extent of enhancement of ε_{eff} is different. These results suggest that the polymer matrix plays a major role in enhancement of ε_{eff} at f_c. Due to the high dielectric constant of PVDF having permanent dipolar polarization, the extent of enhancement in ε_{eff} is tuned while it does not occur in the case of nonpolar LDPE composites. The σ_{eff} of the composites [Fig. 3(b)] in the regime of $f_{con} < f_c$ exhibits a strong frequency dependence while its frequency dependence becomes gradually weaker in the regime of $f_{con} > f_c$. In LDPE/n-Ni, at f_c a mixed conductivity comprising of ac and dc conductivity is also obtained, but the region of dc plateau remains over a very narrow range of frequencies while a broader region of dc conductivity was found for PVDF/n-Ni composites [Fig. 3(b)], which is entirely due to the process conditions and the properties of the polymer matrix.
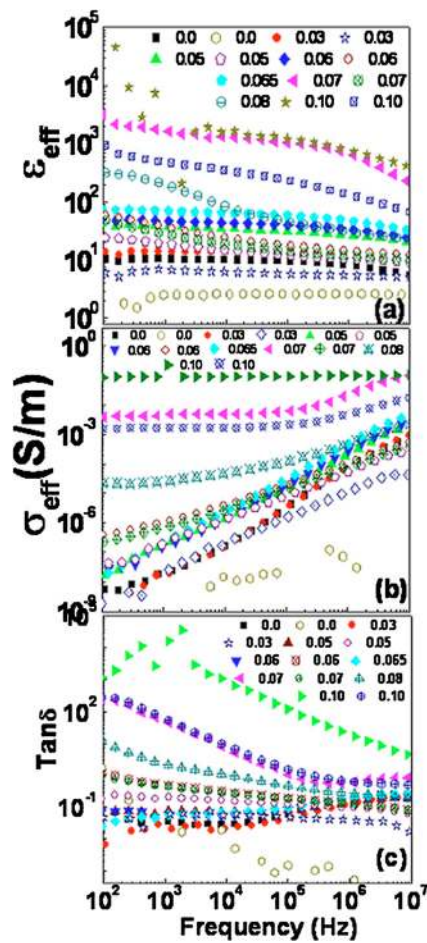
FIG. 3. (Color online) Variation in σ_{eff}, ε_{eff}, and Tan δ as a function of frequency for both the series of PMC. The solid (–■–) and open (– ⊕ –) symbols represent different samples of PMC based on PVDF and LDPE matrices, respectively.

Figure 3(c) shows the value of tan δ of the composites at low frequency undergoes a sharp increase for $f_{con} > f_c$ while maintains a value below 1 at high frequencies ($> 100 kHz$). For the composites with $f_{con} < f_c$, Tan δ is less than 0.1 irrespective of frequency. We also do not observe any dipolar relaxation from LDPE/n-Ni composites unlike that of PVDF/n-Ni composites below f_c which is due to the absence of dipoles in the polymer matrix. We may attribute the higher extent of increment of ε_{eff} in PVDF/n-Ni composites at f_c as compared to the ε_{eff} value in LDPE/n-Ni composites at f_c is due to broader region of dc conductivity. But this is not the case as even for one of highly conducting sample ($> f_c$) in case of LDPE/n-Ni (e.g., $f_{con} = 0.10$) the static ε_{eff} is 1200 as compared to the static ε_{eff} of 3000 at f_c ($f_{con} = 0.07$) for PVDF/n-Ni composites [Fig. 3(a)] although the dc conductivity region in the previous case is larger than the latter [Fig. 3(b)].

In conclusion, we found that the enhancement of ε_{eff} in PMC is largely tuned by the higher dielectric constant of the pure polymer. The polymer matrix plays a major role in the enhancement of ε_{eff} in a PMC which suggests that for higher ε_{eff} with flexibility (which is a major issue in present days), ferroelectric polymer based PMC/PCC should be given preference to be studied. As long as the two polymer matrices used are of the same order of conductivity, with same kind of filler, the value of f_c remains unaltered with the same process conditions. The value of critical exponents is also largely deviated with the change in polymer matrices arising due to the difference in their extent of interaction between the components of PMC due to the difference of their adhesiveness.

[1] Q. M. Zhang, H. Li, M. Poh, F. Xia, Z. Y. Cheng, H. Xu, and C. Huang, Nature (London) **419**, 284 (2002).

[2] L. Qi, B. I. Lee, S. Chen, W. D. Samuels, and G. J. Exarhos, Adv. Mater. (Weinheim, Ger.) **17**, 1777 (2005).

[3] Y. Rao and C. P. Wong, *IEEE Proceedings of the Electronic Components and Technology Conference* (IEEE, Piscataway, NJ, 2002), p. 920.

[4] M. Panda, V. Srinivas, and A. K. Thakur, Appl. Phys. Lett. **92**, 132905 (2008).

[5] M. Panda, V. Srinivas, and A. K. Thakur, Appl. Phys. Lett. **93**, 242908 (2008).

[6] M. Panda, A. K. Thakur, and V. Srinivas, J. Appl. Polym. Sci. **117**, 3023 (2010).

[7] Z. M. Dang, Y. H. Lin, and C. W. Nan, Adv. Mater. (Weinheim, Ger.) **15**, 1625 (2003).

[8] J. K. Yuan, W. L. Li, S. H. Yao, Y. Q. Lin, A. Sylvestre, and J. Bai, Appl. Phys. Lett. **98**, 032901 (2011).

[9] W. J. Li, Q. J. Meng, Y. S. Zheng, Z. C. Zhang, W. M. Xia, and Z. Xu, Appl. Phys. Lett. **96**, 192905 (2010).

[10] J. K. Yuan, Z. M. Dang, S. H. Yao, J. W. Zha, T. Zhou, S. T. Li, and J. Bai, J. Mater. Chem. **20**, 2441 (2010).

[11] Ch. Venkatesh, V. Srinivas, M. Panda, and V. V. Rao, Solid State Comm. **150**, 893 (2010).

[12] F. He, S. Lau, H. L. Chan, and J. Fan, Adv. Mater. (Weinheim, Ger) **20**, A1 (2008).

[13] Z. M. Dang, J. P. Wu, H. P. Xu, S. H. Yao, M. J. Jiang, and J. Bai, Appl. Phys. Lett. **91**, 072912 (2007).

[14] Z. M. Dang, L. Wang, Y. Yin, Q. Zhang, and Q. Q. Lei, Adv. Mater. (Weinheim, Ger.) **19**, 852 (2007).

[15] C. Huang and Q. Zhang, Adv. Funct. Mater. **14**, 501 (2004).

[16] D. Stauffer and A. Aharony, *Introduction to Percolation Theory* (Tayler and Francis, London, 1992).

[17] M. Sahimi, *Applications of Percolation theory* (Taylor and Francis, London, 1994).

[18] K. S. Deepa, M. T. Sebastian, and J. James, Appl. Phys. Lett. **91**, 202904 (2007).

[19] S. H. Yao, Z. M. Dang, M. J. Jiang, H. P. Xu, and J. Bai, Appl. Phys. Lett. **91**, 212901 (2007).

[20] L. Wang and Z. M. Dang, Appl. Phys. Lett. **87**, 042903 (2005).

[21] S. H. Yao, Z. M. Dang, M. J. Jiang, and J. Bai, Appl. Phys. Lett. **93**, 182905 (2008).

[22] M. Fu, Y. Yu, J. J. Xie, L. P. Wang, M. Y. Fan, S. L. Jiang, and Y. K. Zeng, Appl. Phys. Lett. **94**, 012904 (2009).