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Citation: Applied Physics Letters **92**, 132905 (2008); doi: 10.1063/1.2900710
View online: http://dx.doi.org/10.1063/1.2900710
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/92/13?ver=pdfcov
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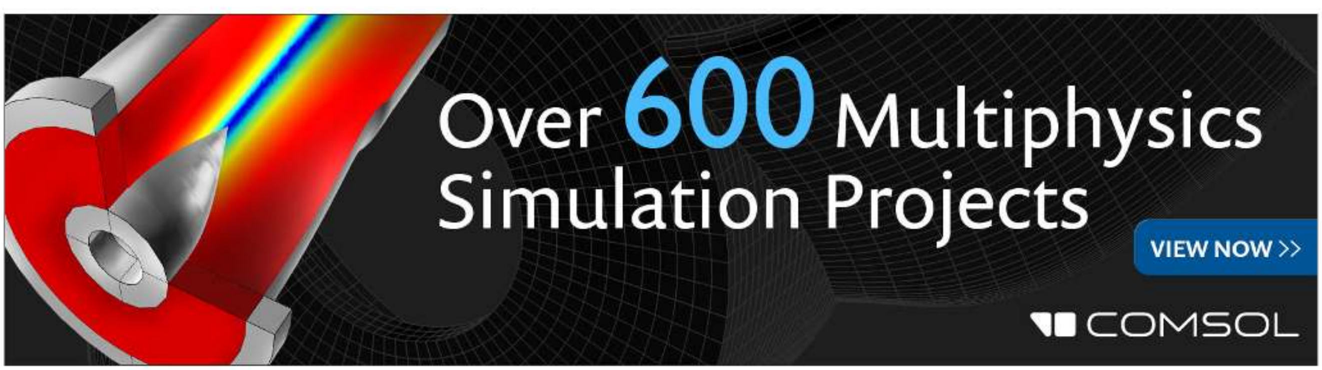

APPLIED PHYSICS LETTERS **92**, 132905 (2008)

On the question of percolation threshold in polyvinylidene fluoride/nanocrystalline nickel composites

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(Received 21 January 2008; accepted 29 February 2008; published online 1 April 2008)

The dielectric behavior of polyvinylidene fluoride (PVDF), nanocrystalline nickel (nc-Ni) composites has been investigated over a broad frequency range of 40 Hz–10 MHz. High effective dielectric constant ($\varepsilon_{\rm eff}$=2050) and low loss (tan δ=10) at 100 Hz have been observed near the percolation threshold. To the best of our knowledge, this is the highest $\varepsilon_{\rm eff}$ value reported to date among the PVDF based metal-polymer composites. The dielectric properties have been explained by using boundary layer capacitor effect and percolation theory while the dielectric anomalies are attributed to process of fabrication leading to thick insulating layer between the filler particles forming a gap in effective tunneling range of two filler particles and also making a difficulty in probability of higher order tunneling. © *2008 American Institute of Physics*.
[DOI: 10.1063/1.2900710]

Recently, there have been several studies on polymer-based composites that exhibit excellent physical properties coupled with mechanical flexibility. In particular, ferroelectric polymers, such as polyvinylidene fluoride (PVDF), poly[(vinylidenefluoride)-co-trifluoroethylene] [P(VDF-TrFE)], and polyvinylidene fluoride-trifluoroethylene-chlorofluoroethylene [PVDF-TrFE-CFE],[1] composites with a variety of fillers, such as ceramics, metals, or metal-ceramic components have been investigated and large changes in the effective dielectric constant ($\varepsilon_{\rm eff}$) have been reported in the neighborhood of percolation threshold.[2–5] Improvement in average dielectric constant of composite is expected when a low dielectric polymer is mixed with high dielectric ceramics. However, interestingly, it has been observed that metal-polymer composites[4–8] exhibit giant enhancement in $\varepsilon_{\rm eff}$ values with low dielectric loss near the percolation threshold, attained at lower filler concentrations compared to ceramic-polymer composites.[2] Such metal-polymer composites are the strong candidates for a broad range of applications, such as high charge-storage capacitors, electrostriction, etc.[9,10] In an effort to further enhance the $\varepsilon_{\rm eff}$, various groups have investigated a variety of composites, such as PVDF/Ni–$BaTiO_3$,[3] PVDF/micron size Ni particle,[5] epoxy/Ag flake,[8] PVDF/multiwall carbon nanotube (MWNT),[10] methyvinyl silicon rubber/MWNT,[11] etc. These investigations suggest that the dielectric behavior of the composites depend on physical properties of the constituents, preparation method, adhesiveness, interactions between fillers and polymer, as well as the size and shape of the fillers[12,13]. On the other hand, the compositions near the percolation threshold are of fundamental interest, as they become a testing bed for various percolation mechanisms formulated from theoretical investigations.

Although several studies show deviations from the percolation theories, interestingly, Dang *et al.* demonstrated ideal percolative behavior in hot-molded PVDF/Ni composites[5] with a percolation threshold $f_{\rm Ni}$=0.16, which is in agreement with the theoretically predicted value.[5,14] The observation of an extraordinary increase in $\varepsilon_{\rm eff}$ and true percolative nature in PVDF/Ni composites prompted us to investigate the effect of nanocrystalline (nc) nickel dispersion. In this communication, we report ferroelectric polymer (PVDF) based nc Ni composites with a very high $\varepsilon_{\rm eff}$ and low dielectric loss, prepared through a simple and cost effective process. We believe such a large enhancement in $\varepsilon_{\rm eff}$ has been observed for the first time in cold compacted PVDF/nc-Ni composites at a threshold composition of 0.28. Further, we also show that the processing conditions and particle size do play significant roles.

nc Ni metal particles of ~20–30 nm size were prepared via high-energy ball milling technique (RETSCH PM-200 model) from high purity (99.9%) nickel powders having initial size of ~20 μm. The polymer PVDF and nc-Ni metal particles were blended together in the form of pellets of diameter 11 mm and thickness ~1.5 mm under 30 MPa at room temperature. The electrical properties were measured using a Precision impedance analyzer (Agilent 4294A) in the frequency range of 40 Hz–10 MHz, with Agilent 16451B dielectric text fixture. The homogeneity of the samples was confirmed using a polarized optical and electron microscope.

A series of polymer-based composites with varying volume fractions of nc-Ni ($f_{\rm Ni}$) were prepared in order to approach the percolation threshold as closely as possible. The optical micrographs of the composites ($f_{\rm Ni}$=0.1, 0.28) shown in Figs. 1(a) suggest a random distribution of nc-Ni clusters at lower concentration in sharp contrast to the formation of self connected network of clusters at higher $f_{\rm Ni}$. From the high resolution micrographs, the Ni clusters in the polymer matrix can be seen in Figs. 1(b) with particle dimensions in the range of 20–30 nm, estimated from high resolution transmission electron microscope image [see inset of 1(b)].

The effective ac conductivity ($\sigma_{\rm eff}$), $\varepsilon_{\rm eff}$ of the composites as a function of $f_{\rm Ni}$ and frequency have been studied at 300 K. As shown in the Fig. 2(a), the $\varepsilon_{\rm eff}$ rises from 215 to 1273 when $f_{\rm Ni}$ increases from 0.27 to 0.28 at 1 kHz while it steeply rises from 255 ($f_{\rm Ni}$=0.27) to 2050 ($f_{\rm Ni}$=0.28) at 100 Hz [see Fig. 3(a)]. This $\varepsilon_{\rm eff}$ is the highest value achieved so far for a PVDF based metal-polymer composites. Similarly, $\sigma_{\rm eff}$ clearly demonstrates an insulator-metal transition in the vicinity of $f_{\rm Ni}$=0.28 [see Fig. 2(b)]. The large enhancement in $\varepsilon_{\rm eff}$ in the neighborhood of percolation threshold can

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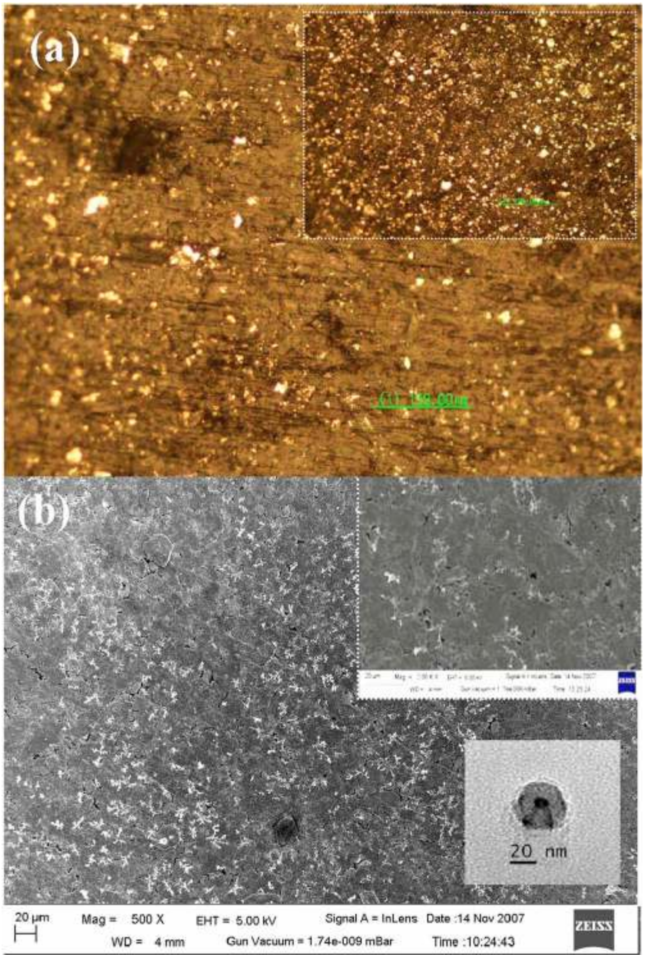

FIG. 1. (Color online) (a) Optical micrographs of $f_{\mathrm{Ni}}=0.10$ composite sample. Inset is for 0.28. (b) FESEM micrographs of the $f_{\mathrm{Ni}}=0.28$ composite sample. Inset: FESEM of $f_{\mathrm{Ni}}=0.28$ composite (top) and HRTEM image of the nano crystalline Nickel (bottom).

be understood on the basis of "boundary layer capacitor effect," i.e, near the percolation threshold, there are many conducting particles isolated by very thin dielectric insulating layer forming large number of microcapacitors which give rise to very high dielectric constant. These microstructural variations could be seen through micrographs (Fig. 1) and from earlier reports.[4–7] The abrupt change in σ_{eff} in the neighborhood of percolation threshold can be understood from percolation theory,[14] i.e., near the percolation threshold, the effective tunneling range of two filler particles overlaps leading to a sudden increment in probability of nearest neighbor as well as higher order tunneling.[12,15] According to percolation theory,[14] the power law dependence of dielectric constant near the percolation threshold is given by

$$\varepsilon_{\mathrm{eff}} \alpha (f_c - f_{\mathrm{Ni}})^{-s} \quad \text{for } f_{\mathrm{Ni}} < f_c, \tag{1}$$

where $\varepsilon_{\mathrm{eff}}$ is the effective dielectric constant, f_c is the percolation threshold and s is the corresponding critical exponent. The measured $\varepsilon_{\mathrm{eff}}$ as a function of f_{Ni} shows a divergence and follows the power law [Eq. (1)], with $f_c=0.278$ and $s=0.82\pm0.07$ [see inset of Fig. 2(a)]. The critical exponent s is in agreement with the earlier reported value of $s=0.89$ (Ref. 5) and universal value of s for a 0–3 composite ($s_{\mathrm{un}}=0.8-1$).[5,14] The dielectric loss factor also undergoes large change near the percolation threshold, i.e., it changes from 0.25 to 2.04 when f_{Ni} increases from 0.27 to 0.28 at 1 kHz

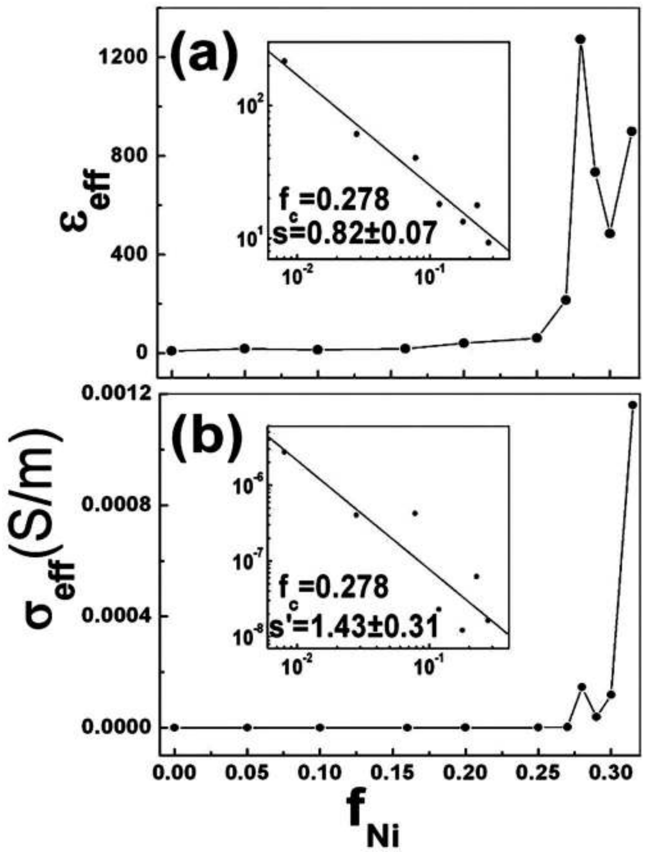

FIG. 2. (a) Effective dielectric constant. (b) Effective conductivity as a function of the volume fraction of Ni, measured at 1 kHz and 300 K. Inset: (a) the least square fit of $\varepsilon_{\mathrm{eff}}$ to Eq. (1). Inset: (b) least square fit of σ_{eff} to Eq. (2).

[see Fig. 3(c)]. As shown in Fig. 2(b), the σ_{eff} as a function of f_{Ni} at 1 kHz abruptly increases near the critical concentration $f_c \sim 0.28$ indicating the formation of the continuous conductive network in the composite. According to percolation theory,[14] the power law dependence of conductivity is:

$$\sigma_{\mathrm{eff}} \alpha (f_c - f_{\mathrm{Ni}})^{-s'} \quad \text{for } f_{\mathrm{Ni}} < f_c, \tag{2}$$

where f_{Ni} is the volume fraction of Ni, f_c is the percolation threshold, and s', is the critical exponent in the insulating region. The best fit of the conductivity data to Eq. (2) yields $f_c=0.278$, $s'=1.4\pm0.3$ [see inset of Fig. 2(b)]. The exponent value s' is higher than the universal value ($s'=0.8-1$) (Refs. 5 and 14) but close to the two phase PVDF-Ni composites, i.e. $s'=1.40$ (Ref. 5). A significant change in f_c (0.278) from the universal value (0.16) of percolation threshold[5,14] could be attributed to sample processing conditions. The other possibility could be because PVDF has a tendency to surround the nickel clusters leading to increase in adhesiveness,[13] such that the nickel clusters are separated by thick insulating layers (for $f_{\mathrm{Ni}}<0.278$) forming a gap in effective tunneling range of two filler clusters which probably inhibits the higher order tunneling,[15] similar to that has been observed in many granular composites which always show a higher value of f_c than the predicted value.[12,16]

The $\varepsilon_{\mathrm{eff}}$ of the composites upto $f_{\mathrm{Ni}}=0.25$ shows a weak dependence of frequency over the whole frequency range but as it approaches percolation threshold, the variation is more pronounced [see Fig. 3(a)]. The changes in $\varepsilon_{\mathrm{eff}}$ may be attributed to the larger leakage currents resulted from the higher conductivity of the composites as $f_{\mathrm{Ni}} \rightarrow f_c$. The σ_{eff}

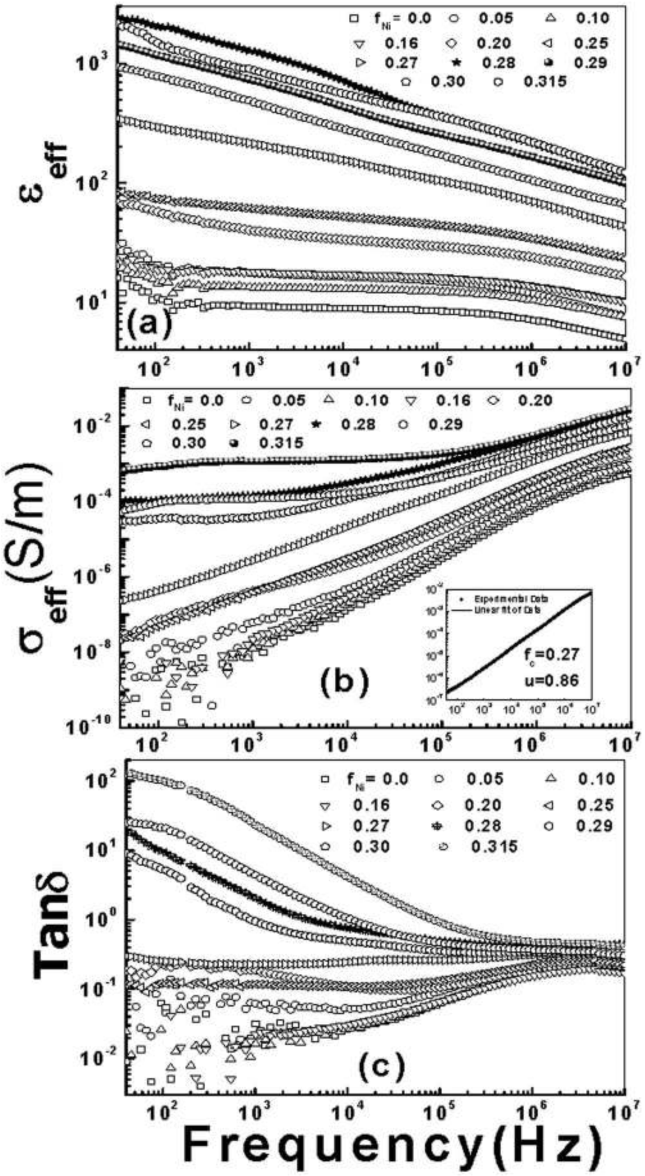

FIG. 3. Dependence of the (a) effective conductivity, (b) effective dielectric constant [Inset shows the best fit of the σ_{eff} values for $f_{Ni}=0.27$ to Eq. (3)], and (c) loss tangent on frequency at room temperature.

of the composites in the regime of $f_{Ni}<f_c$ exhibits a strong frequency dependence while its frequency dependence becomes weaker in the regime of $f_{Ni}>f_c$ [see Fig. 3(b)]. The characteristics, such as high conductivity in the regime of $f_{Ni}>f_c$ and its weak frequency dependence, of the composite may make the PVDF/nc-Ni composite an excellent antistatic media and shielding for electromagnetic or radio-frequency interference of electronic devices.[4] As $f_{Ni} \rightarrow f_c$ the frequency dependence of σ_{eff} can be expressed as a following power law from the percolation theory[5,14]

$$\sigma_{eff}(\varpi,f_c)\alpha\varpi^u, \quad (3)$$

where $\omega=2\pi\nu$, ν is the frequency, and u is the corresponding critical exponent. Equation (3) is best fitted for conductivity data obtained for $f_{Ni}=0.27$ giving $u=0.86$ [see inset Fig. 3(b)], which is a bit higher than the universal value (u_{un} ~ 0.70) and that of reported ($u=0.78$) for a similar composite of PVDF/Ni.[5] The higher u value observed in the present analysis compared to earlier[5] could be due to the deviation[4] of volume fraction of 0.008 between $f_{Ni}=0.27$ and percolation threshold $f_c=0.278$. Figure 3(c) shows the loss tangent of the composite at low frequency, undergoes a sharp increase for $f_{Ni}>f_c$, as reported by Li *et al.*[4] while maintains a value below 1 at high frequencies (>100 KHz). Such sharp rise in loss could be considered as one important feature of the percolative composite and evidence of the large leakage current in the composite. For the composites $f_{Ni}<f_c$, the loss tangent is less than 0.3 irrespective of frequency.

Interestingly dielectric and conductivity data fits yield the same f_c value but is significantly higher than that of the universal value (0.16)[14] which could be attributed to the process conditions. In order to verify this, PVDF/Ni composites were also prepared by following the same processing method but using 20 μm Ni particles. In this case the percolation threshold could not be achieved upto $f_{Ni}=0.5$. Due to increase in density of the particles and interparticle contacts[17] in the case of nc-Ni particles, the tunneling probability is enhanced,[15] leading to lowering of the percolation threshold to 0.28. However, with different process conditions, Dang *et al.* obtained $f_c=0.16$.[5] This suggests that the process conditions affect only the percolation threshold with no significant change in critical exponents.

In conclusion, for PVDF/nc-Ni composites very high values of dielectric constant and low dielectric loss at higher percolation threshold of 0.28 has been observed, attributed to increased adhesiveness between the filler and polymer due to difference in processing conditions. The conductivity and dielectric constant rapidly increase in the vicinity of percolation and the results are explained on the basis of conventional percolation theory.

M. Panda acknowledges financial assistance from CSIR (N. Delhi), India and Mr. Soumen Kar for his help.

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