Multiferroic properties of polyvinyledene fluoride/nickel nano-composites

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Electrical and magnetic properties of ferroelectric polymer (polyvinyledene fluoride) and ferromagnetic metal [nanocrystalline nickel (nc-Ni)] composites have been investigated as a function of volume fractions of nc-Ni (f_{nc}). A significant enhancement in saturation magnetization of 24 emu/g, measure of permeability (μ') of 1.11 and dielectric constant of 2050 at 100 Hz has been observed at the electrical percolation threshold (f_c) of the composite. The critical exponents (x and y) obtained are within the universal regime. The decrease of magnetization of the composite with decrease in f_{nc} is attributed to the dilution effect and magnetic dipolar exchange interaction. The constancy of coercive field (H_c) has been explained on the basis of Stoner-Wohlfarth model. The value of μ' increases linearly with increase of f_{nc} as the magnetic flux concentrates over individual n_c-Ni clusters/particles even beyond f_c. On the other hand, the value of μ' decreases for pure n_c-Ni probably due to the increased connectivity among the n_c-Ni clusters/particles and hence being a conductor results in eddy current generation in alternating magnetic field. The enhancement of dielectric constant near f_c is explained with the help of boundary layer capacitor effect.

Keywords: Composite materials, Percolation, Critical exponent, Permeability, Multiferroic

1 Introduction

The study of composite materials has been the subject of considerable interest in recent years because of their possible technological applications. The soft magnetic nano-composites or insulating polymer magnetic nano-composites (PMC) with nano sized metallic inclusions are common in established industrial applications because of the following properties/reasons. The composite of metal and insulator undergoes an insulator to metal transition (IMT) at a critical concentration of the metal, called electrical percolation threshold (f_c). This is characterized by the divergence in real part of dielectric constant and abnormal increase in its ac conductivity^{1} at f_c. With increase of conductor fraction in the insulating polymer matrix, the effective dielectric constant (ε_{eff}) and effective ac conductivity (σ_{eff}) of the composites have been observed to approach to very large values^{2-6} at f_c and interesting optical properties have also been found^{7}. A similar type of behaviour is also observed in the variation of inductance^{8} and imaginary part of permeability^{9,11} for magnetic metal-insulator composite systems at f_c. In case of ferromagnetic metal nano particles, the nano-dimensional metal granule is considered as a ferromagnetic particle possessing an intrinsic magnetic moment equal to the sum of magnetic moments of the atoms contained in this granule. If the energy of the magneto-static interaction between granules is below k_B T (k_B is Boltzmann constant and T is the absolute temperature), no correlation between the magnetization vectors of such particles takes place, and the composite is expected to show its paramagnetic/super paramagnetic properties. When an infinite network of contacting granules is formed in the insulator matrix, at a critical concentration of the magnetic filler particle called magnetic percolation threshold^{1,12-14} (m_c), conditions favouring exchange interaction between the atoms of the neighbouring granules in the matrix are expected^{12-14}. Hence, the material should acquire a drastic change in its magnetic properties (such as; dc magnetic susceptibility/magnetization/coercivity, etc). The multiferroic behaviour, dielectric relaxation, ferroelectricity and ferromagnetism have also been investigated in a lot of nanosystems^{15,16} and/or composite ceramics^{17-19}. Additionally, the composite of ferroelectric polymer, such as; polyvinylidene fluoride
(PVDF) and magneto-strictive components show recent interest in magneto-electric effect\textsuperscript{20,21}. Recently, magneto-electric effect is also observed in a lot of simple systems of ferroelectric oxides and Ni composites\textsuperscript{22} such as BaTiO\textsubscript{3}/Ni (Ref. 22), PZT/Ni (Refs 23,24), as Ni is the highest magneto-strictive\textsuperscript{22} metal among all the ferromagnetic metals. In the present paper, with the aim of achieving multiferroic/magneto-electric properties in a PMC along with the study of $m_c$ and $f_c$, a composite of PVDF/n$_c$-Ni has been investigated as a function of frequency of applied signal and volume fractions of n$_c$-Ni ($f_{Ni}$).

2 Experimental Details

The synthesis of PVDF/n$_c$-Ni composites and the measurement of their electrical properties can be found from earlier literature\textsuperscript{2}. Structural investigation was done with the help of X-ray diffractometer (Rigaku miniflex). The frequency dependence of initial permeability of the composites were measured with the help of turn coil method\textsuperscript{25} by passing 20 mA ac current through the pick-up coil, using Agilent 4294A impedance analyzer with the help of 42941A probe at room temperature in the frequency range 10 kHz - 10 MHz. FM hysteresis loop measurements were done with the help of a homemade VSM.

3 Results and Discussion

3.1 Structural and Micro Structural Studies

With increase of $f_{Ni}$ in the composites, the intensity of XRD peaks corresponding to fcc-Ni phase increases with a corresponding decrement in intensity of peaks for PVDF (Fig. 1). These changes confirm the formation of a two-phase composite. However, the observed broadening of Ni peaks in the composites is attributed to nano-crystallinity of Ni due to the reduction of it’s particle size.

The presence of two different phases in the composites can be observed from the optical micrographs (Fig. 2). The extent of in-homogeneity of distribution of metallic fillers (brighter clusters) in the polymer matrix increases with increase of $f_{Ni}$ and hence, the cluster size increases.

3.2 Dielectric and Magnetic Studies

The enhancement in $\varepsilon_{eff}$ in the neighbourhood of $f_c$ and the critical exponents ($x$ and $y'$) is explained on the basis of “boundary layer capacitor effect”\textsuperscript{1-6} and “percolation theory”\textsuperscript{1-6}. The universal fractional power laws as a function of frequency in the vicinity of $f_c$,\textsuperscript{26-28} given by

$$\sigma_{eff} (\omega, f_{Ni} \approx f_c) \propto \omega^x$$

and

$$\varepsilon_{eff} (\omega, f_{Ni} \approx f_c) \propto \omega^y$$

where $f_{Ni}$ is the volume fraction of n$_c$-Ni, $\omega$ is the frequency of applied ac signal, $x$ and $y$ are the critical exponents, have been fitted to the experimental results of the composites (Fig. 3). The critical exponents obtained from the fit for $f_{Ni}$$\rightarrow$$f_c=0.27$ ($x=0.86$ and $y=0.16$) are slightly above the universal values\textsuperscript{26,27} ($x=0.72$, $y=0.28$). As predicted under the intercluster polarization model the relation\textsuperscript{26,27} $x+y=1$, is well satisfied for $f_{Ni}$$\rightarrow$$f_c=0.27$ while $x+y > 1$ for $f_{Ni}$ (0.25) < $f_c=0.27$ (Fig. 3). The variation of $\sigma_{eff}$ as a function of frequency at different $f_{Ni}$ is shown in Fig. 4. It is

![Fig. 1—X-ray diffraction pattern of PVDF/n$_c$-Ni composite samples for $f_{Ni}=0.0$ to 0.315 from bottom to top respectively](image)

![Fig. 2—Microstructure/optical micrographs of the polished surface of the pure PVDF and PVDF/n$_c$-Ni composite samples (a) $f_{Ni}=0.0$, (b) $f_{Ni}=0.10$, (c) $f_{Ni}=0.20$ and (d) $f_{Ni}=0.28$, respectively](image)
observed that the plot shows dispersion of ac conductivity with frequency for all the composites and the experimental results agree with the equation

\[ \sigma_{ac}(\omega) = \sigma_{dc} + A\omega^k \]

with the values of \( k \) in the universal limit (0,1).

The \( \varepsilon_{\text{eff}} \) at 100 Hz and the saturation magnetization (\( M_s \)) of the composites as a function of \( f_{\text{Ni}} \) are shown in Fig. 5. The value of \( \varepsilon_{\text{eff}} \) rises from 255 to 2050 when \( f_{\text{Ni}} \) increases from 0.27 to 0.28. All the composites show typical ferromagnetic hysteresis (Fig. 6 and its inset) along with their magnetic saturation (inset, Fig. 5). The value of \( M_s \) increases from 7 emu/g for \( f_{\text{Ni}} = 0.05 \) to 24 emu/g for \( f_{\text{Ni}} = 0.28 \) with increase of \( f_{\text{Ni}} \) (Fig. 5). In order to extract the magnetic parameters, the room temperature \( M-H \) curves of all the composite samples are fitted to the usual function

\[ M(H) = \frac{2M_s}{\pi} \tan^{-1}\left( \frac{H + H_C\tan(\pi S)}{H_C} \right) \]

The quantities \( M_s \) and \( H_C \) give the saturation magnetization and coercivity of the samples, respectively where ‘S’ is known as “squareness” ratio of the ferromagnetic loop and is defined by the ratio of remnant magnetization (\( M_r \)) to saturation magnetization (\( M_s \)) of the ferromagnetic loop, i.e., \( S = M_r/M_s \). Reasonably good fits of Eq. (4) to the magnetization curves have been obtained for all the composite samples (Fig. 6 and its inset). Table 1 compares the magnitude of \( M_s \), \( M_t \) and \( H_C \) for all the samples obtained from the fits. As expected, it is observed from Table 1 that the values of \( M_s \) and \( M_t \) increase with increase of \( f_{\text{Ni}} \) while \( H_C \) remains constant.
the magnetic field, well above 3000 Oe (inset, Fig. 5). The magnitude remains constant with variation of frequency up to 10 MHz (shown up to 1 MHz in Fig. 7). The magnitude of zero field effective permeability ($\mu'$) as a function of $f_{Ni}$ for various frequencies. The magnitude of $\mu'$ decreases with increase of $f_{Ni}$ as can be observed from Fig. 5 that the slope ($dM_s/df_{Ni}$) of $M_s$ vs $f_{Ni}$ curve decreases with increase of $f_{Ni}$. This may be attributed to at lower $f_{Ni}$ the particles/clusters are well separated from one another and the magnetic dipolar interaction between them is weak, which is also minimized because of the insulating, diamagnetic polymer matrix forbidding the interaction between the particles. The value of $M_s$ decreases linearly with increase of $f_{Ni}$ in the region of $f_{Ni} << f_c$ that can be understood on the basis of dilution effect. As $f_{Ni} -> f_c$, the particles are very close to each other and the coupling between the magnetic moments of two or more clusters become prominent because of the increased dipolar interaction and that leads to lowering of rate of increment of $M_s$ with $f_{Ni}$ for $f_{Ni} \geq f_c$.

The value of $M_s$ for all the composites is achieved for the magnetic field, well above 3000 Oe (inset, Fig. 5).

3.3 Permeability Studies

Figure 7 shows the real part of permeability/initial zero field effective permeability ($\mu'$) as a function of $f_{Ni}$ for various frequencies. The magnitude of $\mu'$ remains constant with variation of frequency up to 10 MHz (shown up to 1 MHz in Fig. 7). The magnitude of permeability is considered both due to the ferromagnetic properties of $n_c$-Ni and the generation of eddy currents by an alternating magnetic field.

The value of $\mu'$ of the composites for various $f_{Ni}$ increases with increase of Ni content linearly even beyond $f_c$, i.e., up to $f_{Ni} = 0.315$ and falls for pure $n_c$-Ni. Although the observed $f_c$ value is $f_{Ni} = 0.28$, the observation of magnetic anomaly beyond $f_{Ni} = 0.315$ unlike that of earlier literature may be attributed to the following. From literature, it is observed that the value is $0.25$ is of pure ac conduction while the conductivity for $f_{Ni} = 0.28$ and 0.315 is of mixed type, i.e., the dc conduction in the lower frequency region followed by an ac conduction in the higher frequency region (Fig. 4). This type of mixed conductivity is the complete signature of a microstructure in which, definitely the conducting particles are isolated from each other by a thin insulating polymer layer that prevents the generation of eddy current in the samples. Hence, due to the non-setting of eddy current in the samples, the value of $\mu'$ increases linearly up to $f_{Ni} = 0.315$ since the magnetic flux is more concentrated. But in the case of pure $n_c$-Ni, the value of $\mu'$ decreases as compared to $f_{Ni} = 0.315$ (Fig. 7) which may be due to the combined effect of ferromagnetic properties of $n_c$-Ni and the generation of eddy currents by an alternating magnetic field.

Here the concept of $M_s$ could not be realized in PVDF/$n_c$-Ni composites which may be attributed to

<table>
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<th>$f_{Ni}$</th>
<th>$M_c$(emu/g)</th>
<th>$M_s$(emu/g)</th>
<th>$H_c$(Gauss)</th>
<th>Squareness ratio($S=M_s/M_c$)</th>
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<tr>
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the presence of larger nc-Ni clusters in the polymer matrix giving rise to their individual permanent ferromagnetism arising due to their multi-domain nature. It is interesting to point out the ferroelectric behaviour of PVDF/nc-Ni composites has been explored\(^3\), however, the magneto-electric effect, in such a simple system will be quite interesting and needs further investigation.

4 Conclusions

At \(f_c\) of PVDF/nc-Ni composites, a very high dielectric constant of 2050 at 100 Hz and a high \(M_c\) of 24 emu/g close to pure nc-Ni (30 emu/g) along with a higher value of \(\mu'=1.11\) is observed. The critical exponents found at \(f_c\) were in their universal region. The decrease of magnetization for the composites below \(f_c\) is explained with the help of dilution effect and magnetic dipolar exchange interaction. The increase of \(\mu'\) linearly with \(f_{Ni}\) is explained on the basis of concentrated magnetic flux to the individual nc-Ni clusters/particles and the non-generation of eddy current in the samples while its decrement is explained on the basis of generation of eddy current in the samples. The concept of \(m_c\) could not be realized due the presence of larger nc-Ni clusters in the polymer matrix giving rise to their individual permanent ferromagnetism arising due to their multi-domain nature. The multi-functional properties of the composites may make them suitable for various applications, such as high charge storage capacitors, magnetic memories, high frequency applications, etc.

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References