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Structural and dielectric properties of ferroelectric pvdf/fe$_3$o$_4$ nanocomposites

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ABSTRACT

Magnetic particles embedded in polymer matrix like ferroelectric PVDF have excellent potential application such asmagneto-optical storage devices, flexible electronic devices etc. We report the fabrication Iron oxide (Fe_3O_4) nanoparticle loaded polymer nanocomposites. The prepared nanocomposites were characterized by different techniques. A homogeneous dispersion of Fe_3O_4nanoparticles throughout PVDF matrix was observed in the cryo-fractured surfaces by scanning electron microscopy.X-ray diffraction (XRD) and Fourier transform infra red (FTIR) spectroscopy indicate that the crystal structure is not much affected with the addition of Fe_3O_4 nanoparticles.Broadband dielectric relaxation spectroscopy (DRS) technique is used to investigate the dielectric relaxation and molecular mobility in PVDF/Fe_3O_4 nanocomposites. Dielectric spectroscopy showed an increase in the permittivity of nanocomposites in the whole frequency range studied. Good dispersion of the filler and synergic interaction between filler and polymer were found to enhance the overall properties in nanocomposites.The fabricated nanocomposites very promising for use in electronics packaging substrate as an alternative substrate owing to theiruniquestructural and dielectric properties.

KEYWORDS: PVDF, nanocomposites, dielectric permittivity, Fe_3O_4.

INTRODUCTION

Hybrid inorganic–organic nanocomposite materials are of current interest because of their multifunctionality, ease of processability, and potential for large-scale manufacturing. Many attractive properties of polymers like noncorrosiveness, light weight, mechanical strength, and dielectric tunability can be utilized along with magneticand optical properties of nanoparticles to make multifunctional materials (Singh *et al.*, 2010).The advantages of these materials in electromagnetic interference (EMI) reduction are due to desirable properties like frequency agility, light weight, and noncorrosive nature. This materials also offers potential application various field where high strength magnetic materials with low cost are desired. This led to tremendous boost in the development of organic based nanocomposites.

Inclusion of ferromagnetic nanoparticles in polymers is especially important as magneticnanoparticles have shown promise in various potential applications like spin-polarizeddevices, carriers for drug delivery, magnetic recording media, high-frequency applications, etc. [Srinivasan *et al.,* 2010; Lui *et. al.,* 2010]. However, for most of these highly specialized applications, there is a practical need to disperse the nanoparticles in nonmagnetic media that can be easily processed. Polymer materials are very well suited for this purpose. Magnetic nanoparticles embedded in polymer matrices have excellent potential for electromagnetic device applications like electromagnetic interference suppression [Zhang *et al.*, 2007; Wei *et al.,* 2006]. Advances made to prepare the multifunctional nanocomposites have led great improvement in this field.Several approaches have been developed to synthesize these composites in bulk as well as thin-film forms like sol gel, vacuum evaporation from powders, layer-by-layer self assembly, etc. In the present work, we have synthesized polymer nanocomposites of Poly (vinylidene fluoride) doped with varying concentrations of Fe_3O_4 nanoparticles (~30-50 nm in size).These nanocomposites were processed using simple melt blending technique. The polymer processing conditions were optimized to achieve good uniform dispersion of the nanoparticles in the polymer matrix.

EXPERIMENTAL DETAILS

PVDF Grade, Solef 1008 (with weight average molecular weight of $100X10^3$ g/mol) procured by Solvay Belgium is used for this study. Fe_3O_4 nanoparticles were procured from Aldrich Chemicals. The Fe_3O_4 were used as received for the experiments without any chemical treatment for surface modification. The nanocomposites of PVDF with various wt % of Fe_3O_4 were processed via melt mixing in Thermo Haake Polylab batch mixer.Various wt% of Fe_3O_4 viz. 10, 20, 30% is mixed with PVDF in a 50 gm batch of Thermo Haake Rheochord for 5 min at 200^oC and 60 rpm screw speed. The films of various compositions were processed on Carver Press (Germany) at 200^oC under 5-ton pressure. The thickness of the film was uniform and is about 0.4 to 0.5 mm. The dispersion of Fe_3O_4 nanoparticles in the polymer matrix is determined from the morphology of fractured surfaces of PVDF/Fe_3O_4 nanocomposites using Leica-440 Scanning Electron Microscope.A Rigaku model Dmax 2500 X-ray diffractometer with Cu K_α radiation with a wavelength of 1.54Å and an energy value of 8.05 KeV was used for this purpose.Broadband dielectric measurements were carried out over nine decades of frequency(i.e.100Hz– 10MHz) at different constant temperatures using dielectric analyzer and advanced software obtained from Novocontrol. The sample temperature was stable within less than ±0.1 °K. The effective diameter of the sample was 20 mm, and the thickness of film was about 0.3 mm as already described. The dielectric measurements were carried out using two gold coated cooper electrodes with 20 mm diameter.

RESULTS AND DISCUSSION

Scanning electron micrograph of PVDF/Fe_3O_4 nanocomposites is shown in Figure 1.SEM morphology shows uniform dispersion of Fe_3O_4 in polymer matrix without any obvious agglomeration. The efficiency of the nanoparticles in improving the properties of the polymer materials is primarily determined by the degree of its dispersion in the PVDF matrix.The microstructure of the fractured cross-section of the polymer nanocomposites shows a kind of interconnected network of nanoparticle assembly in polymer matrix.Visibly it appears that nanoparticles are coated by polymer matrix. SEM analysis shows that nanoparticles have strong coating with polymer. TEM micrograph shows the spherical particle shape of Fe_3O_4 nanoparticles. The particle size of Fe_3O_4 was estimated to be 30-50nm.

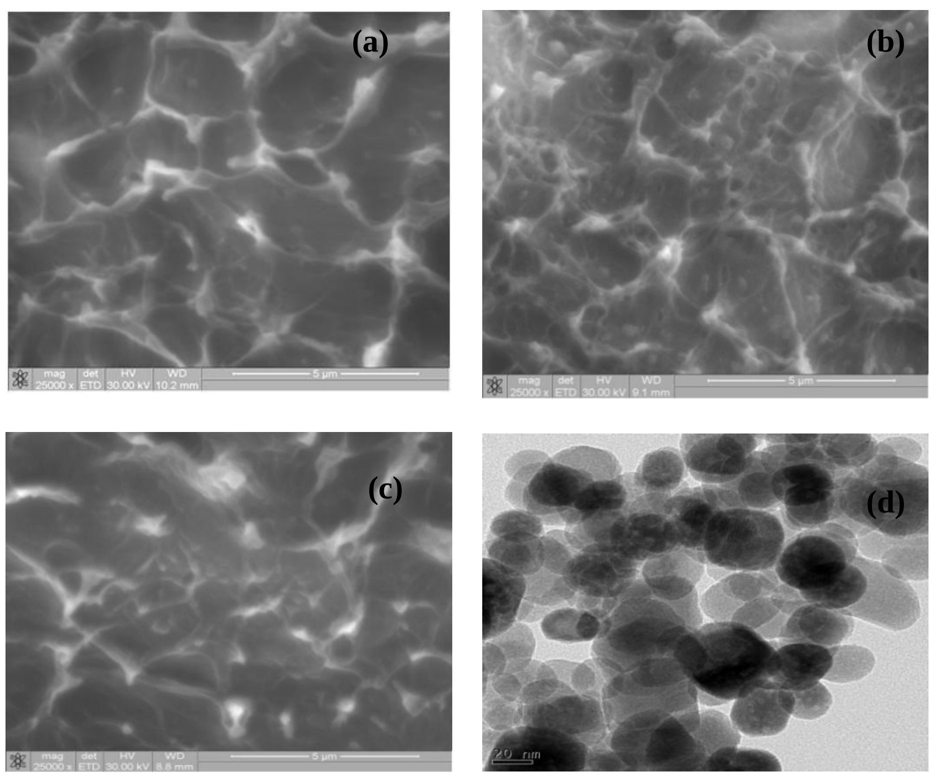

Fig 1: SEM micrographs of PVDF/Fe_3O_4 nanocomposites with different loading of Fe_3O_4 nanoparticles.

X-ray diffraction pattern of PVDF/Fe_3O_4 nanocomposites is shown in Figure 2.X-ray diffraction study indicates that no significant structural changes were occurred in PVDF/Fe_3O_4 nanocomposites. The crystalline morphology remains same in nanocomposites. The diffraction pattern show characteristic peaks of PVDF and sharp increased diffraction peaks of Fe_3O_4were observed with increasing Fe_3O_4 content [Lee et. al. 2002]. The incorporation of Fe_3O_4 nanoparticles produces neither a new peak nor a peak shift with respect to PVDF indicating that Fe_3O_4 filled PVDF nanocomposites consist of two phase structures i.e. polymer and nanoparticle.

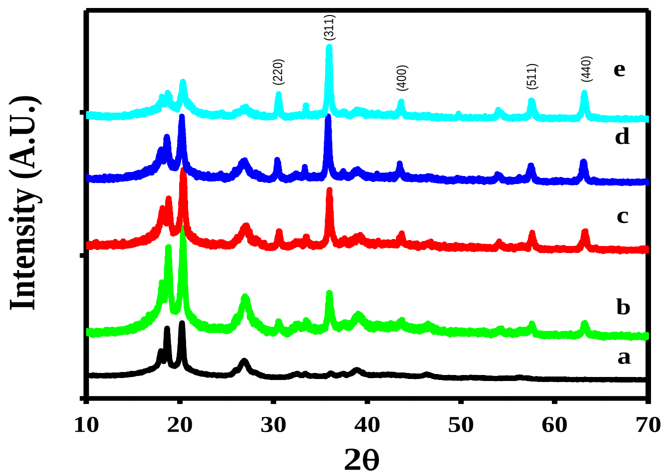

Fig 2: X-ray diffraction pattern of PVDF/Fe_3O_4 nanocomposites

Room temperature dielectric properties

The frequency dependence of the dielectric properties of PVDF/Fe_3O_4 nanocomposites with various volume fraction of the Fe_3O_4 is shown in Figure 3 (a) and (b). It can be seen that the dielectric permittivity is dependent on both frequency and filler loading. The dielectric permittivity for neat PVDF is around 11 and it increases to 38 for 40 wt% of Fe_3O_4 nanoparticles loading. With increasing frequency dielectric permittivity decreases in PVDF and similar trend is followed in nanocomposites. Dielectric constant increases to as high as 38 at frequency 10^{+02} Hz for 40 wt% loading of Fe_3O_4 nanoparticles. It is worth to note that the dielectric permittivity is increased in the whole frequency range of measurement. The increment in the permittivity in the high frequency region brings the interest of these materials for application in high frequency electronic devices. The high values of permittivity observed in the nanocomposites may be due to the interfacial effects in polymer nanocomposites. For PVDF and nanocomposites up to 30% filler loading, dielectric constant is less dependent on frequency and whereas for 40% loading strong frequency dependence is seen in the dielectric spectra.In dielectric permittivity spectra, strong frequency dispersion regions are observed above frequency 10^{+06}Hz and a frequency independent region in between. Generally, dielectric dispersion of Fe_3O_4 nanoparticles is expected to be small up to microwave frequencies. Hence the dispersion observed in the permittivity originates from the dielectric relaxation processes in polymer nanocomposites. The dielectric dispersion located at 2X10^{+07}Hzisattributed to glass transition relaxation respectively.

Figure3(b)shows the variation of loss tangent (tan δ) with frequency for PVDF/Fe_3O_4 nanocomposites at room temperatures. Dielectric loss curve shows broad relaxations corresponding to the glass transition temperature [Shen et. al. 2007; Chu et. al. 2009]. In PVDF/Fe_3O_4 nanocomposites, glass transition relaxation systematic shifts to lower frequency with increasing filler loading. The inclusion of nanoparticles leads to an early onset of dispersion in permittivity with frequency. Moreover, the maximum value of tan δ is less than 0.2 for the entire range of frequencies studied, which is very important for most of dielectric applications.

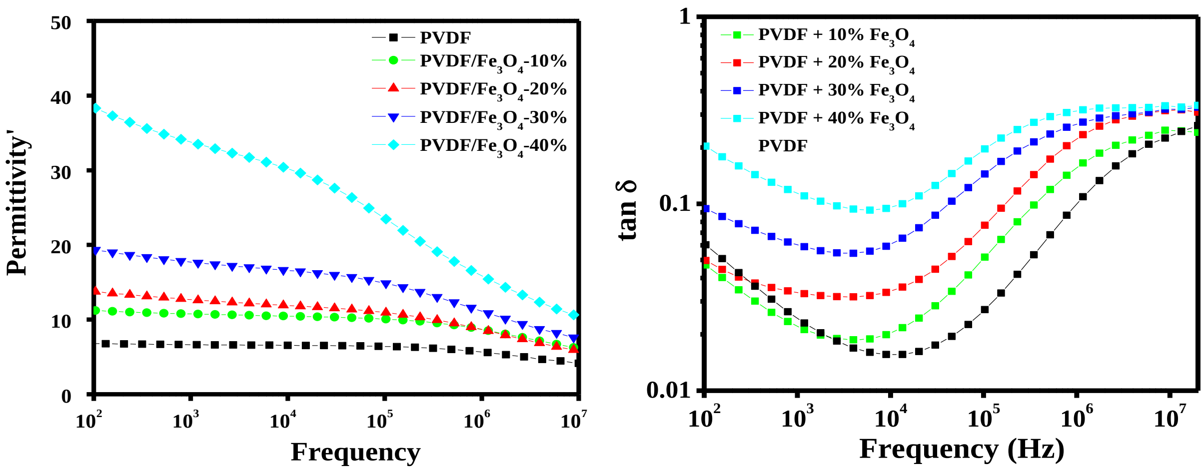

Fig.3: Frequency dependent dielectric spectra of PVDF/Fe_3O_4 nanocomposites.

Fitting to the experimental datausing Log Model

The variation of the permittivity with filler can be studied using various equations [Cheng et. al. 2007]. Log law model is often used to predict the dielectric permittivity of composite systemsand is given by following equation,

$$\log \varepsilon'_{composite} = \log \varepsilon'_{matrix} + \varphi_{filler} \log\left(\frac{\varepsilon'_{filler}}{\varepsilon'_{matrix}}\right) \text{----------(1)}$$

This model takes the filler content and the permittivity of constituent materials into account. Figure4 shows the variation of dielectric permittivity with filler loading. The solid line is fitting line to the observed data which shows that the data can be best fitted using log law model.

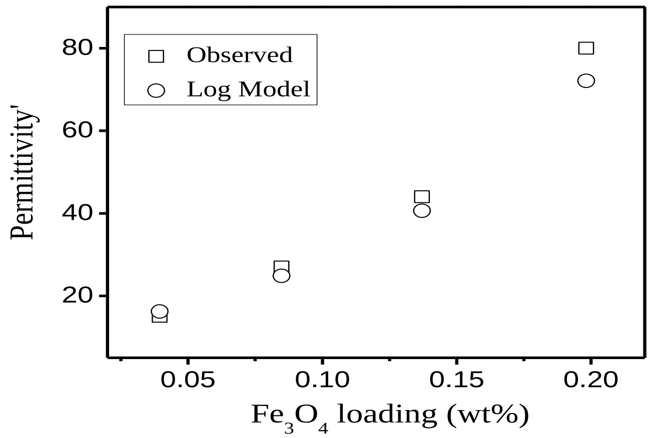

Fig.4: Fitting of observed dielectric data to log law model.

CONCLUSION

This work describes fabrication of PVDF/Fe_3O_4 nanocomposites by simple melt mixing method. The morphology study indicates uniform dispersion Fe_3O_4 nanoparticles in the polymer matrix. The structural analysis shows that addition of Fe_3O_4 nanoparticles does not change the crystal structure of polymer matrix. Significant enhancement in the dielectric properties was observed with the addition of Fe_3O_4 nanoparticles. Moreover the dielectric losses in the nanocomposite are also very low. Further, the observed dielectric permittivity data can be fitted using log law model. Thus, the addition of Fe_3O_4 nanoparticles gives remarkable enhancement in the dielectric properties of polymer.

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