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STUDY OF DIELECTRIC AND PIEZOELECTRIC PROPERTIES OF 0-3 PZT/PVB/CNT NANO-COMPOSITES FOR SENSOR APPLICATIONS

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Abstract : In present work, we prepared PZT-PVB-CNT 0-3 composites with 60% ceramic volume fraction with the inclusion of CNTs from 0 to 1.5 vol%. Dielectric properties of these samples were obtained in a wide frequency range (100 Hz to 1 Mhz) at room temperature. The piezoelectric properties of these composites were analyzed by measuring piezoelectric charge constants (d_{33}). The dielectric and piezoelectric properties of these composites were studied as a function of CNT volume content. Poling voltage required to pole such three phase composites is less than half of that required to pole two phase PZT/PVB composites. It has been observed that the CNTs cause an increase in the dielectric and piezoelectric properties of these composites. The piezoelectric and dielectric properties of composites varied only slightly at low volume concentration of CNT inclusion but the properties were found to change drastically on increasing the volume concentration of CNTs at percolation threshold.

Index Terms **– Three phase Nano composites, Percolation threshold, piezoelectric sensors, Dielectric properties, CNT reinforcement**

Introduction

Composites are formed by incorporating multiple phase components in a material in such a way that the properties of the resultant material are unique and not otherwise attainable. The ceramic –polymer composite posses the mechanical strength, flexibility **,** formability of the polymer **and** high electro-active piezoelectric properties of the ceramic Lead Zirconate Titanate (PZT)[1]**.** A composite having at least one phase in the nanometer scale is called nano-composite. The general idea behind the addition of the nanoscale phase is to create a synergy between the various constituents, such that novel properties capable of meeting or exceeding design expectations can be achieved. 0-3 composites as fabricated by imbedding piezoelectric ceramic powder into a polymer matrix have attracted considerable research interest because of their potential in applications such as piezoelectric sensor, ultrasonic transducer, and pressure sensors etc.[2] A potential way to improve piezoelectric & dielectric properties of theses composites is by inclusion of third reinforcement nano phase i.e. nano fillers such as Carbon nano particles, Carbon Nano Tubes (CNTs). [3]In such composites, the first and third phases are piezoelectric and nano fillers that are distributed within the host matrix, while the second phase is matrix polymeric material that is self-connected in three dimensions. The properties of nano-composites rely on a range of variables, particularly the matrix material, loading, degree of dispersion, size, shape, and orientation of the nanoscale phase and interactions between the matrix Phase and the nano-scale phase. Due to the nanos cale size of the reinforcing phase, the interface-to-volume ratio is significantly higher than in conventional composites. As a result, the volume fraction of the second phase can be reduced, without degradation of the desired properties. Due to reinforcement by nanofillers in such composites , some of the ceramic particles get connected with each other via these nanofillers and thus forms a network in such reinforced nano composites. This conductive path is also referred as percolation path. This conductive path in turn help in developing effective DC poling electric field acting on the ceramic particles. Thus poling efficiency of the composites is increased due to third reinforcing CNT phase. [4]Piezoelectric ceramic-polymer composites are considered as promising materials for applications in high-pressure sensors, hydrophones, vibration sensors and actuators by virtue of their appreciable piezoelectric, dielectric & pyroelctric properties and therefore have attracted considerable research interest.[5, 6, 7, 8]

In this work, we have prepared flexible three phase 0-3 composite were designed with Polyvinyl chloride (PVC) as host phase, ferroelectric ceramic Lead Zirconate Titanate (PZT) as active phase and Carbon Nano particles (CNPs) as third reinforcing phase using hot press technique. Poly (Vinyl Butyral) (PVB) was chosen as a host matrix phase to design 0-3 PZT-PVB composite with varying ceramic volume fractions. Poly(vinyl butyral) (PVB) is sturdy and flexible. Especially, it is known for its high impact strength at low temperatures. Furthermore, PVB has excellent adhesive properties with many materials such as glass, metal, plastics and wood.[9,10,11] Piezoelectric and dielectric properties of such designed composites were studied and analyzed. These campsites were reinforced with CNT as third phase to obtain 0-3-0 PZT/PVB/CNT nano-composites. Effect of third phase reinforcement on the dielectric and piezoelectric properties of the composites were studied and analyzed.

1. EXPERIMENTAL

2.1 Materials & Sample Preparation:

Ferroelectric ceramic Lead Zirconate Titanate (PZT) with structure $Pb(Zr_{1-x}Ti_x)O_3$ was prepared using standard mixed oxide method. The mixed oxide route is the most common route to synthesize PZT ferroelectric ceramics.[12,13] The ingredients PbO, ZrO_2 and TiO_2 were procured from Sigma-Aldrich. Using the step wise procedures of mixed oxide route including ball milling, calcinations etc. , the PZT ceramic powder with particle size in microns was prepared.PVB was procured from Sigma-Aldrich.

The Carbon Nanotubes (CNTs) were procured from Sigma-Aldrich having purity of approximately 93% and diameter 70-90 nm. The surface modification of CNTs was carried out using UV treatment method which is a reported method to increase interface cohesion with the matrix and dispersion in the matrix.[14]

Three phase PZT-PVB-CNT 0-3 composites were prepared using hot press method. To prepare the composite, PVB was first dissolved in Ethanol. PZT Ceramic powder was added for 60% ceramic volume fraction by weight in PVB solution and was blended properly to form mixture. For preparing three phase PZT-PVB-CNT 0-3 nano-composites various volume percentages of CNTs ranging from 0.1 to 1.5 volume % were added in the two phase PZT-PVB composites with 60% ceramic volume fraction (PZT content). For proper dispersion of CNTs in PZT-PVB composite, the CNTs in PZT and PVB mixtures were thoroughly mixed by ultrasonic agitation for one hour.So obtained mixtures for 3 phase composites were kept at 80°C such that solvent gets evaporated until it was almost dry (in order to improve the crystallinity).The mixture was then further dried for 48 hrs to ensure the complete evaporation of solvent. The dries mixtures for 3 phase composites were then molded by pressing at about 150 ◦ C for 30 min under a pressure of 2.5 MPa using Hot Press setup. Disk-shaped composite samples of 100μm thickness were obtained. The composition of so obtained three phase samples composition of three phase CNT reinforced nano -composites can be shown as [x CNT /0.6 PZT/(0.6 −x) PVB] where x= Volume percentages of CNTs ranging from 0.1 to 1.5 volume % . After drying the composites, silver electroding was done at both the sides of the composites. After putting the electrodes, the composite was annealed at 100°C for 2 hrs to improve the crystallinity of the sample and adhesion between the electrode and composite.

For piezoelectric activation, the ceramic-polymer composites were poled under different poling conditions along the thickness direction in a silicon oil bath employing DC poling set up in the laboratory. Both two phase and three phase composites were polarized by applying dc poling field of 2 kV/mm to 4.5 kV/mm at 120°C for one hour. All the samples were aged for 48 hours prior to measuring the dielectric and piezoelectric properties.

. 2.2 Characterization of Samples:

The surface characterization of composite was carried out by SEM. The structural characterization was carried out by XRD. The longitudinal piezoelectric coefficient d_{33} (in pC/N) of the poled two phase and three phase composites were measured using the computer controlled wide range d_{33} piezometer Piezo-Test PM100 (Piezoelectric d33 testing system). The piezotest meter is a flexible, precision range of equipment for testing piezoelectric materials. The measurement is based on comparison of the piezoactivity of standard piezo-ceramic. Dielectric parameters such as relative dielectric constant (εr) and dielectric loss (tan δ)
were measured by using Nova control Impedance spectrometer operated at 1 kHz at room temperature at 1 V initial potential both the two phase (PZT/PVB) with ceramic volume fraction 60%) and three phase (PZT/PVB/CNT) with ceramic volume fraction 60% and CNT ranging from 0.1 to 1.5 vol %) composites.

3. RESULTS AND DISCUSSION

Fig(1) shows the X-ray diffraction pattern of PZT ceramic powder prepared by mixed oxide method.

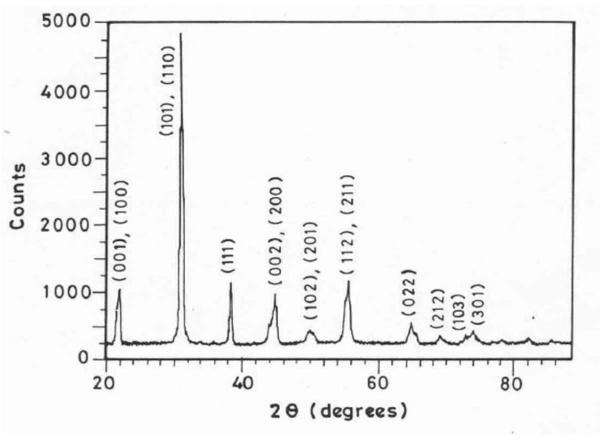

Figure (1): X-ray diffraction of PZT powder prepared with mixed oxide method

The XRD spectra of $PbZr_{0.51}Ti_{0.49}O_3$ (PZT) with peaks at (100), (110), (111), (002), (201), (112), (211), and (102) confirms rhombohedral and tetragonal structure of PZT.

SEM of the composite confirms that the first and third phases are piezoelectric and conductive materials that are distributed within the host matrix, while the second phase is matrix material that is self-connected in three dimensions. Some of the ceramic particles are seen to be connected with each other and thus forming a conducting network or percolation path.

Figure 2 shows variation in dielectric constant (relative permittivity) for [x CNT/0.6PZT/(0.6 −x)PVB] composites with varying x (x= Volume percentages of CNTs ranging from 0.1 to 1.5 volume %) measured at room temperature at 1 kHz.. A slight variation in the dielectric constant was observed with the initial inclusion of CNT phase (for x = 0.1 to 0.7 volume %). We have observed a sharp shoot in the dielectric constant for the composite with CNT concentration of 0.8 volume for x CNT / 0.6 PZT/ (0.6 −x)PVB composite. The sharp shoot in dielectric constant at CNT concentration of 0.8 volume %. may be due to formation of a CNT percolation path through the composites.

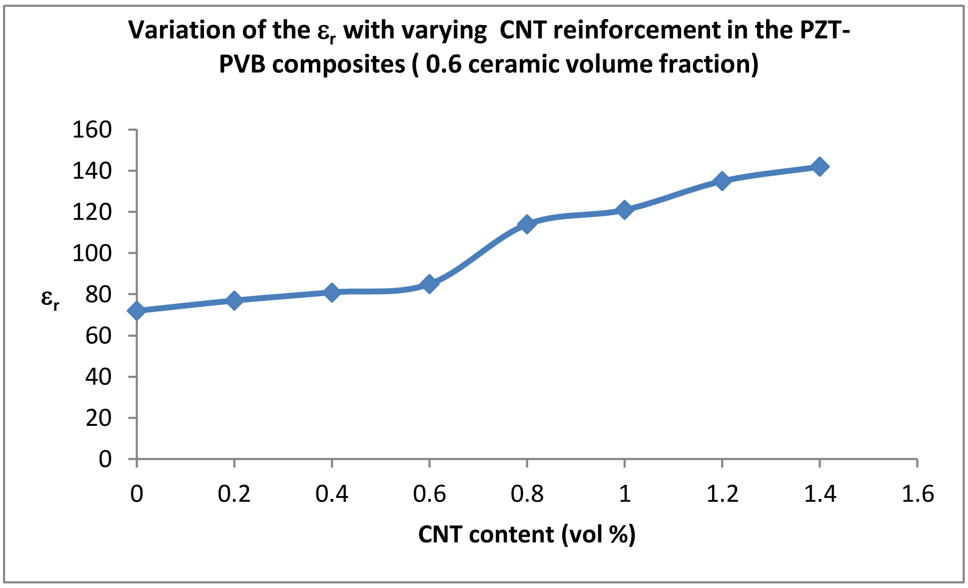

Figure (2): Variation of dielectric constant (ε_r) of three phase reinforced PZT/PVB/CNT composites with varying vol% of CNT

We have also applied analytical model to study the effect of inclusion of third conducting phase in the PZT-Polymer 0-3 composites thus forming 0-3-0 PZT/PVB/CNT composites. The model proposed by S. Banerjee et.al. [15]provides effective dielectric constant of the 0-3-0 composite . Theoretical values of the effective dielectric constant were determined using this model and compared with our experimental data as shown in figure 3.

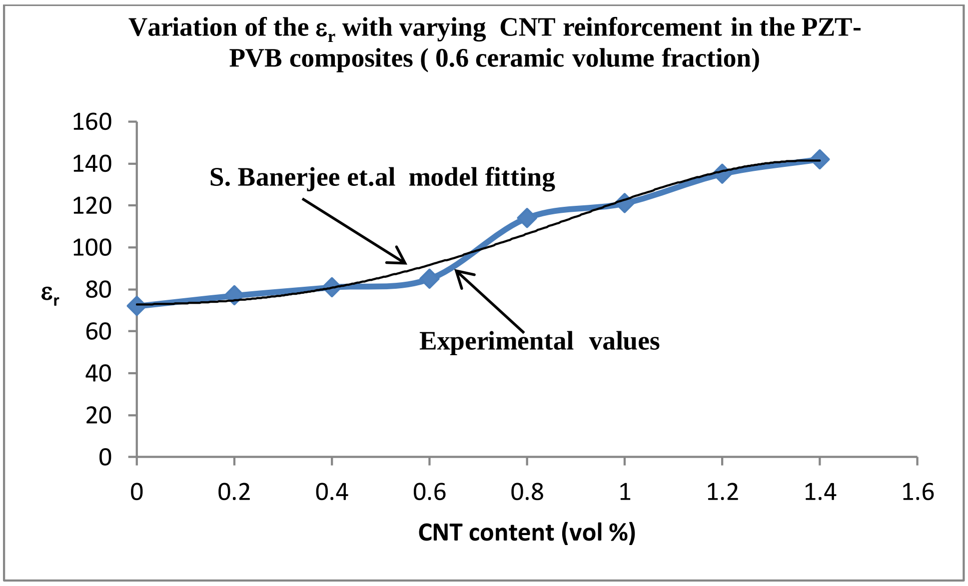

Figure (3): Variation of the ε_r with varying CNT reinforcement in x CNT /0.6 PZT/(0.6 −x) PZT/PVB/CNT composite fitting with theoretical analytical model

Our experimental results of dielectric as measured for these composites were found broadly in agreement with the theoretical results as obtained from the analytical model. In the middle range of third phase loading, little deviation from the experimental data was observed as per this model. Broadly our results regarding comparison of experimental data with analytical model data are in consonance with the results as carried out by S.Banerji et al. with the experimental results from Nan et al.[16]

Figure 4 shows variation in dielectric loss (tan δ) for [x CNT/0.6PZT/(0.6 −x)PVB] composites with varying x (x= Volume percentages of CNTs ranging from 0.1 to 1.5 volume %). The variation in dielectric loss follows the same pattern as that of dielectric constant with varying CNT concentration. It also shows slight variation in the initial range of CNT inclusion and a sharp shoot at with CNT concentration of 0.8 volume %. The sharp shoot in dielectric loss may be due to formation of a CNT percolation path through the composites.

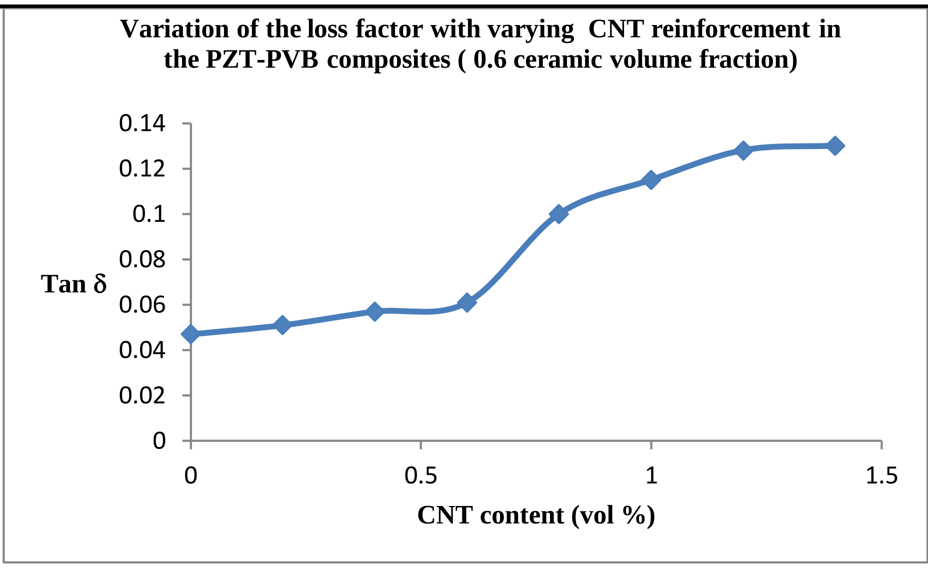

Figure (4) : Variation of loss factor with varying CNT reinforcement in x CNT /0.6 PZT/(0.6 −x) PVB composite

Figure shows variation of piezoelectric coefficient for [x CNT/0.6PZT/(0.6 −x)PVB] composites with varying x (x= Volume percentages of CNTs ranging from 0.1 to 1.5 volume %). Poling voltage required to pole such three phase composites is less than half of that required to pole 0.6PZT/0.4 PVB composites. [17] We obtained 65.7% increase in the d_{33} value for the composite with 0.4 vol% of CNT inclusion in the PZT/PVB/CNT 0-3-0 nano-composite. The piezoelectric coefficient was found to increase initially with increasing CNT vol% and reached maximum (48.7 pC/N) for the composite with 0.4 vol% of CNT inclusion in the PZT/PVB/CNT 0-3-0 nano-composite. On further increasing the CNT vol% in the composite, a decrease in piezoelectric coefficient was observed and d_{33} for the composite with 1.4 vol% of CNT inclusion was obtained as 14.4 pC/N which is even lower than piezoelectric coefficient of 0.6 PZT/ 0.4 PVB. It is because at and beyond percolation threshold (0.8 vol%), the electrical conductivity has increased so much that it becomes difficult to pole the ceramic which in turn causes decrease in the piezoelectric coefficient.

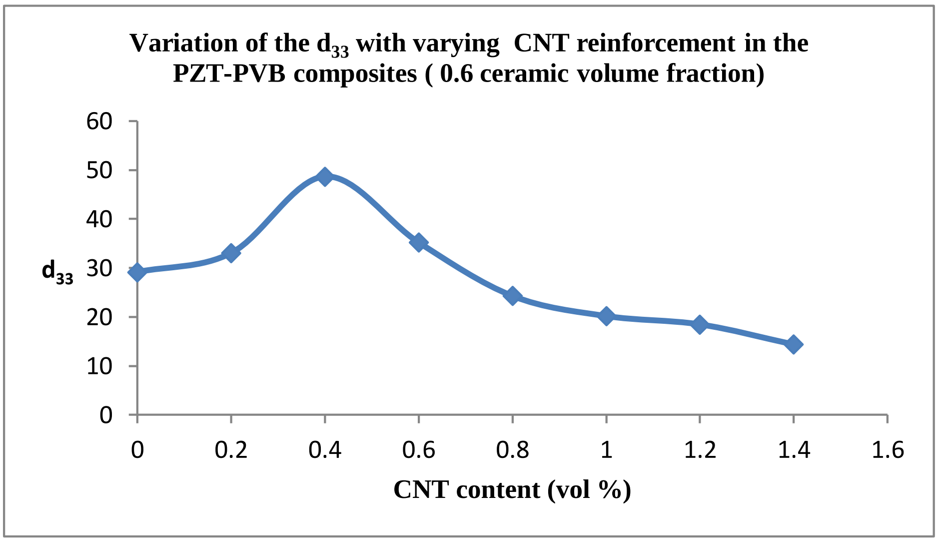

Figure (5) : Variation of the d33 with varying CNT reinforcement in the PZT/PVB/CNT composites (0.6 ceramic volume fraction) (x= Volume percentages of CNTs ranging from 0.1 to 1.5 volume %)

Our results are in agreement with the other reported works on piezoelectric studies of nano-composites. [18]

4. CONCLUSION

The effects of the CNTs on the dielectric and piezoelectric properties of the CNTs/PZT/PVB composites were studied. The CNT additives improved the electrical conductivity of the composites and, as a result, the poling of the composites was more effective. Poling voltage required to pole such three phase composites is almost half of that required to pole PZT-PVB composite without inclusion of CNT. (poling field 4 kV/mm for PZT-PVB composite and 2.5 kV/mm for CNT/PZT/PVB composite). The dielectric constant increased with increasing CNT content, indicating an increase in poling efficiency of the composites. The sharp shoot in dielectric properties a 0.8 vol % of CNT may be due to formation of a CNT percolation path through the composites. This percolation threshold indicates the beginning of formations of CNT networks facilitating the electrical conduction and is responsible for high value of dielectric constant at this point The piezoelectric and dielectric properties of composites varied only slightly at low volume concentration of CNT inclusion but the properties were found to change drastically on increasing the volume concentration of CNTs due to formation of percolation path through the composites. The piezoelectric coefficient was found to increase initially with increasing CNT vol% and reached maximum (48.7 pC/N) for the composite with 0.4 vol% of CNT inclusion in the PZT/PVB/CNT 0-3-0 nano-composite.

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