

Study of piezoelectric and dielectric response of Carbon nano-particles reinforced PZT/HDPE composites

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Abstract-0-3 composites as fabricated by imbedding ferroelectric ceramic particles into a polymer matrix have attracted considerable research interest because of their potential applications such as piezoelectric sensor, ultrasonic transducer and pressure sensors etc. The obtained composites of 0-3 connectivity exhibit piezoelectric properties of ceramics and flexibility, strength and lightness of polymers. For effective polarization of ceramic phase within the host polymer matrix, the composites are reinforced with a third conducting nano phase such as CNTs, metal nano particles etc. causing significant improvement in dielectric and piezoelectric properties. Here we report the effect of inclusion of Carbon nano particles (CNPs) on the piezoelectric and dielectric properties of 0-3 PZT (Lead Zirconate Titanate) / HDPE composites prepared by hot press method. The Carbon nano particles reinforcement concentration varies from 1 to 10 volume % in the 0-3 PZT-HDPE composites (with ceramic volume fraction 0.5). The piezoelectric properties of composite were analyzed by measuring piezoelectric charge constants (d_{33}) employing Piezo-Test PM100 computer interfaced system. The dielectric properties of these samples were measured at 100 Hz at the room temperature. In these reinforced composites, third nano phase dispersed in the matrix facilitates poling and results in an increase of the piezoelectric properties of the composite due to formation of percolation path through the composites. At percolation threshold of CNP content of 6 vol.% in the composite, a significant increase in dielectric properties was observed. Just below percolation threshold, piezoelectric coefficient (d_{33}) was observed to reach its maximum value of 13.2 pC/N. Observed results were analyzed using theoretical models as well. Such designed composites with significant piezoelectric and dielectric response can be used as flexible vibration sensors.

Index Terms- Piezoelectric coefficient, Nano-composites, percolation threshold, Piezo sensors

1. INTRODUCTION

Ferroelectric ceramics possess excellent dielectric properties by virtue of their non centro symmetric structure. Ferroelectric ceramics such as Barium Titanate, Lead Zirconate Titanate (PZT) etc. also have the ability of converting mechanical energy into electrical energy or vice-versa and thus exhibit appreciable piezoelectric properties. Brittle nature of these ceramics hinders their use in various applications. The effective way of utilizing piezoelectric and dielectric properties of these ceramics is by designing their composites with polymers. Such composites have the mechanical strength, flexibility and formability of the polymer with the appreciable dielectric and piezoelectric properties of the ceramic. Piezoelectric ceramic-polymer composites are considered as promising materials for applications in high-pressure sensors, hydrophones, vibration sensors and actuators. Hence various research efforts have been made to develop composites with different ceramics and polymers. [1,2,3]. Composites with 0-3 connectivity are obtained by mixing the ceramic powder with polymer matrix when the particles are not in contact with each other and the polymer phase is self connected in all dimensions.

Polarization of the ceramic phase in the composites is essentially required for activation of piezoelectric properties. Effective polarization of the 0-3 composite is difficult to achieve as the dielectric constant of piezoelectric ceramics is larger than most of the polymers. For a composite with 0-3 connectivity the electric field E_c acting on spherical grain / ceramic particles is given by

$$E_c = \frac{3\varepsilon_1}{\varepsilon_2 + 2\varepsilon_1} E_0$$

where ε_1 and ε_2 are the dielectric constants of the polymer and ceramic, respectively, and E_0 is the applied field. Thus the electric field applied on the composite is effectively controlled by the dielectric constant of polymer matrix. The analog electrical circuit of the composite can be perceived as comprising of two resistance connected in series. Due to high dielectric constant of ceramic phase, major part of the applied voltage is wasted across the polymer phase. To obtain effective polarization of the ceramic particles, a small amount of third conducting phase in nano dimensions is incorporated, which creates electric flux continuity network in the composite. In such composites, the first and third phases are ceramic 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. These nano fillers in the composite,

create a percolative network which in turn causes effective polarization of dipoles aligned to the applied field. This orientation polarization causes a significant enhancement in the dielectric and piezoelectric properties. Various researchers have used different nano-fillers in various composite systems and reported improved performance.[4,5,6,7] Here we report improved piezoelectric and dielectric response of 0-3 composite with High-density polyethylene (HDPE) as polymer host matrix, Lead Zirconate Titanate ($\text{Pb}[\text{Zr}(x)\text{Ti}(1-x)]\text{O}_3$) (PZT) as ceramic phase and Carbon Nano Particles (CNP) as third filler nano-phase.

2. MATERIALS AND METHOD:

2.1. Sample Preparation:

Commercial PZT powder was procured from Concord Electro ceramic Industry India with particle size in microns. The Carbon Nano-particles were procured from Sigma-Aldrich having purity of approximately 93% and particle size 500 nm. High-density polyethylene (HDPE) was also procured from Sigma-Aldrich. The 0-3 composites were prepared using hot press method. To prepare two phase PZT-HDPE 0-3 composite, HDPE was first dissolved in the solvent at 100°C. PZT Ceramic powder was added with different ceramic volume fraction (10% to 60%) by weight in HDPE solution and was blended properly to form mixture. To prepare three phase PZT/HDPE/CNP composite, PZT Ceramic powder was added by weight with 50% ceramic volume fraction in HDPE solution and was blended properly to form mixture. Carbon nano-particles were added to this mixture in the range of 1 vol% to 10 vol% for preparing three phase composites. The heated mixture for both two phase and three phase composites were separately stirred continuously by magnetic stirrer until it became viscous. The mixture was given ultrasonic bath for one hour for proper diffusion of ceramic particles in the host polymer matrix. The mixture was then further dried for 48 hrs to ensure the complete evaporation of solvent. The dried mixtures for two phase and three phase composites were then molded by pressing at about 130°C for 1 hour under a pressure of 4 MPa using Hot Press setup. Disk-shaped composite samples of 100 μm thickness were obtained. The two phase composites PZT/HDPE (with ceramic volume fraction from 10% to 60%) and three phase composites PZT/HDPE/CNP (CNP with 1 vol% to 10 vol% for PZT volume fraction 50%) were obtained. After silver electroding at both the sides, composites were annealed 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 silicon oil

bath employing DC poling set up. Both two phase and three phase composites were polarized by applying dc poling field between 1.5 kV/mm to 3.5 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 and Measurements:

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} Piezo-Test meter PM100 (Piezoelectric d_{33} 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 (ϵ_r) and dielectric loss ($\tan \delta$) were measured by using Nova control Impedance spectrometer operated in the frequency range 100 Hz to 10^6 Hz at 1 V initial potential for both the two phase and three phase composites.

3. RESULTS AND DISCUSSION:

As shown in fig(1), the SEM of the three phase composite confirms the distribution of ceramic particles (first phase) and Carbon nano particles (third phase) within the host polymer matrix (second phase) that is self-connected in three dimensions.

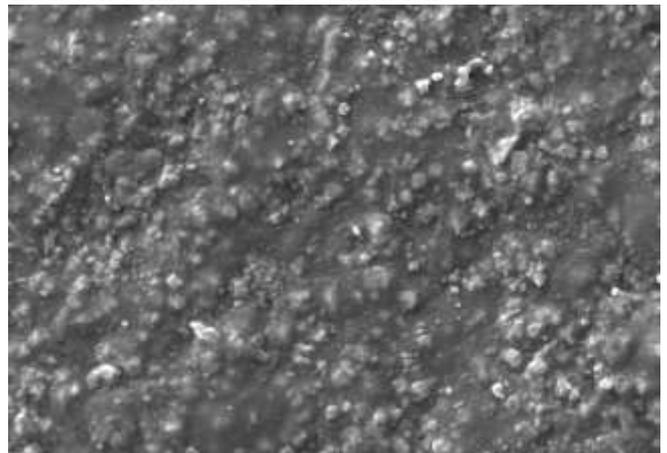


Figure 1 : SEM of the HDPE/PZT composite with Carbon Nano Particles 5 vol%

Figure 2 shows variation in dielectric constant (relative permittivity) for two phase PZT/HDPE composites with ceramic volume fraction varying from 10% to 60%.

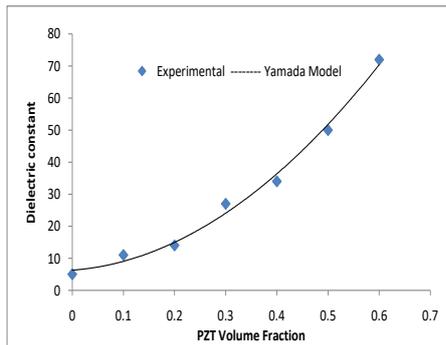


Figure 2: Variation of Dielectric constant(ϵ_r) with varying ceramic volume fraction in the two phase PZT-HDPE composites and comparison with Yamada model

Fig(2) shows variation on dielectric constant of two phase PZT-HDPE 0-3 composite with ceramic volume fractions ranging from 10% to 60% experimentally measured at constant frequency 100 Hz at room temperature. The experimentally obtained values of dielectric constants clearly show that as volume fraction of ceramic phase increases, the dielectric constant ϵ_r also increases. This result is consequential to the fact that ceramic phase majorly governs the dielectric properties of these composites and therefore higher volume fraction of ceramic phase in composite results in higher value of ϵ_r attributed to interfacial polarization.

We have then applied analytical Yamada model to explain dependence of the dielectric constant on the volume fraction. Yamada et al [8] considered a binary system consists of continuous phase (polymer) of the dielectric constant ϵ_1 and the ellipsoidal particles (PZT) of the dielectric constant ϵ_2 . Model considers the composite as a binary system consisting of ellipsoidal ceramic particles dispersed on the continuous medium.

Yamada model defines dielectric constant of the composite as :

$$\epsilon = \epsilon^p \left[1 + \frac{\eta \phi^c (\epsilon^c - \epsilon^p)}{\eta \epsilon^p + (\epsilon^c - \epsilon^p)(1 - \phi^c)} \right]$$

where ϵ^c & ϵ^p are dielectric constants of ceramic and polymer respectively, ϕ is ceramic volume fraction, η is a parameter dependent on the shape of the particles and their orientation in relation to the composite film. The theoretical values of dielectric constants as calculated by this model are also shown in the graph along with the experimentally observed values of dielectric constants for ceramic volume fraction 10% to 60%. This model gave good theoretical fitting for

the composites in the entire range of ceramic volume fraction for $\phi=0.1$ to 0.6. Our results are in agreement with reported ones.

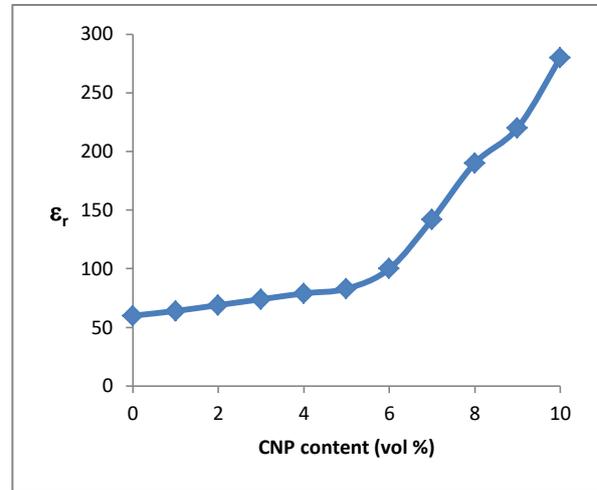


Figure (3): Variation of dielectric constant (ϵ_r) of three phase PZT/HDPE/CNP composites with varying CNP vol%

Fig(3) shows variation of dielectric constant of three phase PZT/HDPE/CNP composites with ceramic volume fraction ($\phi=0.5$) and CNP content varying from 1 vol% to 10 vol% . The dielectric constant was observed to increase gradually with increasing CNP content till 6 vol% content. It may be due to formation of carbon nano particles percolation network through the composites which create electric flux continuity amongst ceramic PZT particles.[9,10] A sharp increase in dielectric constant has been observed at 6 vol% of CNP. It indicates percolation threshold at 6 vol% of CNP contents attributed to the completion of formation of percolating network in the composite at 6 vol% . The values of the effective dielectric constant at room temperature for three phase composite of PZT/HDPE/CNP was observed to reach up to 280 at 10 vol% of CNP from 60 (for two phase PZT/HDPE composite with ceramic volume fraction 50%) .

Fig(4) shows variation in dielectric loss factor for PZT-HDPE composites with CNP content varying from 1 vol% to 10 vol% .

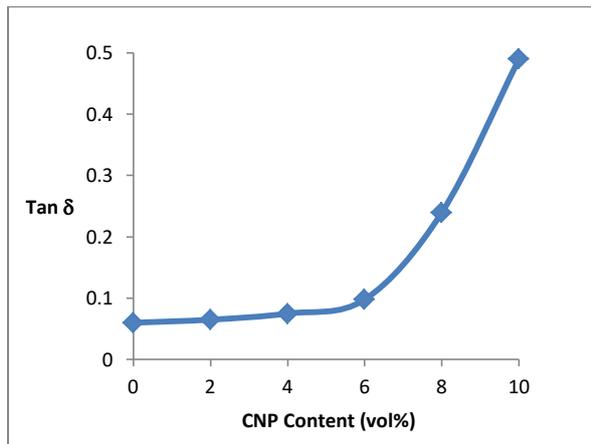


Figure (4): Variation of dielectric loss factor (Tan δ) of three phase PZT/HDPE/CNP composites with varying CNP vol%

The dielectric loss factor variation also follows the same trend and found to increase sharply near the same percolation threshold of Carbon nano particles at 6 vol% content. The enhancement of the dielectric loss is related to the increase of the electrical conductivity of the composite due to formation of conducting path between the PZT particles. A significant increase in the dielectric loss factor has been seen at and beyond 6 vol% of CNPs. The values of the dielectric loss factor at room temperature for three phase composite of PZT/HDPE/CNP was obtained as 0.49 at 10 vol% of CNP from 0.06 (for two phase PZT/HDPE composite with ceramic volume fraction 50%) .

Fig(5) shows variation on piezoelectric coefficient (d_{33}) of two phase PZT-HDPE 0-3 composite with ceramic volume fractions ranging from 10% to 60% experimentally measured at room temperature. It was observed that with the increase in volume fraction of ceramic phase, the piezoelectric coefficient (d_{33}) also increases. This can be attributed to the fact that piezoelectric properties of the composite are governed by ferroelectric ceramic particles. Therefore as volume fraction of ceramic increases, it contributes more to the piezoelectric properties and thus d_{33} increases. The highest value of d_{33} 11.9 pC/N was obtained for two phase PZT/HDPE composite with 0.6 ceramic volume fraction.

The experimentally obtained results were also matched with the theoretical values as obtained using Furukawa model.

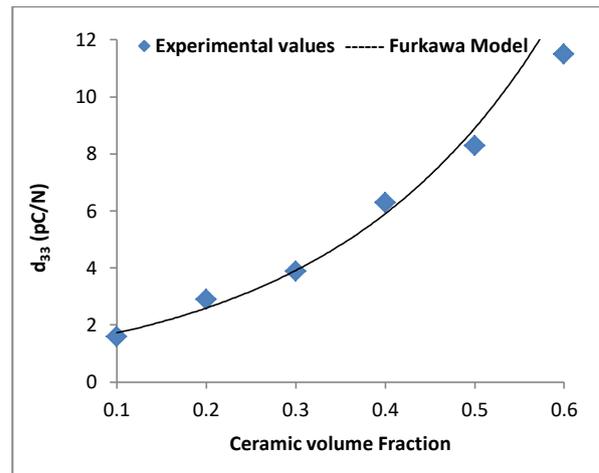


Figure (5): Variation of Piezoelectric coefficient (d_{33}) with varying ceramic volume fraction in the two phase PZT-HDPE composites and comparison with Furukawa model

Furukawa[11] model predicts theoretical values of piezoelectric coefficient for 0-3 ceramic polymer composite as:

$$d_{33} = \frac{15\phi\epsilon_p}{(2 + 3\phi)(1 - \phi)\epsilon_c}$$

where ϕ is the volume fraction of ceramic filler, d_{33} is the piezoelectric voltage constant. ϵ is the dielectric constant with the subscripts c and p corresponding to that of ceramic and polymer phase respectively. The experimentally observed values of d_{33} were found in good agreement with theoretical values as calculated by this model as shown in the fig (5).

Fig(6) shows variation of Piezoelectric Coefficient (d_{33}) of three phase PZT/HDPE/CNP composites with ceramic volume fraction ($\phi=0.5$) and CNP content varying from 1 vol% to 10 vol% . We obtain significant increase in the d_{33} value for the composite with 5 vol% of CNP content. The piezoelectric coefficient was found to increase initially with increasing CNP content (from 8 pC/N for two phase composite with $\phi=0.5$) and reached maximum (13.2 pC/N) for the composite with 5 vol% of CNP. On further increasing the CNP content in the composite, a decrease in piezoelectric coefficient was observed. It is because at and beyond percolation threshold (6 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.

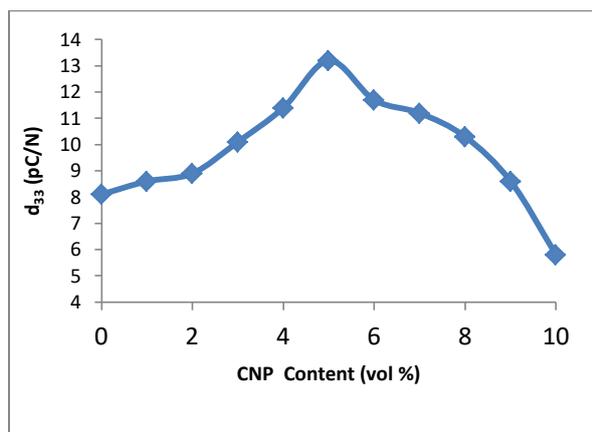


Figure (6): Variation of Piezoelectric Coefficient (d_{33}) of three phase PZT/HDPE/CNP composites with varying CNP vol%

The dielectric and piezoelectric characterization of three phase Carbon nano particles reinforced composites and their comparison with corresponding two phase composites clearly show a significant improvement in the performance of the composites due to the presence of third nano phase. A sharp increase in the dielectric constant and dielectric loss factor at 6 vol% of Carbon nano particles suggests occurrence of percolation threshold at 6 vol% for the composites. At percolation threshold, the third phase nano-particles completely connect the ceramic particles and thus percolation network is completely formed. This in turn increases the poling efficiency of the composite. [12,13,14] Effective DC poling of the ceramic phase locks dipoles into a configuration of near field alignment resulting in permanent polarization. The dielectric constant is a measure of permanent dipole moment in the system. Therefore increase in dielectric constant and dielectric loss factor with increasing volume of CNPs indicates improvement in the poling efficiency of the composites. We observed that poling voltage required to pole such three phase composites is less than that required of required to pole PZT-HDPE composite without inclusion of carbon nano particles. DC poling field of 3.5 kV/mm was required for PZT-HDPE composite whereas it was reduced to 1.5 kV/mm for poling CNT/PZT/HDPE composite. Increasing of interfacial polarization as explained by Maxwell-Wagner may also be a reason for increase in dielectric properties with increasing CNP content. The third phase reinforcement creates a resistance in parallel with that of the polymers resulting into the reduction of the resistance of the polymer phase due to which more voltage is available for the poling of the ceramic phase. [15, 16]

At percolation threshold the percolation network is completely formed and on further increasing CNP loading in the composite beyond percolation

threshold, the conductivity of the composite increases significantly due to beginning of coagulation of carbon nano particles around piezoelectric ceramics. [17,18] This in turn makes poling of the ceramic particles in the composite difficult and thus piezoelectric properties were found to decrease at and beyond percolation threshold (6 Vol%).

4. CONCLUSION

The two phase composites PZT/HDPE (with ceramic volume fraction from 10% to 60%) and three phase composites PZT/HDPE/CNP (CNP with 1 vol% to 10 vol% for PZT volume fraction 50%) were prepared. Observed increase in dielectric and piezoelectric properties of two phase composites with increasing ceramic volume fraction is consequential to the fact that ceramic phase majorly governs these properties of the composites. The obtained results are in good agreement with the theoretical Yamada and Furkawa models. The effects of the carbon nano particles on the dielectric and piezoelectric properties of 0-3 PZT-HDPE composites were studied with CNP content varying from 1 vol% to 10 vol%. Carbon Nano-particles create percolation path between PZT particles in the insulating HDPE matrix. Such percolating network helps in efficient poling of the ceramic particles and locks the dipoles into a configuration of near field alignment resulting in permanent polarization. DC poling field of 3.5 kV/mm was required for PZT-HDPE composite whereas it was reduced to 1.5 kV/mm for poling CNT/PZT/HDPE composite. Both dielectric constant and dielectric loss were increased with CNP content due to percolation network. The values of the effective dielectric constant at room temperature for three phase composite of PZT/HDPE/CNP was observed to reach up to 280 at 10 vol% of CNP. A sharp increase in dielectric properties was observed at 6 vol% of CNP. It suggests occurrence of percolation threshold at 6 vol% for the composites. At percolation threshold, the third phase nano-particles completely connect the ceramic particles and thus percolation network is completely formed. The piezoelectric coefficient d_{33} was found to increase initially with increasing CNP content (from 8 pC/N for two phase composite with $\phi=0.5$) and reached maximum (13.2 pC/N) for the composite with 5 vol% of CNP. The piezoelectric properties were found to decrease at and beyond percolation threshold (6 Vol%) due to increase in electric conductivity which in turn makes poling of the ceramic particles in the composite difficult and causes decrease in the piezoelectric coefficient.

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