AC CONDUCTIVITY AND PIEZOELECTRIC BEHAVIOR OF THREE PHASE FLEXIBLE POLYMER CERAMIC PZT/PVC/CNP 0-3 NANO-COMPOSITE

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Abstract : *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. Disk-shaped two phase PZT/PVC composite and three phase PZT/PVC/Carbon nano particles with ceramic volume fraction 40% and CNP ranging from 1 to 18 vol % with thickness of 200μm were prepared. SEM, XRD, dielectric, AC conductivity and piezoelectric characterization was carried out for these composites. The third phase creates a percolation network in the composite resulting in increasing poling efficiency. Significant enhancement in the dielectric properties, AC conductivity and piezoelectricity was observed on the inclusion of third conducting nano phase especially at and beyond percolation threshold. Dielectric constant and AC conductivity were also studied as function of frequency. These flexible composites can be used in many applications such as sensors and transducers.*

Index Terms *- Three phase percolative composites, Percolation threshold, piezoelectric coefficient, Dielectric properties, AC conductivity, Flexible composites.*

1. INTRODUCTION

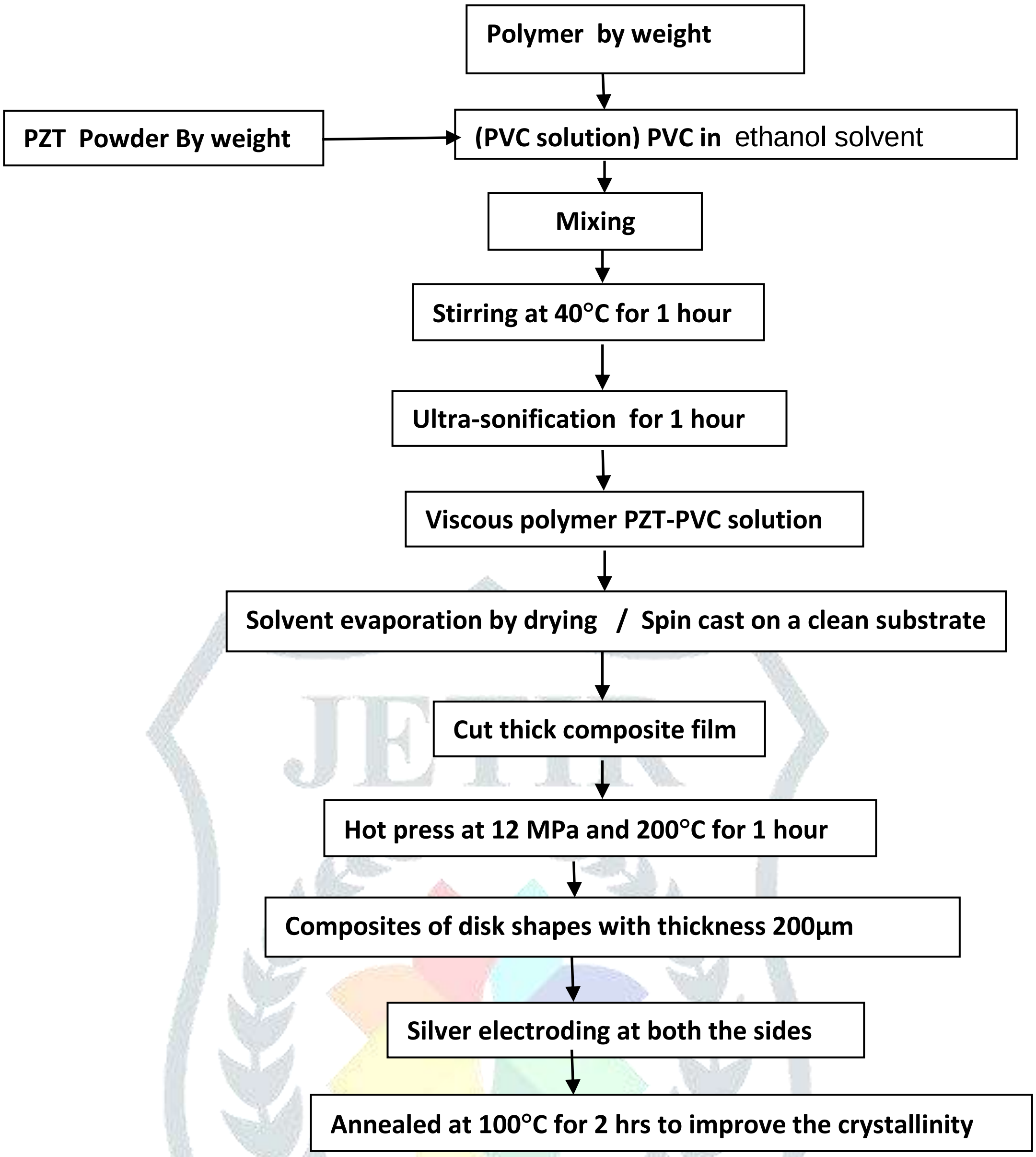
Composites made up of ceramic and polymers are preferred over brittle ferroelectric ceramics for their application as sensors, transducers, actuators by virtue of their flexibility and tailorability. The ceramic particles distributed in the polymer matrix forms a 0-3 composite. The piezoelectric and dielectric performance of such composites depends upon orientational polarization of ceramic particles by applied field. For effective polarization and improved performance, a third conducting phase is incorporated in such composites. There have been various research reports regarding inclusion of third conducting phase in nano dimensions for enhanced functional properties of such composites. [1,2,3] These third phase particles create a continuity percolative network in the composite and thereby increase the effective polarization by making more electric field available to the ceramic particles.[4] In this work, we have prepared flexible three phase 0-3 composite 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. Ferroelectric ceramic Lead Zirconate Titanate (PZT) exhibits appreciable piezoelectric properties due to its rhombohedral and tetragonal structure. Polyvinyl chloride (PVC) is one of widely used polymers. It also exhibit good piezoelectric properties. Therefore PVC was chosen as a polymer phase to design a 0-3 PZT-PVC composite. Disk-shaped two phase PZT/PVC composite and three phase PZT/PVC/Carbon nano particles with ceramic volume fraction 40% and CNP ranging from 1 to 18 vol % with thickness of 200μm were prepared. Here we report improved piezoelectric, AC conductivity and dielectric response of 0-3 composite due to creation of peroclative network by incorporation of third phase of Carbon nano particles in the composites.

2. 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 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. The Carbon Nano-particles were procured from Sigma-Aldrich having purity of approximately 93% and particle size 500 nm. Polyvinyl chloride (PVC) was also procured from Sigma-Aldrich. For designing two phase PZT/PVC composite, firstly PVC was dissolved in ethanol. PZT Ceramic powder was added in PVC the solution by weight for ceramic volume fraction 40% . It was blended properly to form mixture. To include third phase, Carbon nano-particles were added in the PZT-PVC solution with 40% ceramic volume fraction (PZT content). The doping concentration of Carbon Nano particles (CNPs) varies from 1 to 18 vol % in the composites. For proper dispersion, both the two phase and three phase solutions were continuously stirred by magnetic stirrer, slowly warmed until it became viscous. The mixture was given ultrasonic bath for one hour to ensure that the active ceramic phase of PZT and reinforcing third phase of Carbon nano particles get distributed evenly in the host polymer phase. The mixture was then heated such that solvent gets evaporated until it was almost dry. The mixture was then further dried for 48 hrs to ensure the complete evaporation of solvent. The mixture was then molded by pressing at about 110° C for one hour under a pressure of 3 MPa using Hot Press setup. Disk-shaped two phase PZT/PVC composite and three phase PZT/PVC/Carbon Nano particles based composites were obtained with thickness of 200μm . Silver electroding was done at both the sides of the composite. After putting the electrodes, the samples were annealed at 100°C for 2 hrs to improve the crystallinity of the sample and adhesion between the electrode and composite.

A flow chart for the preparation of PZT-PVC two phase 0-3 composites is shown in the following figure .



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 1 kV/mm to 4 kV/mm at 100°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 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 AC conductivity were measured by using Nova control Impedance spectrometer operated in the frequency range 10 Hz to 106 Hz at 1 V initial potential for both the two phase (PZT/PVC) and three phase (PZT/PVC/CNPs with ceramic volume fraction 40% and CNP ranging from 1 to 18 vol %)composites.

3. RESULTS AND DISCUSSION

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

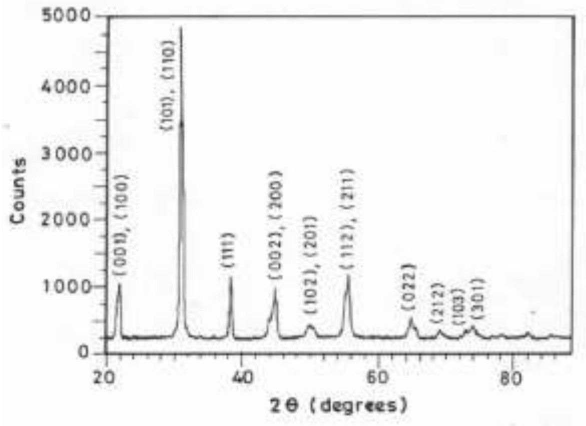


Figure (1): X-ray diffraction of PZT powder prepared with mixed oxide method

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.

Fig(2) shows the SEM of PZT-PVC 0-3 composite with ceramic volume fraction of 40% . Results show that the ceramic filler is distributed close to homogeneously in the polymer matrix.

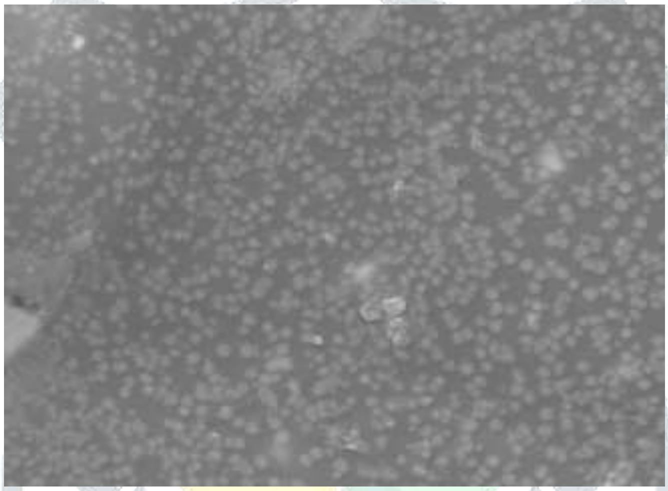


Figure (2): SEM of PZT-PVC 0-3 composite with ceramic volume fraction of 40%

Fig(3) shows the SEM of PZT-PVC 0-3 composite with ceramic volume fraction of 0.4 with Carbon Nano Particles concentration of 8 vol%. As shown in SEM, 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.

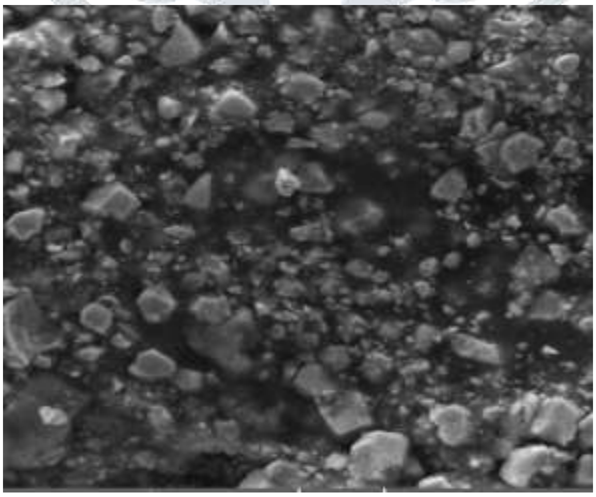


Figure (3): SEM of PZT-PVC 0-3 composite (ϕ= 0.4) with Carbon Nano Particles 8 vol%

There are various parameters contributing to such obtained dielectric constants of these composites. In contrast to single phase materials, dielectric behaviour of particulate composites is much more complicated because of the interfaces between the matrix and the second phase particles dispersed inside it. The effective dielectric constant of such an inhomogeneous medium is a complicated function of the constituents, particle shape and size, volume loading and spatial arrangement of the particle distribution.

Fig(4) shows variation of dielectric constant of three phase PZT/PVC/CNP composites (ϕ=0.4) with varying Carbon Nano Particles content (from 1 vol% to 18 vol%) at 100 Hz and at room temperature . The dielectric constant increases with increasing concentration of Carbon nano particles. It may be due to formation of carbon nano particles percolation network through the composites which create electric flux continuity amongst ceramic PZT particles.[5,6] It was observed that for the lower concentration of Carbon nano particles in these three phase composites, a little increase in the dielectric constant has been observed.

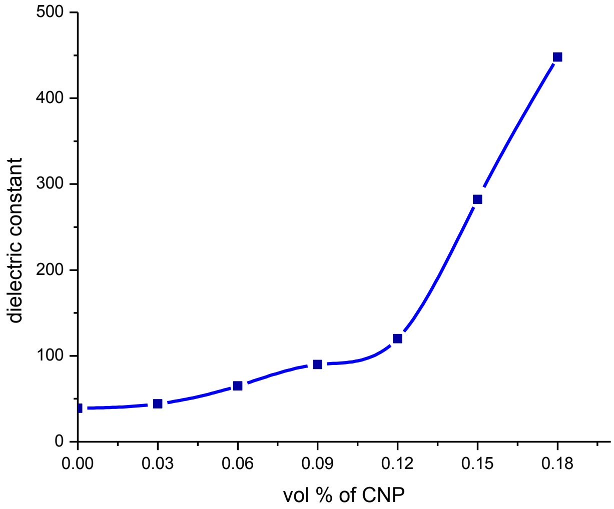


Figure (4): Variation of dielectric constant (ε_r) of three phase reinforced PZT/PVC/CNP composites with varying vol% of Carbon nano particles

At around 15 vol% concentration of Carbon nano particles, a sharp increase in dielectric constant was observed which keeps increasing on higher loading of this third phase. This value of concentration (15 vol%) of Carbon nano particles characterizes the completion of continuity percolating network in the composite and is referred as percolation threshold. This behavior of dielectric permittivity at and beyond the percolation threshold is explained by the power law:

$$\varepsilon = \varepsilon_1 \left|\frac{f_c - f_{CNP}}{f_c}\right|^{-s}$$

where ε_1 is the dielectric constant of two phase PZT/PVC composite with 0.4 volume fraction, f_{CNP} is the volume fraction of the Carbon nano particles, f_c is the percolation threshold and s is the critical component[7,8]. It was observed from the graph that at 100 Hz, the dielectric permittivity of two phase PZT/PVC composite was 41 whereas it reached up to 512 at room temperature at Carbon nano particle concentration of 18 vol% . This can be due to higher value of orientational polarization as achieved due to formation of percolative network.

Fig(5) shows variation of dielectric constant of three phase PZT/PVC/CNP composites (ϕ=0.4) with frequency for different concentration of Carbon nano particles (from 1 vol% to 18 vol%). The dielectric permittivity was measured for a wide range from 10 Hz to 1 MHz at room temperature.

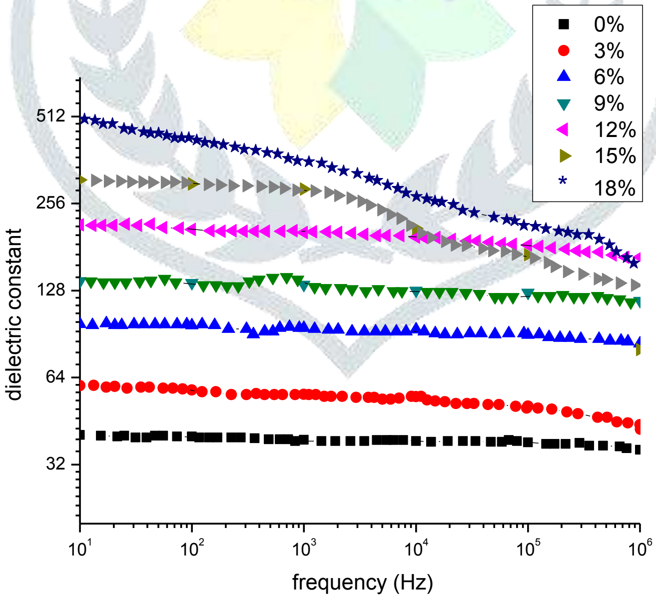


Figure (5): Dielectric constant (ε_r) of three phase reinforced PZT/PVC/CNP composites as a function of frequency for different vol% of Carbon nano particles

The dielectric constant was found to decrease with increase in frequency for all concentrations of Carbon nano particles for these three phase composites. The decrease in dielectric constant is gradual for the composites with CNP concentration less than percolation threshold of 15 vol%. At and beyond percolation threshold, dielectric constant was observed to decrease more rapidly with increase in frequency. The dielectric characteristics show strong frequency dependence in the low frequency region. This can be attributed to interfacial polarization.[9]

Fig(6) shows variation of AC conductivity of three phase PZT/PVC/CNP composites (ϕ=0.4) with frequency for different concentration of Carbon Nano Particles (from 1 vol% to 18 vol%) measured for a wide range from 10 Hz to 1 MHz at room temperature.

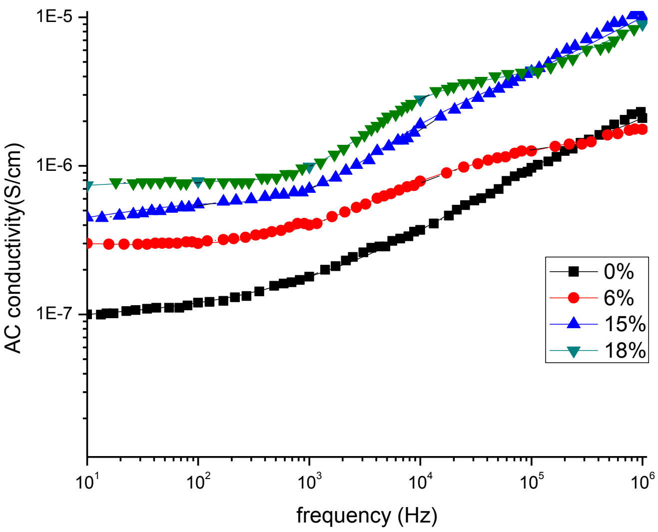


Figure (6): AC conductivity (σ_{AC}) of three phase reinforced PZT/PVC/CNP composites as a function of frequency for different vol% of Carbon nano particles

The AC conductivity was observed to increase with increase in frequency for all concentrations of Carbon nano particles for these three phase composites. It was also observed that on higher loading of Carbon nano particles, AC conductivity of composites increases for all frequencies. The conductivity increases linearly below percolation threshold but at and beyond percolation threshold, it was observed to increase more rapidly with increase in frequency.

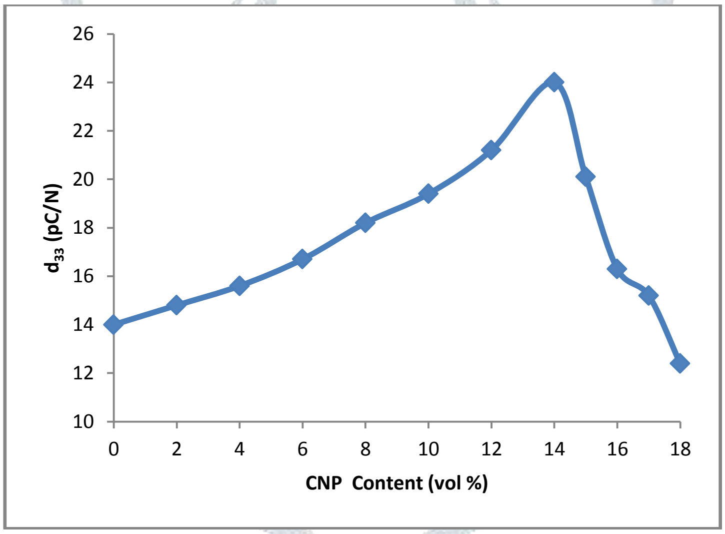


Figure (7): Variation of Piezoelectric Coefficient (d_{33}) of three phase PZT/PVC /CNP composites with varying CNP vol%

Fig (7) shows variation of Piezoelectric Coefficient (d_{33}) of three phase PZT/PVC/CNP composites with ceramic volume fraction (ϕ=0.4) and CNP content varying from 1 vol% to 18 vol% . We obtain significant increase in the d_{33} value for the composite with 14 vol% of CNP content. The piezoelectric coefficient was found to increase initially with increasing CNP content (from 14 pC/N for two phase composite with ϕ=0.5) and reached maximum (24 pC/N) for the composite with 14 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 (15 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.

We have also observed that the poling voltage required to pole three composites is half of that required to pole corresponding two phase composite due to increase poling efficiency by formation of percolative network in the composites. [10,11,12] Thus the dielectric, AC conductivity and piezoelectric behaviour of these flexible composites get substantially improved by addition of third nano phase.

4. CONCLUSION

Disk-shaped two phase PZT/PVC composite and three phase PZT/PVC/Carbon nano particles with ceramic volume fraction 40% and CNP ranging from 1 to 18 vol % with thickness of 200µm were prepared. SEM characterization shows 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. The dielectric constant was found to increase with increasing concentration of Carbon nano particles due to formation of percolation network through the composites. The percolation threshold for three phase composite was obtained at 15 vol% concentration of Carbon nano particles beyond which sharp increase in dielectric constant was observed. The dielectric constant was observed to decrease with increase in frequency whereas the AC conductivity was observed to increase with increase in frequency for all concentrations of Carbon nano particles for these three phase composites. The variation in dielectric permittivity and AC conductivity with frequency becomes more rapid at and beyond percolation threshold. The piezoelectric coefficient was found to increase initially with increasing CNP content (from 14 pC/N for two phase composite with ϕ=0.5) and reached maximum (24 pC/N) for the composite with 14 vol% of CNP. On further increasing the CNP content in the composite, a decrease in piezoelectric coefficient was observed due to increase in electrical conductivity.

5. ACKNOWLEDGMENT

The authors gratefully acknowledge financial support from Department of Science and Technology(DST), New Delhi, India, for the experimental facilities through the major research project.

REFERENCES

[1] Shen Y, Yue ZX, Li M, Nan CW 2005. Enhanced initial permeability and dielectric constant in a double-percolating Ni0.3Zn0.7Fe1.95O4-Ni-polymer composite. Adv. Funct. Mater. 15:1100–1103

[2] Y.e. Mamunya, A. Boudenne, N. Lebovka, L. Ibos, Y. Candau, M. Lisunova 2008. Electrical and thermophysical behaviour of PVC-MWCNT nanocomposites. Compos. Sci. Technol. 68 : 1981-1988

[3] K.-H. Kim, W.-H. Jo 2009. A strategy for enhancement of mechanical and electrical properties of polycarbonate/ MULTI-WALLED CARBON NANOTUBE COMPOSITES. CARBON 47:1126-1134

[4] Wang L, Dang ZM. 2005. Carbon nanotube composites with high dielectric constant at low percolation threshold. Appl Phys Lett. 87:042903

[5] G. Ioannou, A. Patsidis, G.C. Psarras 2011. Dielectric and functional properties of polymer matrix/ZnO/$BaTiO_3$ hybrid composites, Composites: Part A 42 :104–110

[6] Ashok K. Batra,Matthew E. Edwards,Almuatasim Alomari, Adnan Elkhaldy 2015. Dielectric Behavior of P(VDF-TrFE)/PZT Nanocomposites Films Doped with Multi-Walled Carbon Nanotubes (MWCNT). American Journal of Materials Science 5(3A): 55-61

[7]Necira Z, Boutarfaia A, Abba M, et al. 2012. Synthesis of PZT powder by conventional method at various conditions. EPJ Web of Conferences :29:00038.

[8] C. W. Nan, Prog 1993. Mater. Sci. 37, 1.

[9] Dang Z, Shen Y, Nan CW. 2002 . Dielectric behavior of three-phase percolative Ni BaTiO3/polyvinylidene fluoride composites. Appl Phys Lett :81:4814–4816.

[10] Dang ZM, Fan LZ, Shen Y, et al. 2003 . Study on dielectric behaviour of a three-phase CF/(PVDF/$BaTiO_3$) composite. Chem Phys Lett. 369: 95–100

[11] Guangsheng Wang 2010. Enhanced Dielectric Properties of Three-Phase-Percolative Composites Based on Thermoplastic-Ceramic Matrix ($BaTiO_3$ + PVDF) and ZnO Radial Nanostructures. Applied Materials & Interfaces 2(5), 1290–1293

[12] Alex Otavio Sanches, Darcy Hiroe Fujii Kanda, et. al. 2017: Synergistic effects on polyurethane/lead zirconate titanate/carbon black three-phase composites. Polymer Testing 60 :253-259