



ENHANCEMENT IN PIEZOELECTRIC PROPERTIES OF CERAMIC-POLYMER COMPOSITE BY INCORPORATING SEMIMETAL PHASE

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Abstract

Ceramic-polymer composites have extensive application as sensors, transducers etc. by virtue of their significant dielectric, pyroelectric and piezoelectric properties. These composites exploit functional properties of the ceramic and flexible mechanical properties of polymer. The polymer matrix usually serves to provide good protection of the ceramic phase while maintains the compliant mechanical property. These polymer ceramic composites are comparatively flexible and can be used to design large area vibration sensors by establishing intimate contact with the object to be detected. By imbedding piezoelectric ceramic powder into a polymer matrix, 0-3 composites with good mechanical properties and high dielectric breakdown strength can be developed. The electric and dielectric properties of these composites can be modified by mixing required amount of ceramic filler with polymer matrix. The obtained composites of 0-3 connectivity exhibit piezoelectric properties of ceramics and flexibility, strength and lightness of polymers. Another way to enhance piezoelectric properties of these composites is to dope them by third phase as reported in various research studies. In this paper, we have described the piezoelectric properties of composite films of semimetal doped PZT- polymer composites prepared by hot press method for different ceramic volume fraction. Here, we report the effect of inclusion of semimetal phase on the piezoelectric properties of 0-3 PZT-PEG composites (with ceramic volume fraction 0.5). The doping concentration varies from .001 to 0.05 by weight for x semimetal /0.5PZT/(0.5 - x) PEG composite system. The viscous solution of polymer with semimetal doped PZT was heated until all solvent evaporates and then it is further heated so that all the polymer melts. This melt was pressed between two metal discs to obtain sheets of composite of thickness about 200 μm using hot press method having 0-3 connectivity. Samples were poled by applying different poling voltages. The piezoelectric properties of composite were analyzed by measuring piezoelectric charge constants (d_{33}) employing Piezo-Test PM100 computer interfaced system. The dielectric constant of these samples was measured in a wide frequency range (100 Hz to 1 Mhz) at room temperature. Inclusion of third phase causes a significant change in the piezoelectric properties of the composites. Observed results were analyzed using theoretical models as well.

Keywords: piezoelectric coefficient, polymer-ceramic composites, Piezo sensors and hot press method.

1. Introduction:

Ceramic –polymer 0-3 composite system offer several advantages over pure ceramics. These composites have been designed and used for various applications due to their appreciable piezoelectric properties. These

composites can be easily made to large area to increase sensitivity as sensors; they are flexible that intimate contact with the objects to be detected is possible, this is particularly important in vibration sensing and transducer applications. The ceramics provides functional effects and the polymer matrix provide good protection of the ceramic phase while maintains the compliant mechanical property. The obtained composites exhibit piezoelectric properties of ceramics and flexibility, strength and lightness of polymers but electromechanical coupling coefficient, pyroelectric and piezoelectric charge coefficient, relative permittivity and other effective coefficients of these flexible composites are relatively low, which hinders the realization of practical use of the polymer composites.[1,2] Hence, extensive research is going on for optimizing properties of these composites using different ceramics and polymer matrices.[3-5] Different composites of PZT with various types of polymers such as PVDF, PVC and copolymers have been widely studied and reported in literature [6-8]. But one problem with 0-3 connectivity composites which hinders its wide applications is in obtaining effective polarization of ceramic particles /dipoles in such composites as the dielectric constant of piezoelectric ceramics is larger than most of the polymers. [9] For a composite with 0–3 connectivity the electric field E_c acting on spherical grain / ceramic particles is given by [10]

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

where ε_1 and ε_2 are the dielectric constants of the polymer and ceramic, respectively, and E_0 is the applied field. This electric field E_c acting on the ceramic particles in the host polymer matrix is mainly controlled by the dielectric constant of polymer matrix. Due to high dielectric constant of ceramic phase, major part of the applied voltage is wasted across the polymer phase as the analog electrical circuit is two resistances in series for the composite as reported in the literature. Various efforts have been made to obtain the efficient poling of these parameter. One effective way is to create a electric flux continuity amongst ceramic particles by introducing a small amount of third phase (fillers such as graphite, silicon etc.) [11-13]. This 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. Maxwell–Wagner interfacial mechanism well explains the significance of the reduction of such resistance .The influence of introducing third semimetal phase on dielectric, piezoelectric and ferroelectric properties of 0-3 composites is not well explained. Here, we report the results of graphite doping (.001 to 0.5) on the piezoelectric and dielectric properties of PZT- PEG (with ceramic volume fraction 0.5) . We have analyzed the effect of this doping on the piezoelectric and dielectric properties of these composites.

2. Methodology:

2.1 Sample Preparation:

The PZT powder and PEG (in powder form) was procured commercially. A measured quantity of PEG was dissolved in n-Butanol. A proportionate quantity of PZT powder by weight was dispersed in this solution and mixed thoroughly. The solution was stirred and given ultra-sonification treatment for proper mixing. The solution was then heated at 40°C for one hour until it became viscous and finally the solvent evaporates. The dried thick composite film so obtained was then cut , placed in the die and was hot pressed at 10 MPa and 200° C temperature for one hour using hot press technique. The disc shaped 0-3 composites of PZT-PEG of thickness 200 μ m with various ceramic volume fractions (ϕ = 10 % to 60%) were obtained. We have taken PZT- PEG composite with 0.5 ceramic volume fraction to study the effect of inclusion of third phase. The composites with graphite powder (commercially procured) were made in the similar way by mixing PZT powder and graphite powder first and varying the doping concentration from .001 to 0.05 by weight [x graphite/0.5PZT/(0.5 –x)PEG]. The electrodes on both sides of this composite were applied by standard silver paste. 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. PZT- PEG composites with ceramic volume fraction varying from 10% to 60% were polarized by applying dc poling field of 4 KV/mm to 5 KV/mm at 120°C for one hour. Addition of third phase i.e. inclusion of graphite in such composites make it difficult to pole at such high field therefore PZT/Graphite/ PEG composites were poled along the thickness direction in silicon oil bath by applying 2 KV/mm to 3 KV/mm dc poling field for 30 minutes at 120°C. All the samples were aged for at least 24 hours prior to measuring the dielectric and piezoelectric properties.

2.2 Measurements:

Piezoelectric characterization of these poled composites was carried out employing Piezo-Test PM100 computer interfaced system by measuring d_{33} of various composite systems (with and without third phase) . Dielectric parameters such as relative dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) were measured by using Keithely LCZ and HP LCZ impedance analyzer at room temperature at 1 KHz for the composites (0.5 ceramic volume fraction) with varying graphite content.

3. Result & Discussions:

Fig. 1 shows the variation of piezoelectric coefficient of PZT- PEG composites with different ceramic volume fractions. As volume fraction of ceramic increases, the contribution from the ceramic dominates the d_{33} and thus d_{33} increases with increasing volume fraction as ceramic phase gives major contribution to piezoelectric properties of these composites. Such obtained experimental values of piezoelectric coefficients with varying ceramic volume fraction are in well agreement with the theoretical values as calculated using the relation given by Furukawa et.al [14].

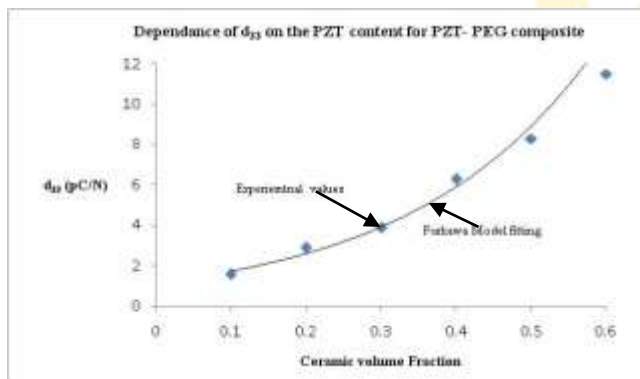


Fig 1 : Piezoelectric coefficient as the function of ceramic volume fraction for 0-3 composites (without introducing third phase)

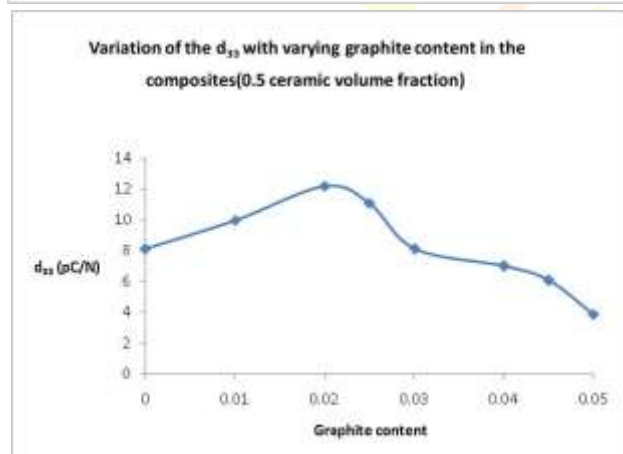


Fig 2: Variation of Piezoelectric coefficient with varying graphite content (.001 to 0.05) in the composites (0.5 ceramic volume fraction)

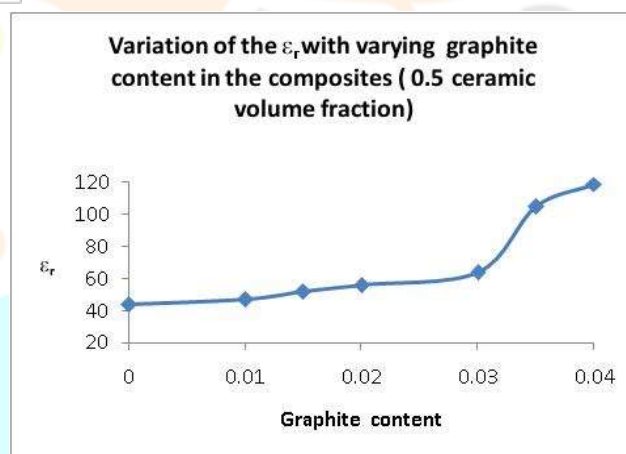


Fig 3: Variation of dielectric constant with varying graphite content (.001 to .05) in the composites (ceramic volume fraction 0.5)

Fig. 2 shows the variation of piezoelectric coefficient for [x graphite/0.5PZT/(0.5 -x) PEG] composites with varying x (graphite doping concentration) from .01 to 0.05 . Poling voltage required to pole such three phase composites is less than half of that required to pole 0.5PZT/0.5 PEG composites. We obtain 46.7% increase in the d_{33} value for the composite with graphite content 0.02. The piezoelectric coefficient was found to increase initially with increasing graphite content and reached maximum (12.2 pC/N) for the composite with 0.02 graphite content. On further increasing the graphite content in the composite, a decrease in piezoelectric coefficient was observed and d_{33} for the composite with graphite content 0.05 was obtained as 4.1 pC/N which is even lower than piezoelectric coefficient of 0.5 PZT/ 0.5 PEG. Our results are in good agreement with similar reported works, wherein inclusion of third phase in PZT-polymer composites enhanced the piezoelectric properties.

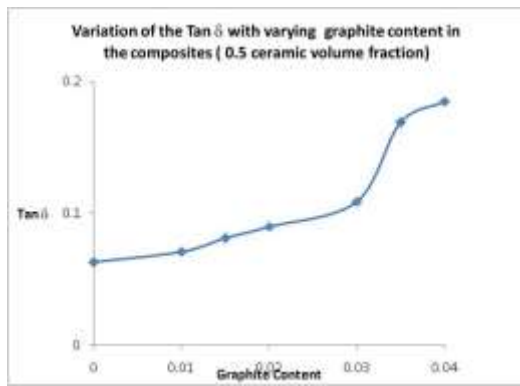


Fig 4: Variation of dielectric loss factor with varying graphite content (.001 to .05) in the composites (ceramic volume fraction 0.5)

Fig. 3 shows variation in dielectric constant (relative permittivity) for [x graphite/0.5PZT/(0.5 - x) PEG] composites with varying x (graphite doping concentration) from .001 to 0.05 . A slight variation in the dielectric constant was observed with the initial inclusion of graphite phase (for $x = 0.01$ to 0.03). We have observed a sharp shoot in the dielectric constant for the composite with graphite content 0.035. An increase of 147 % in dielectric constant was observed at $x = 0.035$ for x graphite/0.5PZT/(0.5 - x) PEG composite. Fig. 5 shows variation in dielectric loss ($\tan \delta$) for [x graphite/0.5PZT/(0.5 - x) PEG] composites with varying x (graphite doping concentration) from .001 to 0.05 . The variation in dielectric loss follows the same pattern as that of dielectric constant with varying graphite content. It also shows slight variation in the initial range of graphite inclusion and a sharp shoot at $x = .035$ loading of graphite. An increase of 164 % in dielectric loss was observed at $x = 0.035$ for x graphite/0.5PZT/(0.5 - x) PEG composite. Obtained results indicate that by introduction of filler in ceramic-polymer composite, poling can be carried out easily resulting in an enhancement in dielectric and piezoelectric properties. As suggested by Sakamoto et al [10] and Liu, X.-F. et al [11,18] , it seems that graphite particle create a continuity network amongst ceramic particles. But when the graphite loading is increased beyond a limit (0.002 in this case) , observed reduction in piezoelectric coefficient may be because the electrical conductivity has increased so much that it becomes difficult to pole the ceramic. The sharp shoot in dielectric constant at $x = 0.035$ graphite content may be due to formation of a graphic particle percolation path through the composites. This percolation threshold indicates the beginning of coagulation of graphite particles around piezoelectric ceramics which is resulting in networks facilitating the electrical conduction and is responsible for high value of dielectric constant at this point . Thus this sharp increase in dielectric constant and dielectric loss may be attributed to formation of a graphic particle percolation path through the composites. Increasing of interfacial polarization may also be a reason for increase in dielectric loss with increasing graphite content. Some models also consider the three phase PZT/Graphite/Polymer composite equivalent to quasi-two-phase composite of conductive graphite particles and insulating PZT/ Polymer mixture matrix, a 0-(1-3) type composite.

4. Conclusion:

PZT- PEG composites have been prepared by hot press technique. A third phase was introduced by inclusion of graphite content and composites [x graphite/0.5PZT/(0.5 - x) PEG, with $x = .001$ to 0.05 by weight] were also prepared. The piezoelectric coefficient was found to increase initially with increasing graphite content and reached maximum for the composite with 0.02 graphite content. An increase of 46.7% in the d_{33} value (12.2 pC/N) for the composite with graphite content 0.02 was observed. Dielectric constant and dielectric loss factors increased significantly at $x = 0.035$ for x graphite /0.5PZT / PEG composite. The result indicates that due to inclusion of graphite phase, poling can be carried out effectively as graphite particles create a continuity network amongst ceramic particles. Sharp increase in dielectric parameters has been analyzed. Results obtained are in good agreement with other studies.

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