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Influence of Phase Transformation in PVDF-PZT Composites of 0-3 Connectivity

P. Gowdhaman, Haresh M. Pandya, P. R. Kumar, V. Annamalai*

Department of Physics, Chikkanna Government Arts College, Tirupur, TN, India.

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Abstract

The 0-3 connected PZT-PVDF ferroelectric composites have been prepared using different solvents as a binder. The phase transformation of polymer phase has been achieved by varying the solvent. The dispersion of ceramic particles into the polymer phase of the composite has been examined using Scanning Electron Microscope (SEM). The poling study on dielectric properties of the PZT-PVDF composites have been analyzed to find a better solvent. The piezoelectric strain coefficient (d_{33}) and piezoelectric voltage coefficient of the PZT-PVDF composite tends to decrease at higher poling fields. The effect of phase change in PVDF on dielectric and piezoelectric properties of the composite has been analyzed and reported in this study.

Keywords: *Dielectric constant; Ferroelectric composite; Piezoelectric strain coefficient; PZT-PVDF; Voltage coefficient.*

1. INTRODUCTION

In the recent few years, there have been numerous research work is going on in the development and investigation of ferroelectric materials due to its unique property called spontaneous polarization. However the ferroelectricity was discovered in the early 1920s, the limitations of these materials make them complicated for practical applications. The discovery of piezoelectric materials like Lead Zirconate Titanate (PZT) and Barium Titanate ($BaTiO_3$) makes them useful for the eclectic range of applications in transducer, sensor and actuator devices (Jain *et al.* 2015).

The ferroelectric ceramic material like PZT has excellent piezoelectric and dielectric properties (Gowdhaman *et al.* 2015), but still its poor mechanical stability makes it under study for real-time applications. Meanwhile ferroelectric polymer such as PVDF (Polyvinylidene Fluoride) possess exceptional flexibility over ferroelectric ceramics (Sampathkumar *et al.* 2013), hence PZT is often combined with PVDF to form biphasic composites. Despite PVDF has reduced dielectric and piezoelectric properties in comparison with PZT, its superior performance as a composite makes them highly compliant for applications where high pressures are involved. Connectivity of the diphasic solid plays a vital role in the properties composite materials. The three dimensional form of ten different connectivity patterns solid composite materials has been described by Newnham *et al*. (1978). Among ten connectivity patterns 0-3 connectivity has been opted in the present study.

The polymer PVDF exists in four different phases (α, β, γ and δ phase). Among different phases β and γ phases of PVDF has been considered in this study. Among several methods available for the preparation of ferroelectric ceramic-polymer composites (Gowdhaman *et al.* 2015; Jain *et al.* 2015), hot press method has been adopted in this study.

2. EXPERIMENTAL METHODS

2.1 Sample Preparation

The PZT-PVDF composite samples were prepared for 0.5 PZT volume fractions. The PZT powder, Navy type VI (APC 855, American Piezoceramics, USA) and PVDF pellets of molecular weight 5,30,000 (Sigma Aldrich Chemicals) were used as ceramic and polymer phase for the composite preparation. Composite samples were prepared by using β and γ phases of PVDF. The β and γ phase of PVDF could be obtained by using cyclohexanone (CYX) and dimethyl sulfoxide (DMSO) as a solvent respectively (Senthilkumar *et al.* 2005). Prepared composites were made into pellets of desired

****V. Annamalai*** ***Tel. no:*** +91 9791493045
Email: *annamalai_140795@yahoo.co.in*

dimensions of the order 2 mm thickness and 6.2 mm diameter by using a hot-press apparatus.

2.2 Electroding and poling

Conductive pure silver paste (Sigma Aldrich Chemicals) has been used for electroding the samples. The subsequent poling has been done on the samples by applying DC electric field using a high voltage power supply. The samples are poled at 120 °C for one hour at different poling field (say 10, 20 and 30 kV/cm). To ensure the homogeneous heating and to avoid arcing the samples was kept inside the silicone oil during the poling process.

3. RESULTS & DISCUSSION

3.1 Morphological studies

The morphological study on PZT-PVDF composite sample prepared at 0.5 volume fraction of PZT have been carried out using Scanning Electron Microscope (JEOL-Model 6390, Oxford Instruments). The SEM micrograph of the PZT-PVDF composite has been presented in fig. 1. The homogeneity in the dispersion of PZT particles in the polymer phase can be inferred from the SEM micrograph of the composite. It is also inferred that the chemical mixing of PZT into PVDF helps to obtain a composite sample with uniform dispersion and the hot press method minimized the possibility of voids. The similar kind of results could be referred from earlier literatures about PZT-PVDF composites (De-Qing *et al.* 2008; Firmino Mendes *et al.* 2009; Thongsanitgarn *et al.* 2010; Gowdhaman *et al.* 2015; Jain *et al.* 2015).

3.2 Dielectric constant (ε_r)

The dielectric constant (ε_r) of the PZT-PVDF composites prepared using β and γ phases of PVDF which are poled at different poling field (E) has been analyzed. The distinction in the dielectric constant with the poling field of the composite with respect to the phase change in PVDF has been plotted in fig. 2. From the fig. 2, it is observed that the dielectric constant of the composite prepared using γ phase of PVDF possess significantly greater response over β phase of PVDF. The variation in dielectric constant may be due to the fact that the relaxation of PVDF in γ phase makes the greater influence of ceramic phase.

3.3 Piezoelectric properties

3.3.1 Piezoelectric strain coefficient (d_{33})

The piezoelectric strain coefficient (d_{33}) of the prepared PZT-PVDF composite has been measured using piezometer PM35 (Take control, UK) and the obtained values have been represented in fig. 3. In comparison with samples prepared using β and γ phases of PVDF, it is found that the d_{33} values obtained in this study are relative to one another. It is also found that beyond the poling field of 20 kV/cm the d_{33} values start to decrease irrespective of the PVDF phases. In ferroelectric materials the domain walls are narrow and hence at higher poling fields the polarization switching takes place from one domain to another which causes the depolarization (Damjanovic, 2006). Therefore d_{33} values tend to decrease at higher poling fields.

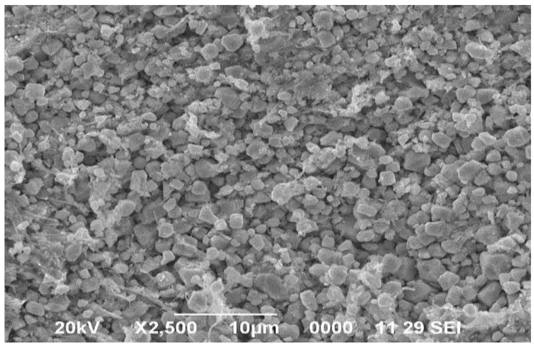

Fig. 1: SEM micrograph of the PZT-PVDF composite at 0.5 volume fraction.

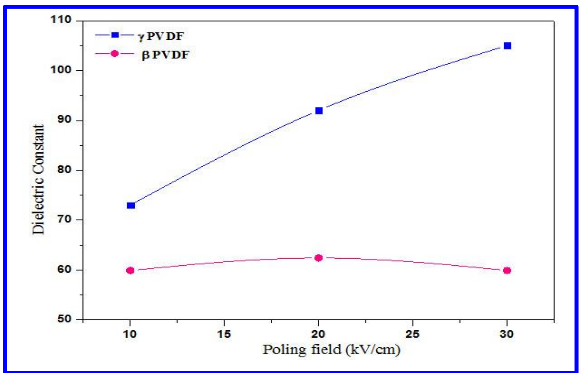

Fig. 2: Comparison of dielectric constant with poling field of the composite at different phases of PVDF

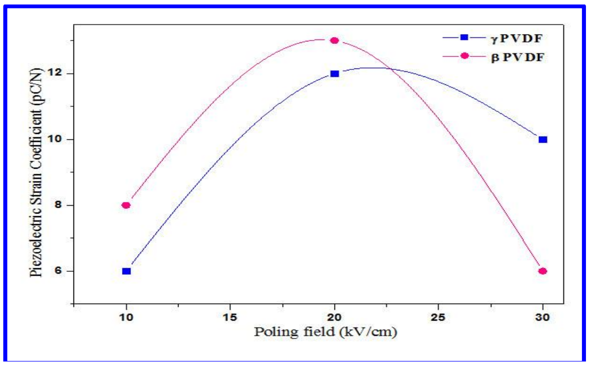

Fig. 3: Variation of piezoelectric strain coefficient with poling field

3.3.2 Piezoelectric voltage coefficient

Piezoelectric voltage coefficient (g_{33}) values of the samples have been calculated from ε_r and d_{33} values by using the relation, $g_{33} = d_{33}/\varepsilon_0\varepsilon_r$ (Sundaram et *al.* 2014), where ε_0 is the permittivity of free space. The calculated g_{33} values have been plotted against the poling field which is shown in fig. 4. The g_{33} values of sample prepared using β phase of PVDF looks pretty good and the maximum value of g_{33} was obtained in the poling field of 20 kV/cm. Since the g_{33} values are proportional to d_{33} values and hence the g_{33} values starts to decrease beyond the poling field of 20 kV/cm due to the depolarization effect of ferroelectric materials.

4. CONCLUSION

The hot press method has been adopted for the preparation of PZT-PVDF ferroelectric composites. The composite samples were prepared using two different phases of PVDF. The SEM studies revealed the homogeneity in the mixture of ceramic and polymer phase. The composite sample with γ phase of PVDF have showed superior dielectric properties and this might be useful for capacitor applications. The piezoelectric properties of the PZT-PVDF composite with β phase of PVDF could be helpful for transducer and sensor applications. The decrease in piezoelectric properties beyond the poling field of 20 kV/cm is due to the depolarization of ferroelectric material at the higher poling field.

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CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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