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Research Article

Significance of Micro and Nano PZT Particles on Dielectric and Piezoelectric Properties of PZT-PVDF Composites

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Abstract

PZT-PVDF composites were prepared using different particle size of PZT and a hot press apparatus has been used for making samples. The structural and compositional analysis of the composite sample was done by using Scanning Electron Microscope (SEM) and Energy Dispersive Analysis of X-rays (EDAX) respectively. The grain size of the ball milled PZT powder was analyzed using powder X-Ray Diffraction (XRD). The samples were poled at a fixed temperature for about an hour under different poling fields. The dielectric constant (ε_r) and the piezoelectric properties like piezoelectric strain coefficient (d_{33}) and voltage coefficient (g_{33}) of composite have been analyzed.

Keywords: lead zirconate titanate, composite, particle size, dielectric constant, strain coefficient, voltage coefficient, ferroelectric materials.

1. Introduction

Ferroelectric materials have recently become so popular due to its spontaneous polarization behavior [1]. Ferroelectric ceramic-polymer composites are one such material which is under the study by many researchers around the world. Ferroelectric materials possess excellent dielectric and piezoelectric properties which make them useful for a diverse range of applications [2–5]. Though ferroelectric ceramics have much better dielectric and piezoelectric properties as a single phase material, it has its own limitations for high pressure applications which constrains their use as raw material. On the other end, ferroelectric polymers become more attractive for its exceptional mechanical stability but they offer very low dielectric and piezoelectric properties. Hence the combined properties of ferroelectric ceramic and polymers are desirable for many practical applications [2, 6–8].

Among several ferroelectric ceramic materials lead zirconate titanate (PZT) has been the material under study because of its superior properties over other ceramic phases. In the meanwhile, polyvinylidene fluoride (PVDF) has been identified to be a one of the suitable ferroelectric polymer. Hence PZT and PVDF have been chosen for the preparation of composites in this study. Ceramic and polymer phases are combined together using a suitable solvent which makes the composite of 0-3 connectivity. Though there are 10 different connectivity patterns reported for a biphasic solid, the 0-3 connectivity become so popular because of its reliability and ease of fabrication [5, 9]. In 0-3 connectivity the volume fraction of PZT can be easily altered, but for the present study it has been chosen as 0.5 whereas the composites were prepared using different particle size of PZT particles.

The different micrometer sized PZT particles (25 µm, 37 µm, and 54 µm) were obtained using nylon sieve plates. The PZT nano particle (17 nm) was obtained from ball milling of PZT powder. The dielectric and piezoelectric properties of the composites with different particle size of PZT have been examined to optimize the particle size of PZT.

2. Experimental methods

The ferroelectric PZT-PVDF composite has been prepared using different particle size of PZT (say 17 nm, 25 µm, 37 µm and 53 µm) at 0.5 volume fraction of PZT. Nylon sieve plates are employed to obtain different particle size of PZT. American Piezo Ceramics (APC 855) PZT ceramic powder and PVDF pellets from Sigma Aldrich chemicals have been used for composite preparation. Cyclohexanone has been used as a solvent for composite preparation. There are numerous methods exist for the composite sample preparation, among which hot press method has been opted for this study [3,5]. The samples were prepared in the form of pellets with fixed dimension [2,5,10]. Further the samples were electroded using conductive silver paste from Aldrich Chemicals. The prepared samples were kept in a silicone oil bath and poled for one hour at 120°C over different poling fields (10, 15, 20, 25, and 30 kV/cm).

2.1 Measurements

The surface analysis and energy-dispersive X-ray spectroscopy (EDAX) analysis were done by using a scanning electron microscope (JEOL-Model 6390, Oxford Instruments). X-ray powder Diffraction (XRD) studies of ball milled pure PZT ceramic powder was done by using Shimadzu Instrument, Model - XRD 6000. The average crystalline size of the PZT powder was calculated using Scherrer formula, $d=0.9\lambda/\beta \cos\theta$, where λ is the wavelength of the CuK-α radiation (1.54Å), β is the full-width half maximum and θ is the Bragg's angle.

The capacitance (C) and the piezoelectric strain coefficient (d_{33}) values were measured using piezometer (Take Control PM 35, UK) at a fixed frequency of 97 Hz. The dielectric constant (ε_r) values were calculated from the capacitance values. The respective voltage coefficient (g_{33}) values were calculated using the relation, $g_{33}=d_{33}/\varepsilon_r\varepsilon_o$, where ε_o is the permittivity of free space.

3. Results and discussion

3.1 Morphological analysis

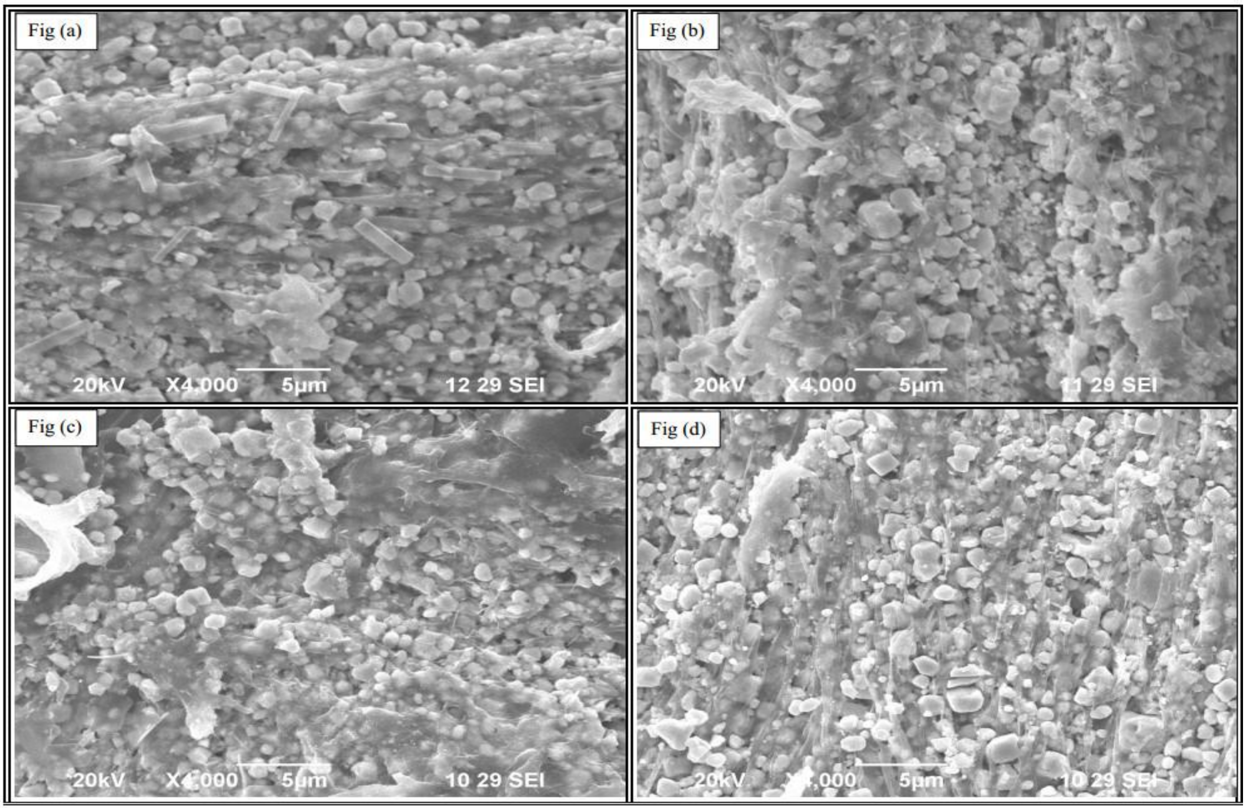

Fig 1 (a-d): SEM micrographs of PZT-PVDF composites of 0.5 volume fraction prepared using PZT particle size 17 nm, 25 μm, 37 μm and 53 μm respectively.

The SEM micrograph obtained for the PZT-PVDF composite made of different particle size of the PZT is shown in figure 1 (a-d). The figure shows that, the PZT particles are mixed well in the polymer matrix and are also distributed uniformly. It can also be noted that the size of the PZT particle dominating the polymer matrix with the increase in PZT particle size in the composite due to the increase in grain size of individual PZT particles.

3.2 Energy dispersive analysis of X-ray (EDAX) analysis

The compositional analysis of the PZT-PVDF composite sample prepared at 0.5 volume fraction of PZT was investigated by EDAX. The corresponding EDAX spectrum shown in figure 2 clearly confirms the purity and content of the composite sample. EDAX analysis also indicates that the influence of ceramic phase is higher than compared to the polymer phase in the composite.

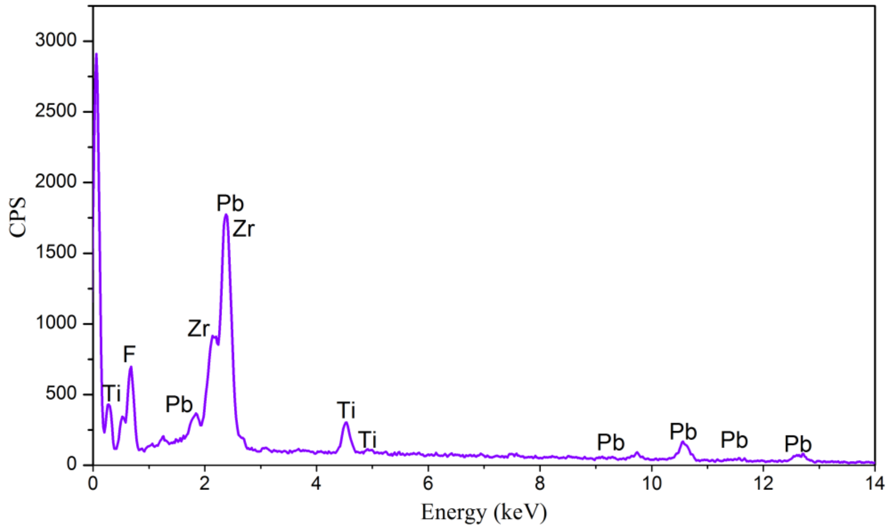

Fig 2: EDAX spectrum of PZT-PVDF composite.

3.3 X-ray diffraction (XRD) of PZT

The X-ray powder diffraction patterns obtained from the ball milled PZT powder is shown in figure 3. The obtained XRD pattern has been compared with the diffraction patterns of PZT, which are presented in earlier literatures. From the analysis, it is confirmed that the obtained results are in proximity with earlier studies and the structure of PZT is identified as a perovskite structure. It is also clear from the patterns that most intense reflection (110) occurs at 2θ~31.14°, which is very close to the value mentioned in literature for pure PZT ceramic phase [6,11–13]. The average grain size of ball milled PZT powder was found to be 0.017 µm (17 nm) which is calculated by using Scherrer formula.

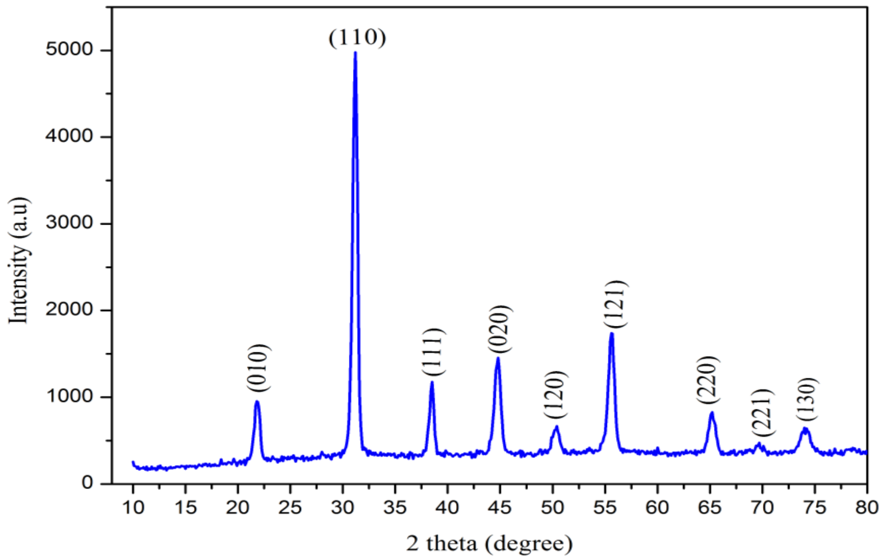

Fig 3: X-ray diffraction pattern for PZT particles.

3.4 Dielectric constant (ε_r)

The samples prepared at different particle size of PZT, which are poled at various poling fields have been analyzed for its dielectric constant and the obtained values were represented in table 1. The figure 4 shows the variation of dielectric constant values with respect to the particle size of PZT for the samples poled at 15 kV/cm. The observed dielectric constant values from the table 1 shows that the dielectric constant increases with increase in particle size of PZT irrespective of the applied poling field. This variation is due to the fact that the ceramic particles are in contact with each other with the increase in particle size of PZT and hence dielectric constant values are greater for 53 µm particles.

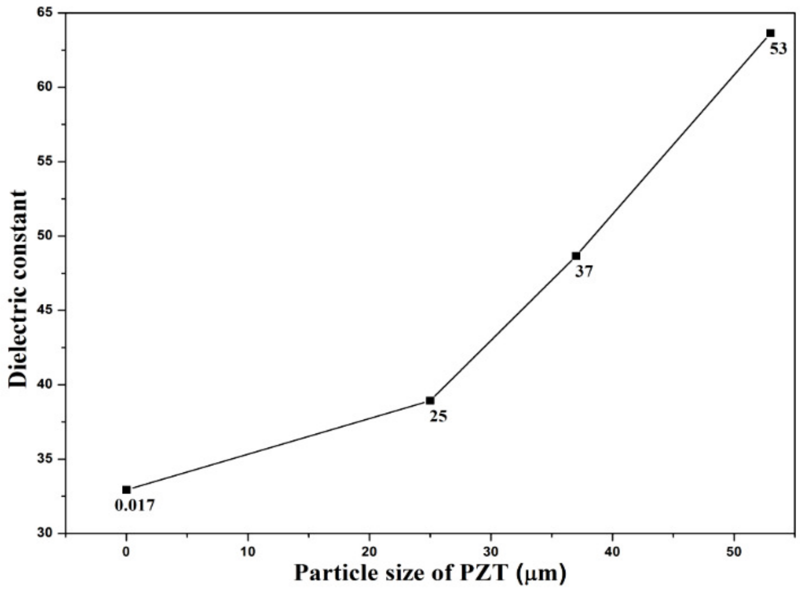

Fig 4: Variation of dielectric constant with particle size of PZT.

3.5 Piezoelectric properties

3.5.1 Piezoelectric strain coefficient (d_{33})

The obtained piezoelectric strain coefficient (d_{33}) values of the composite samples have been presented in table 1. The composite samples with 53 µm particle sizes of PZT was found to have significant d_{33} values rather than compared to the samples with less than 53 µm particle size. The increased particle size of ceramic phase leads to the higher connectivity between the ceramic particles which helps to have efficient poling and thereby d_{33} values become higher for 53 µm.

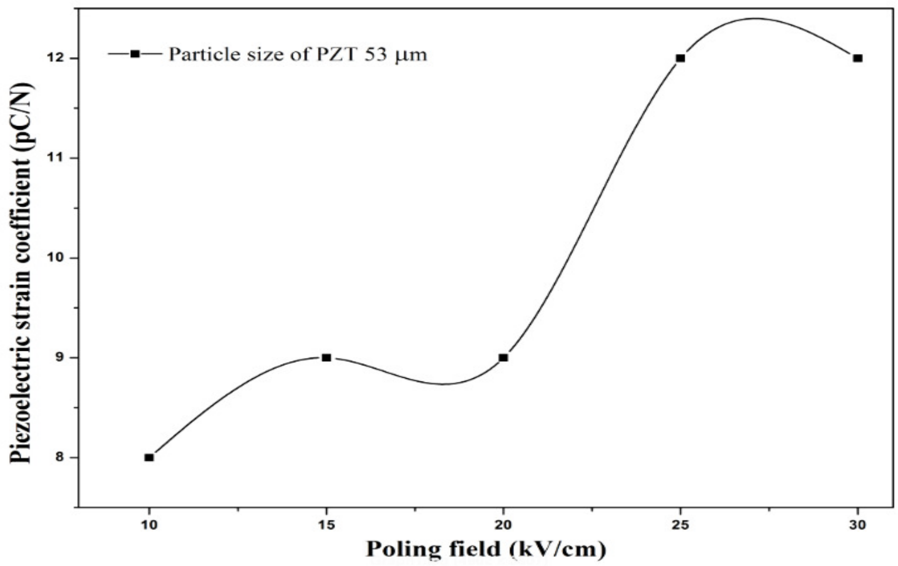

Fig 5: Variation of piezoelectric strain coefficient with poling field.

Figure 5 shows the variation of d_{33} values with poling field for samples with 53 µm particle size. The figure 5 implies that the d_{33} values found to be increased with the increase in poling field, whereas beyond the poling field of 25 kV/cm there was no change in d_{33} values. At higher poling fields the d_{33} values of the ferroelectric materials may tend to decrease due to the depolarization effect [10,14].

3.5.2 Piezoelectric voltage coefficient (g_{33})

The piezoelectric voltage coefficient (g_{33}) values were derived from dielectric constant and d_{33} values by using the relation, $g_{33}=d_{33}/\varepsilon_0\varepsilon_r$. The derived g_{33} values were presented in table 1. The composites with 0.017 µm (17 nm) particle size of PZT, which was poled at 30 kV/cm possess comparatively better g_{33} values. Since the g_{33} values depend on d_{33} as well as ε_r and hence there is a significant variation have been observed in the obtained g_{33} values.

Table 1: Ferroelectric properties of composites with different particle sizes

Poling field kV/cm	Particle Size of PZT											
	17 nm			25 µm			37 µm			53 µm		
	ε_r	d_{33} pC/N	g_{33} 10^{-3} Vm/N	ε_r	d_{33} pC/N	g_{33} 10^{-3} Vm/N	ε_r	d_{33} pC/N	g_{33} 10^{-3} Vm/N	ε_r	d_{33} pC/N	g_{33} 10^{-3} Vm/N
10	29.19	3.0	11.61	46.41	3.0	7.30	53.15	5.0	10.63	67.37	8.0	13.41
15	32.94	6.0	20.57	38.93	4.0	11.61	48.66	5.0	11.61	63.63	9.0	15.98
20	39.28	5.0	14.38	34.43	6.0	19.68	55.12	6.0	12.29	64.38	9.0	15.79
25	35.93	5.0	15.72	35.18	5.0	16.05	51.39	6.0	13.19	67.37	12.0	20.12
30	26.95	8.0	33.53	35.18	7.0	22.47	44.17	6.0	15.34	68.12	12.0	19.90

4. Conclusion

The successful fabrication of PZT-PVDF composites have been made by using different particle size of PZT. The surface morphological analysis revealed the homogeneity of PZT particle in the polymer matrix and the EDAX analysis indicates purity of the content in the composite. The grain size of the ball milled PZT powder was estimated by making use of XRD. The dielectric constant and the piezoelectric strain coefficient (d_{33}) values are found to be greater for 53 µm due to the efficient poling process at a higher particle size of PZT.

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