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On the use of non-MPB lead zirconium titanate (PZT) granules for piezoelectric ceramic–polymer sensorial composites

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Abstract Modern flexible and sensitive sensors based on polymer–ceramic composites employ lead zirconate titanate (PZT) granulates having the morphotropic phase boundary (MPB) composition as the piezo active ingredient, as this composition gives the best properties in fully ceramic piezoelectric sensors. In this study, the possibility of using PZT granulates with compositions, which are not in the MPB region of the PZT phase diagram was investigated. Random 0–3 PZT–epoxy composites were prepared for the complete composition range of PZT ceramics $[\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})_{0.99}\text{Nb}_{0.01}\text{O}_3]$ with x ranging from $x = 0$ to $x = 0.80$. Piezoelectric and dielectric properties of such composites were systematically studied. It is shown that the highest voltage sensitivity (i.e. g_{33}) of the piezoelectric composites is obtained for composition with much lower Zr levels ($x < 0.1$) than the MPB composition. The shift in optimal composition is related to shift in dielectric constant of PZT as a function of the Zr concentration.

1 Introduction

PZT ceramics based on solid solutions of lead zirconate titanate (PZT) are well known piezoelectric materials with widespread technological applications [1]. The compositional dependence of the structure and the electrical

properties of PZT ceramics have been investigated extensively [1–3]. In this system, rhombohedral and tetragonal phases coexist in a region known as the morphotropic boundary or MPB, which is a strong function of composition, $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$, and a weak function of temperature [1, 4]. For fully dense ceramics, those compositions at or close to the MPB composition give the highest dielectric and piezoelectric properties [1]. Hence PZT ceramics and their compositionally modified variants with soft and hard dopants, all having an MPB composition, have been exploited in many sensor and transducer applications [5, 6].

The fact that the best electro-mechanical properties are obtained at the MPB composition is because this composition leads to the highest number of polarisation directions being present simultaneously. Hence, upon application of an electrical field, a good actuation and minimal internal strains are obtained. In contrast, non-MPB compositions have fewer polarisation directions leading to higher inter-granular strains upon actuation and hence lower piezoelectric and dielectric properties. Unlike bulk ceramics, in which the rigid ceramic grains are in contact with each other in all directions, in sensorial composites the PZT granules are surrounded by a flexible polymer. Furthermore, in such composites there is a large mismatch in dielectric properties between the PZT particles (high ϵ) and the matrix (low ϵ). Due to this, the piezoelectric ceramics in composites will exhibit entirely different poling behaviour and polarization mechanisms [7]. Consequently, it is not physically necessary that the use of ceramic filler particles having the MPB or near MPB composition will result in the highest dielectric and piezoelectric properties for the composites. Even though the lack of particle–particle connectivity will result in a relatively low piezoelectric charge coefficient (d_{33}), the significantly lower effective dielectric constant of the polymer matrix will

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result in an enhanced piezoelectric voltage coefficient (g_{33}). Owing to its tailorable properties, a lot of research work have been carried out recently to investigate the effect of various parameters, namely ceramic/matrix type [8, 9] and ceramic–polymer interface [10, 11], in order to enhance the dielectric and piezoelectric properties of composites. This growing interest have opened up doors for a wide range of potential applications of piezoelectric composites [12–14].

In the current study, the piezoelectric and dielectric properties of 0–3 (i.e. isolated particles randomly dispersed in a continuum matrix) PZT–polymer composites containing PZT [$\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})_{0.99}\text{Nb}_{0.01}\text{O}_3$] granulates with compositions ranging from $x = 0$ to 0.80, were investigated. The experimental results obtained are analysed using the Yamada model [15–17] and take into account the compositional dependence of the dielectric constant of the PZT variants.

2 Theory

The dielectric and piezoelectric properties of polymer–ceramic composites are primarily determined by the ceramic particle volume fraction, the particle–particle connectivity and the intrinsic properties of constituent phases. Apart from these obvious factors, the inter-phase interaction between the ceramic particles and polymer matrix, percolation and porosity also have an influence on the final dielectric and piezoelectric properties of the composites. Various models for the prediction of the dielectric and piezo electric properties exist which can be used to analyse and validate the experimental results [15, 16].

The ‘rule of mixtures’ model for the dielectric constant of composites is based on the assumption that the filler particles are uniformly distributed in a continuous matrix and no interactions between these constituents exist [15, 18]. Using these assumptions, the effective dielectric constant of composite containing dielectric fillers embedded in a polymer matrix can be expressed as:

$$(\varepsilon_c)^k = V_f(\varepsilon_f)^k + (1 - V_f)(\varepsilon_m)^k \quad (1)$$

where ε_c , ε_f and ε_m are the dielectric constants of the composite, pure ceramic filler and polymer matrix respectively, k is an empirical parameter that depends on shape and orientation of the filler particles and V_f is the volume fraction of the filler medium. In general, the value of k corresponds to -1 (series model) or 1 (parallel model), with the former being derived by considering the total capacitance (which is later on used to derive dielectric constant) of the composite as the sum of two capacitances in series connection whereas $k = 1$ corresponds to parallel

connection. In addition, for randomly dispersed ceramic filler particles the value of k corresponds to $1/3$ and this version is called as the ‘random’ model [18].

Yamada considered a composite system consisting of ellipsoidal particles homogeneously dispersed in a continuous polymer medium [16, 17]. In this model, the composite dielectric constant and piezoelectric charge coefficient ($d_{33,c}$) of the composite was derived to be given by:

$$\varepsilon_c = \varepsilon_m \left(1 + \frac{nV_f(\varepsilon_f - \varepsilon_m)}{n\varepsilon_m + (\varepsilon_f - \varepsilon_m)(1 - V_f)} \right) \quad (2)$$

$$(d_{33,c}) = \frac{V_f\varphi\alpha n\varepsilon_c(d_{33,f})}{n\varepsilon_c + \varepsilon_f - \varepsilon_c} \quad (3)$$

where n is the shape factor (depends on the geometry of the filler particles and its orientation with respect to the surface of the composite), φ is the ceramic volume fraction and α is the state of poling of the piezoelectric particles compared to that achievable in a fully dense monolithic ceramic sample.

3 Experimental

The ceramic powder used in this study was prepared using the conventional solid state reaction method using lead oxide (PbO), zirconia (ZrO_2), titania (TiO_2) and niobium pentoxide (Nb_2O_5), each of 99.9 % purity, from Sigma Aldrich. The raw materials were mixed according to the stoichiometric proportions based on the desired ceramic composition. The raw materials were ball milled using 5-mm zirconium balls for 7 h in distilled water. The mixture was then dried in an oven in order to remove the distilled water. The dried powder was calcined in a furnace at 750 °C for 2 h at a heating rate of 2 °C/min in order to initiate the formation of perovskite phase. Phase formation was investigated with X-ray diffraction using a Bruker D8 diffractometer (Co $K\alpha_1$, $\lambda = 1.78901 \text{ \AA}$). The powder was milled again as described above for 3 h. The dried powder was calcined again at 1150 °C for 2 h at a heating rate of 2 °C/min. The calcined ceramic powder was milled for 1 h in order to obtain a particle size within the range 2–4 μm . The presence of the tetragonal phase ($x \leq 0.5$), the rhombohedral phase ($x \geq 0.6$) and the coexistence of both phases at morphotropic phase boundary ($x = 0.52$) were observed from the X-ray diffraction patterns. The ceramic powder thus obtained was used as the filler to prepare unstructured 0–3 ceramic–epoxy composites (20 and 40 vol% ceramic granulate of the desired chemical compositions) by the tape-casting method. The 20 and 40 vol% ceramic loading fractions were chosen to get a dilute

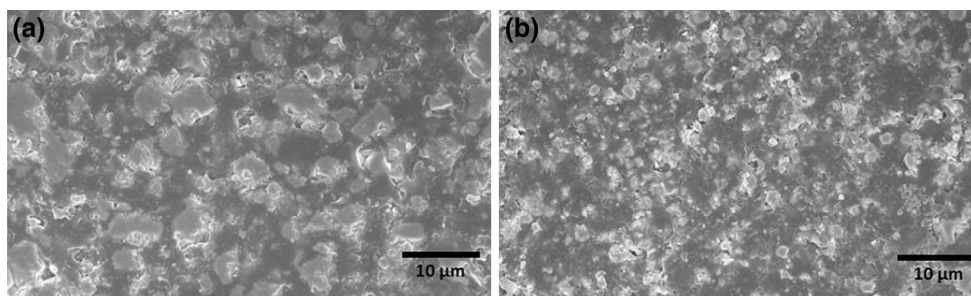


Fig. 1 SEM micrographs of 0–3 PZT (MPB)–epoxy composites with **a** 20 vol% and **b** 40 vol% of ceramic filler

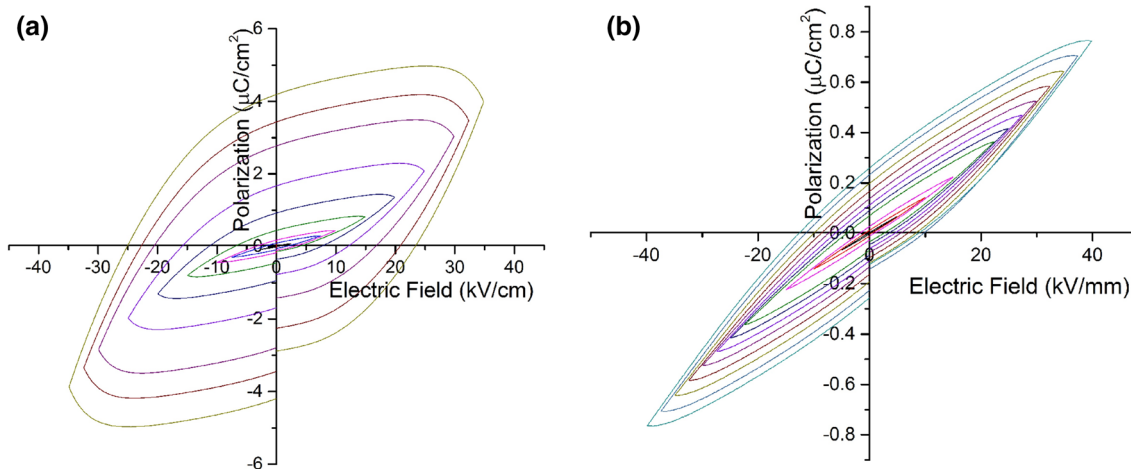


Fig. 2 Polarization hysteresis loops for **a** 20 vol% and **b** 40 vol% of 0–3 PZT (MPB)–epoxy composite

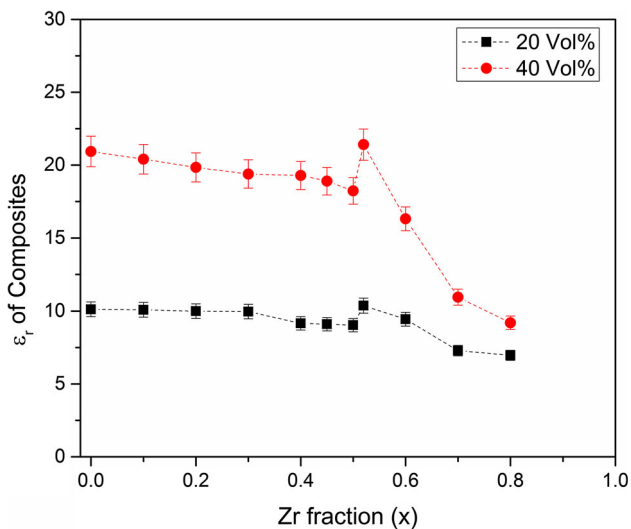


Fig. 3 Dielectric constant (ϵ_r) of the composites as a function of Zr composition in 0–3 composites with 20 and 40 vol% of $\text{Pb}[\text{Zr}_x\text{Ti}_{(0.99-x)}\text{Nb}_{0.01}\text{O}_3$ ceramic filler

system and one with some particle–particle connectivity. The ceramic filler particles having a mean particle size of the order of 2–4 μm were first dispersed into the resin component (EPO-TEC 302-3M 1LB Part A) of the epoxy

and mixed at 3000 rpm for 5 min using a planetary mixer (Speed Mixer DAC 150.1 FVZ). The slurry was degassed for 5 min and subsequently, the curing agent (EPO-TEC 302-3M 1LB Part B) was added to the mix of resin and ceramic particles. Hereafter, it was mixed at 2000 rpm for 5 min. This slurry was degassed for 5 min in order to remove air bubbles. Subsequently, the slurry was poured on a thin aluminium foil and tape-casted using a movable doctor blade at a speed of 2 mm/s, resulting in the formation of 200 micron thin sheets of 0–3 PZT Epoxy composites. The composites thus formed were cured at room temperature for 24 h. After curing, the composites were cut to thin circular disks of 12 mm diameter. Gold electrodes on both sides of the composites were made by sputtering. The composites were poled at 15 kV/mm at 80 °C in silicon oil bath for 1 h. The oil bath containing the composites was then cooled down to 30 °C while maintaining the poling field. The poling temperature was chosen close to the T_g of the epoxy matrix as this temperature leads to a higher electrical conductivity [19–21]. The composites were stored at room temperature for at least 24 h before measuring the dielectric and piezoelectric properties. The dielectric constant of the ceramics and

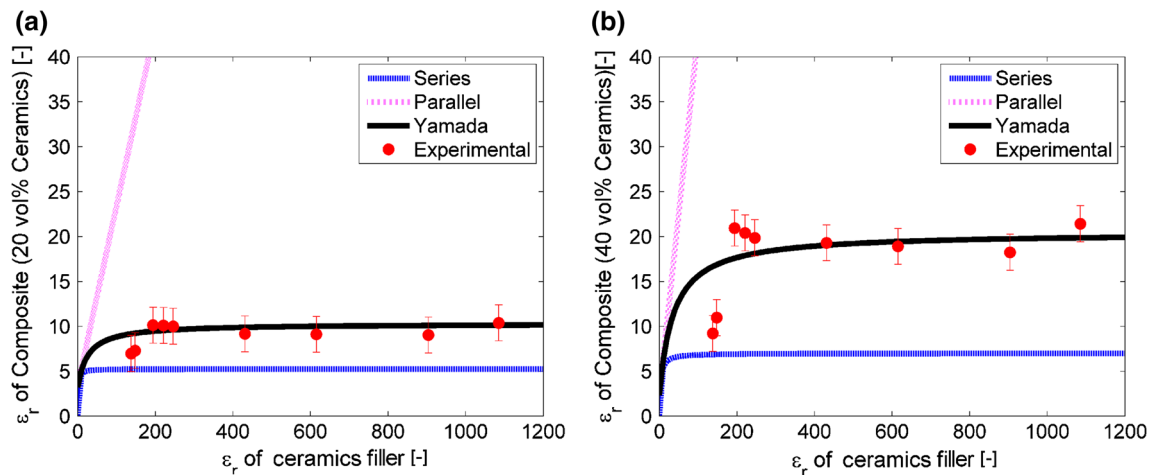


Fig. 4 Comparison of variation of dielectric constant of **a** 20 vol% and **b** 40 vol% composite as a function of the dielectric constant of corresponding $\text{Pb}[\text{Zr}_x\text{Ti}_{(0.99-x)}]\text{Nb}_{0.01}\text{O}_3$ ceramic compositions

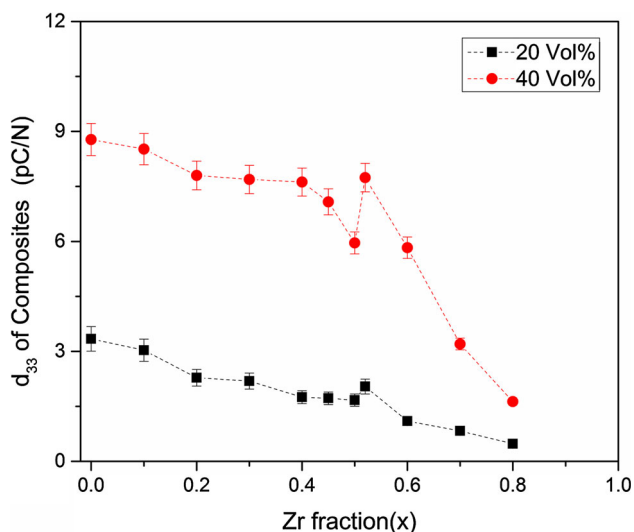


Fig. 5 Variation of room temperature piezoelectric charge coefficient (d_{33}) of 0–3 composites for 20 and 40 vol% of $\text{Pb}[\text{Zr}_x\text{Ti}_{(0.99-x)}]\text{Nb}_{0.01}\text{O}_3$ ceramic filler

composites were measured by parallel plate capacitor method using an Agilent 4263B LCR meter at 1 V and 1 kHz. The piezoelectric charge constant (d_{33}) of the composites was measured using a Berlincourt type d_{33} m and the measurements were carried out at a standard force of 10 N and frequency of 110 Hz. P–E and strain hysteresis loop measurements were carried out to determine the remnant polarization (P_r), spontaneous polarization (P_s) and coercive field (E_c) of the 0–3 composites prepared. The measurements were carried out at room temperature and at an applied field ranging from 5 to 40 kV/mm, using a standardized ferroelectric measurement test system of Radiant Technology. The cross section of the composites

prepared were analysed using a JEOL—JSM 840A scanning electron microscope.

4 Results and discussion

Figure 1 shows the SEM micrographs of the cross section of 0–3 PZT–epoxy composites with 20 and 40 vol% of ceramic filler with MPB composition. It is evident from the micrographs that the ceramic filler particles are homogeneously dispersed in the polymer matrix with minimum porosity. Moreover, a better particle to particle connectivity is observed in 40 vol% composite due to its higher filler content, which results in higher dielectric and piezoelectric properties, as reported in prior works [22, 23].

The polarization hysteresis for 0–3 composites were carried out for different applied fields (5–40 kV/mm) at room temperature and the characteristic loops are shown in Fig. 2. The existence of a hysteresis loop confirms the ferroelectric nature of the 0–3 PZT–epoxy composites prepared. With increasing electric field, the composites exhibited higher polarization due to the reorientation of the dipoles within the ceramic granules, resulting in an increase in the area of the P–E loops. However, the remnant polarization (P_r) remains much lower than that of bulk ceramics due to the influence of the non-ferroelectric polymer phase. It can also be seen that the poling efficiency of composites with 40 vol% of ceramic filler is much higher than that of the ones with 20 vol%. This is due to the better connectivity of the ceramic filler particles in 40 vol% loaded composites.

Figure 3 shows the variation of the dielectric constants of the various composites as a function of the Zr fraction. It has been reported that there is a large difference between

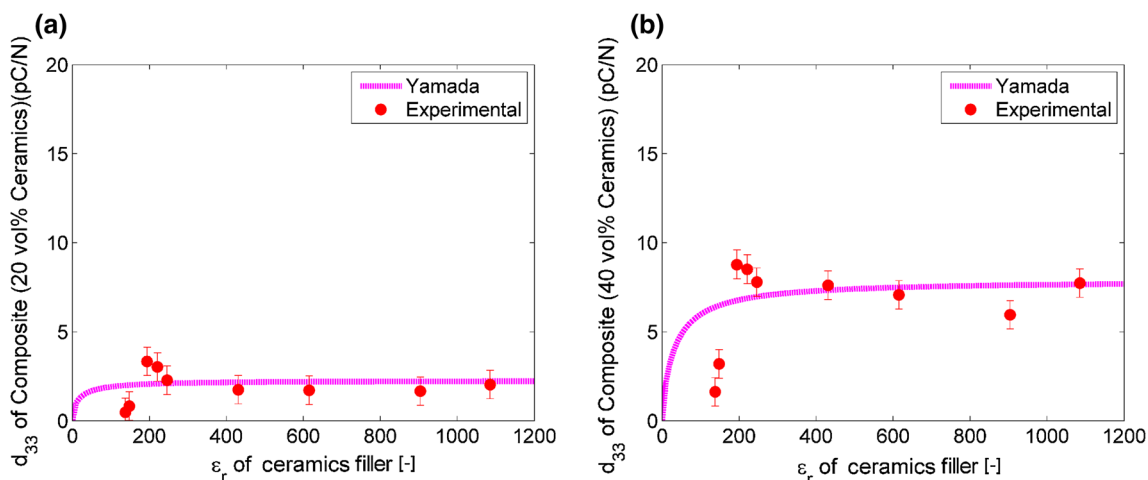


Fig. 6 Variation of room temperature piezoelectric charge constant (d_{33}) of 0–3 composites as a function of filler dielectric constant for **a** 20 vol% and **b** 40 vol% of $\text{Pb}[\text{Zr}_x\text{Ti}_{(0.99-x)}]\text{Nb}_{0.01}\text{O}_3$ ceramic filler

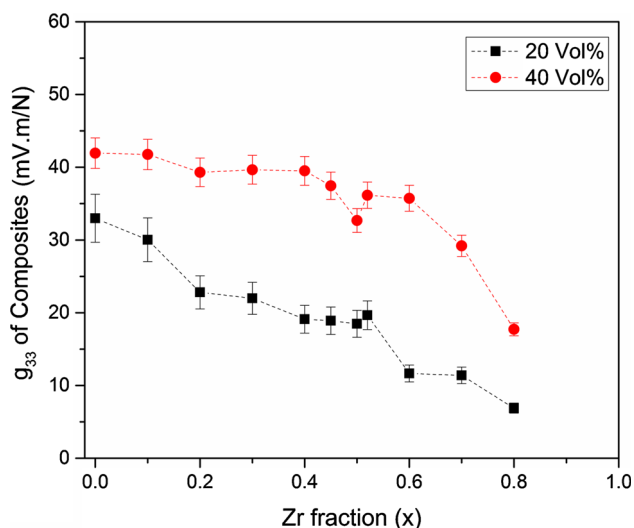


Fig. 7 Variation of room temperature piezoelectric voltage coefficient (g_{33}) of 0–3 Composites for 20 and 40 vol% of $\text{Pb}[\text{Zr}_x\text{Ti}_{(0.99-x)}]\text{Nb}_{0.01}\text{O}_3$ ceramic filler

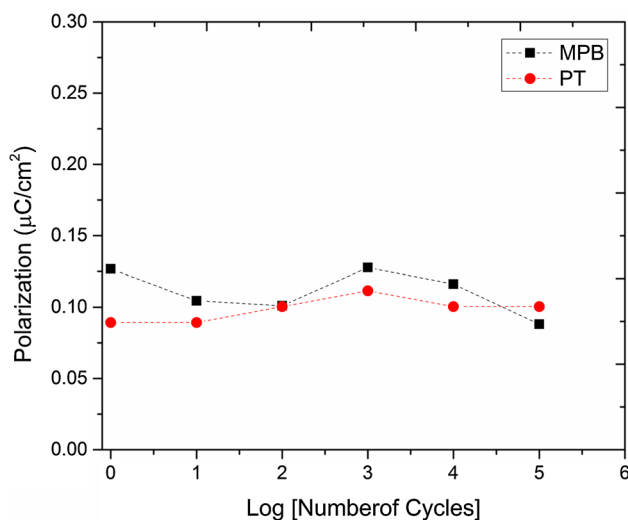


Fig. 8 Polarization fatigue of 0–3 composites with 40 vol% of PT and MPB based ceramic filler

the dielectric constants of PbTiO_3 ($\epsilon = 194$) and MPB ceramics ($\epsilon = 1085$). But when granulates having these compositions are used as filler material in 0–3 composites, the effective dielectric constant of the composite varies less and does not show the pronounced peak value at the composite with MPB ceramic filler. The reason behind this different behaviour of bulk ceramics and composites is related to the difference in the dielectric constant of each constituent (i.e. PZT ceramic filler and epoxy matrix) [24]. For an epoxy–PZT composite with PZT granulates, the dielectric mismatch can be modest (as for PT, i.e. Zr-free PZT) or very large (as for PZT of the MPB composition). A low difference between the dielectric constant of the polymer and ceramic phase results in a better dielectric

homogenization. The dependence of the dielectric constant of the composite on the dielectric constant of the filler material is well supported by the theoretical prediction based on the Yamada model, as shown in Fig. 4. The value of shape factor (n) used in the model is equal to 4.5 due to the nearly spherical morphology of the ceramic filler. The model predicts that the dielectric constant of composites rapidly attains a saturation level as a function of the dielectric constant of constituent ceramic fillers. Once saturated, the increase in the dielectric constant of ceramic filler particles does not have any significant impact on the dielectric constant of its composites. The actual saturation level depends on the granulate volume fraction. This observation is consistent with the experimental results.

Figure 5 shows the piezoelectric charge constant (d_{33}) as a function of Zr fraction for 0–3 PZT–epoxy composites. As reported elsewhere [15, 25], composites with 40 vol% of ceramic filler show a higher d_{33} than those with 20 vol% of filler due to the higher fraction of active ceramic phase and the lower inter particle distance. As in the case of bulk PZT ceramics [1], an increase in the d_{33} of composites is observed for compositions close to the MPB, attaining its maxima at $x = 0.52$ (i.e. MPB composition). For higher Zr fraction (i.e. $x > 0.52$), the anti-ferroelectric rhombohedral phase dominates, resulting in a sharp decline in the d_{33} of ceramic filler and the composites made thereof. Figure 6 shows the results of theoretical predictions for the d_{33} of composites using Yamada's model ($n = 4.5$) as a function of the dielectric constant of ceramic fillers used for two volume fractions. Similarly, as for the effective dielectric constant of composites, the d_{33} of the composites also attains a saturation level after a sharp initial increase of the dielectric constant of the constituent ceramic fillers. This can be correlated to large difference in dielectric constant between the ceramic phase and the polymer phase. In addition to that, the higher depolarization factor of higher dielectric constant filler material also lowers the effective piezoelectric and dielectric properties of the composites made out of it.

Finally, the piezoelectric voltage constant (g_{33}) of the composites as a function of Zr mol% in PZT filler material is shown in Fig. 7. The g_{33} values were obtained by taking the ratio of d_{33} and ϵ_{r33} and ranges from 11 to 42 mV m/N, depending on the vol% of ceramic filler in the composition and the Fig. 7 clearly shows a significant and continuous decrease in g_{33} with increasing Zr fraction. There is no sign of an optimum in performance for compositions at or near the morphotropic phase boundary ($x = 0.52$). The highest value is obtained for composites containing Zr-free or Zr-poor PZT variants. The reason behind the highest voltage sensitivity of PT composites can be attributed to the moderately high d_{33} and relatively lower dielectric constant of PT ceramic filler compared to that of its MPB counterpart.

To conclude, a simple room temperature fatigue experiment, in which the PT and MPB composites with 40 vol% of ceramic filler were exposed to an electric field of 10 kV/mm at a frequency of 1 Hz over a period of 10^5 cycles, was conducted to make sure that the improved sensitivity of the PT epoxy composites is maintained during its use. Figure 8 shows that for both the PT and the PZT composite the polarisation remains more or less constant with the number of cycles. If anything the PT composites perform even better than the PZT containing composites. In case of a monolytic ceramic samples, the stability of PT ceramics is less than that of MPB PZT ceramics [1, 26].

5 Conclusions

The piezoelectric and dielectric properties of unstructured 0–3 PZT–epoxy composites were determined for the complete composition range of PZT ceramics [$\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})_{0.99}\text{Nb}_{0.01}\text{O}_3$] with x ranging from $x = 0$ to $x = 0.80$. While for fully ceramic material the best piezoelectric properties are obtained for a PZT composition at the morphotropic phase boundary, in PZT–epoxy composites the highest voltage coefficient was obtained for the PT composition ($x = 0$). The shift in optimal composition is related to the effect of the low dielectrics of the polymer matrix. The dependence of the piezoelectric and dielectric properties of the composite on the chemical composition of the PZT granulate is well described by the Yamada model. The new insight developed is generic and can also be applied in the development of sensitive sensor materials based on lead-free piezo ceramics.

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