

## Induction of electro-activity in polyvinyl alcohol with addition of nanocrystalline PZT ceramic

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Flexible polymer-ceramic nanocomposites with electro-activity have been prepared by dispersing lead zirconate titanate (PZT) nanoparticles in polyvinyl alcohol (PVA). Thick films of the composites, with volume fractions of nano PZT ranging from 0 to 3 wt %, are cast for experimentation. Their structural, dielectric, thermal and pyroelectric properties are measured and compared with those of pure PVA. It is found that pyroelectricity can be induced into PVA with addition of nanocrystalline PZT ceramic, with pyroelectric coefficient increasing with the concentration of PZT. The Shore hardness of the samples has been measured by indentation technique, and is found to increase with PZT addition. The relevant pyroelectric figures of merit have been estimated, which also increase with PZT addition. Since the flexibility of the composite decreases with hardness, enhancement in pyroelectric figures of merit is at the expense of flexibility and formability. The results presented in this work offer possibility to design material with optimum property for applications requiring moldable pyroelectric detectors.

**Keywords:** Polymer-ceramic nanocomposite, Polyvinyl alcohol, Nanocrystalline PZT, Pyroelectric coefficient, Pyroelectric figures of merit

### 1 Introduction

There has been a great deal of interest in developing flexible electro-active polymer-ceramic composites for various applications such as sensors, actuators and various electro-mechanical components and systems<sup>1-4</sup>. Such materials possess the advantages of the ceramic as well as the polymer. Conventional ceramic materials with high internal polarization possess considerably high ferroelectric properties as well as electro-activity. Correspondingly these materials often exhibit high piezoelectric, pyroelectric, birefringence and nonlinear optical properties. However, ceramics suffer from disadvantages such as high brittleness which limits their mechanical formability, flexibility and mouldability. There are many applications that require flexible, at the same sensitive, piezoelectric/pyroelectric sensors and actuators. Polymers are known to possess desirable properties of ductility, flexibility and formability. So it is natural to think of developing composites by mixing ceramics and polymers so that smart materials possessing both these characteristics are available for applications. Composites based on piezoelectric/pyroelectric ceramic particles embedded in polymers possess hybrid properties derived from individual components, including large piezoelectric/pyroelectric coefficients

of the ceramic material and the excellent mechanical strength, formability, and robustness of the polymer, eventually useful for thermal/infrared detectors without the use of a substrate for support. Several researchers have prepared such materials and studied their properties<sup>5,6</sup>. Special attention has been paid to prepare composites by mixing strong piezoelectric ceramics with polymers that are inherently electro-active. Typical ceramics in this category are lead titanate (PT), lead zirconate titanate (PZT), barium titanate (BT), triglycine sulphate (TGS) etc and the popular electro-active polymers have been polyvinylidene fluoride (PVDF), polyvinylidene fluoride-trifluoroethylene [P(VDF-TrFE)], and polyetherketone (PEKK), polyurethane (PU) etc. Such composites have been experimented for their use as piezoelectric as well as pyroelectric sensors and actuators. Recent studies of ceramic-polymer based pyroelectric composites show potential usefulness in terms of large area, light weight, enhanced strength, flexibility and formability for infrared sensor applications.

Polyvinyl alcohol (PVA) is a popular synthetic polymer which has a good number of applications, particularly as a biomaterial. PVA hydrogels also find a wide range of technological applications. PVA finds applications as biocompatible materials, bio-sensors,

drug delivery systems etc because PVA hydrogels are essentially non-toxic, non-carcinogenic, biodegradable, biocompatible, water soluble and are comparatively inexpensive<sup>7</sup>.

Lead zirconate titanate (PZT) is a very widely used electro-strictive transducer material because of its high piezoelectric coefficient and electro-mechanical coupling. PZT-based piezoelectric materials exhibit excellent and stable electro-mechanical properties, and so are widely used as ultrasonic resonators, ceramic filters, high power transducers, actuators, piezoelectric drives and so on<sup>8</sup>. Even though PZT and similar materials are good piezoelectric materials with high dielectric constants, they are brittle in nature and also are not suitable for high frequency applications due to high acoustical impedance. Their poor mechanical strength and lack of ductility (or high brittleness) also pose problems for applications requiring moldable sensors. Even though polymers do not possess desirable piezoelectric or dielectric properties, they do not suffer from the drawbacks of PZT-like piezoceramics and also serve as excellent host media to incorporate ceramic fillers. In the light of these, the idea of developing polymeric nanocomposites with piezoelectric nanoceramics dispersed in polymer matrix evolved. Such combinations are found to be promising materials because of their combined features of high mechanical strength, elastic properties of host polymer and electro-activity of the piezoceramic.

Different PZT-polymer composites have been prepared and properties studied for their piezoelectric, pyroelectric and dielectric applications by different groups<sup>9,10</sup>. Most of these studies have been on mixtures of traditional PZT, with particle sizes in the micrometer range or above, and the desired polymer. Polymers being materials with low dielectric constant, the preparation of polymer-ceramic composites with high dielectric constant is a challenging task. The composites encapsulating nanoparticles of PZT in polymer matrix display novel and often enhanced properties as compared to traditional materials<sup>10</sup> and also open up possibilities for new technological applications, which include microwave communication devices, embedded capacitors for micro-mechanical systems, flexible actuators, artificial muscles etc. The aim of the present work is to induce pyroelectric/piezoelectric properties in PVA so that formable bio-friendly materials for transducer and actuator applications can be developed. Nanoparticles of PZT are embedded in a matrix of

PVA hydrogel to prepare PZT-PVA nanocomposites and their relevant properties measured following appropriate techniques. The purpose of selecting PZT in the nanocrystalline form is to obtain higher sensitivity and better formability at as low a filler concentration as possible.

Initial characterization of the prepared nano-composites has been carried out using powder XRD and dielectric measurements. The pyroelectric figures of merit of such a sensor material are determined from their pyroelectric coefficients as well as thermal properties, such as specific heat and thermal conductivity. The pyroelectric figures of merit have been compared with the Shore hardness of the materials, and it is shown that enhancement in pyroelectric sensitivity is at the expense of flexibility (or inverse shore hardness) of the material.

## 2 Experimental Details

The host polymer used in this work was commercially available PVA (Aldrich, molecular weight: 90,000-1, 20, 000, degree of hydrolysis: 99 mol %). A definite amount of PVA was dissolved in de-ionized water at 90°C for 6 h. The PVA aqueous solution so obtained was kept undisturbed for a day to obtain clear, foam-free gelatinous solution.

The starting materials used for the preparation of PZT nanopowders were zirconyl oxychloride ( $ZrOCl_2 \cdot 8H_2O$ ), lead nitrate ( $PbNO_3$ ), titanium dioxide ( $TiO_2$ ) and potassium hydroxide (KOH). PZT nanoparticles were prepared following the hydrothermal method, with de-ionized water used in all preparation process. In order to accommodate the high pressure involved in hydrothermal synthesis, a home made, oven heated, acid digestion bomb (autoclave) was used. The device consisted of a PTFE liner in which the precursors were taken, surrounded by a screw top steel casing. A thermostatically controlled laboratory oven was used to heat the autoclave to the desired temperature.

The hydrothermal procedure followed in this work was similar to the one followed by Deng *et al*<sup>11</sup>. For the synthesis of PZT nanopowders, stoichiometric amounts of  $ZrOCl_2 \cdot 8H_2O$ ,  $PbNO_3$  and  $TiO_2$  were taken in the autoclave of volume 100 ml, filled with water up to 80% of its capacity and the mixture stirred vigorously. Then potassium hydroxide flakes were added slowly with continuous stirring to obtain an initial mineralizer concentration of 5mol/l. The autoclave was maintained at 160°C for 4 h and then cooled to room temperature naturally. The product so

obtained was filtered and washed with distilled water and ethanol in sequence. Finally, the yellow product obtained was dried at 80°C.

PZT powder at the required weight percentage was dispersed ultrasonically in PVA aqueous solution and stirred for about 2 h. The gelatinous mass so obtained was then introduced into a rectangular polyethylene container and allowed to dry at room temperature. This was kept undisturbed for about a week, after which thin solid sheets of PZT-PVA nanocomposites were obtained. The concentration of nano PZT in the PVA polymer matrix was varied by dispersing different weight percents (0.5%, 1%, 2% and 3%) of PZT in PVA aqueous solution. A thin pure PVA sheet was also prepared following the same procedure for comparison.

Powder X-ray diffraction (XRD) technique was used to characterize pure PZT nanopowder first. The prepared nanocomposite samples were also subjected to powder XRD measurements. The diffractometer (Bruker, Model D8 Advance) was operated at 30 kV and 20 mA at a glancing angle of 2 degrees to record the diffraction patterns.

The dielectric constant and dielectric loss of the dry composite samples were measured with an Impedance analyzer (Hewlett Packard, Model 4194 A) in the frequency range 100 Hz-1 MHz, keeping the signal strength at 0.5 Vrms. In order to carry out dielectric measurements, samples of diameter 10 mm each were cut from each sheet and used as the dielectric medium of a parallel plate capacitor. The capacitance of the capacitor was measured as a function of frequency, from which the dielectric constant and loss of the medium at various frequencies were determined. The dielectric properties of cast films of pure PVA as well as composites of PVA/PbTiO<sub>3</sub>, PVA/PbO and PVA/NiCl<sub>2</sub> have appeared in literature<sup>12-15</sup>.

The pyroelectric coefficients  $p(T)$  of the nanocomposites were determined following the standard heating technique and calculated following the well known relation<sup>6</sup>:

$$p(T) = I/A (dT/dt) \quad \dots(1)$$

where  $I$  is the pyroelectric current,  $A$  is the sample area and  $dT/dt$  is the heating rate (1°C/min in our measurements).

The photopyroelectric (PPE) technique was used to determine the thermal transport properties, thermal diffusivity ( $\alpha$ ) and thermal effusivity ( $e$ ), by measuring the frequency dependence of the PPE signal amplitude and phase in a photopyroelectric

spectrometer<sup>16,17</sup>. From the values of  $\alpha$  and  $e$ , the thermal conductivity ( $k$ ) and specific heat capacity ( $c$ ) of the samples were obtained. The Shore D hardness values for the samples, including pure PVA, were measured following the indentation method, measuring the penetration depth of a Durometer indenter with a shore hardness meter (Hardmatic Mitutoyo, Model: 321JAA283).

### 3 Results and Discussion

Figure 1(a) shows a typical powder XRD pattern of pure PZT nanoparticles obtained by hydrothermal synthesis. The XRD pattern matches with that of Pb<sub>0.52</sub>Zr<sub>0.48</sub>O<sub>3</sub> (JCPDS Card No: 33-0784). The average diameter of the particles, calculated using the Debye-Scherrer formula, is in the range 10-15 nm. Figure 1(c) shows the XRD pattern of one sample of PZT-PVA nanocomposite with 1 wt. % of PZT dispersed in PVA. The peaks obtained confirm the presence of PZT particles in the polymer matrix. The XRD pattern for pure PVA is also shown Fig. 1(b) for comparison.

The variations of dielectric constant and dielectric loss factor with frequency for the composite samples with different concentrations of nano PZT, as well as for pure PVA, are shown in Figs 2(a and b), respectively. The variations of dielectric constant and loss tangent with concentration of PZT, at frequency 1 kHz, are shown in Fig. 3. It can be noted that the dielectric constant as well as loss factor increases as

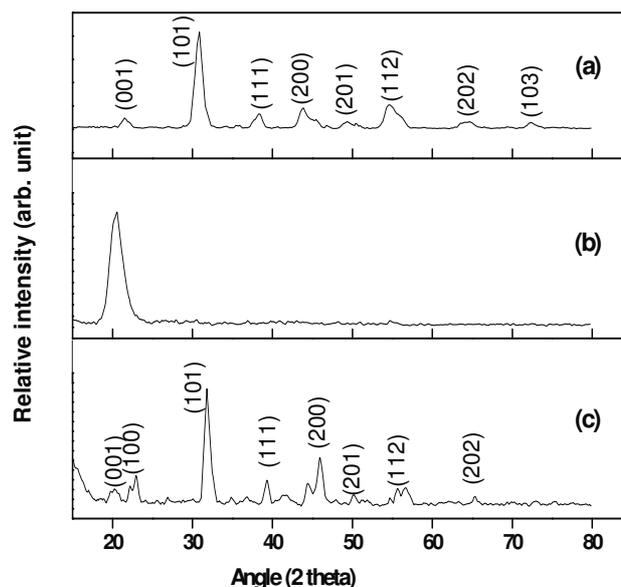


Fig. 1 — Powder XRD patterns of (a) pure PZT nanopowder (b) pure PVA (c) PZT-PVA nanocomposite with 1 wt. % of PZT dispersed in PVA

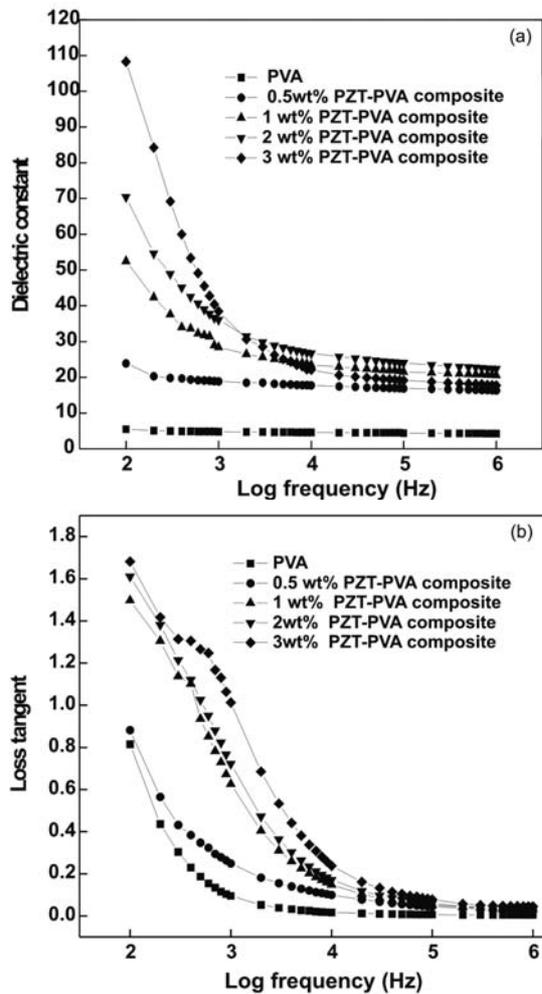


Fig. 2 — Variation of dielectric (a) constant and (b) loss with frequency for PZT-PVA composites with different wt % of PZT

the PZT content in the PVA matrix increases. The increase in dielectric constant with increase in PZT content can be attributed to increase in internal polarization of the sample. The increase in the dielectric loss with increasing PZT content can be attributed to the formation of electric dipoles in the medium. In the hydrogel composite at lower frequencies the conduction losses dominate over the domain losses and hence the  $\tan\delta$  loss is high at low frequencies.

The variation of pyroelectric coefficient for samples with different concentrations of nano PZT is shown in Fig. 4 (a). It can be seen that the pyroelectric coefficient increases monotonically as the PZT content in the PVA matrix increases. The variation of Shore D hardness with weight per cent of PZT is plotted in Fig. 4(b). It can be seen that the Shore D hardness also increases with wt % of PZT. The

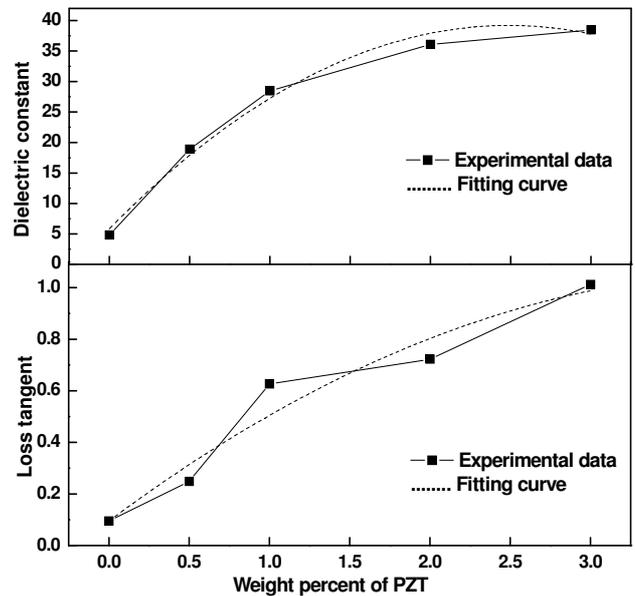


Fig. 3 — Variations of dielectric constant and loss factor with wt% of PZT for PZT-PVA composites at 1 kHz

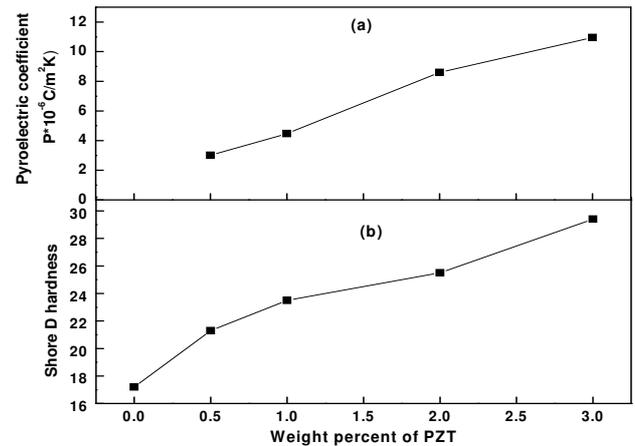


Fig. 4 — Variations of (a) pyroelectric coefficient and (b) Shore D hardness with wt % of PZT in PZT-PVA nanocomposites

variations of specific heat capacity and thermal conductivity with weight per cent of PZT are shown in Fig. 5. It can be seen that specific heat decreases with wt % of PZT, while thermal conductivity shows a corresponding increase. The pyroelectric figure of merit for each of the samples has been evaluated using the expression:

$$\Theta = p(T)/cke' \quad \dots(2)$$

where  $\epsilon'$  is the dielectric constant of the material.

Values of the specific heat, thermal conductivity, pyroelectric coefficient and pyroelectric figure of merit for the different samples are tabulated in

Table 1. It can be seen that among the four composite samples investigated, the pyroelectric figure of merit is the best for the sample with 3 wt % PZT loading. Still higher PZT loading leads to particle agglomeration, which makes the sample brittle, which is undesirable for the envisaged applications.

Since the hardness of a material scales inversely with the flexibility (or formability) of a material, we plotted the inverse Shore D hardness with wt % of PZT. This variation, along with the variation of pyroelectric figure of merit with wt % of PZT, is shown in Fig. 6. As the wt % of PZT increases the Shore hardness increases or inverse Shore hardness decreases. The inverse shore hardness curve meets the pyroelectric figure of merit curve at the composition around 1.7 wt % PZT. This means that for a pyroelectric figure of merit of nearly  $3.2 \pm 10^{-10}$  (or pyroelectric coefficient of nearly  $6.5 \pm 10^{-10} \text{C/cm}^2\text{K}$ ), the optimum inverse Shore hardness is nearly 0.041 (or Shore hardness nearly 24.4).

As it follows from Eq. (2), the important properties to look for in a thermal/infrared sensor material are low dielectric constant and loss, high pyroelectric coefficient, low specific heat capacity and thermal conductivity. For infrared pyroelectric detector materials, the following important figures-of-merit are also defined<sup>18-21</sup>,

$$\text{Current sensitivity, } F_I = \frac{p(T)}{c} \quad \dots(3a)$$

$$\text{Voltage responsivity, } F_V = \frac{p(T)}{c\epsilon'} \quad \dots(3b)$$

$$\text{Detection sensitivity, } F_D = \frac{p(T)}{c\sqrt{\epsilon''}} \quad \dots(3c)$$

where  $\epsilon''$  is the dielectric loss. These have been calculated for the PZT-PVA nanocomposites and found that these figures-of-merit increases with increase of filler concentration, as shown in Fig. 7.

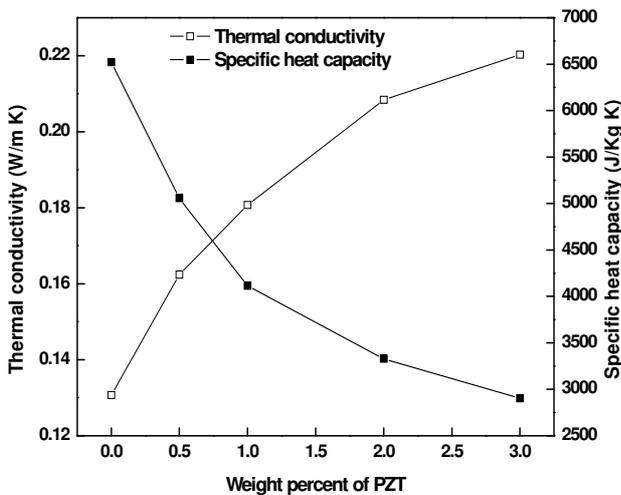


Fig. 5 — Variations of specific heat capacity and thermal conductivity with weight percent of PZT in PZT-PVA nanocomposites

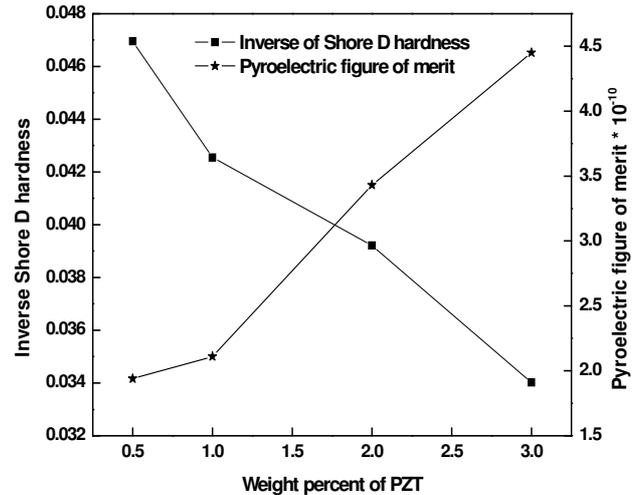


Fig. 6 — Variations of Inverse Shore D hardness and Pyroelectric figure of merit (as defined by equation 2) with weight percent of PZT in PZT-PVA nanocomposites

Table 1 — Specific heat capacity, thermal conductivity, pyroelectric coefficient, dielectric constant, Shore D hardness and pyroelectric figure of merit for pure PVA film as well as different PZT-PVA nanocomposites at room temperature

Sample	Specific heat capacity, c J/kg-K	Thermal conductivity, k W/m-K	Pyroelectric coefficient (303K) $\rho \cdot 10^{-6} \text{C/cm}^2 \text{K}$	Dielectric constant	Shore D hardness	Pyroelectric figure of merit $\Theta = P \cdot 10^{-10} / c k \epsilon$
Pure PVA	6521	0.1307	-	4.8	17.2	-
0.5wt% PZT-PVA	5057	0.1624	3.01	18.89	21.3	1.94
1wt% PZT-PVA	4115	0.1807	4.47	28.46	23.5	2.11
2wt% PZT-PVA	3327	0.2084	8.6	36.07	25.5	3.43
3wt% PZT-PVA	2903	0.2203	10.96	38.46	29.4	4.45

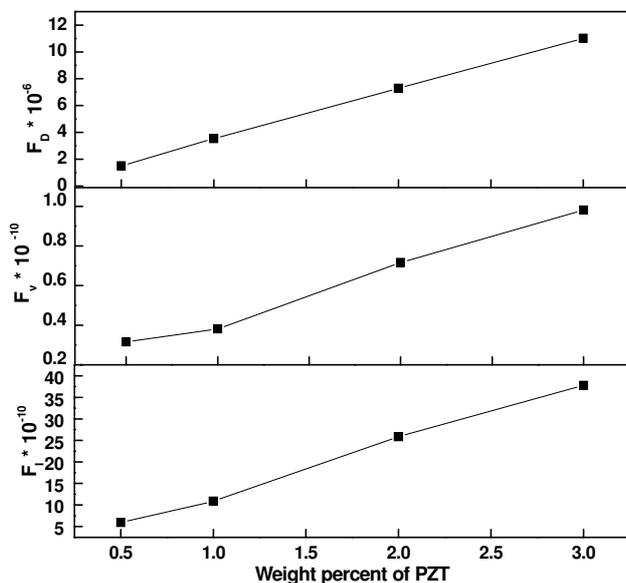


Fig. 7 — Variations of the figures of merit, current sensitivity ( $F_L$ ), voltage responsivity ( $F_V$ ) and detection sensitivity ( $F_D$ ) (as defined by eqns.3) with PZT filler concentration

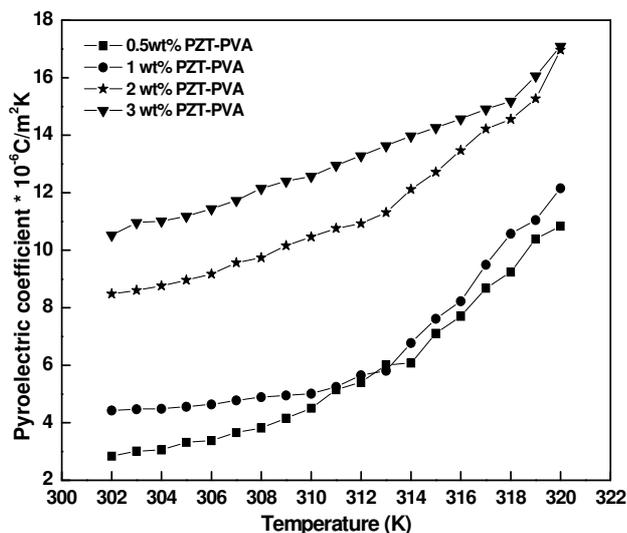


Fig. 8 — Variations of pyroelectric coefficients with temperature for different samples of PZT-PVA nanocomposites

The variations of pyroelectric coefficients for different samples with temperature, varying from room temperature 303 K to about 320 K, have also been measured. These variations are shown in Fig. 8. It can be seen that the pyroelectric coefficient increases with temperature. However, use of these materials as pyroelectric detectors beyond this temperature is not advisable as the material gets damaged at high temperatures.

#### 4 Conclusions

Thin sheets of PZT-PVA hydrogel nanocomposites, with the concentration of PZT varying from 0 to 3 wt. %, are obtained by a solid casting method. The incorporation of PZT nanoparticles in to the polymer matrix results in an increase in dielectric constant of the samples. This is likely due to PZT nanoparticles getting embedded in to the micropores of PVA, making it a homogenous composite material with enhanced internal polarization. The dielectric loss of the PZT-PVA nanocomposite decreases with increasing PZT concentration. These studies reveal that the dielectric constant of PZT-PVA hydrogel nanocomposite sheets can be tuned by varying PZT loading in the polymer matrix. We show that it is possible to induce and tune electric polarization in a polymer base, without significantly changing its polymer characteristics, which will have several practical applications.

The pyroelectric coefficient, thermal conductivity and specific heat capacity of the samples have been measured, and it found that pyroelectricity gets induced in to PVA with the addition of PZT, with pyroelectric coefficient increasing with PZT concentration. The thermal conductivity increases, but specific heat capacity decreases with increase in PZT concentration. The shore hardness of the samples has also been measured, and it is found that the hardness increases with addition of PZT. It is found that beyond about 3 wt % concentration of PZT, the sample becomes brittle losing flexibility and formability which are characteristics of a soft polymer like PVA. All the relevant pyroelectric figures of merit of the samples have been determined, and found that these also increase with wt % of PZT. A comparison of the variations of inverse shore hardness and pyroelectric figures of merit reveal that the increase in pyroelectric figure of merit is at the expense of the flexibility of the composite. If more flexibility is desired for any application, it automatically puts a limit on the detection sensitivity of the material. Depending on the application, one shall design the material.

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