

Effect of poling procedure on the properties of lead zirconate titanate/vinylidene fluoride-trifluoroethylene composites

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Lead zirconate titanate/vinylidene fluoride-trifluoroethylene [PZT/P(VDF-TrFE)] 0–3 composites for pyroelectric sensor and piezoelectric transducer applications have been fabricated by incorporating PZT powder into a P(VDF-TrFE) copolymer matrix. The properties of these composites can be tailored to suit designated applications by varying the ceramic volume fraction and by using different poling procedures. As both phases in the composite are ferroelectric, and the piezoelectric coefficients of the ceramic and copolymer phases have opposite signs while the pyroelectric coefficients have like signs, special ways can be used to produce three groups of samples with (1) only the ceramic phase poled, (2) two phases poled in the same direction to achieve reinforced pyroelectric activity and reduced piezoelectric activity, and (3) two phases poled in opposite directions to obtain reinforced piezoelectric activity and reduced pyroelectric activity. In this work, original experimental results on the properties of PZT/P(VDF-TrFE) composites poled under different conditions are presented and possible reasons behind the reinforcement and cancellation of piezoelectric and pyroelectric properties are discussed. © 1999 American Institute of Physics. [S0003-6951(99)01120-1]

The P(VDF-TrFE) 70/30 mol % copolymer (supplied by Piezotech) used in the present study has a Curie temperature T_{ch} at 103 °C upon heating and T_{cc} at 70 °C upon cooling as measured by differential scanning calorimetry. The lead zirconate titanate (PZT) powder PKI 502 is supplied by Ultrasonic Powders Ltd.. The copolymer pellets are dissolved in methyl-ethyl-ketone and suitable amounts of PZT powder are blended into the P(VDF-TrFE) solution to form composites with different volume fractions of ceramic ϕ . After evaporation of the solvent, the composites were compression molded into disk samples 15 mm in diameter and about 0.4 mm thick. The poling procedure for the three groups of samples is as follows:

Group 1: Samples are heated to 120 °C (above T_{ch}) and an electric field E_0 of ~35 kV/mm is applied to the composite for 1 h. The field E_0 is then switched off before cooling to room temperature. As E_0 is switched off above T_{ch} while the copolymer is still in a paraelectric state, only the ceramic phase is poled. To verify this, the same procedure is applied to a copolymer sample. The copolymer sample has no detectable piezoelectric and pyroelectric activities, thus showing that it is not polarized.

Group 2: The poling procedure is similar to that applied to group 1 samples except that E_0 is maintained while cooling to room temperature. As the sample cools through T_{ch} and T_{cc} with E_0 still applied, the copolymer phase is poled in the same direction as the ceramic phase.

Group 3: The poling procedure is similar to that applied to group 2 samples to produce composites with both phases poled in the same direction. In order to polarize the ceramic phase in an opposite direction relative to the copolymer, these samples are reheated to 50 °C and then a poling field of

10 kV/mm is applied in the reverse direction for 0.5 h. The samples are then cooled to room temperature with the reverse poling field kept on. As the applied field is much lower than the coercive field of P(VDF-TrFE), the polarization in the copolymer phase is not affected but the polarization in the PZT phase is reversed.

The piezoelectric d_{33} coefficient of the samples was measured using a Pennebaker model 8000 piezo d_{33} meter from American Piezo-Ceramics Inc.. The pyroelectric coefficient p of the samples was measured using the digital integration technique.¹

Below the Curie temperature (~350 °C), PZT has a tetragonal ABO_3 unit cell structure² which gives it a spontaneous polarization P_s as its center of positive charge does not coincide with its negative charge center (Fig. 1). Poling causes P_s to align in the thickness direction. When subjected

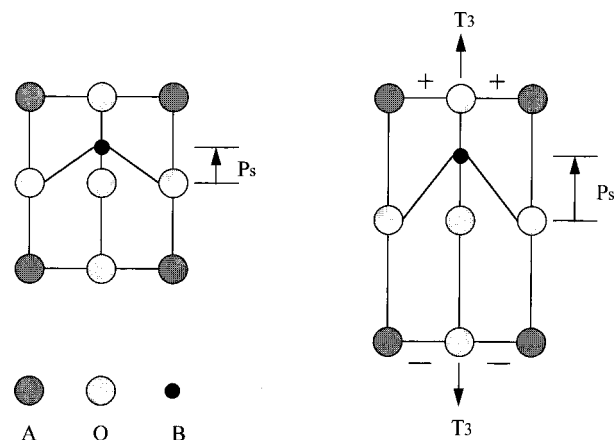


FIG. 1. Piezoelectric effect in a ceramic with tetragonal ABO_3 structure (e.g., PZT), (a) before tension, (b) under tension. The polarization increases as the separation of the positive and the negative charge centers increases.

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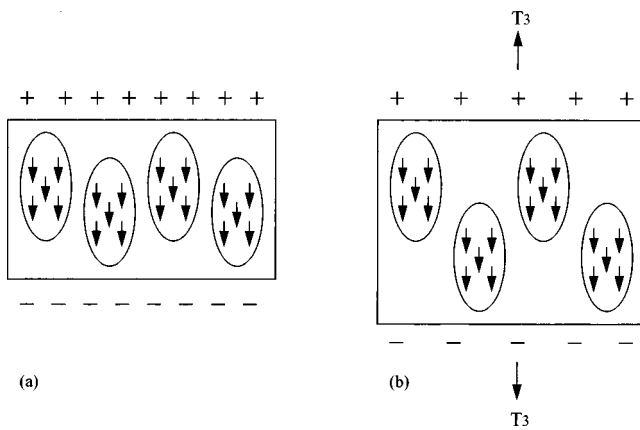


FIG. 2. Piezoelectric effect in a P(VDF-TrFE) copolymer, (a) before tension, (b) under tension. The spontaneous polarization decreases as the volume increases.

to a tensile stress, the separation between the two charge centers increases thereby resulting in a longer dipole moment arm and hence a higher P_s . As P_s increases, positive charges will be generated on the anode (the electrode subjected to positive voltage during poling) and hence PZT has a positive piezoelectric d_{33} coefficient. P(VDF-TrFE) has a semicrystalline structure; the dipoles exist in the rigid crystal lamellas³ and can be aligned along the thickness direction by the application of an external poling field. After being poled and then subjected to a tensile stress, the thickness increase arises largely from the deformation of the amorphous region,⁴ so the rigid crystal lamellas are dispersed in a larger volume (Fig. 2), thereby causing a decrease in P_s (P_s is proportional to the dipole moment per unit volume) and hence a decrease of the positive charges on the anode. Hence, P(VDF-TrFE) copolymer has a negative piezoelectric d_{33} coefficient due to this dimensional effect.⁴ As the piezoelectric coefficients in the ceramic and the copolymer have opposite signs, hence when the ceramic and copolymer phases in the PZT/P(VDF-TrFE) composites are poled in the same direction (group 2), their piezoelectric activities partially cancel and when they are poled in opposite directions (group 3), their piezoelectric activities are reinforced (Fig. 3). Samples with only the ceramic phase poled (group 1) have piezoelectric coefficients in between those of group 2 and group 3 samples (Fig. 3).

For most pyroelectric ceramics, their pyroelectric coefficients are negative because the spontaneous polarization decreases as the temperature increases. This is because as the temperature increases, the increase in thermal energy causes the disordering of dipoles which results in a decrease of positive charges on the anode. For pyroelectric polymers, their pyroelectric coefficients are also negative because the disordering of crystalline dipoles increases with increasing temperature which causes a decrease in spontaneous polarization.⁵ Hence, when the ceramic and the copolymer phases in the PZT/P(VDF-TrFE) composites are poled in the same direction (group 2), their pyroelectric activities are reinforced and when they are poled in opposite directions (group 3), the pyroelectric activities partially cancel (Fig. 4). Group 1 samples have pyroelectric coefficients in between that of group 2 and group 3 samples (Fig. 4).

In summary, we have prepared PZT/P(VDF-TrFE) 0–3

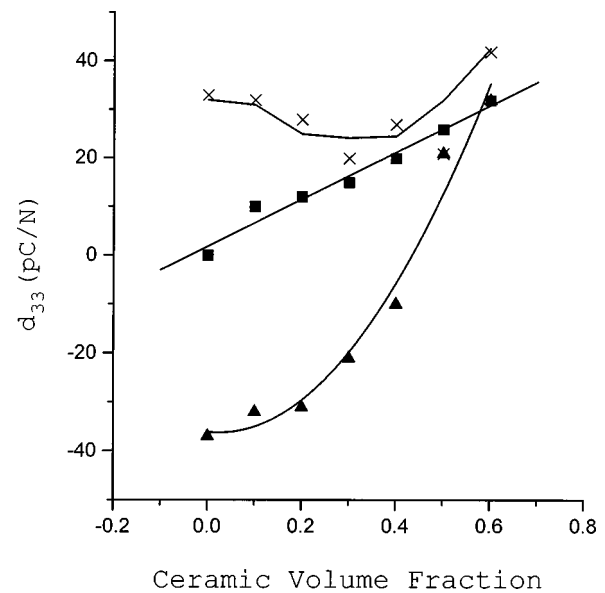


FIG. 3. Piezoelectric d_{33} coefficient of the composites as a function of volume fraction of ceramic ϕ . When the ceramic and copolymer phases are poled in the same direction (▲), partial cancellation occurs. When the two phases are poled in opposite directions (×), reinforcement is obtained. (■) represents d_{33} of composites with only the ceramic phase poled.

composites with the ceramic and copolymer phases poled in special ways. The piezoelectric and pyroelectric properties of these composites vary greatly with the poling procedures. Composites with the ceramic and copolymer phases poled in the same direction can be used as sensing elements in pyroelectric sensors⁶ as they have enhanced pyroelectric activity but reduced piezoelectric activity, thereby minimizing the vibration induced electrical noise. Composites with the ceramic and copolymer phases poled in opposite directions can be used to fabricate ultrasonic transducers⁷ as they have reinforced piezoelectric property but reduced sensitivity to temperature fluctuation.

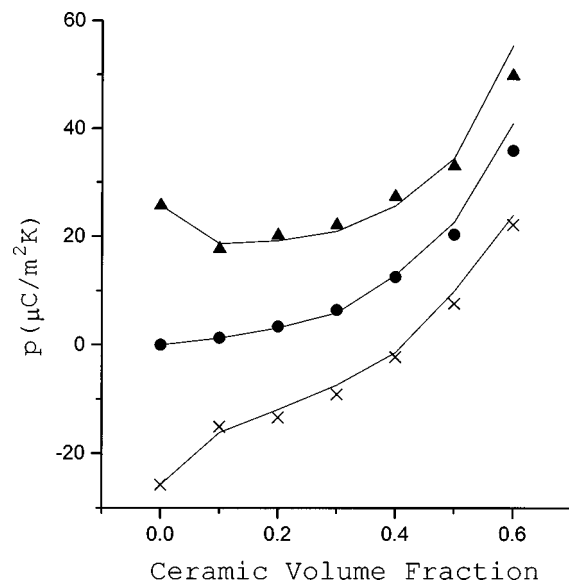


FIG. 4. Pyroelectric coefficient p of the composites as a function of volume fraction of ceramic ϕ . When the ceramic and copolymer phases are poled in the same direction (▲), reinforcement occurs. When the two phases are poled in opposite directions (×), partial cancellation is obtained. (●) represents p of composites with only the ceramic phase poled.

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