

PIEZOELECTRIC AND PYROELECTRIC PROPERTIES OF
PT/P(VDF-TrFE) 0-3 COMPOSITES

H.L.W. CHAN, W.K.CHAN, C.L. CHOY and Deming LEI
Department of Applied Physics and Materials Research Centre,
The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

Abstract

Lead titanate (PT)/vinylidene fluoride-trifluoroethylene (P(VDF-TrFE)) copolymer 0-3 composites have been fabricated by solution blending followed by compression-molding. In order to obtain piezoelectric and pyroelectric activities the composites have been polarized by a stepwise poling method. Samples with (i) polarization in the ceramic phase only and (ii) parallel polarization in the ceramic and copolymer have been prepared. The piezoelectric and pyroelectric coefficients of these two types of composites have been measured and the results are discussed.

1. Introduction

Conventional ferroelectric ceramics such as lead zirconate titanate (PZT) and modified lead titanate (PT) are popular choices in piezoelectric or pyroelectric sensor applications. These materials have high thickness electromechanical coupling coefficients (k_t), a wide range of dielectric permittivity and low dielectric and mechanical losses. However, their high acoustic impedances result in poor acoustic coupling to water or human tissues. Ferroelectric polymers such as polyvinylidene fluoride (PVDF) and vinylidene fluoride/trifluoroethylene (P(VDF-TrFE)) have a low acoustic impedance but also have low k_t and ϵ and high dielectric losses. PT/P(VDF-TrFE) 0-3 composites have attracted considerable research interests [1,3] as they offer properties intermediate between PT and P(VDF-TrFE). After combining the two phases in a 0-3 connectivity, the composite must be poled by exposure to a high electric field. In the present study, electric field was first applied at a temperature above the Curie temperature for heating ($\uparrow T_c$) of the copolymer in order to polarize the ceramic. After cooling to room temperature the composites were heated to a temperature below $\uparrow T_c$ and then poled again by an electric field aligned parallel to the polarization of the ceramic. The piezoelectric and pyroelectric properties of these composites were studied.

2. Sample fabrication

The P(VDF-TrFE) copolymer pellets supplied by Piezotech have a nominal TrFE content of 35 mol%. The endotherms of the as-supplied pellets was measured at a heating rate of 10°C/min and at a cooling rate of -10°C/min using a Perkin Elmer DSC7 Thermal Analyzer. The Curie temperature of the copolymer for heating $\uparrow T_c$ was 102°C ($\uparrow T_c = 101.7^\circ\text{C}$ for first heating and $\uparrow T_c = 102.5^\circ\text{C}$ for second heating) and $\downarrow T_c = 62^\circ\text{C}$ upon cooling. The melting temperature T_m was 153°C.

The calcium modified lead titanate ($\text{Pb}_{0.76}\text{Ca}_{0.24}$)[$(\text{Co}_{0.5}\text{W}_{0.5})_{0.04}\text{Ti}_{0.96}\text{O}_3$] was supplied by Zhongshan University in China and was prepared by the conventional ball-milling mixed

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oxide process. It was calcined at 900°C for 2 hours and sintered at 1130°C for about 7 hours. The PT ceramic powder was obtained by grinding a sintered ceramic block in a ball-milling machine.

A predetermined amount of copolymer pellets was dissolved in acetone at room temperature and the required quantity of PT powder was blended into the solution. The mixture was then poured onto a petri-dish and after evaporation of the solvent in air, the mixture was placed in an oven at 120°C for 2 hours to ensure that the solvent has completely evaporated. The dried composite was cut into small pieces and was molded into disc shape by pressing in a compression machine at 200°C and at a pressure of 48.8 kg/mm². Composite discs with various volume fractions of ceramic ϕ and of thickness 0.5 mm and diameter 12.8 mm were prepared using the method described above.

3. Relative permittivity measurements

The relative permittivities of the unpoled 0-3 composite samples were measured as functions of temperature at 1 kHz using an HP 4194A impedance analyzer. The sample was heated or cooled at a rate of about 1°C/min in a temperature controlled oven until a certain temperature was reached, and then kept at that temperature for half an hour before measurement was made. The resulting relative permittivities for PT, P(VDF-TrFE) and composites with various volume fractions of ceramic ϕ are shown as functions of temperature in Fig.1. The relative permittivity of PT (Fig. 1a) is about 250 at 30°C and increases roughly linearly with temperature at a rate of 0.43 % per degree. Thermal hysteresis was observed for the copolymer and 0-3 composites and abrupt changes in the relative permittivities occurred at different temperatures upon heating and cooling.

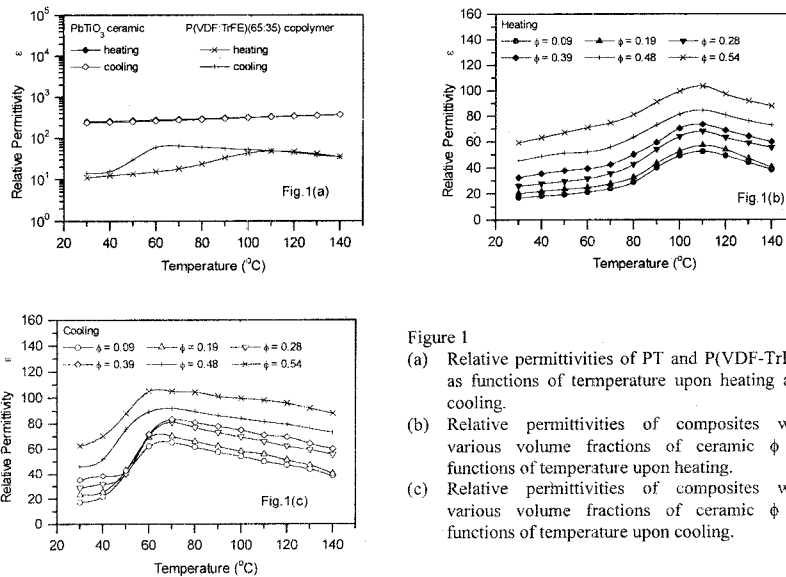


Figure 1

- Relative permittivities of PT and P(VDF-TrFE) as functions of temperature upon heating and cooling.
- Relative permittivities of composites with various volume fractions of ceramic ϕ as functions of temperature upon heating.
- Relative permittivities of composites with various volume fractions of ceramic ϕ as functions of temperature upon cooling.

Similar to the results reported for lead zirconate titanate/vinylidene fluoride-trifluoroethylene 0-3 composites [4], below the Curie temperature of the copolymer, the relative permittivities of PT/P(VDF-TrFE) 0-3 composites (shown in Fig. 2) agree reasonably well with the values calculated using the Bruggeman equation [5,6]:

$$(\epsilon_c - \epsilon)/(\epsilon)^{1/3} = (1 - \phi)(\epsilon_c - \epsilon_p)/(\epsilon_p)^{1/3} \quad (1)$$

where ϵ_c , ϵ_p and ϵ are the dielectric constants of the ceramic, copolymer and composite, respectively.

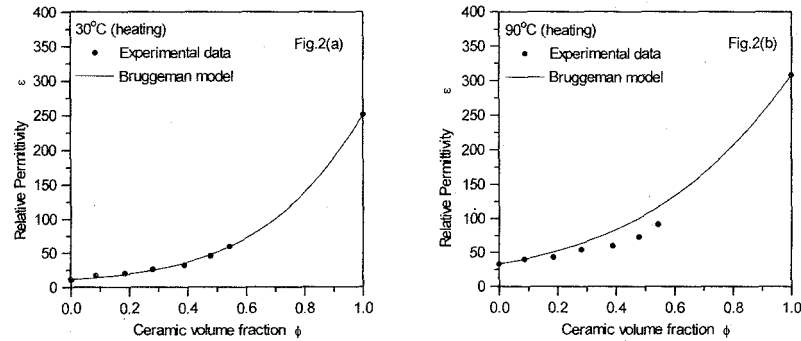


Figure 2 (a) The relative permittivity of PT/P(VDF-TrFE) 0-3 composites as a function of the volume fraction of ceramic ϕ at 30°C upon heating.
(b) The relative permittivity of PT/P(VDF-TrFE) 0-3 composites as a function of the volume fraction of ceramic ϕ at 90°C upon heating.

4. Electric field acting on the PT particles inside a composite

After a d.c. electric field has been applied to a composite for a time long compared to the interfacial relaxation time, the ratio of the electric field in the two phases estimated from the Maxwell-Wagner model is given by $E_c/E_p = \rho_c/\rho_p$, [2,3] where ρ_c and ρ_p are the resistivity of the ceramic and the copolymer, respectively. For a time short compared to the interfacial relaxation time, the electric field ratio is determined by the relative permittivities: $E_c/E_p = \epsilon_p/\epsilon_c$, [2,3]. For a composite containing a spherical particle of dielectric constant ϵ_c embedded in a continuous medium of relative permittivity ϵ , the local field experienced by the particle is given by [7]

$$E_c = 3\epsilon E_o / (2\epsilon + \epsilon_c) \quad (2)$$

where E_o is the applied electric field. The observed values of ϵ were used in eqn. (2) to calculate E_c/E_o . As shown in Fig. 3, at temperatures above 90°C, the electric field acting on the PT particles in a composite with a ceramic volume fraction of 0.48 is as high as 0.5 of the applied field.

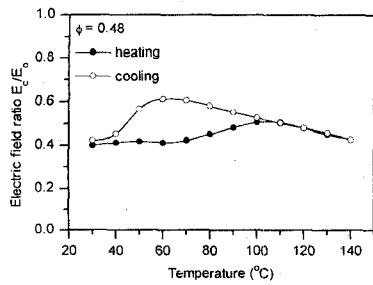


Figure 3
Electric field ratio (E_c/E_0) for PT/P(VDF-TrFE) 0-3 composite ($\phi = 0.48$) as a function of temperature upon heating and cooling

5. Poling of PT/P(VDF-TrFE) 0-3 composites

5.1 Poling of the PT ceramic

Attempts were made to polarize the composites in the regime where the electric field ratio was determined by the relative permittivities. Composites with $\phi = 0.48$ were heated to 120°C (which is above $\uparrow T_c$ of the copolymer) and stepwise poling method [8] was used. The electric field was increased from 0 to E_1 and kept at E_1 for a time t_p (~4 min.); the field was then switched off and the sample short-circuited for time t_s (~8 min.). Electric field was then increased to E_2 ($> E_1$) and kept constant for time t_p and then the field was switched off and the sample short-circuited for a time t_s . The electric field was increased after each short-circuited step and a field as high as 27 kV/mm can be reached. With this stepwise process, the risk of electric breakdown was reduced. This may result from the short-circuited periods during which the mechanical stress and the injected space charges were partially relaxed, thereby leading to a more homogeneous electric field distribution.

Since the electric field was switched off at 120°C (above the Curie temperature of the copolymer) and the composites were cooled to room temperature under zero field, only the ceramic phase was polarized and contributed to the pyroelectric and piezoelectric properties.

After cooling to room temperature, the ceramic poling ratio α was estimated from the peak heights $I_{(200)}$ and $I_{(002)}$ of the (200) and (002) x-ray reflections arising from the PT ceramic[9]

$$\alpha = I_{(002)} / [I_{(002)} + I_{(200)}] \quad (3)$$

5.2 Poling of the copolymer

Composites with a polarized PT ceramic phase were heated to 75°C and poled again by the stepwise poling method and with the polarity of the field applied to the sample in a direction parallel to the polarization of the ceramic. A maximum field of 27 kV/mm could be applied. The samples were short-circuited and annealed at 70°C for 15h before measurement.

6. Measurement of piezo- and pyro-electric coefficients

The impedance of the samples was measured using an HP 4194A impedance analyzer and the thickness mode electromechanical coupling coefficient k_t calculated from the impedance according to the IEEE standard [10]. The pyroelectric coefficient p was measured using the digital integration method. [11] The d_{33} coefficient of the samples was determined using a Pennebaker model 8000 piezo d_{33} tester from American Piezo-Ceramics, Inc.. The measured properties of the composite samples together with the properties of PT and the copolymer were tabulated in Table 1.

As shown in Table 1, the copolymer has a d_{33} value smaller than PT but of opposite sign, hence when both phases are polarized, the piezoelectric properties cancel each other resulting in lower d_{33} and k_t values. Unlike the piezoelectric coefficient, the pyroelectric coefficient increased by 50% after the copolymer have been poled in the same direction as PT.

Table 1 Piezo and pyro-electric properties of PT, P(VDF-TrFE) and PT/P(VDF-TrFE) 0-3 composite with $\phi = 0.48$.

Sample	poling ratio α	d_{33} (pC/N)	k_t	p $\mu\text{C}/\text{m}^2\text{K}$ (25°C)
Lead titanate PT	0.75	61.9	0.40	152.1
65/35 P(VDF-TrFE)	-----	-37.2	0.21	25.7
Composite: with polarized PT	0.47	20.4	0.17	40.7
Composite: field applied to P(VDF-TrFE) parallel to field applied to PT	0.42	15.4	0.15	60.3

7. Laser-induced pressure pulse measurements

The laser induced pressure pulse (LIPP) method [12] was used to determine the polarization distribution in the samples and to distinguish whether the piezoelectric property arose from the ceramic or the copolymer. As the piezoelectric coefficient e_{33} of PT and the copolymer have opposite signs, the pressure pulses generated would have opposite polarity, with the signal for PT larger than that of the copolymer. After the composite had been poled at 120°C, a large negative pressure pulse was detected at the anode side (the side connected to positive poling voltage) and the LIPP signal indicated that the sample was uniformly poled, with the piezoelectric coefficient $(e_{33})_1$ contributed mainly by PT. After the composite was poled again at 75°C with the applied field parallel to the polarization of the PT phase, the LIPP signal became smaller, implying a reduction in the piezoelectric coefficient due to the negative contribution from the polarized copolymer matrix. To verify this further, the sample with both phases polarized was annealed at 120°C for 15h to remove the polarization of the copolymer and the LIPP measurement was repeated. The annealed sample was found to have a piezoelectric coefficient almost the same as the coefficient prior to poling of the copolymer.

8. Conclusion

The permittivity ϵ of PT/P(VDF-TrFE) 0-3 composites have been determined from 20°C to 140°C. The observed ϵ agree quite well with the predictions of the Bruggeman model. The polarization distribution in a PT/P(VDF-TrFE) 0-3 composite with a ceramic volume fraction of 0.48 was determined by the laser-induced pressure pulse method. It was found that a polarized copolymer matrix gave rise to a reduction in the piezoelectric coefficients but an increase in the pyroelectric coefficient. Studies on the piezoelectric and pyroelectric properties of PT/P(VDF-TrFE) composites with other volume fractions of ceramic are in progress.

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