

Study on PZT4/VF₂/VF₃ Piezoelectric 0-3 Composites

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ABSTRACT

PZT4/VF₂/VF₃ 0-3 composites with different volume percent of ceramic have been fabricated. The dielectric constants and electrical resistivities of the composites were measured as functions of temperature in order to find the optimum poling conditions. The electromechanical properties of the piezoelectric composites were also measured and compared to model calculations.

INTRODUCTION

Piezoelectric ceramic/piezoelectric polymer 0-3 composites represent a class of piezoelectric materials having potential to replace conventional piezoceramics and piezopolymers. After combining the two phases in a 0-3 connectivity, the composite must be poled in a high electric field in order to elicit piezoelectric response. One important parameter we need to consider in the poling of a composite is the ratio of the resistivities ρ of the constituent phases since it governs the effective poling field across each phase. (Maxwell-Wagner effect [1]). Another parameter is the relaxation time τ of the composite, which determines the poling time. Both ρ and τ are functions of temperature. In order to find the optimum poling temperature and poling time, the dielectric constants and resistivities of the PZT-4 ceramic, VF₂/VF₃ copolymer and 0-3 composites with different volume fraction of ceramic were measured as functions of temperature.

COMPOSITE PREPERATION

The VF₂/VF₃ copolymer supplied by Atochem North America Inc. has a nominal VF₃ content of 30%. The DSC (Differential Scanning Calorimetry) endotherms of the as-supplied pellets was measured at a heating rate of 10°C/min using a Perkin Elmer DSC7 Thermal Analyzer. The Curie transition temperature for the first heating ($\uparrow T_c$) of the copolymer was 105°C and the melting temperature T_m was 155°C. This indicated that the VF₃ content of the copolymer was several percent higher than 30. [2]

The PZT powder supplied by the Shanghai Institute of Ceramics has a grain size between 1 and 3 μm and has properties similar to the Vernitron (Morgan Matroc Ltd.) PZT-4 composition. The copolymer pellets were first dissolved in Methyl-Ethyl-Ketone (MEK), and then a suitable amount of ceramic powder was blended into the solution. The mixture was then poured onto a petri-dish and after

evaporation of the solvent, the mixture was triturated. Then the composite was moulded into disc shape by hot pressing at 37.7 kg/mm² and 200°C in a compression machine. Composite discs with different volume percent of ceramic formed using the method described above have a diameter of 12.5 mm and thickness ranging from 0.5 to 0.9 mm.

RESISTIVITY MEASUREMENTS

Polymers tend to have higher resistivities while ceramics have somewhat lower resistivities. The resistivities of both the ceramic and polymer decrease as the temperature increases but usually the gradient is higher for the polymer. Experimental measurements of the ceramic and the copolymer resistivities ρ_c and ρ_p were carried out in order to find a suitable poling temperature for the composite.

The constant voltage method [3] was used to measure the resistance of the unpoled samples, a 100V d.c voltage was applied to the sample using the built-in voltage source of Keithley 617 Electrometer, and the resistance of the sample was measured using the same electrometer. Resistivities of the samples are shown in Fig.1. A sharp decrease of the copolymer resistivity was observed at about the Curie temperature (105°C). This indicated that if the composites were poled above 100°C, the resistivity ratio ρ_p/ρ_c would be about 10, which is close to the ratio of the coercive field of the copolymer and ceramic at high temperature.

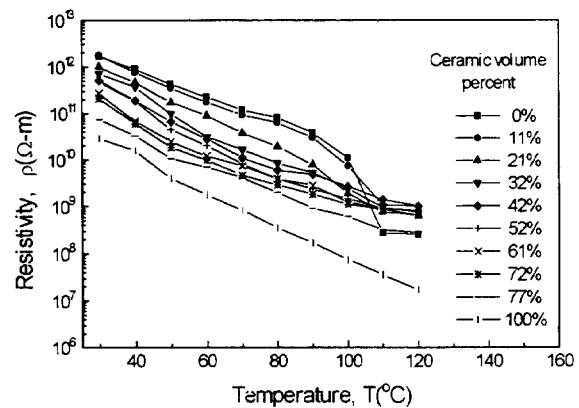


Fig.1 Resistivities of the 0-3 composites vs temperature.

DIELECTRIC CONSTANT MEASUREMENTS

The capacitance of the unpoled disc samples at 1 kHz was measured using an HP4194A Impedance Analyzer and the resulting dielectric constants at different temperatures are shown in Fig. 2. A relaxation peak was observed near the Curie temperature of the copolymer [4]. This peak is prominent for the pure copolymer but becomes broader as the volume percent of ceramic increased.

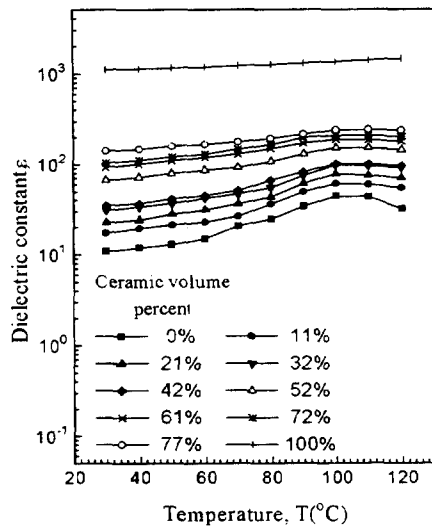


Fig.2 Dielectric constants of the composites vs temperature.

Values of the measured dielectric constants were compared to various models, namely, the Voigt (parallel) model, Reuss (series) model, Yamada model [eqn. (1)] and Furukawa model [eqn.(2)] for 0-3 composites [5-7]. In the Yamada model:

$$\epsilon = \epsilon_p \left\{ 1 + \frac{[n\phi(\epsilon_c - \epsilon_p)]}{[n\epsilon_p + (\epsilon_c - \epsilon_p)(1 - \phi)]} \right\} \dots \dots \dots (1)$$

where ϵ , ϵ_c and ϵ_p are the dielectric constants of the composite, ceramic and copolymer respectively, ϕ is the volume fraction of the ceramic and n is a parameter describing the shape of the ellipsoidal particles [5]. In the Furukawa model for dispersed spherical particles, the dielectric constant of a composite was given as:

$$\epsilon = \epsilon_p [2\epsilon_p + \epsilon_c - 2\phi(\epsilon_p - \epsilon_c)] / [2\epsilon_p + \epsilon_c + \phi(\epsilon_p - \epsilon_c)] \dots \dots \dots (2)$$

It was noted that at a lower temperature (e.g. 30°C, as shown in Fig. 3a), the experimental results agreed very well with the Yamada model with a shape parameter n of 4.3,

which is different from the previously reported value of 8.5 for the PZT-PVDF 0-3 composites [5], the Furukawa model gave values slightly lower than the experimental measurements. However, as the temperature increased, for high volume percent of ceramic, the Furukawa model agreed better with the experimental results (Fig. 3b) than the Yamada model with $n=4.3$. If $n=3$ was used in eqn. (1), the predicted values from the Yamada model and Furukawa model were identical.

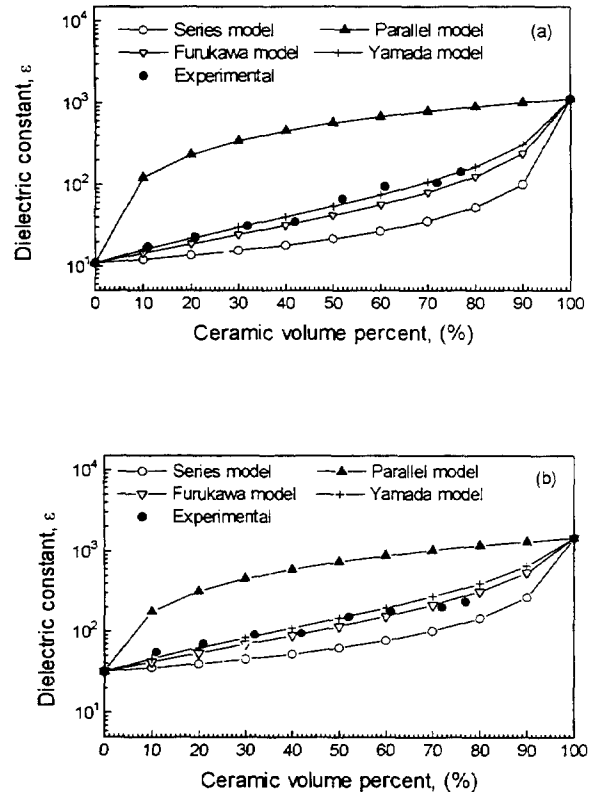


Fig.3 Dielectric constant of the composites as a function of volume percent of ceramics. (a) at 30°C, (b) at 120°C.

In previous reports [5-8], 0-3 composites were prepared by mixing the copolymer and ceramic powder in a hot rolling mill. As the copolymer was still highly viscous in its molten state, clustering of the ceramic powder might become a problem. In the present work, since the ceramic powder was dispersed in a very dilute copolymer solution, it is very likely that each ceramic particle would be coated with a layer of copolymer. This is consistent with the assumptions of the Yamada and Furukawa models [5,6] and hence a close agreement can be obtained even for high volume percent of ceramic.

RELAXATION TIME OF THE 0-3 COMPOSITES

If the composite disc samples were modeled as a parallel plate capacitor having the measured values of resistivity ρ and dielectric constant ϵ , the RC constant and hence the relaxation time $\tau = 1/(RC) = \rho\epsilon$ can be evaluated. It is seen from Fig. 4 that the relaxation time τ dropped from several hundred seconds to several seconds as the temperature increased from 30 to 120°C. However, during poling, a very high d.c. electric field was applied to the sample. Since the resistivity of a dielectric increases in an electric field [9], the value of ρ (and hence τ) during poling may be much higher than ρ (and τ) measured under normal condition. Hence much longer poling time t_p (typically two hours) was used to ensure that $t_p \gg \tau$.

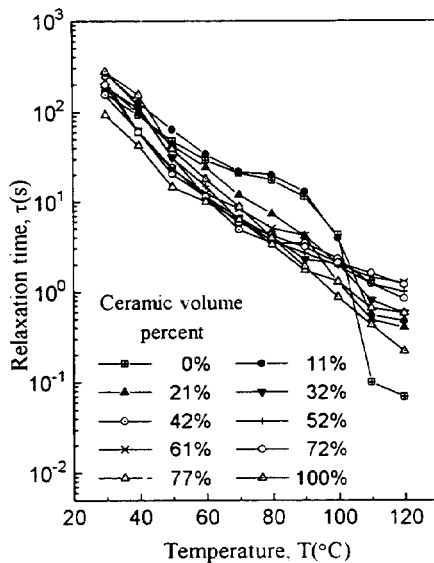


Fig.4 Relaxation time of the composites vs temperature.

POLING AND PIEZOELECTRIC PROPERTIES OF THE SAMPLES

DC thermal poling was used to pole the samples in an oil bath at 120°C, and the typical poling conditions were tabulated in Table 1. Values of the thickness electromechanical coupling coefficient k_t were evaluated using the method proposed by Sherrit et al [10] taking into account the high loss in the copolymer. The charge constants d_{33} was measured using a Pennebaker model 8000 piezo d_{33} tester from American Piezo-Ceramics, Inc.. The volume fraction of ceramic ϕ was calculated using the measured density.

TABLE I
THE PROPERTIES OF PZT-4/P(VDF/TrFE) 0-3 COMPOSITES.

Ceramic volume fraction ϕ	ρ (kg/m ³)	Dielectric constant ϵ	k_t	d_{33} (pC/N)	Poling condition (120°C)
0	1878.5	9.81	0.27	-38.4	3h, 26kv/mm
0.11	2515.1	14.75	0.23	-30.9	2h, 24kv/mm
0.21	3033.8	22.57	0.21	-26.5	2h, 22kv/mm
0.32	3635.9	31.29	0.16	-23.2	2h, 19kv/mm
0.42	4237.4	35.21	0.19	-22.8	2h, 16kv/mm
0.52	4775.5	63.72	--	-14.9	2h, 14kv/mm
0.61	5273.9	94.11	--	13.2	2h, 12kv/mm
0.72	5907.6	101.5	0.13	26.2	2h, 11kv/mm
0.77	6193.6	134.12	0.19	33.4	2h, 12kv/mm
1.00	7452.0	910.05	0.47	177.3	1h, 1kv/mm

From Table 1, it can be seen that the d_{33} constants of the composites decreased from -30.9 pC/N at $\phi = 0.11$ to a small value of -14.9 pC/N at $\phi = 0.52$, then changed sign to +13.2 pC/N at $\phi = 0.61$, and remain positive for higher value of ϕ . This strongly suggested that the copolymer phase also contributed to the d_{33} value of the composite. As a first estimate of the contribution of both phases to the d_{33} constant, assume

$$d_{33} = \alpha\phi Gd_{33c} + (1-\phi)d_{33p} \dots\dots\dots(3)$$

where α is the ceramic poling ratio, d_{33c} and d_{33p} are the charge constants of the ceramic and copolymer respectively, and G represents the local field coefficient [5],

$$G = n\epsilon / [n\epsilon + (\epsilon_c - \epsilon)] \dots\dots\dots(4)$$

Using $n = 4.3$ and $\alpha = 0.6$, d_{33} of the composites were calculated and shown in Fig. 5 together with the measured values. It is clear that equations (3) and (4) give the right trend indicating that the d_{33} contribution of the copolymer tended to cancel the contribution of the ceramic.

The thickness electromechanical coupling coefficient k_t of the composites was smaller than that of the ceramic or the copolymer, especially around $\phi = 0.5$ to 0.66. The

thickness mode resonance peaks, although visible, were very weak.

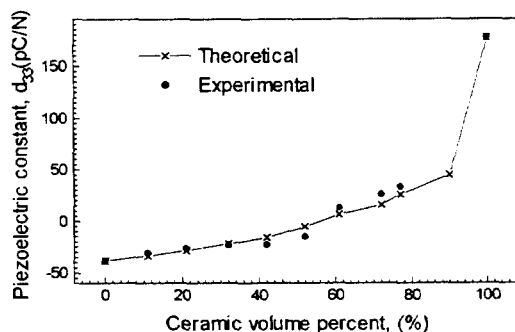


Fig. 5 Measured d_{33} values compared to the theoretical values calculated using eqn. (3)

CONCLUSION AND DISCUSSION

0-3 composites of PZT4/VF₂/VF₃ copolymer with different volume percent of ceramic were fabricated using solution cast and hot-press method. The dielectric strength of these composites is lower than that prepared using hot two-roll mill and hence breaks down more easily under high poling field. However, using a dilute solution of the copolymer can help to circumvent powder clustering problem and the ceramic particles are likely to be surrounded by copolymer layers as modeled by previous workers, hence the dielectric constants of the composites agreed very well to the model predictions even for high volume percent of ceramic.

The poling temperature was chosen to be 120°C, at which the copolymer resistivity was rather low, hence the resistivity ratio of the two phases was about 10, which is close to the ratio of their coercive fields. However, since the Curie temperature of the copolymer used in this experiment was 105°C, in order to pole the copolymer, the electric field must be kept on when the composite was cooled through its Curie temperature T_c (T_c for the composites was also around 100°C).

The contribution to the piezoelectric activities by the two piezoelectric phases seemed to cancel each other resulting in a variation of d_{33} from negative to positive as the ceramic content increased. k_t was also fairly small. In transducer applications, it is not desirable to have a cancellation effect, hence, we are trying to pole the two phases oppositely so that reinforcement will occur. Details of this poling study will be reported later [11].

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