

# Studies of Proton Irradiated 0.9PMN-0.1PT/P(VDF-TrFE) 0-3 Composites

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**Abstract:** Polyvinylidene fluoride-trifluoroethylene [P(VDF-TrFE) 70/30 mol%] copolymer can be transformed from a ferroelectric to a relaxor material after proton irradiation. The phase transition peak broadens and shifts towards lower temperature as the measurement frequency decreases. In the present study, 0-3 composites are fabricated by incorporating 0.9Pb(Mg<sub>1/3</sub>Nb<sub>2/3</sub>)O<sub>3</sub>-0.1PbTiO<sub>3</sub> ceramic powder into a P(VDF-TrFE) 70/30 mol% copolymer matrix. 0.9PMN-0.1PT ceramic is a relaxor ferroelectric with high dielectric permittivity. It was found that the relative permittivity of PMN-PT/P(VDF-TrFE) 0-3 composite increases with increasing ceramic volume fraction. Composites with 0.3 and 0.4 volume fraction of 0.9PMN-0.1PT were subjected to proton irradiation. With a 80 Mrad (4.76 x 10<sup>13</sup> ions/cm<sup>2</sup>) proton dosage, the relative permittivity of the 0.4 volume fraction 0-3 composites can go up to 130 near room temperature (at 1kHz).

## INTRODUCTION

Piezoelectric ceramic / polymer composites have the compliance of polymers which overcome the problems of brittleness in piezoceramics. By imbedding piezoelectric ceramic powder into a polymer matrix, a 0-3 composite with good mechanical properties and high dielectric breakdown strength can be developed. This composite can be used in capacitor and energy storage devices [1-2].

Since a polymer matrix has low relative permittivity  $\epsilon$ , the resulting 0-3 composites also have low  $\epsilon$ . In order to improve the energy storage capability, the relative permittivity of this type of composite needs to be increased. Hence, different ceramics and polymer matrix have been used in the past to optimize  $\epsilon$ . The ceramic phase used in composites is usually lead based relaxor-based ceramics and lead titanate (PT) based ceramics [3-5]. P(VDF-TrFE) ferroelectric copolymer is used as the polymer matrix because it has high  $\epsilon$  compared to other polymers [6]. Besides using different materials, irradiation was also used to improve the dielectric properties of composites. It was found that the

dielectric properties of copolymer can be changed significantly after electron irradiation [7]. When the irradiated copolymer was used as the matrix, the resulting composites have higher relative permittivity which improves their charge storage capability [8, 9].

In this work, 0.9PMN-0.1PT and P(VDF-TrFE) 70/30 mol% were used as the ceramic inclusion and polymer matrix, respectively. The 0-3 composites were treated with high-energy proton irradiation. 0.9PMN-0.1PT is a lead-based relaxor material with very high dielectric permittivity near room temperature. The properties of the composites with different ceramic volume fractions and irradiation dosages were investigated.

## EXPERIMENTAL

0.9PMN-0.1PT ceramic powder was fabricated using the Columbite method [10]. First, magnesium oxide and niobium pentoxide were pre-reacted at 1100°C to form a columbite magnesium niobate. After the pre-reaction, the columbite magnesium niobate was reacted with lead oxide and titanium oxide to give PMN-PT. This method suppressed the growth of the pyrochlore phase and thus produced PMN-PT ceramic powder with a pure perovskite phase. The powder was calcinated at 850°C and sintered at 1200°C for 2 hours. In order to minimize the particle size, the powder was ball-milled in ethanol for 10 hours. The P(VDF-TrFE) 70/30 mol% copolymer powder was supplied by Piezotech Co., St. Louis, France.

0-3 composites were prepared by solvent casting. The copolymer powder was dissolved in methylethylketone (MEK) and then the ceramic powder was added. Ultrasonic agitation was used to disperse the powder. The mixture was continuously stirred at 60°C during evaporation of solvent until the gel was almost dry. Then, the gel composite was dried at 80°C in an oven overnight to ensure the complete evaporation of solvent and moisture.

The bulk composites were fabricated by hot pressing. The dried composite was cut into small pieces and then compression-molded at 230°C into composite film with thickness of ~30 $\mu$ m. Composites

with ceramic volume fractions ranging from 0.05 to 0.40 were fabricated. The bulk composites were annealed under pressure at 120°C for 2 hours. Crystallinity of the composite film was analysed using an X-ray diffractometer (XRD, Philips PW3710). The distribution of ceramic powder inside the copolymer matrix was investigated by scanning electron microscopy (Leica stereo scan 440).

Proton ( $H^+$  ions) irradiation was carried out in an accelerator (High Voltage Engineering) located at the Chinese University of Hong Kong. The energy of protons should be high enough to go through the composites so that the microstructure of the whole composite film can be modified but no protons were implanted in the polymer. The samples were irradiated by 3MeV protons at ambient temperature in vacuum. The irradiation dosages were chosen for maximizing the relative permittivity of the composites near room temperature. Three dosages,  $3.57 \times 10^{13}$  ions/cm<sup>2</sup> (60 MRad),  $4.76 \times 10^{13}$  ions/cm<sup>2</sup> (80 MRad),  $5.96 \times 10^{13}$  ions/cm<sup>2</sup> (100 MRad) were used. The samples were then electroded with chromium-gold by evaporation for further measurements. After electroding, the samples should be annealed under pressure at 120°C for 2 hours to improve the adhesion between the electrode and the composite. The capacitance of the samples was measured as a function of temperature using a Hewlett-Packard 4194A impedance/gain phase analyzer and the relative permittivity can be calculated.

## RESULTS AND DISCUSSION

Once the composite film was fabricated, the distribution of ceramic powder inside the composites can be revealed by using scanning electron microscopy. Fig. 1 shows that in a composite with 0.3 ceramic volume fraction, the powder is uniformly distributed throughout the copolymer matrix and the average particle size is around 1 $\mu$ m. The crystallinity of the samples can be investigated by using X-ray diffractometry. The XRD patterns of 0.9PMN-0.1PT ceramic powder, un-irradiated and proton-irradiated

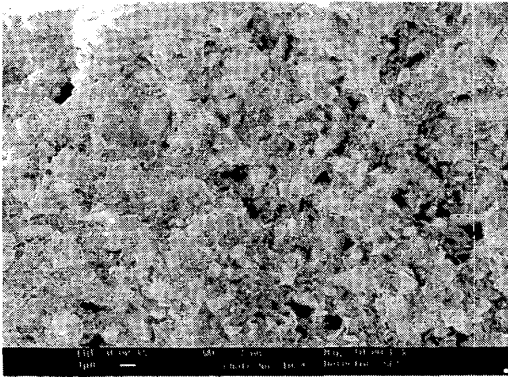


Fig. 1 Scanning electron micrograph of the 0-3 composite with 0.3 ceramic volume fraction.

composites (dosage:  $4.76 \times 10^{13}$  ions/cm<sup>2</sup>) of 0.3 ceramic volume fraction are shown in Fig. 2. As shown in the XRD patterns, the sample has pure perovskite phase and no pyrochlore phase. Both ceramic and copolymer peaks can be found in the pattern of the composite. Besides, the effect of proton irradiation on the composites can also be observed in the XRD patterns. Proton irradiation has no significant effect on the ceramic phase of composites. However, there are effects on the XRD peaks of the copolymer phase after irradiation. Before irradiation, the (201) + (111) peaks of the copolymer can be clearly observed at around  $2\theta \sim 40.5^\circ$ . After irradiation, the peak disappears. The (200) + (110) peaks at  $2\theta \sim 19^\circ$  moved towards a lower angle after irradiation. During proton irradiation, the lattice spacing expands perpendicular to the chain direction resulting in the larger lattice constant [11].

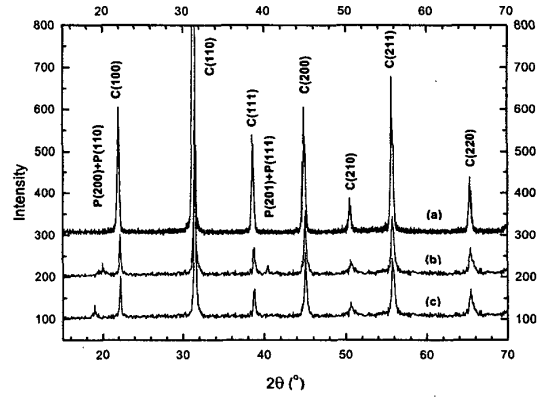


Fig. 2 XRD patterns of (a) 0.9PMN-0.1PT ceramic powder, (b) un-irradiated composite and (c) proton-irradiated composite (dosage:  $4.76 \times 10^{13}$  ions/cm<sup>2</sup>) with 0.3 ceramic volume fraction. [C – ceramic phase; P – copolymer phase]

Before the proton irradiation, the dielectric properties of composites were characterized. The relative permittivity and loss tangent ( $\tan\delta$ ) of the composites were measured at 1 kHz at room temperature as a function of the ceramic volume fraction as shown in Fig. 3. The relative permittivity and dielectric loss increase with the ceramic volume fraction. It was found that the experimental data agree quite well with the Bruggeman model [12]:

$$\frac{\epsilon'_c - \epsilon'_p}{(\epsilon'_c)^3} = \frac{(1-\phi)(\epsilon'_c - \epsilon'_p)}{(\epsilon'_p)^3} \quad (1)$$

$$\epsilon'' = \frac{(\epsilon'_c - \epsilon'_p)(\epsilon'_c + 2\epsilon'_p)\epsilon'_p}{(\epsilon'_c - \epsilon'_p)(\epsilon'_c + 2\epsilon'_p)\epsilon'_p} \epsilon''_p + \frac{3(\epsilon'_c - \epsilon'_p)\epsilon'_c}{(\epsilon'_c - \epsilon'_p)(\epsilon'_c + 2\epsilon'_p)} \epsilon''_c \quad (2)$$

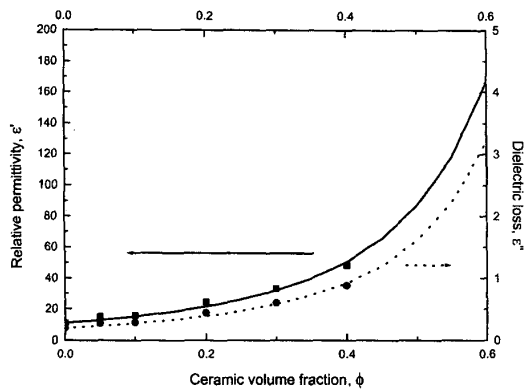


Fig. 3 Dielectric properties (1 kHz) of un-irradiated composites at 25°C as a function of PMN-PT volume fraction. The solid curve ( $\epsilon'$ ) and dashed curve ( $\epsilon''$ ) are calculated from the Bruggeman model. Solid circles and solid squares are the experimental data.

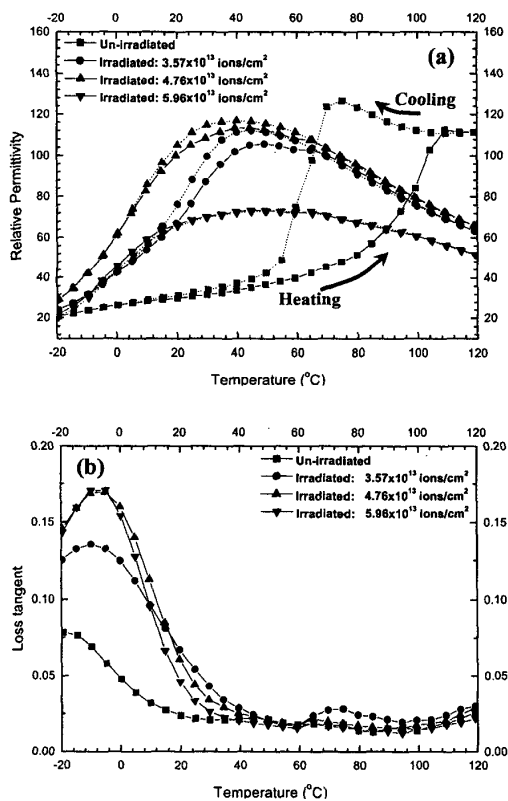


Fig. 4 Temperature dependence of dielectric properties (1 kHz) of composites with 0.3 PMN-PT volume fraction with different irradiation dosages. (a) Relative permittivity [Solid line: Heating process; Dotted line: Cooling process] (b) Loss tangent

where  $\phi$  is the ceramic volume fraction of the composite,  $\epsilon'$  and  $\epsilon'' (= \epsilon' \tan\delta)$  are the relative permittivity and dielectric loss of the composite,  $\epsilon_c'$  and  $\epsilon_c'' (= \epsilon_c' \tan\delta_c)$  are the relative permittivity and dielectric loss of the ceramic inclusion,  $\epsilon_p'$  and  $\epsilon_p'' (= \epsilon_p' \tan\delta_p)$  are the relative permittivity and dielectric loss of the polymer matrix respectively. In the theoretical calculation, the relative permittivity and loss tangent of pure copolymer ( $\epsilon_p' = 11$ ;  $\tan\delta_p = 0.018$ ) and sintered ceramics ( $\epsilon_c' = 15000$ ;  $\tan\delta_c = 0.065$ ) at room temperature were measured at 1 kHz.

Fig. 4 shows the dielectric properties (1 kHz) of the composite with 0.3 ceramic volume fraction as a function of temperature after different irradiation dosages. As shown in Fig. 4(a), broader permittivity peaks and higher relative permittivity can be obtained after irradiation. Since the peaks move towards lower temperatures, the relative permittivity  $\epsilon$  at room temperature increases significantly. Compared with the un-irradiated composite,  $\epsilon$  of the irradiated composite shows weaker temperature dependence. Moreover,  $\epsilon$  of the irradiated composites have little or no thermal hysteresis during the heating and cooling process. It indicates that the composite is no longer a normal ferroelectric after irradiation. Besides, the relative permittivity and temperature dependence can be varied by using different irradiation dosages. Among the three irradiation dosages, a proton dosage of  $4.76 \times 10^{13}$  ions/cm<sup>2</sup> can maximize the relative permittivity of the composites near room temperature. It is noted that the loss of composites also becomes higher after irradiation.

Fig. 5 shows the temperature and frequency dependence of the permittivity and loss of the irradiated composite with 0.4 ceramic volume fraction

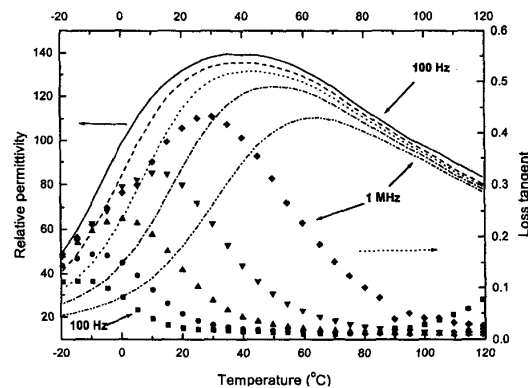


Fig. 5 Temperature dependence of relative permittivity and loss tangent of irradiated composites (dosage:  $4.76 \times 10^{13}$  ions/cm<sup>2</sup>) with 0.4 ceramic volume fraction are plotted at different frequencies (100 Hz, 1 kHz, 10 kHz, 100 kHz, 1 MHz) [Line: relative permittivity; Symbols: loss tangent]

(dosage:  $4.76 \times 10^{13}$  ions/cm<sup>2</sup>). Both peaks of the relative permittivity and loss tangent move towards higher temperature with increasing frequency. This broad diffuse and frequency dependent transition peak is a major characteristic of relaxor ferroelectrics [13]. The relative permittivity of the composite is as high as 130 (at 1 kHz) at room temperature.

#### CONCLUSION

0.9PMN-0.1PT / proton irradiated P(VDF-TrFE) 0-3 composites have been fabricated. With the combination of these two high relative permittivity phases, the dielectric properties of the composites can be improved significantly. After irradiation, the dielectric peak broadens and the transition temperature shifts to lower temperature (from 75°C to 35°C). With an irradiation dose of  $4.76 \times 10^{13}$  ions/cm<sup>2</sup>, the room temperature relative permittivity of a 0-3 composite with 0.4 ceramic volume fraction is 130.

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