The Effect of Solvent Type on the Pyroelectric Activity of PVDF Composites

By:

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Abstract:

The behavior of pure poly (vinylidene fluoride), PVDF doped with 20 wt% of TiO_2 prepared in pure acetone and acetone/DMF mixture are investigated. They are subjected to constant electric field strength in order to attain pyroelectric activity. Quasi static method with several heating rates has been employed to elucidate the pyroelectric properties of PVDF/TiO_2 composites. IR spectroscopy has been examined to study the effect of solvent on the pyroelectric activity of the polymer composites.

I. INTRODUCTION

The discovery of strong piezoelectricity and pyroelectricity in polyvinylidene fluoride (PVDF) in 1969 and 1971 respectively has drawn much attention to these polymers [1,2]. PVDF is famous with its semicrystalline properties that contain polar crystals in which the direction of polarization can be reversed by applying an appropriate electric field [3]. PVDF consists of four α, β, γ, and δ crystalline phases where both of α and β phases are the

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most favorable phases to be discussed. The nonpolar α phase in PVDF has a *trans-gauche-trans-gauche* (TGTG) conformation, and the dipoles in a unit cell are antiparallel. The β phase with the all-*trans* (TTTT) molecule conformation exhibits a large spontaneous polarization and all dipoles in a crystallite are aligned in parallel [4]. The essential strong polar domains due to the large dipole moment of the C-F bond which is perpendicular to the long molecular axis play a main role to the significant exhibition of pyroelectric properties in PVDF thin films [5].

Pyroelectricity is defined as the temperature dependence of the spontaneous polarization in solid state. Spontaneous polarization which emerges in the dielectric crystal in the absence of an electric field is the dipole moment per unit volume of the pyroelectric materials. The dipole moment per unit volume has to be non-zero and equivalent to a layer of bound charge on each flat surface of the sample in order to observe pyroelectric activity. This can only be observed when there is a temperature change in a system [6,7].

Most studies of the pyroelectric properties are mainly focused on PVDF and its related copolymer with trifluorethylene , P(VDF-TrFE). In this study however, PVDF doped with TiO_2 has been chosen to form PVDF composites due to its unique properties such as high chemical stability, mechanical resistance and high optical transmittance in the visible-IR spectral range. A survey in the published literature shows that very little work has been done on the dielectric properties, surface and structural morphology of this particular PVDF/TiO_2 composite. The PVDF films derived from polar solvents, such as dimethylacetamide (DMSO), dimethylformamide (DMF), and dimethylacetamide (DMAc) have been suggested to be used to enhance the β phase in PVDF [8]. This paper reports the effect of solvent type on the pyroelectric activity of PVDF composites.

II. EXPERIMENT

Primarily, pure PVDF (supplied by Sigma-Aldrich Pte Ltd) powders doped with 20 wt% TiO_2 powders were dissolved in acetone and mixture of acetone/DMF in the ratio of 1:1. Both samples were then name as PT2 (a) and PT2 (b) respectively. The solutions were then agitated in the ultrasonic bath to ensure complete dissolution of the mixtures. The PVDF/TiO_2 thin film composites were prepared by spin casting the polymer composite solution onto the glass substrate which was previously coated with aluminum electrode of 50 nm thick. The thickness of the thin films were measured by Tencor Alpha Step 2000 mechanical profiler and found to be approximately 2 μm. The films were annealed at 120°C for 2 hours and kept overnight to remove the solvent residual. An aluminum top electrode of 20 nm thick was then thermally evaporated on the top surface of the films to produce the desired metal-insulator-metal (MIM) structure.

A direct current (d.c.) voltage with a constant electric field, 5 MV/m was then applied to the thin films for 1 hour at 110°C in order to align the orientation of polar domains and also to attain the pyroelectric activity. Usually, poling field strength, temperature and time selected must produce polar domains that are reoriented to their optimum orientations in the thin films. However, in this work, the above mentioned parameters are simply chosen according to our instrument limitations and the applied poling electric field strength used seems to be less than the coercive field of the composite thin films which is 80 MV/m for pure PVDF at room temperature [4]. The quasi-static method was employed to measure the pyroelectric coefficient. The temperature of the sample was set to increase/decrease at constant rates in order to generate a triangular

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temperature waveform while recording the short-circuited pyroelectric current. The triangular temperature waveform range was generated using LakeShore temperature controller. The pyroelectric current, I_p which was generated when the PVDF and PVDF/TiO$_2$ films were heated and cooled repeatedly was measured by Keithley 617 electrometer. The crystalline phases of the samples were examined by Perkin Elmer Fourier Transform infrared (FTIR) spectroscopy system 2000.

III. RESULTS

A. Pyroelectric properties

The change in spontaneous polarization which is due to the accumulated surface charge density on a pyroelectric material can be evaluated by measuring the short circuit current that flows in the circuit, typically performed without external mechanical stress. The rate of change of polarization can be represented by pyroelctric current, I_p, when the surface charge is allowed to flow. The pyroelectric current, I_p is expressed as

$$I_p = pA \frac{dT}{dt} \qquad (1)$$

where p is the pyroelectric coefficient, A is the effective area of the sample and dT/dt is the rate of temperature change.

Fig. 1 compares the pyroelectric coefficient, p of the PVDF/TiO$_2$ composites which were dissolved in pure acetone (PT2 (a)) and the mixture of acetone/DMF (PT2 (b)). Both samples PT2 (a) and PT2 (b) exhibit pyroelectric coefficient, $p \approx 9.4$ μCm^{-2}K^{-1} and 9.8 μCm^{-2}K^{-1} respectively when they were subjected to the electric field strength of 5 MVm^{-1}. Sample prepared in the mixture of acetone/DMF shows higher pyroelectric coefficient as

compare to the sample prepared in pure acetone. This suggests that PVDF thin films dissolved in polar solvent such as DMF may induce the spontaneous polarization of the polymer. However, the mixed solution of acetone/DMF can not completely dissolve the TiO_2 particles from PVDF/TiO_2 composite. Whereas, PVDF/TiO_2 composite prepared in pure acetone does not experience this difficulty.

B. IR spectroscopy analysis

Fig. 2 shows the transmission Fourier transforms infrared spectra from 400-1300cm^{-1} of pure PVDF and PVDF/TiO_2 composites. The presence of both α phase and β phase in Fig. 2 denote the most important characteristic which can enhance the pyroelectric activities in PVDF films. The characteristic vibration spectra of the α-phase are well defined at 408, 532, 614, 764, 796, 855 and 976cm^{-1} absorption bands and the bands at 445, 510 and 840cm^{-1} indicate the characteristic of the β phase in PVDF film. As the TiO_2 was doped in PVDF, the infrared spectra peaks of α and β phase in sample PT2 (a) and PT2 (b) decrease significantly. It is known that the pyroelectric activity of pure PVDF is mainly governed by the β-phase which produces a large dipole moment to contribute to a strong spontaneous polarization [9,10]. Sample PT2 (a) and PT2 (b) with lower intensity of β-phase peaks in its infrared spectra however, can still exhibit strong pyroelectric coefficient in the electric field strength of 5 MVm^{-1} (under its coercive field). Even though the reported pyroelectric coefficient of pure PVDF at room temperature as indicated by C. Birlikseven et. al. [11] and R.W. Newsome et. al. [12] is higher around 20 $\mu Cm^{-2}K^{-1}$ – 25 $\mu Cm^{-2}K^{-1}$, but, the thickness of the PVDF films used in their works were thicker (greater than 9 μm). In this work, the thickness of the samples used is thinner (≈ 2 μm). Thickness and solution

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concentration have been found to influence the magnitude of pyroelectric coefficient of PVDF films. W. Eisenmenger et. al [13] had proved that PVDF films prepared in different thickness and poling time will definitely influence the polarization (which contribute to the pyroelectric activity) in PVDF. Optimum thickness and appropriate poling time and temperature are important parameters in order to obtain the most favorable pyroelectric coefficient. In this study, high pyroelectric coefficient could be easily maintained by increasing the weight ratio of TiO_2 in the composites up to a certain limit and the weight ratio or the concentration of PVDF also played an important role in enhancing pyroelectric activity of the thin films. This indicates that the presence of TiO_2 in PVDF increases the magnitude of dipole moment per unit volume of this pyroelectric composite.

IV. CONCLUSION

It has been found that PVDF/TiO_2 thin film composite prepared in acetone/DMF mixture exhibit higher pyroelectric coefficient compared to that prepared in pure acetone. However, the solution mixture has dissolution problem with TiO_2 ceramic filler. Pure acetone however has the advantage of flexibility to dissolve the PVDF/TiO_2 composites. There are more works need to be carried out in order to understand the mechanism of how TiO_2 influence the dipole moment per unit volume of the PVDF composite system.

ACKNOWLEDGMENT

REFRENCES

[1]   H. Kawai, Japan J. Appl. Phys. **8**, 975-976 (1969).

[2]   J.G. Bergmann Jr., J.H. McFee and G.R. Crane, Appl. Phys. Lett. **18**, 203 (1971)

[3]   E.R. Neagu, J.S. Hornsby and D.K. Das-Gupta, J. Phys. D: Appl. Phys. **35**, 1229-1235 (2002).

[4]   D. Rolik, S. Bauer and R. Gerhard-Multhaupt, J. Appl. Phys. **85**, 3282 (1999).

[5]   K. Nakamura and Y. Wada, J. Polym. Sci. Polym. Phys. Ed. **9**, 161, (1971).

[6]   S.B. Lang, Ferroelectrics, **230**, 401 (1999).

[7]   W.H. Abd. Majid, T.H. Richardson, D. Lacey and A. Topacli, Thin Solid Films, **376**, 225-231 (2000).

[8]   D.T. Grubb and K.W. Choi, J. Appl. Phys. **52**, 5908 (1981).

[9]   R. Gregorio Jr., J. Appl. Polymer Science **100**, 3272 (2006).

[10]   K. Doughty, P. Pantelis, J. Materials Science **15**, 974 (1980).

[11]   C. Birlikseven, E. Altintas and H.Z. Durusoy, J. Materials Science: Materials in Electronics, **12**, 601 (2001).

[12]   R.W. Newsome, Jr. and E.Y. Andrei, Physical Review B **55**, 11 (1997).

[13]   W. Eisenmenger, H, Schmidt and B. Dehlen, Brazilian J. Phys. **29**, 295 (1999).

List of figure captions:

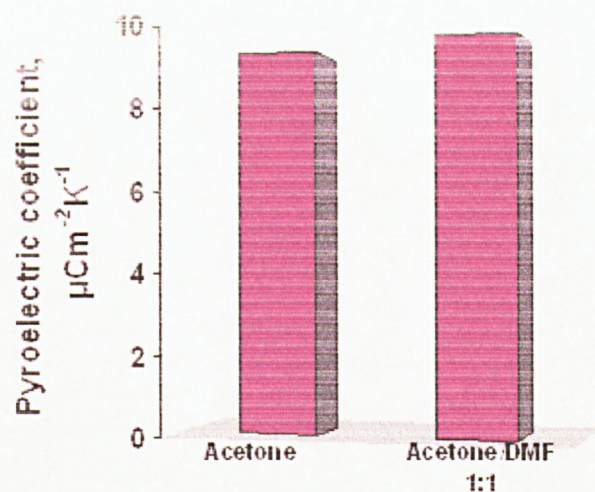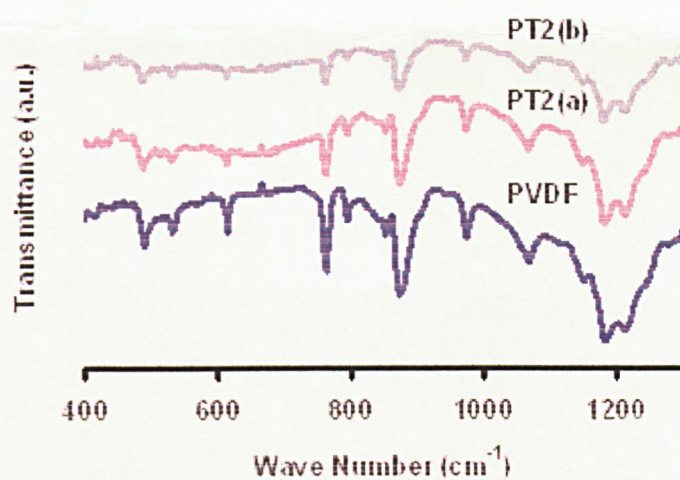Fig. 1 The dependence of solvent on pyroelectric properties of PVDF/TiO$_2$ thin film composites.
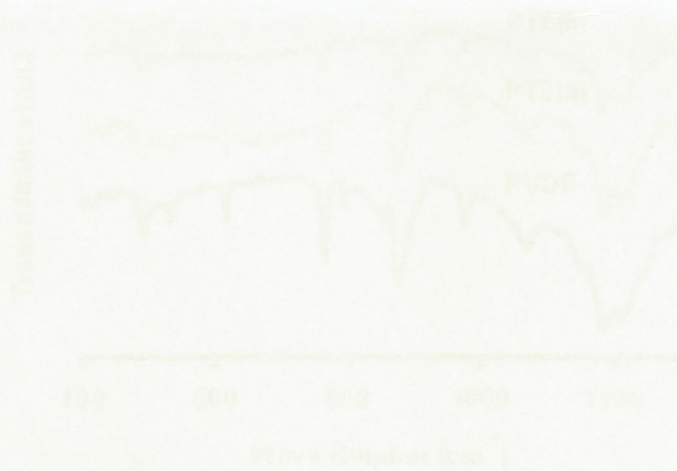
Fig. 2 Fourier transforms infrared spectra of PVDF and PVDF composites.