

CHAPTER VI

FERROELECTRIC AND PIEZOELECTRIC PROPERTIES OF 0-3 CONNECTIVITY AIR BUBBLES/PVDF COMPOSITES

6.1 Abstract

The phase inversion and chemical blowing agent were produced 0-3 connectivity of Air bubbles/PVDF composites of defined porosity and spherical dimensions. Measurements of ferroelectric as well as piezoelectric are presented and compared between spherical and ellipsoid shapes. Additionally, the results show that the ellipsoidal can enhance piezoelectric of porous PVDF films and hysteresis loop can be confirms as a soft ferroelectric material. The results have been explained on the basis of charge storage in the bubbles components when the high fields generated, in the PVDF matrix. These can be a choice material for low-density piezoelectric application, with thermal stability and acoustic impedance matching.

Keywords: Poly (vinylidene fluoride); Microporous; Hyteresis properties; Piezoelectric coefficient; Bubble Shapes

6.2 Introduction

Poly(vinylidene fluoride) (PVDF) is the first available piezoelectric polymer film that has the highest piezoelectric properties among all synthetic polymers. There have widely used as bone for sound applications and underwater hydrophone devices because of their wide bandwidth, high sensitivity, good electromechanical properties, low power requirements, and high generation force. In the case of underwater hydrophone device, PVDF films need to add bubbles inside for light weight applications, low acoustic (close acoustic match of water) and mechanical impedance [Lines M E and Glass A M (1979) J. Lekkala, *et al* (1996)]. Due to the low dielectric and piezoelectric constant when compared with ceramic, many researchers have been studying to improve the electromechanical properties of the PVDF film by first making PVDF-copolymer such as Poly(VDF-co-TrFE) and Poly(VDF-co-TeFE). Secondly, a polymer/ceramic composite is fabricated by adding ceramic into the polymer matrix. Later, electrically-charged polymer foams were discovered, such as cellular PP film and cellular PETP film, so-called ferroelectret which are strongly piezoelectric materials [Neugschwandtner *et al.* (2001)],

resulting in a significant change of the dipole moment which leads to strong electrical signals between the film electrodes. Those concepts are very interesting but not many researchers are investigating space-charge in cellular PVDF for improving disadvantage of PVDF film.

The purpose of this work is to investigate a novel concept that induces internal bubbles in PVDF film and observe the ferroelectric and piezoelectric behavior. The two main techniques for producing the PVDF porous or microcellular film are; first, “Phase Inversion Technique”, which the PVDF solution is immersed into a non-solvent that can form different membranes for example cellular, sponge and spherulite structure, second, “Compression Molding Technique” which using blowing agent to create bubbles inside PVDF films. In this study, pores or internal bubbles was proposed to be another candidate to use instead of ceramic filler for improving the piezoelectric properties.

6.3 Experimental

A. Characterization of porous PVDF films

Porous PVDF films are prepared by two techniques; the isothermal immersion-precipitation method and the chemical blowing agent method. The suitable condition for preparation both of them are discussed from previous work. The SEM (SEM; JSM-5200, JEOL) and OM (SZH 10, OLYMPUS) micrographs of Air/PVDF at different ways were clearly seen that the pore or internal bubbles had a connectivity zero while the PVDF polymer had a connectivity of 3 which shown in Figure 6.1-6.2.

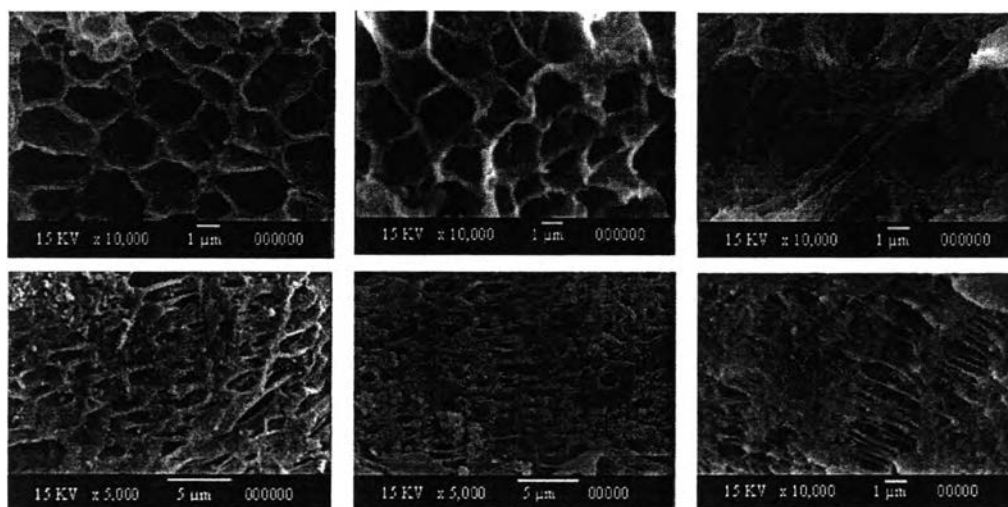


Figure 6.1 The SEM micrograph of porous PVDF by phase inversion with different shape of bubbles; (top) spherical and (bottom) ellipsoidal shape.

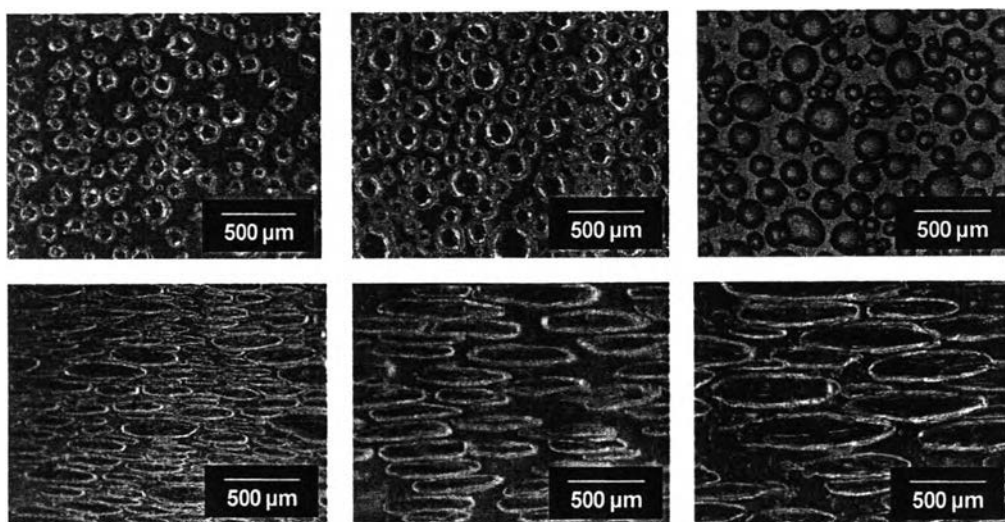


Figure 6.2 The OM micrograph of porous PVDF by AZDC compression molding with different shape of bubbles; (top) spherical and (bottom) ellipsoidal shape.

The ferroelectric and piezoelectric properties of porous PVDF films in different shape were investigated by using a Sawyer-Tower circuit RT66A and stress piezoelectric coefficients (d_{33}) of the polarized films were obtained from d_{33} meter (APC Int. Ltd., model 8000) operating at frequency of 1000 Hz and a time interval of 24 h after film polarization.

6.4 Results and Discussion

6.4.1 Ferroelectric Properties

The ferroelectric behavior of Air/PVDF composites were investigated from relationship between polarizations (P) and applied electric field (E) at room temperature. In Figure 6.3, it was found that the hysteresis loop of porous PVDF films can be observed, which shows characteristic of ferroelectric. For pure (non-porous) PVDF films, it shows linearly relation of polarization and electric field indicating weak ferroelectric properties (dipole moments are random) [G. M. Sessler, (1998)]. On the other hand, the ferroelectric properties are obviously exhibited in drawn PVDF at 1:1 ratio which confirm that β crystalline phase is ferroelectric more than α crystalline phase. From this reasons, the orientation of chain molecule into the β phase is suitable phase for ferroelectric application. Also, the variations of these parameters with change shape are shown in Figure 6.4-6.5.

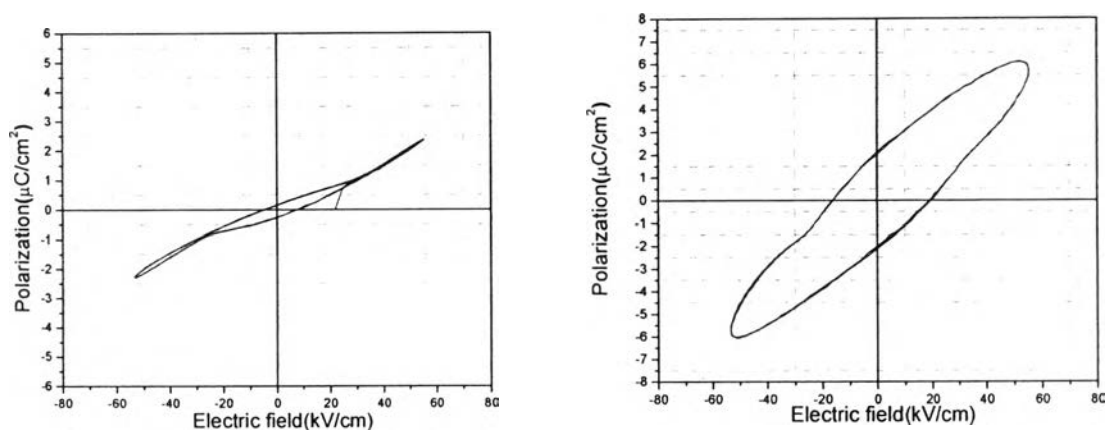


Figure 6.3 comparative hysteresis loops between non-strain and strain in non-porous PVDF films.

The hysteresis loops of porous PVDF films by phase inversion (Fig.6.4) are show space charge polarization phenomena in non-strain depend on the number of traps or polarizable molecules in material. There can be changed the dipole direction of PVDF film easier than non-porous PVDF films. Due to non-porous PVDF need a high E-field for switch the direction of vinyl chain. So, the spontaneous polarization (P_s) not occurred. The sizes of loop are increased with increasing β -phase and introduce bubbles.

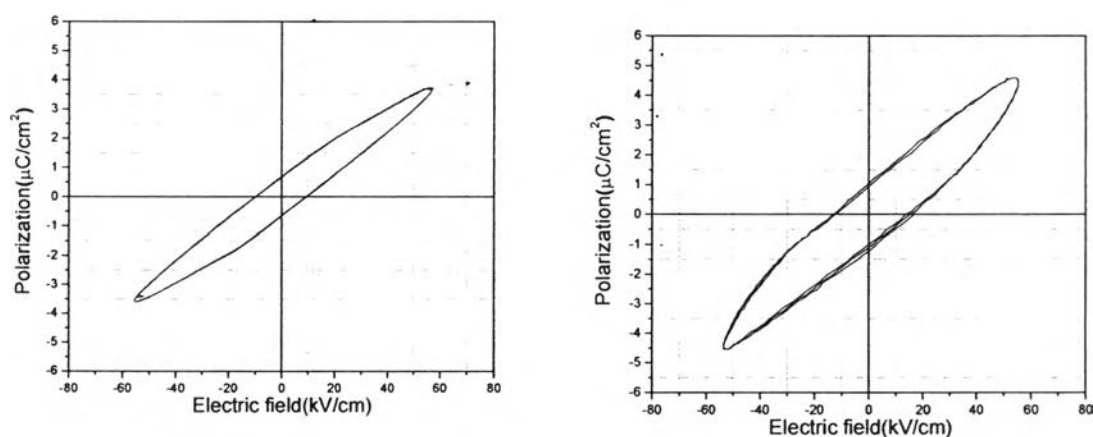


Figure 6.4 Comparative hysteresis loop between (a) spherical and (b) ellipsoidal bubble shapes in PVDF matrix by phase inversion method.

In Figure 6.5, the hysteresis loop can be suggested that this material have ferroelectric properties and can be classified in soft ferroelectric material when compare with other polymer. The remanent polarization (P_r) of ellipsoidal bubble shape in porous

PVDF films has a higher than spherical shapes that can be yielded a chance to get higher piezoelectric properties.

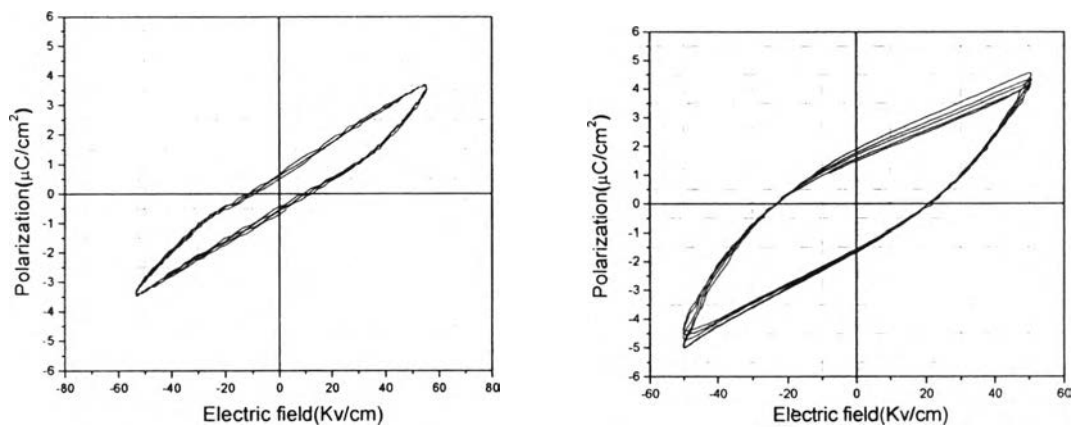


Figure 6.5 Comparative hysteresis loop between (a) spherical and (b) ellipsoidal bubble shapes in PVDF matrix by phase inversion method.

These results show 2 main effects on Ferro-characteristic which are β -phase and space charge polarization in porous PVDF films. The ellipsoid shape in blowing agent method has a P_{max} higher than phase inversion technique due to there are different structures in cellular and non-cellular. It is interesting to see that there can induce polarization easily.

6.4.2 Piezoelectric Properties

Stress piezoelectric coefficients (d_{33}) can be determined by d_{33} meter (APC Int. Ltd., model 8000). Before measurement, sample should have poled in oil bath under a constant electric field 50 kV/mm, at 90°C.

A. Flat PVDF film

Table 6.1 Comparative data of d_{33} between non-stretching and stretching in PVDF films

Materials	Piezoelectric coefficient (d_{33})pC/N	
	Before poling	After poling
Undrawn flat PVDF	0	2
Drawn flat PVDF(ratio 1:1)	0	10

*All film were exposed under constant electric field of 50 kV/mm and constant temperature of 90°C.



Figure 6.6 Piezoelectric of flat PVDF films shown (a) non-stretching and (b) after stretching at 50 kV/mm.

The flat film and porous films before poling show zero value of d_{33} . After poling the film show 2 pC/N of piezoelectric coefficient as quite low % β -phase. The stretching of flat film before poling show zero value but poling of stretching film was found that the piezoelectric coefficient is 10 pC/N. So, it can be suggested that d_{33} coefficient increases with an increasing of stretching and fraction of β crystalline phase that shown in Table 6.1 and confirm by Figure 6.6.

B. Porous PVDF film

a) Phase inversion technique

Table 6.2 The piezoelectric constant (d_{33}) of different porous structure in non-stretching PVDF films (spherical shape)

Materials	Piezoelectric coefficient (d_{33})pC/N	
	Before poling	After poling
Porous PVDF 20% films by DMAc	0	2
Porous PVDF 20% films by DMF	0	2
Porous PVDF 20% films by TEP	0	2

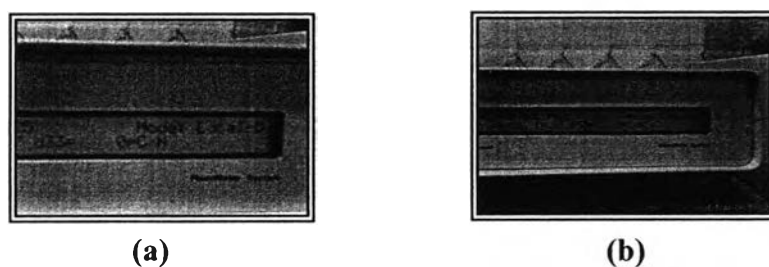
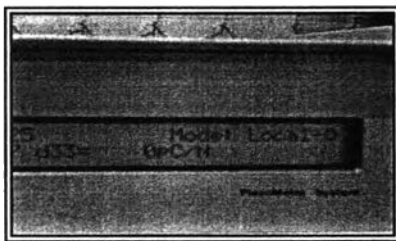


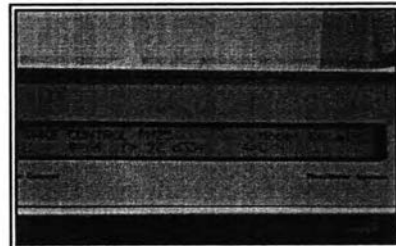
Figure 6.7 Piezoelectric of spherical porous PVDF films shown (a) non-poling and (b) after poling in DMAc, DMF, and TEP at 50 kV/mm.

Table 6.3 The piezoelectric constant (d_{33}) of different porous structure in stretching PVDF films (ellipsoidal shape)

Materials	Piezoelectric coefficient (d_{33}) pC/N	
	Before poling	After poling
Porous PVDF 20% films by DMAc	0	4
Porous PVDF 20% films by DMF	0	4
Porous PVDF 20% films by TEP	0	4



(b)



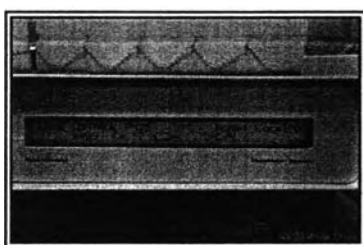
(b)

Figure 6.8 Piezoelectric of ellipsoidal porous PVDF films shown (a) non-poling and (b) after poling in DMAc, DMF, and TEP at 50 kV/mm.

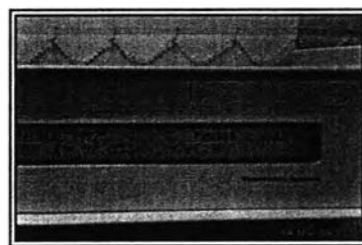
b) Blowing agent technique

Table 6.4 The piezoelectric constant (d_{33}) of different bubble shapes in PVDF films

Materials	Piezoelectric coefficient (d_{33}) pC/N	
	Before poling	After poling
Porous PVDF films by AZDC blowing agent (spherical shape)	0	2
Porous PVDF films by AZDC blowing agent (ellipsoidal shape)	0	7



(a)



(b)

Figure 6.9 Piezoelectric of porous PVDF films shown after poling (a) spherical and (b) ellipsoidal bubble shape at 50 kV/mm.

Therefore non-poling of spherical bubble shape (both phase inversion and blowing agent technique) show a zero piezoelectric coefficient. When poling nearly external breakdown phenomena (poling under a constant electric field of 50 kV/mm, at 90°C) in porous PVDF films are show value of piezoelectric coefficient. There can cause “Phaschen law” [R. Gerhard-Multhaupt, *et al* (2000)], interfacial polarization or Maxwell Wagner-Sillar (MWS) were produced from the accumulation of charges at the interface between pore and polymer resulting in a large scale field called “space charge”, which is different from the other types of polarization (atomic, electronic, dipolar), being produced by the displacement or orientation of bound charge.

Table 6.2-6.4 show the different shapes of bubbles or porous in PVDF films affected on d_{33} coefficient. For spherical shape, poling can slightly improve piezoelectric coefficient. On the other hand, the stretching of porous films to produce ellipsoidal shape exhibit that poling has much effect on increasing of d_{33} coefficient. Clearly, the charge was accumulated at the surface boundary of pores or bubbles. When the film is stretched, the charges inside the bubbles or pores were separated far apart into the negative and positive charges creating strong dipoles in microstructure of the film.

In Table 6.4, it was found that the increasing of piezoelectric d_{33} constants up to 7 pC/N can be obtained with these composites, that their activity can be explained by a model assuming the presence of charges of opposite sign on the upper and lower surfaces of the air enclosures. [J. Hillenbrand, G. M. Sessler (2000)]. In this case the β crystalline phase is slightly effect on piezoelectric that can be confirmed by XRD results.

In this paper, PVDF-based, heterogeneous piezoelectric charge electrets are lower piezoelectric than PP electret with outstanding d_{33} D 150 pC/N. Due to PP is non-polar polymer that have capacities to keep the real charge greater than PVDF (polar polymer).

6.5 Conclusions

The piezoelectric coefficient of undrawn and drawn non-porous PVDF under the same poling conditions increases with an increasing fraction of β crystalline phase, the ferroelectric properties governed by β phase. For porous PVDF films, at high alternating E-field (nearly breakdown 50 kV/mm at 90°C), the gas in the pore may be ionized and generated the space charge. Also, the switching of dipole of porous PVDF film can be occurred easily compare to those in non-porous PVDF films. When the

mechanical deformation provides ellipsoid shape in porous PVDF film, piezoelectric was up to 7 pC/N. These values are slightly more than some PVDF inorganic piezoelectric composites. Consequently, the accumulations of space charges in porous PVDF films are one of internal effect to enhance the piezoelectric properties. Finally, Air/PVDF composite is a promising material for electronic applications in a 1 kHz-10 MHz range, and be potentially used as low-density piezoelectric applications.

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