CHAPTER VI
DIELECTRIC AND PIEZOLECRIC PROPERTIES OF LAMINATE MULTILAYER PVDF/BST COMPOSITE

6.1 Abstract

Lamination or multilayer thin films of PVDF and PVDF/BST composite were produced by compression molding technique. PVDF-PVDF/BST bilayer films, PVDF-PVDF/BST40%-PVDF trilayer films and PVDF/BST-PVDF-PVDF/BST trilayer films were fabricated and compared the properties with single structure of PVDF and composite film. The microstructural layers of PVDF and composited film of laminate films was observed in SEM image which showed dense and smooth surface. The multilayer system revealed dielectric constants and dissipation factor as the function of frequencies and temperatures using Impedance/Gain-Phase Analyzer. The dielectric constant showed a frequency dependency while temperature independency of dielectric constant was found in short range. The effective dielectric constant of the multilayer structures was related a series connection model of each layer dielectrics. The hysteresis loops of laminate films showed a ferroelectric behavior and the highest piezoelectric coefficient, d_{33} was observed in PVDF/BST composite film.

Keywords: Lamination; Multilayered film; Dielectric properties; Ferroelectric behavior

6.2 Introduction

The nature of piezoelectricity of multilayered polymer system depends on the physical and chemical properties of their components. The most heterogeneous polymer films can have piezoelectric properties to some degree, even if they are not polarized [Greaves *et al.*, 1974, Hayakawa *et al.*, 1973, Wada *et al.*, 1976]. This may be related to heterogeneity and embedded charges accidentally present in the film. The laminated system or multilayer structure of different materials fulfills the heterogeneity condition, moreover the charges can be stored at the interfaces of the layers as a result of the equilibrium electrification and some effects. The piezoelectric laminate film comprised two or more layers wherein the surface of each layer can be accomplished by surface lamination to each other by melting to cause the respective surface and have one or more ferro- or piezoelectric properties superior to those of individual properties. The individual surfaces were placed in contact with each other by melting to form the laminate which had different material characters. More than two piezoelectric materials can be laminate to form trilayer or higher level of lamination and the properties over the expected properties. This invention involved individual surface which are capable to being polarized. Mazur in 1989 studied the piezoelectricity of multilayered polymer system by making multilayer film indifferent internal layer, sandwich by PVDF film. Uncharged laminate PVDF-PMMA/$BaTiO_3$-PVDF exhibits the highest piezoelectric properties but the better piezoelectric stability can be obtained in polarized PVDF-PUE-PVDF laminate. However all laminated film had higher piezoelectric coefficient when compared with the single PVDF film. The piezoelectric strain constant d_{31}, piezoelectric stress constant e_{31} and remanent polarization, P_r of Nylon 11-PVDF bilaminated film were investigated compare to those of individual Nylon 11 and PVDF film [Scheinbiem, *et al.*, 1994]. The Nylon 11-PVDF bilaminated film show significantly higher remanent polarization, P_r ,which is 44% higher than that of either Nylon 11 or PVDF film, which were produced in an identical procedure. The piezoelectric strain constant, d_{31}, and piezoelectric stress constant, e_{31} of Nylon 11-PVDF bilaminated film show significant improvement at both room and evaluated temperatures when compare with Nylon 11 or PVDF film.

A presently desired laminate film coming with this invention comprised a PVDF film and PVDF/BST composite film laminate to form laminate film in different series: PVDF-PVDF/BST bilayer, PVDF-PVDF/BST-PVDF trilayer and PVDF/BST-PVDF-PVDF/BST trilayer films. This particular piezoelectric laminate film coming within invention has provided significant ferroelectric and piezoelectric properties in comparison.

6.3 Experiment

6.3.1 Materials

Stretched PVDF film 4x prepared by stretching PVDF from solution-casting technique and PVDF/BST40% composite film from compression molding technique.

6.3.2 Laminate Film Fabrication

PVDF-PVDF/BST40% bilayer films, PVDF-PVDF/BST40%-PVDF trilayer films and PVDF/BST40%-PVDF-PVDF/BST40% trilayer films were fabricated by Labtech compression machine. They were compressed at 90°C for 20 min under pressure 10 tons.

6.4 Results and Discussion

6.4.1 Scanning Electron Microscope (SEM)

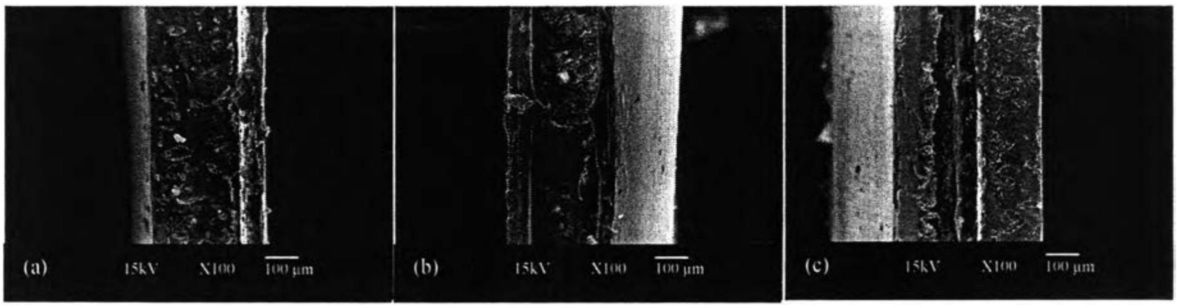


Figure 6.1 SEM cross section image of (a) PVDF-PVDF/BST40% bilayer films, (b) PVDF-PVDF/BST40%-PVDF trilayer film and (c) PVDF/BST40%-PVDF-PVDF/BST40% trilayer film.

The interface in the resulting multilayered PVDF and PVDF/BST composite films was evidenced by SEM as shown in Figure 6.1. Each layers of PVDF and PVDF/BST composite film were clearly observed which confirmed multilayer film made by compression technique.

6.4.2 Dielectric Properties

Stretched PVDF film x4 and PVDF/BST40% composite film was used as starting materials of multilayer film because stretched PVDF film x4 had the good dissipation factor, smooth surface and its thickness was not too thin. PVDF/BST40% composite film had good dielectric properties and also it was flexible enough to prepare multilayer films. The frequency dependant dielectric behavior of PVDF film, PVDF/BST composite film and bilayer film were shown in Figure 6.2. which showed room temperature values for the dielectric constant and dissipation factor as a function of the frequency. It can be observed that the dielectric constant of all materials showed a slight frequency dependency. the dielectric constant of PVDF/BST composite film yielded highest dielectric constant than those of individual single film which can be seen from Figure 6.2 (a), however, that there is a tendency for a decrease in the dielectric constant and an increase in the dissipation factor at higher frequencies, possibly related to interfacial polarization of space charges [Sutton *et al.*, 1960, Tomozawa *et al.*, 1977]. Similar dielectric constant vs. frequency behavior has also been observed for other thin films [Joshi *et al.*, 1997, Lu *et al.*, 1999].

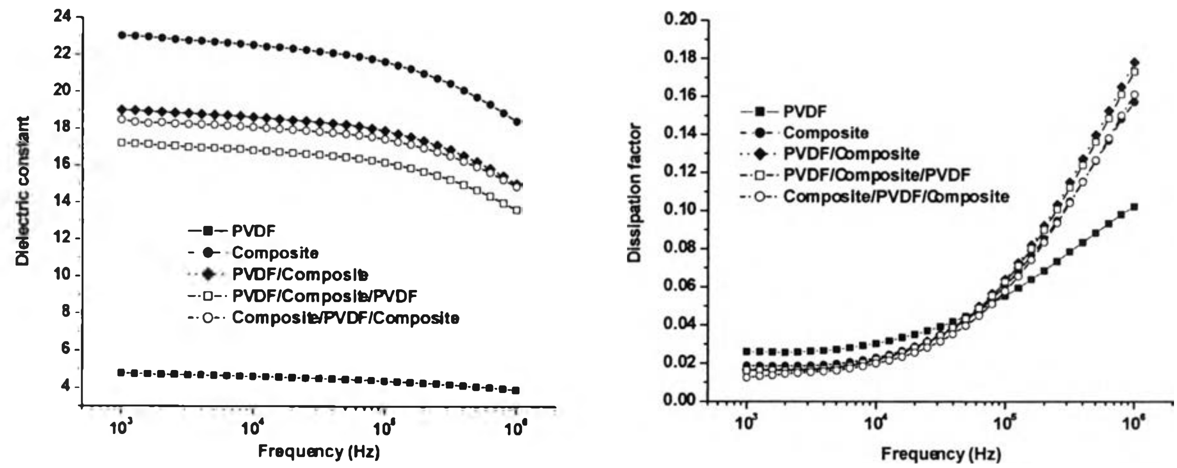


Figure 6.2 (a) Dielectric constant and (b) Dissipation factor as the function of frequency at room temperature of PVDF film x4, PVDF/BST composite film and Multilayer films.

The effective dielectric constant of the multilayer structure is a series connection model of PVDF and PVDF/BST composite layer dielectrics. the effective dielectric constant, ε_{eff}, can theoretically be expressed as:

$$\frac{1}{\varepsilon_{eff}} = \left[\frac{1}{\varepsilon_1} + \frac{1}{\varepsilon_2} + \frac{1}{\varepsilon_3} + ...\right] / (t_1 + t_2 + t_3 + ...) \qquad (1)$$

where t is thickness of each layer. The dielectric constant was very close to those calculated assuming the series connection model of three components. The calculated dielectric constant of PVDF/BST40%-PVDF-PVDF/BST40% trilayer film has a difference lower than 0.7% those ($\varepsilon_r \approx 18.48$) experimental dielectric constant of the trilayer film. The dielectric constant of the multilayer thin films can thus be explained by a series connection of individual components [Pontes *et al.*, 2001]. By using compression technique, all films showed low dissipation factor which yielded the values less than 0.03 and 0.2 at the frequency of 1 kHz and 1 MHz respectively.

Table 6.1 Dielectric constant at 1 kHz from calculation and measurement in comparison

Sample	Dielectric constant at 1 kHz	
	Calculation*	**Measurement**
PVDF-composite	15.57	19.01
PVDF-composite-PVDF	12.45	17.22
Composite-PVDF- Composite	18.35	18.48

*calculation form equation 1.

Figure 6.3 to Figure 6.7 showed temperature dependence of PVDF 4x, PVDF/BST composite and all laminate films at different frequencies. It can be seen that the dielectric constant of all materials except PVDF 4x showed the temperature independency in shot range of temperature. However, the dielectric value of all samples tend to increase with the temperature which is the nature of piezoelectric materials.

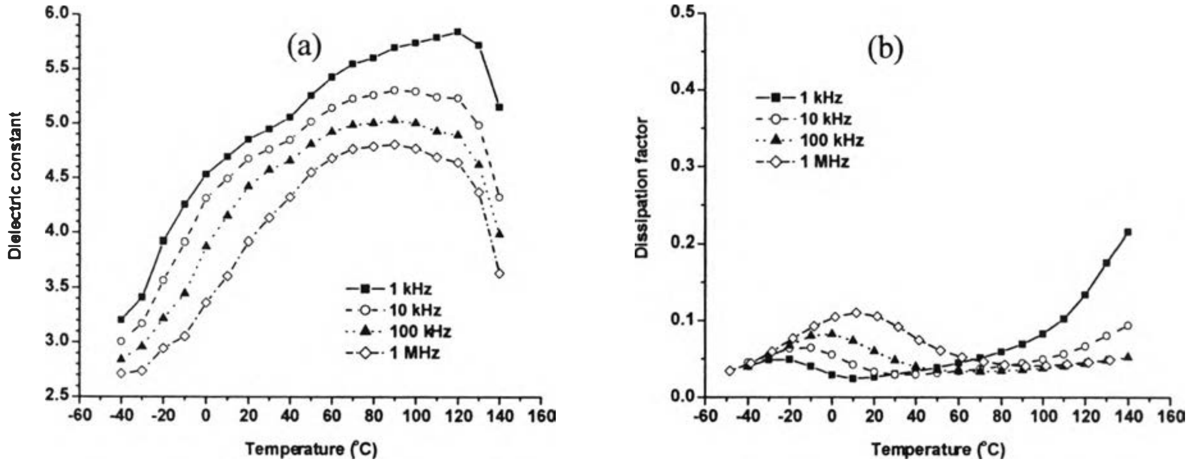


Figure 6.3 (a) Dielectric constant and (b) Dissipation factor as the function of temperature at different frequency of PVDF film 4x.

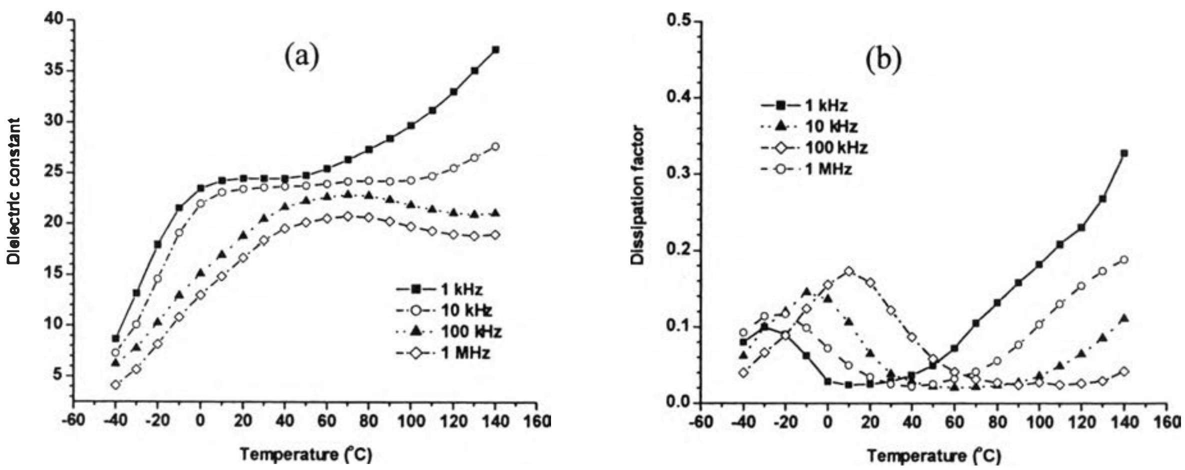


Figure 6.4 (a) Dielectric constant and (b) Dissipation factor as the function of temperature at different frequency of PVDF/BST composite film.

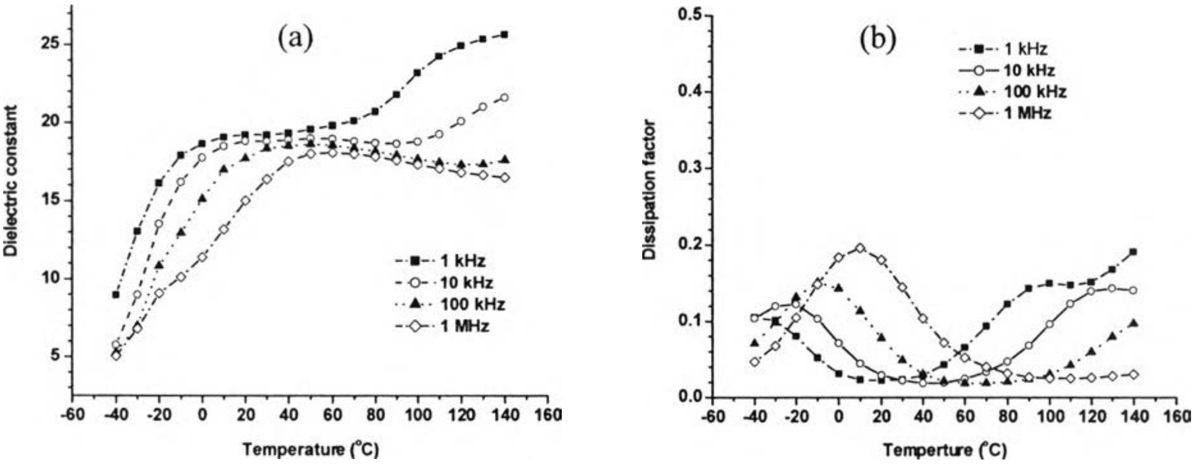


Figure 6.5 (a) Dielectric constant and (b) Dissipation factor as the function of temperature at different frequency of PVDF-PVDF/BST40% bilayer film.

The pattern of dissipation factor of all series in various temperature showed that molecular relaxation of PVDF polymer did not be interfered from lamination method.

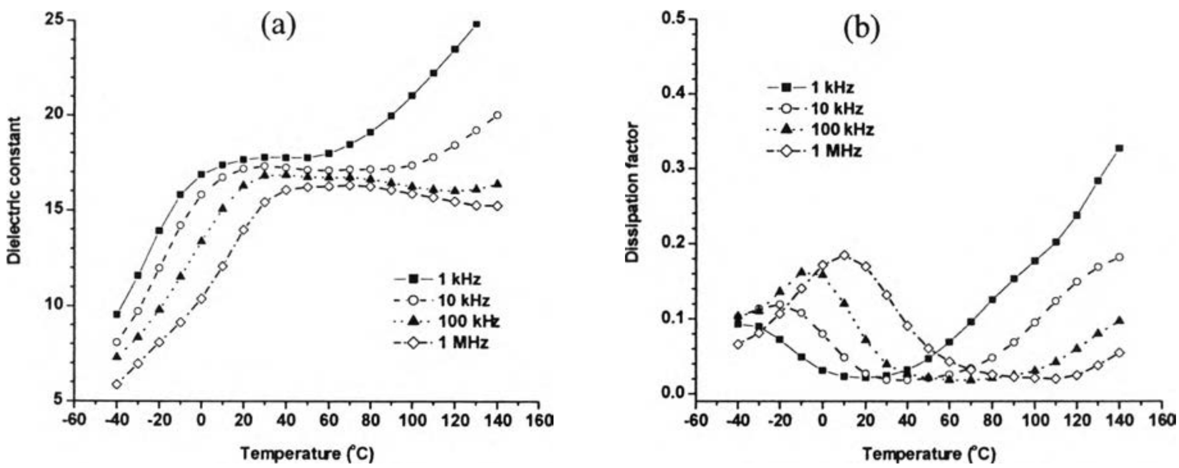


Figure 6.6 (a) Dielectric constant and (b) Dissipation factor as the function of temperature at different frequency of PVDF-PVDF/BST40%-PVDF trilayer film.

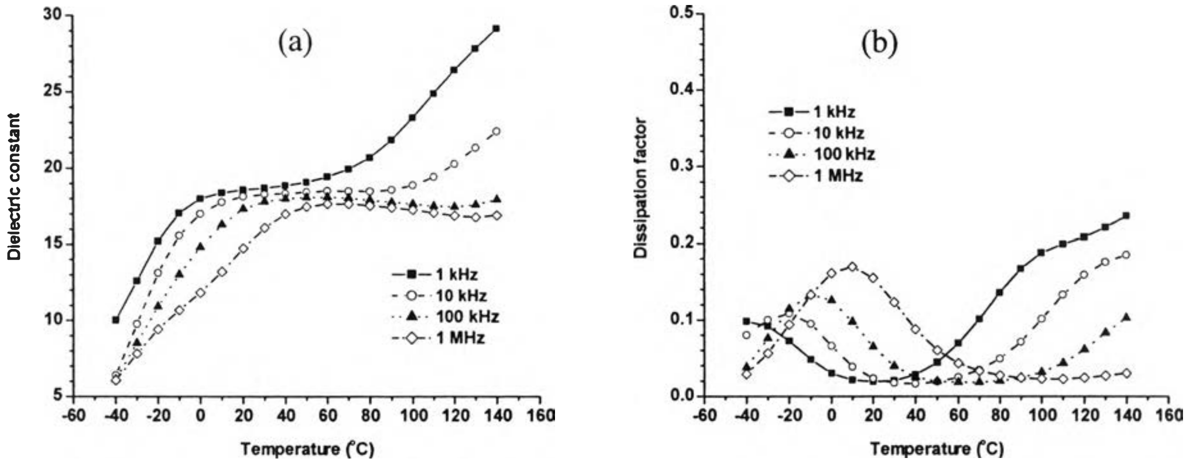
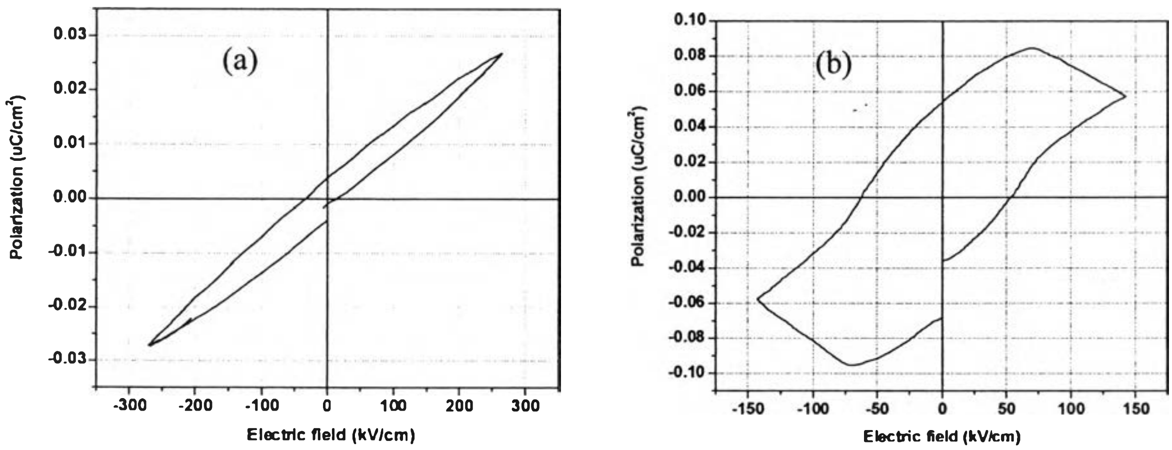


Figure 6.7 (a) Dielectric constant and (b) Dissipation factor as the function of temperature at different frequency of PVDF/BST40%-PVDF-PVDF/BST40% trilayer film.

6.4.3 <u>Piezoelectric Properties</u>

Figure 6.8 shows a typical polarization electric field *(P-E)* hysteresis loop at room temperature for PVDF, PVDF/BST composite and multilayer films. Ferroelectric behaviors of all material were showed by field *(P-E)* hysteresis loop with individual remanent polarization (P_r) and the coercive field (E_c).



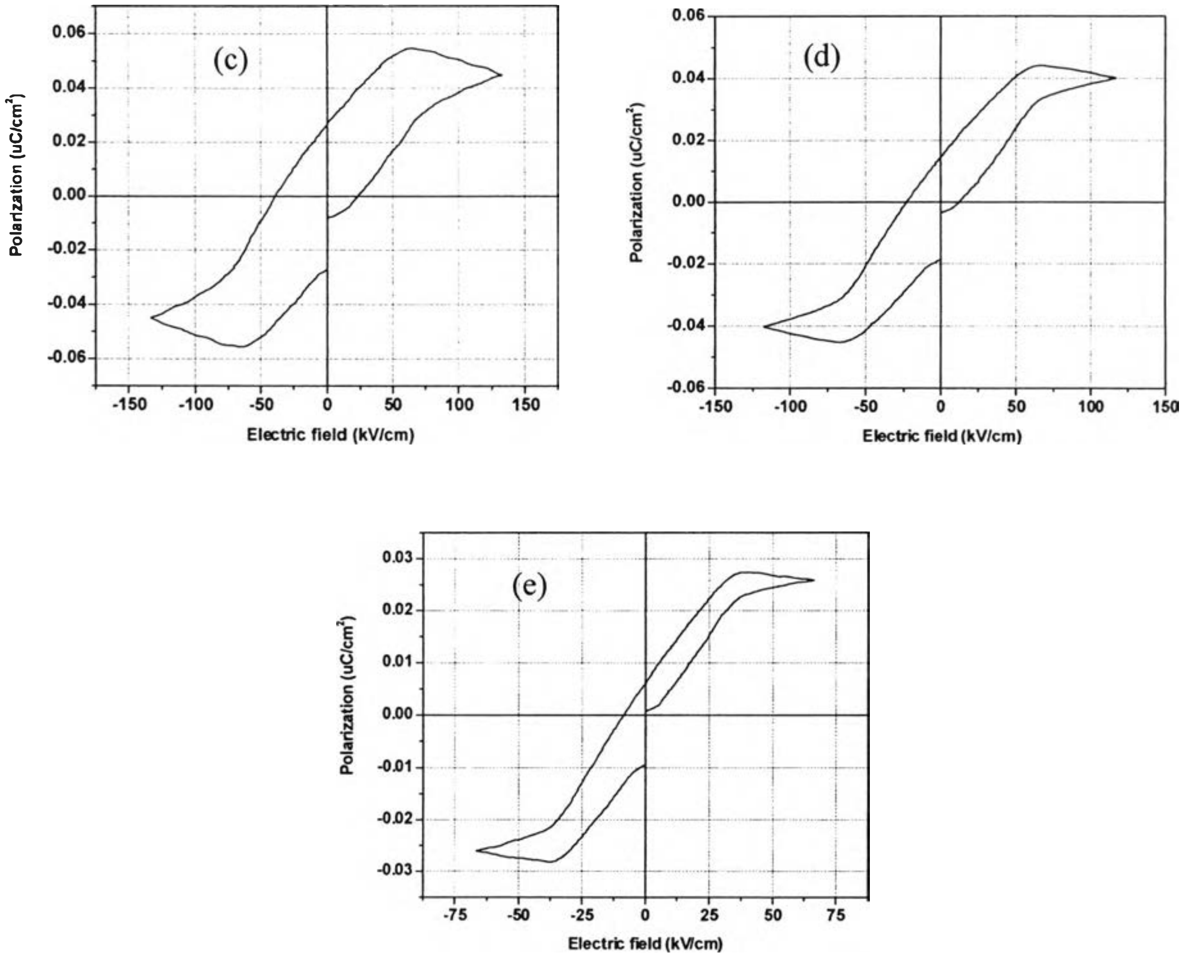


Figure 6.8 Hysteresis loop of (a) PVDF film 4x, (b) PVDF/BST composite film, (c) PVDF-PVDF/BST40% bilayer film, (d) PVDF-PVDF/BST40%-PVDF trilayer film and (e) PVDF/BST40%-PVDF-PVDF/BST40% trilayer film.

Figure 6.8 (a) showed the hysteresis loop of PVDF 4x which exhibit the paraelectric properties with small remanent polarization (P_r) and the coercive field (E_c) while the composite film and multilayer film film show ferroelectric properties. The greatest remanent polarization (P_r) and the coercive field (E_c) were shown in PVDF/BST composite film (as shown in Figure 6.8 b) with the highest piezoelectric coefficient (d_{33}) which showed the value after poling of 16 pC/N. The piezoelectric constants of all series of lamination in table 6.1 showed corresponding with the dielectric constant and hysteresis loops, shown in Figure 6.7 and Figure 6.8 respectively. The highest piezoelectric coefficient was yielded from the highest remanent polarization (P_r) and the lower piezoelectric coefficients were showed from smaller one.

Table 6.1 Piezoelectric coefficient (d_{33}) of all samples before and after Poling

Material	Piezoelectric coefficient, d_{33} (pC/N)	
	Before Poling	**After Poling**
*PVDF x4	0	2
PVDF/BST composite film	0	16
PVDF-PVDF/BST40% bilayer film	0	12
PVDF-PVDF/BST40%-PVDF trilayer film	0	9
PVDF/BST40%-PVDF-PVDF/BST40% trilayer film	0	7

* poling conditions, the electric field is 50 kV/cm in oil bath at 90°C

Due to the limitation of piezoelectric ceramics, this research tends to increase and improve dielectric and piezoelectric properties of PVDF film by lamination or multilayer system in order to use in mechanical sensor applications which require high flexibility of the polymer. Unfortunately, laminated film did not show higher piezoelectric coefficients than that of single layer of PVDF/BST composite film (as shown in Table 6.1). Two hypotheses obtained from this research were described as follows :first reason might yield from the preparation section of laminated film. Each layer of multilayer structure was not individually poled before lamination by compression so charges may not be completely induced and stored as review in the propose. Second was the fusion of PVDF matrix, PVDF matrix of PVDF and PVDF/BST composite film which used as starting materials in lamination may be fused in some area between the interlayer of laminated film. This reason could be supported by a literature research; Mazur (1989) obtained high piezoelectric coefficient from trilayer film made from PMMA/$BaTiO_3$ sandwiched by PVDF layer. Their successful PVDF-PMMA/$BaTiO_3$-PVDF film with good interlayer was obtained from different polymer matrix of starting materials. And also the induced positive and negative charges occurred from functional group of PMMA and PVDF respectively.

6.5 Conclusion

Multilayered thin films were successfully prepared by the compression molding technique. A smooth, dense surface was observed by SEM images. The interface in the resulting multilayered PVDF and PVDF/BST composite films was very clearly evidenced by SEM. The dielectric constants and dissipation factor of multilayer thin films were investigated as the function of frequencies and temperature. All materials showed a slight frequency dependency at room temperature. But the dielectric constants of all laminate films showed thermal independency in short range of temperature which were as the same as the composite films. The dielectric constant of multilayered films was explained by the series connection of the component films. The effective dielectric constant calculated from the series connection equation well related to the experimental measurement. And hysteresis loops of multilayer film showed ferroelectric behavior.

6.6 Acknowledgements

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6.7 References

Greaves, R.W., Fowler, E.P., Goodings, A. and Lambs, D.R. (1974) The Direct Piezoelectric Effect in Extruded Polyethylene. Journal of Materials Sciences, 9, 1602-1608.

Hayakawa, R. and Wada, Y. (1973). Piezoelectricity and Related Properties of Polymer Films. Advances in Poymer Sciences, 11, 1-55.

Joshi, P.C. and Desu, S.B. (1997) Structural, electrical, and optical studies on rapid thermally processed ferroelectric $BaTiO_3$ thin films prepared by metallo-organic solution deposition technique. Thin Solid Films, 300, 289-294.

Lu, C.H. and Wen, C.Y. (1999) New non-fatigue ferroelectric thin films of barium bismuth tantalite. Materials Letters, 38, 278-282.

Pontes, F.M., Leite, E.R., Lee, E.J.H., Longo, E., Varelab, J.A. (2001) Dielectric properties and microstructure of $SrTiO_3/BaTiO_3$ multilayer thin films prepared by a chemical route. Thin Solid Films 385, 260-265.

Sutton, P.M. In: Birks, J.B. and Schulman, J.H., (Eds.). (1960) Progress in Dielectric. Wiley: New York.

Tomozawa, M. in: Tomozawa M., Doremus, R.H. (Eds.). (1977) Treatise on Materials Science and Technology. Academic: New York.

Wada, Y. and Hayakawa R. (1976) Piezoelectricity and Pyroelectricity of Polymers, Japan Journal of Applied Physics, 15, 2041-2057.