CHAPTER VI
DIELECTRIC AND FERROELECTRIC PROPERTIES OF PVDF/BT COMPOSITES

6.1 Abstract

Film mechanical sensors, one of the piezoelectric applications, which are focused on this research, are used to measure or detect various mechanical quantities. This work extended the range of material properties by fabricating poly vinylidene fluoride (PVDF)/barium titanate (BT) composite film. The piezoelectric ceramic, BT, is induced into composite to increase the dielectric constant and piezoelectric properties. A certain weight fraction of 0.3, 0.5 and 0.7 of calcined and sintered BT powder was embedded in a matrix of PVDF before compression molding into 100-200 μm thick sheets. The dielectric constant and the loss tangent of composites at different %wt ceramic were observed. The piezoelectric properties of PVDF/BT composite were investigated. Subsequently, microstructure of the composite was observed using scanning electron microscopy (SEM).

6.2 Introduction

Polymer/ceramic composites have received much attention as new piezoelectric materials for applications in electromechanical transducer, such as microphones, hydrophones, medical ultrasound and pyroelectric detector, *etc* [Olszowy, M. (1997)]. Poly vinylidene fluoride, PVDF, was used as a piezoelectric polymer matrix. The dielectric constant of PVDF is higher than most polymers, and makes PVDF attractive for integration into devices as the signal to noise ratio is less for higher dielectric materials. The weak points of PVDF are possessed low the dielectric constant compare to those of ceramic and exhibit relaxation behavior. From these concerns, the composite of PVDF and ceramic with high dielectric constant would be expected to have higher dielectric constant and less relaxation behavior. Barium titanate, BT, was used as ferroelectric ceramic because of capability in wide applications in many electronic applications [Lu, Q. *et al.*, (2004)].

BT is of high interest since it provides a unique combination of high dielectric constant, low dc leakage, low loss tangent up to high frequencies, and stable operation at high temperatures. BT belongs to the general class of ferroelectric materials based on the perovskite structure [Wua, D. *et al.*, (2000)]. The simplest fabrication of PVDF/BT composites is the composites of 0-3 connectivity. To design a polymer/ceramic composite, a fine powder is dispersed in a PVDF matrix [Lu, Q. *et al.*, (2004)]. The composites are mainly characterized the dielectric properties, piezoelectric properties, and microstructure. These composite would be promising for electronic application due to the characteristics of lead-free, low-cost, light weight, and high dielectric constant.

6.3 Experimental

Barium Titante Preparation

BT powder was prepared by sol-gel process. Barium acetate was dissolved into methyl alcohol 20ml in the presence of glacial acetic acid 10 ml. The solutions were then mixed and stirred for 20 minutes at room temperature. The prescribed amount of titanium-n-butoxide was added into the mixture. All the materials mentioned above were thoroughly mixed to prepare a stable solution with uniform composition until gel solution occurs. After that the gel solution was poured into an alumina crucible and heated by using a 2-step thermal decomposition method with calcining temperature of 1000 °C in order to decompose the precursors and to crystallize the barium titanate. The calcined BT powder was compressed to fabricate BT ceramics sintered at 1350 °C. The BT ceramic was ground to fabricate sintered BT powder.

PVDF/Barium Titante Composite Preparation

PVDF powder supplied by Solvay (Solef 1008) was dissolved in dimethly formamide (DMF) at 60°C for PVDF solutions. For composite preparation the polymer/solvent ratio was 10g/100 ml. Proportionate quantity of calcined and sintered BT powder were added in the polymer solution. It was homogenized by magnetic stirrer. Additional mixing by ultrasonic was used to guarantee that the powder agglomerated were broken. The solution was dried by heating at 100 °C. The composite film was prepared by a Wabash compression as pressing dried solution at 174 °C for 20 minutes under pressure of 10 tons. The thickness of the prepared films was ranged between 100-200 μm. Follows the above method, the composite of 30, 50 and 70 % by weight of ceramic were fabricated.

Characterization

The distribution of ceramic powders in composites was observed using scanning electron microscope (SEM; JSM-5200, JEOL). The piezoelectric properties was investigated by using 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. The dielectric properties of composites were measures using Hewlett-Packard 4194A impedance/gain phase analyzer. The measurements were performed at room temperature with a frequency range of 1 kHz-1 MHz.

6.4 Results and Discussions

6.4.1 Dielectric measurement

The frequency dependant dielectric constant of PVDF/calcined BT composites is shown in Figure 6.1 which is very large about 16.7 at 1 kHz and at weight fraction of 30/70.It is obviously noticed that the value of dielectric constant increases with increasing weight fraction from 100/0 to 30/70 of PVDF/BT ratio. As the weight fraction of BT is added up to 70%, the dielectric constant of composites shows the value of 16.7 at 1 kHz. Figure 6.2 shows the dielectric loss tangent which lower than 0.08 at frequency up to1 MHz at all weight proportions.

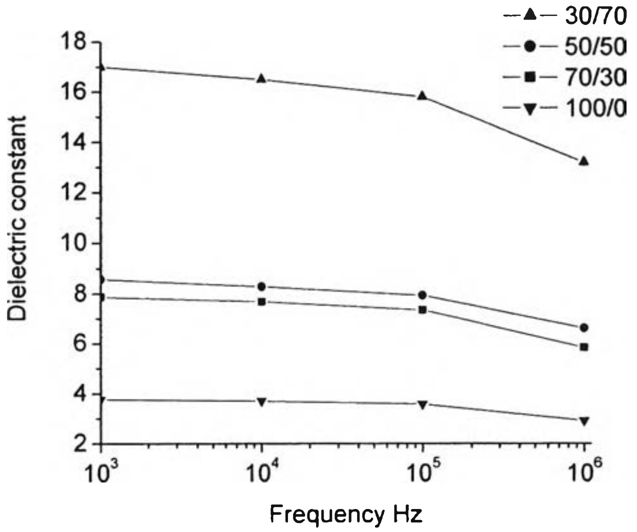

Figure 6.1 The frequency dependence of the dielectric constant of PVDF/ calcined BT composites at weight proportions of 100/0, 70/30, 50/50 and 30/70.

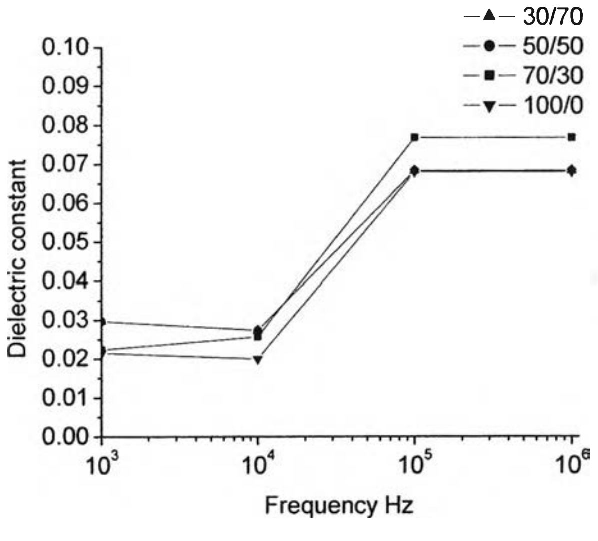

Figure 6.2 The frequency dependence of the dielectric loss tangent of PVDF/ calcined BT composites at weight proportions of 100/0, 70/30, 50/50 and 30/70.

The frequency dependant dielectric constant of PVDF/sintered BT composites is shown in Figure 6.3. It is observed that the dielectric constant of sintered BT composite show high value about 24.4 at 1kHz and at weight fraction

30/70. Figure 6.4 shows the dielectric loss tangent which lower than 0.08 at frequency up tol MHz at all weight proportions.

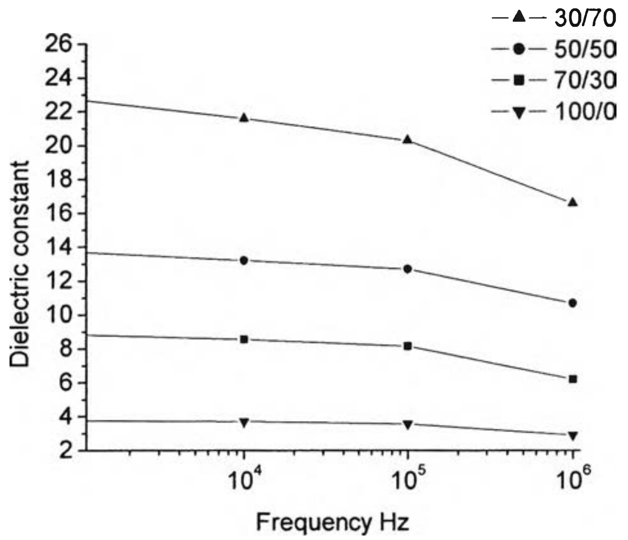

Figure 6.3 The frequency dependence of the dielectric constant of PVDF/ sintered BT composites at weight proportions of 100/0, 70/30, 50/50 and 30/70.

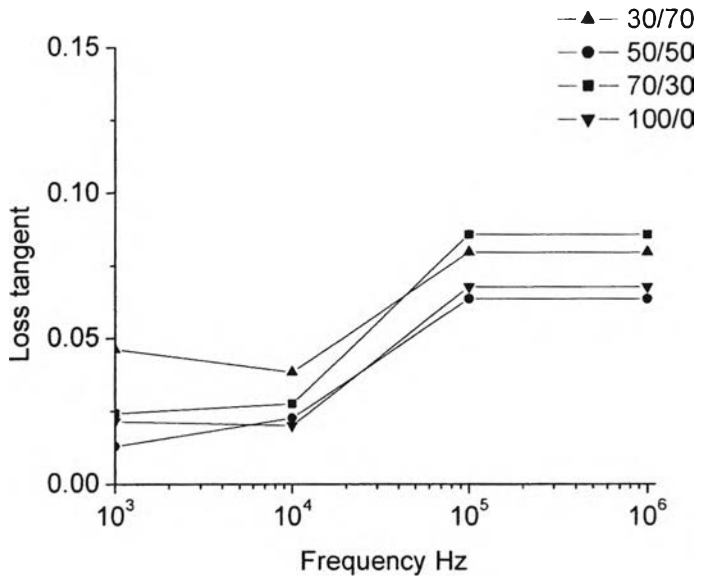

Figure 6.4 The frequency dependence of the dielectric loss tangent of PVDF/ sintered BT composites at weight proportions of 100/0, 70/30, 50/50 and 30/70.

The comparison of dielectric constant in PVDF/calcined BT and PVDF/ sintered BT is shown in Figure 6.5. The dielectric constant of PVDF/sintered BT is higher than those of PVDF/calcined BT for all compositions. The BT powder ground from sintered pallet contribute higher dielectric constant in composite because the larger grain size

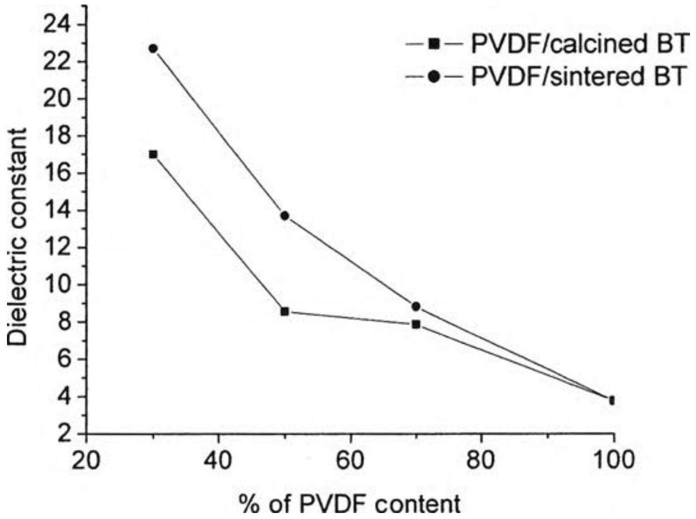

Figure 6.5 The % of PVDF content versus dielectric constant at 1 kHz .

6.4.2 *X-ray diffraction (XRD)*

XRD patterns of calcined and sintered BT powder were shown in Figure 6.6. The BT powder after sintered at 1350 °C reveals tetragonal phase as observed by the splitting at 2θ ~ 46 °C. This can be explained from the fact that BT shows tetragonal after sintering process. The lattice parameter of BT was shown in table 6.1.

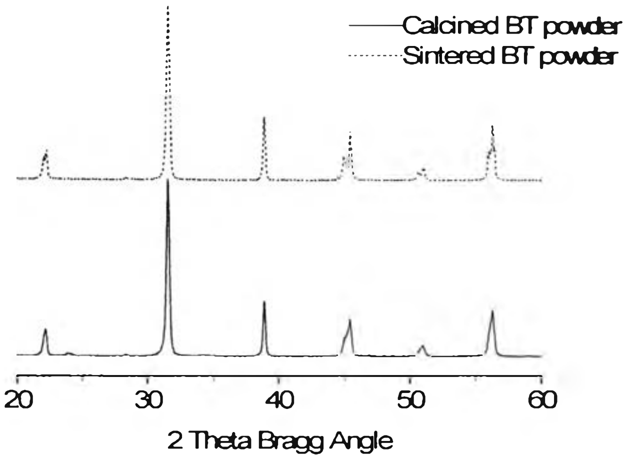

Figure 6.6 X-ray diffraction patterns of calicned and sintered of BT ceramic powder.

Table 6.1 Lattice parameter of the calicned and sintered of BT ceramic powder.

Materials	Unit cell parameter		Unit cell volume	Tetragonal
	a_0(nm)	c_0(nm)	$v_0 \times 10^3$(nm)	ratio c_0/a_0
Calcined BT powder	4.004806	4.004806	64.23095	1
Sintered BT powder	3.98867	4.028652	64.73624	1.010024

6.4.3 Piezoelectric Properties

The ferroelectric behavior of the PVDF/ calcined and sintered BT composites are investigated from relationship between polarization (P) and electric field (E) at room temperature, as shown in Figure 6.7 The ferroelectric properties are obviously exhibited in PVDF/ sintered BT which confirm that sintered BT powder is ferroelectric more than calcined BT powder. From this reasons, the sintered BT powder is suitable phase for ferroelectric application. Stress piezoelectric coefficients (d_{33}) of the polarized films were obtained from d_{33} meter. The film composites before poling show zero value of d_{33}. After poling under a constant electric field of 10 kV/mm, at 90°C, the PVDF/ sintered BT composites show value of piezoelectric coefficient but PVDF/ calcined BT composites remain show zero value as not showing ferroelectric properties (confirmed from Figure 6.7). It was found that the piezoelectric coefficient of PVDF/sintered BT under the same poling conditions increases with an increasing of % wt of BT ceramics (shown in Table 6.2).

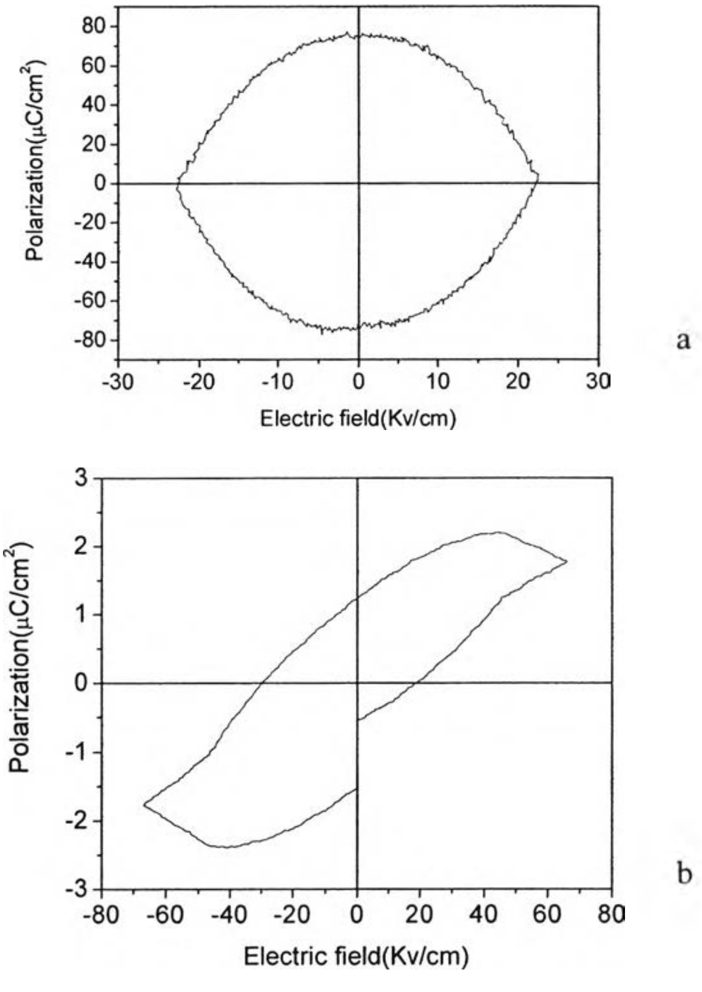

Figure 6.7 Hysteresis loop of (a) PVDF/ calcined BT (b) PVDF/ sintered BT at ratio between PVDF and BT is 30/70.

Table 6.2 Comparative data of d_{33} between calcined and sintered BT powder embedded in PVDF matrix

Composition		**Piezoelectric coefficient(d33) after poling**	
PVDF	BT	Calcined BT powder	Sintered BT powder
70	30	0	1
50	50	0	2
30	70	0	9

*All film were exposed under constant electric field of 10 KV/mm and constant temperature of 90°C.

6.4.4 Scanning electron microscopes-SEM

The SEM surface micrographs of PVDF/ BT at weight proportions 70/30, 50/50 and 30/70 were clearly seen that the BT particles had a connectivity zero while the PVDF polymer had a connectivity of 3 which shown in Figure 6.8. However, the images show homogeneous images at 70/30 and tend to show larger agglomeration when increasing weight fraction of BT particles which may occur due to Van der Waals force.

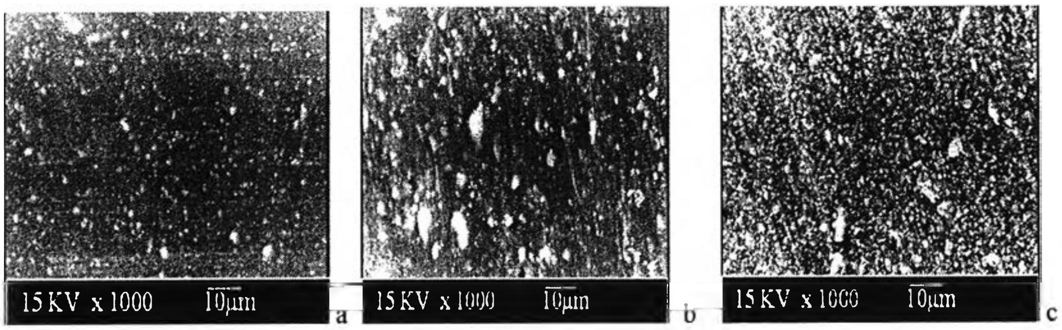

Figure 6.8 Scanning electron microscope (SEM) of the PVDF/ BT composites at weight proportions (a) 70/30, (b) 50/50and (d) 30/70.

6.5 Conclusion

The PVDF/ BT composite with 0-3 connectivity were successfully fabricated. The BT powders which come from calcining and sintering process was dispersed in PVDF matrix; however, large of agglomeration were found in composites at high BT content (70%wt). It was found that increasing the amount of ceramic powders in composites enhances the dielectric constant of composites and sintered powder can enhance dielectric constant of composite also. The PVDF/sintered BT powder displays ferroelectric application more than PVDF/calcined BT powder because grain ceramic of sintered BT powder occurs.

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