CHAPTER IV
DIELECTRIC AND MECHANICAL PROPERTIES OF POLY(BUTYLENE SUCCINATE) THIN-FILM COMPOSITE INCORPERATED WITH BARIUM STRONTIUM TITANATE POWDERS

5.1 Abstract

High dielectric constant barium strontium titanate ($Ba_{0.7}Sr_{0.3}TiO_3$ or BST) powder was prepared by low temperature sol-gel method to be used as filler in poly(butylene succinate)-composite in 0-3 connectivity system. Moreover, the thermal properties and dielectric behavior of poly(butylene succinate) integrated with BST powder were studied. The result showed the improvement of thermal stability and dielectric constant with increasing amount of BST powder. Finally, the composite thin film with good dielectric properties, flexibility, and process ability will be applicable as thin film capacitor for high-frequency electronic devices.

5.2 Introduction

Biodegradable polymers are commonly used in packaging, agricultural and medical purposes. Although, the electrical utilization of biodegradable polymer have been slightly studied. Some biodegradable polymers were investigated their utilization as electrical insulators regarding to the conductivity, dielectric properties and breakdown strength compared to those of low density polyethylene (LDPE) [1]. Among those biodegradable polymer, poly(butylene succinate) (PBS) has adequate physical and dielectric properties besides it has lower glass transition temperature than that of poly-L-lactic acid (PLLA) and polyethylene terepthalate succinate (PETS). PBS is a biodegradable thermoplastic which can be synthesized from 1,4-butanediol and succinic acid [2]. Similar to commonly used polymeric material, PBS has very low dielectric constant in terms of electrical utilization. Early purposed method is to integrate high dielectric constant ceramic filler in the polymer matrix as a composite material in order to improve the dielectric properties [3]. One of the promising material that has been used to produce capacitor and high frequency electronic devices are barium titanate and its solid solution such as barium strontium titanate [4-5]. The most well-known approach of mixing this two-phase material is "0-3 connectivity" which means the ceramic filler is randomly dispersed in polymer matrix [6]. Besides the obtained high dielectric constant, by using PBS would fulfill the flexibility, feasibility, and more importantly, bring biodegradability to the dielectric 0-3 composites.

In this work, barium strontium titanate powder was prepared by low-temperature sol-gel method to be incorporated in poly(butylene succinate)/barium strontium titanate ($Ba_{0.7}Sr_{0.3}TiO_3$) composite thin films at various composition of filler content from 0 to 50 wt% have been prepared to study the dispersion state, thermal stability, mechanical properties, frequency-dependent and temperature-dependent dielectric properties.

5.3 Experimental

5.3.1 Preparation of barium strontium titanate powders

Barium strontium titanate, $Ba_{0.7}Sr_{0.3}TiO_3$ ceramic powder was prepared by dissolving the stoichiometric amount of barium acetate and strontium acetate in 50 ml of acetic acid for 10 min. Following by mixing of those two precursor solution and adding 50 ml of methyl alcohol. The solution were mixed and stirred to obtain a homogenously mixed solution. Then an equimolar amount of titanium-n-butoxide was added into the mixture under vigorous stirring. The molar ratio of Ba:Sr:Ti was equal to 0.7:0.3:1.0. After 20 hr, the solution became a white gel, the gel was taken to calcination process by using "2-step thermal decomposition" method in order to decompose of the organic compounds and crystallize the $Ba_{0.7}Sr_{0.3}TiO_3$ powders, and the temperature profile in 2-step thermal decomposition is shown in Figure 5.1.

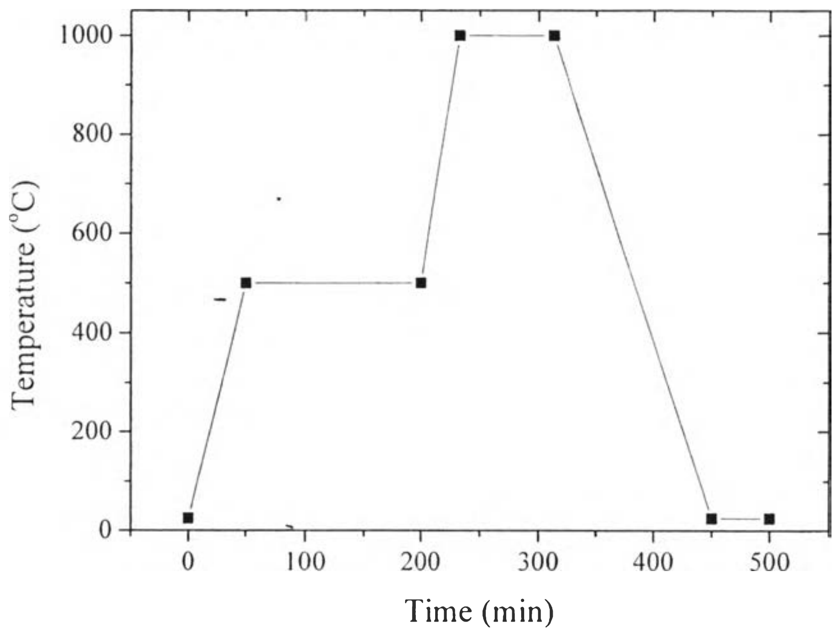

Figure 5.1 Two-step thermal decomposition temperature profile.

5.3.2 Preparation of Poly(Butylene Succinate)/Barium Strontium Titanate Composite

The thin-film composite of poly(butylene succinate)/barium strontium titanate powder, $Ba_{0.7}Sr_{0.3}TiO_3$ were prepared by using solution mixing method. Firstly, PBS pellets were dissolved in the chloroform solvent in the ratio of 16g/100ml. Secondly, $Ba_{0.7}Sr_{0.3}TiO_3$ powder were added to the PBS solution in the composition of 0, 10, 20, 30, 40, and 50wt%. Then, the PBS-BST solutions were casted in the aluminum tray, dried in the oven at 60℃ for 5 hours and cut into small flakes. Finally, the composite flakes were spread in rectangular-shaped mold with the thickness of 0.2 mm and pressed by compression molding at the temperature about 150℃ and the pressure about 2500 psi.

5.3.3 Characterizations and Testing

The morphological investigation of PBS/BST composite thin-film was determined by using Scanning Electron Microscope (SEM) which study the dispersion state of fracture surface. Thermal stability of PBS/BST composite films were measured by using Thermogravimetric Analysis (TGA). The film specimens were heated from room temperature to 1,100℃ in air by using a heating rate of 10℃/min. Mechanical properties of neat PBS and PBS-composite thin-film were measured according to ASTM D882 by using universal testing machine (UTM) in tensile mode with gauge length of 50 mm and 10 mm width, the speed was 50 mm/min. To prepare thin-film samples for dielectric properties measurement, the films were cut into square-shape of 2cm x 2cm and Pt coated both side of the film in circle diameter of 1 cm to be used as electrode. The dielectric properties [dielectric constant (ε'), and loss tangent (tan δ ; ε"/ε')] of PBS/BST thin-film composite were determined by using an E4991A_RF impedance/material analyzer equipped with a 16453A dielectric material test fixture. Agilent Technologies, Inc., USA). The frequency-dependent dielectric properties were measured by using scan frequencies ranged from 10 MHz to 1 GHz. To study the temperature-dependent dielectric properties, the PBS-composite thin films were placed between two electrodes inside an Espec SU-261 temperature and humidity control chamber. First, the sample was heated from room temperature to 70℃ and then cooled down by 10℃ to reach -50℃. The data were collected every 5 min after temperature is decreased.

5.4 Results and Discussion

5.4.1 Poly(butylene succinate)/Barium Strontium Titanate composite Characterizations

5.4.1.1 Morphological Investigation

The dispersion state of barium strontium titanate (BST) powder in poly(butylene succinate) (PBS) matrix were morphologically characterized by SEM technique. The SEM images of the fracture surface of neat-PBS and PBS- composites with various BST contents are shown in Figure 5.2. It can be clearly seen that when BST content increases, the larger agglomeration started to form. However, the PBS-composites were consistent with 0-3 connectivity theory due to the possession of 0-dimensional barium strontium titanate powder dispersed in 3-dimentional poly(butylene succinate) matrix.

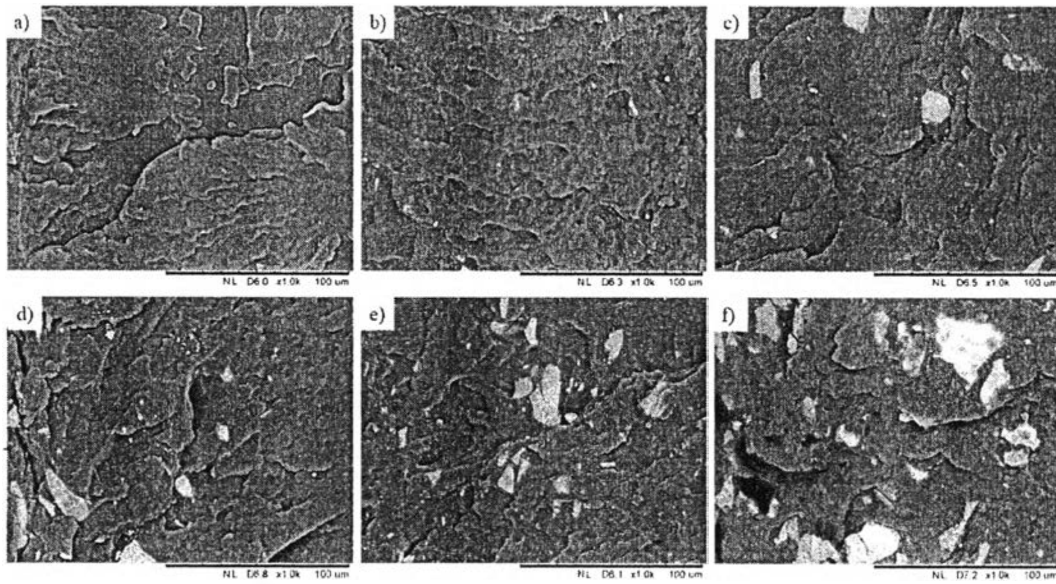

Figure 5.2 SEM images of PBS-composite in various composition of BST powder (a) 0 wt% (b) 10 wt% (c) 20 wt% (d) 30 wt% (e) 40 wt% (f) 50 wt%.

5.4.1.2 Thermal Properties

Table 5.1 and Figure- 5.3 show the thermal stability improvement and %residue of neat-PBS and PBS-composite thin-films. The result show the improvement of 5wt% and 10wt% degradation temperature as BST powder content increases as a result of the BST powder, inorganic compound, act as heat barrier at the beginning of thermal decomposition [7].

Table 5.1 Degradation temperature and %Residue of PBS-composite

PBS/BST	Degradation temperature		Residue (%)
	$T_{0.05}$	$T_{0.10}$	
100/0	268.50	284.67	0.00
90/10	276.17	292.17	6.87
70/30	277.83	293.83	21.07
50/50	287.67	308.33	47.66

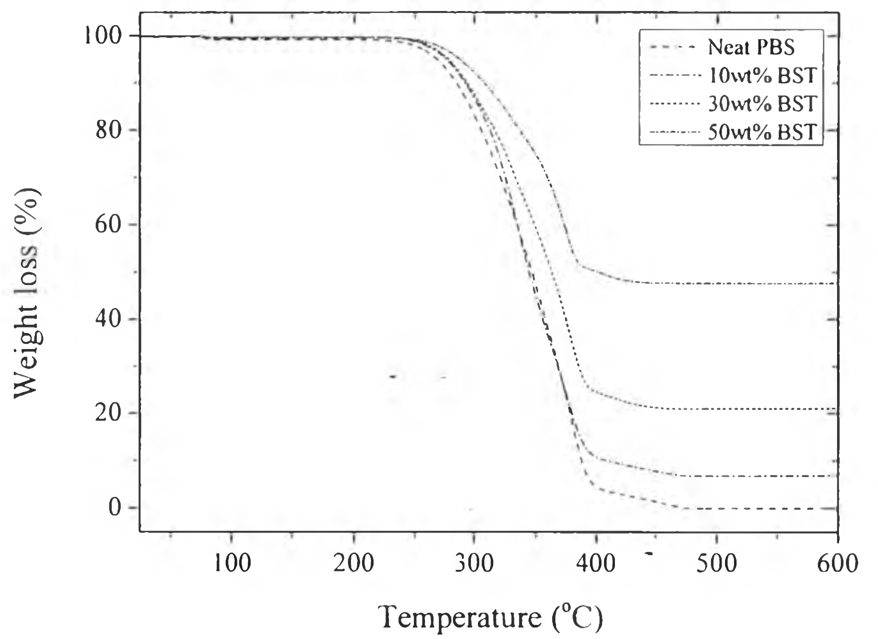

Figure 5.3 TGA curves of neat PBS and PBS-composite samples.

5.4.1.3 Mechanical Properties

The tensile strength and percentage strain at break of PBS/BST composite, as shown in Figure 5.4 and 5.5, decreases with increasing BST loadings. The more content of the filler, the less interaction between the filler surface and polymer matrix [8]. However, the PBS-composite show the improvement of tensile modulus (Figure 5.6) as a function of BST content. Likewise, the stress-strain curve, in Figure 5.7, show the increment of the slope. Which can be implied that, the material have become more brittle.

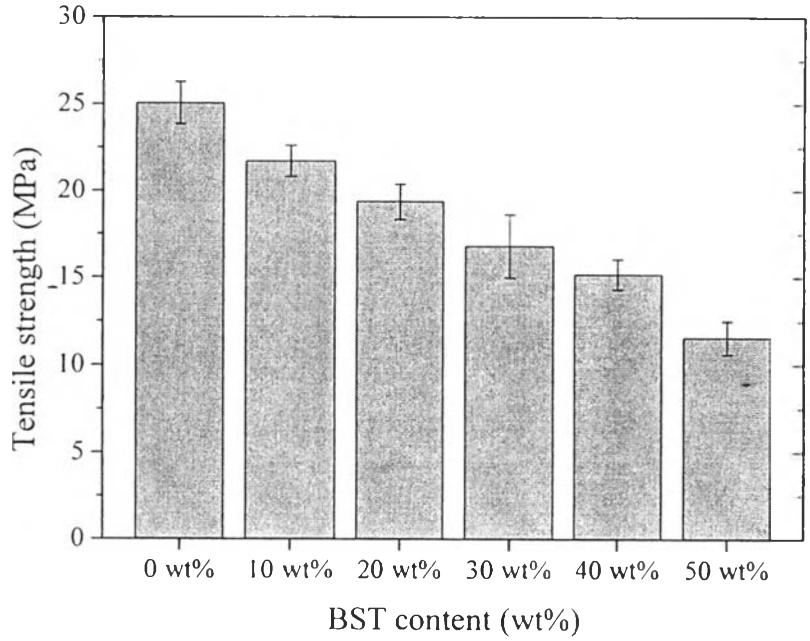

Figure 5.4 Tensile strength of PBS-composite.

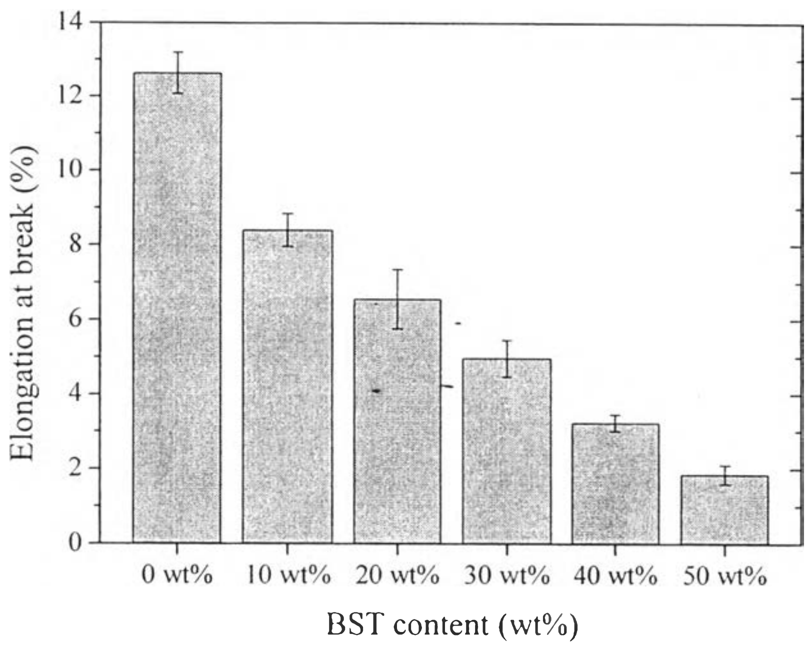

Figure 5.5 Percentage elongation at break of PBS-composite.

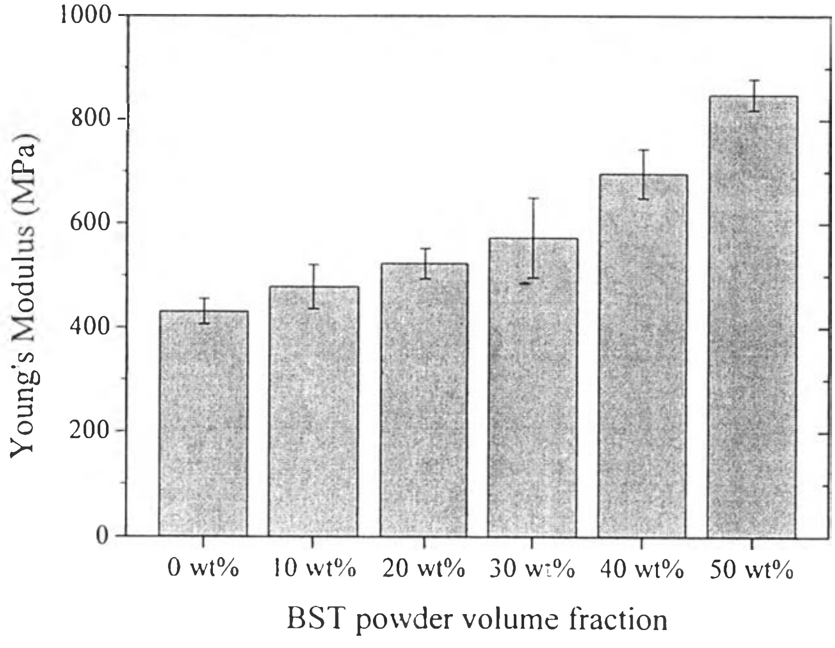

Figure 5.6 Young's modulus of PBS-composite.

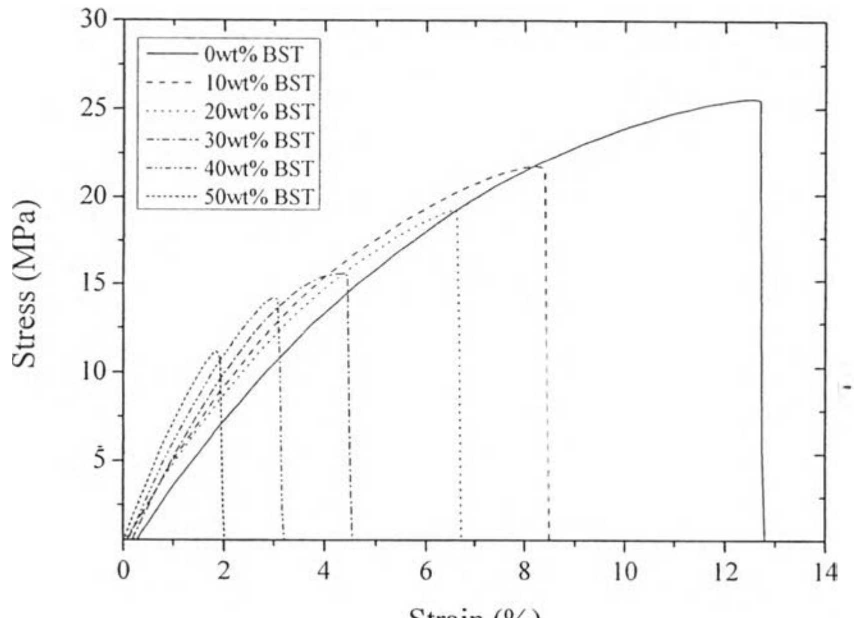

Figure 5.7 Stress-strain curve of PBS-composite.

5.4.1.4 Frequency-dependent Dielectric Properties

The frequency-dependent dielectric properties of PBS-composite thin-film are shown in Figure 5.8 and 5.9. The improvement of dielectric constant of PBS-composite was found to be a function of BST filler content. Due to BST has higher dielectric constant than that of PBS matrix. The frequency dependence of dielectric constant of PBS/BST composite measured at room temperature in the frequency ranging from 10^7 Hz to 10^9 Hz (Figure 5.9) show the higher dependency at higher content of BST in PBS-composite compare to that of neat-PBS, which has smallest dependency. It is the same manner as loss tangent, as shown in Figure 5.10. the highest loss tangent occurred at $2x10^7$ Hz which caused the steep reduction of dielectric constant.

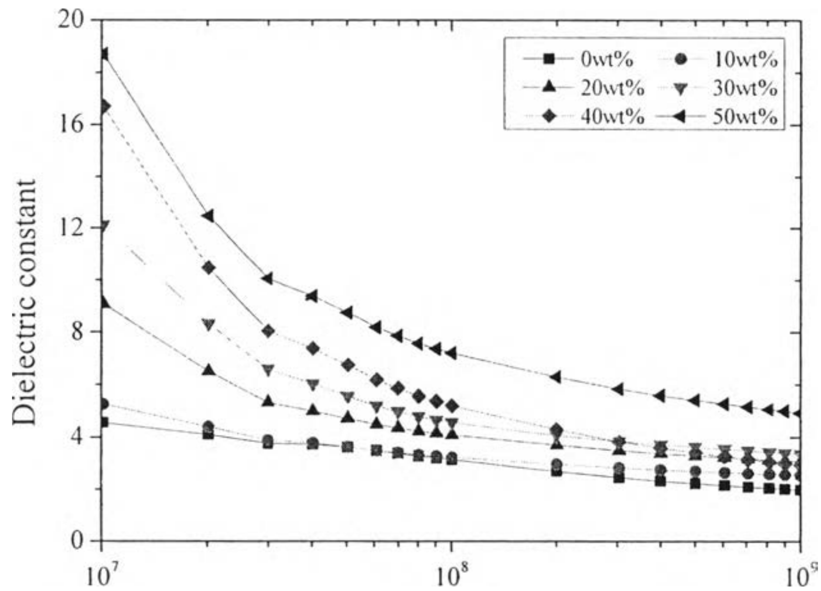

Figure 5.8 Frequency-dependent dielectric constant PBS-composite.

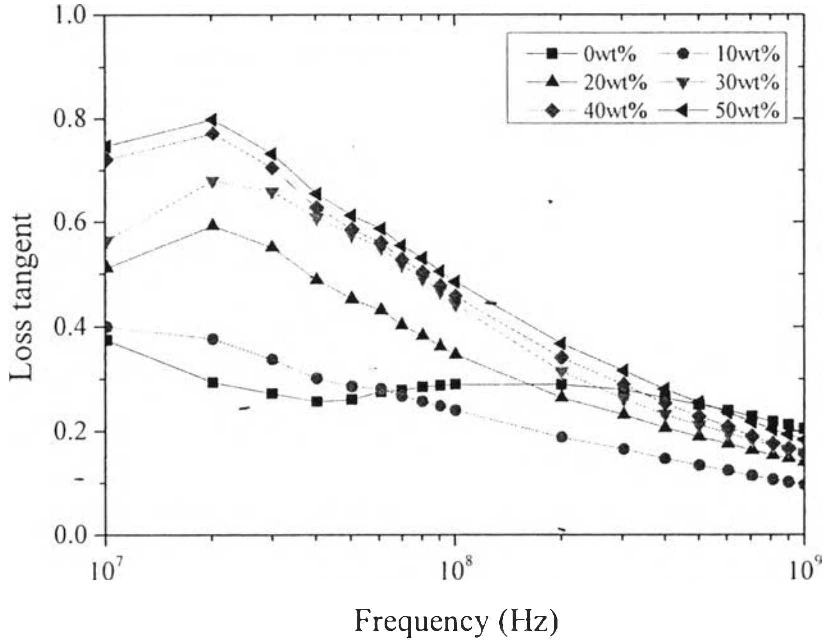

Figure 5.9 Frequency-dependent loss tangent PBS-composite.

5.4.1.5 Temperature-dependent Dielectric Properties

Figure 5.10 and 5.11 show the temperature-dependent dielectric constant and loss tangent measured at 10 MHz, respectively. The temperature variation of dielectric constant in Figure 5.11 was small at low content of BST powder. With increasing temperature, the polymer chain flexibility have been slightly enriched causing the polarization movement [9]. As increasing amount of BST content, the temperature variation of dielectric constant slightly increases (Figure 5.10). At temperature of 10℃ in loss tangent curve (Figure 5.11) gave the highest value of loss tangent, which exhibit the highest increment of dielectric constant.

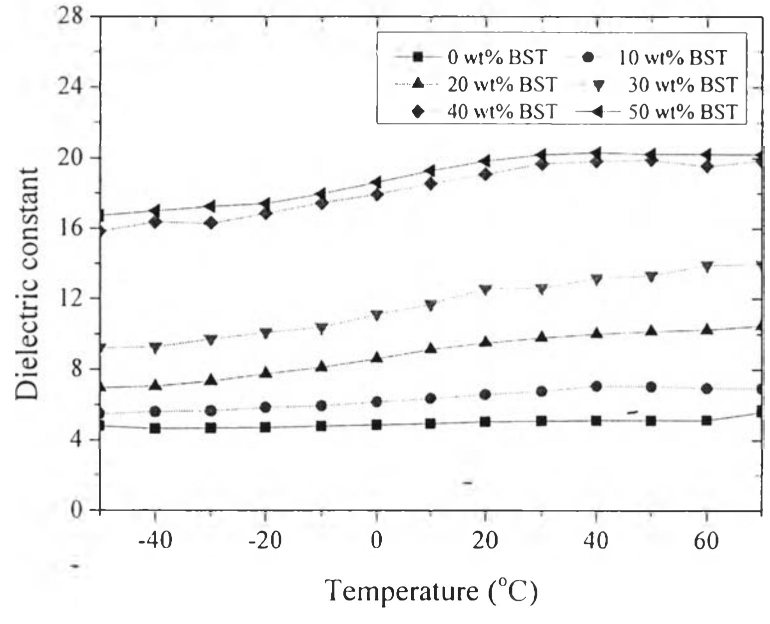

Figure 5.10 Temperature-dependent dielectric constant of PBS-composite.

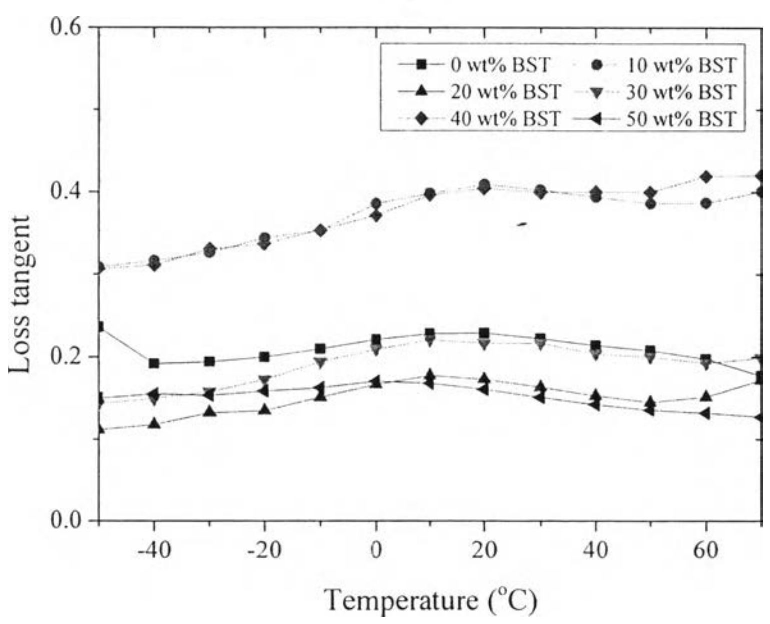

Figure 5.11 Temperature-dependent loss tangent of PBS-composite.

5.5 Conclusions

PBS/BST composite thin-films were prepared by using two-step method including solution mixing and compression molding. Their dispersion state showed the increasing agglomeration as BST filler content increases. The tensile strength and elongation at break were decreased as a function of BST filler content. The modulus and stress-strain curve showed the thin-film became more brittle. However, the dielectric properties of PBS/BST composite thin-film were increased as a function of BST filler content.

5.6 Acknowledgements

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5.7 References

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