CHAPTER V

EFFECT OF THE SURFACE MODIFICATIONS TO MICROWAVE DIELECTRIC PROPERTIES OF THE NOVEL COMPOSITES

5.1 Abstract

For microwave substrate application, the high dielectric constant and low loss tangent are required but from previous work, the polybenzoxazine – BST composites that were prepared by compression molding exhibited the high dielectric constant and loss tangent. The main cause of low loss tangent is the present of agglomerated BST filler in polymer matrix when ceramic volume fraction increases. In order to solve the incompatibility problem of the composite, the surface modification method was suggested. In this work, the surface of BST filler was treated with three different chemical agents such as 3-aminopropyl- trimethoxy silane, phthalocyanine and benzoxazine monomer. Then, study the surface morphology and microwave dielectric properties of the treated composites compare with untreated composites. It was found that at all of ceramic content, the treated composites showed that BST can disperse well in polymer matrix when compare with untreated composites and contribute to lower in loss tangent. For the dielectric constant, silane coupling agent is the best choice in three chemicals because it could improve the dielectric constant over than the others. While, the lower value in loss tangent were found in the composites of phthalocyanine and benzoxazine monomer treated BST powder.

Keyword: Polybenzoxazine, Barium strontium titanate, microwave dielectric properties, surface modification, agglomeration

5.2 Introduction

Nowadays, the passive electronic device, capacitor, technology plays an important role for the miniaturization products. These devices will require the excellence electrical performance, higher reliabilities, small size and improved designed options. Recently researches have studied the polymer-ceramic composites because these materials can combine ceramic's electrical properties and the mechanical flexibility, chemical stability, and processing possibility of polymers. In polymer-ceramic composites, polymer matrix possesses lower dielectric constant in comparison to ceramic particles. The dielectric properties of the composites are strongly influenced by the ceramic phase, including content, particle size, and distribution. In addition, it can be also affected by porosity and filler distribution. There are many research works which studied the dielectric properties of the polymer-ceramic composites with different type of polymer matrixes and ceramic filler. Barium Strontium Titanite (BST) is the one type of ferroelectric ceramic materials that was generally studied in the polymer-ceramic composites due to its high dielectric constant. For polymer matrix phase, thermosetting polymer such as polyimide, phenolic resin, epoxy and polybenzoxazine are widely used in telecommunicate electronic application because their higher thermal stability and low viscosity properties [1-3].

The incompatibility between the polymer and ceramic phases is the major problem which usually occurs in the composites in form of the ceramic agglomeration. Most of polymers have the hydrophobic surface while ceramics with residual hydroxyl group are the hydrophilic. To modify the properties of polymer-ceramic composites, many additives have been developed. Among these additives, coupling agent have obtained more interesting due to their special structure, which have two different functional groups, one is attracted to polymer and other one is attracted to ceramic surface. Coupling agents are usually used for inorganic fillers contained polymers to improve the adhesion between fillers and matrix. Many research reported that the uniform distribution of ceramic filler is the mainly factors which influences on the dielectric properties of the composites furthermore, the dielectric properties of the polymer matrix, the ceramic content and the porosity of the composites [4-6].

5.3 Experimental

5.3.1 Surface modification of BST Powder

- Surface Modification by Silane Coupling

Dissolve the 3-aminopropyl-trimethoxysilane 1 g. in water 5 ml: ethanol 95 ml solution then mixed that solution with BST powders 40 g. This suspension was ultrasonicated at room temperature for 10 min and stirred at 70°C for 1 h. The treated suspension was centrifuged and subsequently washed by ethanol and dried in a vacuum oven at 50°C. Finally, the coupling agent modified BST particles were obtained

- Surface Modification by Benzoxazine monomer

Dissolve 5wt% of aniline based benzoxazine monomer in THF. The solution was slowly added drop wise to stirring BST particle/THF slurry. Then the mixture was stirred for 1 h. and evaporated THF out at about 70°C. Lastly, treated BST was dried in a vacuum oven overnight in order to remove the residual solvent.

- Surface Modification by Phthalocyanine

Dissolve 0.1 wt% of phthalocyanine powder in DMAc solvent then added the solution into stirring BST particle/DMAc slurry. The mixture was then stirred for 1 h. and evaporated DMAc out at 200°C. After that the residual solvent was removed again by drying in a vacuum oven overnight.

5.3.2 Composite Preparation

The composite between polybenzoxazine based and BST ceramic ($Ba_{0.3}Sr_{0.7}TiO_3$) were prepared. Owing to the much difference between the densities of two substrate, then mix the benzoxazine monomer and BST powder with 30, 40, 50, 60, 70 and 80 wt% by melt mixing process to prevent the separation of 2 phases. After that, the mixtures was fabricated as composite specimens with the thickness of 1.2 mm. and 2.0 mm in diameter by compression molding with curing conditions which given in Table 5.1.

Table 5.1 Temperature profile for compression molding process

Temperature (°C)	Time (minute)	Applied load (150 kg.)
120	30	-
140	30	-
160	30	-
180	30	-
200	30	+
230	60	+

5.3.3 Characterizations

To measure and confirm the successful functional groups of the surface modification of BST powder Fourier transformation infrared spectrophotometer (NEXUS 670 FTIR) were used. All spectra were recorded with absorbance mode in the wave number range of 400-4000 cm^{-1} and 32 scans per resolution. For the dielectric properties of the treated composites as frequency dependence, the dielectric properties of the composites were measured at room temperature (25 °C) with an Agilent E4991A RF Impedance/Material Analyzer (Agilent Technologies Inc., USA) at frequency range of 1MHz – 1GHz and were investigated at -50 to 150°C for temperature dependant. Microstructure and surface morphology of BST powders and the composite were observed by a scanning electron microscope (SEM; HITACHI S-4800) at voltage of 15 kV. And the distribution of ceramic filler in the composites was observed by a scanning electron microscope (SEM; HITACHI S-4800) at voltage of 15 kV.

5.4 Results and Discussions

5.4.1 Characterization of polybenzoxazine-modified BST

5.4.1.1 Surface modification of BST powder

- BST powder treated with phathalocyanine

Figure 5.1 shows the FTIR spectra of the Phthalocyanine treated BST powder. It was found that at the region of 1596 cm^{-1} – 1562 cm^{-1} show the characteristic peak of the aromatic rings of the phthalocyanine. The peak at 1444 cm^{-1} refer to C=O stretching mode of the carbonate ion impurities (CO_3^{2-}) and the peak at 552 cm^{-1} attributes to the Ti-O stretching vibration of TiO_6 octahedral of the BST powder. There are no peaks that corresponding to the bond formation of C-Sr or C-Ba that mean the phthalocyanine did not form the bond on the surface of BST on the other hand, phatalocyanine just coated on the BST particles.

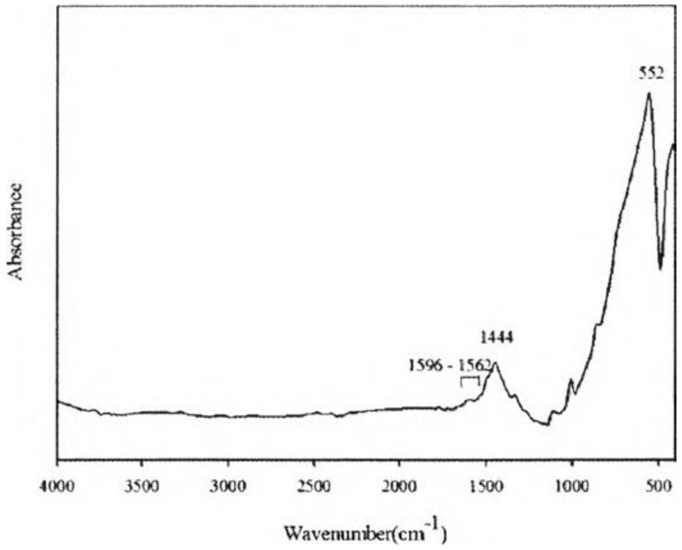

Figure 5.1 The FTIR spectra of BST treated with phthalocyanine.

- BST powder treated with silane coupling agent

The dielectric properties of the composites were improved by enhances the dispersion of BST filler on polybenzoxazine matrix. The surface was BST was chemically modified with 3-aminopropyl trimethoxy silane by taking advantage of hydroxyl groups (-OH group) which detected on the surface of BST powder. The IR spectra of 3-aminopropyl trimethoxy silane treated BST powder as shown in Figure 5.2.The absorption band at wave number of 855 cm^{-1} attributes to the characteristic of Si-O-Si unit from the hydrolysis of silane. At 1449 cm^{-1} of absorption band refer to C=O stretching mode of the carbonate ion impurities (CO_3^{2-}) and the peak at 559 cm^{-1} belong to the Ti-O stretching vibration of TiO_6 octahedral of the BST powder. From this result, it confirms that the silane coupling agent was hydrolyzed and reacted onto the surface of BST particles[7].

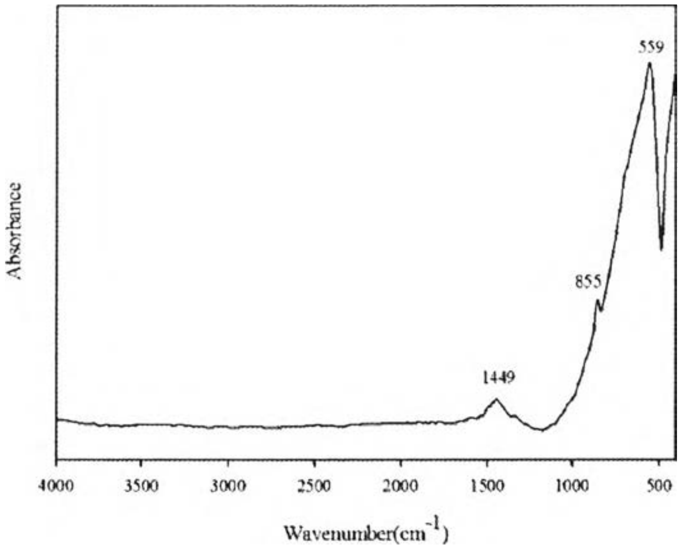

Figure 5.2 The FTIR spectra of BST treated with 3-aminopropyl trimethoxy silane.

- BST powder treated with aniline based benzoxazine monomer (BA-a)

The spectrum of BST powder coated 5 wt% BA-a monomer showed the absorption band at 1203 cm^{-1} which belong to asymmetric stretching mode, and at 1108 cm^{-1} corresponding to C-N-C stretching mode of the BA-a monomer. The IR peak at 1444 cm^{-1} refer to C=O stretching mode of the carbonate ion impurities (CO_3^{2-}) and at 552 cm^{-1} attributes to the Ti-O stretching vibration of TiO_6 octahedral of the BST powder as shown in Figure 5.3. It was indicated that the BST particles was already coated by BA-a monomer.

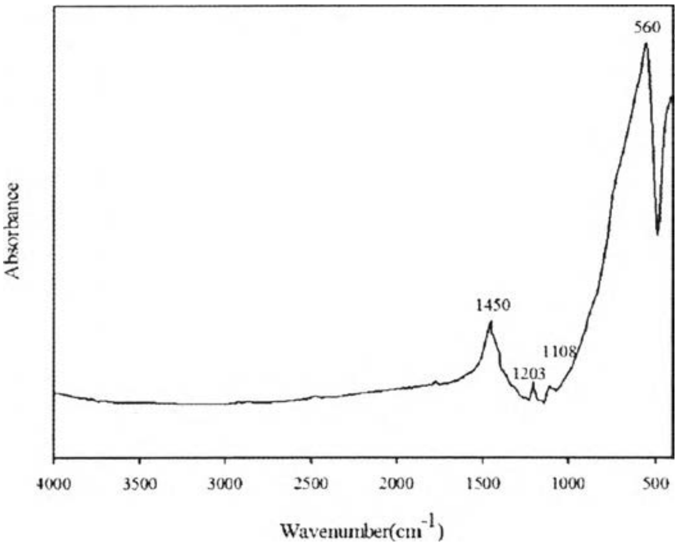

Figure 5.3 The FTIR spectra of BST treated with 5 wt% BA-a monomer.

5.4.1.2 Microstructure of PBA-a/treated BST composites and the effect of surface modification on BST particle distribution

The surface morphology of PBA-a/treated BST composites which used for study the effect of surface modification on BST particle distribution was shown at Figure 5.4 for 30 wt% and Figure 5.5 for 80 wt% (a)-(d) which is untreated-composites, silane coupling agent treated composite, phthalocyanine treated composite and BA-a monomer treated composite, respectively. From the result, it was shown that the dispersion of the treated BST in polymer matrix (at every filler volume fraction) is better than untreated BST. The composites that treated with phthalocyanine and treated with the BA-a monomer exhibited that the BST particles can disperse (de-agglomeration) better than the composites that treated with silane compound. These can explain in term of molecular structure because the main structure of the phthalocyanine and benzoxazine monomer consist of the aromatic rings (bulky group) so it related to the molecular packing efficiency decrease and obstructs the ceramic particle to come closer[8].

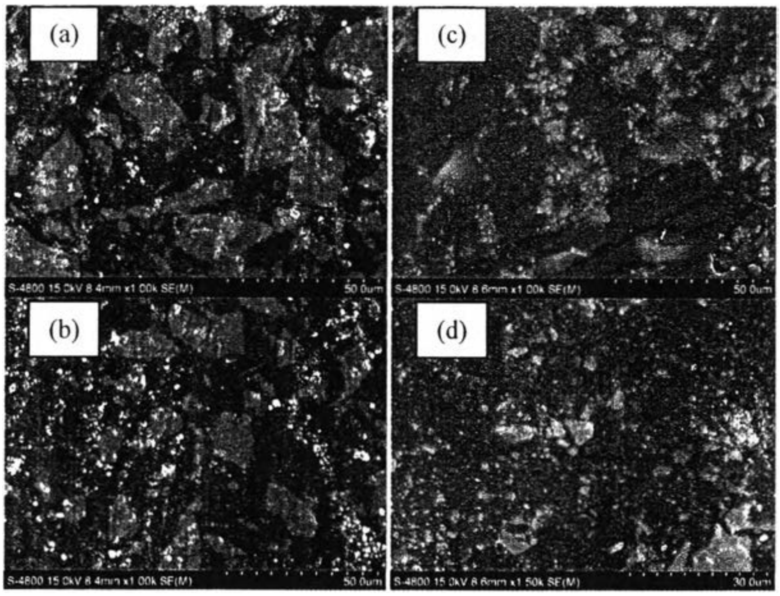

Figure 5.4 SEM micrographs of PBA-a/BST composite at 30 wt% of BST with (a) untreated BST, (b) silane treated BST, (c) phthalocyanine treated BST and (d) BA-a monomer treated BST.

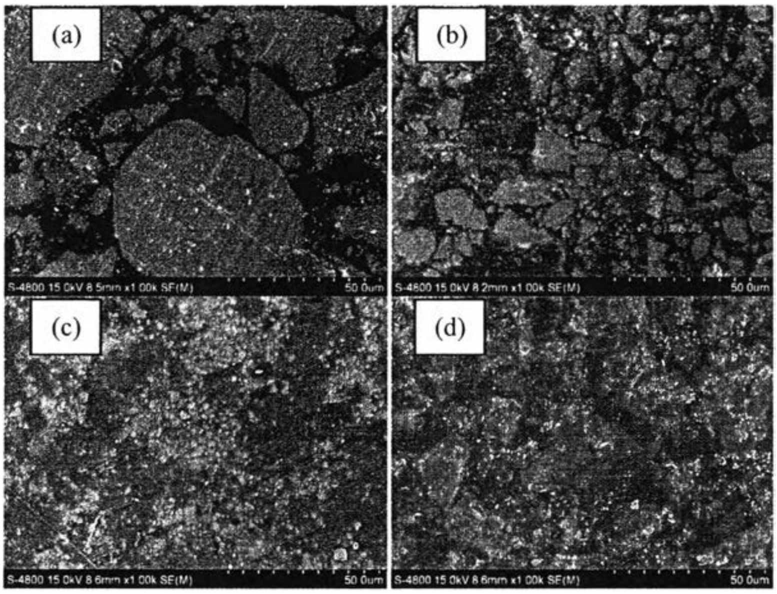

Figure 5.5 SEM micrographs of PBA-a/BST composite at 80 wt% of BST with (a) untreated BST, (b) silane treated BST, (c) phthalocyanine treated BST and (d) BA-a monomer treated BST.

5.4.1.3 Microwave dielectric properties of the untreated and treated surface of the PBA-a/BST composites

- Effect of frequency dependent

For the frequency dependence, it was measured at 1 MHz to 1 GHz and room temperature. The dielectric constants with difference surface treatment agent at various ceramic loading from 30 wt% to 80 wt% were observed at Figure 5.6 - 5.11, respectively. The result from Figure 5.6 - 5.11 shows that the silane compound can improve the dielectric constant of the composites compared with other surface treatment agents. Because silane coupling agent act as molecular bridges between polymer and ceramic filler, lead to the covalent chemical bonds across the interface of polymer and ceramic phase so, the polarizability could be enhanced and also increase dielectric constant. In case of loss tangent, Figure 5.12 – 5.17, phthalocyanine and the benzoxazine monomer could help BST filler prevent agglomerate which link with the SEM image. Moreover, improve an adhesion that leads to the decreasing of loss tangent of the composite. The lower in dielectric loss was due to the dispersion enhancement of phthalocyanine and benzoxazine monomer, consequent in lower of porosity in composites which could be generated from the segregation of difference surfaces between polymer and ceramic [9].

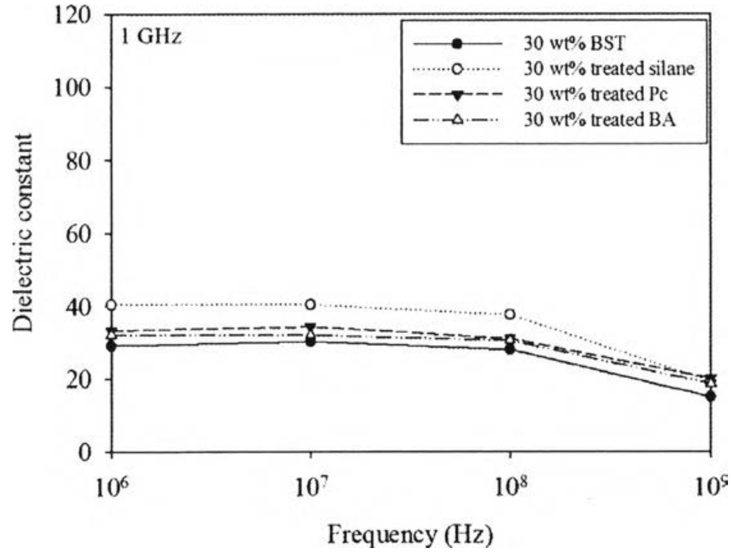

Figure 5.6 Frequency dependence of dielectric constant for the 30 wt% BST composites with different surface treatment agent.

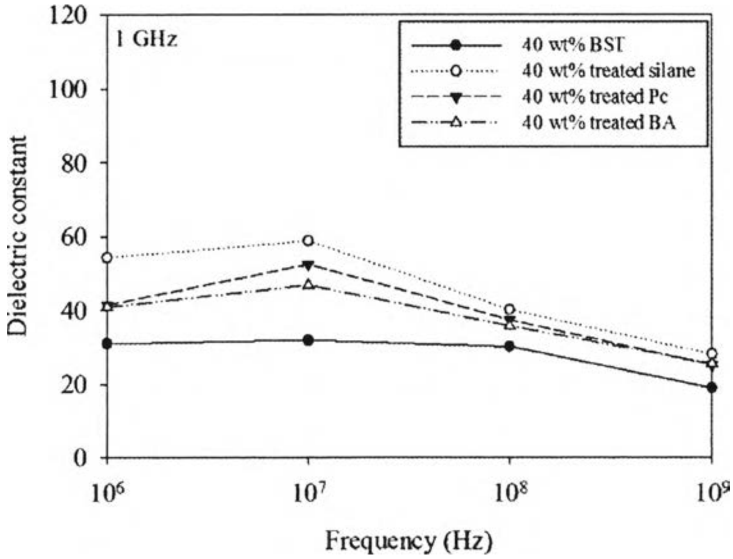

Figure 5.7 Frequency dependence of dielectric constant for the 40 wt% BST composites with different surface treatment agent.

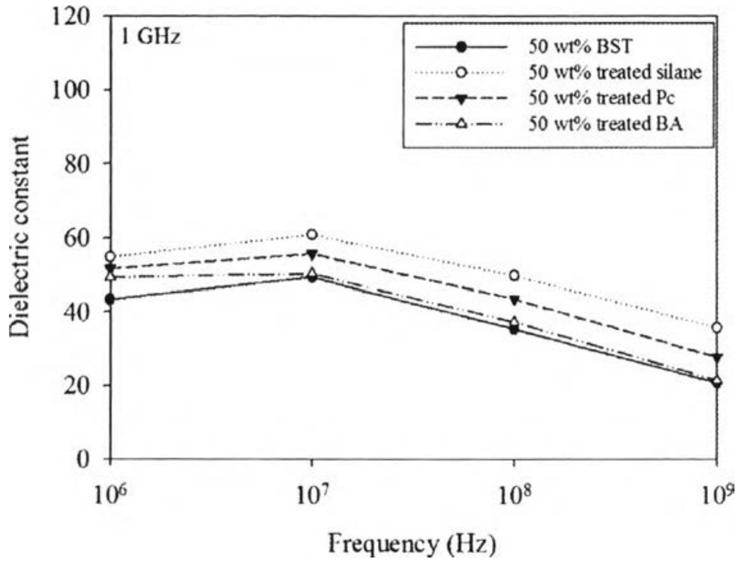

Figure 5.8 Frequency dependence of dielectric constant for the 50 wt% BST composites with different surface treatment agent.

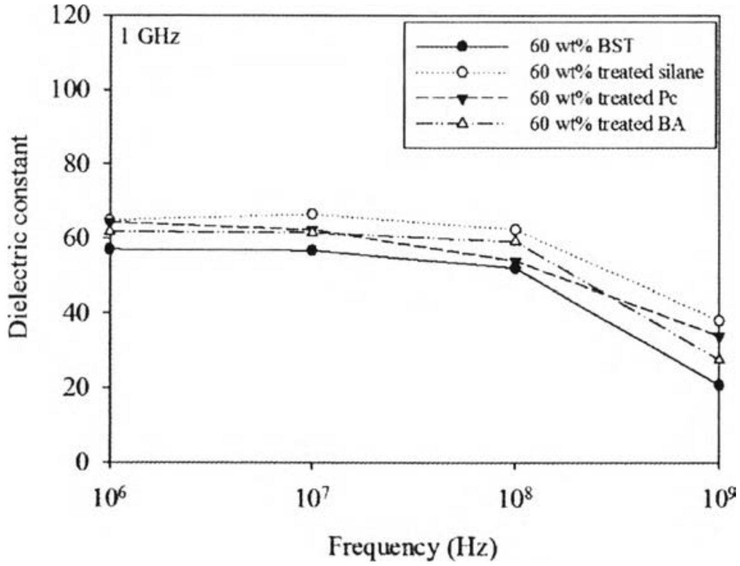

Figure 5.9 Frequency dependence of dielectric constant for the 60 wt% BST composites with different surface treatment agent.

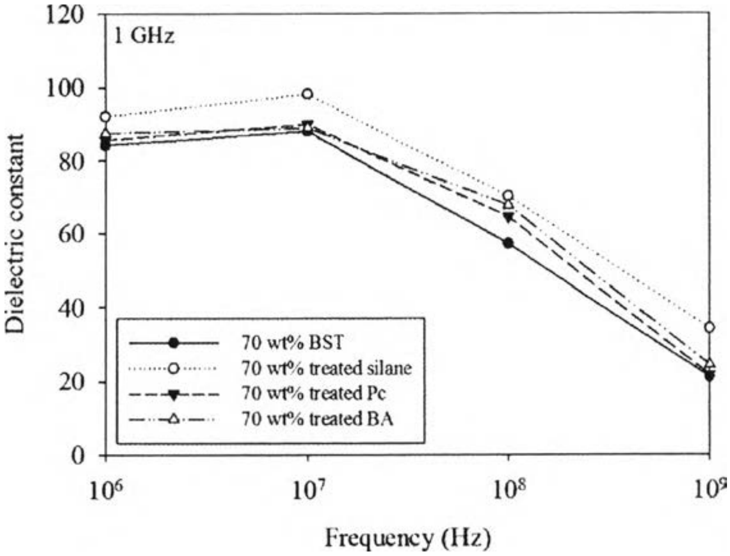

Figure 5.10 Frequency dependence of dielectric constant for the 70 wt% BST composites with different surface treatment agent.

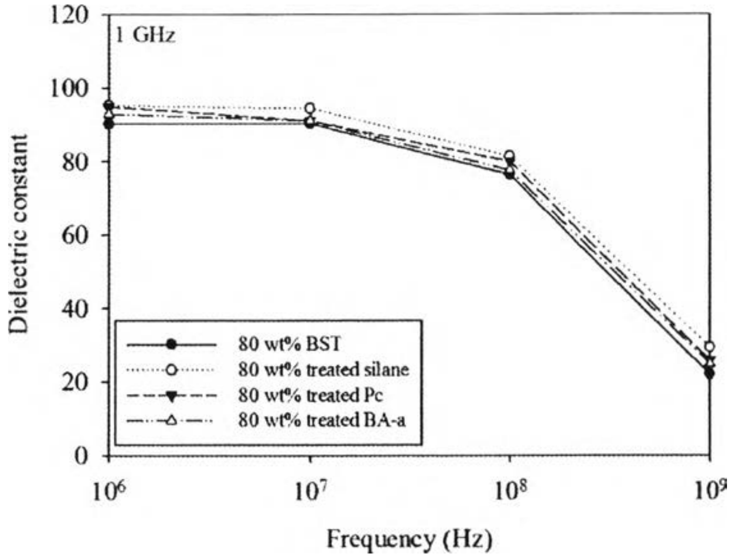

Figure 5.11 Frequency dependence of dielectric constant for the 80 wt% BST composites with different surface treatment agent.

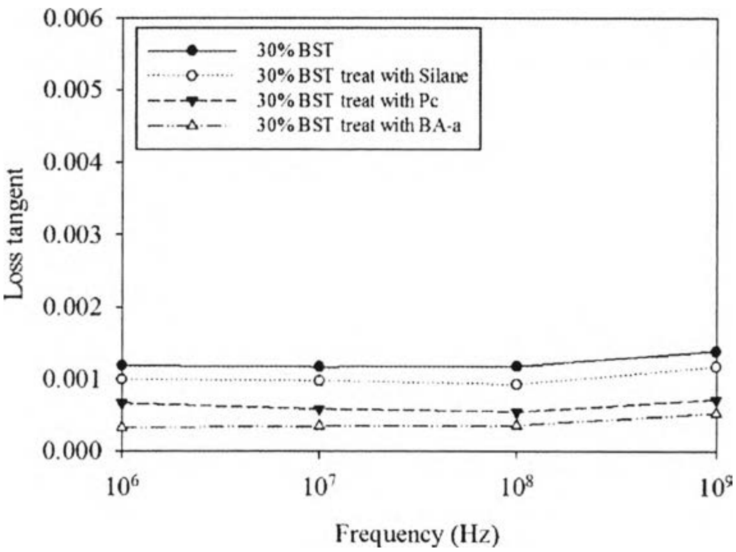

Figure 5.12 Frequency dependence of loss tangent for the 30 wt% BST composites with different surface treatment agent.

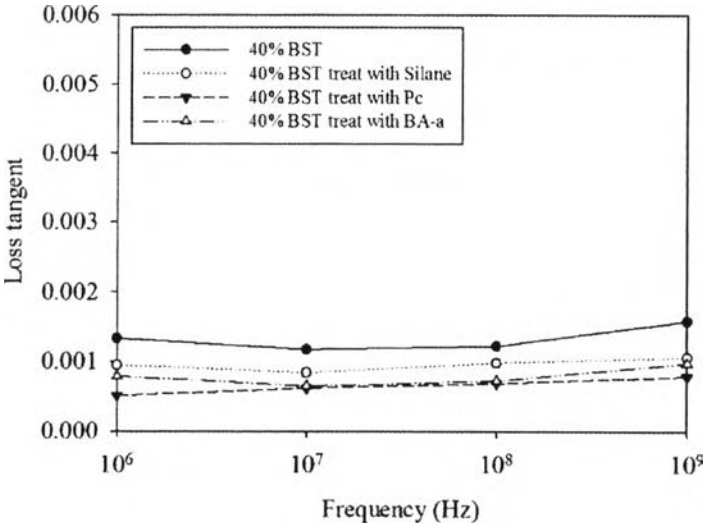

Figure 5.13 Frequency dependence of loss tangent for the 40 wt% BST composites with different surface treatment agent.

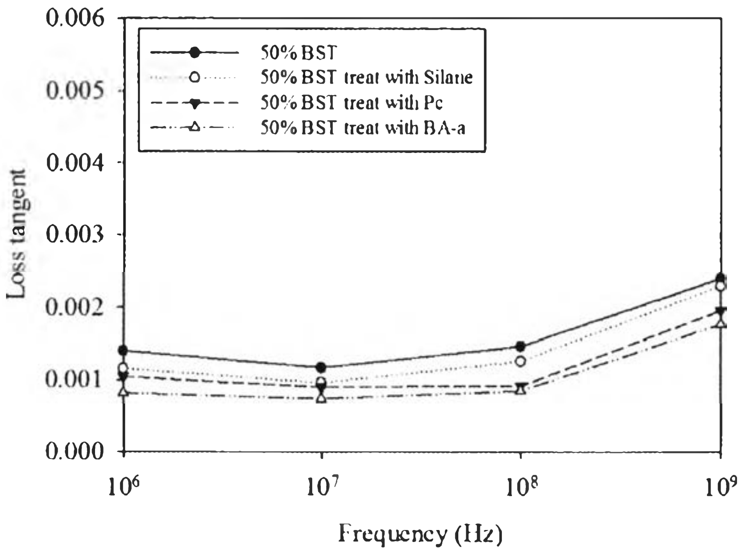

Figure 5.14 Frequency dependence of loss tangent for the 50 wt% BST composites with different surface treatment agent.

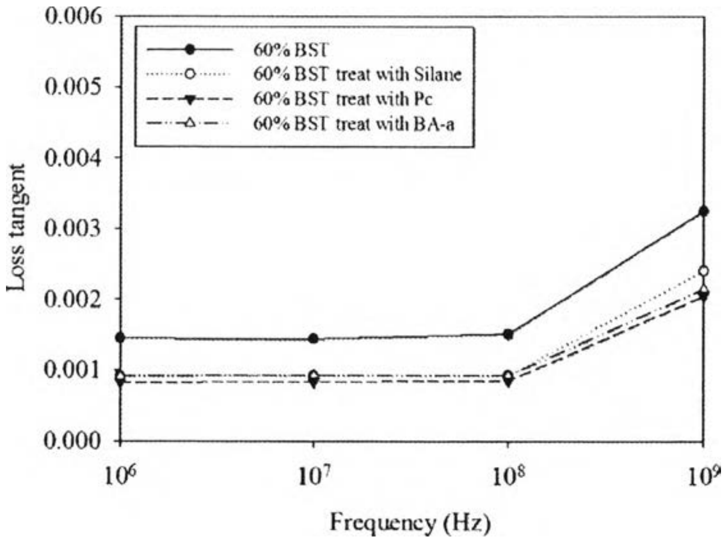

Figure 5.15 Frequency dependence of loss tangent for the 60 wt% BST composites with different surface treatment agent.

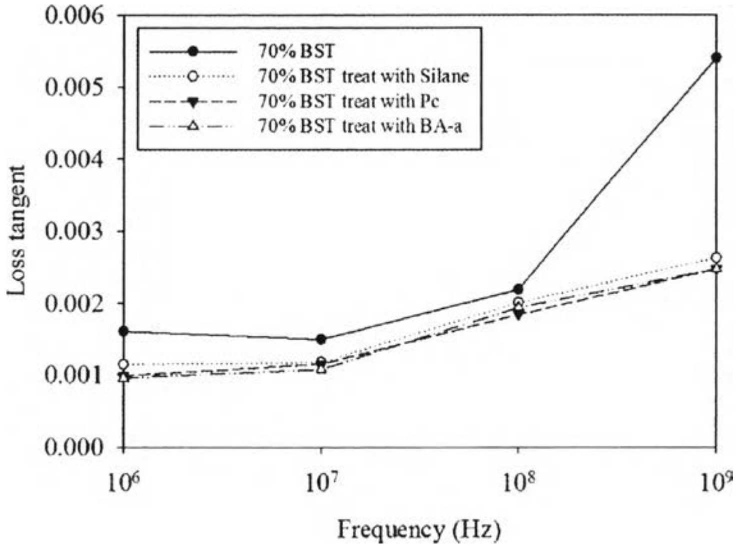

Figure 5.16 Frequency dependence of loss tangent for the 70 wt% BST composites with different surface treatment agent.

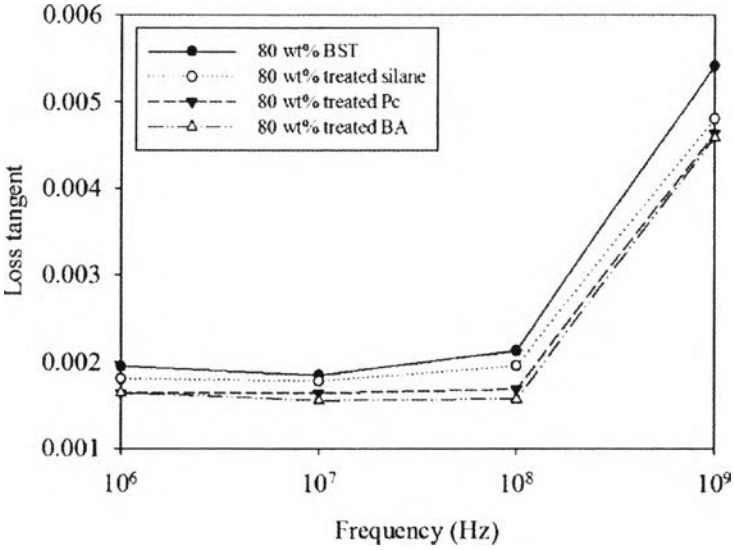

Figure 5.17 Frequency dependence of loss tangent for the 80 wt% BST composites with different surface treatment agent.

- Effect of temperature dependent

In case of temperature dependence of dielectric constant and loss tangent for the composites at various ceramic content from 30 wt% - 80wt% and with different surface treatment agent at 1GHz as shown in Figure 5.18 - 5.29., respectively. The results showed the constant of dielectric constant with temperature increase while did not show the fluctuation in loss tangent too. It refer to the surface treatment agents did not separate or change to the void that make the loss tangent was constant. This can conclude that for high frequency application (1 GHz), the temperature did not affect to the dielectric properties of the treated composites in -50 °C to 150 °C ranges or it means that the surface treatment agent did not separate or change to the void when temperature increase[10].

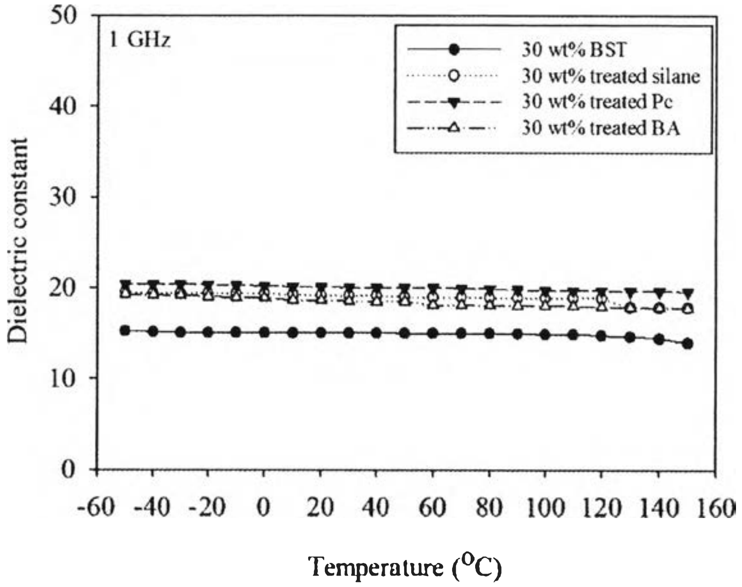

Figure 5.18 Temperature dependence of dielectric constant for the 30 wt% BST composites with different surface treatment agent.

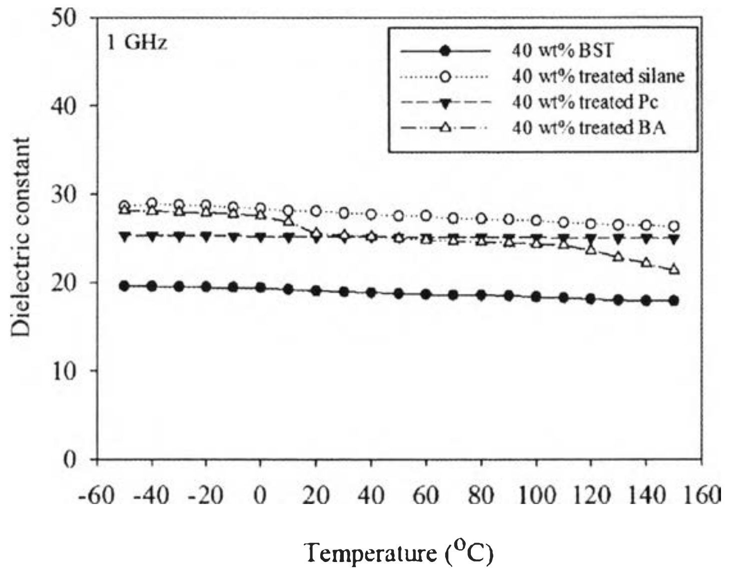

Figure 5.19 Temperature dependence of dielectric constant for the 40 wt% BST composites with different surface treatment agent.

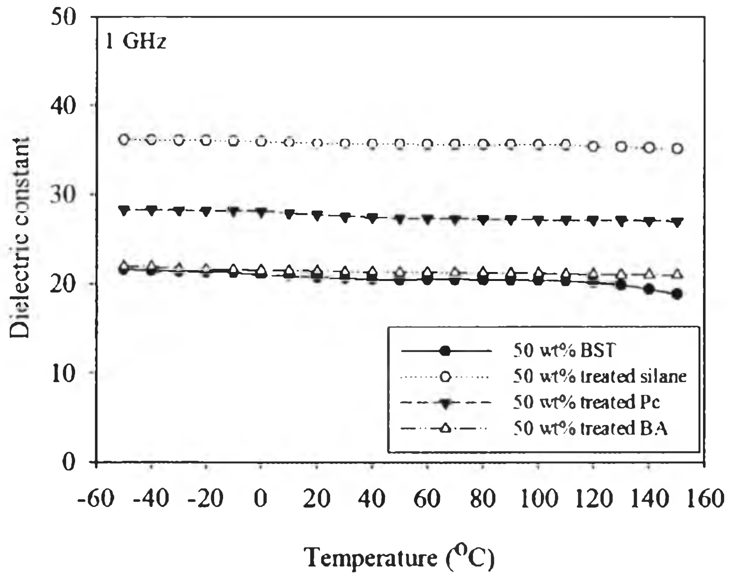

Figure 5.20 Temperature dependence of dielectric constant for the 50 wt% BST composites with different surface treatment agent.

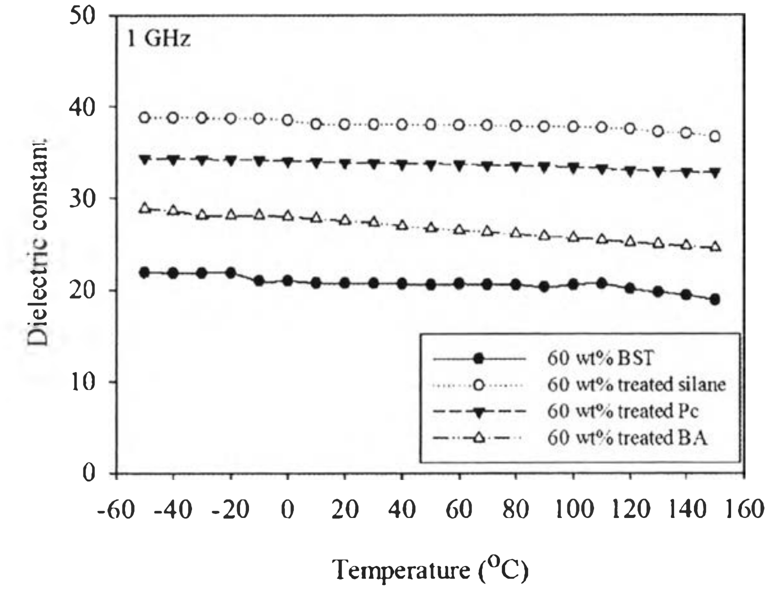

Figure 5.21 Temperature dependence of dielectric constant for the 60 wt% BST composites with different surface treatment agent.

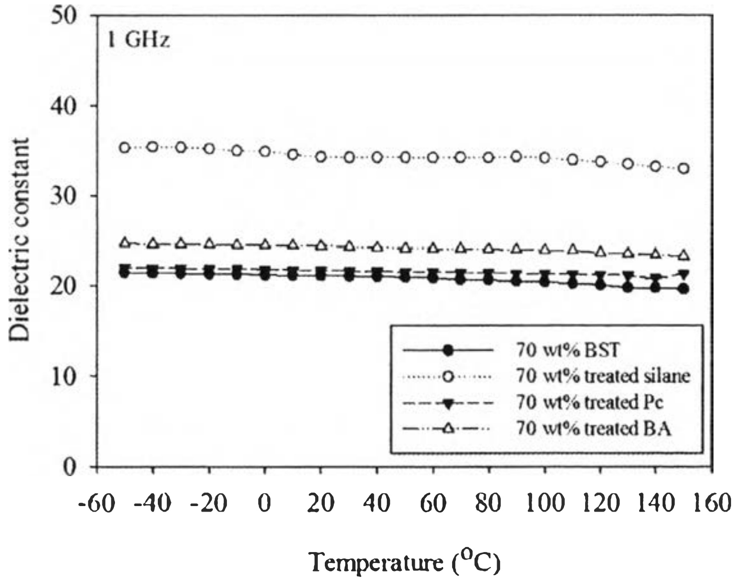

Figure 5.22 Temperature dependence of dielectric constant for the 70 wt% BST composites with different surface treatment agent.

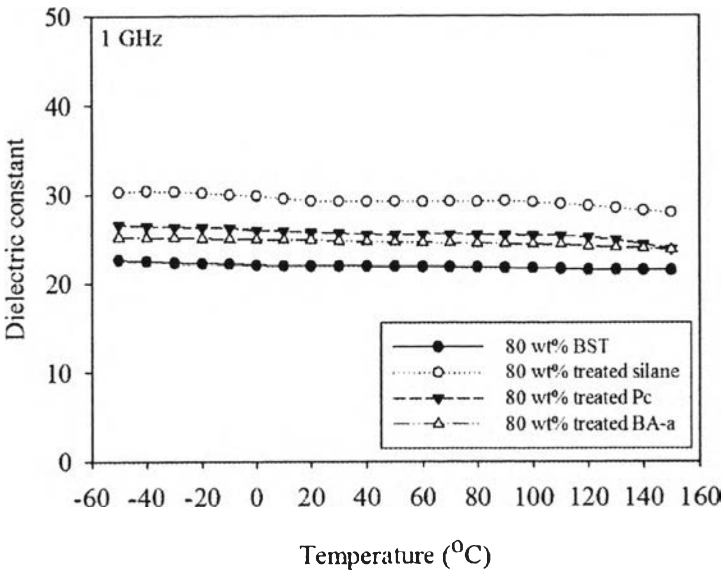

Figure 5.23 Temperature dependence of dielectric constant for the 80 wt% BST composites with different surface treatment agent.

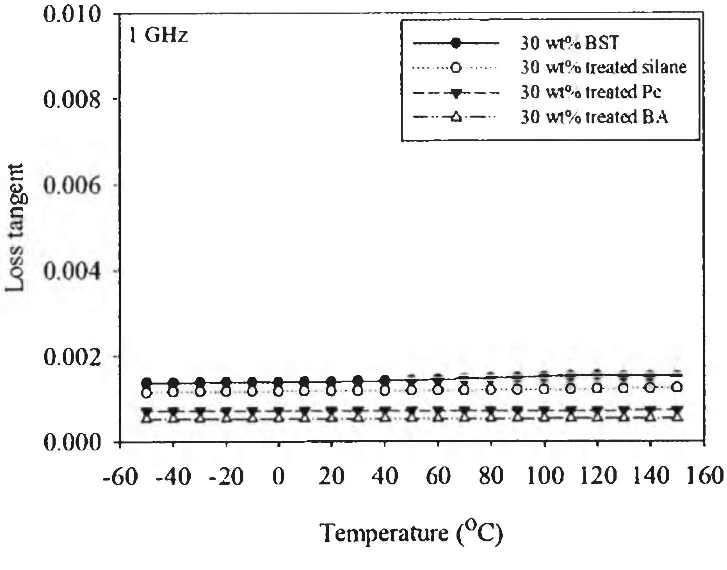

Figure 5.24 Temperature dependence of loss tangent for the 30 wt% BST composites with different surface treatment agent.

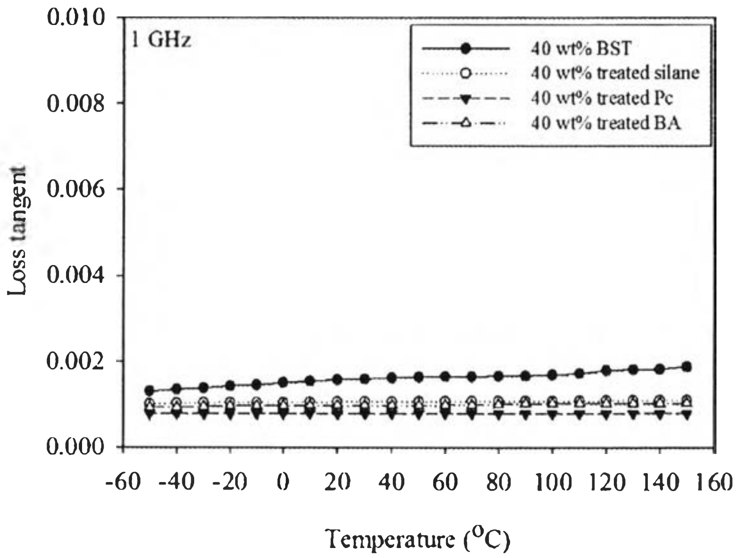

Figure 5.25 Temperature dependence of loss tangent for the 40 wt% BST composites with different surface treatment agent.

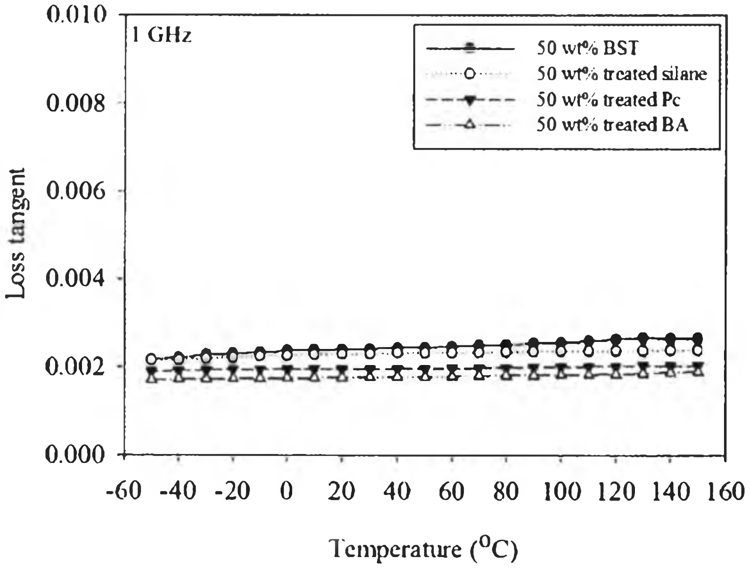

Figure 5.26 Temperature dependence of loss tangent for the 50 wt% BST composites with different surface treatment agent.

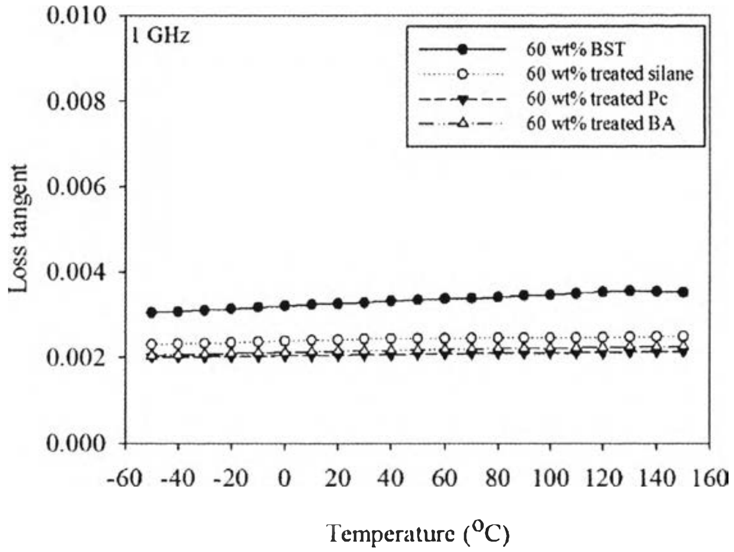

Figure 5.27 Temperature dependence of loss tangent for the 60 wt% BST composites with different surface treatment agent.

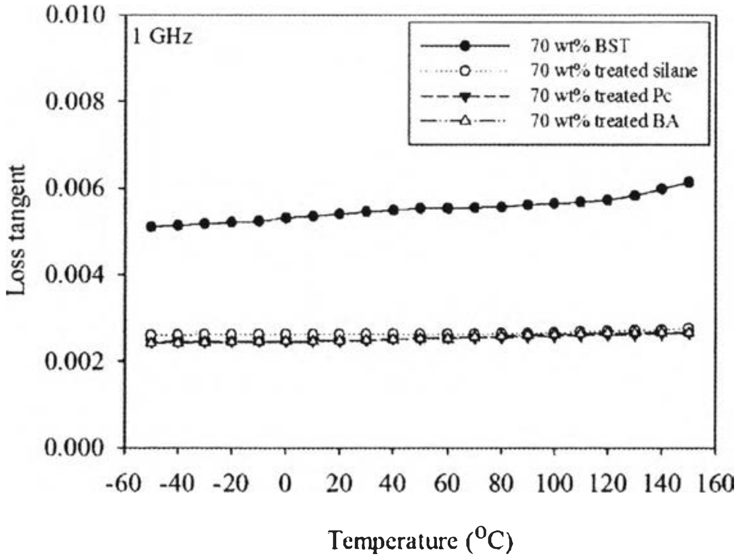

Figure 5.28 Temperature dependence of loss tangent for the 70 wt% BST composites with different surface treatment agent.

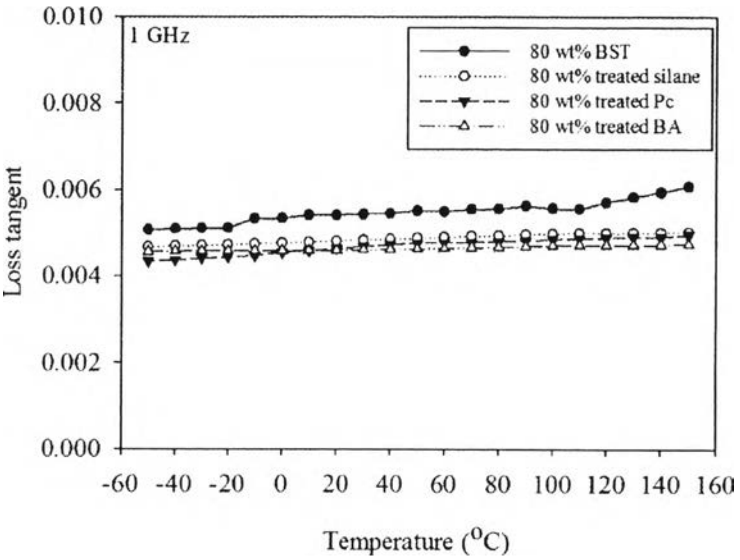

Figure 5.29 Temperature dependence of loss tangent for the 80 wt% BST composites with different surface treatment agent.

5.5 Conclusions

Surface modification process is the one method which can solve the incompatibility problem between the ceramic filler and polymer matrix in composites and result to higher dielectric constant. The silane coupling agent, phthalocyanine and benzoxazine monomer were used for surface modification method in this work. It was found that the Polybenzoxazine-treated BST composites show the better dispersion of the treated BST ceramic on polymer matrix compare with untreated BST composites. For the dielectric properties, silane coupling agent could improve the dielectric constant to highest value compared with other surface treatment agents due to the covalent bonds which occur between interface of polymer and ceramic phase that lead to total polarizability of the composites increase. While, phthalocyanine and benzoxazine monomer consist of aromatic rings (bulky group) in their structure that could prevent the BST come closer and contribute to BST de-agglomerate in polymer matrix resulting in lower dielectric loss. Additionally, the dielectric constant and loss tangent of the modified composite were independence on frequency and temperature. In conclusion, the surface treatment of BST filler in polybenzoxazine composite improves dielectric property at microwave frequencies.

5.6 Acknowledgements

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