

CHAPTER V
DIELECTRIC PROPERTIES OF DURABLE POLYBENZOXAZINES
COMPOSITES IN THE MICROWAVE FREQUENCY REGION

5.1 Abstract

High performance thermosetting resins made of high molecular weight polybenzoxazines, for electronic applications, were produced in order to eliminate brittleness as a major shortcoming of usual monomeric benzoxazines. methylenedianiline (BA-mda)- and hexamethylenediamine (BA-hda)-based polybenzoxazines were prepared via the solvent method. The two different diamine-based polybenzoxazines were investigated for dielectric behaviors in the microwave frequencies. Dielectric characteristics of the samples were observed in the frequency range of 300 MHz to 1 GHz, from -50 °C to 150 °C. The results showed that the relative permittivity (ϵ') and loss tangent ($\tan \delta$) of poly(BA-mda) were 4.57 and 0.022, respectively, which were higher than that of poly(BA-hda) ($\epsilon' = 3.04$ and $\tan \delta = 0.008$) measured at room temperature (1 GHz). With the exceptional dielectric properties including thermal characteristics, poly(BA-mda) was further developed by combining with BST to uplift the dielectric properties. The composites between BA-mda and barium strontium titanate, $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$, (BST) fillers were studied as a function of the ceramic content and surface modification. It was found that by adding 60 wt.% of silane modified BST, the dielectric constant and loss tangent were 8.16 and 0.03, respectively. In addition, the dielectric properties of poly(BA-mda) composites were nearly stable with variations of temperature and frequency, indicating temperature and frequency independence.

Keyword: High molecular weight polybenzoxazine, barium strontium titanate (BST); dielectric materials; microwave frequency

5.2 Introduction

Dielectric materials operated at high frequency operation have been expanded to modern microelectronics and electrical products. The materials used must have attractive properties such as moderate relative permittivity, low loss tangent, and good mechanical properties [1-2]. To obtain these properties, polymer/ceramic composites have been considered to be potential candidates for integration into electronic devices. With the recent progress, high performance polybenzoxazine/BST composites were successfully prepared and proposed for being used in capacitor applications at low frequency. Diamine-based polybenzoxazine/BaTiO₃ composites with 0-3 connectivity were studied the dielectric properties in the frequency range of 1 kHz to 10 MHz. The dielectric constant and loss tangent of the composite with 70 wt.% of BST were 13.8 and 0.013, respectively [3]. Krueson *et. al.* later developed the material by introducing fluorine- and amine-based polybenzoxazine as polymer matrices and doped barium titanate with strontium. Thus the Curie temperature was shifted to a lower temperature obtaining a higher dielectric constant at room temperature. This research revealed the improvement in dielectric properties of the composites. At 80 wt.% of BST loading, the dielectric constant and loss tangent were 40 and 0.120, respectively (1 kHz) [4]. Although polybenzoxazine thermosets have shown a number of appealing properties including high glass transition temperature, good thermal stability, excellent mechanical properties, near zero shrinkage, and low water absorption. Their application in some research areas has been limited due to the brittle nature of short molecular weight polybenzoxazines [5]. Various alternatives have been proposed to minimize this problem. It is well-known that polybenzoxazines can be prepared in a variety of ways by varying the phenol or amine groups, thus producing substantial molecular design flexibility. Therefore, the main chain benzoxazine polymer (MCBP) approach is also one of the preferred ways to overcome the shortcoming of the traditional short molecular weight polybenzoxazine and to improve the processing capability [6]. Dielectric behaviors of high molecular weight polybenzoxazine composites, applied for high frequency applications have not been reported to date. As a result, in this work, a series of high molecular weight methylenedianiline-based (BA-mda) and

hexamethylenediamine-based benzoxazine (BA-hda) polybenzoxazines were firstly studied for dielectric behaviors at microwave frequency with a wide range of temperatures. The effect of the molecular structure of the polybenzoxazines using two diamines—one aliphatic (hexamethylenediamine) and—one aromatic (methylenedianiline) on dielectric characteristics was described. Furthermore, the suitable polymer matrix was used for composite fabrications. For increasing dielectric constant, nanoparticle-barium strontium titanate ($\text{Ba}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$) was introduced into polymer matrix at various contents. To enhance the compatibility between polymer and ceramic, the surface of BST powder was also modified by using 3-aminopropyl-trimethoxysilane and polymer matrix based. The dielectric properties under temperature and frequency variations of composites on the amount of BST loading were investigated and discussed. The theoretical models have been calculated and proposed for predicting the dielectric constant of the polymer-ceramic composite.

5.3 Experimental

5.3.1 Synthesis of Methylenedianiline- (BA-mdm) and Hexamethylenediamine-Based (BA-hda) Benzoxazine Precursors

To Synthesize BA-mdm precursor through the solvent method, mdm (40.0 mmol, 7.93 g), bisphenol-A (40.0 mmol, 9.13 g) and paraformaldehyde (172 mmol, 5.15 g) were added into 250 ml round-bottom flask with 100 mL of chloroform as the solvent. The reaction was carried out under reflux at 100°C for 5 h. The obtained mixture was filtered and sequentially washed with 0.5 N NaHCO_3 aqueous solution (200 mL). To eliminate water, the sample solution was dried with anhydrous sodium sulfate for one night. After evaporation, the white crystal benzoxazine precursors were solid at room temperature. The synthesized precursors were ground into a fine powder and taken for material characterizations. Preparation of BA-hda used the same approach, substituting hda in the place of mdm.

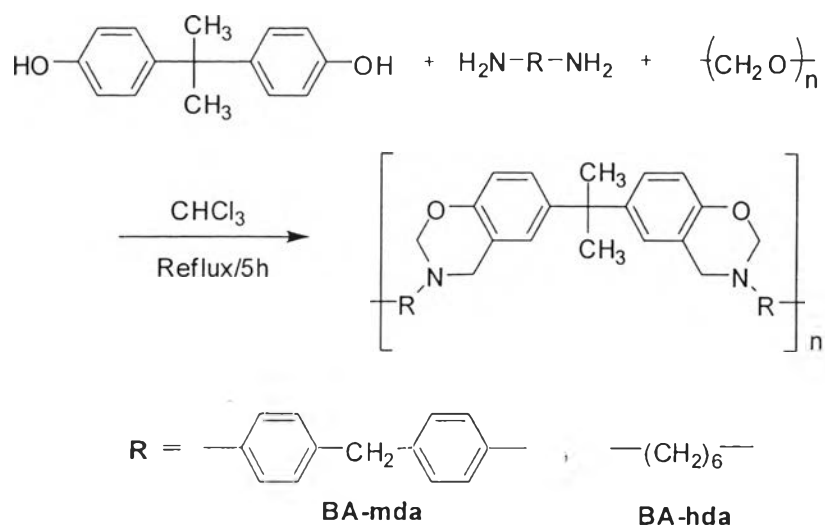


Figure 5.1 Chemical route for synthesis of methylenedianiline- (BA-mda) and hexamethylenediamine-based (BA-hda) benzoxazine precursors [6]

5.3.2 Preparation of poly(BA-mda) and poly(BA-hda) specimens

The BA-mda precursors (~2 g) were dissolved in 3 g of dimethylformamide. Firstly, the mixture was heated to 100 °C and vigorously stirred until becoming a homogeneous solution. The solution was then poured into an aluminium mold. To avoid bubbles being trapped inside the specimen, the temperature was gradually increased up to 200°C. After the curing process, the fully cured specimen gave the transparent dark brown and was used for characterizations. The preparation of the BA-hda specimen was performed in the same way.

5.3.3 Poly(BA-mda) Composite Preparation

The fabrication of composites was prepared by dissolving BA-mda in dimethylformamide. The mixture was vigorously stirred until obtaining homogeneous solution. Then BST powders at desirable amount (30, 40, 50, and 60 wt.% of BST) were added and followed by curing process as mention in 5.3.2.

5.3.4 Surface Modification by BA-mda Benzoxazine Precursor Surface

To modify BST by BA-mda precursor, The 5 wt.% of BA-mda was dissolved in THF. The prepared solution was slowly added dropwise to the stirring

BST particle/THF slurry system. Then the mixture was continuously stirred for 1 h. and evaporated THF out at 70°C. Lastly, BA-mda treated BST was dried in a vacuum oven overnight in order to remove the residual solvent.

5.3.5 Characterizations and testing

The proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$) was used to confirm molecular structure of polybenzoxazine precursors. The spectra were obtained on a Varian Mercury NMR spectrometer operated at 400.00 MHz by using deuterated chloroform (CDCl_3) as the solvent to which the chemical shifts (δ) were given. The functional groups related to structure of the materials were also investigated by using a Nicolet Nexus 670 fourier transform infrared spectrophotometer (FTIR). All FTIR spectra were obtained in a spectral range of $4000\text{-}400\text{ cm}^{-1}$ as a function of time with 64 scans at a resolution of 2 cm^{-1} . The KBr pellet technique was applied in the preparation of sample powder. The samples prepared were sufficiently thin with optical thickness small enough according to Beer-Lambert's law. The curing profile of benzoxazine precursors was carried out using a Perkin-Elmer DSC 7 instrument. The sample was first heated from 30°C to 300°C and cooled down at a rate of $5^\circ\text{C}/\text{min}$ under a N_2 atmosphere with a flow rate of $25\text{ ml}/\text{min}$. Glass transition temperature (T_g) of polybenzoxazine based was measured under tension mode by GABO EPLEXOR 100 N operated at 1 Hz and a strain value of 0.1% were applied. The temperature was scanned from 25°C to 250°C with a heating rate of $2^\circ\text{C}/\text{min}$ under N_2 atmosphere with flow rate of $100\text{ ml}/\text{min}$. The TG-DTA curves were collected using a Perkin-Elmer Pyris Diamond TG/DTA instrument. The sample was loaded $\sim 5\text{ mg}$ on the alumina pan and heated from 30°C to 900°C at a heating rate of $10^\circ\text{C}/\text{min}$ under N_2 flow of $100\text{ mL}/\text{min}$. The true density of benzoxazine precursor were measured by pycnometer (Quantachrome, Ultrapycnometer 1000) under helium purge at pressure of 20 psi. Relative density of materials (polymer and polymer-composites) was measured in order to observe the existence of void by following the test method A of ASTM D 792-00. The dimension of samples was $20\text{ mm} \times 5\text{ mm} \times 2\text{ mm}$. Analytical balance with density kit consists of Balance SARTORIUS research RC210S and kit SARTORIUS YDK201. Dielectric properties [dielectric constant (ϵ'), and loss tangent ($\tan \delta$;

ϵ''/ϵ'] of poly(BA-mda) and poly(BA-hda) specimens were determined by using an E4991A RF impedance/material analyzer equipped with a 16453A dielectric material test fixture, Agilent Technologies, Inc., USA). The scan frequencies ranged from 300 MHz to 1 GHz. The prepared sample was placed inside a Espec SU-261 temperature chamber (variable temperature oven) and temperature was controlled from -50 °C to 150 °C. First, the sample was heated from room temperature to 150 °C and then cooled down by 10 °C increment until reaching -50 °C. During the temperature ramp down, data collection was delayed for 2 min. after each step in order to increase the accuracy of the dielectric measurement. Microstructure of the composites was examined using a scanning electron microscope (SEM; HITACHI S-4800) at voltage of 15 kV. The surface of specimens was coated with platinum under vacuum before observation to make them electrically conductive. Atomic force modulate mode (AFM) was used to measure Young's modulus and hardness of each region of copolymer which can be referred to the distribution of urethane content in benzoxazine phase. In this mode, at 10 μm of scan size and 0.2 Hz of scan rate were set so as to analyze those parameters of the materials.

5.4 Results and Discussions

5.4.1 Benzoxazine Precursors and Polymers Characterizations

5.4.1.1 Nuclear Magnetic Resonance Spectroscopy (NMR) Analysis

The structures of the synthesized polybenzoxazines precursors were characterized by ^1H NMR, and FTIR techniques to identify the formation of high molecular weight polybenzoxazine precursors.

The ^1H NMR spectrum of BA-mds can be seen in Fig. 5.2. The aromatic protons are found at 6.60–7.25 ppm. The characteristic peaks, assignable to methylene ($\text{O}-\text{CH}_2-\text{N}$) and methylene of oxazine ($\text{Ar}-\text{CH}_2-\text{N}$), appear at 5.24 and at 4.50 ppm, respectively. Moreover, the methyl proton of bisphenol-A and methylene proton of mda are observed at 1.52 and 3.79 ppm, respectively.

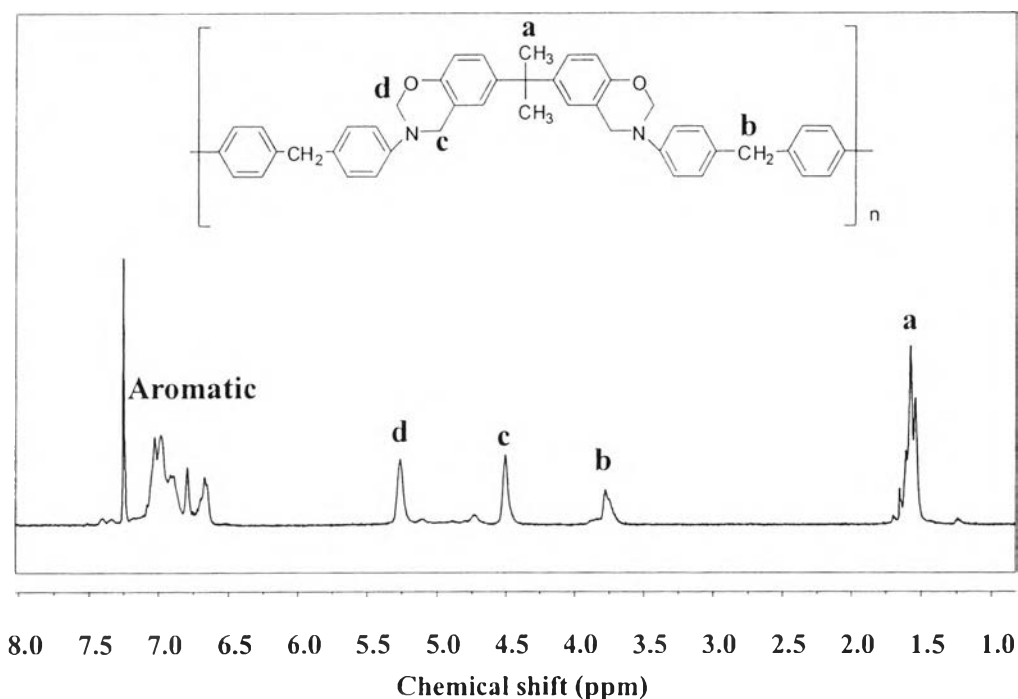


Figure 5.2 The ^1H -NMR spectra of methylenedianiline-(BA-mds) based polybenzoxazines.

The characterized molecular structure of BA-hda by ^1H NMR spectrum as shown in Fig. 5.3, the characteristic peaks assignable to methylene ($\text{O}-\text{CH}_2-\text{N}$) and methylene ($\text{Ar}-\text{CH}_2-\text{N}$) of oxazine ring are observed at 4.81 and at 3.92

ppm, respectively. Additionally, the methyl proton of bisphenol-A appears at 1.58 and the methylene proton of hda is observed at 2.70 and 1.34 ppm. The appearance of chemical shifts strongly confirms the formation of the precursors [6].

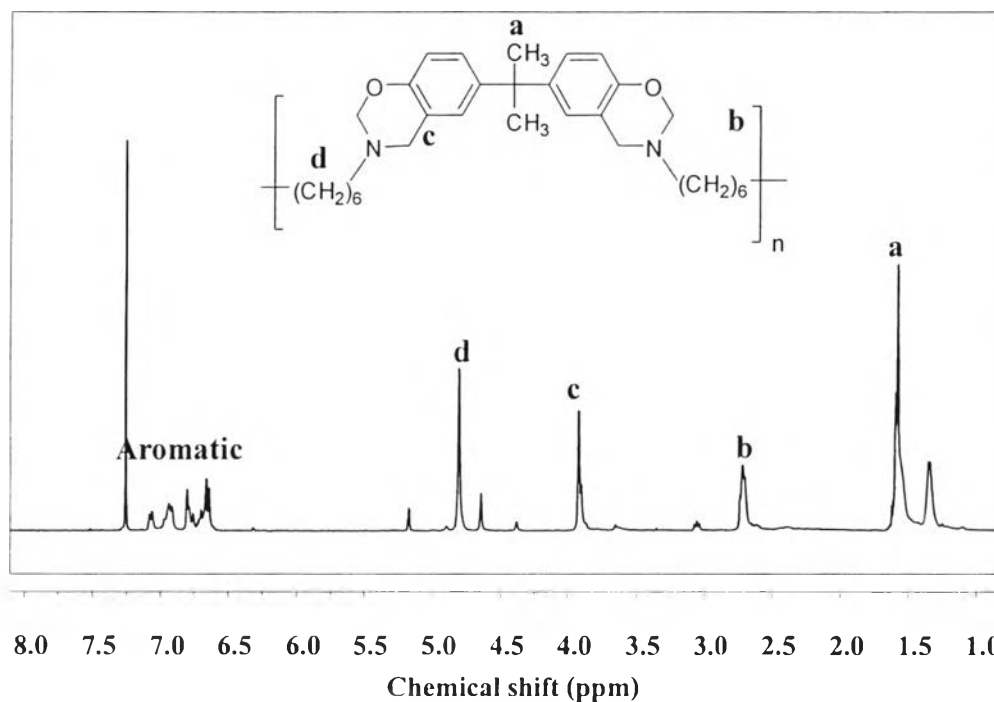


Figure 5.3 The ¹H-NMR spectra of hexamethylenediamine-based (BA-hda) polybenzoxazines.

5.4.1.2 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

The FTIR spectra of methylenedianiline-(BA-*mda*) and hexamethylenediamine-based (BA-*hda*) benzoxazines precursors are shown in Fig. 5.4 and 5.5, respectively. Asymmetric stretching of C–O–C (1234 cm^{-1}), asymmetric stretching of C–N–C ($1180\text{--}1187\text{ cm}^{-1}$), and CH₂ wagging of oxazine ($1325\text{--}1328\text{ cm}^{-1}$) are found. In addition, the characteristic absorptions, which are subject to trisubstituted benzene ring at $1502\text{--}1511\text{ cm}^{-1}$ and out of plane bending vibrations of C–H at $937\text{--}943\text{ cm}^{-1}$ are observed. These absorption bands demonstrate that the precursors containing the benzoxazine structure in the backbone have been acquired

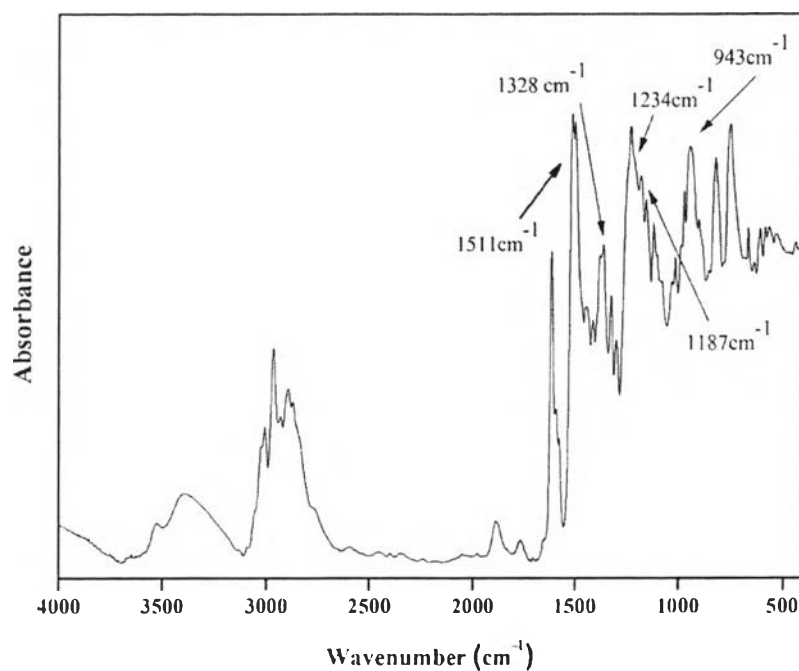


Figure 5.4 The FTIR spectra of methylenedianiline-(BA-mda) based polybenzoxazines.

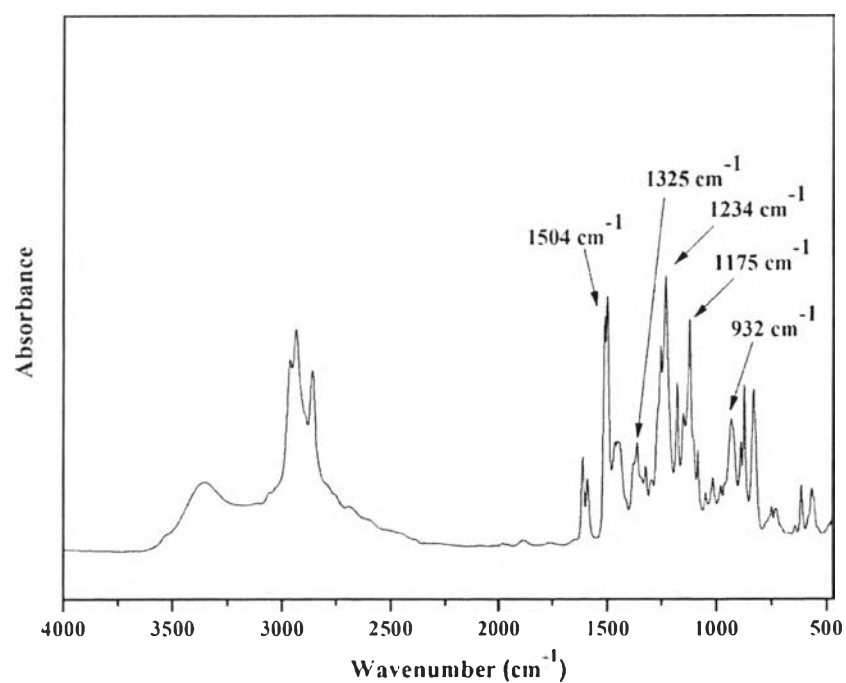


Figure 5.5 The FTIR spectra of hexamethylenediamine-based (BA-hda) polybenzoxazines.

5.4.1.3 Differential Scanning Calorimetry (DSC) Analyses

The DSC diagrams of BA-mda and BA-hda as precursors are shown in Figure 5.6. The exothermic onsets are related to the ring-opening of monomers and the formation of phenolic hydroxyl group in polybenzoxazine network. The onsets of high molecular weight precursor, BA-mda and BA-hda exhibit at 204°C and 198°C. In addition, exothermic peak temperatures of them are presented at 237°C and 232°C, respectively. A single exothermic peak of the curing reaction suggests that the reaction of both BA-mda and BA-hda monomers form a network structure simultaneously at the same temperature range.

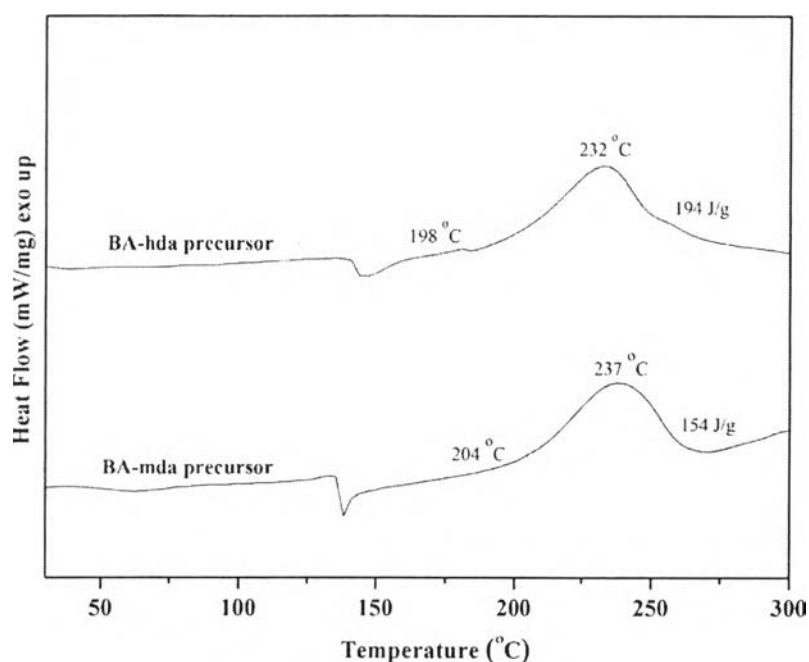


Figure 5.6 DSC patterns of methylenediamine (BA-mda)-and hexamethylenediamine-based (BA-hda) polybenzoxazines precursors.

5.4.1.4 Microwave Dielectric Properties Measurements

The high molecular weight poly(BA-mda) and poly (BA-hda) specimens were investigated for dielectric characteristics in the frequency range of 300 MHz to 1 GHz under temperature variation ranging from -50 °C to 150 °C. The dielectric properties of poly (BA-mda) are shown in Fig. 5.7.

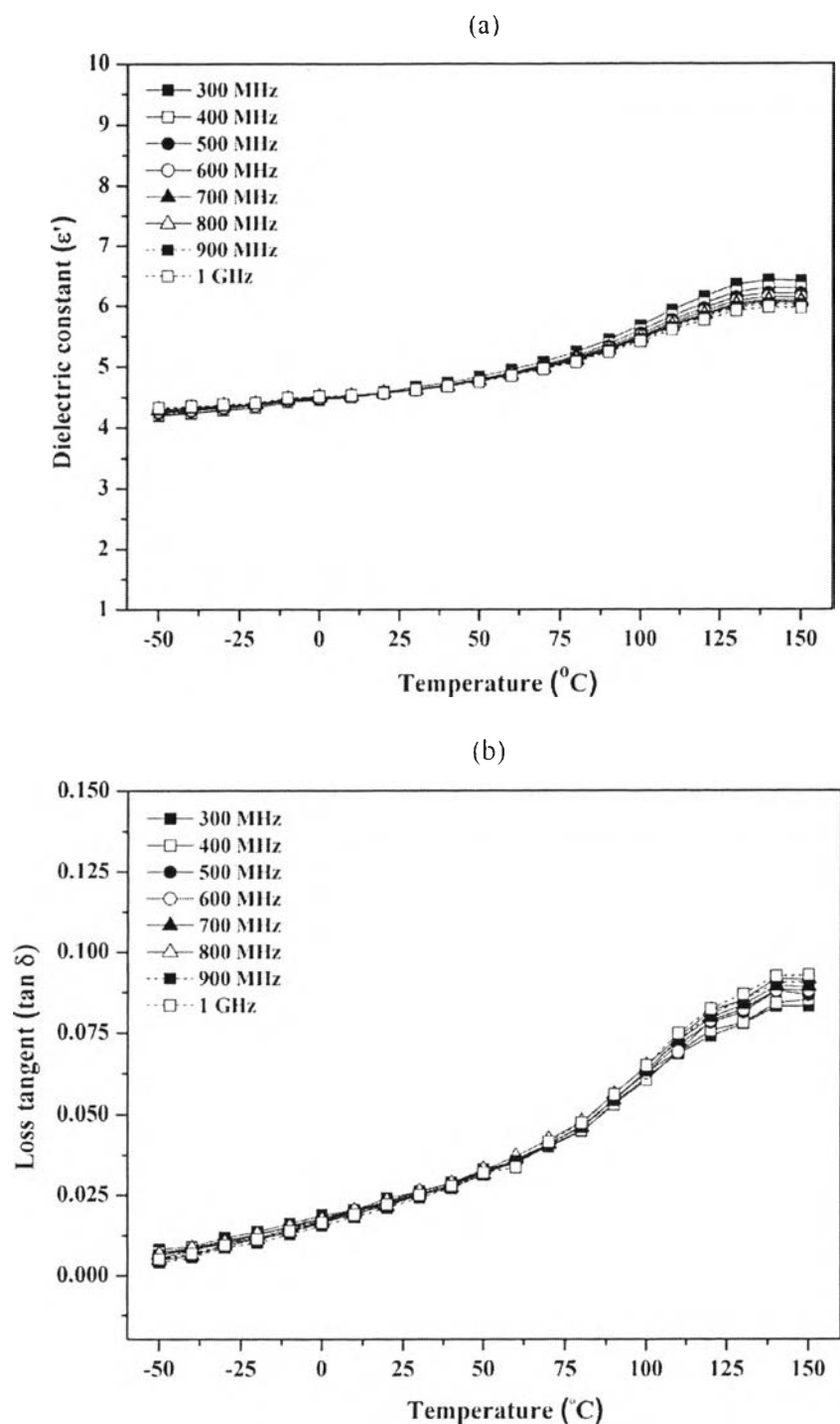


Figure 5.7 Temperature and frequency dependence of a) dielectric constant and b) dielectric loss tangent of aniline-based polybenzoxazine (BA-mda).

At room temperature (1 GHz), the dielectric constant and loss tangent ($\tan \delta$) of poly(BA-mda) are 4.57 and 0.022, respectively. It can be seen that the

dielectric constant and loss tangent of poly(BA-mdm) slightly increase when the temperature increases. At temperatures above 50 °C, there are significant enhanced in the dielectric property values and frequency dependence. However, the gap between the highest and the lowest values of the dielectric constant under temperature variation of the poly(BA-mdm) is within 2, indicating that the fluctuation atmosphere has a small influence on this polymer type. For the dielectric characteristics of aliphatic diamine-based, poly(BA-hda) as seen in Fig. 5.8. It is found that the relative permittivity (ϵ') and dissipation factor ($\tan \delta$) of poly(BA-hda) are 3.04 and 0.008, respectively observed at room temperature (1 GHz). The dielectric constant is stable at different atmospheres and small deviation of loss tangent is found at various temperatures. These characteristics prove that poly (BA-hda) is not dependent on temperature and/or frequency.

In principle, the dielectric properties are directly related to the dependence on the chemical structures of polymers. When comparing the dielectric characteristics of the two diamine-based polybenzoxazines, it is found that poly(BA-mdm) exhibits a higher dielectric constant and dissipation factor than poly(BA-hda). This is because poly(BA-mdm) is comprised of a large number of aromatic rings leading to more unsaturated, conjugated, and phenyl groups. These conjugated double bonds of aromatic system are more polarizable than the C–H bonds and C–C bonds of aliphatic diamine-based polybenzoxazines [7-8]. In this study, the dielectric constant and loss factor for both poly(BA-mdm) and poly(BA-hda) do not show any significant fluctuation under temperature and frequency variations. These superior behaviors are derived from high glass transition temperature (T_g) of the two resins. According to the Takeichi reported [5], T_g values of poly(BA-mdm) and poly(BA-hda) were around 228 and 247 °C, respectively. Thus the relaxation process of poly(BA-mdm) and poly(BA-hda) are less than those of traditional polymers.

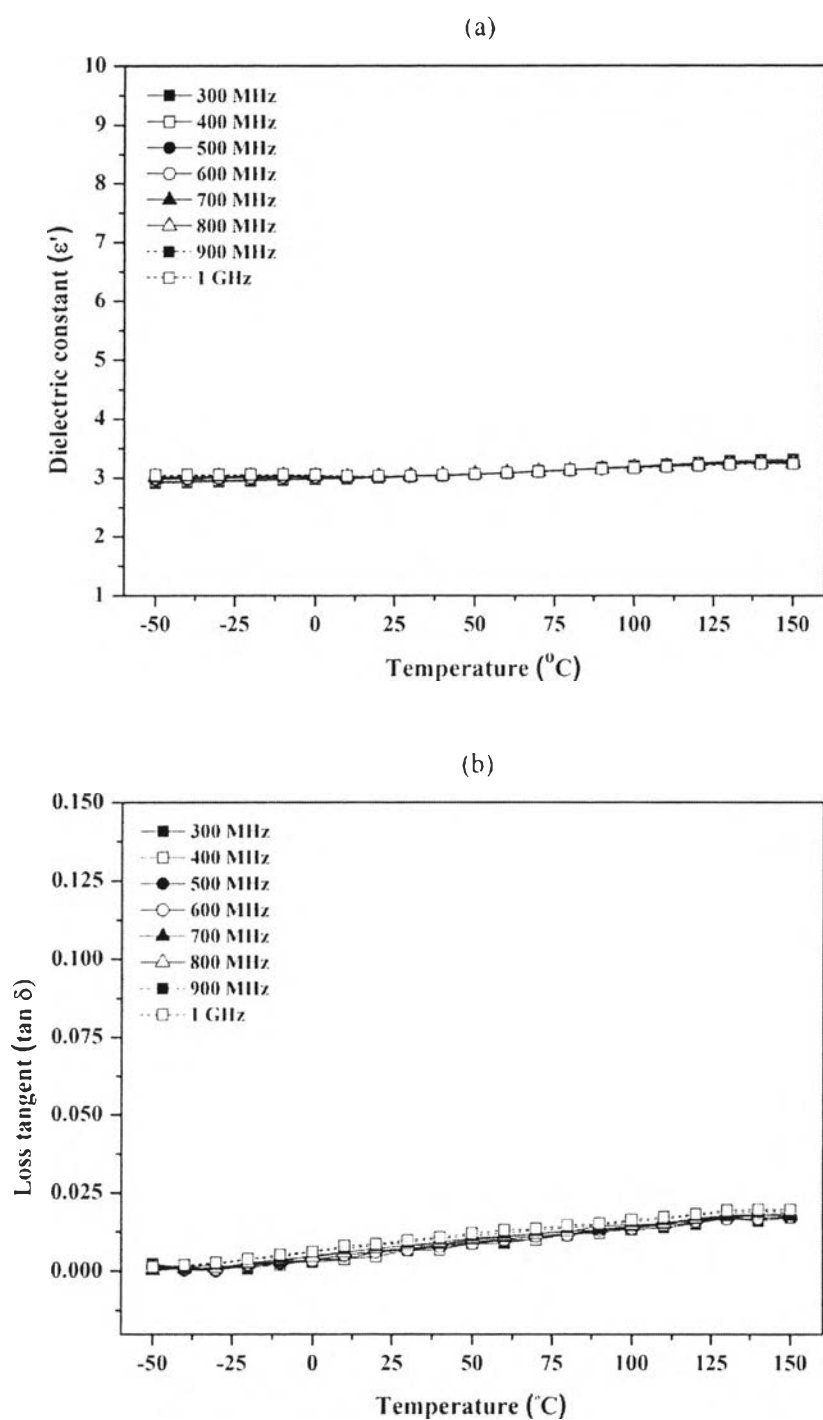


Figure 5.8 Temperature and frequency dependence of a) dielectric constant and b) dielectric loss tangent of hexamethylenediamine-based polybenzoxazine (BA-hda).

5.4.1.5 Thermal Gravimetric Analysis (TGA)

TGA thermogram and thermal properties of high molecular weight poly(BA-mda) and poly(BA-hda), which reported at 5% and 10% weight losses with the residual weight at 900 °C are presented in Figure 5.9. The cured products exhibits high degradation temperature. The thermal stability and char yield of Poly (BA-mda) were higher than Poly(BA-hda) due to the high aromatic content in the backbone of poly(BA-mda) [9].

Table 5.1 Thermal properties of methylenediainline (BA-mda)-and hexamethylenediamine-based (BA-hda) polybenzoxazines

Materials	T _{d5} (°C)	T _{d10} (°C)	Residual weight (%) at 900°C
Poly(BA-hda)	295.0	330.8	16.4
Poly(BA-mda)	316.7	353.2	31.9

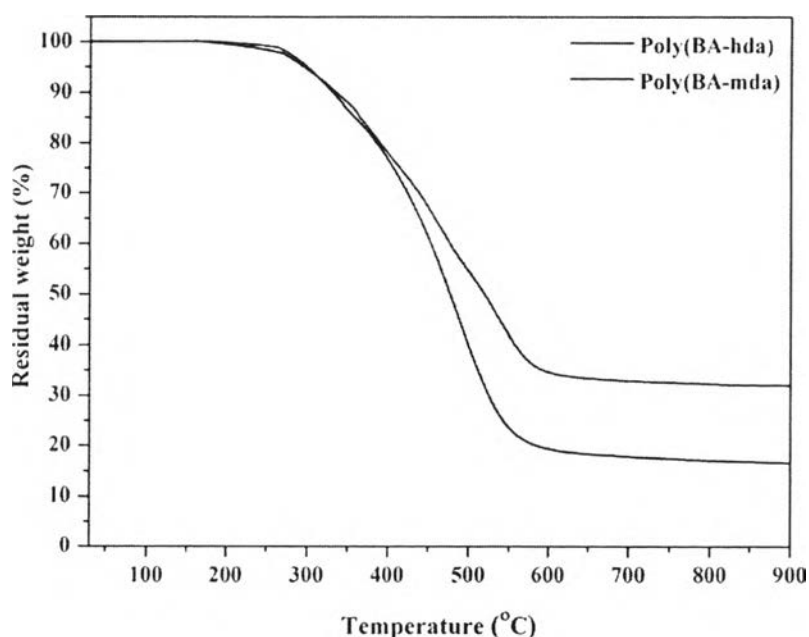


Figure 5.9 TGA thermogram of of methylenediainline (BA-mda)-and hexamethylenediamine-based (BA-hda) polybenzoxazines.

5.4.2 Poly(BA-mdm)/Barium Strontium Titanate Composites

Characterizations

5.4.2.1 Microwave Dielectric Properties Measurements

For concerning with various aspects, poly(BA-mdm) is superior to poly(BA-hda) both of thermal and dielectric properties. Hence poly(BA-mdm) was used as polymer matrix for combining with barium strontium titanate (BST). The composite materials were prepared by varying BST from 30 to 60 wt.%. The dielectric characteristics of the composites were studied in the frequency range of 300 MHz to 1 GHz with the temperature variation from -50 °C to 150 °C. The temperature dependence of the permittivity and dissipation factor of composites with various BST loadings is shown in Figure 5.10a and b, respectively.

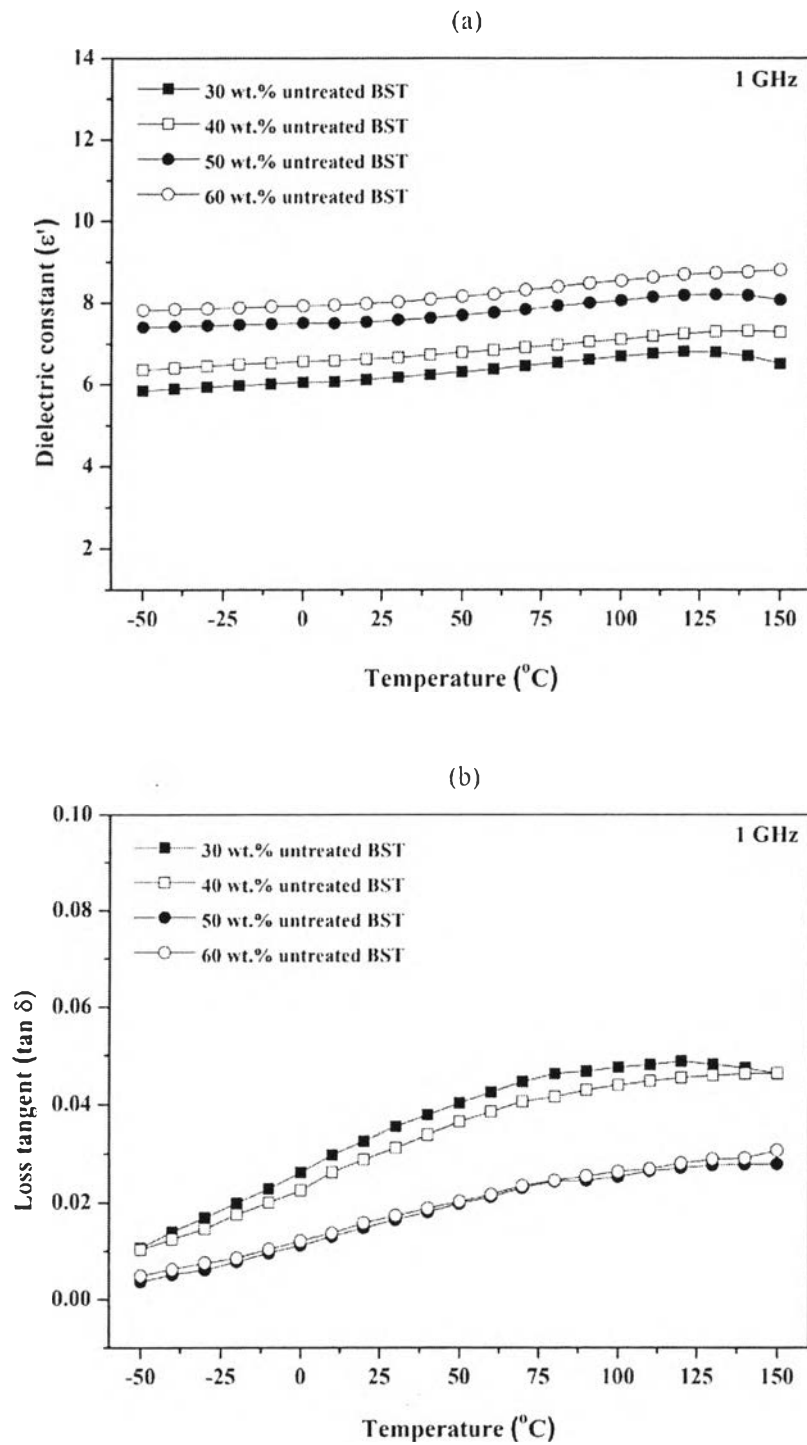


Figure 5.10 Temperature dependence of a) dielectric constant and b) loss tangent of poly(BA-mda) composites by varying BST contents measured at 1 GHz.

Fig. 5.10a shows that the amount of BST loading has an influence on dielectric characteristics. The dielectric constant of the composites is gradually increased with higher amount of BST adding. In the present of ceramic filler, the ceramic particles come closer, resulting in an increased dipole-dipole interaction. This phenomenon provides a higher dielectric constant [10]. With a wide range of temperature observation, the relative permittivity of all components in the existence of BST is nearly stable. This outstanding property stems from the synergism between the polymer and ceramic phases. As a consequence, the rigidity part from the ceramic filler could help weaken the relaxation process of the polymer matrix. On the contrary, loss tangent is independent on the amount of BST loading but slightly dependent on temperature variation as shown in Fig 5.10b. This is because the loss relies on several factors related to the whole sample characteristics [11]. Nevertheless, in this study, the dissipation factor of all composites is still less than 0.05. Besides, the study as a function of frequency (300 MHz to 1 GHz) is observed. The dielectric constant and loss tangent of poly(BA-mda) composites under varying BST weight ratios (30, 40, 50, and 60 wt.%) measured at room temperature are illustrated in Fig. 5.11a and b.

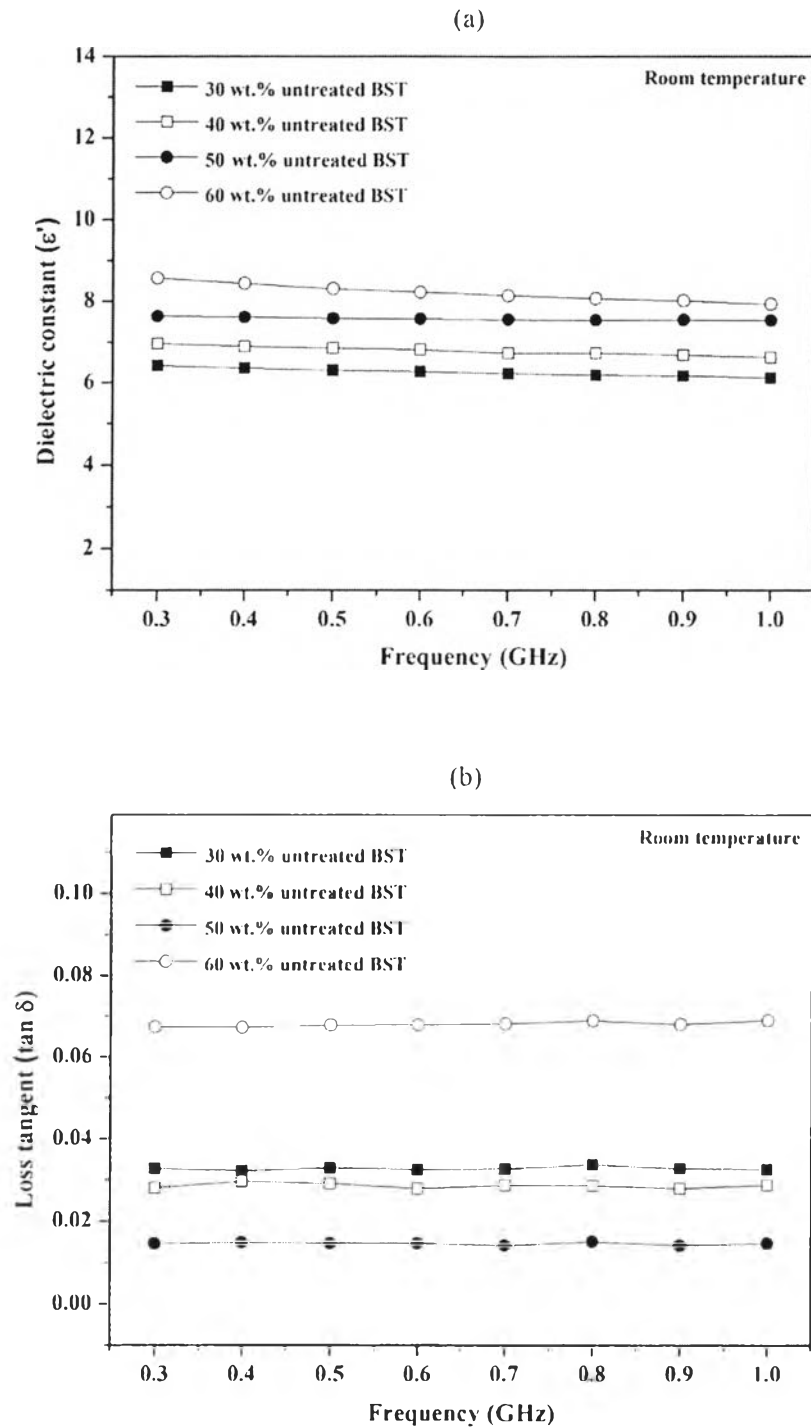


Figure 5.11 Frequency dependence of a) dielectric constant and b) loss tangent of BA-mda composites by varying BST contents measured at room temperature.

The dielectric constant of the composite demonstrates small improvement. It is shifted from 6.12 to 7.93 at 30 wt.% and at 60 wt.% of BST

loading, respectively, As an observed frequency, the relative permittivity and dissipation factor of prepared composites exhibit nearly the same, which refers to the frequency independence characteristic (Fig. 5.11a). Also, the values of dielectric loss tangent for the composites loaded with 30 wt.% and 60 wt.% are 0.032 and 0.069, respectively.

5.4.2.2 Density Measurement

The measurement on density was performed to observe the presence of voids or porosity in poly(BA-mda) composite specimens at various BST contents. This analysis was based on ASTM D792-00. The experimental density as relative density was compared with the theoretical density calculated by using equation (4.3). Density of Poly(BA-mda) and BST nanopowder is 1.182 and 5.412 g/cm³, respectively. The density of the poly(BA-mda)/BST composites at desirable BST weight fractions are summarized as shown in Table 5.2 and Fig. 5.12. Moreover, the experimental density can fit well with the theoretical density at the variation of BST content in the composite as shown in Figure 5.12. Evidently, the experimental density at 50, 60 wt.% of BST loading is found to be decreased when compared with the theoretical density. The result implies that the entrapment of air or bubble was present in the composite specimens. This effect is corresponding to the small improvement in dielectric constant at high BST loading.

Table 5.2 Density of the poly(BA-mda) composites at various contents

Poly(BA-mda)/BST (wt.%)	Volume fraction	Density (g/cm ³)	
		Relative	Theoretical
70/30	0.0917	1.477	1.569
60/40	0.1357	1.730	1.176
50/50	0.1906	1.778	1.988
40/60	0.2610	1.950	2.286

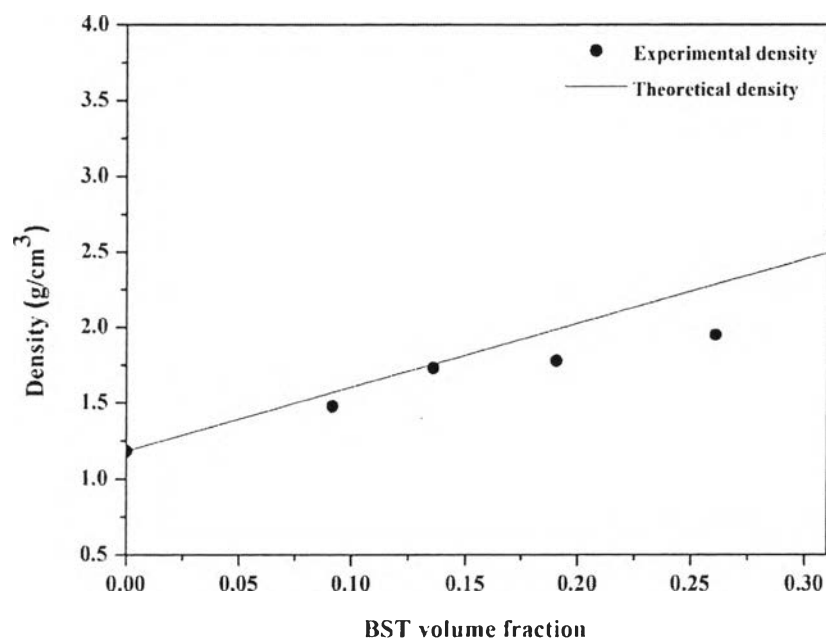


Figure 5.12 The comparison between (•) experimental and (-) theoretical density as a function of BST volume fraction.

5.4.2.3 Thermogravimetric analysis (TGA) thermogram.

Thermogravimetric analysis (TGA) thermograms of poly(BA-mda) composites at various BST contents are displayed in Table 5.3. Degradation temperature (T_d) of the composites was reported at 5% and 10% weight losses with the residual weight at 900 °C. It is found that the thermal stability of the composites is significantly enhanced with higher amount of BST. By adding 60 wt.% of BST, the degradation temperature (T_{d5}) of the materials is shifted from 316.7 to 365.0. The result originates from the attachment of BST particle to the polymer matrix resulting in the restriction of chain movement of the polymer phase. As a result, the interconnection between two phases is improved, which is able to retard the degradation of the composites by shifting decomposition temperature to higher values. Char yield of the composite systems is found to increase linearly with increasing the mass fraction of the BST. The presence of void did not affect the thermal stability of the composites because the nature of BST structure is thermally stable up to very high temperatures. As can be seen in Table 5.3, 31.9 % of the

residual weight of the neat poly (BA-mda) is uplifted to 77.5 after adding 60 wt.% of BST. It is confirmed that the existence of higher amount of BST improves not only the dielectric properties as former mention but also thermal properties [12-13].

Table 5.3 Thermal properties of poly(BA-mda) composites at various compositions with 30, 40, 50, and 60 wt.% of BST loading

Poly(BA-mda)/BST (wt.%)	BST Volume fraction	T _{d5} (°C)	T _{d10} (°C)	Residual weight(%) at 900°C
100/0	0	316.7	353.2	31.9
70/30	0.0917	326.3	361.4	50.9
60/40	0.1357	335.1	372.2	60.9
50/50	0.1906	360.0	377.2	72.2
40/60	0.2610	365.0	404.6	77.5

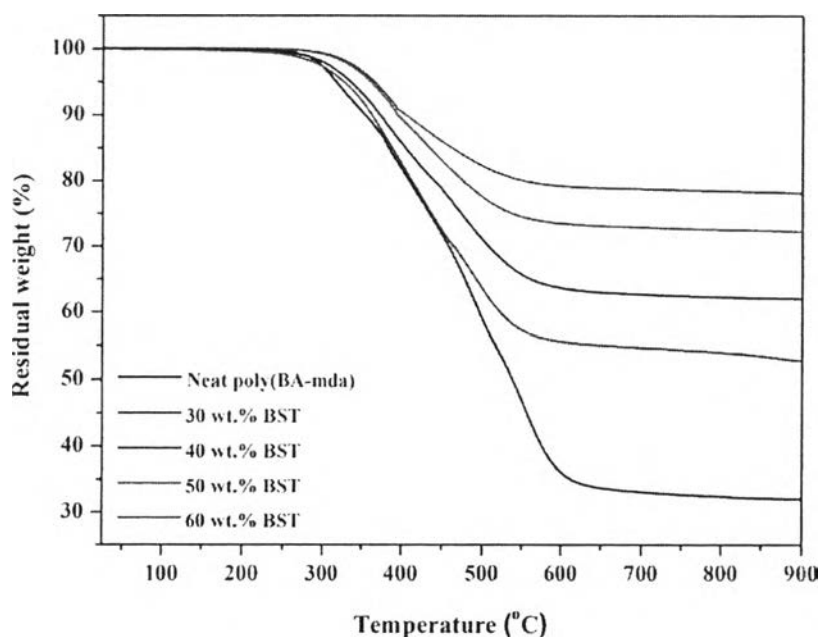


Figure 5.13 TGA thermogram of poly(BA-mda) composites at various compositions with 30, 40, 50, and 60 wt.% of BST loading.

5.4.2.4 Atomic force microscopy (AFM) Analysis

According to FMM operation, the mechanical data including Young's modulus and hardness are presented in Table 5.4. It is found that the Poly(BA-mda) composites yield higher Young's modulus and hardness in comparison to the neat polymer based. The hardness of adding 60 wt.% of BST in the poly(BA-mda) significantly shifts from 2.2 to 2.6 kPa. Similarly, the modulus value is also enhanced from 108 to 151 kPa. These phenomena are derived from the higher stiffness of BST filler. On account of the identical embedded characteristic of BST in polymer matrix and also determination of mechanically microscopic level, the different in the amount of BST do not largely affect to those factors.

Table 5.4. The mechanical properties in microscopic level of poly(BA-mda) composites at various BST contents monitored by AMF in FM-mode

Poly(BA-mda)/BST (wt.%)	Hardness (kPa)	Young's modulus (kPa)
100/0	2.2 ± 0.2	108 ± 10
70/30	2.9 ± 0.3	138 ± 9
60/40	3.2 ± 0.1	152 ± 6
50/50	2.9 ± 0.2	151 ± 8
40/60	3.6 ± 0.5	151 ± 10

5.4.2.5 Experimental Data Fitting

Under various assumptions concerning arrangement of inclusions and filler shape, different laws have been proposed to fit the experimental dielectric constants for two component mixtures, and to predict the effect of each phase on the dielectric properties. In this study, series, Lichtenecker model, Maxwell-Wagner equation and Kerner expression modified by Jayasundere-Smith (J-S prediction) were used for dielectric prediction of pol(BA-mda) composites, as shown in Figure 5.14. The equations of these models are described as follow:

Series model	$\frac{1}{\varepsilon} = \frac{\phi_c}{\varepsilon_c} + \frac{\phi_p}{\varepsilon_p}$
Lichtenecker model	$\log \varepsilon = \phi_p \log \varepsilon_p + \phi_c \log \varepsilon_c$
Maxwell-Wagner equation	$\varepsilon = \varepsilon_p \frac{2\varepsilon_p + \varepsilon_c + 2\phi_c(\varepsilon_c - \varepsilon_p)}{2\varepsilon_p + \varepsilon_c - \phi_c(\varepsilon_c - \varepsilon_p)}$
Kerner expression	$\varepsilon = \frac{\varepsilon_p \phi_p + \varepsilon_c \phi_c [3\varepsilon_p / (\varepsilon_c + 2\varepsilon_p)] [1 + 3\phi_c(\varepsilon_c - \varepsilon_p) / (\varepsilon_c + 2\varepsilon_p)]}{\phi_p + \phi_c [3\varepsilon_p / (\varepsilon_c + 2\varepsilon_p)] [1 + 3\phi_c(\varepsilon_c - \varepsilon_p) / (\varepsilon_c + 2\varepsilon_p)]}$

where ε is the dielectric constant of the composites; ε_p and ε_c refer to the dielectric constants of the polymer matrix and the BST ceramic, respectively; ϕ_c and ϕ_p are the volume fraction of the ceramic and polymer, respectively

From the experimental data obtained by calculated of five theoretical models, as indicated in Figure 5.14, It is found that the measured dielectric constant of the Poly(BA-mda) composites is fit with Maxwell-Wagner equation. It considers the composite as a random mixture of nearly rough spherical inclusions [4, 14-15].

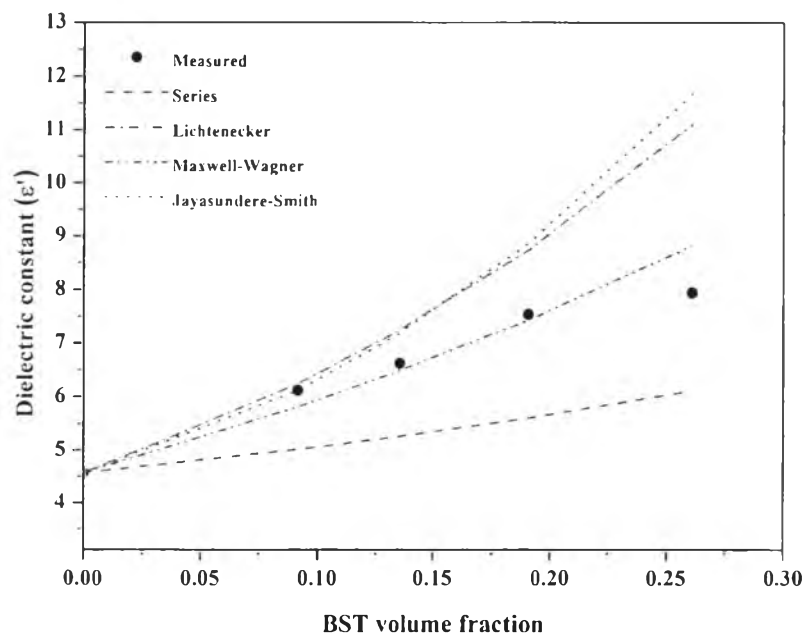


Figure 5.14 Plot of theoretical models and the measured dielectric constant for different BST volume fractions at room temperature and 1 GHz.

5.4.3 Characterization of Poly(BA-mda)-Modified BST

5.4.3.1 Fourier Transform Infrared Spectroscopy (FTIR) Analysis

By raising the dielectric capability of poly(BA-mda) composites, the compatibility between polymer and ceramic should be improved. For the BST coated by 5wt.% of BA-mda system, it is evidently from Fig 5.15 that BST powder modified by 5 wt.% of the Ba-mda matrix displays the absorption peak around 1125-1225 cm^{-1} belonging to the asymmetric C-O-C stretching mode and additionally C-N-C antisymmetric stretching mode. presented at 1175 cm^{-1} and 1227 cm^{-1} confirm that surface modification on BST surface by BA-mda is successful [35].

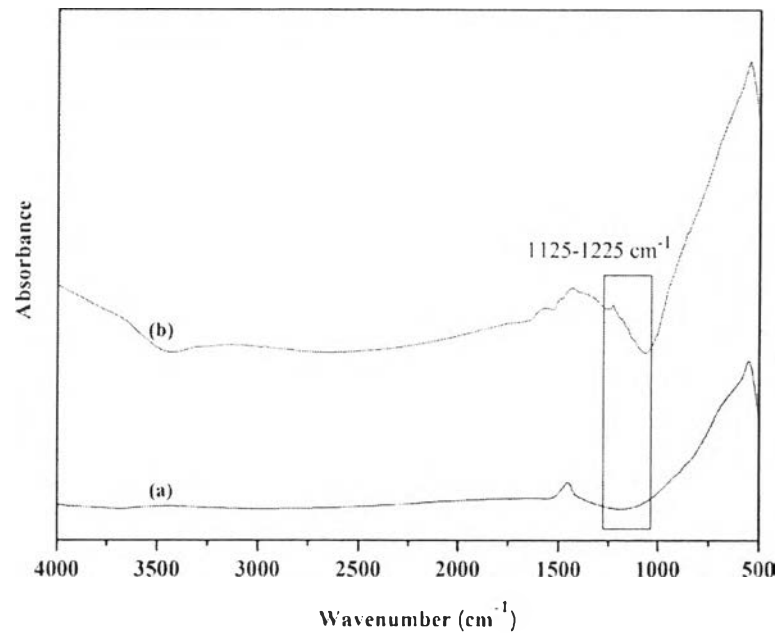


Figure 5.15 The FTIR spectra: (a) BST powder and (b) BST treated with 5 wt.% BA-mda.

5.4.3.2 Scanning Electron Microscopy (SEM) Analysis

The effect of BST surface modification on the distribution of ceramic filler in poly(BA-mda) matrix was investigated using SEM technique.

Figure 5.16 (a)-(c) demonstrates cross-sectional morphologies of the composites at 50 wt.% of BST particles which are untreated, treated with silane coupling agent and treated with BA-mda, respectively. From the SEM images, it

could be seen the agglomeration and the poor dispersion of various modified BST approaches. These phenomena result from the silane coupling agent and BA-mda as surface modifiers could not work effectively. This may be due to the unsuitable composite preparation method, which those of specimens were prepared by using solvent with the fact that the starting polymer matrix cannot melt by itself. Therefore, the interconnection that attached to BST surface was destroyed causing higher incompatibility between two phases again. Since, the distribution is directly related to dielectric properties. Therefore, the study of dielectric properties has been further investigated.

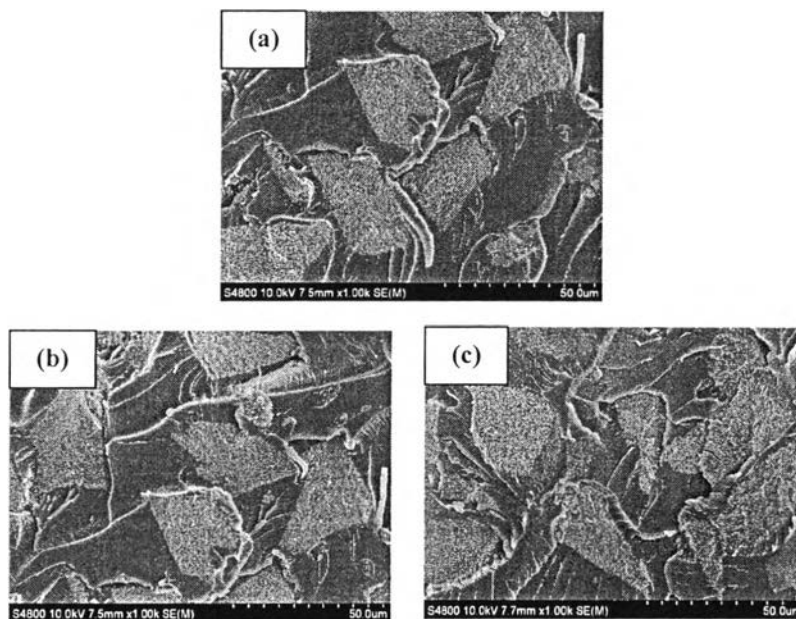


Figure 5.16 SEM micrographs of poly(BA-mda) composites at 50 wt.% of BST with (a) untreated BST powder, (b) silane treated BST powder, and (c) BA-mda treated BST powder.

5.4.3.3 Microwave Dielectric Properties Measurements

The dielectric characteristics including the relative permittivity and loss tangent on surface modification routes by using BA-mda and 3-aminopropyl trimethoxysilane as surface modifiers were compared with untreated BST system. The dielectric measurement was carried out under the temperature dependence ranging from $-50\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$ as shown in Fig. 5.17-5.20, respectively. The study

under frequency dependence in the range of 300 MHz to 1 GHz was also performed at the same composition as presented in Fig.5.21-5.24, respectively. It is clear that the dielectric constant at every BST fraction of untreated and treated BST is nearly the same. The higher amount of BST loading and also surface treatment could not shift the dielectric constant to higher values as expected. The study on morphologies by SEM as discussed earlier is related to the observed dielectric properties. Poor distribution of ceramic filler results in obtaining lower polarizability and also creating higher dielectric loss, which ruins the dielectric characteristic. However, the prominent of this system that has been found is the nearly stable of dielectric constant with various atmospheres. The loss tangent is slightly dependent on temperature where this factor is still less than 0.05 for all compositions.

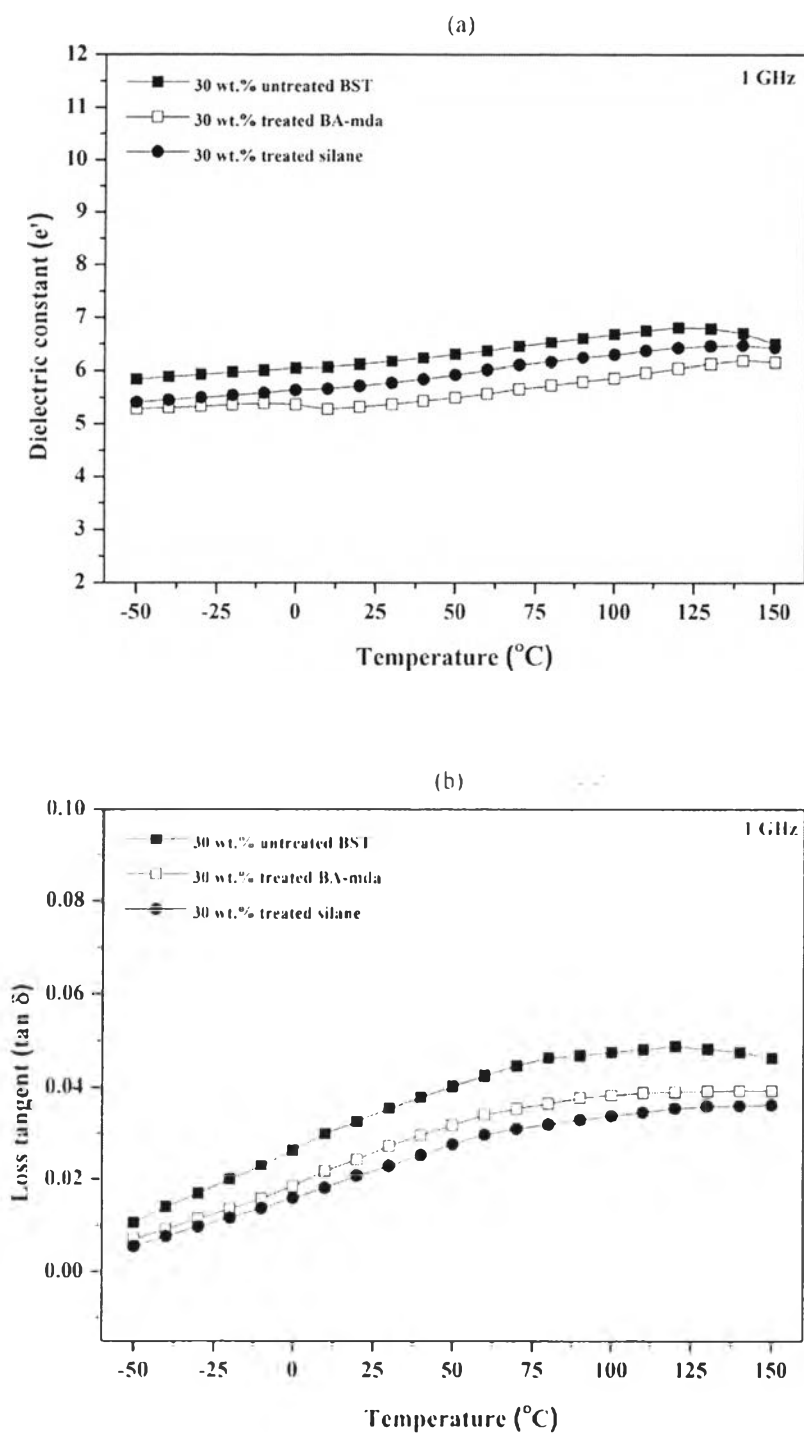


Figure 5.17 Temperature dependence of a) dielectric constant and b) loss tangent of poly(BA-mda) composite at 30 wt.% of BST measured at 1 GHz.

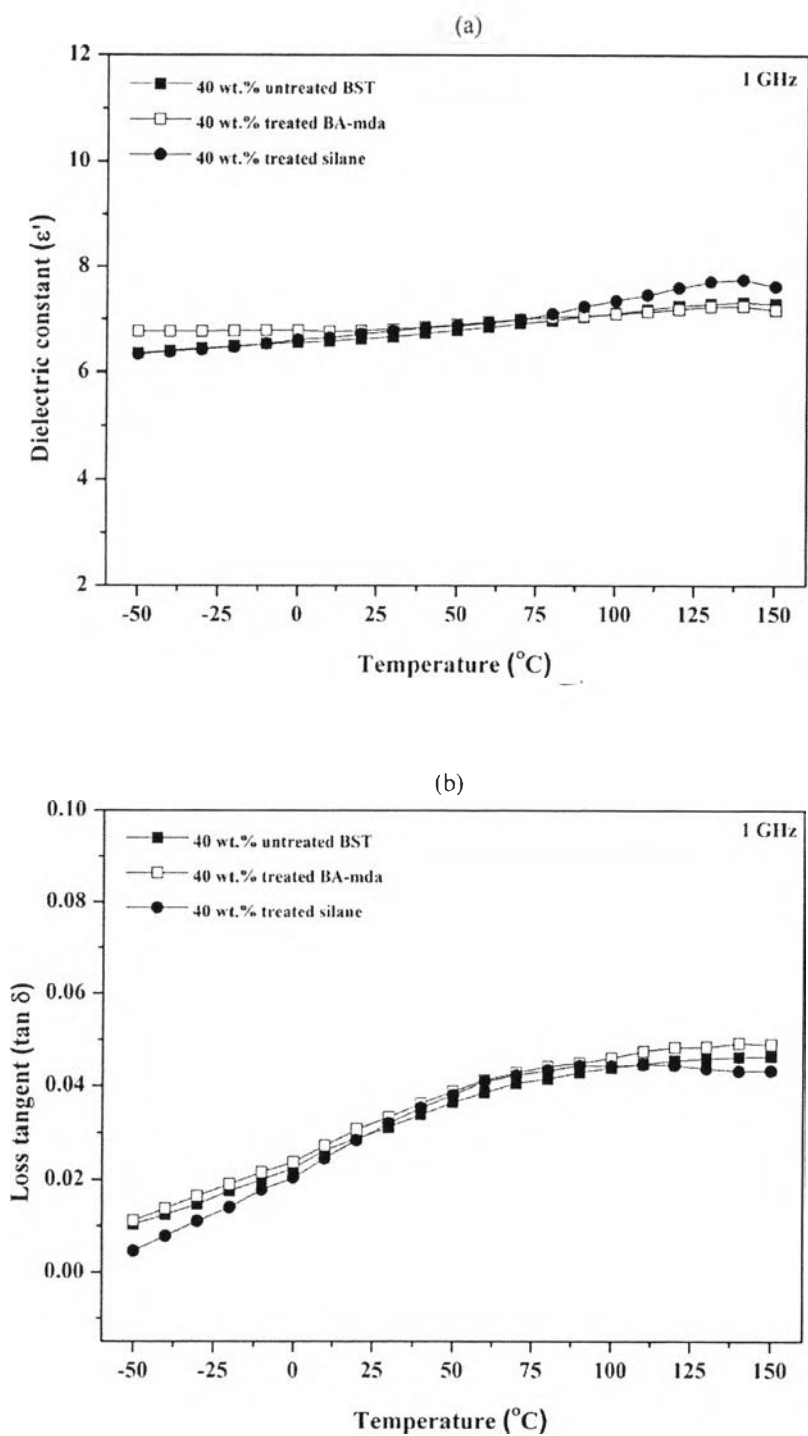


Figure 5.18 Temperature dependence of a) dielectric constant and b) loss tangent of poly(BA-mda) composite at 40 wt.% of BST measured at 1 GHz.

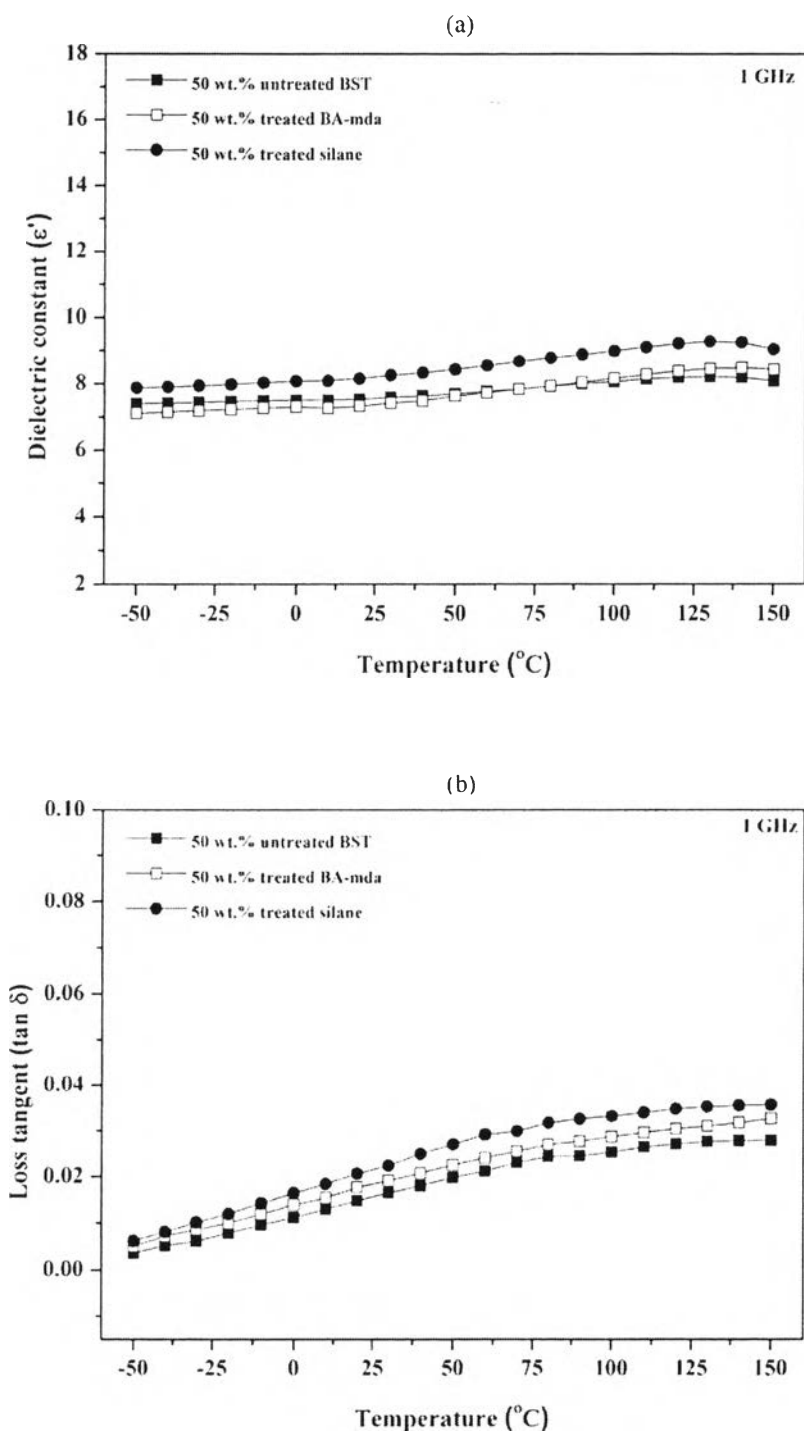


Figure 5.19 Temperature dependence of a) dielectric constant and b) loss tangent of poly(BA-mda) composite at 50 wt.% of BST measured at 1 GHz.

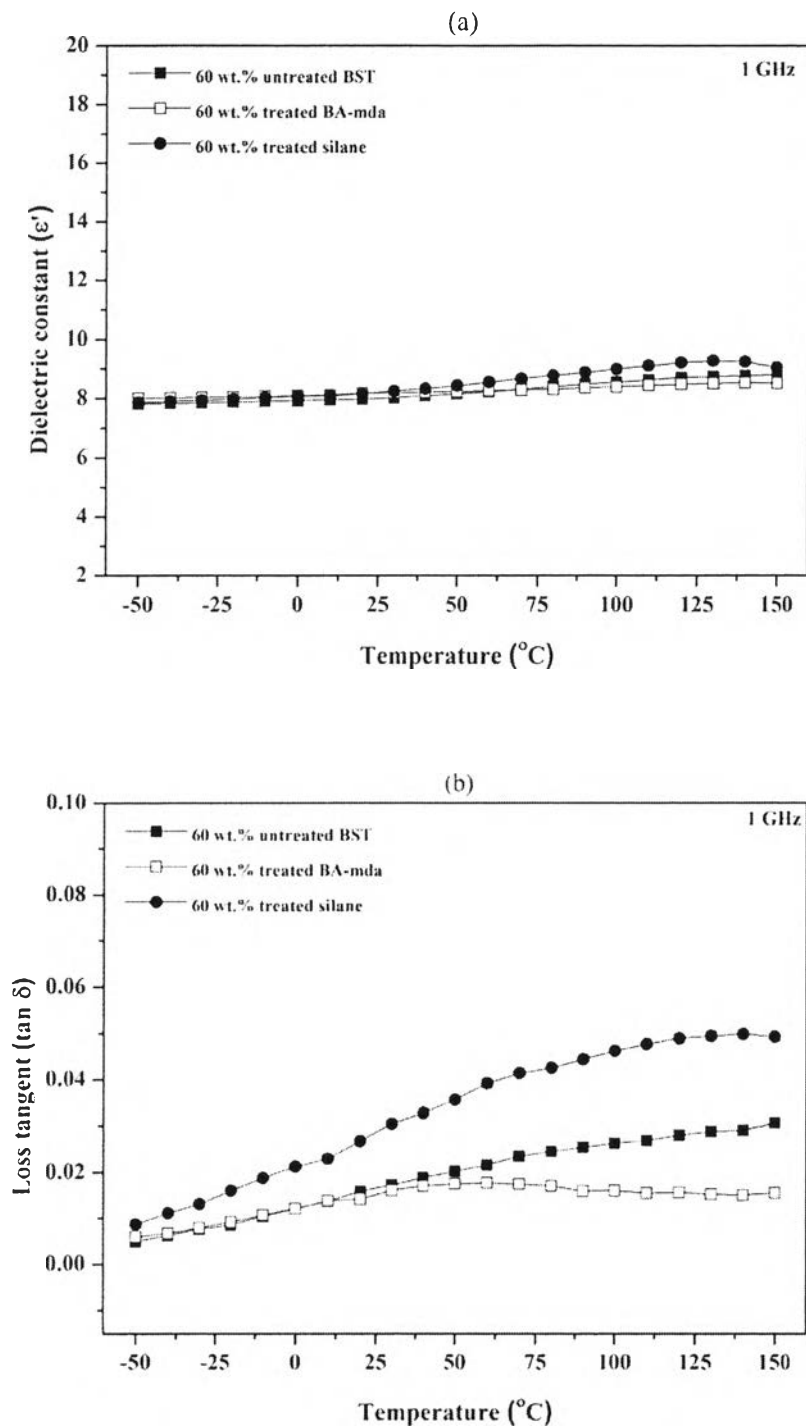


Figure 5.20 Temperature dependence of a) dielectric constant and b) loss tangent of poly(BA-mda) composite at 60 wt.% of BST measured at 1 GHz.

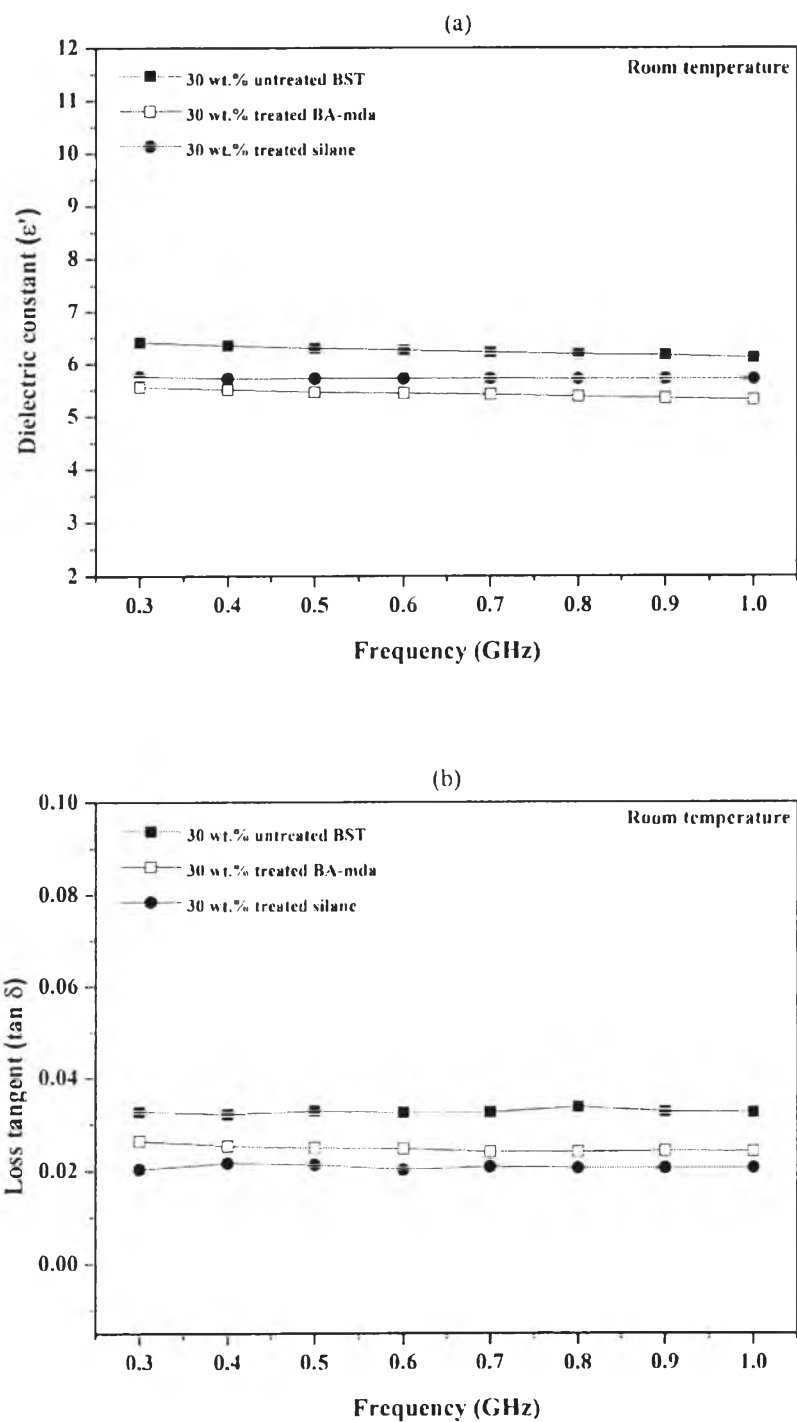


Figure 5.21 Frequency dependence of a) dielectric constant and b) loss tangent of poly(BA-mda) composite at 30 wt.% of BST measured at room temperature.

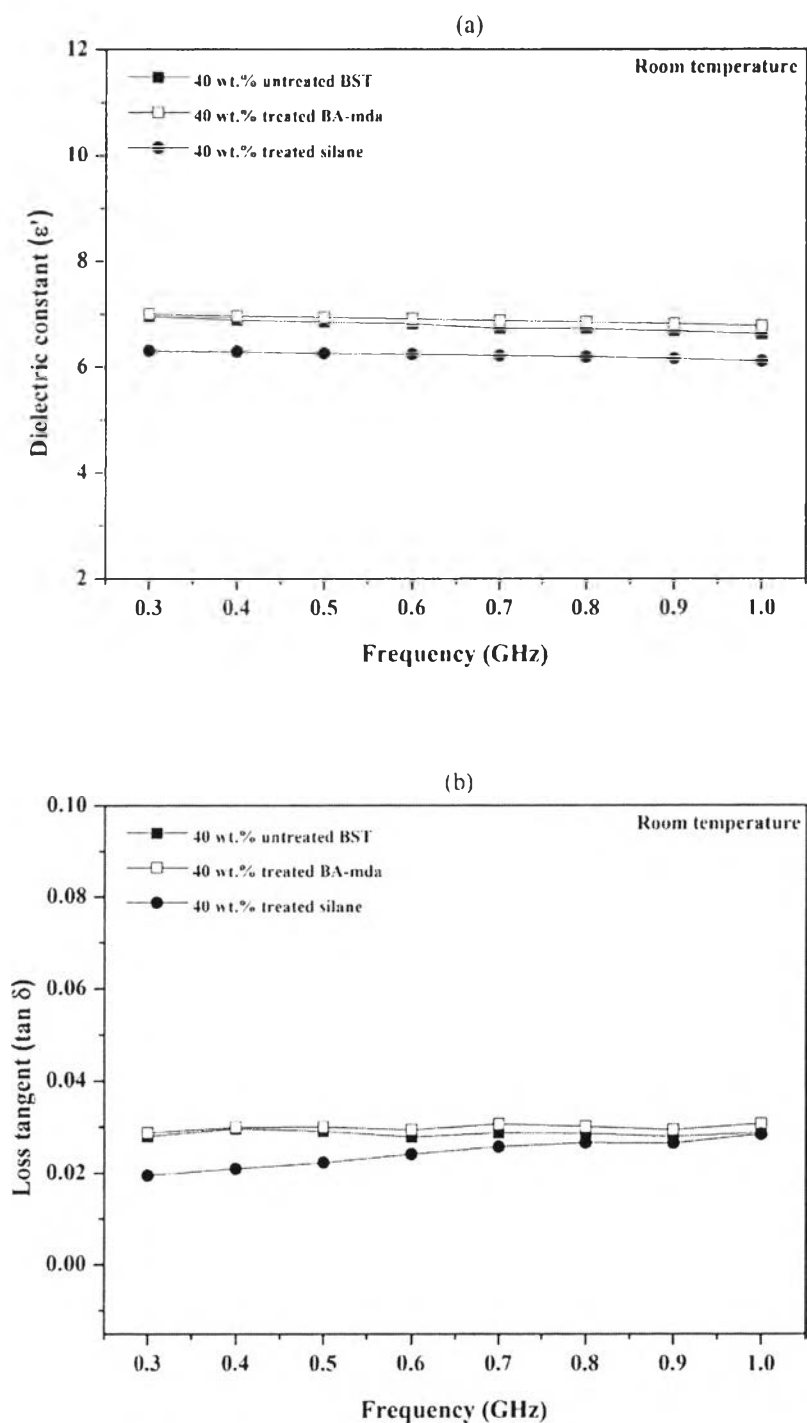


Figure 5.22 Frequency dependence of a) dielectric constant and b) loss tangent of poly(BA-mda) composite at 40 wt.% of BST measured at room temperature.

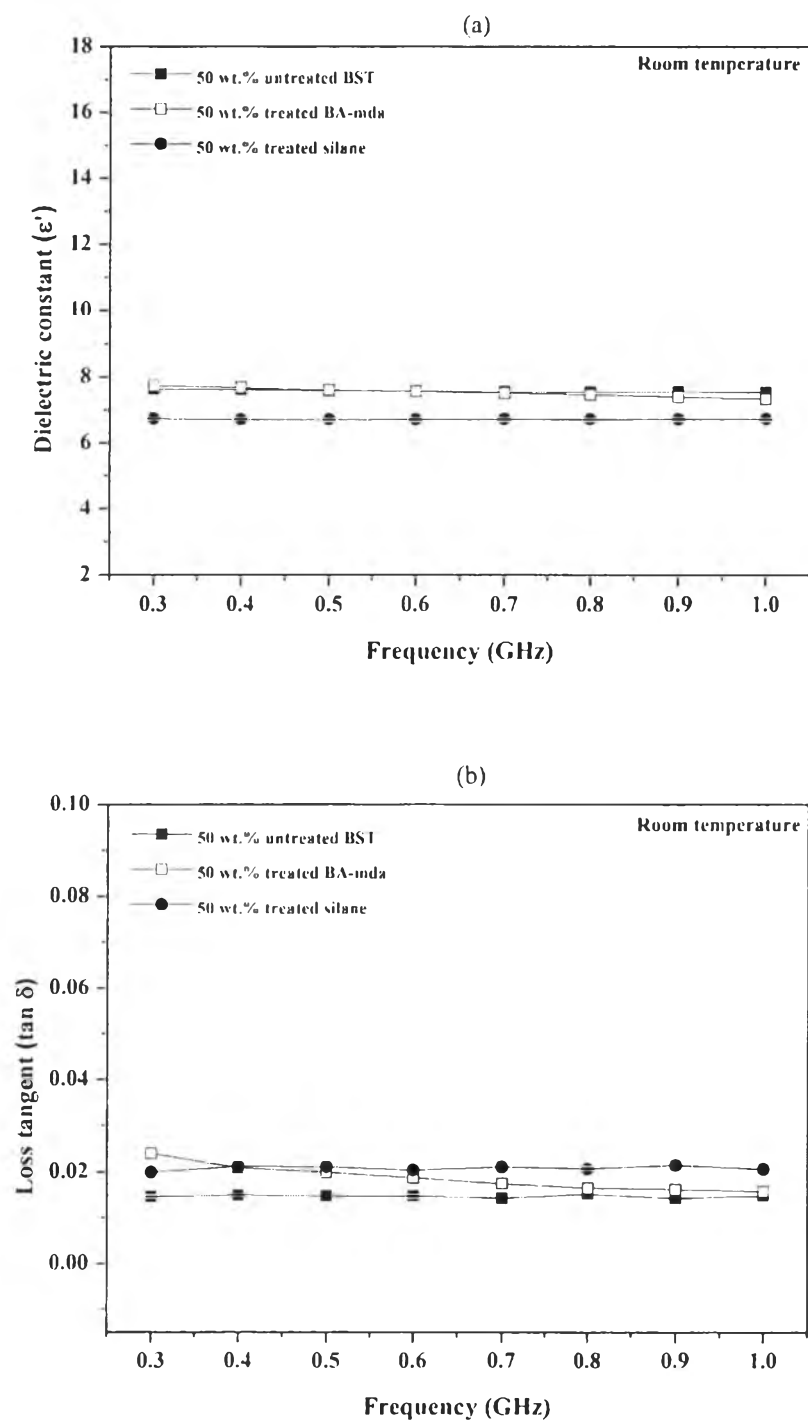


Figure 5.23 Frequency dependence of a) dielectric constant and b) loss tangent of poly(BA-mda) composite at 50 wt.% of BST measured at room temperature.

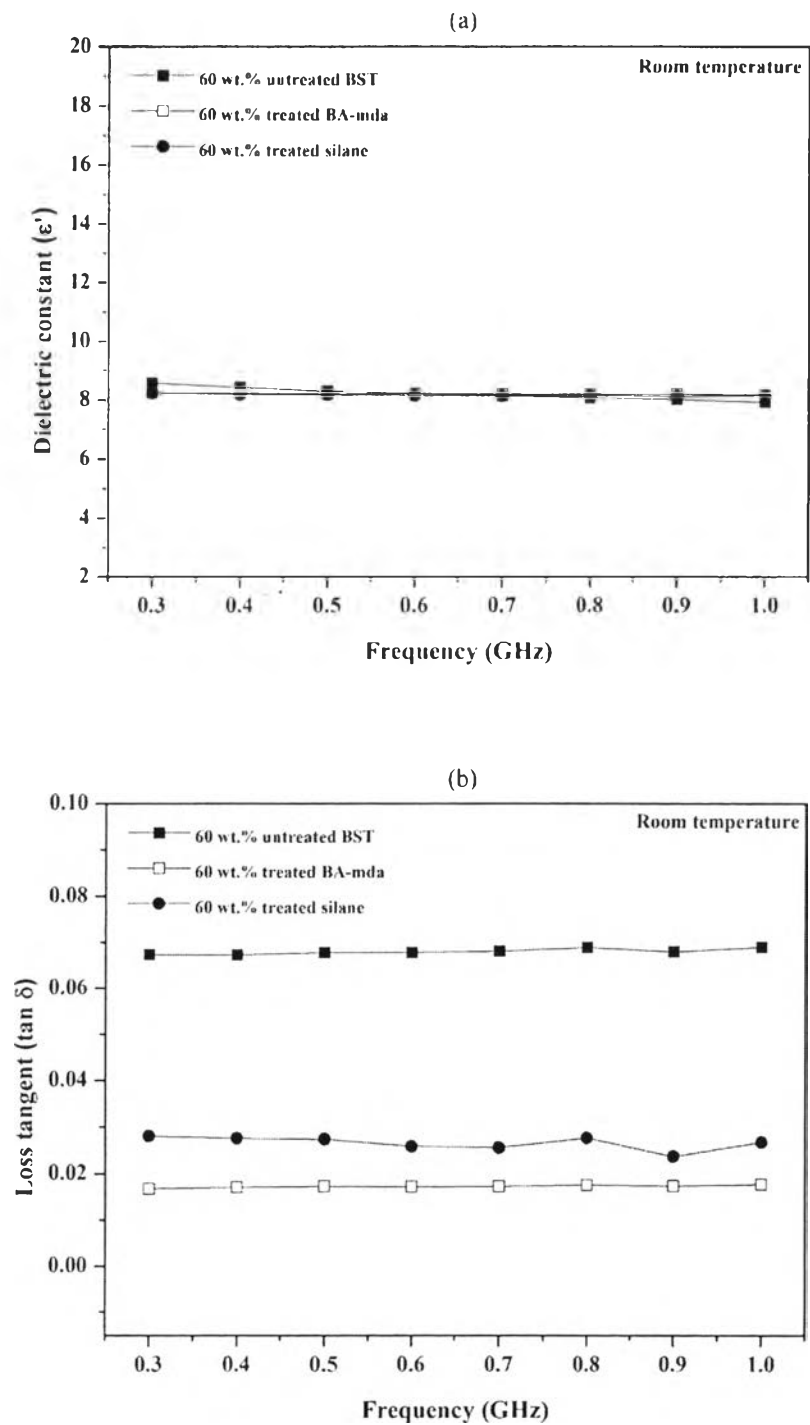


Figure 5.24 Frequency dependence of a) dielectric constant and b) loss tangent of poly(BA-mda) composite at 60 wt.% of BST measured at room temperature.

5.5 Conclusions

Using high molecular weight polybenzoxazines could help expand the applications of polybenzoxazine resin. After observed their properties, these main chain types possessed good thermal stability, suitable toughness, and high glass transition temperature. For the dielectric study, it was found that the dielectric properties were strongly dependent on molecular structure. High molecular weight methylenedianiline- (BA-mda) based polybenzoxazine containing aromatic backbone provided better dielectric properties compared to that of BA-hda. Therefore, poly(BA-mda) was used as a polymer matrix. For the poly(BA-mda)/BST composites, it was found that the dielectric constant can slightly increase by the higher ceramic content. By adding 60 wt% (26 vol.%) of untreated BST powder, the dielectric constant increased from 6.1 to 8.0 at 1GHz (room temperature). Surface modification using 3-aminopropyl trimethoxy silane and BA-mda did not help improve the dispersion of ceramic filler. The dielectric results derived from untreated and treated systems are nearly the same. For theoretical model prediction, poly(BA-mda) composites were fit well with Maxwell-Wagner equation considered that composites are as a random mixture of nearly rough spherical inclusions.

5.6 Acknowledgements

The authors thank the partial scholarship and partial funding of the research work provided by the Petroleum and Petrochemical College, Chulalongkorn University and Center of Excellence on Petrochemical and Materials Technology (PETRO-MAT) and the 90th Anniversary of Chulalongkorn University Fund (through the Ratchadaphiseksomphot Endowment Fund).

5.7 References

- [1] Tian, M.B. (2003) Substrates for High Density Package Engineering. Tsinghua University Press, Beijing. (pp 22–24).
- [2] JS, M. and LokeNgai, K. (2011) Microwave properties of dielectric materials, microstrip antennas. Malaysia: InTech.
- [3] Panomsuwan, G., Kaewwatal, S., Ishida, H., and Manuspiya, H., (2007) Proceedings of the 2nd IEEE International conference on nano/micro engineered and molecular systems, Bangkok, Thailand. 497-501.
- [4] Krueson, N., Manuspiya, H., Laoratanakul, P., and Ishida, H. (2008) Dielectric properties enhancement in polybenzoxazine composite at multi-frequency range. Advanced Materials Research. 55-57, 105–108.
- [5] Ning, X. and Ishida, H. (1994) Phenolic materials via ring-opening polymerization: synthesis and characterization of bisphenol-A based benzoxazines and their polymers. Journal of Polymer Science Part A: Polymer Chemistry, 32(6), 1121–1129.
- [6] Takeichi, T., Kano, T., and Agag, T. (2005) Synthesis and thermal cure of high molecular weight polybenzoxazine precursors and the properties of the thermosets. Polymer, 46(26), 12172-12180.
- [7] Manuspiya, H. and Ishida, H. (2011) Polybenzoxazine-Based Composites for Increased Dielectric Constant. In Ishida, H. and Agag, T. Polybenzoxazine Applications and Potential Applications. Ohio: Elsevier. (pp. 621-637).
- [8] Hougham, G., Tesoro, G., Viehbeck, A., and Chapple-Sokol, J.D. (1994) Polarization effects of fluorine on the relative permittivity in polyimides. Macromolecules, 27(21), 5964–5971.
- [9] Ishida, H. (2011). Overview and Historical Background of Polybenzoxazine Research. In Ishida, H. and Agag, T. Polybenzoxazine Applications and Potential Applications. Ohio: Elsevier. (pp 24-69).
- [10] Kuo, D.H, Chang, C.C., Su, T.Y., Wang, W.W., and Lin, B.Y. (2001) Dielectric behaviours of multi-doped BaTiO₃/epoxy composites. Journal of the European Ceramic Society. 21(9), 1171–1177.

- [11] Bai, Y., Cheng, Z.Y., Bharti, V., Xu, H.S., and Zhang, Q.M. (2000) High-dielectric-constant ceramic-powder polymer composites. Applied Physics Letters, 76(25), 3804–3806.
- [12] Zhang, J., Xu, R., and Yu, D. (2007) A novel poly-benzoxazinyl functionalized polyhedral oligomeric silsesquioxane and its nanocomposite with polybenzoxazine. European Polymer Journal, 43(3), 743–752.
- [13] Du, W., Shan, J., Wu, Y., Xu, R., and Yu, D. (2010) Preparation and characterization of polybenzoxazine/trisilanol polyhedral oligomeric silsesquioxanes composites. Materials and Design, 31(4), 1720–1725.
- [14] Rao, Y., Takahashi, A., and Wong, C.P. (2003) Di-block copolymer surfactant study to optimize filler dispersion in high dielectric constant polymer–ceramic composite. Composites Part A: Applied Science and Manufacturing, 34(11), 1113–1116.
- [15] Cho, S.D. and Paik, K.W. (2001) Relationships between suspension formations and properties of BaTiO₃/epoxy composite films for integral capacitors. Proceedings of the 51st IEEE electronic component technology conference, Piscataway, USA. 1418–1422.
- [16] Ishida, H. and Podriguez, Y. (1995) Curing kinetics of a new benzoxazine-based phenolic resin by differential scanning calorimetry. Polymer, 36(16), 3151–3158.