



CHAPTER IV RESULT AND DISCUSSION

4.1 Characterization of Benzoxazine

4.1.1 SEC

The mannich reaction illustrated in Figure 2.3 was completed within 6 hrs. This result was obtained from thin layer chromatography. The precursor of benzoxazine, the mixture of monomer and oligomers, was purified with 3 N NaOH to obtain more benzoxazine monomer components. The oligomer that have phenol group in the structure were dissolved into the aqueous solution during washing with NaOH. This composition and structure of purified precursor were confirmed by SEC and FTIR. The SEC chromatograph of the purified benzoxazine is shown in Figure 4.1. The

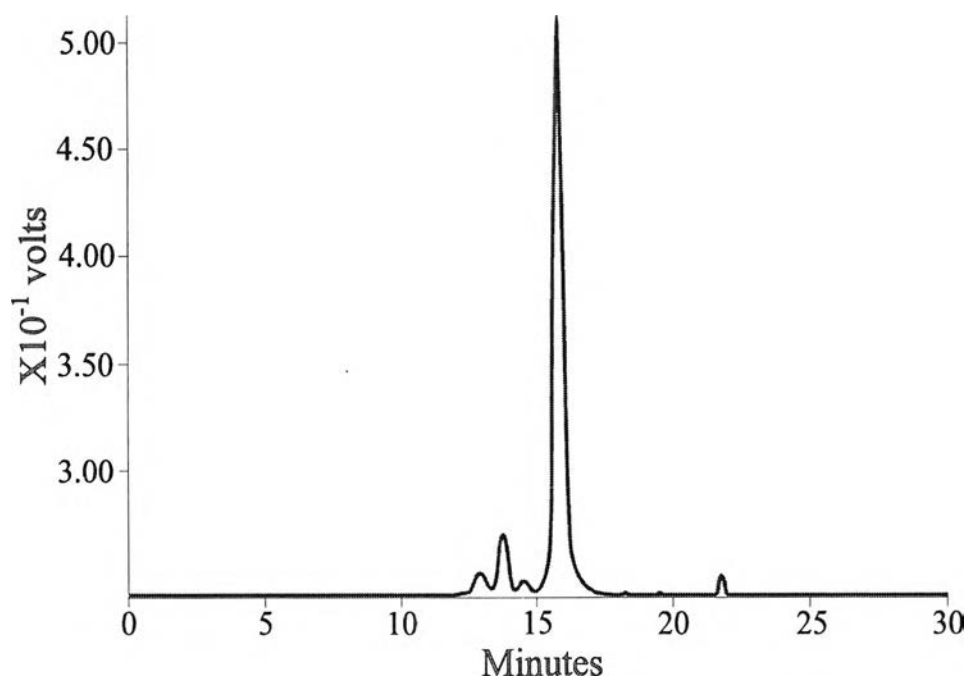


Figure 4.1 SEC chromatograph of washed precursor polybenzoxazine.

strongest peak at 15.6 min retention time is assigned to the difunctional benzoxazine monomer while the peaks with shorter retention times represent the dimers and higher oligomers. The percentage of benzoxazine monomer can be calculated from the peak area of the monomer and is about 88%. The structure of benzoxazine was studied by FTIR in the following section.

4.1.2 FTIR

The yellow clear viscous fluid of purified precursor benzoxazine was characterized with FTIR. This FTIR spectrum was collected from a thin film of viscous fluid coated onto a ZnSe disk shown in Figure 4.2. From the figure, the benzoxazine monomer shows bands at 2957, 2931 and 2870 cm^{-1} which are assigned to the asymmetric C-H stretching of CH_3 , CH_2 and symmetric C-H stretching of CH_3 , respectively. The specific characteristic peaks of benzoxazine consist of 1498, 1321, 1232, 933 and 822 cm^{-1} which can be referred to the tri-substituted benzene ring mode in the oxazine ring structure, tertiary amine, aromatic ether, C-H stretching of benzene ring and the

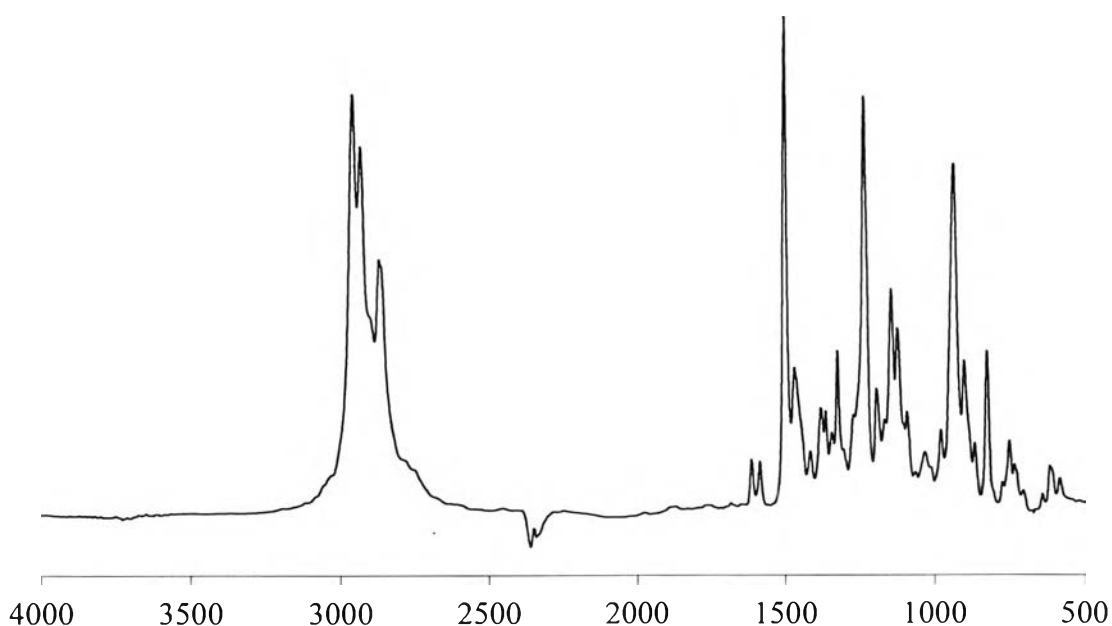


Figure 4.2 FTIR spectra of washed precursor benzoxazine.

tri-substituted benzene ring mode. Moreover, FTIR region between 1550 to 1400 cm^{-1} is the region of interest that can be used to distinguish between monomer and oligomer structure. The difference in the cyclic rings structure from polymeric linear bridge structure show their characteristic peaks in this region shown in Figure 4.3. The band at 1499 cm^{-1} is attributable to the tri-substituted benzene ring mode in the oxazine ring structure while the absent band at 1481 cm^{-1} is assigned to the tetra-substitute benzene ring mode in ortho-substituted position. Thus, the existing of benzoxazine monomer in purified benzoxazine precursor as a major product is confirmed which is consistent with the SEC result.

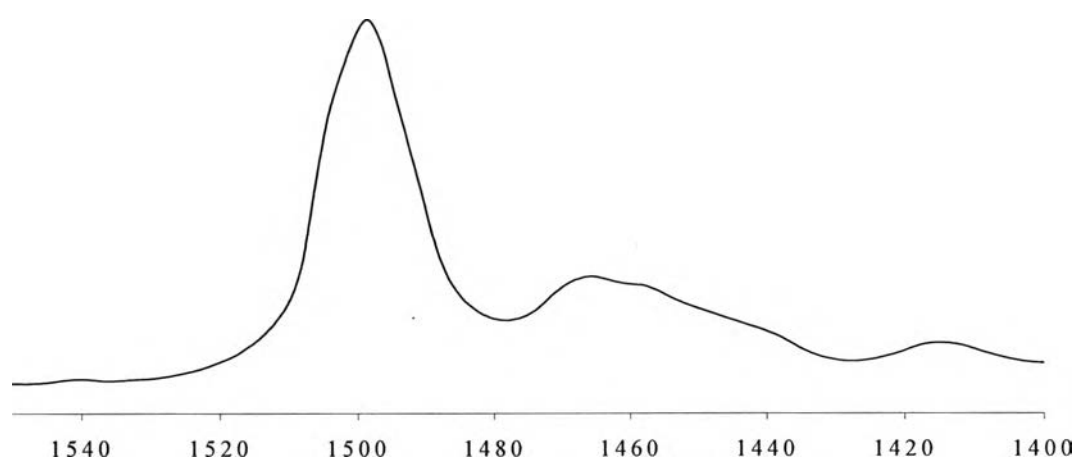


Figure 4.3 FTIR spectra in the range between 1550 and 1400 cm^{-1} of washed precursor benzoxazine.

4.1.3 DSC

The curing of benzoxazine gives out heat for ring opening polymerization of the oxazine ring. Differential scanning calorimeter was used for determination the empirically suitable condition of curing this kind of benzoxazine monomer. Figure 4.4 shown the non-isothermal experiment for detection the heat of reaction. This spectrum shows the starting and ending

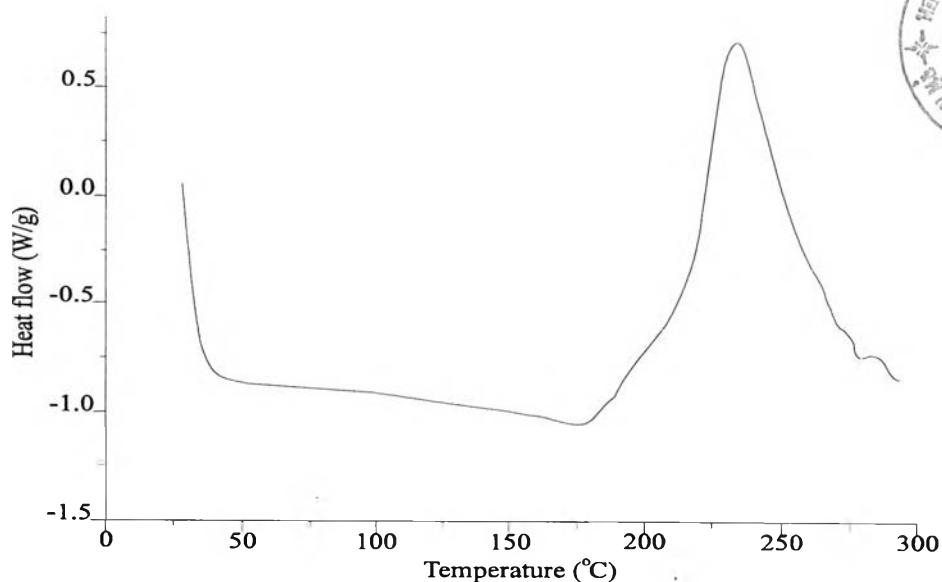


Figure 4.4 DSC spectrum of non-isothermal experiment of benzoxazine monomer.

temperature of curing reaction equal to 175 to about 300 °C and the exothermic peak at about 230°C. Because this exothermic peak can be correlated with the rate of reaction, the peak temperature is the temperature of the highest curing rate. This temperature was then chosen to use for the curing of benzoxazine monomer.

4.2 Characterization of Organically Modified Na⁺-Montmorillonite

4.2.1 AAS

The atomic absorption spectroscopy was used to determine amount of Na⁺ ion exchange with protonated form of modifying agent that was shown in eq (3.1). The results are shown in Table 4.1. The percentage of Na⁺ ion exchange was calculated by multiplying 100 to the ratio of averaged Na⁺ content obtained from AAS to that of the original montmorillonite (see also Appendix I). The amount of ion exchange is strongly depended on type of clay and type of modifying agent, which concern about relative affinity between Na⁺ ion and modifying agent.

Table 4.1 The percentage of Na⁺ ion exchanged from clay.

Modifying agent	Percentage of exchangeable Na ⁺ ions
DODEC	83.7
CAPRO	87.8
ANDAD	90.8
PHEN	95.6
TMAN	92.1

Most of modifying agents shown very high ability to exchange with Na⁺ ion; as a result silicate surfaces are mainly covered by modifying agent. These modified montmorillonites were further characterized by FTIR in the following section.

4.2.2 FTIR

FTIR was used for characterized Na⁺-montmorillonite and organically modified montmorillonite (OMOM) shown in Figure 4.5. The specifically characteristic peak of the individual modifying agent was shown in all OMOM's but not present in the pristine Na⁺-montmorillonite. The Na⁺-montmorillonite shows their characteristic peaks at 3630, 3455, 1040, 521 and 466 cm⁻¹ which can be associated with OH stretching, OOH stretching, Si-O stretching, Al-O stretching and Si-O bending respectively. The original modifying agents are presented in the form of primary amine salt, and show the boarding peak in the range 3300-2700 cm⁻¹ in every spectrum of OMOM. Not only the modified montmorillonites show those peaks but also show some characteristic peaks that depend on kind of modifying agent. These chemical structures of modifying agent are shown in Figure 3.1. For example dodecylamine modified montmorillonite (MOM_DODEC) shows C-H stretching while the caproic acid modified montmorillonite (MOM_CAPRO) shows a small peak of C=O stretching of carboxylic group and a very small

peak of C-H stretching. The 4-amino-N,N-dimethylaniline dihydrochloride, p-Phenetidine and 2,4,6-trimethylaniline modified montmorillonite (MOM_ANDAD, MOM_PHEN and MOM_TMAN) containing the benzene ring structure show C=C stretching of skeletal benzene ring mode ($1500 \pm 25 \text{ cm}^{-1}$). Moreover, the MOM_PHEN and MOM_TMAN still show Ar-O-R and very weak stretching of C-H band respectively. All of these characteristic peaks imply the success of the modifying of silicate layers material, and this is confirmed by more studying with TGA.

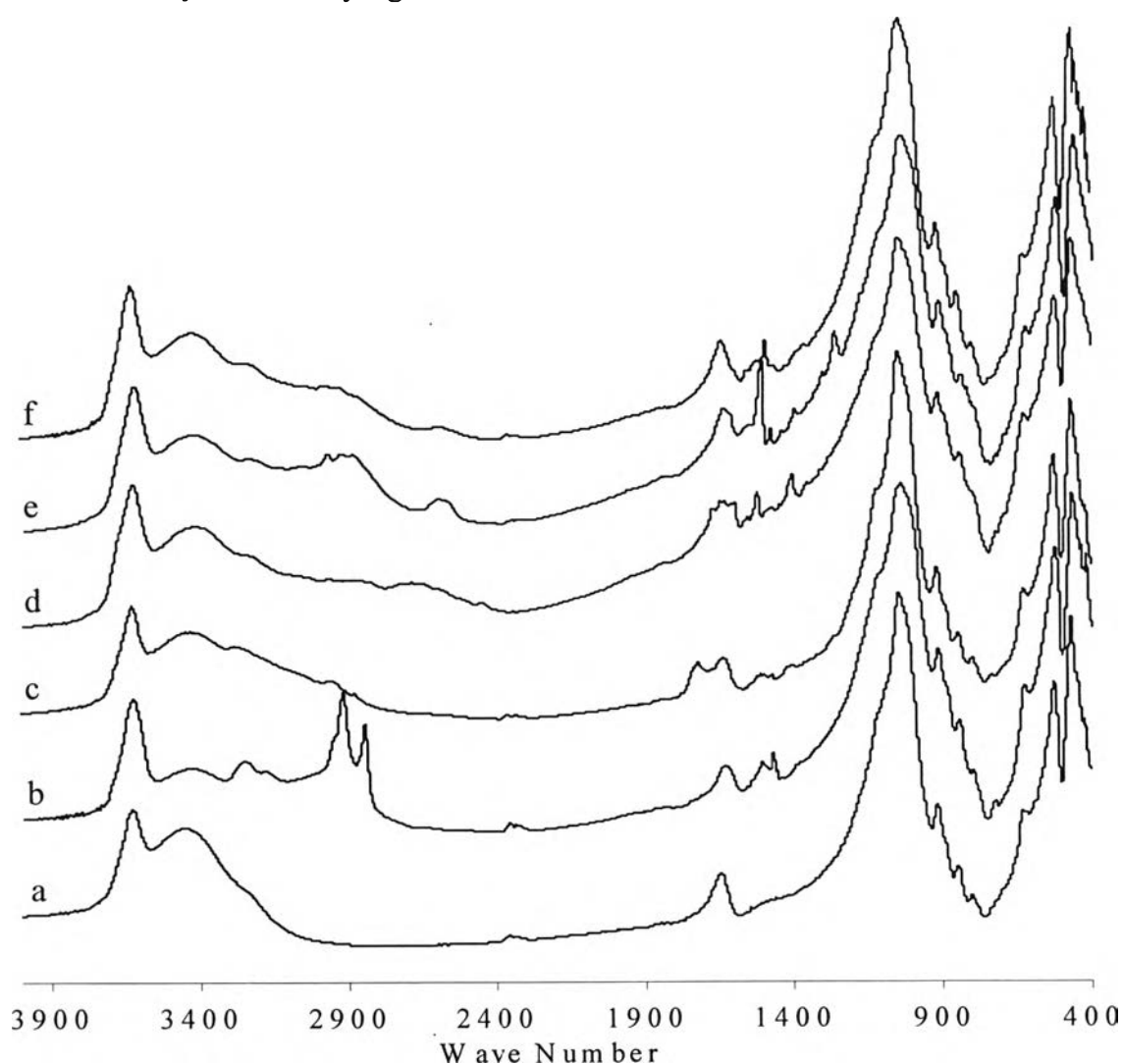


Figure 4.5 FTIR spectra of (a)Montmorillonite, (b)MOM_DODEC, (c) MOM_CAPRO, (d)MOM_ANDAD, (e)MOM_PHEN and (f) MOM_TMAN.

4.2.3 TGA

The thermogravimetric analysis was also used for characterization and can be applied for the determination of the content of organic compound in the gallery path of silicate layers. Figure 4.6 shows the TGA thermograms of dodecylamine, dodecylamine-modified montmorillonite and pristine montmorillonite. The nature of the montmorillonite structure is lost at temperature about 600°C and dodecylamine is decayed at temperature 160°C. However the weight of dodecylamine in the OMOM is lost at higher temperature when compared with pure dodecylamine. This consistency with more stability of dodecylamine occurred from ionic bonding between dodecylamine salt and silicate layers and trapped between the gallery pathway of silicate layers of montmorillonite. The others of OMOM have the same relationship like the dodecylamine-modified montmorillonite in that the intercalation agent compound lose at higher temperature compared with their pure compounds (see also Appendix II). Moreover, the thermograms of TGA can be used for determination the total organic content in the modified montmorillonite. The weight loss of all OMOMs were found to occur at

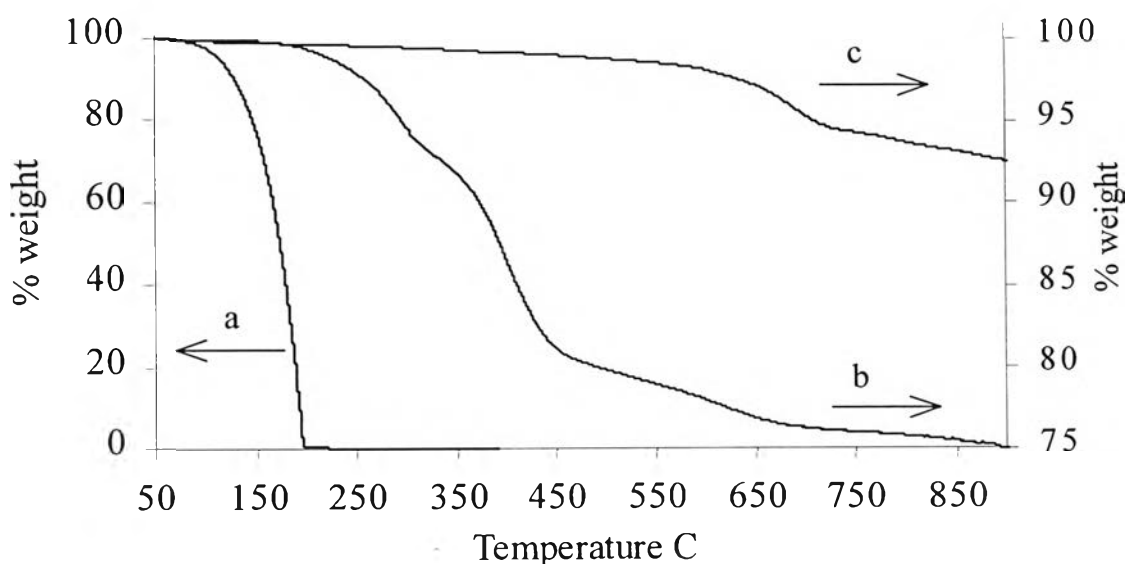


Figure 4.6 TGA thermograms of (a) dodecylamine, (b) dodecylamine modified montmorillonite and (c) dried Na⁺-montmorillonite.

Table 4.2 The percentage of total organic content from the TGA results.

OMOM	Modifying agent	δ	% Organic content	Td (°C)
MOM_DODEC	Dodecylamine	8.39	19.96	235
MOM_TMAN	2,4,6-trimethylaniline	9.31	3.86	238
MOM_ANDAD	4-amino-N,N-dimethylaniline	10.02	3.03	205
MOM_PHEN	p-Phenetidine	10.51	3.83	286
MOM_CAPRO	6-aminocaproic acid	10.71	7.49	257

δ = Solubility parameter (cal.cm^{-3})^{1/2} (benzoxazine monomer $\delta = 9.44$)

temperature within the range of lost temperature of their organic compounds and montmorillonite (~600 °C). Table 4.2 shows the percentage of total organic content in OMOM and solubility parameter of individual modifying agent. In the case of MOM_ANDAD, MOM_PHEN, and MOM_TMAN, the percentage of organic content are very low. These results are seemed to contradict with the previous result of AAS that show very high exchange capacity of ANDAD, PHEN and TMAN. However this TGA result can not use to correlate with the percent ion exchange because it can not confirm that all chemical components of each modifying agent will be lost their weight before 600°C. It is true that some carbon compounds of the modifying agent still remain in the gallery pathway of silicate layers; such as, carbon lamella nanocomposite (F. Beguin et al, 1996).

The organic modifying agent travelling inside the silicate layers of montmorillonite affects to expand the layer spacing of 001 plane. Hence, the d001 of OMOM is expected to increase from the original d001 of montmorillonite. This can be studied by XRD which was shown in the following section.

4.2.4 XRD

XRD results of various types of OMOM are shown in Table 4.3 and their spectra shown in Figure 4.7. These data show the relationship between molecular size that correlates with molecular weight of modifying agent and d001 spacing of OMOM. The first group of four types of the OMOM shows almost the same increasing of d001 spacing, about 4 Å, that corresponds to the radius of methylene group (-CH₂-) of hydrocarbon. Because this entire group of modifying agent has nearly the same of molecular weight (130-138 g/mol) so the expansion of silicate is almost the same.

In the case of MOM_DODEC shows the expansion equal to 6.9 Å that correlates with its bigger size or higher molecular weight (185 g/mol) than the other. This expansion of MOM_DODEC is greater than 4 Å but is less than 8 Å that mean some part of dodecylamine molecule are stacking on itself. All of the modifying agents align themselves in the horizontal direction parallel

Table 4.3 The d 001 spacing and the increasing of 001 spacing of OMOM and pristine montmorillonite.

Type of MOM	001 spacing (Å)	Increasing of 001 spacing (Å)	M.W. of modifying agent (g/mol)
MOM_TMAN	14.0	4.4	135
MOM_ANDAD	13.0	3.4	136
MOM_PHEN	13.7	4.1	137
MOM_CAPRO	13.3	3.7	131
MOM_DODEC	16.5	6.9	185
MOM	12.5	2.9	
MOM_Dry*	9.6	0	

* From Jordan J. W. (1949)

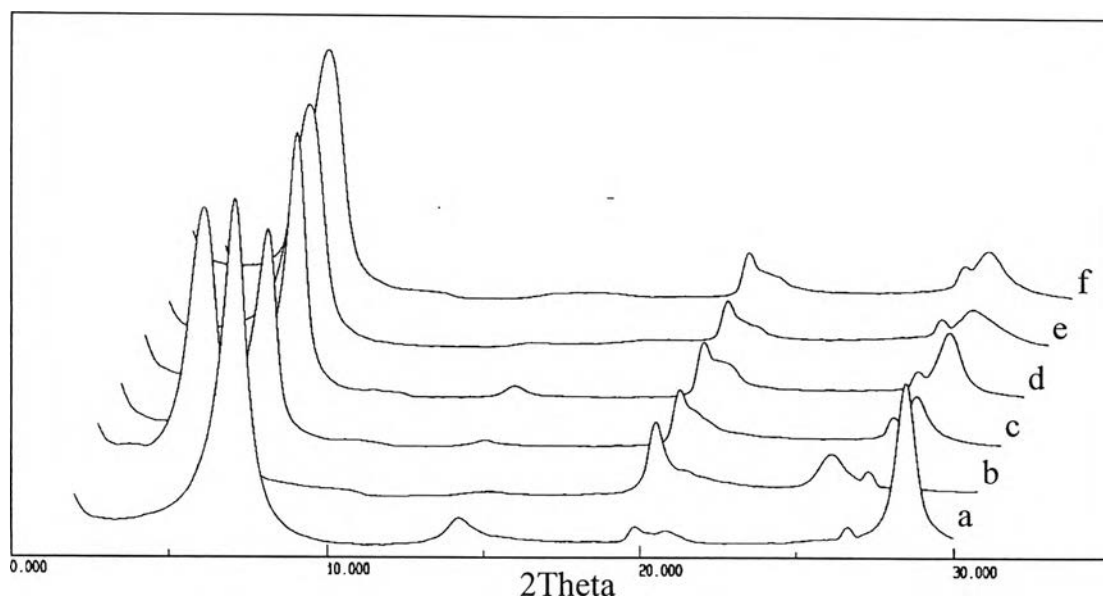


Figure 4.7 Wide angle X-ray diffraction spectra (2-30 deg.) of (a) MOM, (b) MOM_DODEC, (c) MOM_CAPRO, (d) MOM_ANDAD, (e) MOM_PHEN and (f) MOM_TMAN.

with the surface of silicate layers and thus most of the surface of silicate layer was coated with organic compound. Montmorillonite (MOM) also shows some expansion. It is known that the d spacing of montmorillonite varies greatly with the nature of the ions and solvent being sorbed. Like in this case of Na⁺-montmorillonite, it absorbs moisture very quickly and hence the d spacing is about 12 Å while the d spacing is about 9.6 Å in the dry form.

4.3 Studying of OMOM Swelling in Various Type of Solvent

These studying are based on the preparation of OMOM with good dispersion in various types of solvent system. It is important that the good delamination of OMOM can be achieved with suitable polarity medium. The solvent selected to study in this work is based on capability to dissolve

benzoxazine monomer. This is to provide and promote delamination of OMOM, and those can be divided into two part of mono solvent and binary solvent system.

4.3.1 Mono Solvent System

Figure 4.8 shows the total volume of swollen OMOM in various types of solvent. These swelling exhibit the relationship between type of modifying agent and kind of solvent. The good swelling renders more delamination where solvent can penetrate into gallery pathway. Hence, there is more the probability for benzoxazine monomer to intercalate too. Most of OMOM show the best swelling in the toluene solvent except MOM_PHEN that shows the best swelling in ethanol. However, MOM_PHEN exhibits good swelling in toluene. So, toluene was selected and used for nanocomposite

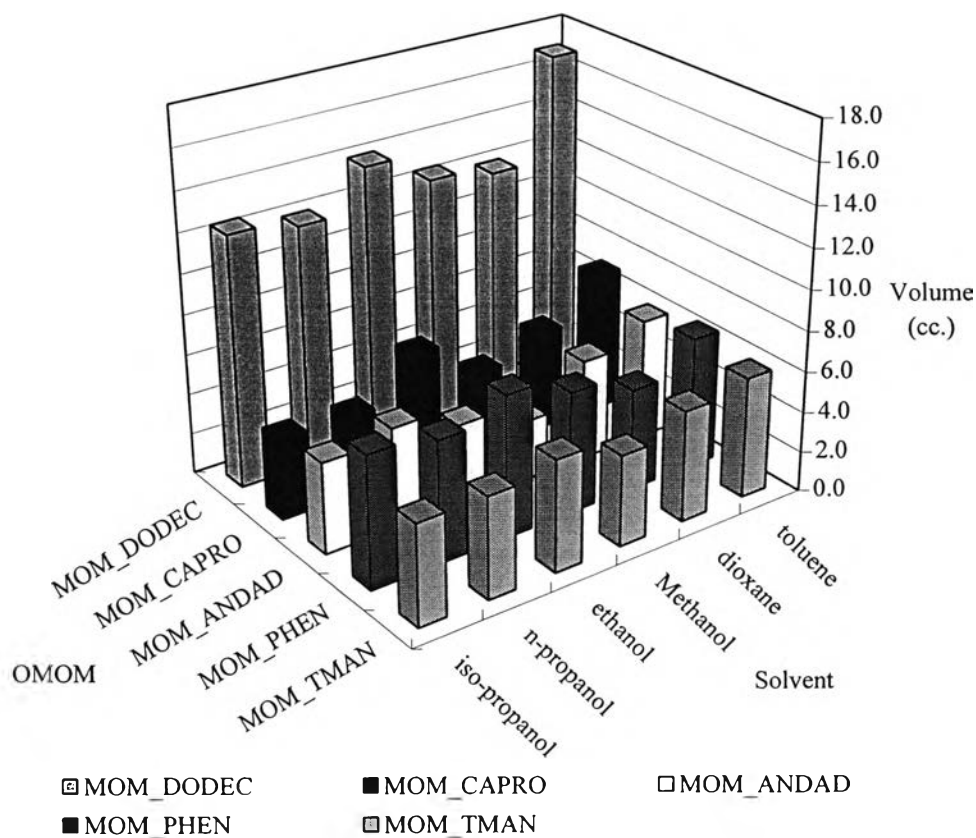


Figure 4.8 Volume of swollen OMOM in various types of solvent.

preparation. Moreover, dioxane, used for synthesis of benzoxazine monomer was also selected for composite preparation because it dissolved benzoxazine monomer very well. In addition, the solubility parameter of benzoxazine is closed to that of dioxane.

4.3.2 Binary Solvent System

An alternative solvent system is binary solvent system. This system has some properties that can not obtain from mono solvent system. Figure 4.9 shows swelling ability of OMOM in binary solvent system of methanol and toluene. Most of OMOM showed the better swelling in binary solvent than in mono solvent system of methanol and toluene. The composition of 5% methanol in toluene exhibits the best swelling of OMOM. These small amount of methanol can promote the swelling of OMOM because the methanol molecules can form hydrogen bonding on the surface of silicate layers and shield the uncoated area that can not be coated by modifying agent. So, all of silicate surfaces are more organic like and hence more gain

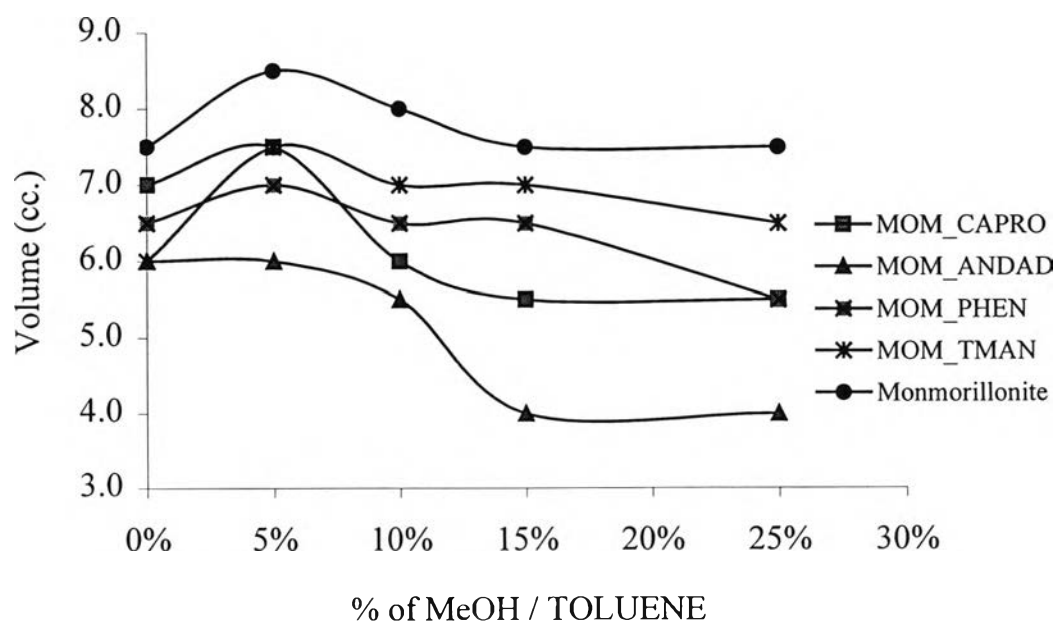


Figure 4.9 Volume of swollen OMOM in binary solvent system.

probability to have better dispersion of OMOM. It is further expected that benzoxazine monomer could be intercalate easier due to the improved organic nature. Especially MOM_DODEC showed very good dispersion in the binary solvent system but the result didn't show in the Figure because it can be explained that the physical gel for all composition of methanol and toluene mixed solvent is form. It is occurs from the hydrogen bonding between silicate layer and methanol molecule in addition to good solubility of dodecylamine in MOM_DODEC with both toluene and methanol. However, when methanol content increased, the physical gel was soften much more. This is affected by the excess of methanol interrupting the gel formation.

This binary solvent with small amount of methanol in toluene is shown the good alternative route to achieve substantial delamination of OMOM. So, the 5% methanol in toluene was selected and used for nanocomposite preparation.

4.4 Composite Characterization

4.4.1 XRD

The composite films of polybenzoxazine with various type of modifying agent was mounted on the standard holder of XRD for determination of the d spacing of silicate layers. The results of d_{001} spacing of silicate are shown in Table 4.4. The mixing time, type of modifying agent and the method that used for preparation of polybenzoxazine composite films were considered. These d spacing results do not show any significant change when compare with the mixing time. The only mechanical force with long time of mixing does not effectively provide better dispersion or greater delamination of silicate layers. From the various types of modifying agent selected with the reason of compatibility between modifying agent with benzoxazine according

Table 4.4 The d_{001} spacing of silicate layer in various types of composite film.

	Modifying agent	2 hrs.	4 hrs.	6hrs.
NON SOLVENT	DODEC	13.4	13.3	13.8
	TMAN	13.1	13.5	13.2
	ANDAD	13.3	13.5	13.1
	PHEN	13.5	13.3	13.8
	CAPRO	13.5	13.2	13.5
DIOXANE	DODEC	13.6	13.4	13.6
	TMAN	13.6	13.7	13.6
	ANDAD	13.6	13.6	13.8
	PHEN	13.4	13.8	13.3
	CAPRO	13.5	13.5	13.4
TOLUENE	DODEC	13.6	13.6	13.6
	TMAN	13.8	13.7	13.8
	ANDAD	13.5	13.6	13.5
	PHEN	13.5	13.5	13.5
	CAPRO	13.0	13.5	13.5
5%MeOH in TOLUENE	DODEC	13.4	13.3	13.5
	TMAN	13.6	13.7	13.8
	ANDAD	13.6	13.6	13.6
	PHEN	13.5	13.7	13.8
	CAPRO	13.6	13.3	13.5

to compatibility reason(see also Table 4.2), increase of solubility between modifying agent and benzoxazine not really affect the expansion of d_{001} . However, the result of MOM_DODEC is quite different in that the d spacing decreased. The dodecylamine molecules in the gallery pathway of silicate

layers may contract themselves during mixing with benzoxazine monomer. This behavior comes from the incompatibility of dodecylamine and benzoxazine and hence dodecylamine try to reduce its surface to contact with benzoxazine monomer. The other four types of OMOM having modifying agent that are more compatible with benzoxazine than dodecylamine do not help to give greater expansion than the original form of OMOM. It may be explained that these modifying agents are still not compatible enough with benzoxazine due to some discrepancy of solubility values. The compatible between modifying agent and polymer matrix is very important; for example, polycaprolactone with dimethyl dioctadecyl ammonium modified montmorillonite did not exhibit the good delamination of silicate layers in the composite. But when 12 aminododecanoic acid was used as a modifying agent, the excellent delaminations into the individual of silicate layer are occurred (Messersmith, P. B., 1995).

Moreover, in this work, the polarity of the medium in the mixing step that performed by using various types of solvent is concerned. It is including of non-solvent system, mono solvent system and binary solvent system. Those various types of solvents used for composite preparation provide better expansion ability of silicate layer in the matrix during mixing and thus compensate the incompatible between the modifying agent and benzoxazine monomer. But solvent type does not show any effect to the d spacing. For example, MOM_DODEC in the binary solvent system can form into physical gel indicating excellent expansion, but the good delamination of silicate layers in the polymer matrix cannot be obtained.

In the non-solvent system, OMOM were mixed with benzoxazine monomer and the mixture were then cured to produce the polymer-clay composite. These products from non-solvent preparation show the same value of d_{001} as those found in the mono and binary solvent system. Since, non solvent system reveals the true interaction between OMOM or modifying agent

and polybenzoxazine. The d_{001} value obtained by non solvent preparation can use as reference to indicate the compatibility effect. This leads to the conclusion that among these main effects, the compatibility is the most important.

4.4.2 TEM

The structural characterization of the polybenzoxazine-clay nanocomposite films was obtained by Transmission Electron microscopy (TEM). Figure 4.10 show transmission electron micrographs of polybenzoxazine with two type of modified clay of (a) MOM_DODEC and (b)

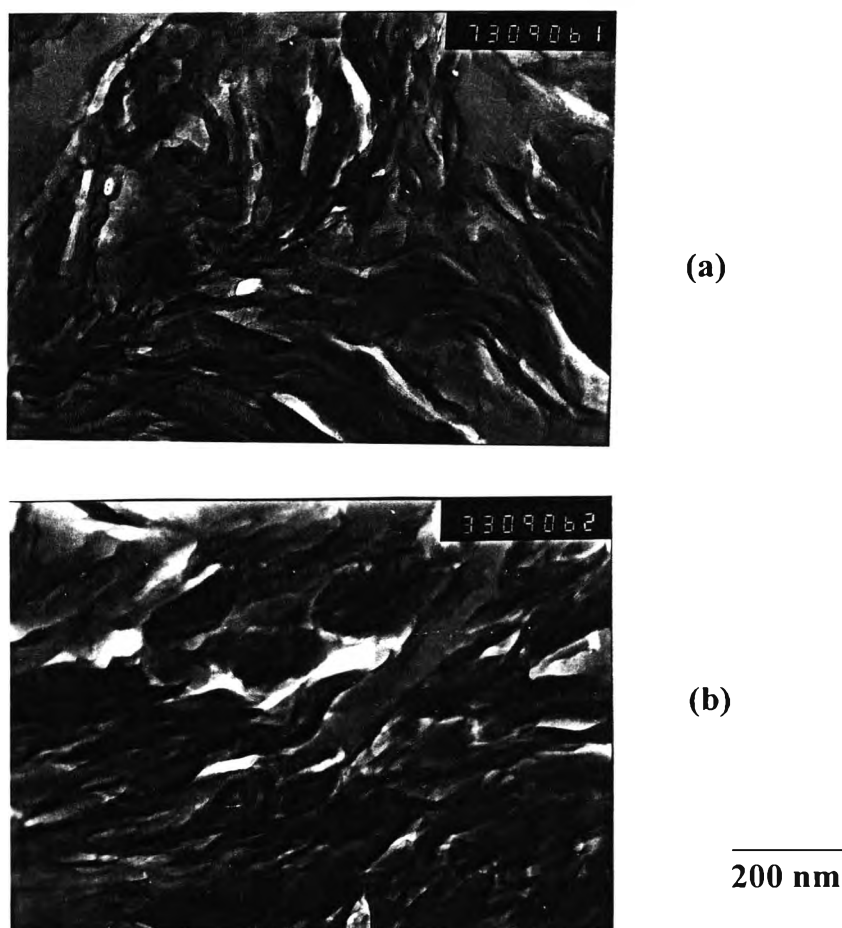


Figure 4.10 Transmission electron micrographs of polybenzoxazine composite of (a) MOM_DODEC and (b) MOM_TMAN via non solvent preparation.

MOM_TMAN which these composite films were prepared via non solvent system. These figures show the aggregation of silicate layer in the benzoxazine matrix that consistence with the XRD result in the previous part that every type of modified clay in the polymer was shown nearly the same of d_{001} spacing. The effect of solvent that used to improve the polarity of medium to further expand of silicate layers was considered and showed the same expansion distance as non solvent method (TEM results in Appendix III).

4.5 Properties of Composite

4.5.1 Heat Resistance

Thermogravimetric analysis was used for study on the heat resistance property of polybenzoxazine composite films. The TGA results of various types of composite films are shown in the Table 4.5 and in Appendix IV. The ash weight of composite film (28.9-37.2%) is greater than ash from the polybenzoxazine film (28.6%). The increasing of weight is correlated with the content of modified clay in the polymer matrix (~3%). Heat resistance of composite film is improved as seen by the increase of the first onset of degradation temperature of the composite film from the pristine polybenzoxazine film. However, the second onset of degradation temperature of composite film decreases as compared with polybenzoxazine film. The decreasing of second onset temperature may effect from obstructive of silicate layers in the crosslinking of polymer matrix. It is noted that both transitions are quite closed. So, the total degradation of composite film has sharper transition than the polybenzoxazine film. The effect of composite preparation method on the heat resistance property of composite film does not show any significant change because the dispersion of silicate layers in the composite film is not quite different in various preparation methods. The effect of modifying agent on the heat resistance property is very small or can be neglect

Table 4.5 The first and second onset temperatures of composite film together with percent ash in the composite film.

	Modifying agent	Td #1	Td #2	% ash
Polybenzoxazine		292	405	28.6
NON SOLVENT	DODEC	296	387	29.2
	TMAN	293	388	29.2
	ANDAD	298	391	32.5
	PHEN	296	393	32.2
	CAPRO	300	390	28.4
DIOXANE	DODEC	301	399	29.9
	TMAN	295	401	31.8
	ANDAD	301	400	33.7
	PHEN	298	398	31.2
	CAPRO	304	397	31.3
TOLUENE	DODEC	298	394	28.9
	TMAN	296	386	34.3
	ANDAD	298	390	29.2
	PHEN	296	388	31.3
	CAPRO	296	391	32.1
5% MeOH in TOLUENE	DODEC	297	400	29.7
	TMAN	298	398	29.9
	ANDAD	297	396	32.9
	PHEN	303	393	37.2
	CAPRO	301	393	30.3

Td = Degradation temperature taken at the onset of mass drop (°C).

because these agent are small molecules and its content in the composite film is very small.

The silicate layer in the polybenzoxazine composite film has improved heat resistance property because the silicate layer itself has very high heat resistance property. However, a little change in the heat resistance properties is shown and correlates with the dispersion of silicate layer in the polymer matrix. The good delamination and dispersion of silicate layer show better improvement of the heat resistance due to the increase of surface area of silicate to prevent heat penetration into the polymer matrix.

4.5.2 Water Absorption

Thermogravimetric analysis was used for study on water absorption of polymer and polymer composite films and shown in Table 4.6 and Appendix V. The sample films were immersed in the water at 30°C for 48 hrs before experiment run. The TGA thermograms of polybenzoxazine film

Table 4.6 The first and second onset temperatures of composite film of non solvent preparation with percent ash of composite film from water absorption experiment.

	Modifying agent	Td #1	Td #2	% ash	% H ₂ O*
Polybenzoxazine	-	282	396	23.5	5.1
Polybenzoxazinec Composite	DODEC	303	396	30.7	-1.5
	TMAN	300	395	27.4	1.8
	ANDAD	302	401	27.1	5.4
	PHEN	299	396	26.8	5.4
	CAPRO	302	397	28.2	0.2

Td = Degradation temperature taken at the onset of mass drop (°C).

* Calculated from %ash of dry (Table 4.5) minus %ash of wet composite film.

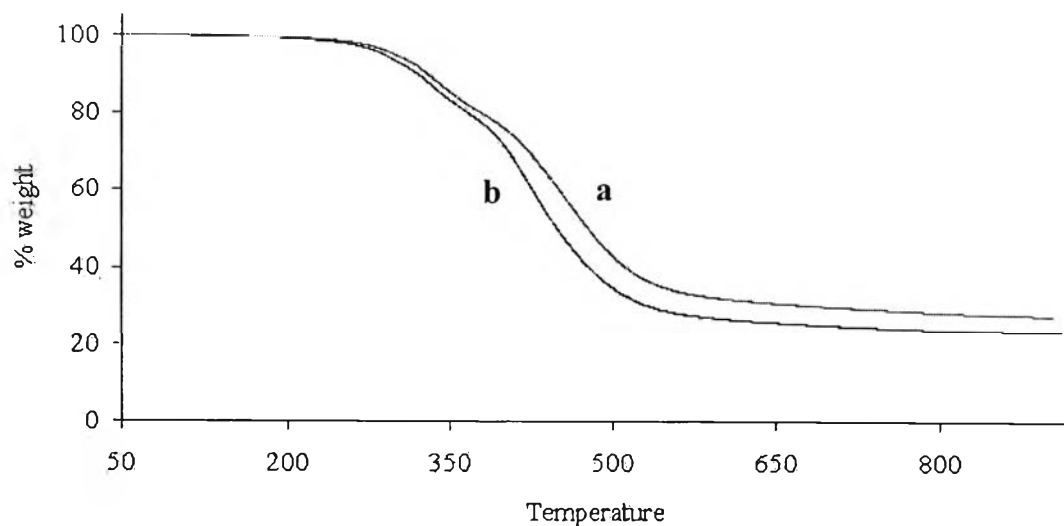


Figure 4.11 TGA thermograms of (a) polybenzoxazine film and (b) water immersed polybenzoxazine film.

both water immersed and non-immersed films are shown in Figure 4.11 while Figure 4.12 shows the thermograms of polybenzoxazine composite both water immersed and non-immersed films. Both water-immersed sample films in two figures do not show any significant change in the beginning of thermograms

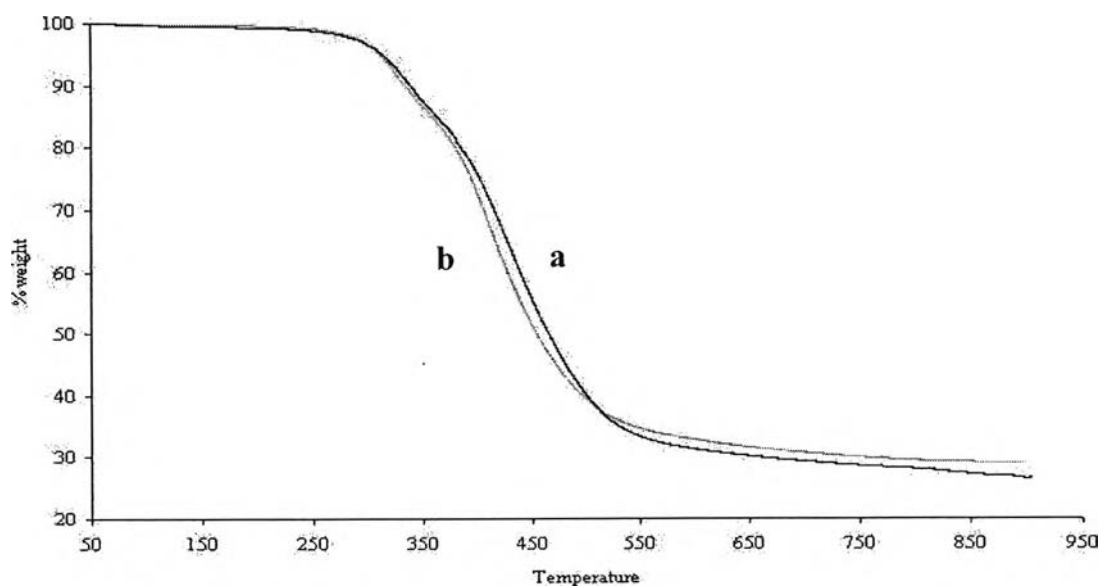


Figure 4.12 TGA thermograms of (a) water immersed and (b) not immersed 3% MOM_TMAN-polybenzoxazine composite film.

that should reveal lost of water. However, decreasing of percentage of ash in both polymer and composite films shown in the figures that can refer to lost of water during experimental. The decreasing of percent ash of water-immersed polybenzoxazine film is 5.1 percent while the composite film shows only about 2.3 percent (calculated from the average value of all type of modifying agent). Because the shape of silicate layers like flakes which retard the penetration of water to the polymer matrix, so the water absorption of the composite film is smaller than pristine polybenzoxazine film. However, in the case of the well dispersed silicate in the polymer matrix, it shows less water absorption than the conventional composite. That affects from the increasing aspect ratio of silicate layers which directly effect to the path length of water penetration. For example, this behavior was found in the poly(ϵ -caprolactone)-clay nanocomposite as reported by Messersmith and Giannelis (1995).