CHAPTER III
RESULTS AND DISCUSSION

3.1 Monomer Characterization

The FTIR spectra of the purified B-a and B-m are shown in Figures 3.1 and 3.2. For both monomers, the C-H stretching of the methylene groups in benzoxazine ring can be seen in the spectral region from 3100-2700 cm^{-1}, the methyl group vibrations occuring at 2967 and 2870 cm^{-1}. The symmetric methylene wagging and twisting bands are shown by weak bands around 1370-1250 cm^{-1}. The region from 1490-1460 cm^{-1} can be assigned to the methylene antisymmetric deformation. The C-H out-of-deformation of the 1,2,4-tri-substituted benzene ring can be found in the region from 940-920 cm^{-1}.

The band at 1496 cm^{-1} attributes to the tri-substituted benzene ring mode in the oxazine ring structure, while the band at 1481 cm^{-1} is assigned to the tetra-substituted benzene ring mode in the orho-substituted (methylene-amine-methylene bridge) phenolic structures. The antisymmetric and symmetric C-N-C stretching modes are shown in the regions from 1240-1020 cm^{-1} and 830-740 cm^{-1} respectively. The region of 1240-1210 cm^{-1} is due to the C-O-C antisymmetric stretching mode, while the symmetric stretching mode can be found in the region from 1040-1020 cm^{-1}.

For benzoxazine monomer based on methylamine, the methyl group on nitrogen atom appears at 2810 and 2794 cm^{-1}(J.P. Dunker, 1995).

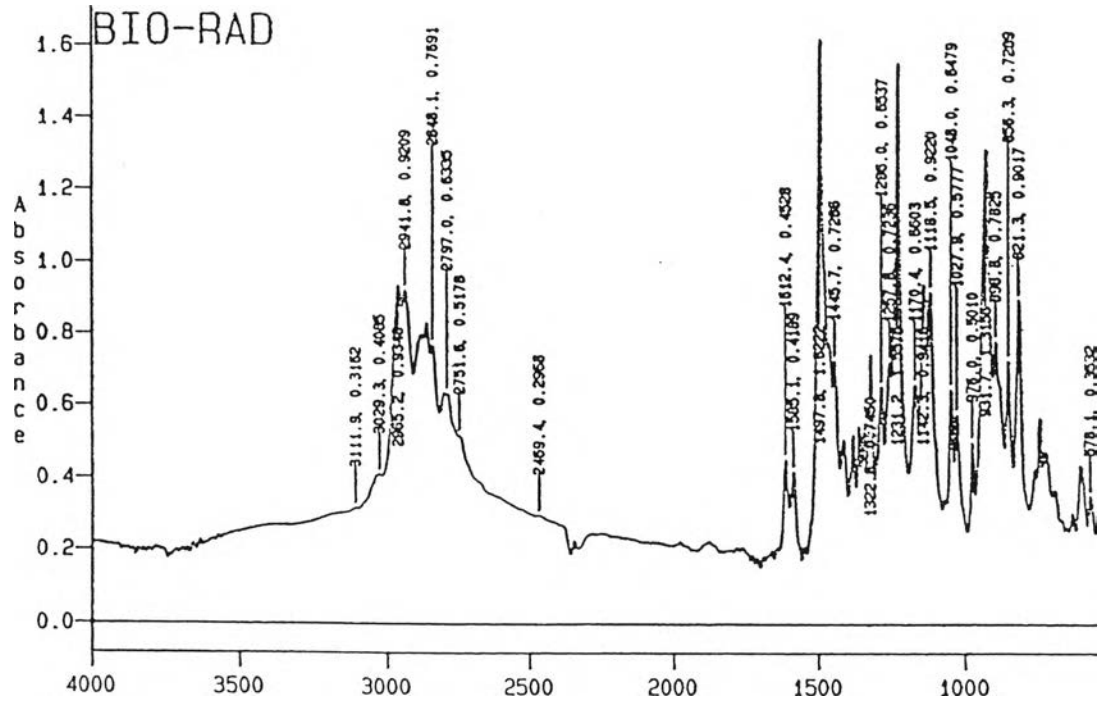

Figure 3.1 FTIR spectrum of purified benzoxazine based on methylamine, B-m, monomer.

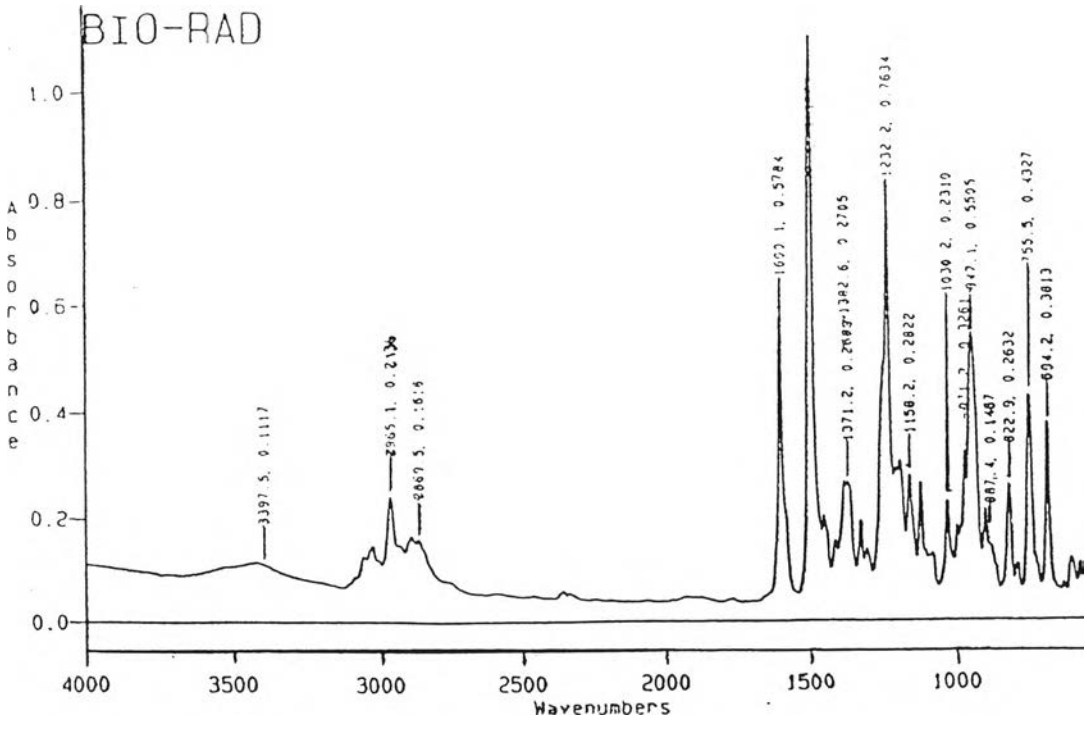

Figure 3.2 FTIR spectrum of benzoxazine based on aniline, B-a, monomer.

3.2 Physical Characterization

Polybenzoxazine paper composites are expected for the unique properties comparing to other composites. Paper is a natural fiber having hydroxyl groups which lead to the high hydrophilicity, while the benzoxazine exhibits hydrophobicity to the overall material. Hence, it is instructive to study the effects of the paper fiber on the composites.

The applications of paper composites can be expected due to the cost performance and mechanical endurance together with the natural availablility merit. However, since paper can be affected from the environment easily, it is necessary to study the environmental resistance of the materials as the first step.

In this section, paper composites are investigated in terms of their water absorption property. Normally, paper absorbs water by more than hundred fold. However, it can be expected that the composites will be protected from water attack by the polymer component and the absorption will not be significant compared to the pure paper raw material. In this case, the interface of paper and the polybenzoxazines matrix will play an important role regarding the water absorption property. The effect of the interface of the composites should be related to the duration of soaking time, which is the time for paper soaking in the molten resin, and as a result, the penetration of water molecule will be controlled. The fiber content of the composite will also affect the water absorption property. It can be expected that when the fiber content becomes higher, the water penetration will be more significant.

3.2.1 Density Measurement

The density at room temperature of polybenzoxazines and their composites were calculated and summarized in Tables 3.1 and 3.2.

Table 3.1 Summary of the physical properties of B-a, and B-a composites

Soaking Time* (min)	Specific Gravity (g/cm^3)	Density (g/cm^3)	Water Absorption (%)				
			1 day	7 days	14 days	28 days	30 days
B-a	1.1817	1.1789	0.230	0.516	0.696	0.875	0.899
B-a + paper 0†	1.2785	1.2754	2.369	7.265	8.473	8.755	8.776
B-a + paper 30†	1.2674	1.2644	1.808	5.782	7.254	8.097	8.107
B-a + paper 60†	1.2650	1.2620	1.144	4.293	5.470	6.616	6.728
B-a + paper 90†	1.2792	1.2761	2.574	7.447	8.457	8.706	8.713
B-a + paper 120†	1.2687	1.2657	2.865	7.702	8.489	8.701	8.721

* Soaking time is the time for melting the resin and allowing the paper to soak in the molten resin before compression at higher temperature

† Soaking time in minutes

B-a composites showed higher density than B-a polymer. The density values of composites were approximately the same, i.e. in the range of 1.2620-1.2754 g/cm^3, while the density of B-a polymer is 1.1789 g/cm^3.

Table 3.2 Summary of the physical properties of B-m and B-m composites

Soaking Time* (min.)	Specific Gravity (g/cm^3)	Density (g/cm^3)	Water Absorption (%)				
			1 day	7 days	14 days	28 days	30 days
B-m	1.1316	1.1289	0.248	0255	0.720	0.815	0.859
B-m + paper 0	1.2584	1.2554	5.062	9.682	9.829	9.950	9.962
B-m + paper 120	1.2241	1.2212	2.174	5.906	7.622	8.529	8.549

* Soaking time is the time for melting the resin and allowing the paper to soak in the molten resin before compression at higher temperature

In the case of B-m and B-m composites, the density values reveal similar results to that of B-a and B-a composites in the range of 1.2667 to 1.2212 g/cm^3 while the density of B-m polymer was 1.1289 g/cm^3.

In the cases of B-a composites and B-m composites, it is found that the density was higher than the polymer systems due to the addition of fiber to the composites.

Density of the composites can be influenced mainly by two factors. The one is the molecular weight of the polymer main chains in the composites and the other is amount of the polymer penetrated into the paper.

The former depends directly on the polymer itself while the latter is related to the interaction between the interface of polymer and paper, which is related to hydrophobicity and hydrophilicity balances between paper and polymer main chains.

From the results, it is found that B-a composites give higher densities than B-m composites. However, it is difficult to conclude this because the aniline moieties gives the higher molecular weight than B-a compared with methylamine groups of B-m. It should be noticed that the increasing density value of B-a is less than in the case of B-m. This suggests that the amount of polymer and paper per volume for B-a composites is lower than for B-m composites. Thus, it can be concluded that the interaction between paper and B-m is higher than B-a, which may be due to the balance of hydrophilicity of methylamine-based benzoxazine and paper fiber. However, the apparent density value of B-m composite is less than B-a, since the molecular weight of the aniline moiety is 5 fold higher than the methylamine moiety.

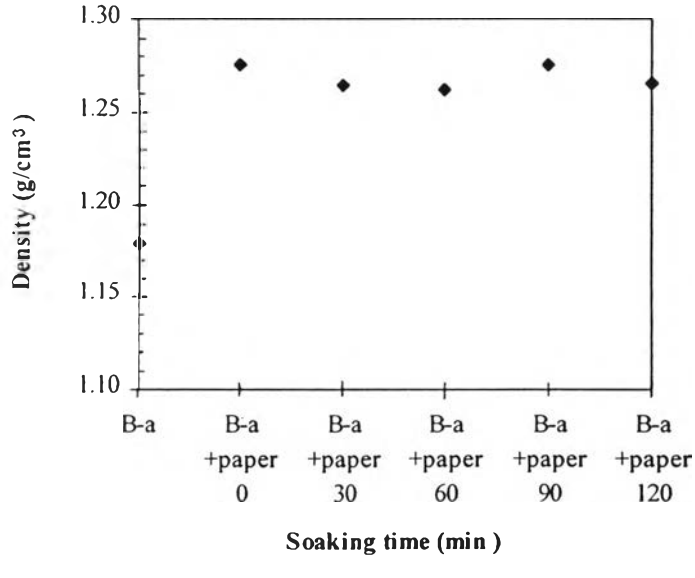

Figure 3.3 Density of B-a and B-a composites with various soaking times.

Figure 3.3 shows the density with various soaking times. It is expected that curing at an appropriate soaking time and soaking temperature, will produce the composites of high density. It is known that benzoxazine precursors can be molten and polymerized approximately above 100°C. In order to study the soaking condition, it is necessary to operate under conditions of molten temperature. At 100°C soaking condition, it was found that the polymer melt could not fill the mold uniformly. Thus, the curing condition was focused on the molten temperature. A homogeneous polymer melt was produced at 120°C. At a soaking temperature of 120°C the density of the composites did not show any differences among the various conditions of soaking times. From these results it appears that at 120°C the molten polymer is initially polymerized and the polymer molecules tend to exist in a viscous polymer state rather than penetrate into the paper fiber.

3.2.2 Water Absorption Measurement

Water absorption is one of the paper composites properties which is directly related to the interface between paper and benzoxazine. In a previous section the density of the composites has been discussed in terms of the interfacial property of the composites. However, in this section the fiber volume contents and the effect of the composites interface will be discussed.

It is found that the % fiber volume content of B-a composites are 38.99, 37.80 , 37.30 , 38.68 and 38.54, respectively. For B-m composites, the fiber volume contents are 38.86% and 37.97%, respectively. Hence the different densities of composites.

Table 3.1 and 3.2 summarize the water absorption values for various

periods of immersion time. The curves of water absorption (%) as a function of time of immersion in distilled water for 30 days are plotted as shown Figures 3.4 and 3.5 for B-a and B-a composites and for B-m and B-m composites, respectively.

Water Absorption and Hydrophilicity of polymer system

Water absorption (%) of B-a composites is higher than B-a polymer by approximately 7.48-9.76 folds, while the water absorption (%) of B-m composites is approximately 9.95-11.60 times higher than B-m polymer. It can be concluded that water absorption onto the polymer matrices is mainly owing to the hydrophilicity of the polymer chains. Thus, it is found that B-m polymer shows higher water absorption at the initial step than B-a polymer (Figures 3.4 and 3.5), owing to the more hydrophilicity of the methylamine group compared with the aniline group.

In the case of the B-a and B-m composites, which composed of cellulose fiber, the hydrophilicity of fiber may play an important role for the water absorption. Thus, the composites should have more affinity to water than the cases of pure B-a and B-m polymers.

However, it is found that B-a and B-m composites show less water absorption than cellulose fiber. From the results, it is clear that in the case of the composites water absorption will increase aproximately 2% a day which will be much less than paper fiber, absorbed water more than 100% a day (A.K. Mohanty and M. Misra, 1995). Comparing to cellulose fiber reinforced cement composites, which show 25-50% of water absorption, polybenzoxazine paper compasites have shown better water absorption property.

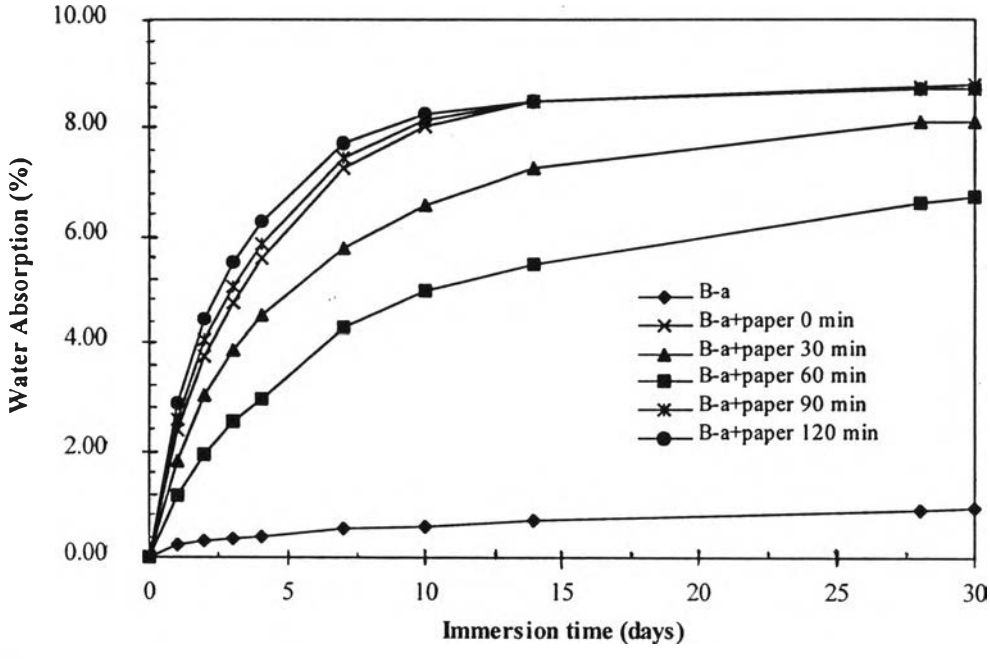

Figure 3.4 Water absorption (%) of B-a and B-a composites with various soaking times as a function of immersion time.

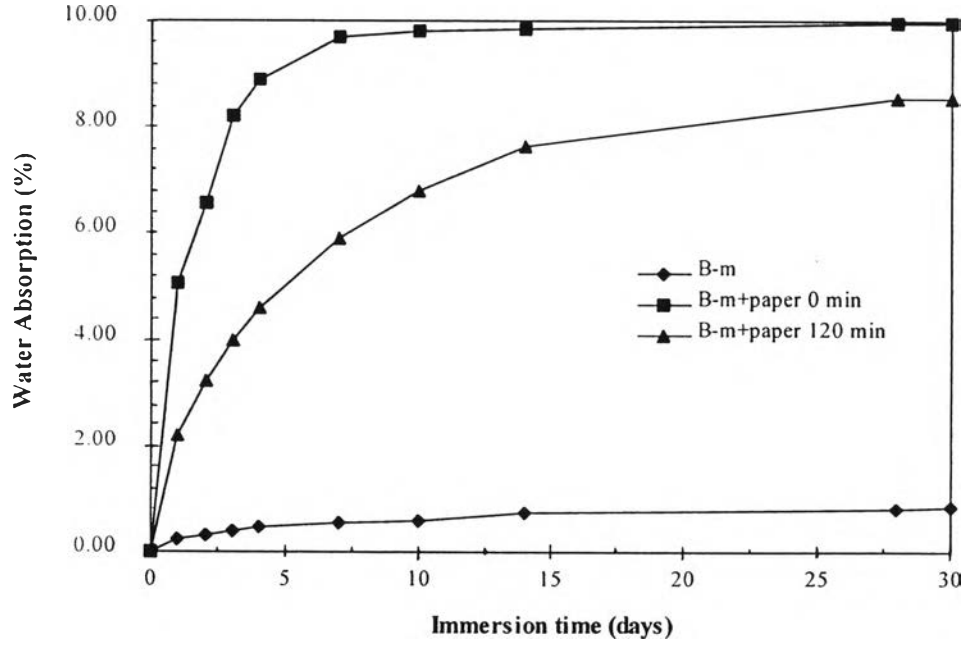

Figure 3.5 Water absorption (%) of B-m and B-m composites with various soaking times as a function of immersion time.

This can be explained that benzoxazines can protect the fiber from the water environment, owing to the hydrophobicity of benzoxazines part.

Paper fiber content is also an important factor concerning the system of composites. For high percentages of fiber content in the composites, it can be expected that water absorption will increase proportionally. However, the interface between the polymer chains and paper fiber will also play an important role, i.e. if the interface of the composites shows almost no defects, the water absorption would be low. As mentioned in the previous section, the soaking time is one of the approaches to study the interfacial effect.

Water Absorption and Soaking Time

Figure 3.6 shows the relationship of the soaking times and water absorption. Since in this work, the fiber content is not varied in the processing step, the fiber contents calculated in this section then were the values calculated from the prepared samples at each soaking time, according to equation 2.4.

It can be expected that with different soaking times, polymer volume content in the composites will be affected, owing to the molten state when the compression mold close. In contrast, the amount of the fiber will be constant while the amount of the polymer will be changed according to the processing step. A soaking time of 0 minutes, the fiber content is found to be the highest (38.99 %). This may be due to the molten polymer being squeezed from the mold at low viscosity compared to other soaking time cases. At longer soaking time the polymer viscosity will increase proportionally. However, in most cases, the fiber content is within the small range of 37.30 to 38.99 %.

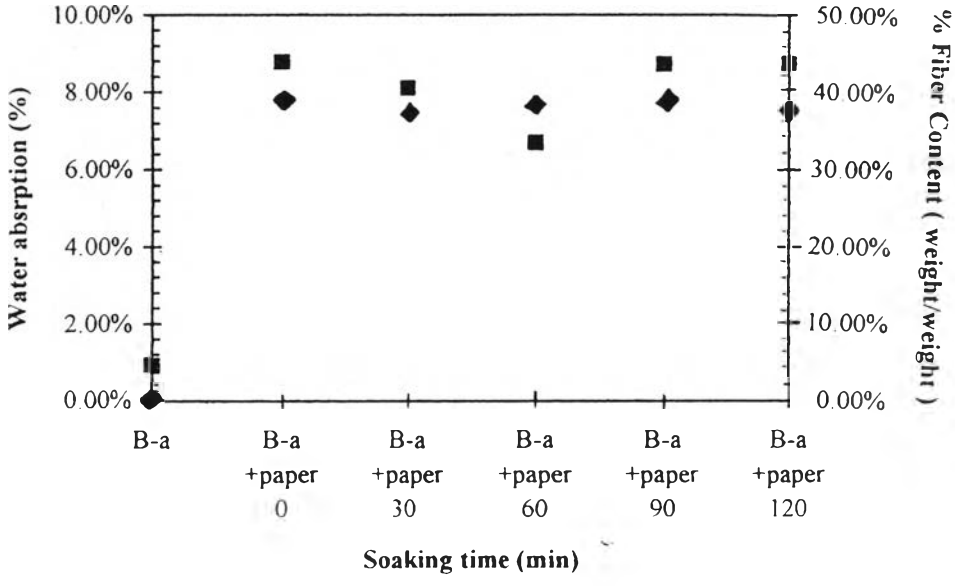

Figure 3.6 % Fiber content and water absorption (%) at various soaking time of B-a and B-a composites.(◆) : % Fiber content, and (■) : Water absorption (%).

The water absorption (%) are presented as a function of soaking time (Figure 3.6). In the case of B-a, by varying the soaking time from 0 to 120 minutes, it is found that water absorption (%) is in the range of 6.7 to 8.8% . The water absorption decreases from the soaking times of 0 to 60 min, suggesting that the long soaking time provides time for molten polymer to penetrate into the paper fiber and as a result the composites show less water absorption. However, in the case of 90 and 120 min., water absorption increases gradually. This can be explained that soaking time at that level (90 or 120 min.) will provide the curing environment to the polymer rather than the penetration to the paper fiber. It can be concluded that in order to minimize the water absorption for the composites it is important to specify the conditions for presoak, soaking and curing in terms of temperature and time.

Comparing glass fiber composites (H.Y. Low, M.S. thesis, 1995), which show a water absorption of 0.5% (for 30 days), it is clear that paper fiber composites show considerably higher water absorption owing to the hydrophilicity of three hydroxyl groups of cellulose fiber.

By considering the structure of the B-a oligomer, which has strong inter- and intra-hydrogen bonding between each monomer, it may be difficult for the benzoxazine precursor, which is cured to oligomer, to penetrate into the paper fiber and form the interaction with cellulose.

In the case of B-m, it is found that water absorption (%) also depends on the soaking time of B-m resin. In this case at long soaking times (120 min) the water absorption decreases due to the structure of B-m which is less bulky than B-a, therefore, B-m resin is easier to penetrate the fiber strands. It should be noted that B-m was prepared with excess solvent and the purification was complete. Thus, B-m shows low viscosity in the form of monomer precursors which can penetrate the cellulose moiety of paper fiber.

Water Absorption study based on fiber weight

In a previous section, water absorption was studied related to the composite weight. However, water absorption is mainly induced by the paper fiber in the composites. Thus, it is of interest to study the effect of paper fiber on the water absorption.

In order to study the effect of fiber on the water absorption, it is necessary to evaluate the percent of water absorption as a function of fiber

content. Figure 3.7 shows the water absorption as a function of percent of fiber in the composites (according to equation 2.5).

It is found that the percent of water absorption for all cases ranges from 23 to 26%. It is clear that the paper fiber in the composite is being protected by the polymer matrix.

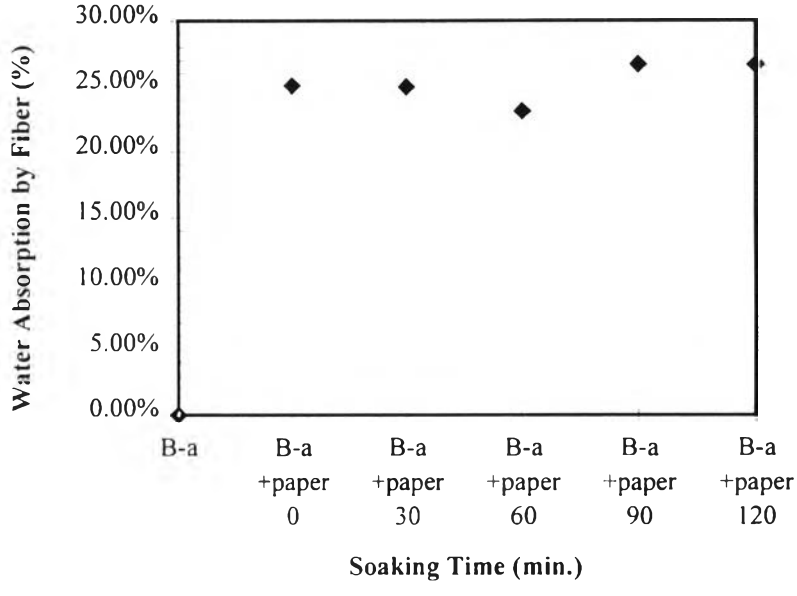

Figure 3.7 Water absorption (%) calculated by weight of fiber as a function of soaking time.

3.3 Mechanical Characterization

3.2.1 Flexural Testing

The Flexural testing data of B-a and their composites with various soaking times investigated in this work are summarized in Table 3.3. The

flexural property is the average value obtained from multiple tests according to ASTM D790-92.

Table 3.3 Mechanical properties of B-a and B-a composites

Soaking Time (min.)	Modulus (GPa)	Strength (MPa)	Strain (%)
B-a (only)	5.466	75.732	1.935
B-a+paper 0 min.	6.195	114.609	3.121
B-a+paper 30 min.	7.190	116.917	3.269
B-a+paper 60 min.	6.578	113.086	3.117
B-a+paper 90 min.	6.876	106.653	3.248
B-a+paper 120 min.	7.109	128.234	3.392

For some advanced applications, it is necessary to study the mechanical properties to evaluate the composite materials. In this case, paper composites are expected to show high mechanical properties by virtue of the benzoxazine polymer.

Ishida et al. (H.Y. Low, M.S. thesis, 1995) has shown that glass fiber composites produce improved mechanical properties, such as flexural strength, strain and modulus. Hence, it is of interest to study paper-based composite mechanical properties and consider the factors concerned with this system.

The B-a composites shows flexural properties superior to the B-a polymer (Table 3.3). The B-a and B-a composites show their brittle property, i.e. low % strain values. However, B-a composites exhibit higher elongation

at break than B-a polymer. The B-a samples are found to fail at an average of 1.935 % strain while the B-a composites experienced fracture when the strain average is between 3.117-3.392 %. The results reveal that the fiber addition to the composite structure has played an important role in stress transfer.

The flexural moduli of B-a and B-a composites are 5.466 GPa and 6.195 to 7.190 GPa respectively. The strength at break of the B-a composites (106.653 to 128.354 MPa,) are higher than that of B-a polymer (75.732 MPa).

Figures 3.8 and 3.9 are flexural modulus and % strain as a function of soaking time, respectively.

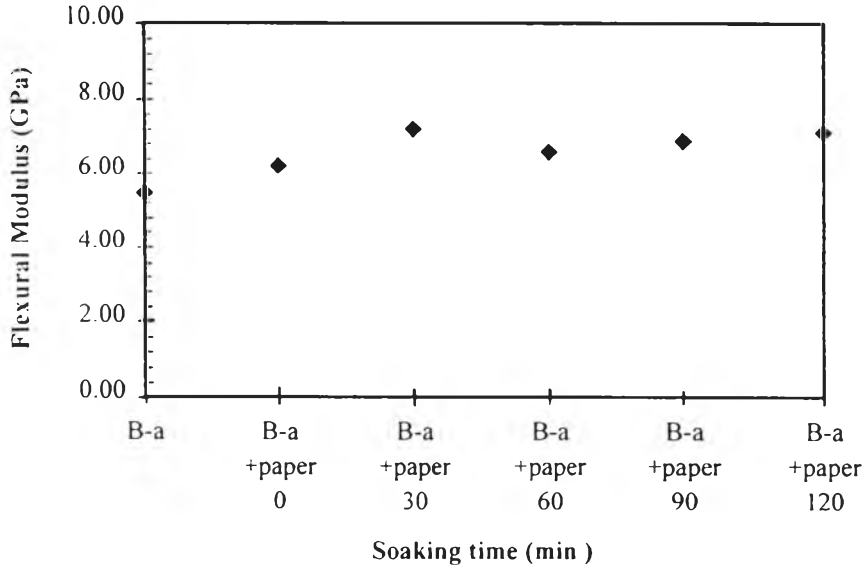

Figure 3.8 Flexural modulus of B-a and B-a composites as a function of soaking time.

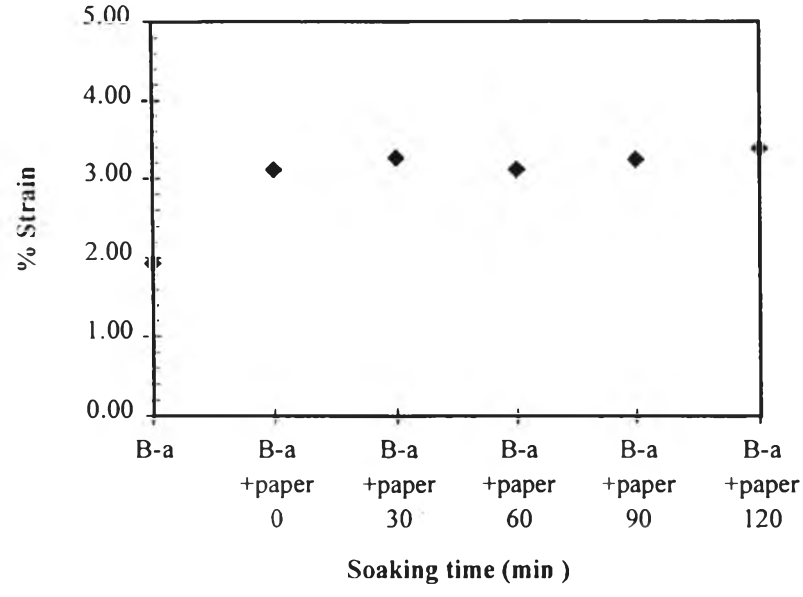

Figure 3.9 % strain at break of B-a and B-a composites as a function of soaking time.

As shown in Figure 3.8, the flexural modulus of B-a composites are approximately the same and slightly higher than B-a polymer. It can be concluded that the strength at break and elongation at break for those composites are increased due to the fiber in the composites.

The same tendency can be found in the case of strain at break (Figure 3.9). It is found that the % strain or elongation at break depend on the % fiber volume content.

The strain of B-a polymer is 1.935%, which is lower than other cases, indicating the effect of fiber in the composites. For the B-a composites, the % strain is improved for 1-1.5 folds. It should be noted that the varying soaking times at 120°C are not the main factor concerning strain improvement.

3.2.2 Dynamic Mechanical Measurement

Dynamic mechanical analysis is another useful property to evaluate the properties of composites. With the temperature sweep mode, paper composites were investigated for storage modulus, glass transition temperature and tangent delta (tanδ) in order to evaluate mechanical properties.

Generally, dynamic mechanical test results provide data on storage modulus at room temperature (G'_{RT}), loss modulus (G") and damping curve or tangent delta (tanδ). Tg of B-a, B-m and their paper composites are determined by the sudden change in the loss modulus (G") curve. Storage modulus at room temperature (G'_{RT}) and Tg are summarized in Table 3.4.

Table 3.4 Summary of storage modulus at room temperature (G'_{RT}) and Tg of B-a, B-m and paper composites

Soaking time (min)	G'_{RT} (GPa)	Tg (°C)
B-a	1.958	164.0
B-a+paper 0 min.	3.792	173.7
B-a+paper 30 min.	3.774	171.8
B-a+paper 60 min.	3.131	172.1
B-a+paper 90 min.	3.968	173.9
B-a+paper 120 min.	4.307	171.9
B-m	1.894	176.6
B-m+paper 0 min.	3.899	213.1
B-m+paper 120 min.	3.107	216.4

Dynamic mechanical spectra of polymer system of B-a and B-m and composite material systems of B-a and B-m are shown in Figures 3.10-3.13, respectively.

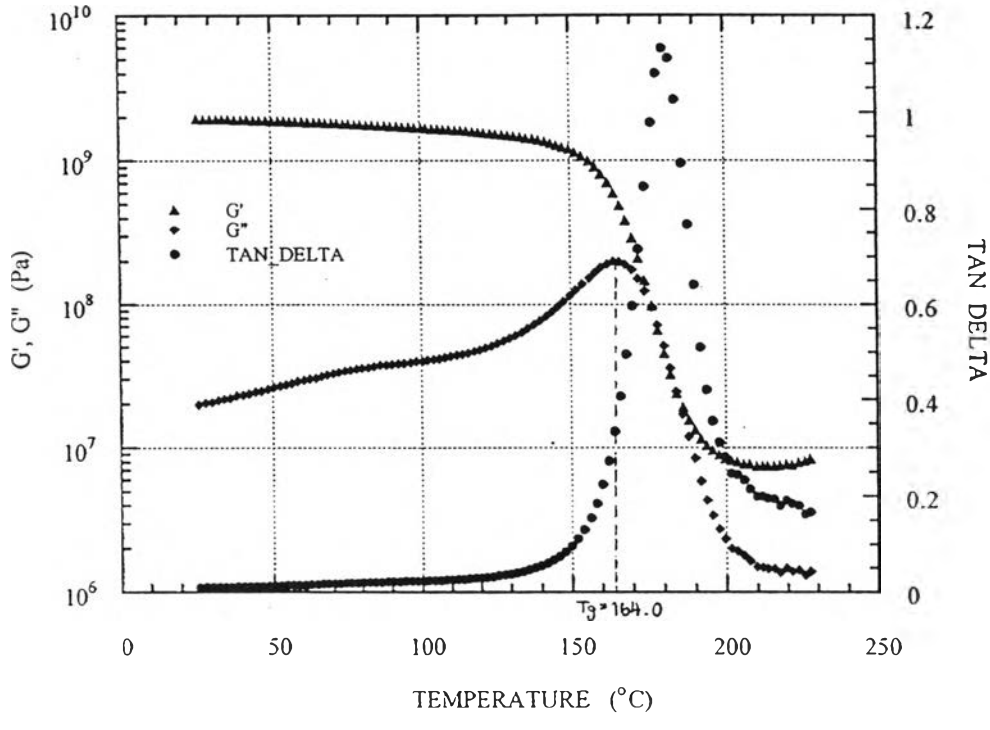

Figure 3.10 Dynamic mechanical spectrum of B-a, (▲) : storage modulus (G'), (◆) : loss modulus (G"), and (●) : tanδ.

Due to inter- and intra-hydrogen bondings, the strong network contributes to the high Tg (D.J. Allen, 1996). Thus, polybenzoxazines have high Tg (above 160 °C) while their crosslink densities are low. From Figures 3.10 and 3.11 respectively, the Tg of B-a is 164°C while the Tg of B-m is 176.6°C. The Tg of thermosetting resins are strongly influenced by their free volume (D.J. Allen, 1996).

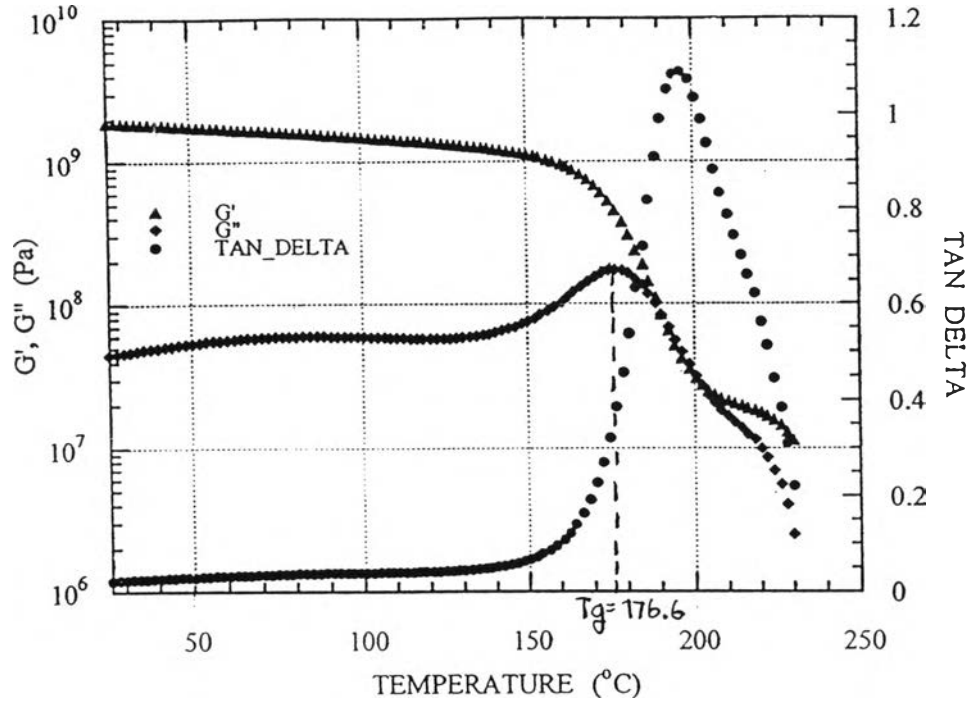

Figure 3.11 Dynamic mechanical spectrum of B-m, (▲) : storage modulus (G'), (◆) : loss modulus (G"), and (●) : tanδ.

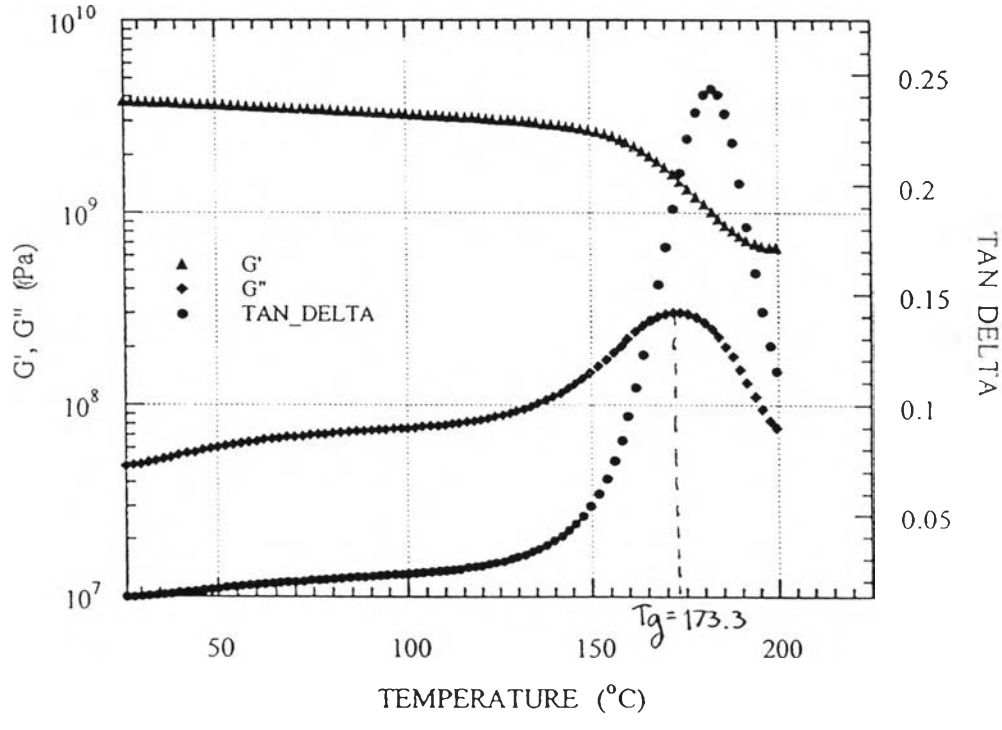

Figure 3.12 Dynamic mechanical spectrum of B-a composite for 0 min soaking time, (▲) : storage modulus (G'), (◆) : loss modulus (G"), and (●) : tanδ.

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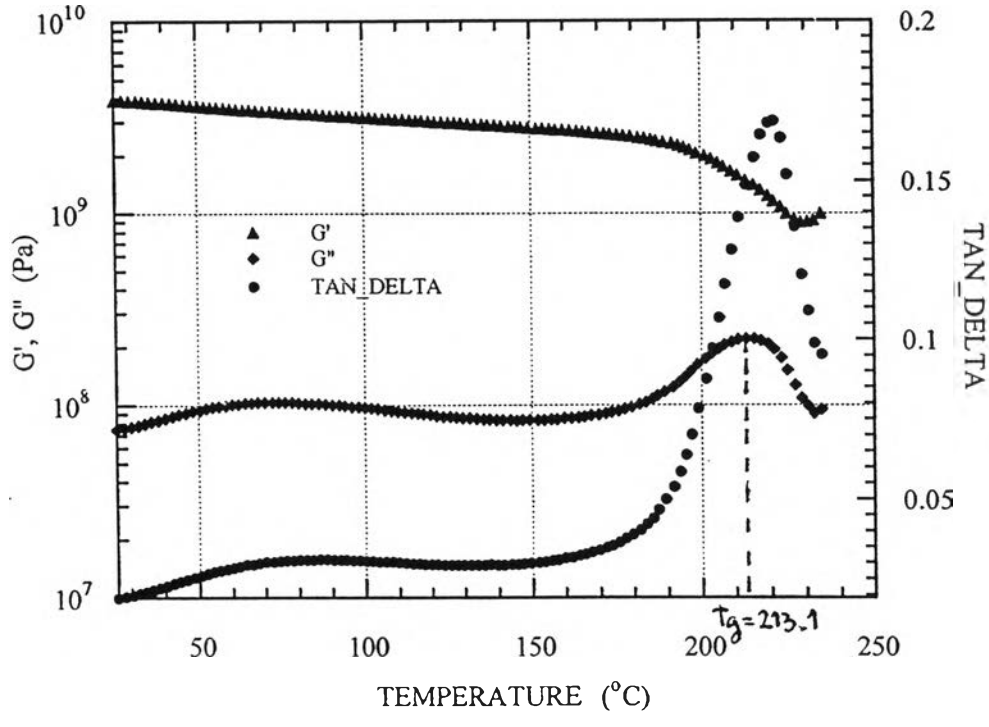

Figure 3.13 Dynamic mechanical spectrum of B-m composite for 0 min soaking time, (▲) : storage modulus, (G'), (◆) : loss modulus (G"), and (●) : tanδ.

It should be noted that B-a contains a greater amount of free volume than B-m due to the rigid benzene ring on the chain and thus provides an amorphous like structure. Therefore, the Tg of B-a polymer is lower than B-m polymer.

In the case of composites, glass transition temperatures were also determined. From Figures 3.12 and 3.13, the Tg of both B-a composites and B-m composites are higher than those of the B-a and B-m resins. This may be

due to the fiber that was added to the composites restricting the mobility of the polymer chains at the glass transition temperature.

Generally, in composite materials which consist of filler and matrix, there will be some of the deformation energy to dissipate, mainly in the matrix but also at the interface. In this case, the interface of polymer and paper fiber provide the additional source of energy lost by any mechanism. During deformation , a composite material with poor interfacial bonding will tend to dissipate more energy than the same composite with good interfacial bonding (N.Suprapakorn, M.S.Thesis, 1996). However, since the soaking temperature and curing temperature are in the same range, it is difficult to vary the soaking condition in order to study the interfacial effect on energy dissipation.

A comparison of G', G" and tan δ of B-a and B-a composites are shown in Figures 3.14-3.16. In Figure 3.14, the storage modulus (G') of B-a composite is higher than that of the B-a polymer. This may be due to the fiber making the composite more elastic. The decrease in the G' curve, due to the transition from glassy state to rubbery state, of the B-a composites is shifted to the higher temperature compared with the B-a polymer system. In Figure 3.15, the loss modulus (G") of B-a composite is found to be higher than B-a polymer. The result reveals that in case of B-a composite, the fiber/matrix interface dissipates more energy than the B-a polymer. It can be concluded that the appropriate loss modulus will be achieved by the improvement of fiber/matrix interface in the B-a composite.

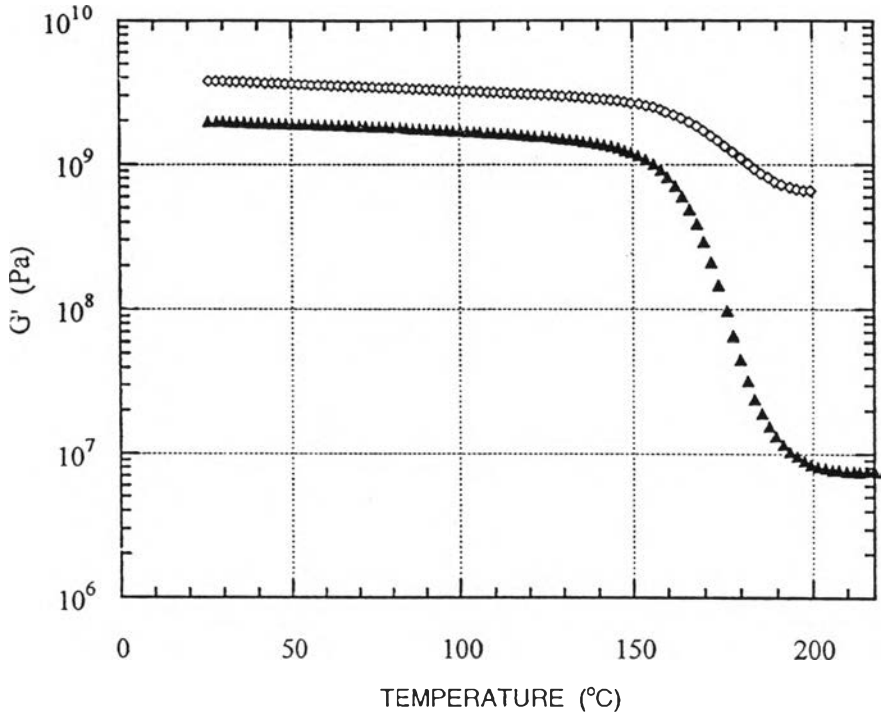

Figure 3.14 Storage modulus (G') compared between (▲) : B-a polymer and (◇) : B-a composite for 0 min soaking time.

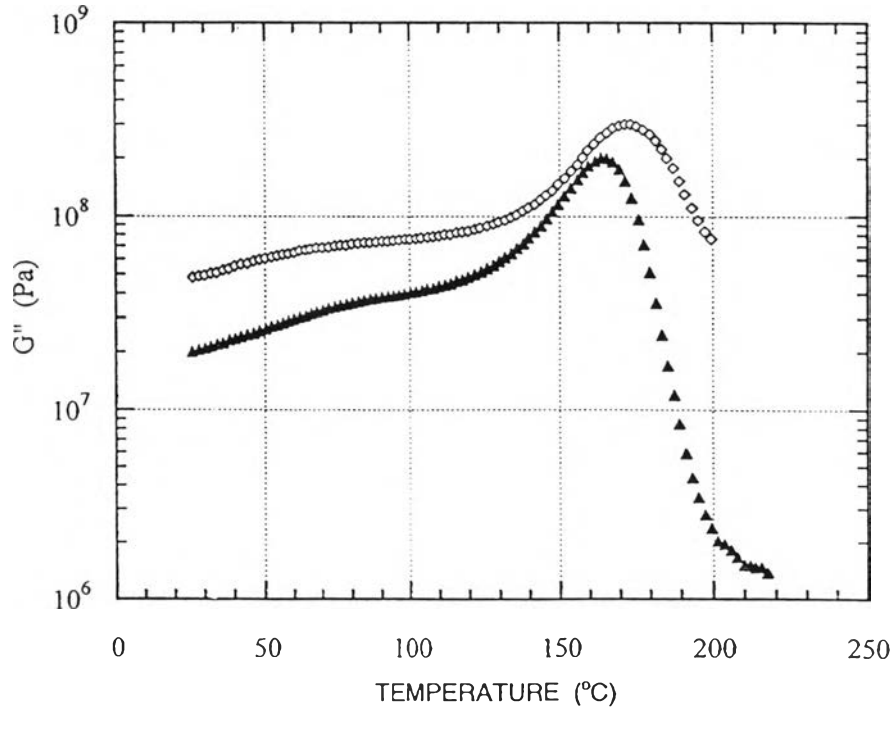

Figure 3.15 Loss modulus (G") compared between (▲) : B-a polymer and (◇) : B-a composite for 0 min soaking time.

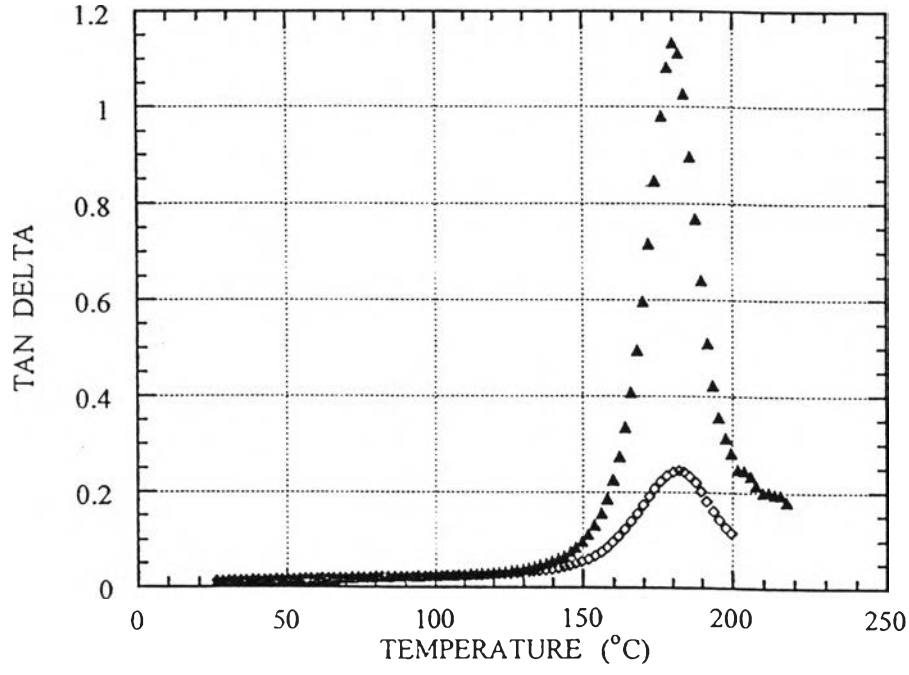

Figure 3.16 Damping curve (tanδ) compared between (▲) : B-a polymer and (◇) : B-a composite for 0 min soaking time.

B-m polymer and B-m composites show the same results as in Figures 3.17-3.18. As the storage modulus (G') of B-m polymer is 1.958 while B-m composites are approximately 3.131 to 4.307 GPa.

The damping curve (tanδ) is sensitive to transitions, relaxation processes, and structural changes. The damping curve reflects the energy loss at the fiber/matrix interface in the composite systems. Tanδ values have, therefore, been used in many studies to evaluate the adhesion of the fiber/matrix in the composite systems. The tanδ plot of B-a and B-a composite are shown in Figure 3.16. It can be seen that the tanδ of B-a composite is lower than that of B-a polymer. This could be because of the interface of the paper and B-a polymer. B-m and B-m composites gave similar results. Tanδ peak of B-a composite is broader than B-m composite indicating the higher degree of inhomogeneity of B-m composites compared with B-a composites (Figures 3.16 and 3.19).

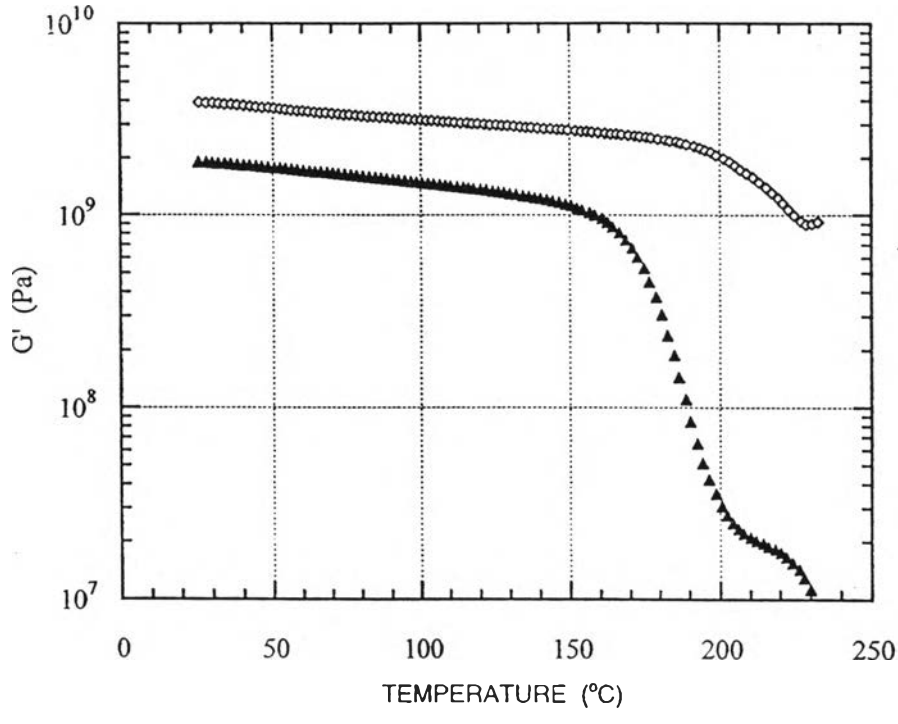

Figure 3.17 Storage modulus (G') compared between (▲) : B-m polymer and (◇) : B-a composite for 0 min soaking time.

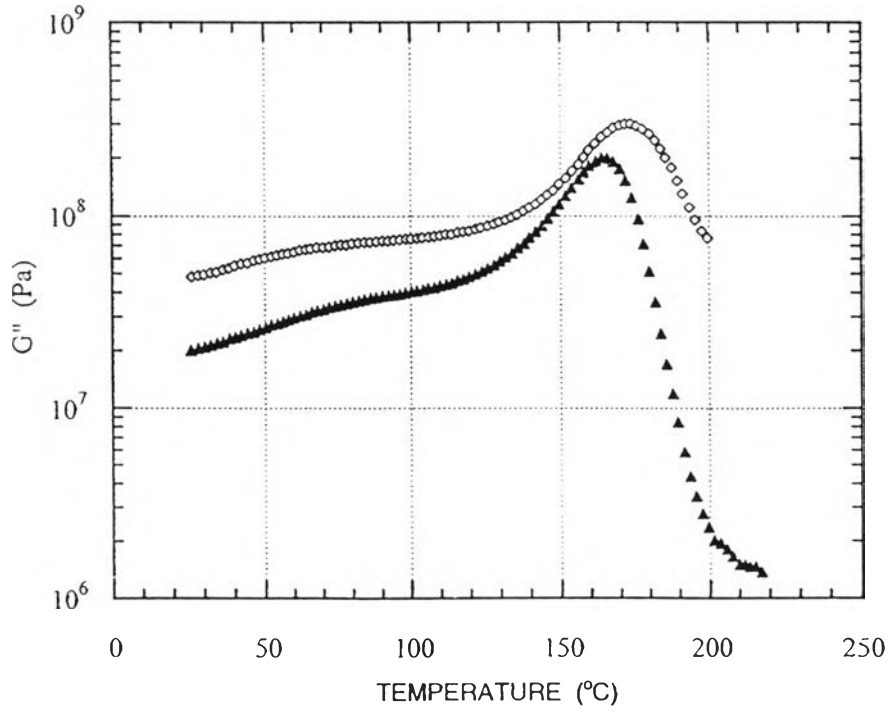

Figure 3.18 Loss modulus (G") compared between (▲) : B-m polymer and (◇) : B-m composite for 0 min soaking time.

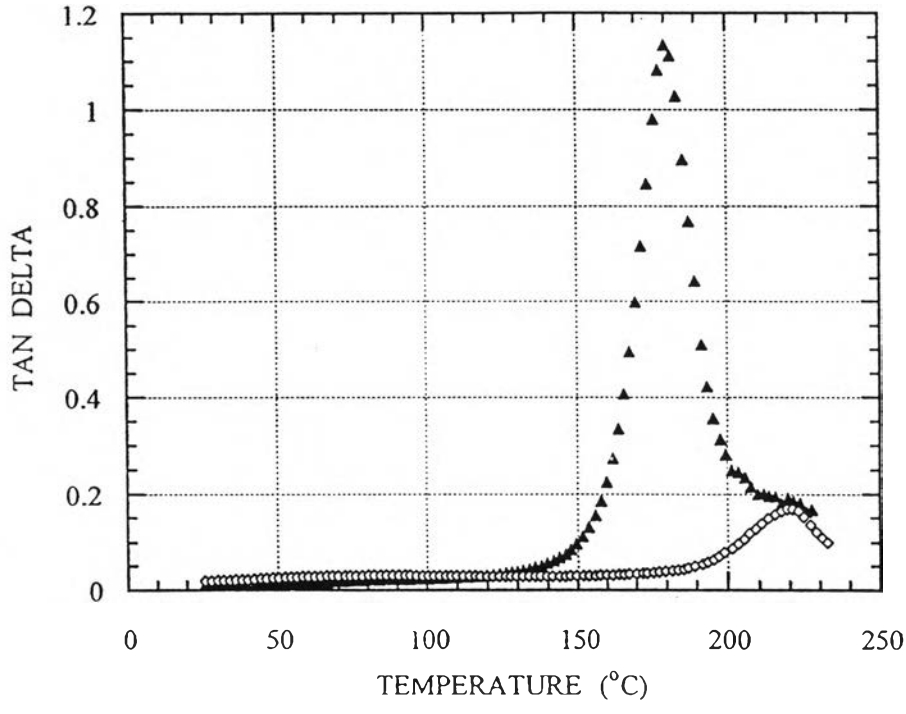

Figure 3.19 Damping curve (tanδ) compared between (▲) : B-m polymer and (◇) : B-m composite for 0 min soaking time.

A weak interface between the fiber and matrix is prone to water absorption which will decrease the mechanical properties. Water molecules can penetrate into the void or free volume. Water also shows the affinity to bond with the hydrophilic functional groups of both the fiber and matrix of the composites. Thus, it is expected that B-m will be more affected by water absorption than B-a due to aniline groups in B-a structure being more hydrophobic than the methyl groups in B-m structure.

In another case, water absorption at equilibrium is mainly dependent on void or free volume in the polymer structure. The bulky aniline groups make B-a polymers more amorphous-like than B-m. Thus, water molecules

are easier to penetrate through the B-a amorphous-like polymer. So, there are two structural effects for the water absorption mechanism. The former one is the hydrophilicity which is the dominant factor at the initial state of water absorption, while the latter is the void or free volume in the polymer structure which is dominant factor at the equilibrium state. Water absorption in the fiber will reduce the overall stress transfer by effectively plasticizing the fiber and matrix, thus weakening the fiber/matrix interface.

The storage modulus (G') and loss modulus (G") of B-a polymer compared to B-a polymer after immersion in distilled water for 24 hours are shown in Figures 3.20 and 3.21 respectively.

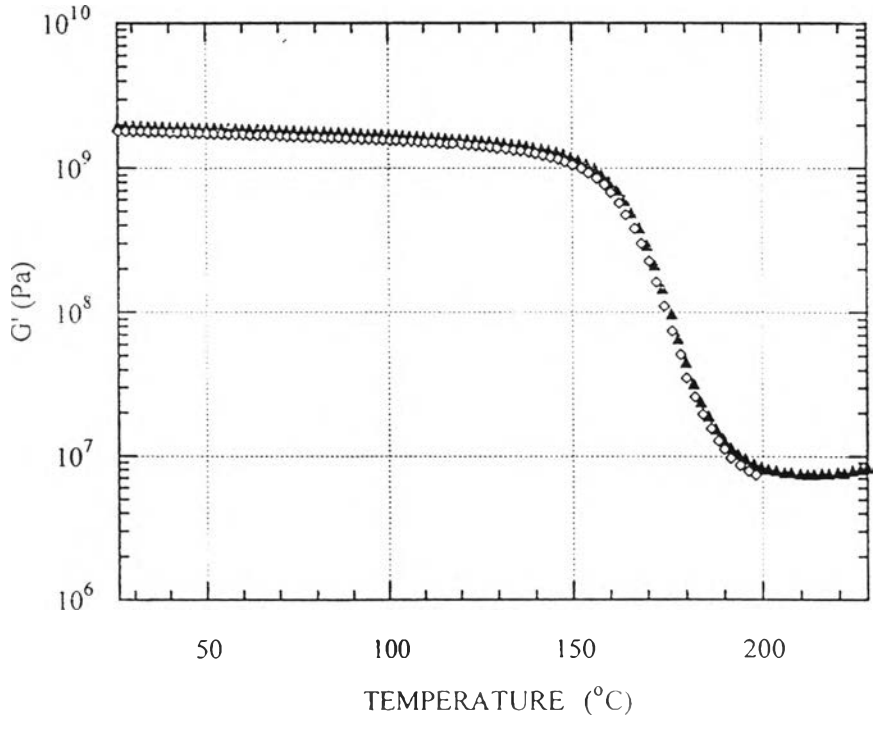

Figure 3.20 Storage modulus (G') compared between (▲) : B-a polymer and (◇) : B-a polymer after immersion in distilled water for 24 hours.

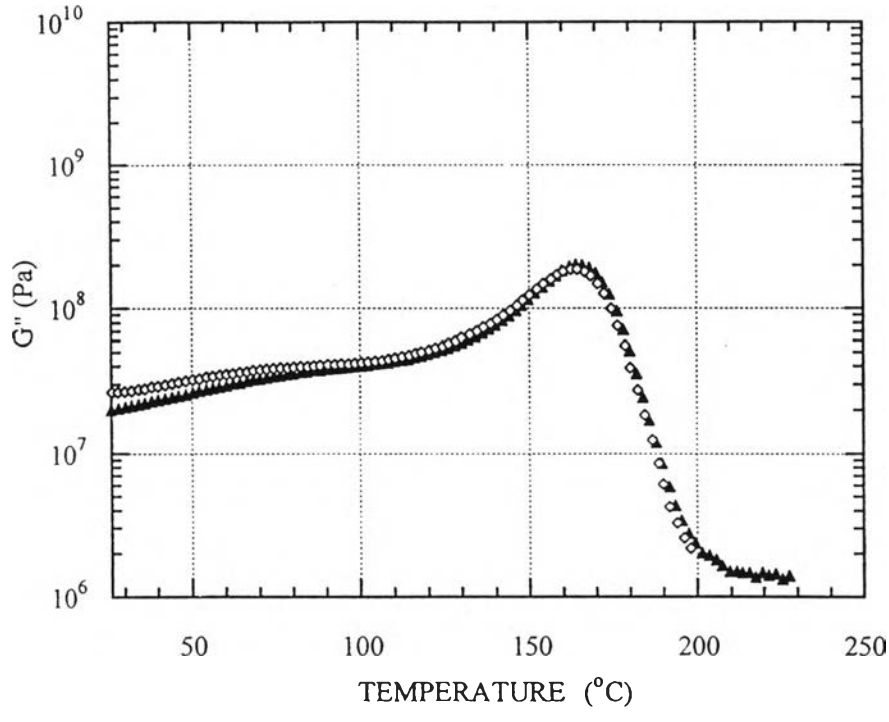

Figure 3.21 Loss modulus (G") compared between (▲) : B-a polymer and (◇) : B-a polymer after immersion in distilled water for 24 hours

In the case of B-a polymer, the storage modulus (G') and loss modulus (G") and Tg of B-a polymer and a B-a polymer immersed in distilled water for 24 hours were almost the same. In this case, it can be considered that water absorption (%) of the B-a polymer has a relatively low effect due to low hydrophilicity of B-a during the initial state of water absorption. Therefore, the water does not show much effect of the dynamic mechanical properties.

In the case of B-a composites, the storage modulus (G') of B-a composite which was immersed in distilled water for 24 hours has lower G' than that of the dry one. It can be concluded that the effect of water absorbed mostly by the fiber and performed the defects on the composites, as a result, more energy dissipation in this system.

The maximum peak of loss modulus G" of the wet B-a composite is lower than the dry one indicating the decreasing of Tg. As the B-a composite absorbs much more water, the effect from water will be more significantly. The Tg moves to the lower temperature due to the water that plasticized the fiber and matrix, and caused more energy dissipation. As shown in Figures 3.22 and 3.23 respectively.

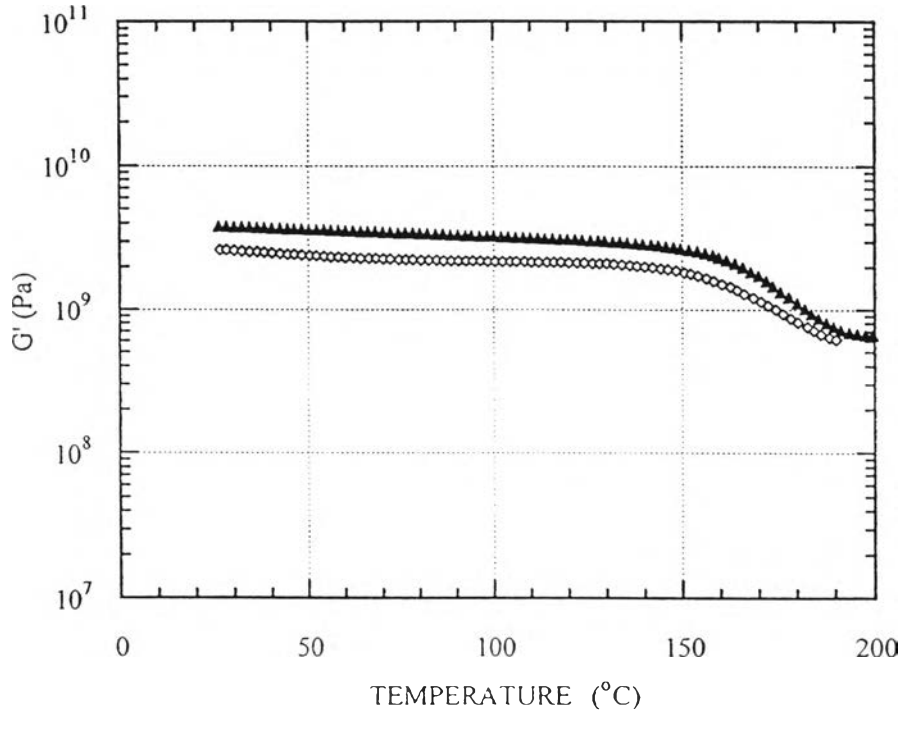

Figure 3.22 Storage modulus (G') compared between (▲) : B-a composite and (◇) : B-a composite after immersion in distilled water for 24 hours.

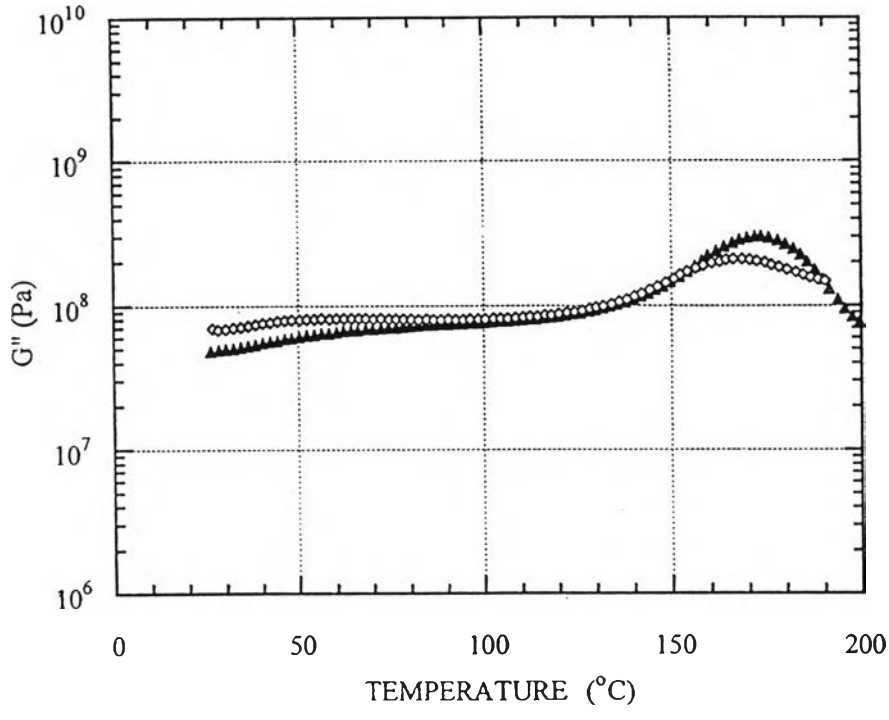

Figure 3.23 Loss modulus (G") compared between (▲) : B-a composite and (◇) : B-a composite after immersion in distilled water for 24 hours.

3.4 Interfacial Characterization

In order to investigate the fiber/matrix interface of the composite. The dry B-a composite and wet B-a composite (flexed until breakage) were observed by SEM technique. The digitized photographs are shown in Figures 3.24 and 3.25 respectively.

The dry B-a composite, in Figure 3.24, shows that the fiber/matrix interface was clearly separated. The fiber layer and matrix layer was laid

alternatively. The numbers shown in both images are the thickness of paper and polymer part in paper composites. For the wet B-a composite in Figure 3.25, the image exhibits the swelling of the fiber due to the water that was mostly absorbed by the fiber. The reduction of mechanical properties after immersed in distilled water can be said to be caused by the swelling of fiber and separation at the fiber/matrix interface.

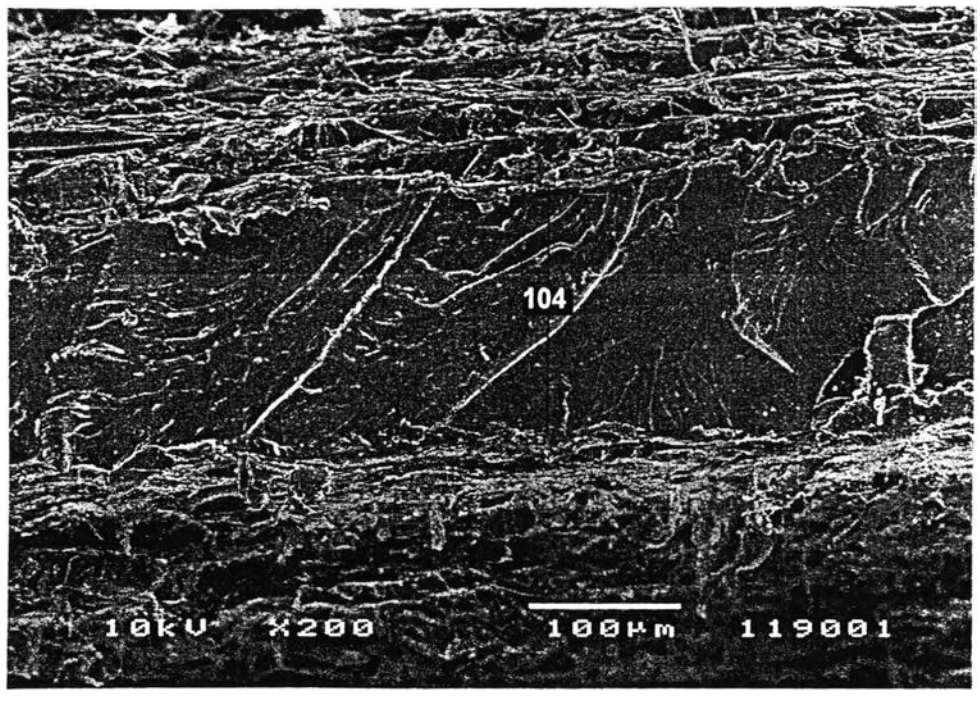

Figure 3.24 SEM image of dry B-a composite (Number in this image represent the thickness of polymer phase).

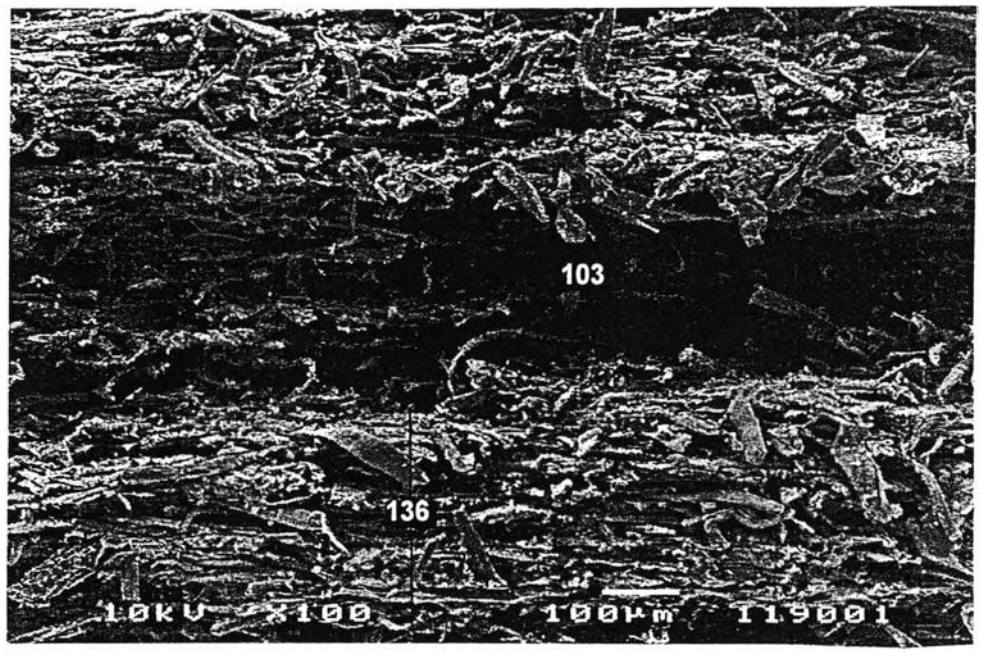

Figure 3.25 SEM image wet B-a composite after immersion in distilled water for 24 hours (Number in this image represents the thickness of the fiber and polymer phase).