



CHAPTER V

RESULTS AND DISCUSSION

5.1 Aniline-based Benzoxazine Resins and Novolac Epoxy Resin Characterization

5.1.1 Chemorheological Properties

The effect of epoxy on the gelation behaviors of benzoxazine-epoxy mixtures was investigated using rheological technique. Figure 5.1 shows the plot of dynamic viscosity (Pa.s) as a function of temperature ($^{\circ}\text{C}$) of the aniline based benzoxazine resins. From the figure, the major thermal event on the left hand side or low temperature range is called the liquefying point which is the transition of solid to liquid and on the right hand side or high temperature range is called the gel point which is the transition of liquid to solid, in other words the transition of monomer to polymers. At these points, the complex viscosity of resin rapidly approaches its minimum value. Furthermore, the temperature range from the liquefying point to the gel point is called processing window which is the range of the lowest viscosity useful for polymer compounding or processing. On the left hand side of Figure 5.1 presents the plot of dynamic viscosity (Pa.s) as a function of temperature ($^{\circ}\text{C}$) exhibiting processing windows of BA-a mixed with novolac epoxy resin at various epoxy contents. The liquefying temperature or transition of solid of the resin mixtures was observed to increase from 66 to 88.5 $^{\circ}\text{C}$ with an increasing amount of the epoxy resin from 0%wt, 20%wt, 40%wt and 60%wt in the resin mixture. A benzoxazine (BA-a) and novolac epoxy mixture was systematically shifted to higher temperature from 66 $^{\circ}\text{C}$, 67 $^{\circ}\text{C}$, 85 $^{\circ}\text{C}$ and 88.5 $^{\circ}\text{C}$ with the increasing amount of novolac epoxy respectively.

Figure 5.2 shows the gel temperatures of benzoxazine and novolac epoxy mixture which were observed to systematically shift to higher temperature from 200.5 $^{\circ}\text{C}$, 206.5 $^{\circ}\text{C}$, 213 $^{\circ}\text{C}$ and 222 $^{\circ}\text{C}$ with the amount of novolac epoxy.

The liquefying point or transition of solid to liquid of the resin mixtures increased with increasing amount of novolac epoxy and the gel point or transition of liquid to solid of the resin mixtures also increased with increasing amount of novolac epoxy. Therefore, the processing window of the mixtures was found to shift to higher temperature range by increased amount of the epoxy resin as showing in Figure 5.3. However, all the mixture resins are low viscosity liquid within the temperature range of 100 to 195°C which provides sufficient processing window, particularly for the compounding process.

5.1.2 Curing Characteristics

The ring opening polymerization of the benzoxazine (BA-a) and novolac epoxy copolymers can be completed by thermal treatment alone and does not yield any by-product. The curing reaction can also take place either with or without catalyst. The curing behaviors can be analyzed by a differential scanning calorimeter. Figure 5.4-5.6 illustrates the plot of the DSC heat flow (mW/mg) as a function of temperature (°C). The curing behaviors due to the ring opening polymerization of the benzoxazine (BA-a) and novolac epoxy resins are shown in Figure 5.4.

All of the benzoxazine (BA-a) and novolac epoxy mixtures were observed to have a softening point (T_g of resin) in respective of the novolac epoxy component. The softening point was also found to increase with an addition of the epoxy as compared with that of the pure benzoxazine (BA-a). The DSC thermograms of benzoxazine (BA-a) with changing the component of novolac epoxy are shown in Figure 5.5. The positions of the softening points of benzoxazine (BA-a) and novolac epoxy mixtures at 100:0, 80:20, 60:40 and 40:60 mass ratio were determined to be approximately 47, 51, 58 and 63°C, respectively.

From the Figure 5.6, it can be observed that benzoxazine (BA-a) and novolac epoxy mixtures at mass ratio 100:0, 80:20, 60:40 and 40:60 showed exothermic peaks at 230, 235, 242 and 250°C, respectively. As a consequence, the degree of curing retardation was increased with the increasing amount of the novolac epoxy in the binary mixtures. This indicates that benzoxazine (BA-a) and novolac epoxy mixtures at composition 40:60 mass ratio was the

most difficult to be thermal cured i.e. required higher temperature or longer time to be fully cured.

The curing condition of the benzoxazine (BA-a) and novolac epoxy mixtures was determined from the disappearance of the area under the curve of the exothermic peak in DSC experiment. Figure 5.7 indicates the DSC thermogram of the benzoxazine (BA-a) and novolac epoxy mixtures at a mass ratio of 40:60 at various curing conditions. This composition was selected to represent all mixtures for determining the fully cured condition as this ratio of the resin blend required the most curing temperature for achieving a fully cured stage. From the figure, the heat of reaction determined from the area under the exothermic peak of the uncured benzoxazine (BA-a) blends with novolac epoxy resin, the top curve, was 320.1 J/g corresponding to the 0% conversion. The area under the curing peak tended to decrease with increasing the curing temperature or curing time. The heat of reaction was reduced to 249.7 J/g (22% conversion) after curing at 150°C for 1 hour, and decreased to 80.0 J/g (75% conversion), 54.4 J/g (83% conversion), 16.0 J/g (95% conversion) and 9.6 J/g (97% conversion) after further curing at 170°C for 1 hour, 190°C for 1 hour, 200°C for 1 hour and 200°C for 2 hours, respectively. After final cure at 200°C for 2 hours, the exothermic heat of reaction was completely disappeared (100% conversion) which corresponds to the fully cured stage of the mixtures.

5.1.3 Fourier Transform Infrared Spectroscopy Investigation

In this research, aniline based benzoxazine resins were blended with novolac epoxy resin at various compositions. The chemical structures of aniline-based benzoxazine resins, novolac epoxy resin and their network formation reactions were studied by FTIR spectroscopic technique. The important functional groups of the benzoxazine monomers are the oxazine ring and the tri-substituted benzene ring in the benzoxazine ring structure whereas that of the epoxy is its epoxide ring. These functional groups were used to characterize the presence of the monomer in the polymerization reaction. Figure 5.8 shows the FTIR spectra of aniline-based benzoxazine monomers and the novolac epoxy resin in the spectral region from 1900 cm^{-1} to 600 cm^{-1} . From Figure 5.8 (a), the absorption bands appeared at 942 and 1492 cm^{-1} were

assigned to the oxazine ring [23] and the tri-substituted benzene ring [28] in the benzoxazine ring structure, respectively while the absorption bands at 745 cm^{-1} was assigned to a mono-substituted benzene in BA-a. Figure 5.8 (b) FTIR showed spectra of novolac epoxy monomer. The appearance of the peaks at about 966 , 823 , 1105 , and 1180 cm^{-1} in the novolac spectra are due to the ortho substitution in benzene nuclei confirmed also by the bands appeared at 1637 and 1727 cm^{-1} .

Figures 5.9-5.12 display the FTIR spectra of benzoxazine (BA-a) mixed with novolac epoxy resin of monomers and the fully cured polymers. As the curing process proceeded upon heat treatment, and infinitely three dimensional network was formed. According to the polymerization mechanism reported [24, 30], the oxazine ring is opened by the breakage of a C-O bond of the oxazine ring. Then the benzoxazine molecule transformed from a ring structure to a network structure, During this process, the tri-substituted benzene ring, backbone of benzoxazine ring, became tetra-substituted benzene ring with the characteristic absorption band appeared at 1485 cm^{-1} [24]. It also leads to the formation of a phenolic Mannich base polybenzoxazine structure. The network structure of a fully cured BA-a was composed of the phenolic Mannich bridge network. A broad intensive IR absorption band observed at 3350 cm^{-1} was assigned to the phenolic hydroxyl group [31]. These phenomena confirmed that benzoxazine monomers were thermally polymerized through its ring-opening reaction to yield polybenzoxazine network

The infra-red spectra of aniline-based benzoxazine monomers copolymerized with novolac epoxy resins were shown in Figures 5.9-5.12. The absorption bands at 942 cm^{-1} assigned to the oxazine ring in benzoxazine structure and 900 cm^{-1} assigned to the epoxide ring of epoxy resin. After being fully cured, both bands were disappeared as seen in Figures 5.9a. It was realized that the benzoxazine and epoxy rings opened, and the crosslinking reaction proceeded quantitatively without the use of curing accelerators. The epoxy appeared to react with the phenolic hydroxyl groups as soon as the ring opening polymerization made them available. Thus, the epoxy was found to be completely consumed at the later stage of cure.

5.2 Characterization of Aniline-based Polybenzoxazine and Novolac Epoxy Copolymers.

5.2.1 Density Measurement

In this study, the density measurement based on water displacement principle of all specimens was used to investigate the presence of void in polymeric copolymers. The density of benzoxazine-epoxy copolymer at room temperature was calculated using equation 4.2. Figure 5.13 exhibits the density of polybenzoxazines (BA-a) copolymers with novolac epoxy at various weight ratios. From the figure, the density of pure polybenzoxazine (BA-a) was calculated to be about 1.185 g/cm^3 . Moreover, an addition of the novolac epoxy into the polybenzoxazines (BA-a) caused systematic variation in the copolymer densities. The density of the copolymers trended to slightly increase from 1.185 g/cm^3 of the neat polybenzoxazine (BA-a) to about 1.188 g/cm^3 with increasing the epoxy resin contents from 0 to 60%wt. The density of the novolac epoxy used equals to 1.191 g/cm^3 [11]. The density of the copolymers seems to follow a simple rule of mixture. In addition, for mass ratio of novolac epoxy above 40 wt%, the density of the copolymers was unlikely to be in line with a simple rule of mixture because the amount of epoxy resin may exceed its stoichiometric amount for infinite network formation. At this point, some unreacted of the novolac epoxy resin may exist in the copolymers network. The density of the obtained network system thus needed to consider that of the unreacted of the novolac epoxy resin as well.

5.2.2 Dynamic Mechanical Properties

Dynamic mechanical analysis (DMA) is useful to investigate thermomechanical properties of polymeric materials, especially the transitions and relaxations of the materials. Knowledge of the transitions and relaxations of the materials will lead to an understanding of how materials behave at different temperatures and to an identification of a suitable service temperature. The change in molecular mobility of the specimen when temperature changed was sensed by dynamic mechanical analysis. Figure 5.15 and 5.17 shows the dynamic mechanical behaviors of the neat polybenzoxazines (BA-a). Figure 5.15 displays the plot of the loss modulus (MPa) as a function of temperature ($^{\circ}\text{C}$) and the glass transition temperature T_g

was taken at the maximum point on the loss modulus curves. From the figure, the interesting feature of the in cooperation of epoxy at 20% and 40% on dynamic mechanical property was a splitting of the loss modulus peaks. The appearance of the two modulus peaks suggested the presence of two T_g 's in the copolymer and signified the phase separation to occur in the polymer hybrids. The glass transition temperatures (T_g) of the polybenzoxazines (BA-a) and novolac epoxy copolymers at various compositions were shown in Figure 5.16. From the figure, the first T_g at high temperature of polybenzoxazine (BA-a) copolymers with the novolac epoxy resin tended to decrease from 168°C, 164°C, 145°C and 115°C while the second T_g at lower temperature was from 168°C, 112°C, 118°C and 115°C with increasing the epoxy resin contents from 0%, 20%, 40% and 60%wt, respectively. The additional crosslinks of epoxy in the benzoxazine matrix have the effect on decreasing the glass transition temperature of the copolymers material over the pure. While the T_g of novolac epoxy lower than the pure polybenzoxazine (BA-a) was likely to be due to the fact that the stoichiometric ratio of components is approached, unreacted epoxy molecules may remain in the network formed and may interfere with network formation or act as a plasticizer [17].

Figure 5.17 illustrates a plot of storage modulus (MPa), a material stiffness, as a function of temperature (°C) of the polybenzoxazine (BA-a) copolymers with novolac epoxy as a function of epoxy contents (%wt). From the figure, the storage modulus at room temperature was found to decrease systematically from 5.99 GPa of the neat polybenzoxazine (BA-a) to 4.76 GPa with increasing the amount of the epoxy resin from 0 to 60%wt. This is due to the more flexibility or less stiffness of the novolac epoxy compared to the polybenzoxazines used. The less stiffness was likely from the presence of the softer molecular segments of epoxy than those of polybenzoxazine. [12].

5.2.3 Thermal Expansion Properties

Figure 5.18 shows the plot of coefficient of thermal expansion (ppm/°C) as a function of epoxy content (%wt). The coefficient of thermal expansion (CTE) of the neat aniline-based polybenzoxazines was calculated from the slope based on the thermal expansion curve of each specimen of the plot of the probe position as a function of temperature. The coefficient of

thermal expansion in the glassy state was taken from the same temperature range of 30°C to 120°C. From the figure, the coefficient of thermal expansion of polybenzoxazine (BA-a) and novolac epoxy copolymers were reduced from 46.80 ppm/°C to 20.97 ppm/°C with increasing amount of the epoxy from 0 to 40%wt. However, with the incorporation of novolac epoxy up to 60% lead to the coefficient of thermal expansion was increased to 33.84 ppm/°C. The typical of novolac epoxy resins have a CTEs value at 18.4 ppm/°C. As a result, the increase of novolac epoxy fraction in the copolymers caused the reduced in their CTEs. The result of coefficient of thermal expansion of the copolymers seems to follow a simple rule of mixture. In addition, for mass ratio of novolac epoxy above 40 wt%, the CTEs of the copolymers was unlikely to be in line with a simple rule of mixture because the amount of epoxy resin may exceed its stoichiometric amount for infinite network formation.

5.2.4 Thermal Degradation and Thermal Stability of Benzoxazine-Epoxy Copolymer

Thermogravimetric analyzer (TGA) is a technique which a change in sample mass is monitored as a function of temperature or time. Degradation temperature (T_d) is one of the key parameters that needed to be considered for high temperature applications of materials. In this study, degradation temperatures of the copolymers were defined as the temperature at 5% weight loss and the char yields were obtained at 800°C under nitrogen atmosphere for each polymer.

Figure 5.20 shows the TGA thermograms of the aniline-based polybenzoxazine copolymers with novolac epoxy resin at various compositions. The degradation temperature (T_d) of polybenzoxazine (BA- a) and novolac epoxy copolymers were found to increase from 329°C for the neat BA-a to 362°C for the copolymer with epoxy content of 60wt% as depicted in Figure 5.21. Meanwhile, the polymerized network structure of polybenzoxazine (BA-a) was a pure phenolic Mannich bridge network but novolac epoxy contained additional structure phenolic network structure. The incorporation of epoxy into polybenzoxazine had been reported to help improve crosslinked density of the resulting copolymers. [Ref. ternary systems] This may explain the thermal stability enhancement of the copolymers comparing with the neat polybenzoxazine.

However, the char yields of benzoxazine/epoxy binary systems were found to decrease with increasing amount of the epoxy as shown in Figure 5.22. This is due to the fact that polybenzoxazines are known to possess higher char yield than the epoxy [12].

5.2.5 Flexural Properties

The flexural properties of polybenzoxazine (BA-a) copolymers with novolac epoxy resin at various epoxy contents are shown in Figure 5.26-5.29. The specimens for flexural analysis were loaded until failure such that both flexural stress and strain at breakage could be measured for the polybenzoxazine-epoxy copolymers. Flexural strength and strain represent an ability of materials to absorb maximum force at rupture. This ability concerns with storing and dissipating forces in polymers in the form of movement, rotation and vibration of molecule, which is transformed to heat, deformation or sound, etc [24]. Figure 5.26 exhibits the plot of the flexural strength (MPa) as a function of the epoxy content (%by weight) of polybenzoxazines-epoxy copolymers at various compositions. The flexural strength of a thermosetting resin is influenced by a number of interrelated parameters including T_g , molecular weight between crosslinks, free volume, chemical structure, network regularity and perfection, and many other contributing factors [24]. From the figure 5.27, it can be observed that the flexural strength of the polybenzoxazine (BA-a) was found to be about 114.6 MPa, with in the cooperation of novolac epoxy by mass fraction of the epoxy resin from 0 to 60% the flexural strength of the copolymers were increasing from 114.6 to 157.9 MPa. Also, it was suggested by Ishida and Allen, 1996 that the benzoxazine homopolymer and copolymers with low concentrations of epoxy may contain clusters of branched chains or at best may be characterized as a loosely crosslinked network. The addition of epoxy molecules allows the clusters to be joined, the network tightened, and the perfection of the network improved with a subsequent increase in flexural strength [24].

Figure 5.28 exhibits the plot of the flexural strain at break (%) of the aniline-based polybenzoxazines (BA-a) copolymer with novolac epoxy resin as a function of epoxy contents (% by weight). From the figure, the flexural strain at break of polybenzoxazine was observed to

be about 2.0%. The flexural strain at break of aniline-based polybenzoxazines (BA-a) copolymer with novolac epoxy resin was also observed to increase from 2.1, 2.3, 2.8 and 3.7%, with increasing the amount of the epoxy resin from 0 to 60% wt. Generally, intermolecular packing, free volume, molecular architecture, and molecular weight between crosslinks influence the large strain glassy state properties [2]. The extensibility of a crosslinked polymer in its glassy state is constrained largely by its available free volume. A higher free volume decreases chain interactions and enhances the ability of molecular chain segments to flow under load by such means as rotational configurationally changes. These effects on free volume may be at least partially responsible for the improved strain behavior observed in the copolymers. The ability of chain segments to reach their fully extended state is also dependent on the intermolecular flexibility of the segments as well as their intermolecular packing constraints. Thus, the addition of the more flexible epoxy segments to the polybenzoxazine matrix should also contribute to the increased strain at breakage for the copolymers [24].

Finally, the plot of flexural modulus (GPa) of aniline-based polybenzoxazines alloyed with epoxy resin as a function of epoxy contents (% by weight) is shown in Figure 5.29. The flexural modulus shows a behavior nearly identical to that of the storage modulus at room temperature from FMA thermograms. From the figure, the flexural modulus of the polybenzoxazine (BA-a) was found to be about 4.7 GPa. For the copolymers with novolac epoxy, the flexural modulus of all copolymers decreased from 4.7 to 4.4 GPa with increasing the amount of the novolac epoxy resin from 0 to 60%wt. The phenomenon was due to the basic principle that the addition of the more flexible or less stiff epoxy in the more rigid polybenzoxazine can cause the softening of the resulting polymer copolymers. These results are consistent with those of DMA.

5.2.6 Water Absorption Investigation

Water has a T_g of -130°C . Polymers that absorb water are also plasticized by water. Therefore, water generally has a negative effect on the T_g 's of polymers and reduces the upper temperature limit for the polymers applications. Typical phenolic materials are fairly hydrophilic because each phenolic repeat unit contains a free hydroxyl group. By adding a hydrocarbon

substituent, such as a methyl group, in close proximity of the hydroxyl groups, such as in the case of polybenzoxazine and novolac epoxy, the polymer chains should become less polar and absorb less water.

Equilibrium moisture uptake was studied at room temperature for a series of polybenzoxazine (BA-a) and novolac epoxy copolymers. Three samples of each specimen were measured at room temperature and the results were illustrated in Figure 5.34. The water absorption levels for polybenzoxazine (BA-a) and novolac epoxy copolymers were relatively unaffected by the contents of the epoxies (Figure 5.34). The 80:20 benzoxazine/epoxy copolymer absorbed slightly more water than the 60:40 and 40:60 benzoxazine/epoxy copolymers, probably as a result of having more polar phenolic hydroxyl groups in the higher novolac compositions.

5.2.2 Hardness (Shore D) Measurement

Figure 5.36 illustrates hardness of polybenzoxazines copolymers with novolac epoxy resin at various epoxy contents (0%, 20%, 40% and 60%). From the figure, the hardness was observed to decrease from 91 to 90 Shore D with increasing the amount of the epoxy resin from 0 to 60%wt. This is due to the lower hardness of the epoxy compared with the polybenzoxazine. The novolac epoxy possessed a hardness value is 88-90 shore D.

5.3 Characterization of fiber glass-reinforced Polybenzoxazine and Novolac Epoxy Copolymers.

5.3.1 Density Measurement

Figure 5.14 exhibits the density at 80% of fiber glass-reinforced polybenzoxazines (BA-a) copolymers with novolac epoxy at various weight ratios. The theoretical densities of the fiber glass-reinforced were calculated based on the density of fiber glass (E-glass) of 2.540 g/cm^3 , the density of polybenzoxazine (BA-a) of 1.185 g/cm^3 and the density of novolac epoxy of 1.191 g/cm^3 . The theoretical calculation results of fiber glass reinforcement of polybenzoxazines (BA-a) copolymers with novolac epoxy at 100:0, 80:20, 60:40 and 40:60 were 2.2690, 2.2692, 2.2694 and 2.2695 g/cm^3 , respectively. The density measurement based on water

displacement principle of all specimens was used to investigate the presence of void in polymeric copolymers. Indicate that the results were showed at 1.9435, 1.9547, 1.9430 and 1.9471 g/cm³, respectively. The reinforcement of the fiber glass was confirmed again by using TGA.

Most observed fiber glass reinforcement densities showed difference values with the calculated and the analyzed by TGA. The reasons that the densities of fiber glass reinforcement were lower than theoretical calculation at amount 14% of voids content in fiber glass-reinforced polybenzoxazine and novolac epoxy copolymers.

5.3.2 Thermal Expansion Properties

The thermal expansion behavior of fiber glass-reinforced polybenzoxazine and novolac epoxy composite specimens was taken from the same temperature range of 30°C to 120°C. The test specimens produced by compression molding layers at 80% of fiberglass cloth (E-glass) with 20% of polybenzoxazine and novolac epoxy copolymers matrix. From Figure 5.19, this indicated thermal expansion coefficient values of fiberglass-reinforced BA/EP at 100:0, 80:20 and 60:40 were decreased from 24.26, 23.77 and 20.97 ppm/°C respectively. However, fiber glass-reinforced BA/EP at 60:40 was increased to 33.84 ppm/°C, whereas some unreacted of the novolac epoxy resin may exist in the copolymers network. Very interesting that the fiber glass-reinforced of the pure polybenzoxazine was significant decrease of the CTE to 24.26 ppm/°C which pure polybenzoxazine given CTE at 46.8 ppm/°C.

5.3.3 Thermal Degradation and Thermal Stability Properties

The plot of degradation temperature against percentage polybenzoxazine and novolac epoxy copolymer is given in Figure 5.24. It is observed from Figure 5.24 that the degradation temperature increases with the increasing percentage of novolac epoxy, which in turn implies that the novolac epoxy incorporation enhances the thermal stability in addition to the decrease in percentage weight loss. The heat distortion temperature of unreinforced matrix systems and matrix systems reinforced with E-glass are presented in figure 5.25. The delay in degradation of

fiber glass-reinforced composite when compared with unreinforced benzoxazine and epoxy resin may be explained due to the presence of a fiber glass, which in turn stabilizes the matrix system against thermal degradation. Hence, a delay in degradation was observed for various of novolac epoxy systems over the polybenzoxazine system (Figure 5.20). However, the glass reinforcement imparts a high value due to the inorganic silicate nature. Hence, the novolac epoxy introduction into polybenzoxazine resin improves the service temperature of the matrix systems.

5.3.4 Flexural Properties

The flexural stress and flexural strain of fiber glass-reinforced polybenzoxazine and novolac epoxy copolymers as a function of the composition of the epoxy in the binary system are shown in Figures 5.30. The figure shows that the flexural stress and flexural strain of composite was increased when the composition of the epoxy was increased because the more toughness between the fiber glass and matrix. Figure 5.31 exhibits the plot of the flexural strength (MPa) as a function of the epoxy content of polybenzoxazines-epoxy copolymers at various compositions. From the figure 5.31, fiber glass-reinforced with in the cooperation of binary matrix by mass fraction of the epoxy resin from 0 to 40% the flexural strength of the copolymers were increasing from 241.8 to 416.0 MPa. However, the increasing of epoxy more than 40% (60%) by weight was decreased a flexural strength to 378.0 MPa because the soft segments of novolac epoxy content was increased.

From the figure 5.32, the flexural strain at break of polybenzoxazine was observed to be about 1.5%. The flexural strain at break of fiber glass-reinforced polybenzoxazines copolymer with novolac epoxy resin was also observed to increase from 1.5, 2.2, 2.3 and 3.0%, with increasing the amount of the epoxy resin from 0%, 20%, 40% and 60% wt, respectively.

In Figure 5.33, the flexural modulus of fiber glass-reinforced copolymers composite was increased by increasing the weight content of epoxy because novolac epoxy has higher modulus than polybenzoxazine polymer. In the figure was observed to increase from 18.7 to

22.2 GPa. The increased flexural strength and the increased flexural modulus of composite were improved by increasing the composition of the epoxy copolymers.

5.3.5 Water absorption

Figure 5.35 illustrates the water absorption of fiber glass-reinforced composite at various of novolac epoxy copolymer contents. From the figure, the water absorption at 80% of fiberglass reinforcement of novolac epoxy content at 0%, 20%, 40% and 60% were 1.83%, 1.60%, 1.67% and 1.35%, respectively. However, the glass reinforcement imparts a high water absorption value due to the high content of fiber glass-reinforced (80%). Hence, if decreasing the fiber glass reinforced and increasing polybenzoxazine and epoxy copolymer matrix will be improves the water absorption of the composite systems.

5.3.6 Hardness (Shore D) Measurement

Figure 5.37 showed the hardness of fiber glass-reinforced polybenzoxazines copolymers with novolac epoxy copolymers composite at various epoxy contents. From the figure, the hardness of the polybenzoxazine and novolac epoxy copolymers were observed to increase from 85, 88 and 93 Shore D, with increasing the amount of the epoxy resin from 0%, 20% and 40%wt, respectively. This is due to the tougher of the epoxy compared with the polybenzoxazine leading to the copolymers matrix less brittle. However, the increasing amount of an epoxy more than 40% the hardness slightly dropping to 90 Shore D. Because of the effecting from epoxy matrix was leading to softer and more flexible in copolymer composite.

5.3.7 Scanning Electron Microscope (SEM)

The SEM photograph obtained for fracture studies of composites specimens are presented in Figure 5.39(a) and (b). From Figure 5.39(a), it is observed that the matrix system reinforced with E-glass shows that the high interfacial strength is due to better wetting of E-glass. From the SEM photograph, it can also seen that the residues of matrix resins are left with fractured glass, whereas no residual resins are attached with the fractured E-glass. This may be

explained due to the strong polar active sites present on the surface of fiber glass imparted by ionic sites of silicon and oxygen atoms and are responsible for the formation of strong intermolecular adhesion between E-glass and matrix resin.

However, from the SEM photograph, it can be seen in the case of E-glass are sharply broken under the conditions of test. This may further be explained due to polymeric crystalline nature of the former and inorganic amorphous character of the latter. Benzoxazine and novolac epoxy mixture improves wettability of reinforcements, as benzoxazine possesses low surface tension, better wetting and spreading characteristics even over smooth polished surfaces. SEM photographs obtained for fractured surface of E-glass reinforced matrix systems show that the very good intermolecular adhesion between matrix and E-glass reinforcement. It is concluded that the improved wetting and bonding between matrix resin and reinforcements can be achieved by polybenzoxazine and novolac epoxy resin. The resulting copolymers matrix materials can be utilized for the fabrication of composites using E-glass reinforcement for high performance of printed circuit board (PCBs) material for a higher service temperature with better performance.

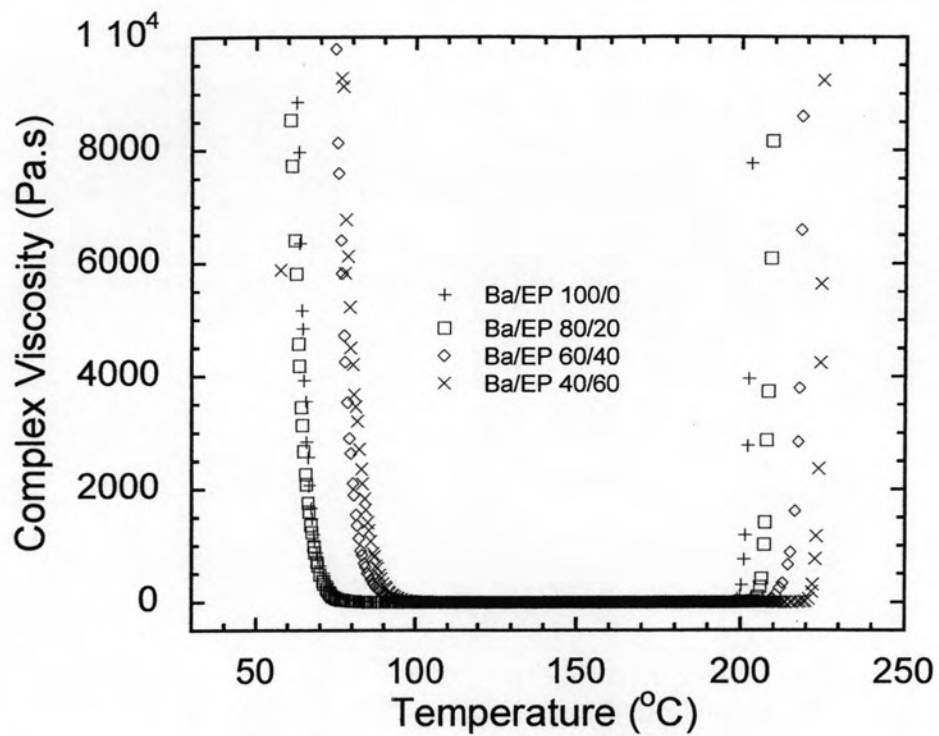


Figure 5.1; Processing window of benzoxazine (BA-a) mixed with novolac epoxy resin at various compositions: (+)100:0, (□) 80:20, (◇) 60:40 and (x) 40:60.

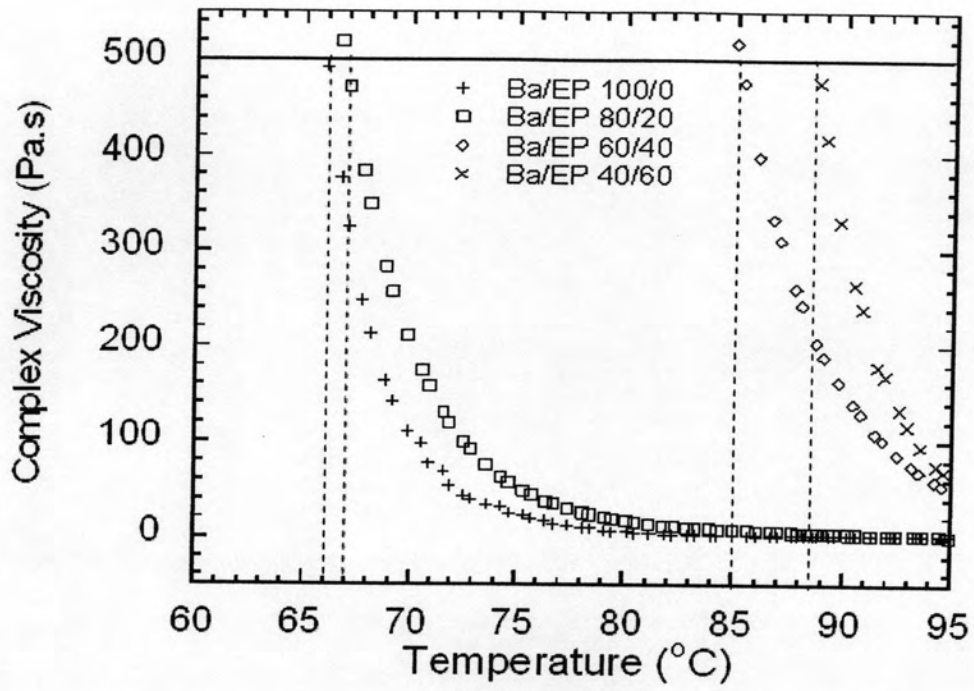


Figure 5.2; Liquefying temperature of benzoxazine (BA-a) mixed with novolac epoxy resin at various compositions: (+)100:0, (□) 80:20, (◇) 60:40 and (x) 40:60.

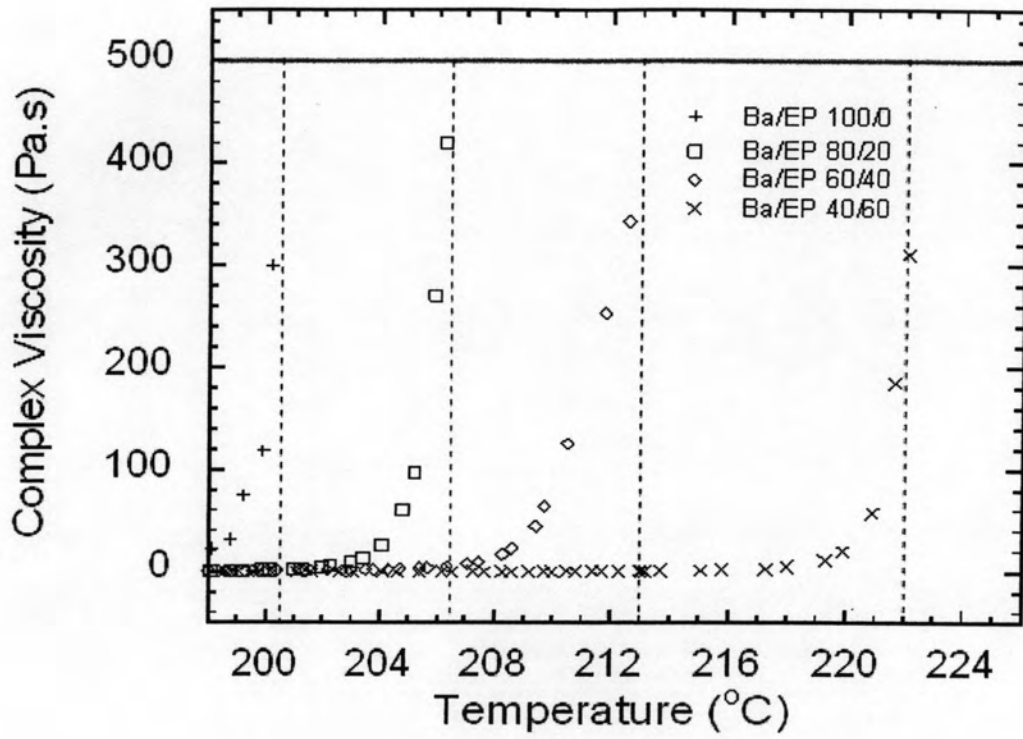


Figure 5.3; Gel temperature of benzoxazine (BA-a) mixed with novolac epoxy resin at various compositions: (+)100:0, (□) 80:20, (◇) 60:40 and (x) 40:60.

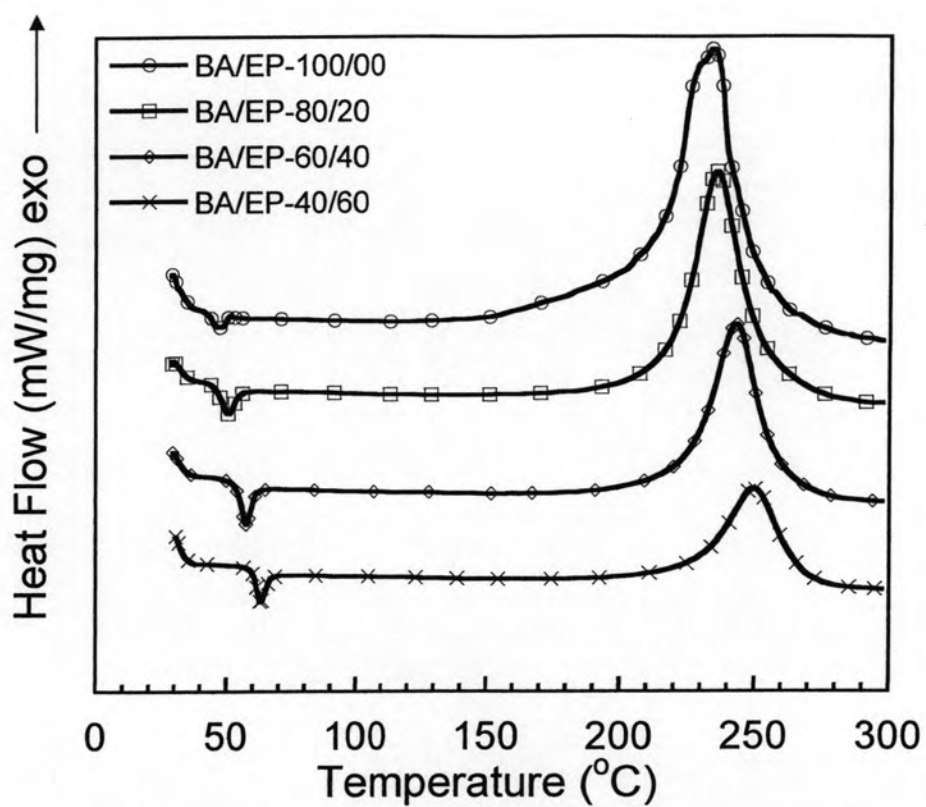


Figure 5.4 ; DSC plot of benzoxazine (BA-a) mixed with novolac epoxy resin at various compositions: (○)100:0, (□) 80:20, (◇) 60:40 and (×) 40:60.

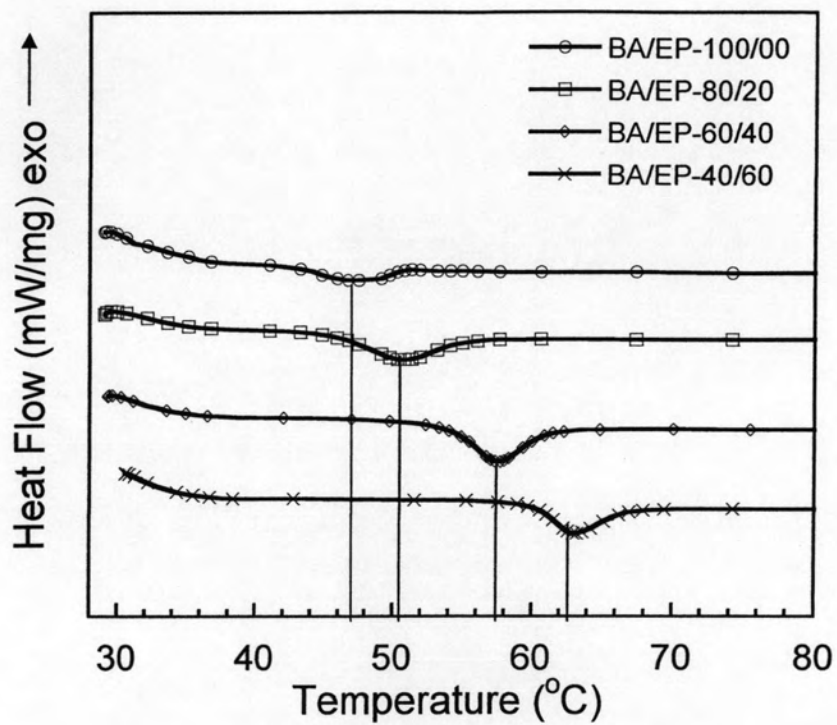


Figure 5.5; Softening point of benzoxazine (BA-a) mixed with novolac epoxy resin at various compositions: (○) 100:0, (□) 80:20, (◇) 60:40 and (×) 40:60.

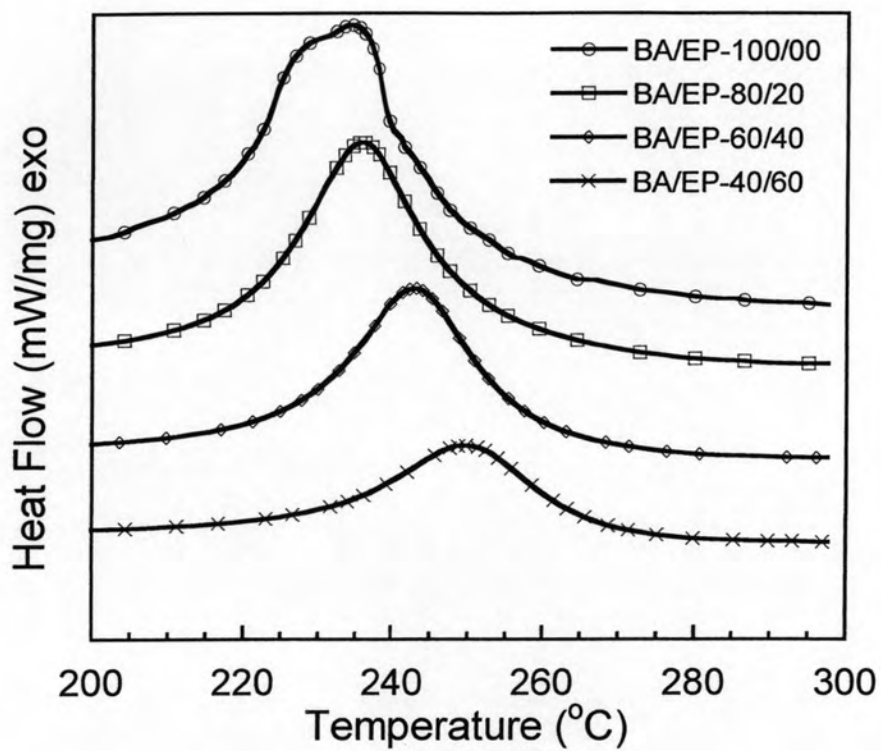


Figure 5.6; Exothermic peak plot form DSC for of benzoxazine (BA-a) mixed with novolac epoxy resin at various compositions: (○)100:0, (□) 80:20, (◇) 60:40 and (×) 40:60.

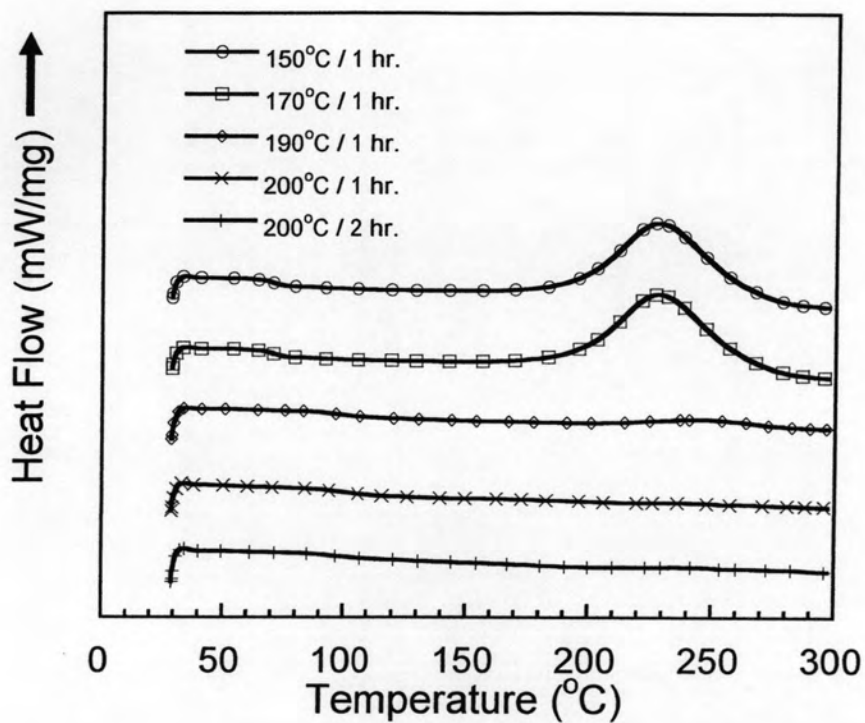


Figure 5.7; DSC thermograms of the benzoxazine (BA-a) mixed with novolac epoxy resin at a mass ratio of 60:40 at various curing condition: (—○—) 150°C/1hr, (—□—) 150°C/1hr+70°C/1hr, (—◇—) 150°C/1hr+70°C/1hr+90°C/1hr, (—×—) 150°C/1hr+70°C/1hr+90°C/1hr+200°C/1hr, and (—+—) 150°C/1hr+70°C/1hr+90°C/1hr+200°C/1hr+200°C/2hrs.

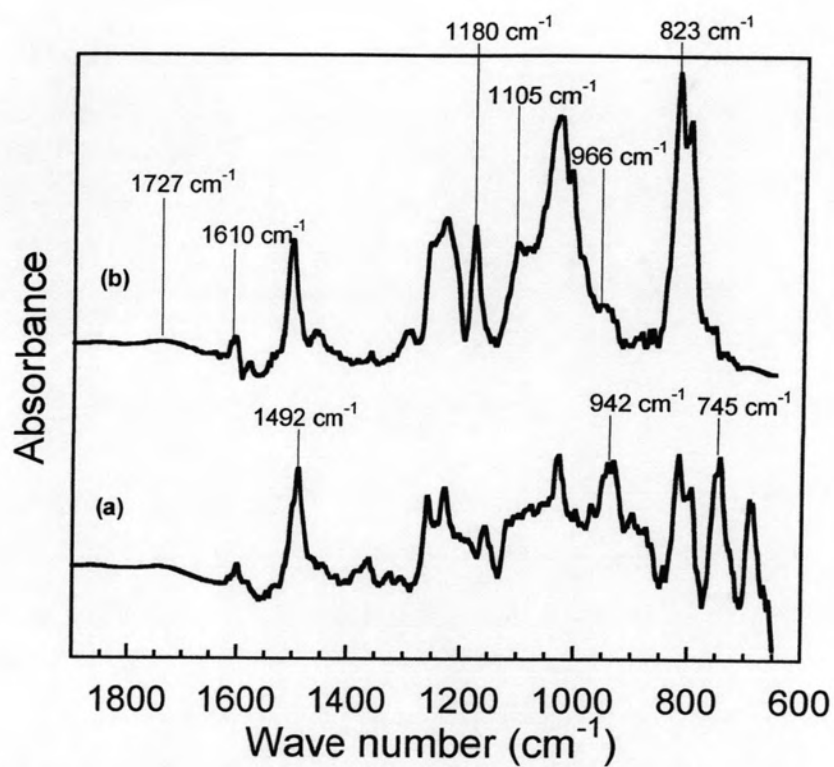


Figure 5.8 ; FTIR spectra of benzoxazine (BA-a) and novolac epoxy monomer :
benzoxazine monomer and (b) novolac epoxy monomer

(a)

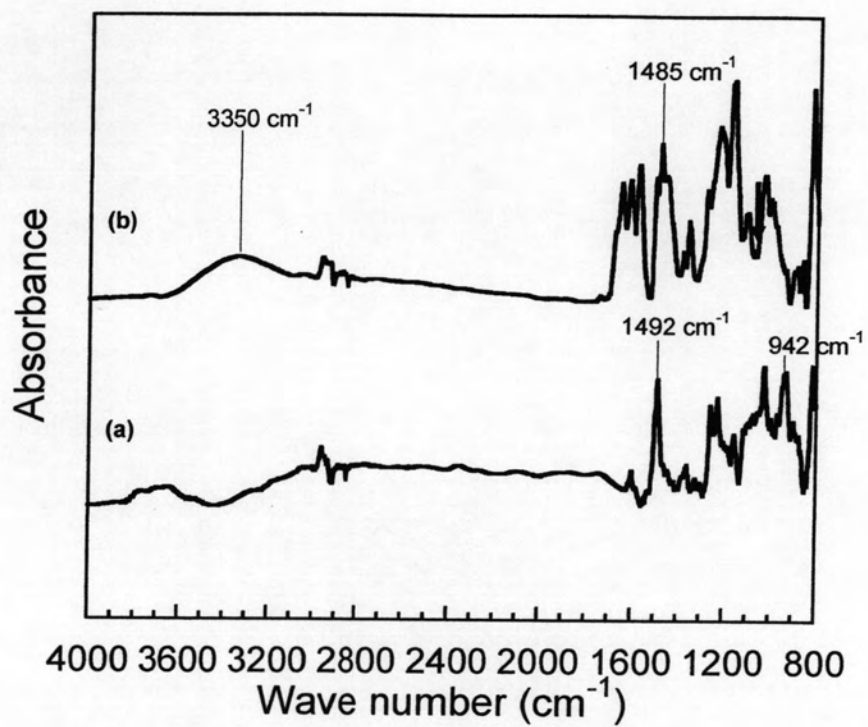


Figure 5.9 ; FTIR spectra of pure benzoxazine (BA-a) : (a) polymer and (b) monomer

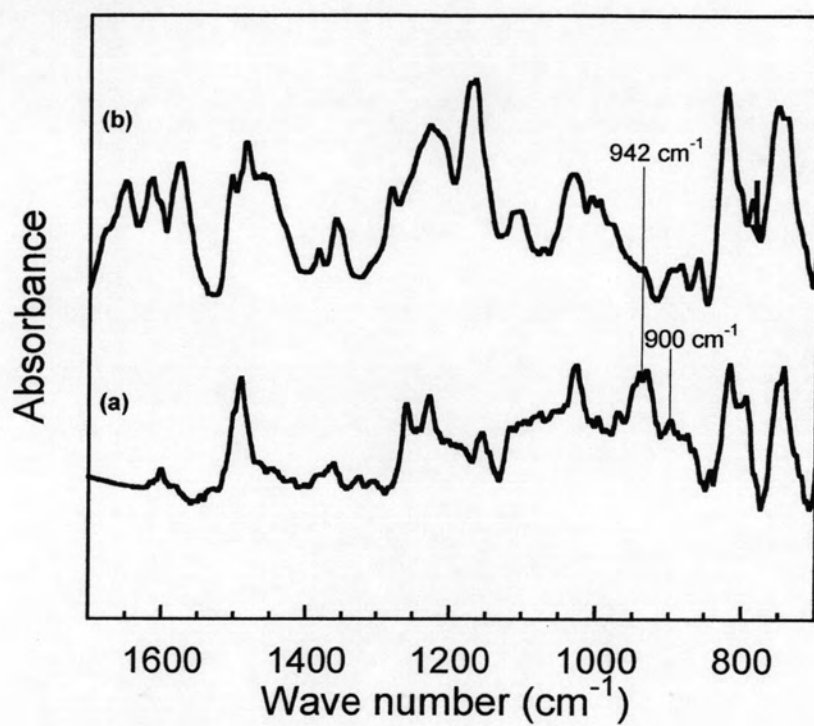


Figure 5.9a ; FTIR spectra of pure benzoxazine (BA-a) : (a) polymer and (b) monomer

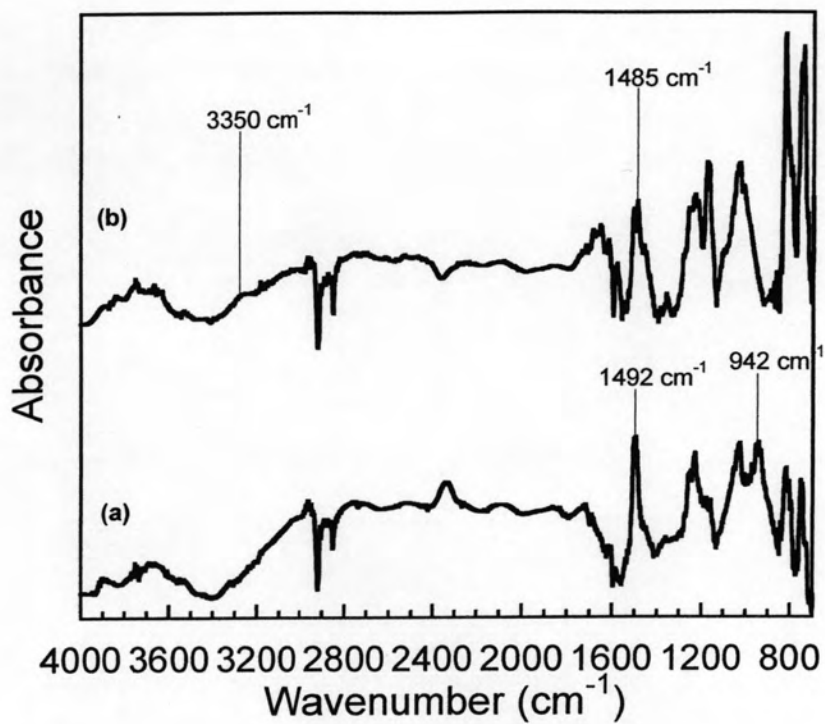


Figure 5.10 ; FTIR spectra of benzoxazine (BA-a) mixed with novolac epoxy resin at 80:20 mass ratio : (a) polymer and (b) monomer

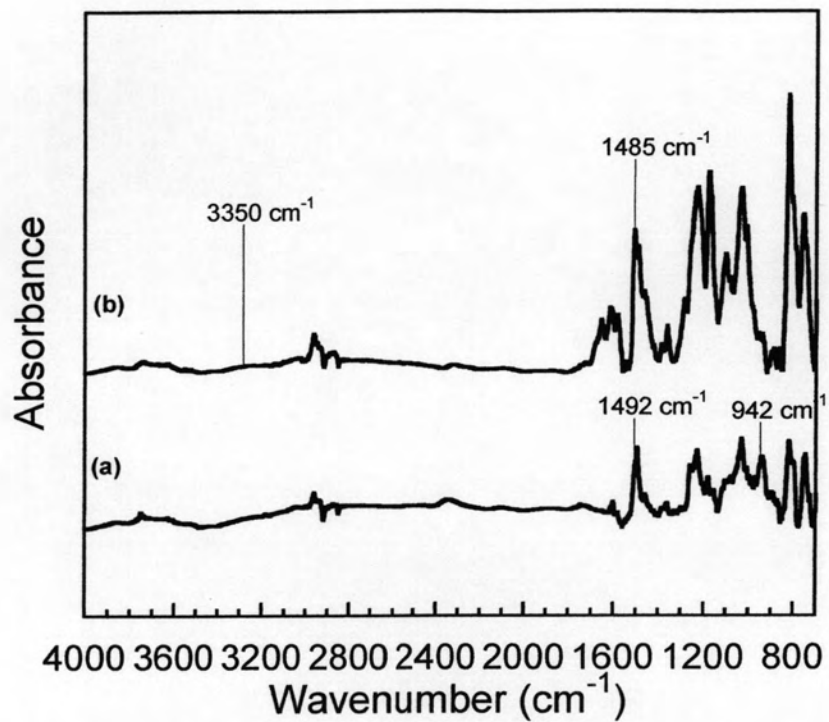


Figure 5.11 ; FTIR spectra of benzoxazine (BA-a) mixed with novolac epoxy resin at 60:40 mass ratio : (a) polymer and (b) monomer

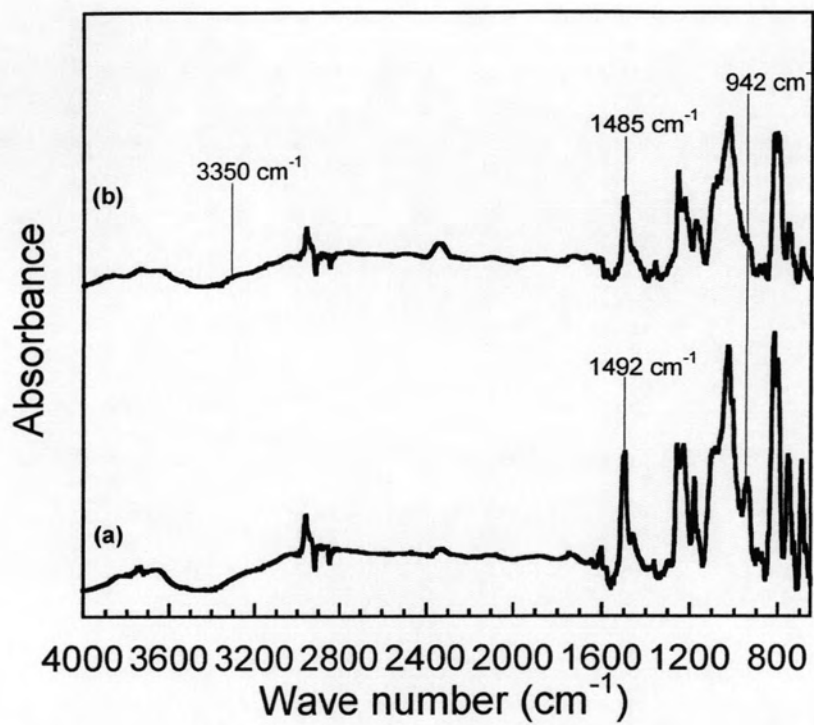


Figure 5.12 ; FTIR spectra of benzoxazine (BA-a) mixed with novolac epoxy resin at 40:60 mass ratio : (a) polymer and (b) monomer

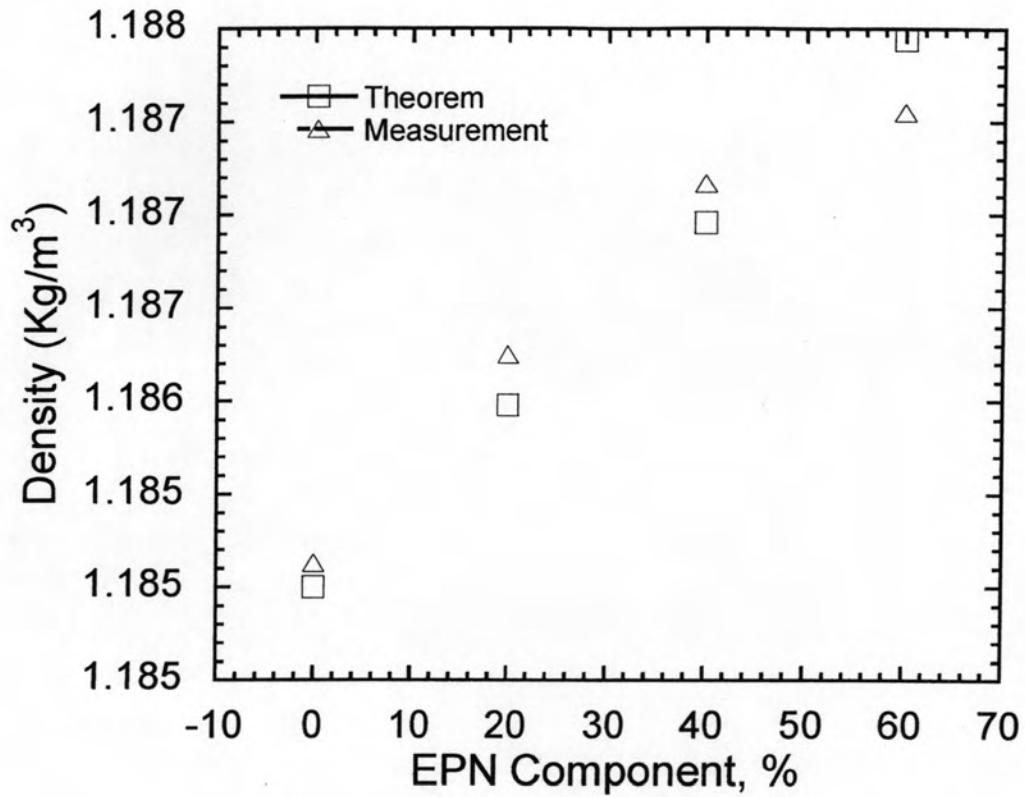


Figure 5.13; Density plot of benzoxazine (BA-a) mixed with novolac epoxy resin at various compositions: (Δ) Measurement , (\square) Theorem

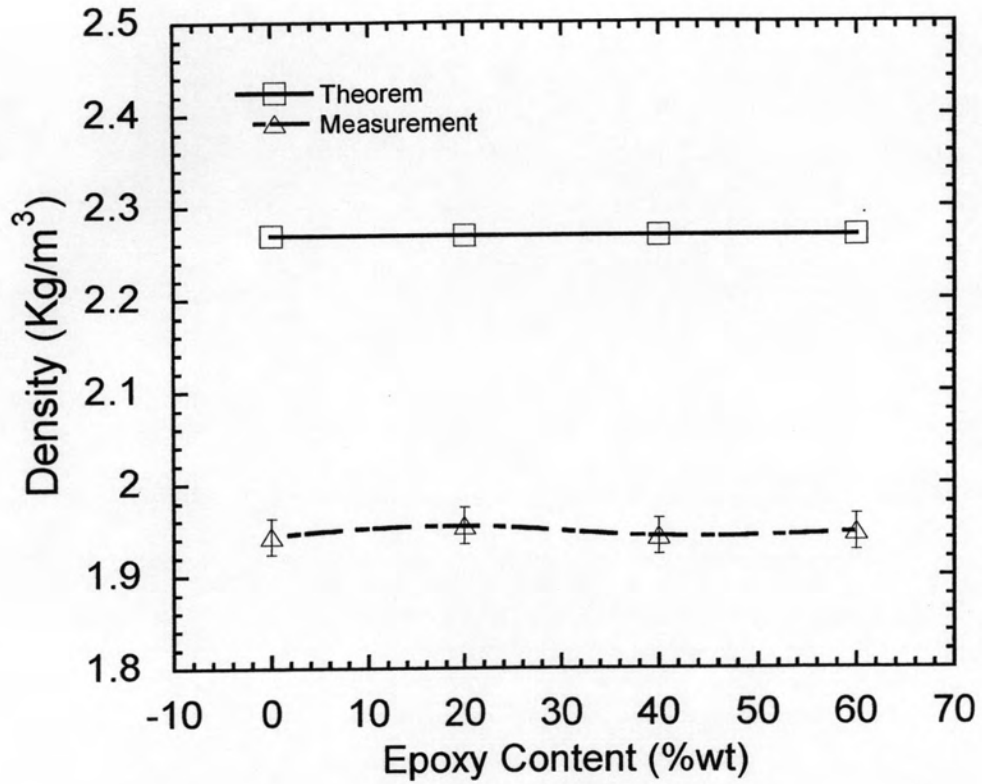


Figure 5.14; Density plot of fiber glass-reinforced polybenzoxazine (BA-a) and novolac epoxy resin at various compositions: (Δ) Measurement, (\square) Theorem

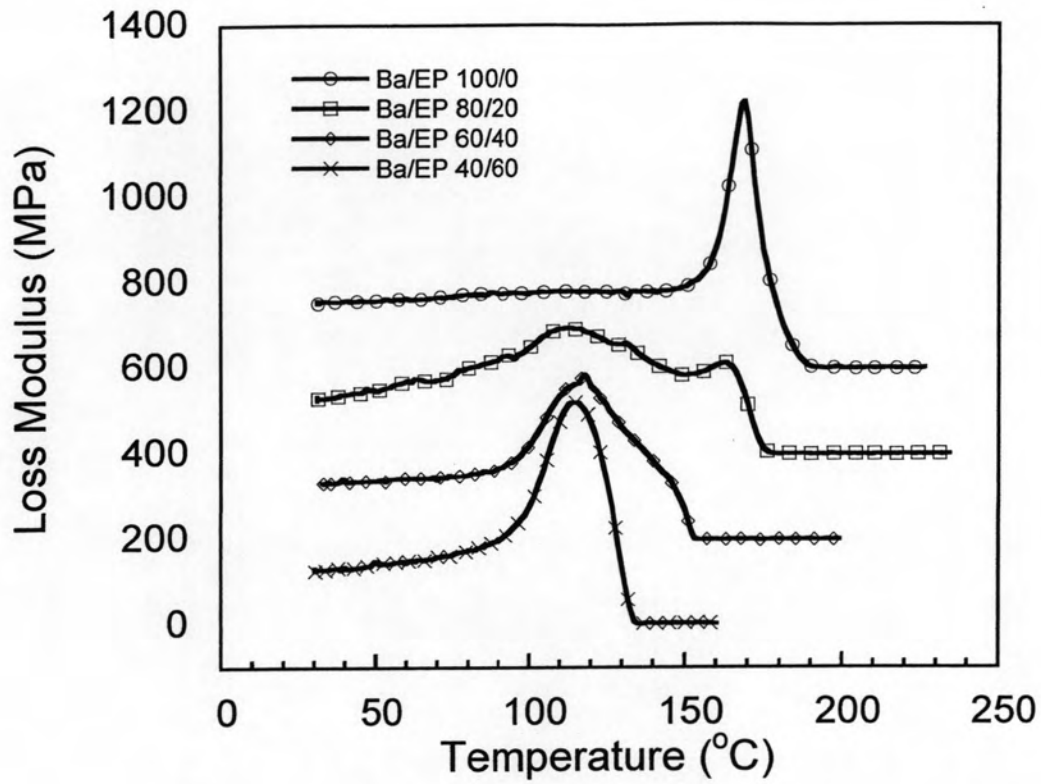


Figure 5.15; Loss modulus as a function of temperature of polybenzoxazine and novolac epoxy resin at various compositions: (\square)100:0, (\square) 80:20, (\diamond) 60:40 and (\times) 40:60.

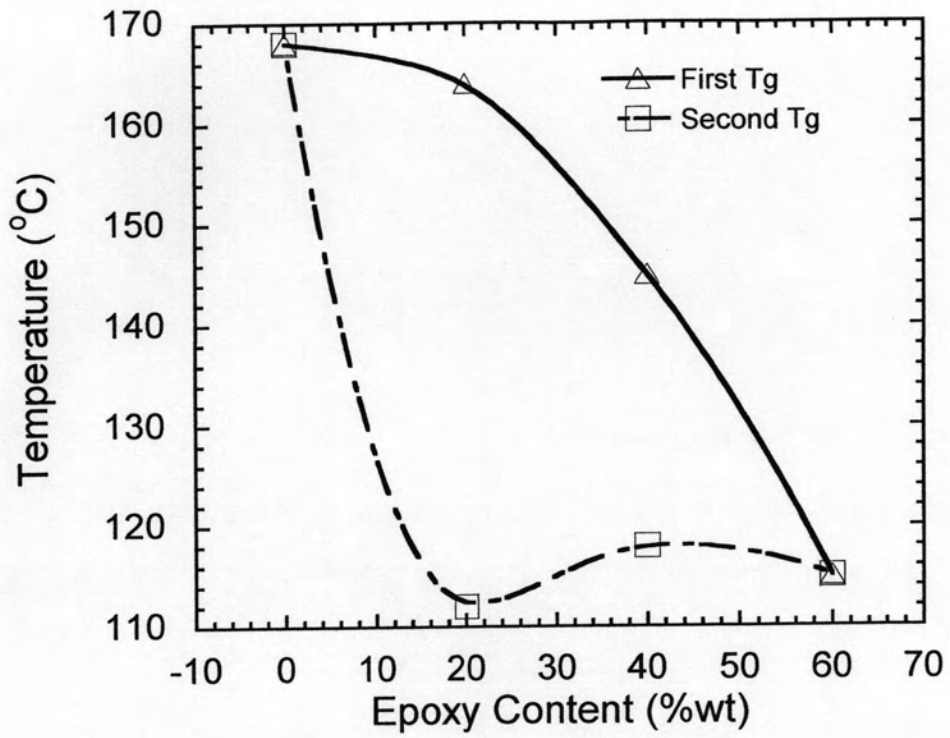


Figure 5.16; Glass transition as a function of temperature of polybenzoxazine (BA-a) and novolac epoxy resin at various compositions : (Δ) First Tg , (\square) Second

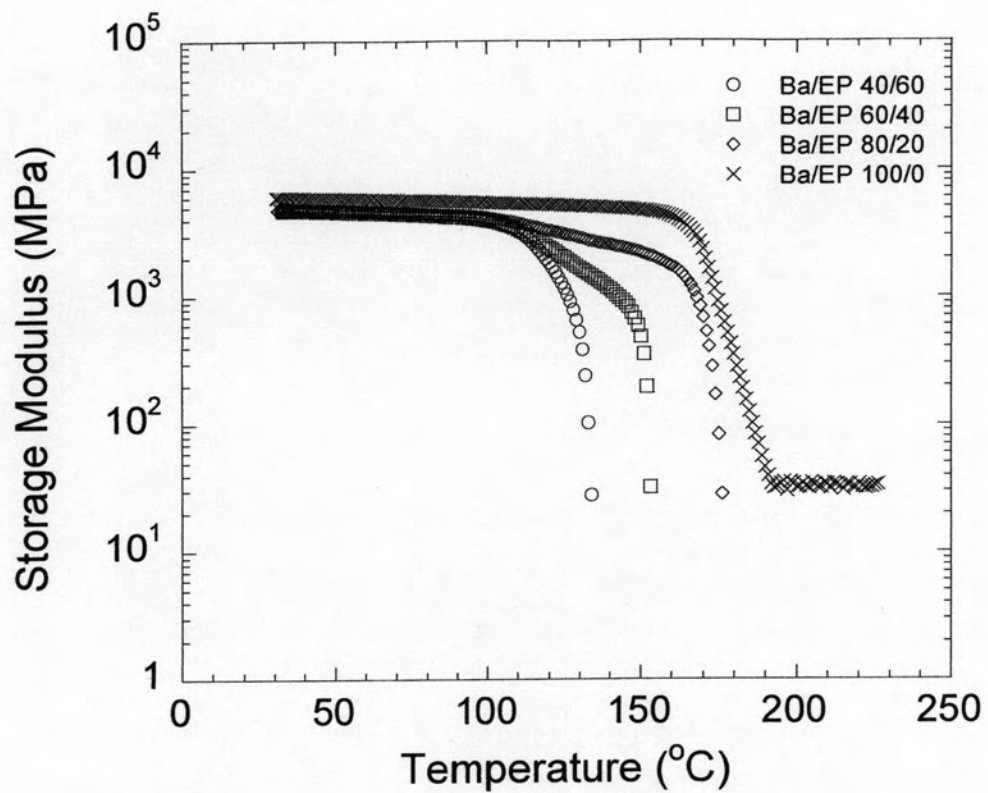


Figure 5.17 ; Storage modulus as a function of temperature of polybenzoxazine (BA-a) and novolac epoxy resin at various compositions: (o)100:0, (□) 80:20, (◇) 60:40 and (x) 40:60.

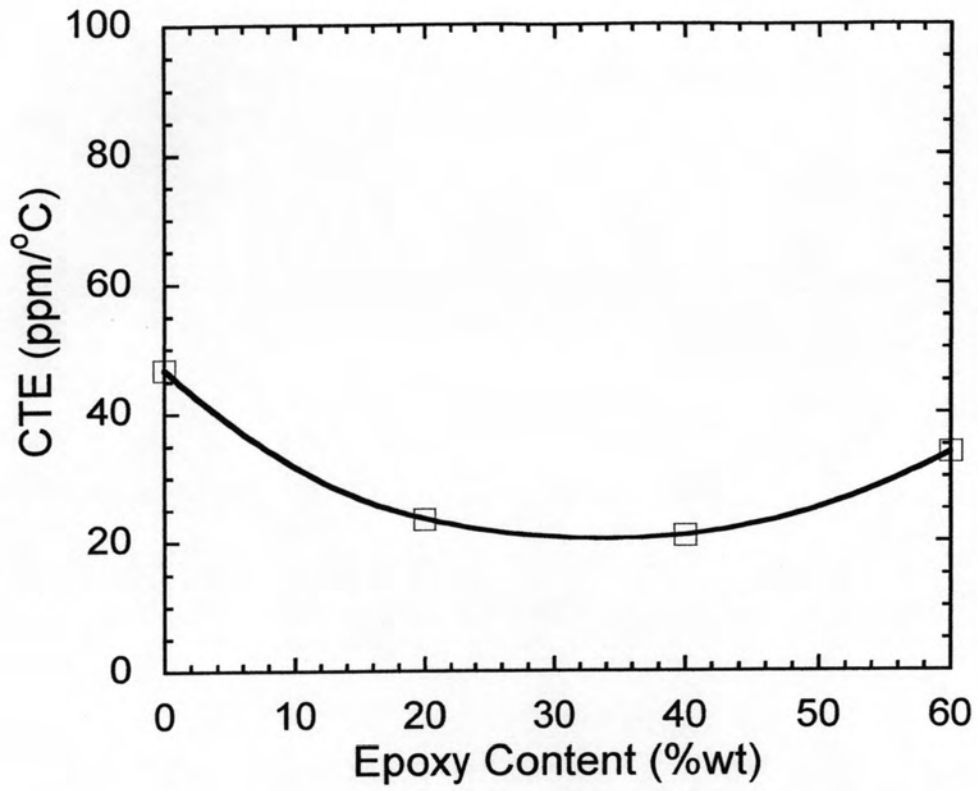


Figure 5.18 ; Coefficient of thermal expansion (CTE) of polybenzoxazine and novolac epoxy copolymers at various compositions.

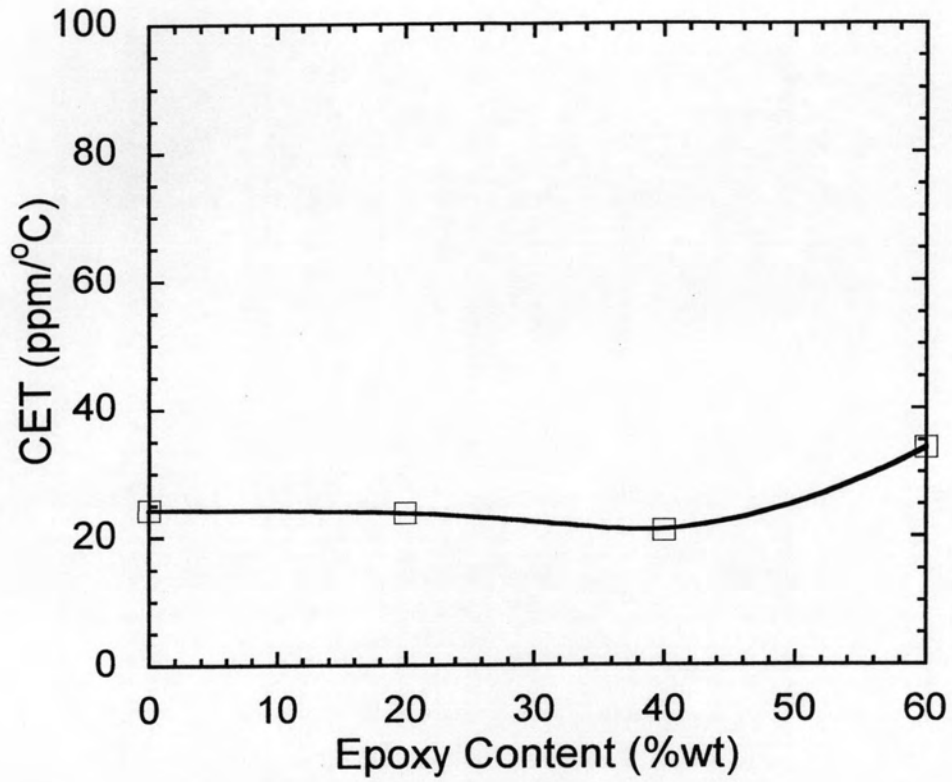


Figure 5.19 ; Coefficient of thermal expansion (CTE) of fiber glass-reinforced polybenzoxazine and novolac epoxy copolymers at various compositions.

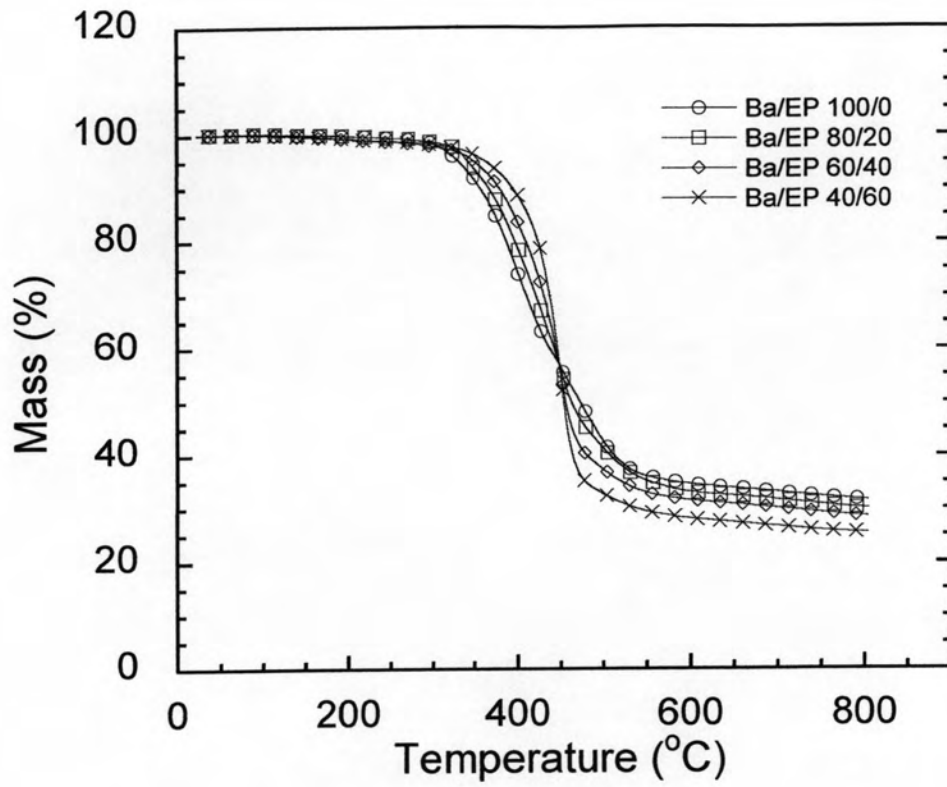


Figure 5.20 ; TGA thermogram of the polybenzoxazine (BA-a) and novolac epoxy resin at various compositions: (+)100:0, (\square) 80:20, (\diamond) 60:40 and (x) 40:60.

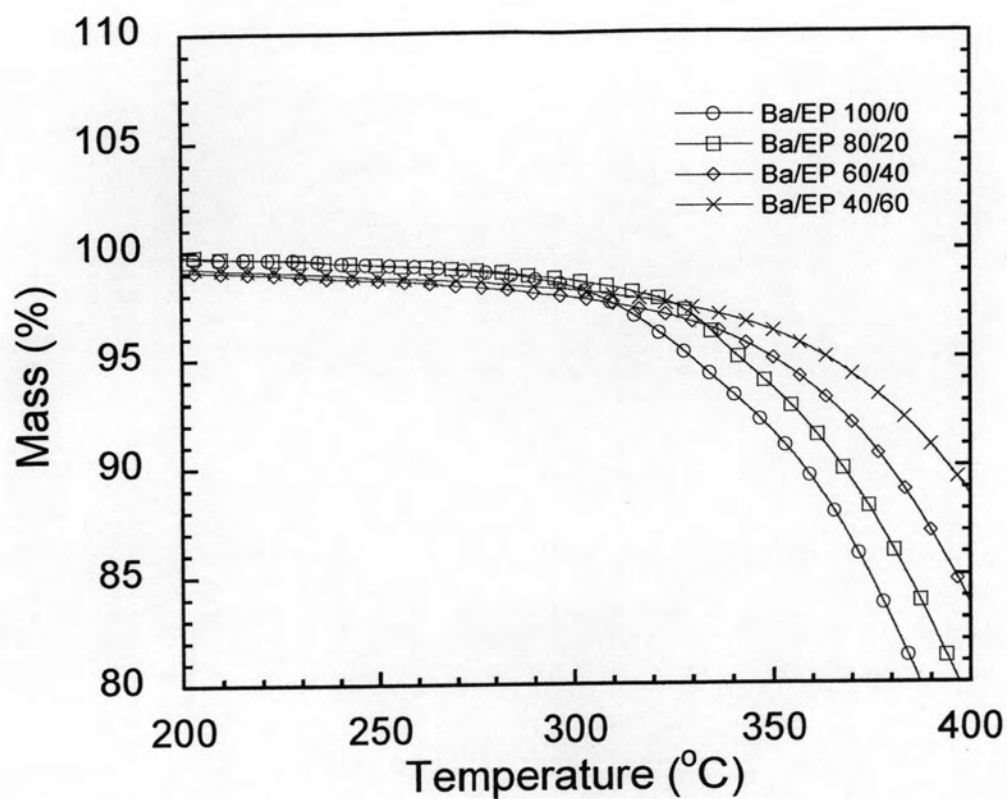


Figure 5.21; Degradation temperature as a function of temperature of benzoxazine (BA-a) and novolac epoxy resin at various compositions: (+)100:0, (\square) 80:20, (\diamond) 60:40 and (\times) 40:60.

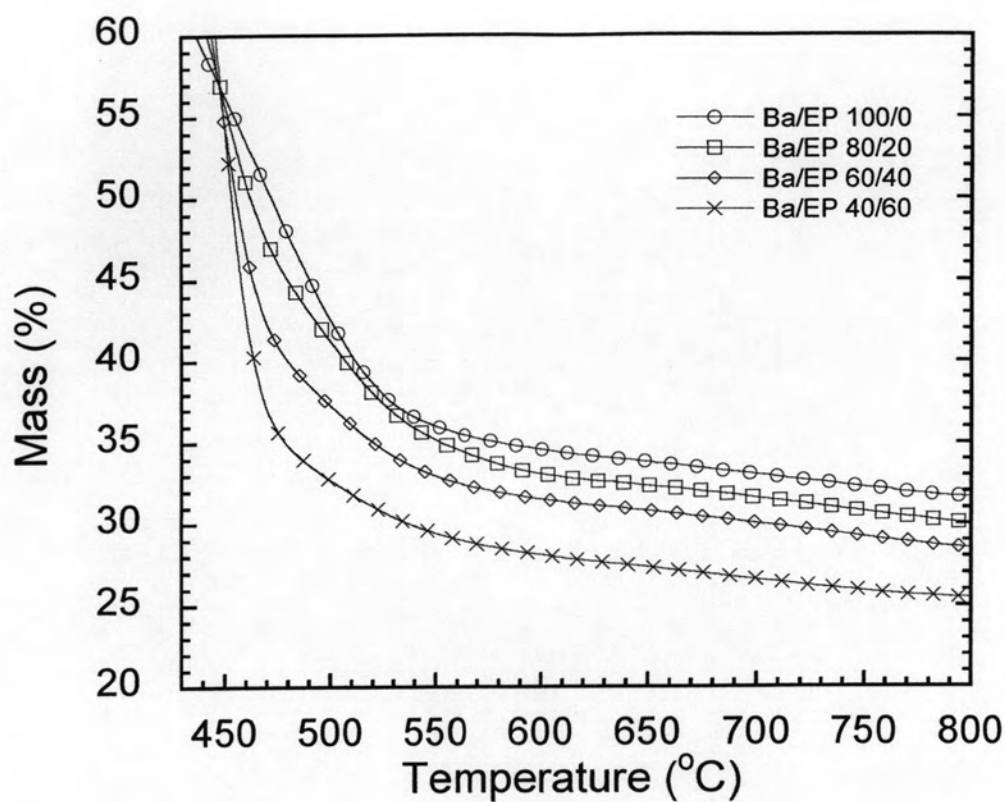


Figure 5.22; Char yields as a function of temperature of polybenzoxazine (BA-a) and novolac epoxy copolymers at various compositions: (o)100:0, (\square) 80:20, (\diamond) 60:40 and (x) 40:60.

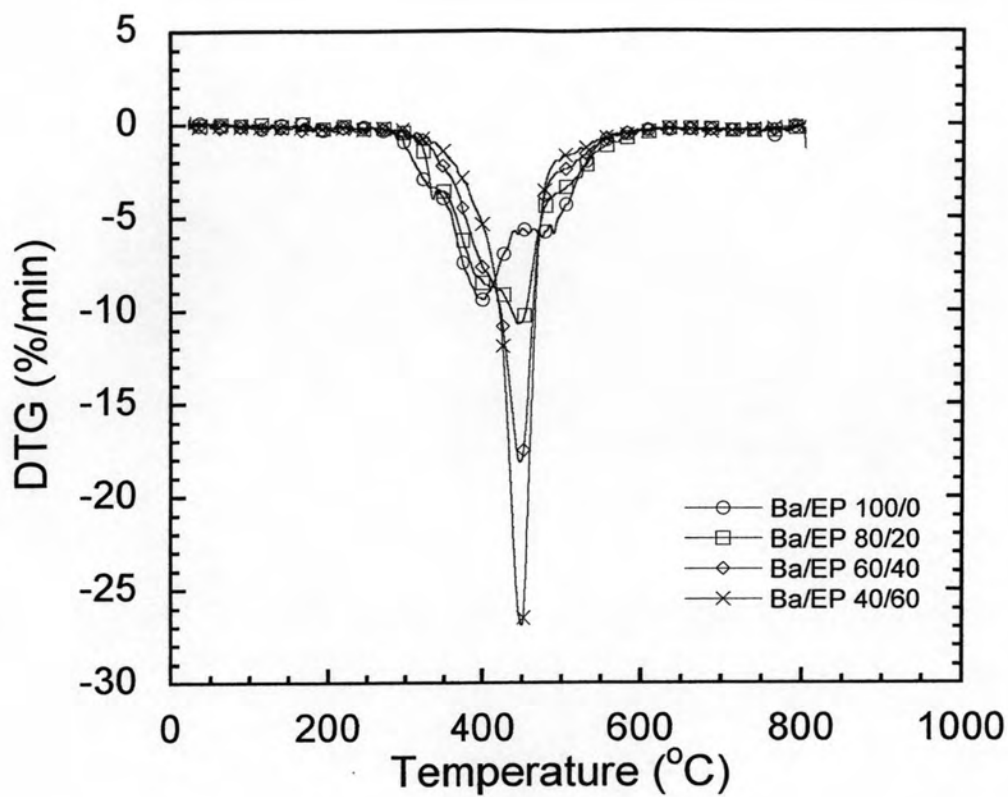


Figure 5.23; DTG(%/min) as a function of temperature of polybenzoxazine (BA-a) and novolac epoxy copolymers at various compositions: (+)100:0, (\square) 80:20, (\diamond) 60:40 and (\times) 40:60.

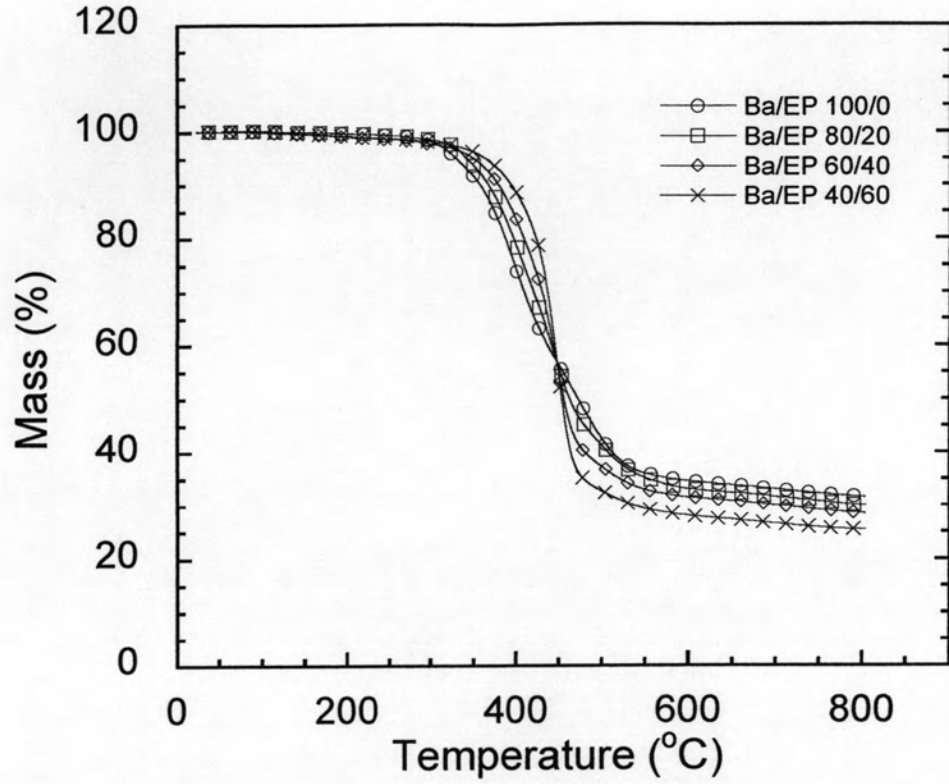


Figure 5.24 ; TGA thermogram of the fiber glass-reinforced polybenzoxazine (BA-a) and novolac epoxy copolymers at various compositions: (+)100:0, (\square) 80:20, (\diamond) 60:40 and (\times) 40:60.

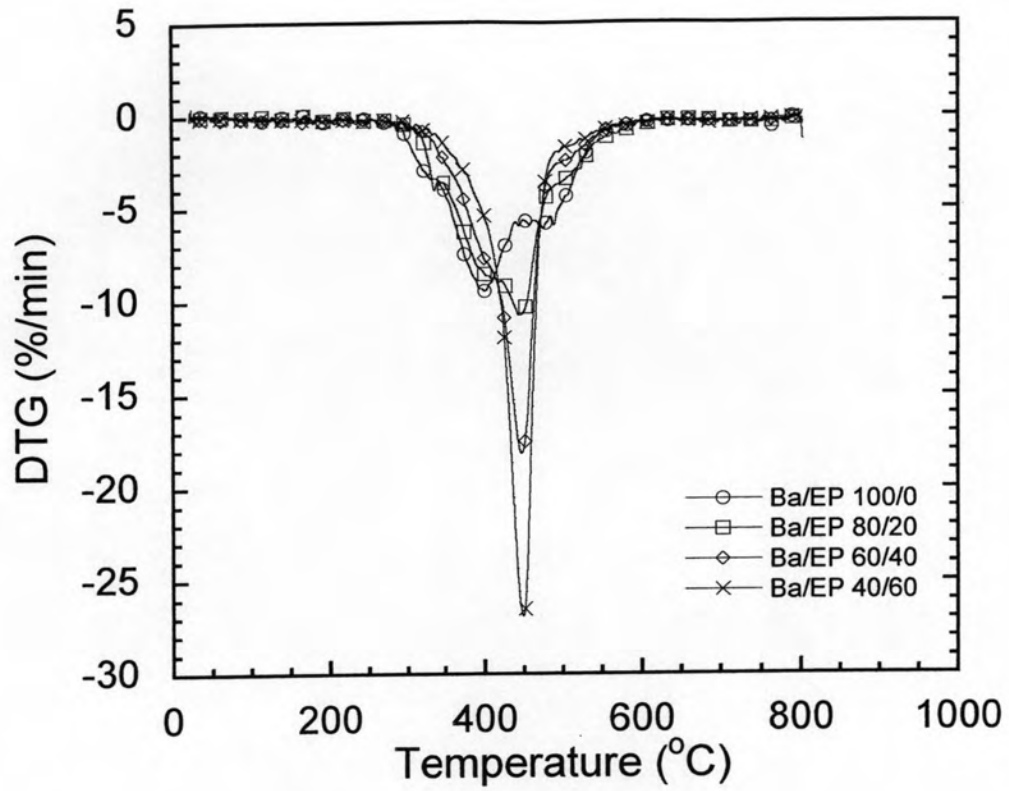


Figure 5.25; DTG(%/min) as a function of temperature of fiber glass-reinforced polybenzoxazine (BA-a) and novolac epoxy copolymers at various compositions: (+)100:0, (\square) 80:20, (\diamond) 60:40 and (x) 40:60.

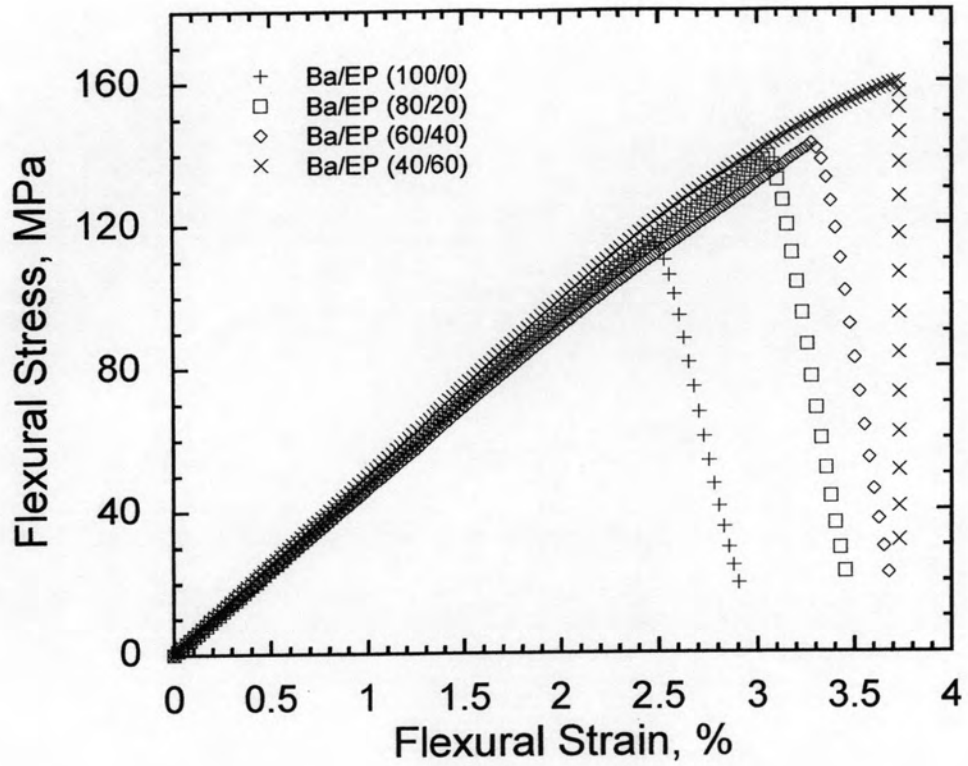


Figure 5.26 ; Flexure Stress (MPa) and Flexure Strain (%) of benzoxazine (BA-a) mixed with novolac epoxy resin at various compositions: (+)100:0, (□) 80:20, (◇) 60:40 and (×) 40:60.

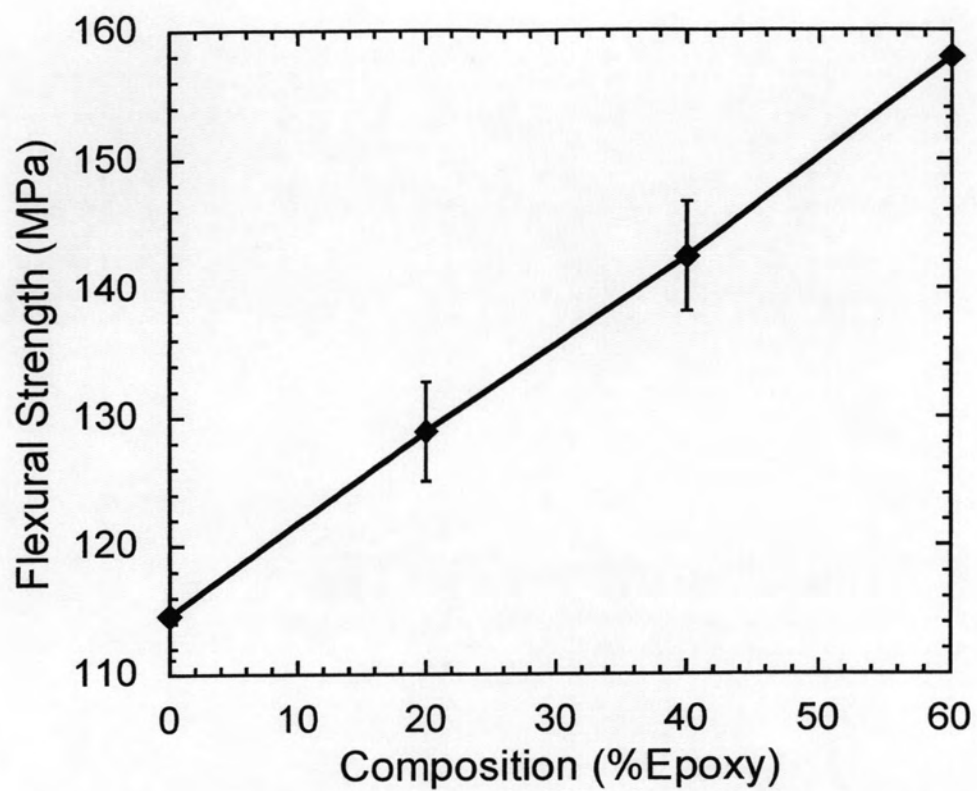


Figure 5.27; Flexural Strength (MPa) of benzoxazine (BA-a) mixed with novolac epoxy resin at various compositions

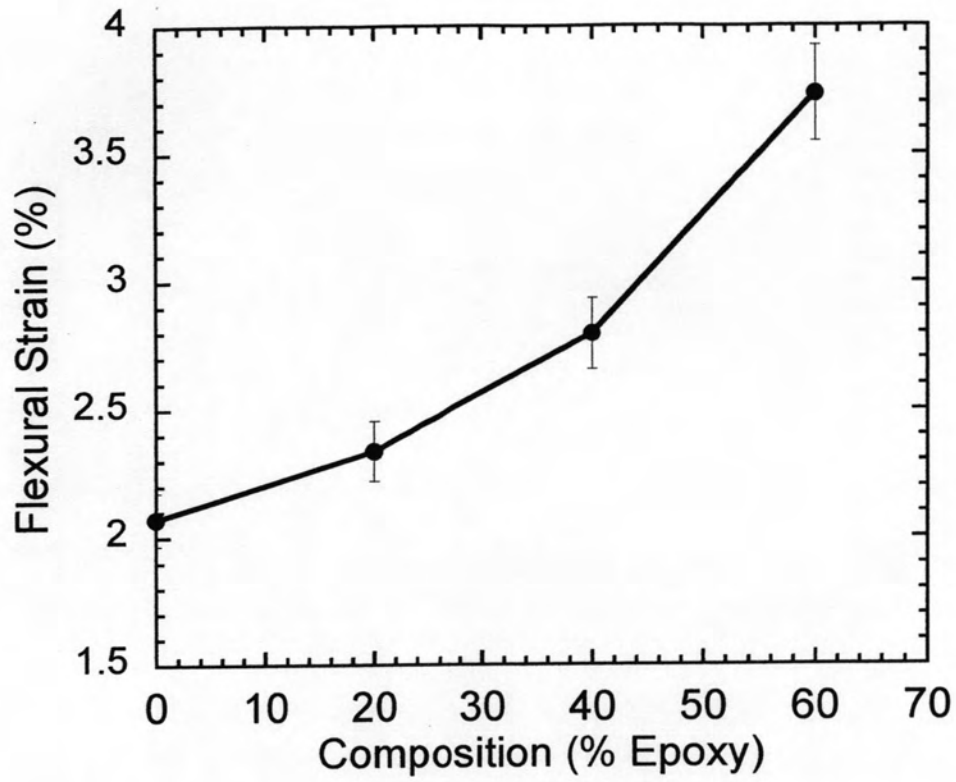


Figure 5.28; Flexural Strain (%) of benzoxazine (BA-a) mixed with novolac epoxy resin at various compositions.

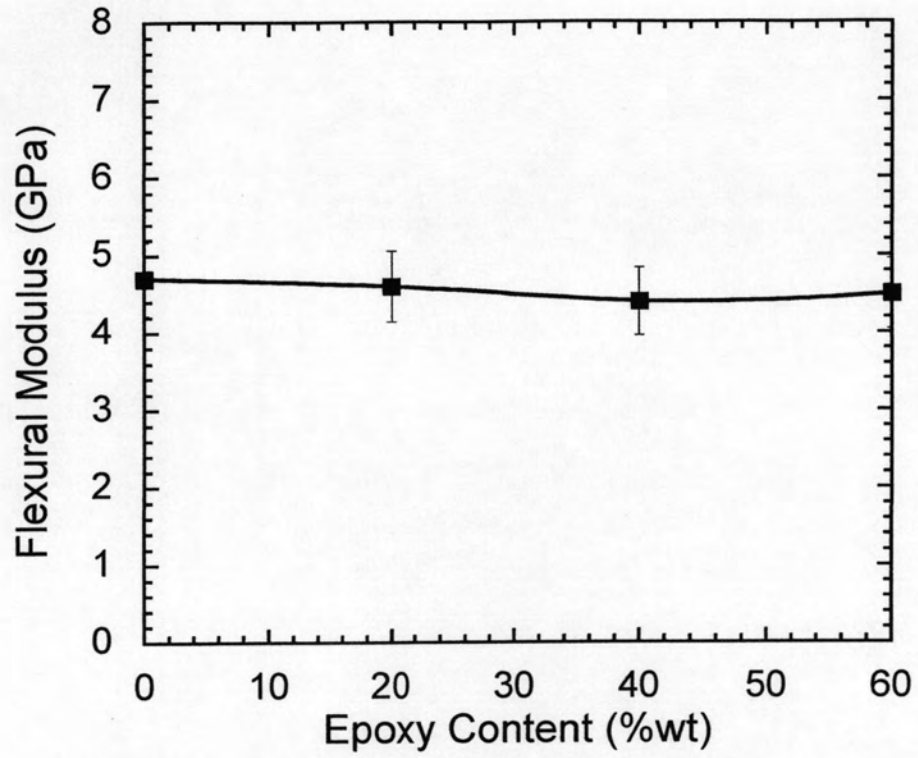


Figure 5.29; Flexural Modulus (GPa) of benzoxazine (BA-a) mixed with novolac epoxy resin at various compositions.

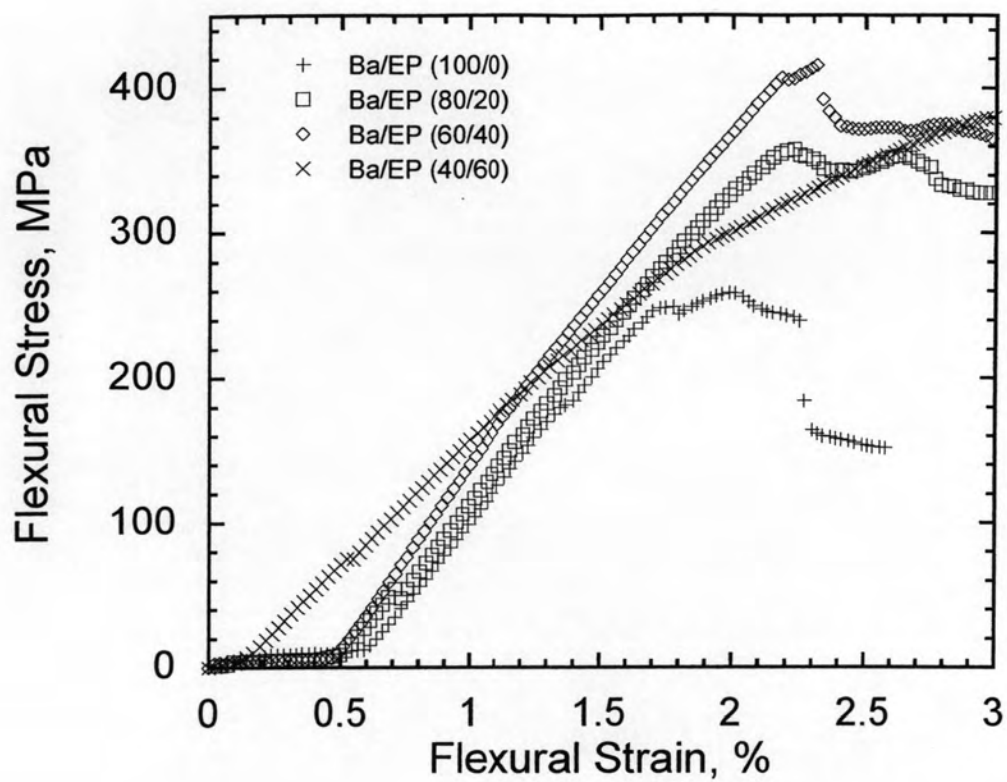


Figure 5.30; Flexural Stress with glass reinforcement of benzoxazine (BA-a) mixed with novolac epoxy resin at various compositions: (+)100:0, (□) 80:20, (◇) 60:40 and (x) 40:60.

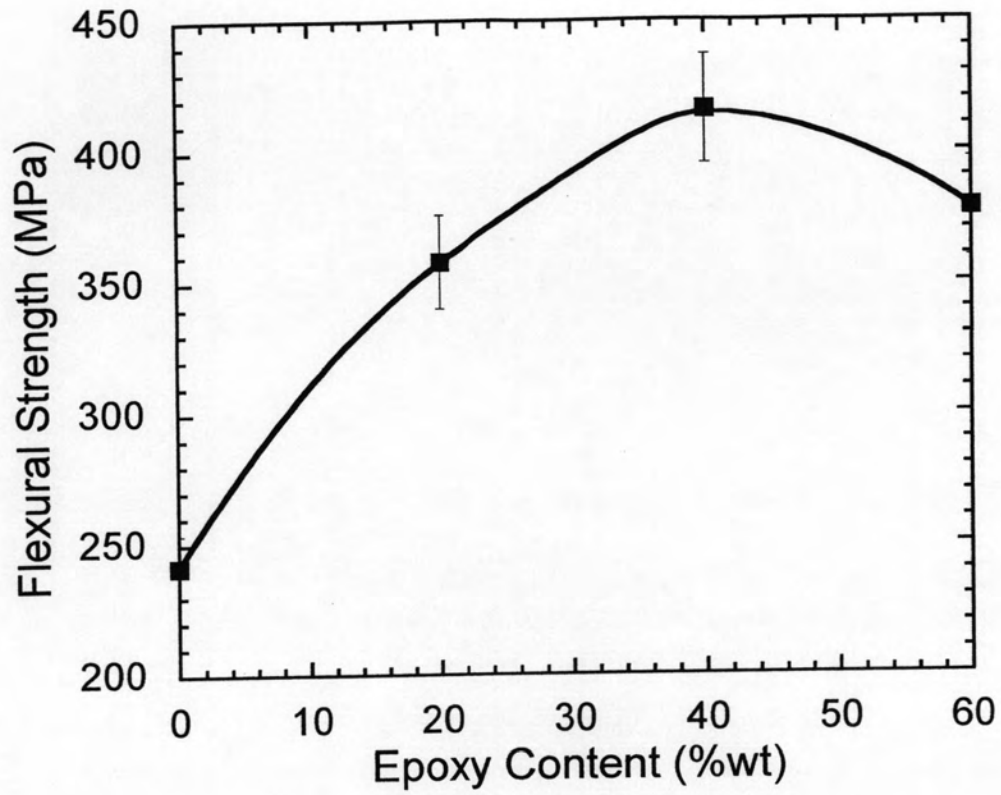


Figure 5.31; Flexural Strength (MPa) with glass reinforcement of benzoxazine (BA-a) mixed with novolac epoxy resin at various compositions.

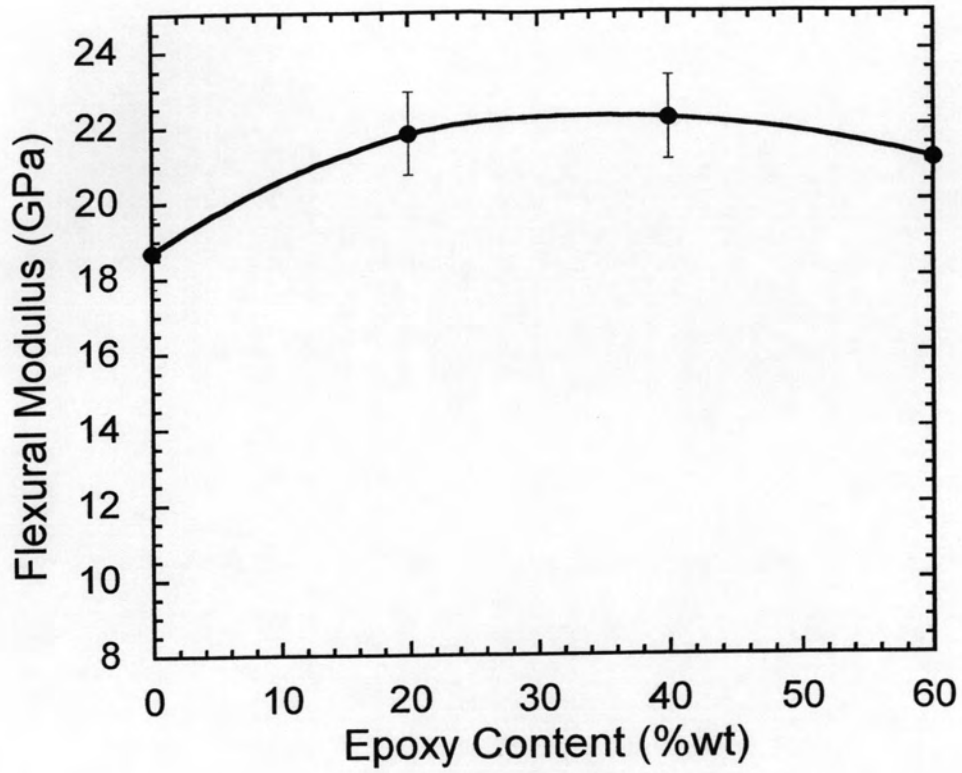


Figure 5.32; Flexural Modulus (GPa) with glass reinforcement of benzoxazine (BA-a) mixed with novolac epoxy resin at various compositions.

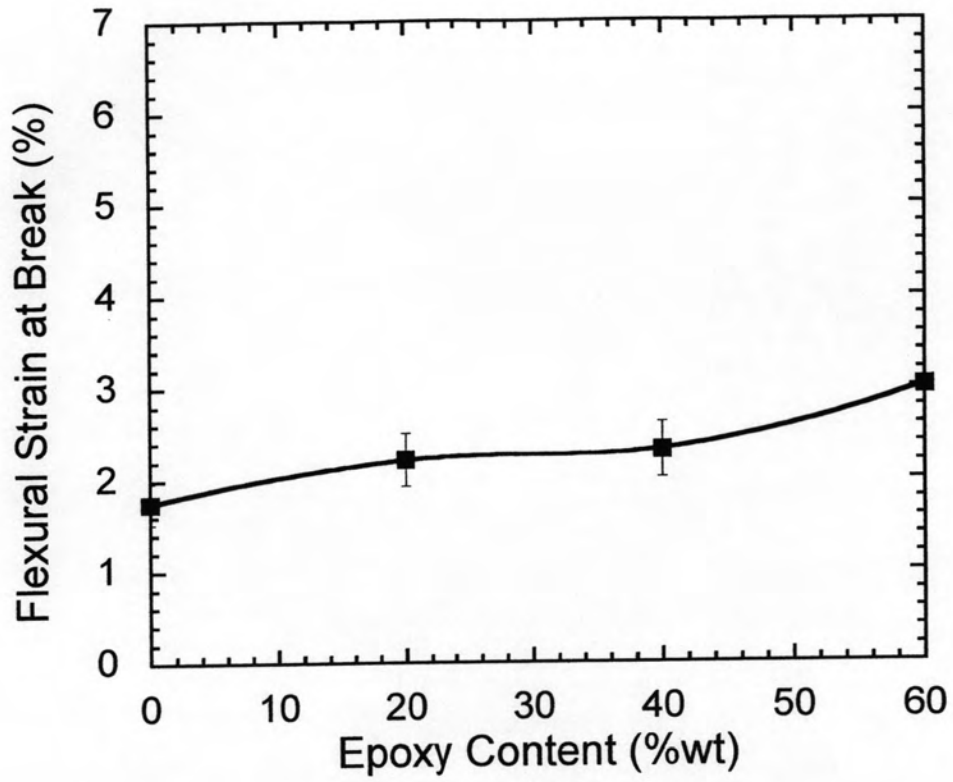


Figure 5.33; Flexural Strain (%) with glass reinforcement of benzoxazine (BA-a) mixed with novolac epoxy resin at various compositions.

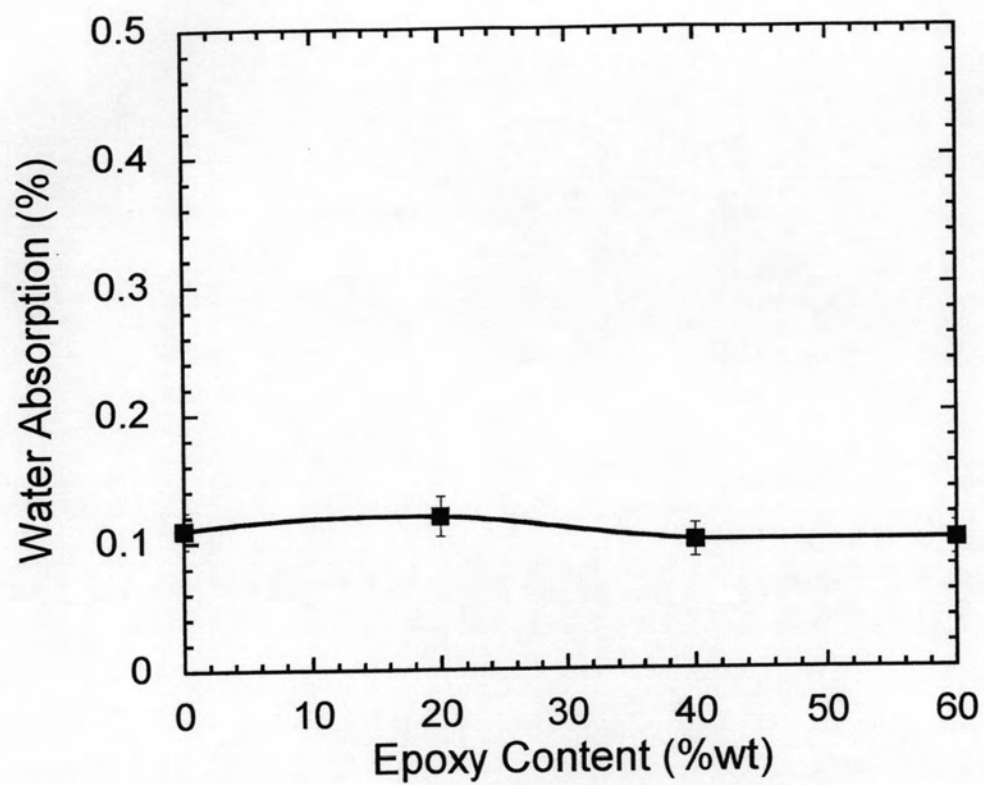


Figure 5.34; Water absorption plot of benzoxazine (BA-a) and novolac epoxy copolymers at various compositions.

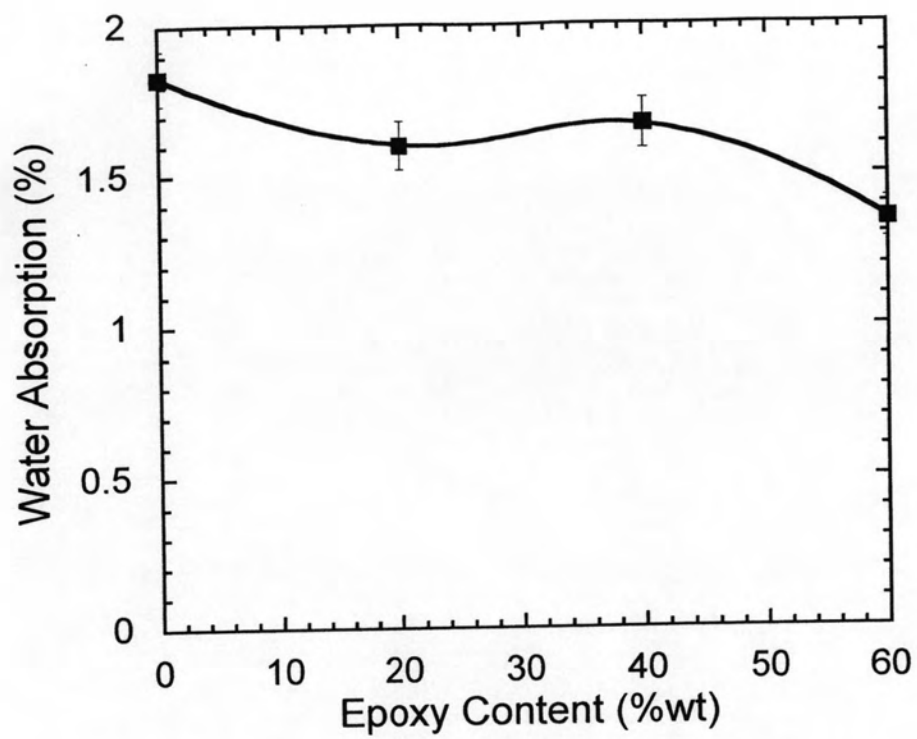


Figure 5.35; Water absorption plot of fiber glass-reinforced benzoxazine (BA-a) mixed with novolac epoxy resin at various compositions.

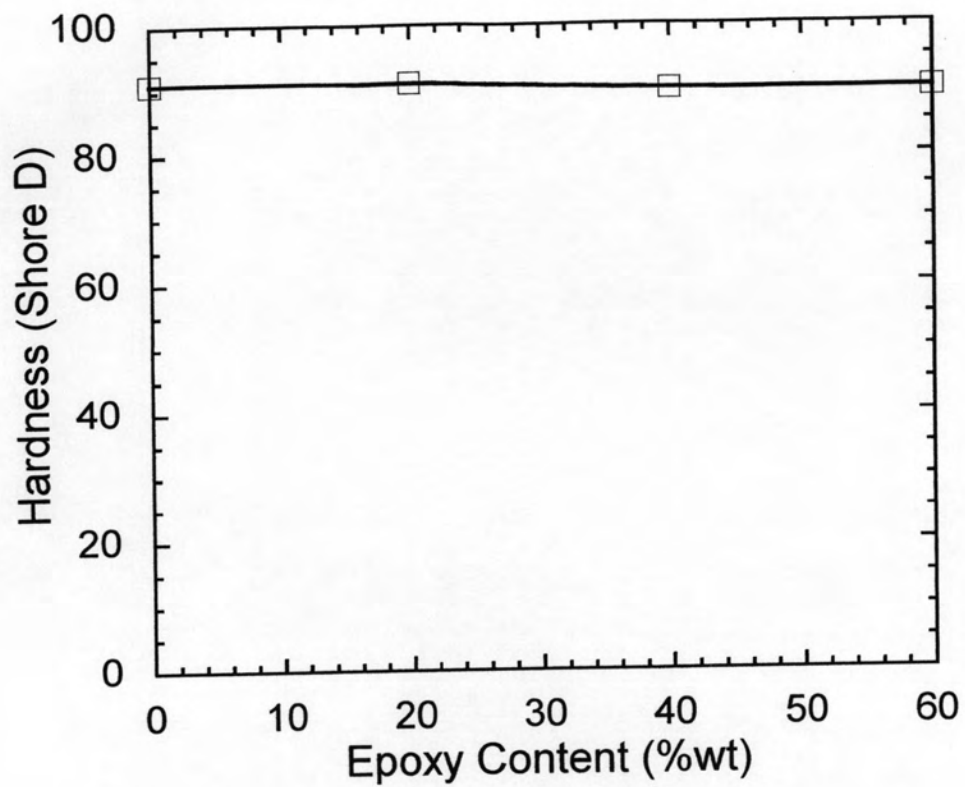


Figure 5.36 ; Hardness of polybenzoxazine (BA-a) mixed with novolac epoxy resin at various compositions.

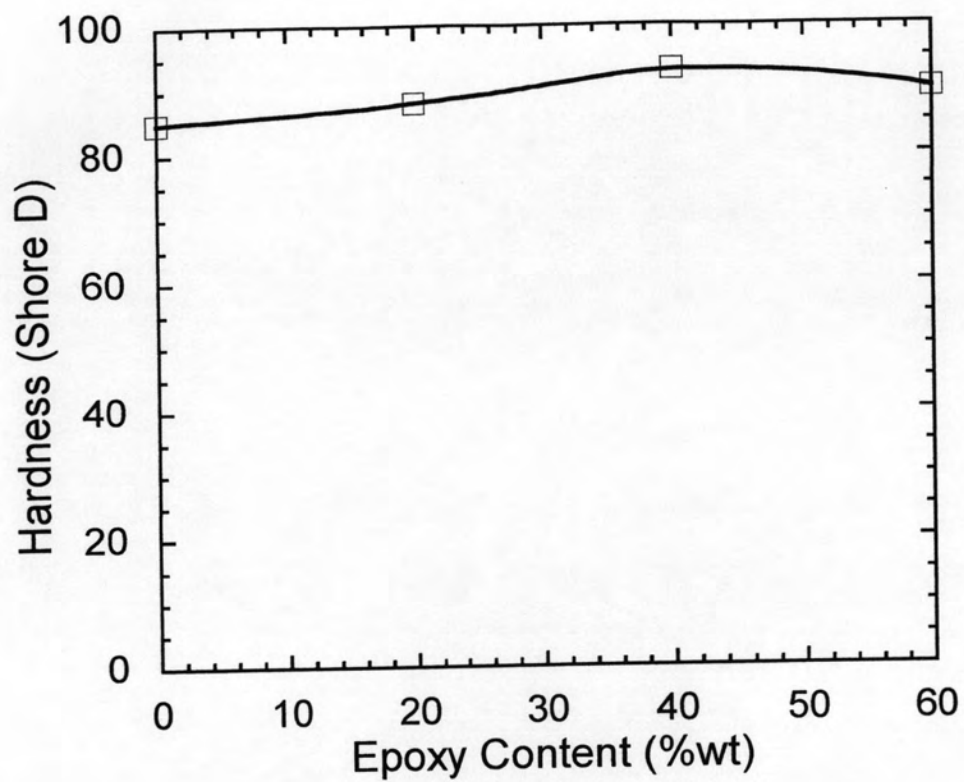


Figure 5.37; Hardness of fiber glass-reinforced polybenzoxazine (BA-a) mixed with novolac epoxy resin at various compositions.