

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Monomer Characterization

4.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of as-synthesized Ph-a and BA-a are shown in Figures 4.1 and 4.2. For both monomers, the C-H stretching region can be found around 3100-2700 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-plane deformation of the 1,2,4-tri-substituted benzene ring can be found in the region from 940-920 cm^{-1} .

The band around 1495-1497 cm^{-1} attributes to the tri-substituted benzene ring mode in the oxazine ring structure. The antisymmetric and symmetric C-N-C stretching modes can be found in the regions 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, while the symmetric stretching mode appears at 1040-1020 cm^{-1} .

For BA-a monomer, the methyl group vibration occurs at 2968 and 2872 cm^{-1} . The hydroxyl group of the phenolic structure appears at 3421 cm^{-1} (Ishida and Rodriguez, 1995).

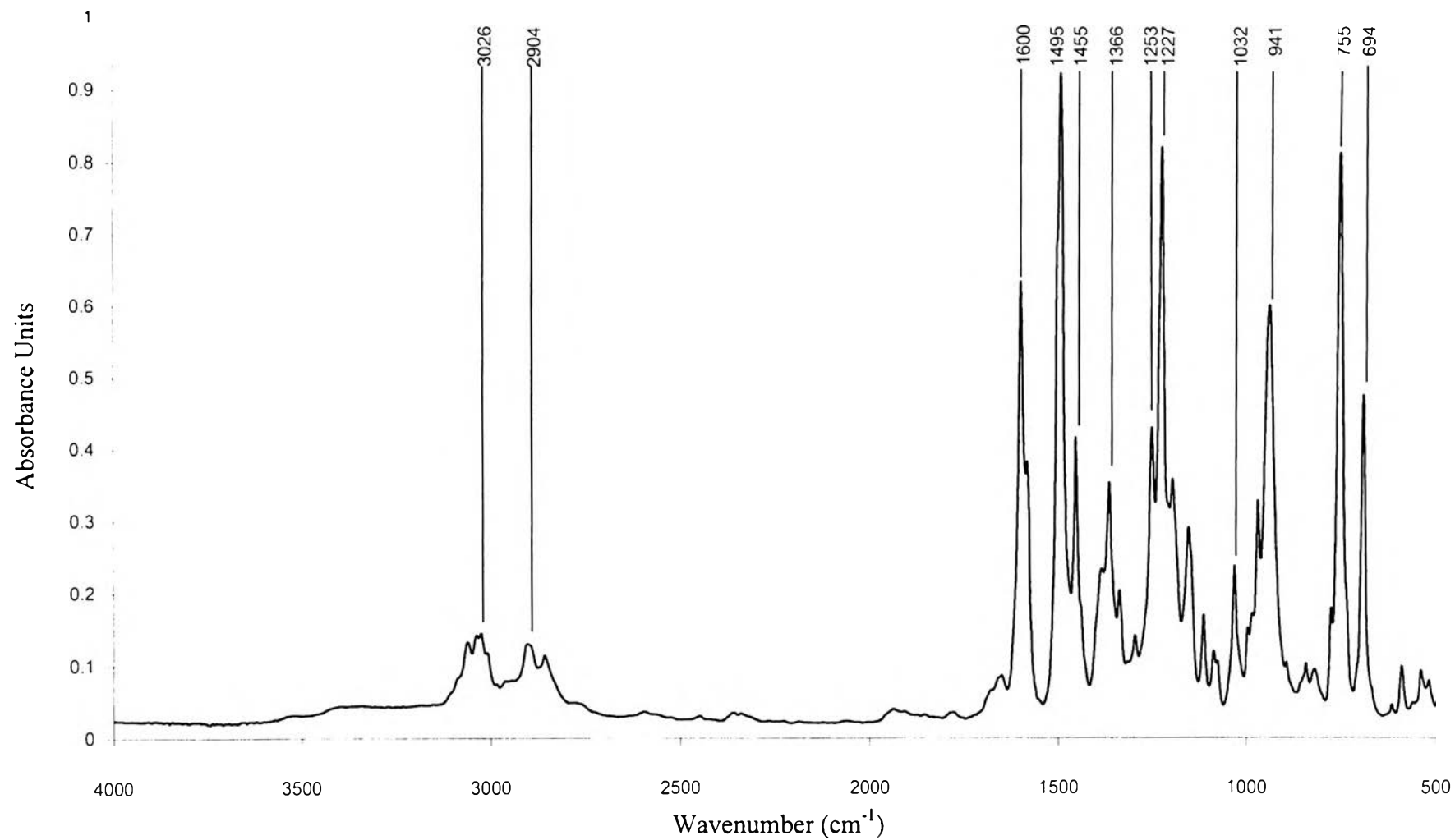


Figure 4.1 FTIR spectrum of as-synthesized Ph-a monomer.

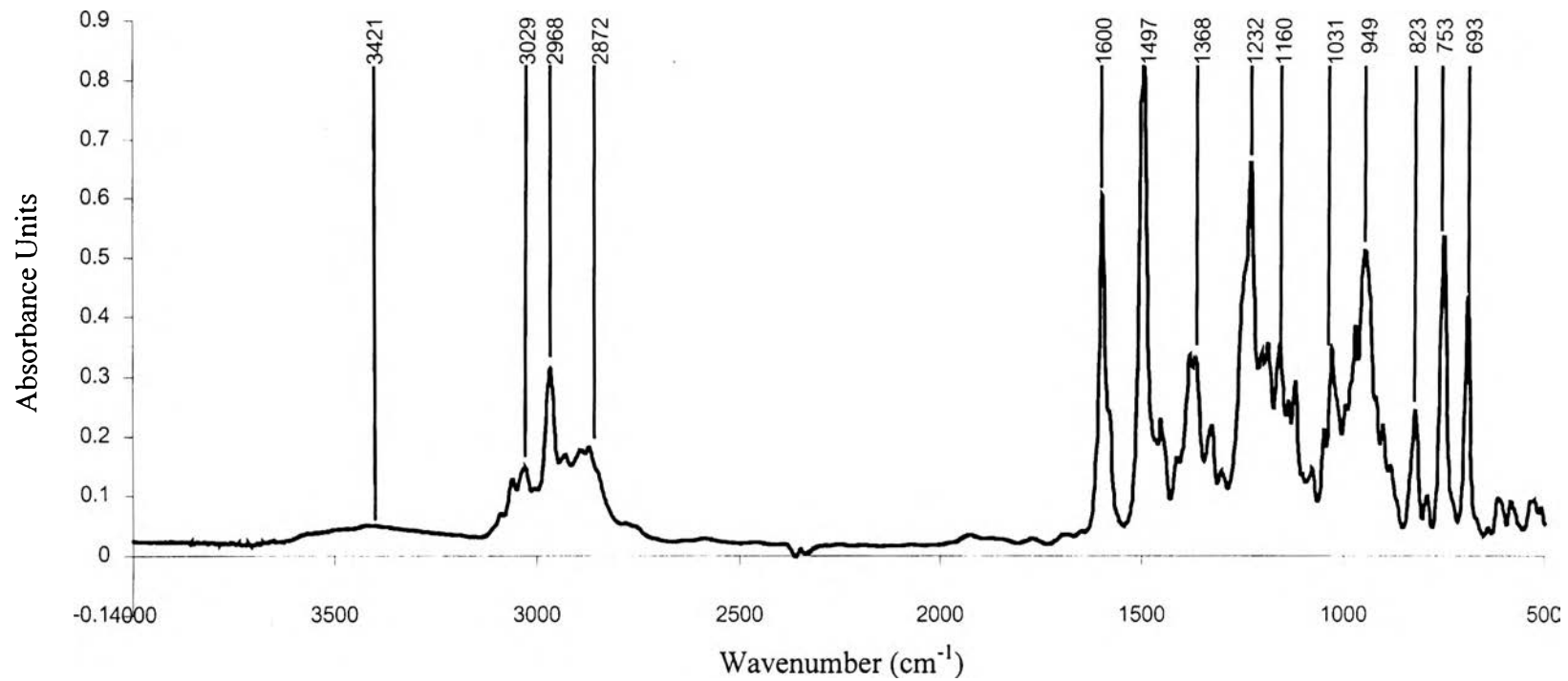
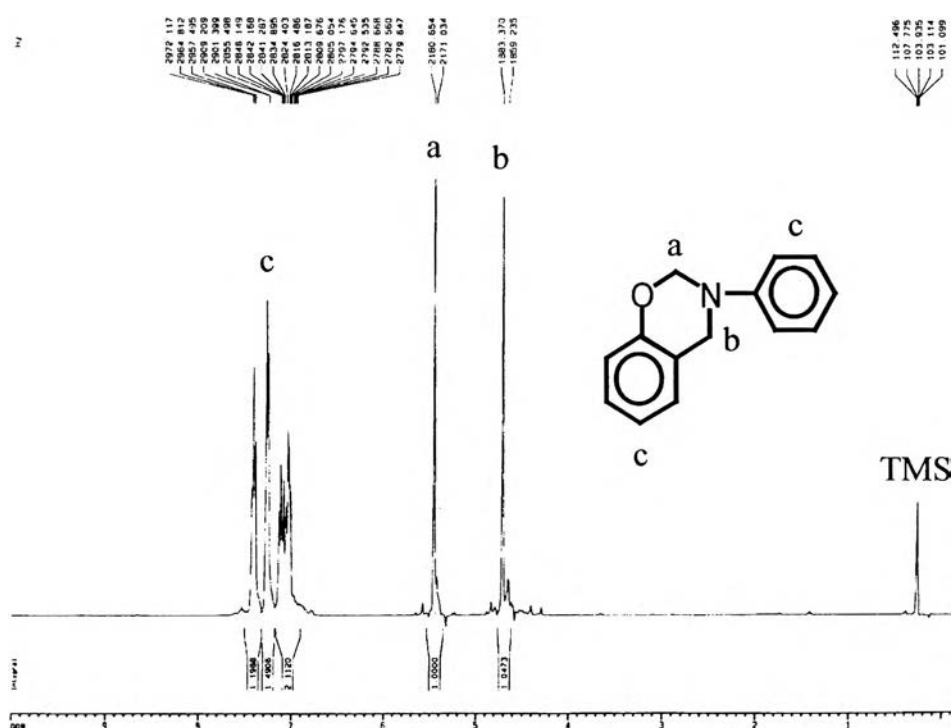


Figure 4.2 FTIR spectrum of as-synthesized BA-a monomer.

4.1.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

The ^1H -NMR spectra of as-synthesized Ph-a and BA-a monomers are depicted in Figures 4.3 and 4.4. The important peak assignments are indicated. For Ph-a monomer, the peak around 0.2-0.3 ppm is the internal reference tetramethylsilane (TMS). The signal of methylene units (a and b) in the oxazine ring occurred as singlets at 4.7 and 5.45 ppm. The nine aromatic protons (c) showed multiplets around 7-7.45 ppm.

For BA-a monomer, the peak around 0-0.1 ppm is the internal reference TMS. Six methyl protons (a) showed a singlet at 1.6 ppm. The signal of methylene units (b and c) in the oxazine ring occurred as singlets at 4.6-5.35 ppm. The sixteen aromatic protons (d) showed multiplets around 6.7-7.3 ppm. These NMR spectra indicate the purity of the monomers to be approximately in the range of 97-98% (Ishida and Rodriguez, 1995).



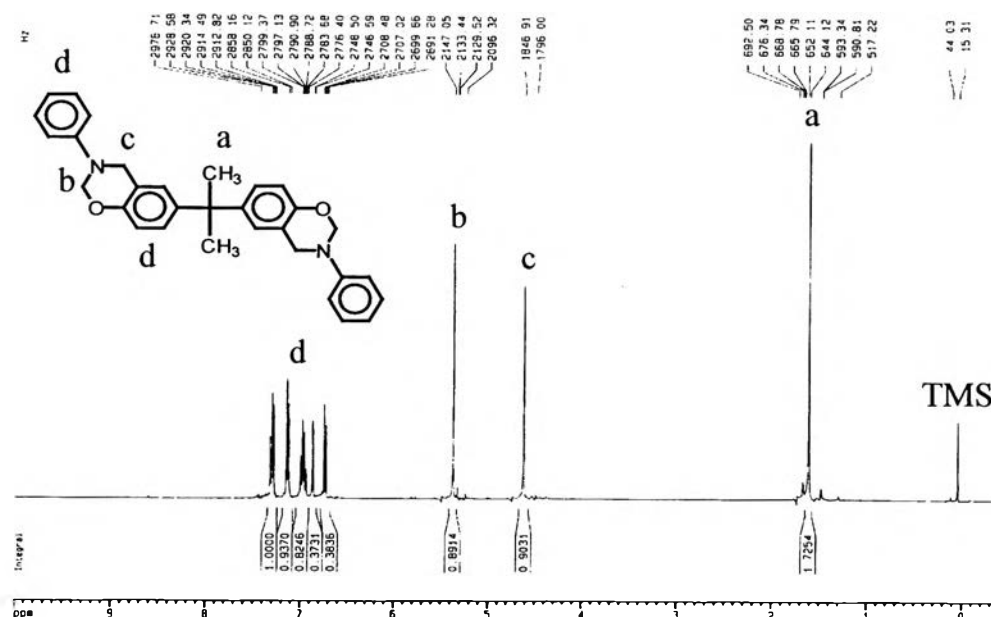


Figure 4.4 NMR spectrum of as-synthesized BA-a monomer.

4.2 Properties of Polybenzoxazine Resin

4.2.1 Effect of Varying the Resin Composition

4.2.1.1 *Flexural properties*

The effect of varying BA-a:Ph-a ratio in the resin on flexural properties of polybenzoxazine resin with different curing conditions are shown in Figures 4.5 and 4.6. Regarding to the curing conditions of 150°C for 3 h + 160°C for 3 h, the results showed that an increase in BA-a:Ph-a ratio led to an increase in flexural strength but the flexural modulus decreased. This may be because molecules in BA-a are more bulky than that of Ph-a, so the packing of BA-a molecules is not as good as for Ph-a. There will therefore be more free volume in the resin with high BA-a:Ph-a ratio and hence the lower

modulus. For the curing conditions of 150°C for 3 h + 170°C for 3 h, it showed that the flexural strength and modulus increased with increase in BA-a:Ph-a ratio. The results showed that curing at higher temperature led to better packing and higher cross-linking, hence better mechanical properties were achieved.

4.2.1.2 Impact strength

The effect of varying BA-a:Ph-a ratio on impact strength of polybenzoxazine resin with different curing conditions is shown in Figure 8. It was observed that the impact strength increased slightly with increase in BA-a:Ph-a ratio. This is because BA-a is difunctional benzoxazine which can produce crosslinked structure, so its mechanical properties in terms of flexural and impact strength is better than that of Ph-a. While Ph-a can also crosslink to some at the aniline side group, the degree of crosslinking is less than that when BA-a was used. Moreover, the results showed that the flexural strength, flexural modulus, and impact strength increased with increase in curing temperature.

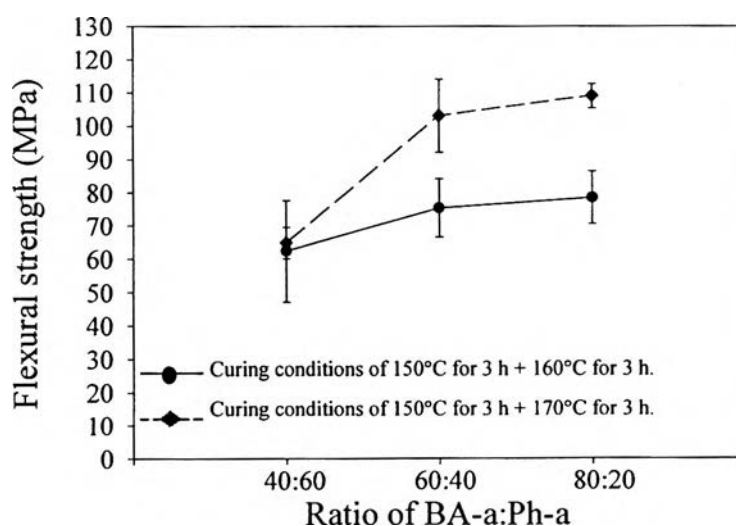


Figure 4.5 Flexural strength of polybenzoxazine resins with different BA-a:Ph-a ratios.

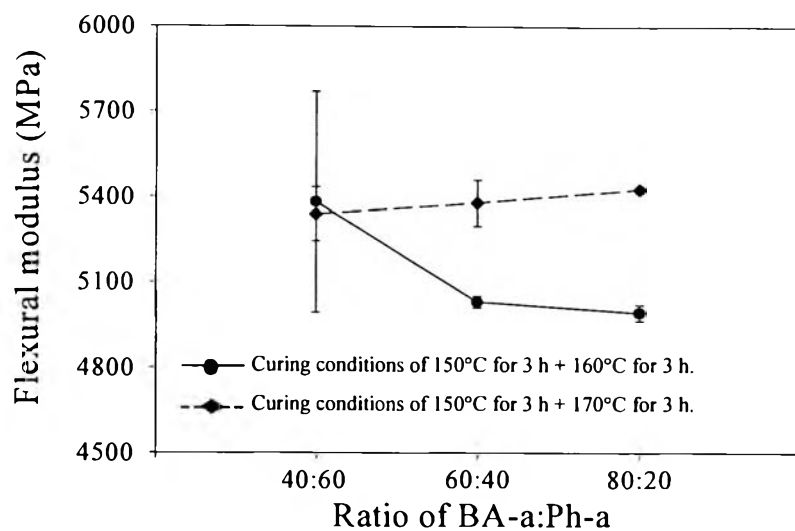


Figure 4.6 Flexural modulus of polybenzoxazine resins with different BA-a:Ph-a ratios.

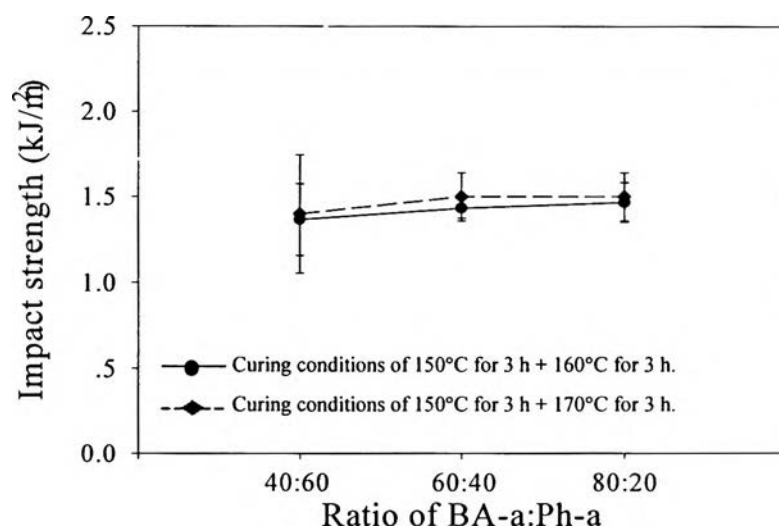


Figure 4.7 Impact strength of polybenzoxazine resins with different BA-a:Ph-a ratios.

4.2.2 Effect of Curing Conditions

4.2.2.1 *Flexural properties*

The effect of curing conditions on flexural properties of polybenzoxazine resin is shown in Figures 4.8 and 4.9. The results show that both the flexural strength and flexural modulus increase with increases in curing temperature and curing time.

4.2.2.2 *Impact strength*

The effect of curing conditions on impact strength of polybenzoxazine resin is shown in Figure 4.10. The impact strength increased slightly with increases in curing temperature and curing time.

For thermosetting materials, as the curing temperature and curing time increase, the mechanical properties also increase due to the formation of cross-links.

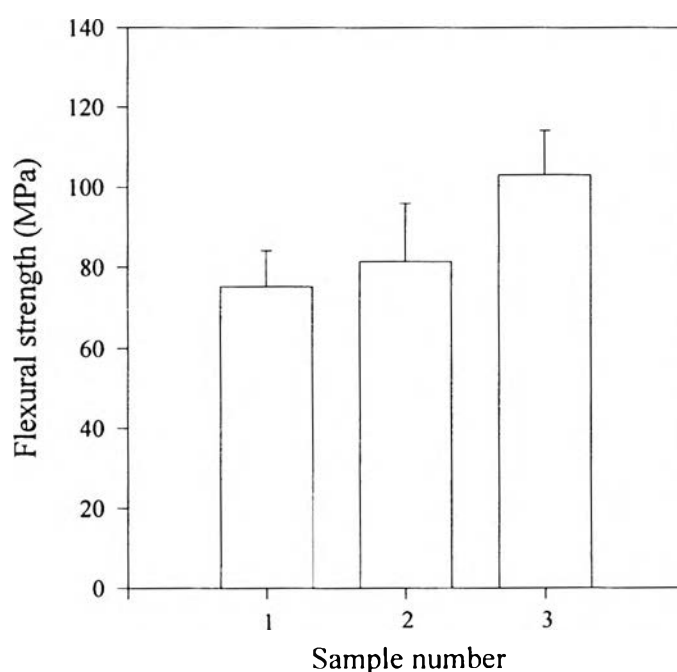


Figure 4.8 Flexural strength of polybenzoxazine resins cured under different conditions

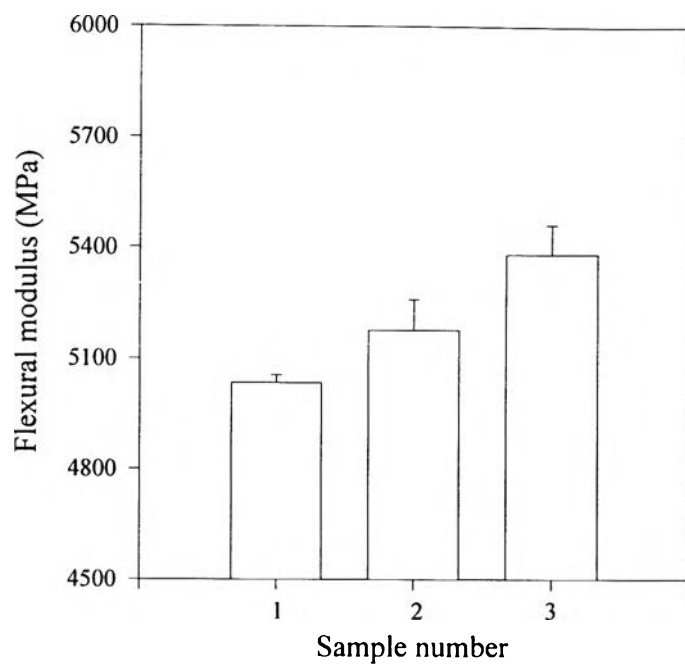


Figure 4.9 Flexural modulus of polybenzoxazine resins cured under different conditions.

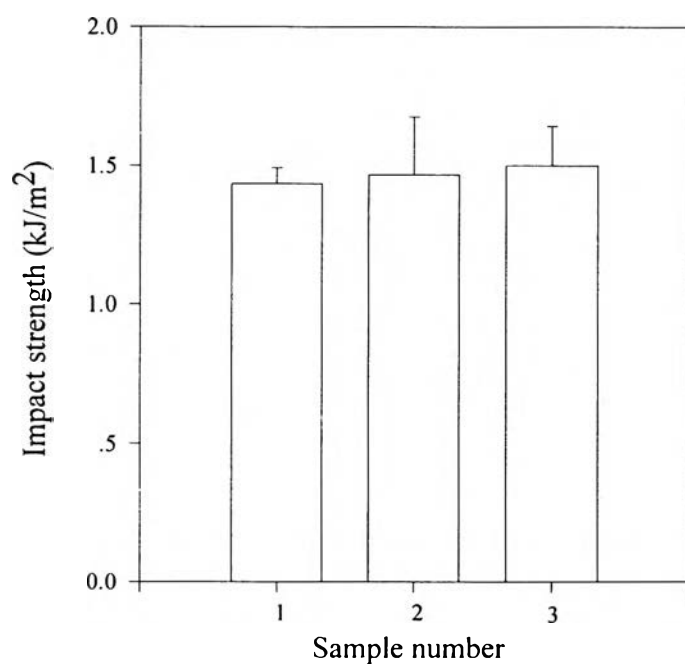


Figure 4.10 Impact strength of polybenzoxazine resins cured under different conditions.

where

Sample number 1 = curing conditions of 150°C for 3 h + 160°C for 3 h.

Sample number 2 = curing conditions of 150°C for 6 h + 160°C for 3 h.

Sample number 3 = curing conditions of 150°C for 3 h + 170°C for 3 h.

4.2.3 Comparison of Properties of Polybenzoxazine and Unsaturated Polyester Resins

4.2.3.1 *Mechanical properties*

The mechanical properties of polybenzoxazine and unsaturated polyester resins are compared in Table 4.1.

Table 4.1 Comparison of mechanical properties of polybenzoxazine and unsaturated polyester resins.

Resin type Property	PBZX resin at different BA-a:Ph-a ratio			UPE resin
	40:60	60:40	80:20	
Flexural strength (MPa)	64.7 ± 4.7	103.1 ± 11.0	109.0 ± 3.6	90.5 ± 12.0
Flexural modulus (MPa)	5341 ± 94.3	5381 ± 80.1	5426 ± 11.6	4049 ± 69.2
Impact strength (kJ/m ²)	1.4 ± 0.3	1.5 ± 0.1	1.5 ± 0.1	1.4 ± 0

The flexural strength of PBZX resin at BA-a:Ph-a ratio of 40:60 was lower than that of UPE resin but PBZX resins at BA-a:Ph-a ratios of 60:40 and 80:20 had higher flexural strength. The flexural modulus of PBZX resin was more than UPE resin at all BA-a:Ph-a ratios and its impact

strength was similar to UPE resin. Ishida and Allen (1996) studied the mechanical properties of PBZX resins. They found that PBZX resins had high tensile and flexural moduli.

4.2.3.2 Water absorption

The water absorption of polybenzoxazine at BA-a:Ph-a ratio of 60:40 and unsaturated polyester resins are shown in Figure 4.11.

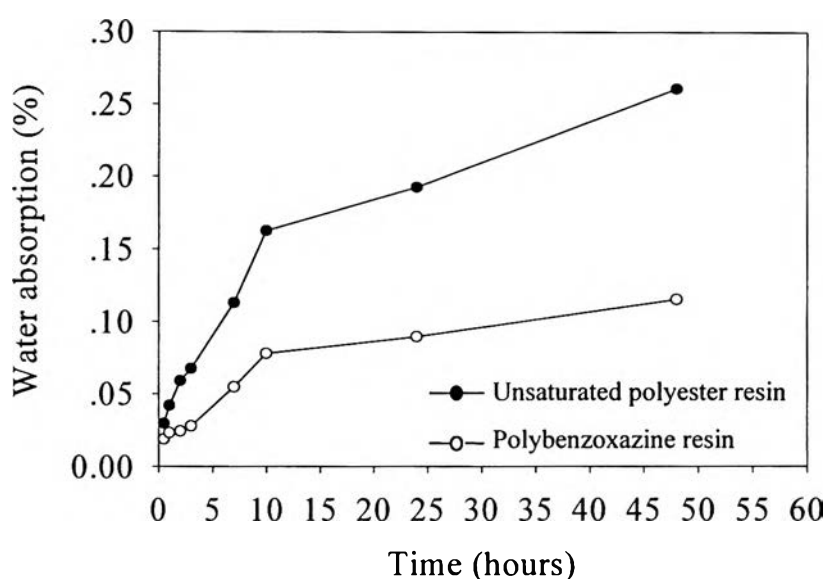


Figure 4.11 Water absorption of polybenzoxazine and unsaturated polyester resins.

It was observed that both types of resins had very low water absorption of not more than 0.3% even after 48 hours immersion. However, polybenzoxazine resin was found to have a lower water absorption than unsaturated polyester resin. The saturation water content of PBZX derived from BA-a was reported to be 1.9% by weight after immersion in water for 600 days at room temperature (Ishida and Allen, 1996).

4.3 Properties of composites

4.3.1 Comparison of Properties of Pure Polybenzoxazine Resins and their Composites

Polybenzoxazine composites were prepared by RTM technique with 20 wt% fiber content, BA-a: Ph-a ratio of 60:40, curing temperature and curing time of 150°C for 3 h + 160°C for 3 h and 150°C for 3 h + 170°C for 3 h. The mechanical properties of pure polybenzoxazine resins and their composites are compared in Table 4.2.

Table 4.2 Mechanical properties of polybenzoxazine resins (ratio of 60:40) and kenaf-reinforced polybenzoxazine composites at different curing conditions.

Property \ Sample	Curing conditions of 150°C for 3 h + 160°C for 3 h.		Curing conditions of 150°C for 3 h + 170°C for 3 h.	
	Pure PBZX resin	PBZX composite	Pure PBZX resin	PBZX composite
Flexural strength (MPa)	75.3 ± 8.9	75.5 ± 5.2	103.1 ± 11.0	78.2 ± 5.2
Flexural modulus (MPa)	5035 ± 20.5	7227 ± 162	5381 ± 80.1	7513 ± 482.3
Impact strength (kJ/m ²)	1.4 ± 0	2.6 ± 0	1.5 ± 0.1	2.7 ± 0.3

For PBZX resin and its composite at curing conditions of 150°C for 3 h + 160°C for 3 h, there was no change in the flexural strength but the flexural modulus and impact strength of the composite were much higher than those of the pure resin when the fibers were added into the resin.

For PBZX resin and its composite at curing conditions of 150°C for 3 h + 170°C for 3 h, it showed that the flexural strength of composite was lower than the pure resin but the flexural modulus and impact strength of the composite were much higher than those of pure resin. It is known that at low fiber content, fibers act as defects in the resin matrix (Devi *et al.*, 1997), so normally a minimum amount of fiber is required to improve the strength of the composite. In this work, the results show that the fiber content of 20 wt% was not high enough to increase the strength of composite. However the modulus and impact strength of the composite generally increased as soon as fiber was added. Therefore there was an improvement in both the modulus and impact strength of the composite compared to pure resin. These results imply that the fiber/matrix adhesion of the systems studied is relatively poor as the fiber surface is hydrophilic and the matrix is hydrophobic. If the strength improvement is desired, it can be achieved by mixing a small amount of an amino or epoxy functional silane coupling agent.

Table 4.3 Mechanical properties of polybenzoxazine resins and kenaf-reinforced polybenzoxazine composites using different BA-a:Ph-a ratio of 40:60 and 60:40 (curing conditions of 150°C for 3 h + 170°C for 3 h).

Property	BA-a :Ph-a ratio of 40:60		BA-a:Ph-a ratio of 60:40	
	Pure PBZXresin	PBZX composite	Pure PBZX resin	PBZX composite
Flexural strength (MPa)	64.7 ± 4.7	74.0 ± 3.6	103.1 ± 11.0	78.2 ± 5.2
Flexural modulus (MPa)	5341 ± 94.3	7134 ± 97.7	5381 ± 80.1	7513 ± 482.3
Impact strength (kJ/m ²)	1.4 ± 0.3	2.4 ± 0.2	1.5 ± 0.1	2.7 ± 0.3

Table 4.3 compares the mechanical properties of PBZX resins and their composites of BA-a:Ph-a ratios of 40:60 and 60:40, the results showed that the mechanical properties of pure PBZX resin and PBZX composite of BA-a:Ph-a ratio of 60:40 were higher than that of BA-a:Ph-a ratio of 40:60.

4.3.2 Comparison of Properties of Composites from Polybenzoxazine and Unsaturated Polyester Resins

The properties of composites from polybenzoxazine at BA-a:Ph-a ratio of 60:40 and unsaturated polyester resins with 20 wt% fiber content are presented in Table 4.4.

Table 4.4 Mechanical properties of composites from polybenzoxazine and unsaturated polyester resins with 20 wt% kenaf fiber.

Property \ Sample	Composite from Polybenzoxazine resin (BA-a:Ph-a ratio of 60:40)	Composite from Unsaturated polyester resin
Flexural strength (MPa)	78.2 ± 5.2	95.8 ± 12.3
Flexural modulus (MPa)	7513 ± 482.3	6728 ± 241
Impact strength (kJ/m^2)	2.7 ± 0.3	5.2 ± 0.5
Tensile strength (MPa)	46.1 ± 7.4	54.0 ± 1.0
Tensile modulus (MPa)	4768 ± 416.0	4756 ± 285.6
% Strain at break (%)	0.3 ± 0	0.8 ± 0

It was observed that the flexural strength, impact strength, tensile strength, and % strain at break of composites made from polybenzoxazine resin were lower than that for unsaturated polyester resin composites, but their tensile moduli were about the same. The flexural modulus of polybenzoxazine composites was however significantly higher than that of unsaturated polyester composites.

Based on the above results, it can be concluded that polybenzoxazine composite is suitable for applications where flexural modulus is the most important property. As the current formulation does not include a toughness modifier, a significant potential exists to improve the flexural and impact strengths because the composite tend to fail prematurely by the brittleness of the resin.