CHAPTER 3

EXPERIMENT

3.1 Materials

3.1.1 2,2′-(3-phenyl-4-dihydro-1,3,2-benzoxazine) propane

The benzoxazine monomer, 2,2′-(3-phenyl-4-dihydro-1,3,2-benzoxazine) propane, was synthesized by the following procedure. A 0.2 mole aniline in 20 ml dioxane is slowly added to an aqueous solution of 0.4 mole formaldehyde in 80 ml dioxane. The temperature of mixture is kept below 10 $^\circ$C during the addition of aniline. The mixture is stirred for 10 min and then 0.1 mole bisphenol-A in 100 ml dioxane is added into the system. The temperature is raised and the mixture is refluxed for 6 hours. A clear yellowish solid resin is obtained after solvent (dioxane) is removed. This resin is used without further purification. The chemical structure of benzoxazine monomer is shown in figure 3.1. The obtaining precursors are a mixture of monomer, dimer and oligomers formed in the reactions during the synthesis. Some of the possible structures of this precursor are shown in figure 3.2. FT-IR spectrum of the benzoxazine monomer is shown in figure 3.3.
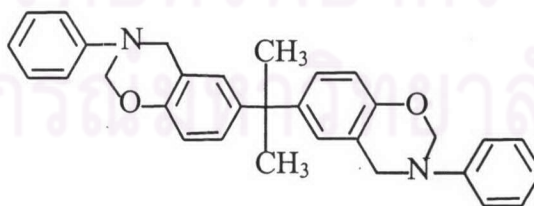

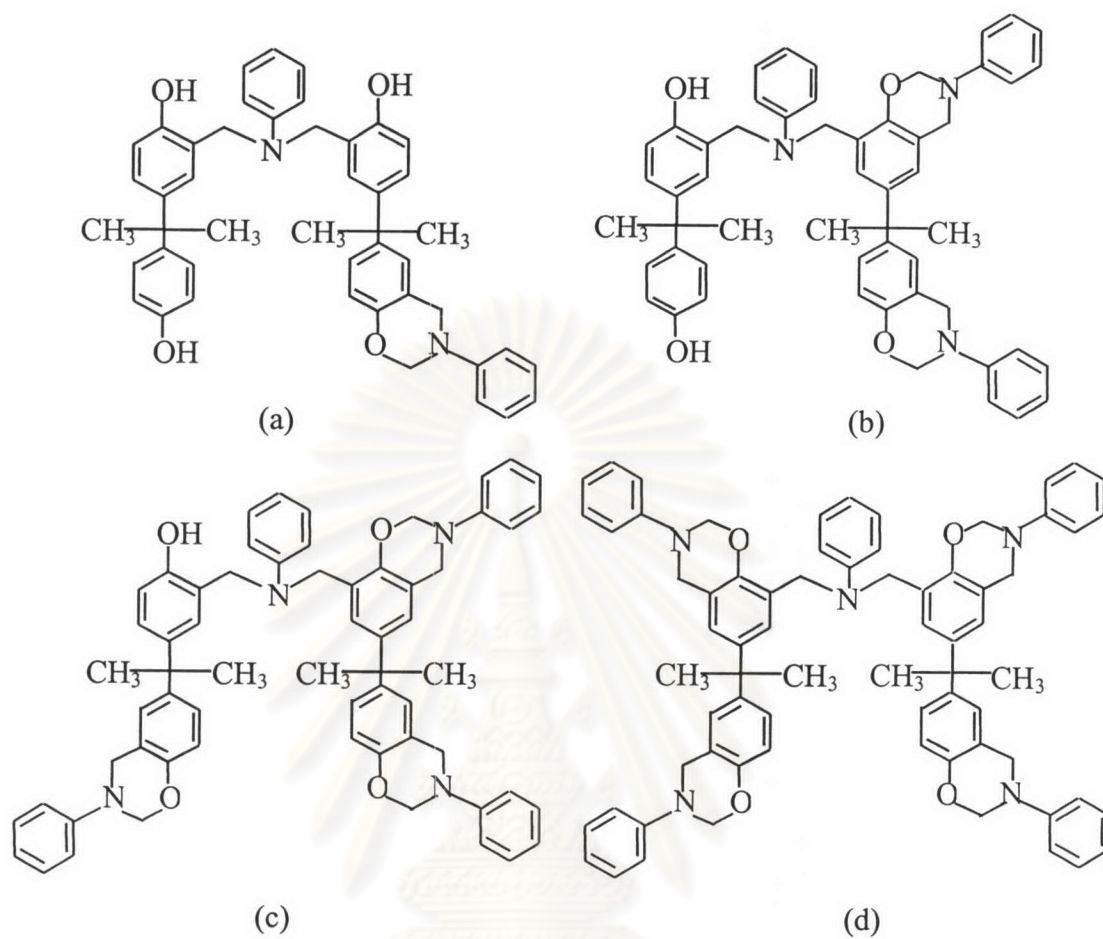**Figure 3.1**   The chemical structure of benzoxazine monomer.

Figure 3.2   Some of the possible structures in benzoxazine precursor: (a) dimer, (b) trimer, (c) tetramer, and (d) pentamer.
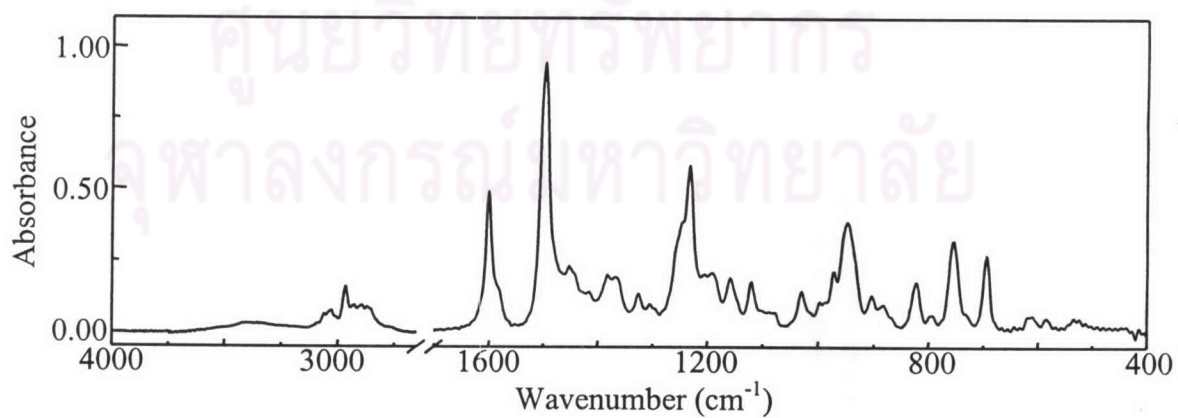

Figure 3.3   FT-IR spectrum of benzoxazine precursor.

Table 3.1   Infrared peaks assignment of benzoxazine precursor.

Peak position (cm^{-1})	Assignment
3029	C-H stretching of benzene ring
2966	C-H asymmetric stretching of methyl group
2928	C-H asymmetric stretching of methylene group
2894	C-H symmetric stretching of methyl group
2869	C-H symmetric stretching of methylene group
1600, 1497, 1453	C=C stretching of benzene ring
1383, 1366	C-H symmetric deformation of geminated methyl group of bisphenol-A
1233	C-O(-Ar) asymmetric stretching of aliphatic aromatic ether
1121	C-H in plane deformation of 1,2,4-tri-substituted mode of oxazine ring
948	C-H out of plane deformation of 1,2,4-tri-substituted mode of oxazine ring
823	C-H out of plane deformation of 1,4-di-substituted mode of bisphenol-A
756, 649	C-H out of plane deformation of mono-substituted mode of benzene ring

3.1.2 Diglycidyl ether of bisphenol-A (DGEBA) epoxy resin

The diglycidyl ether of bisphenol-A (DGEBA) epoxy resin, Epon 825, was obtained from Shell Chemicals. The chemical structure of DGEBA epoxy resin is shown in figure 3.4. The resin is a clear viscous liquid at room temperature. The

resin contains an epoxide content of 173 to 179 mole/kg. FT-IR spectrum of the DGEBA epoxy resin is shown in figure 3.5.
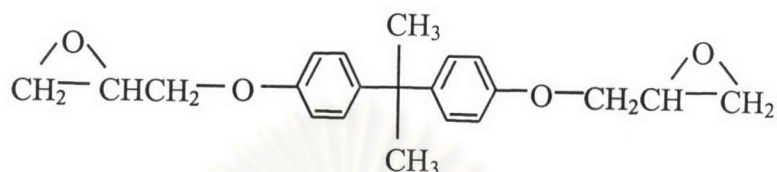
Figure 3.4   The chemical structure of diglycidyl ether of bisphenol-A epoxy resin.
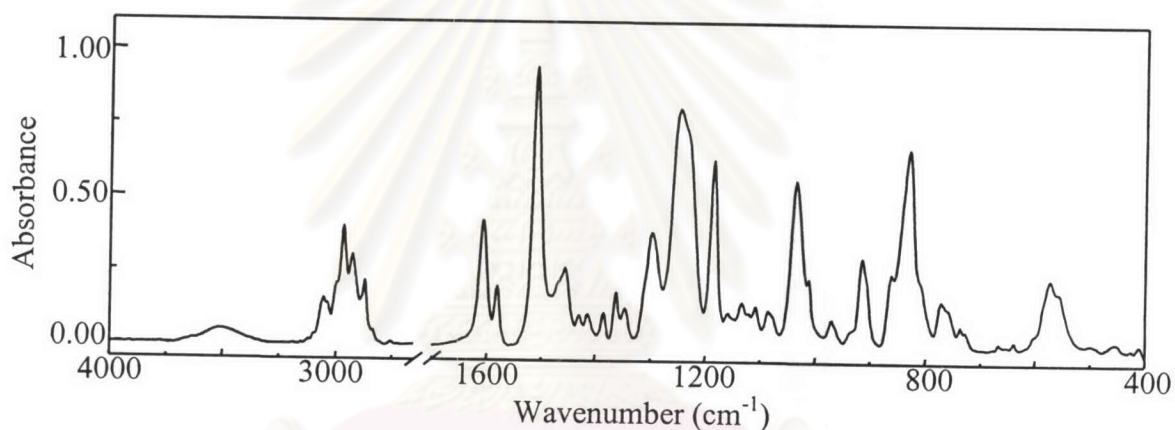
Figure 3.5   FT-IR spectrum of DGEBA epoxy resin.

Table 3.2   Infrared peaks assignment of epoxy resin

Peak position (cm^{-1})	Assignment
3516	O-H stretching of 2° alcohol
3056	C-H asymmetric stretching of methylene of epoxide ring
3037	C-H stretching of benzene ring
2966	C-H asymmetric stretching of methyl group
2928	C-H asymmetric stretching of methylene group

Table 3.2 (continued)

Peak position (cm^{-1})	Assignment
2872	C-H symmetric stretching of methyl group
1608, 1582, 1510, 1456	C=C stretching of benzene ring
1385, 1362	C-H symmetric deformation of geminated methyl group of bisphenol-A
1297	C-O(-Ar) asymmetric stretching of aliphatic aromatic ether
1247	C-O(-C) symmetric stretching of epoxide ring
1184	C-H in plane deformation of 1,4-di-substitued of benzene ring
1036	C-O(-Ar) symmetric stretching of aliphatic aromatic ether
915, 831	C-O(-C) asymmetric stretching of epoxide ring

3.1.3 Phenolic novolac resin

Phenolic novolac, HRJ1166, was obtained from Schenectady International., USA. The resin is a dark red solid at room temperature. The chemical structure of phenolic novolac resin is shown in figure 3.6. FT-IR spectrum of the phenolic novolac resin is shown in figure 3.7.
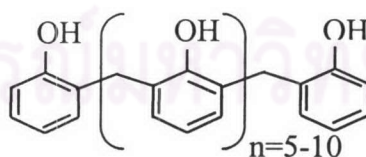
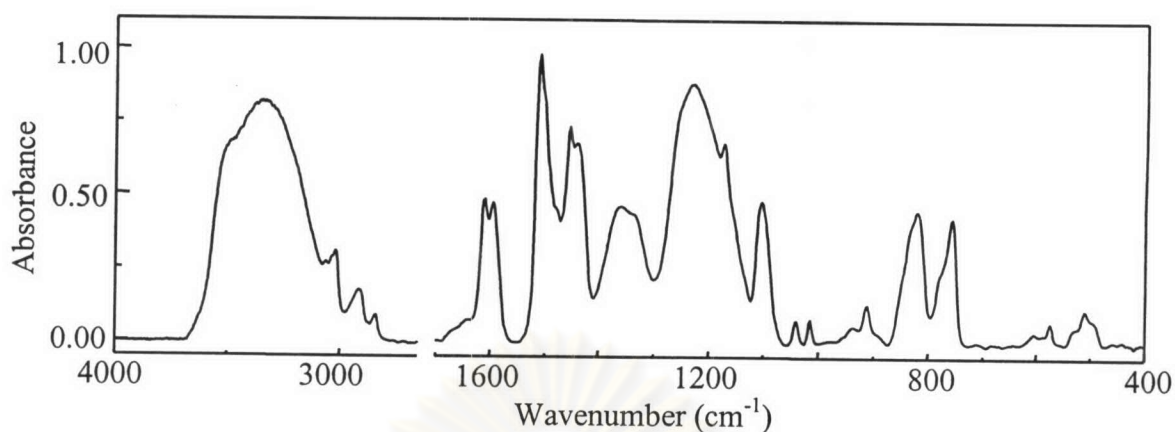**Figure 3.6**   The chemical structure of phenolic novolac resin.

Figure 3.7 FT-IR spectrum of phenolic novolac resin.

Table 3.3 Infrared spectra peaks assignment of phenolic novolac resin

Peak position (cm^{-1})	Assignment
3332	O-H stretching of phenol
3020	C-H stretching of benzene ring
2914	C-H asymmetric stretching of methyl group
2840	C-H symmetric stretching of methylene group
1619, 1596, 1510, 1455	C=C stretching of benzene ring
1360	O-H in plane deformation of phenol
1230	C-O asymmetric stretching of phenol
1172, 1104	C-H in plane deformation of 1,2,3-tri-substituted mode of benzene ring
821	C-H out of plane deformation of 1,2,3-tri-substituted mode of benzene ring

3.2   Sample preparation

All samples were used as received without further purification. The binary and ternary mixtures were prepared by mixing the desired mass fraction of each resin. The mixture was heated to 80 °C in an aluminum pan and was stirred until a homogeneous mixture was obtained. The ternary mixture is a clear solid at room temperature. All mixtures were kept in a closed container at room temperature until used.

In this study, the abbreviation of binary and ternary mixtures is assigned as follows: the letters B, E, and P, respectively stand for benzoxazine, epoxy, and phenolic resins. The numbers that follow the abbreviation are the mass ratio of the corresponding resins. For example; BE11 comprise of benzoxazine and epoxy resins with the mass ratio of 1:1, while BEP352 represents benzoxazine, epoxy, and phenolic mixture with the mass ratio of 3:5:2, respectively.

3.3   Differential scanning calorimetry

A differential scanning calorimeter (DSC model 2910) from TA instruments was used to study the polymerization and the thermal properties of the prepared sample. All samples were crimped in hermetically sealed aluminum pans with lids. All experiments were carried out in the scanning mode from room temperature to 300 °C. The sample weight was about 5 mg. The weight of reference and sample pan with lids were within 26 ± 0.3 mg. Dry nitrogen gas was introduced into the DSC cell as the purging gas. For kinetic measurements, three different heating rates were investigated: 5, 10, and 20 °C/min. The reaction is considered complete when the curved leveled off to the baseline and no signals of heat evolution peaks in the curve are observed. The areas under the curves were measured above the base line, a straight-line extension of both sides of each exotherm using DSC-4 software.

3.4   Fourier transform infrared spectroscopy

FT-IR spectra of samples under various curing conditions were acquired *via* Bruker Vector 33 FT-IR spectrometer equipped with a KBr beamsplitter and a deuterated triglycine sulfate (DTGS) detector. All spectra were taken as a function of time with 36 scans at a resolution of 4 cm^{-1} and spectra range of 4000-400 cm^{-1}. *In situ* monitoring of the structural change is deduced from the observed spectrum. The polymerization reactions of the samples were examined from room temperature to 300 $^{\circ}$C. All experiments were always performed below 300 $^{\circ}$C to prevent any possible degradation of the polymer inside the chamber. Premelted samples, 0.5-1.0 mg, were cast as thin films on potassium bromide (KBr) disks at 80 $^{\circ}$C. All of the samples used in this study were sufficiently thin with optical thickness under the Beer-Lambert's law. The samples were then mounted on a sample holder and located in a hot cell in order to maintain the reaction temperature.

Because the thickness of the sample in the IR beam may be altered during the reaction due to the low viscosity of the monomers at the high temperature, an internal reference band is assigned for quantitative analysis. The band at 2967 cm^{-1}, which is assigned to the C-H stretching of methyl group, was chosen as the internal standard.