

CHAPTER III

RESULTS AND DISCUSSION

3.1 Characterization of Benzoxazine Monomer

3.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the purified B-a is shown in Fig 3.1. The C-H stretching region can be found around 3100-2700 cm^{-1} , the methyl group vibration occurs at 2967 and 2870 cm^{-1} . Due to methylene structure, the peak at 2775 cm^{-1} is occurred. The symmetric methylene wagging and twisting bands are shown by weak bands around 1370-1250 cm^{-1} . The region 920-940 cm^{-1} is unique to the C-H out-of-plane deformation of the 1,2,4-tri-substituted benzene ring.

The band at 1496 cm^{-1} is attributable 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 ortho-substituted (methylene-amine-methylene bridge) phenolic structures formed by the reaction between the oxazine ring and the free ortho position of a phenol structure. The hydroxyl group of the phenolic structure occurs at 3300 cm^{-1} .

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 $1240\text{-}1210\text{ cm}^{-1}$ is due to the C-O-C antisymmetric stretching, while the symmetric stretching mode appears at $1040\text{-}1020\text{ cm}^{-1}$.

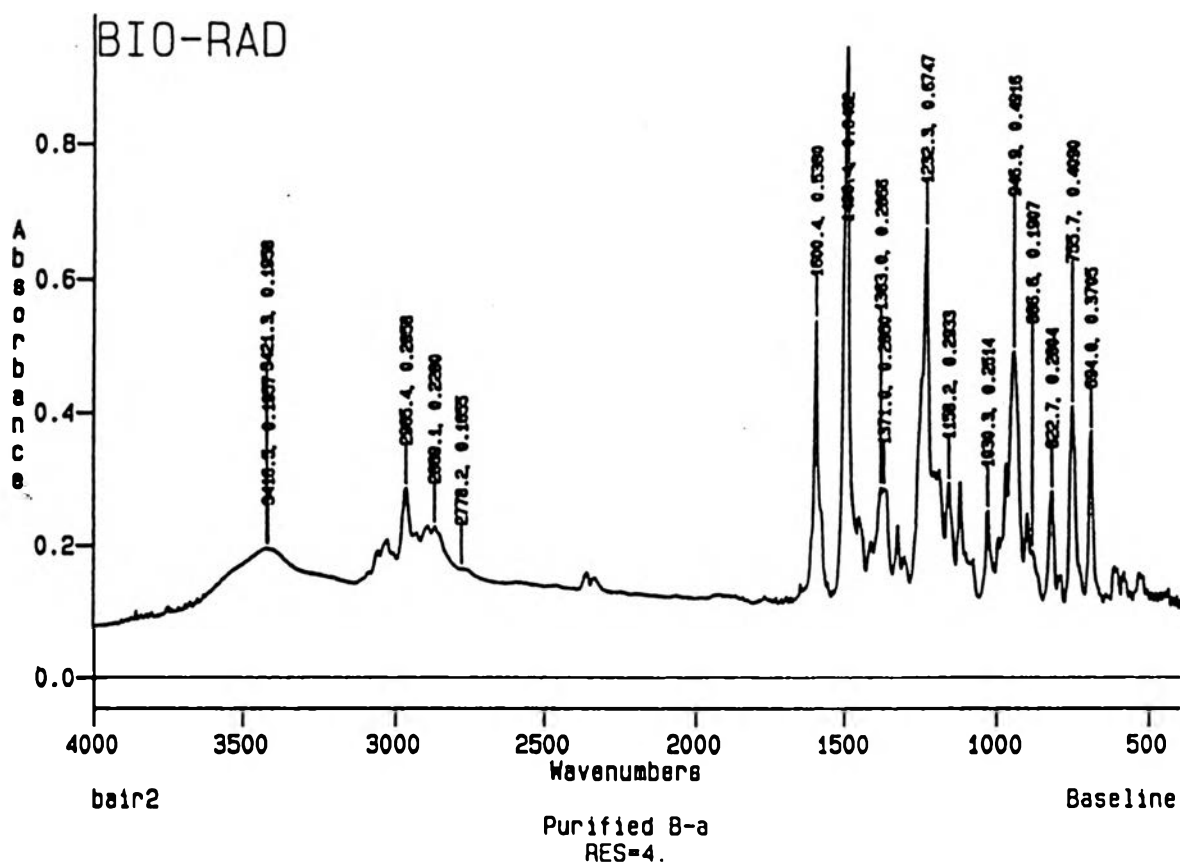


Figure 3.1 FTIR spectrum of purified B-a.

3.1.2 Size Exclusion Chromatography (SEC)

The SEC chromatograph from UV detector of the purified B-a composition is presented in Fig 3.2. The strongest peak at 10 min retention time is assigned to the difunctional B-a benzoxazine monomer. The shoulder of the strongest peak, which occurs at shorter retention time, represents dimers and higher oligomers. The purity computed by comparing the area under the highest peak to the shoulder is 98 %.

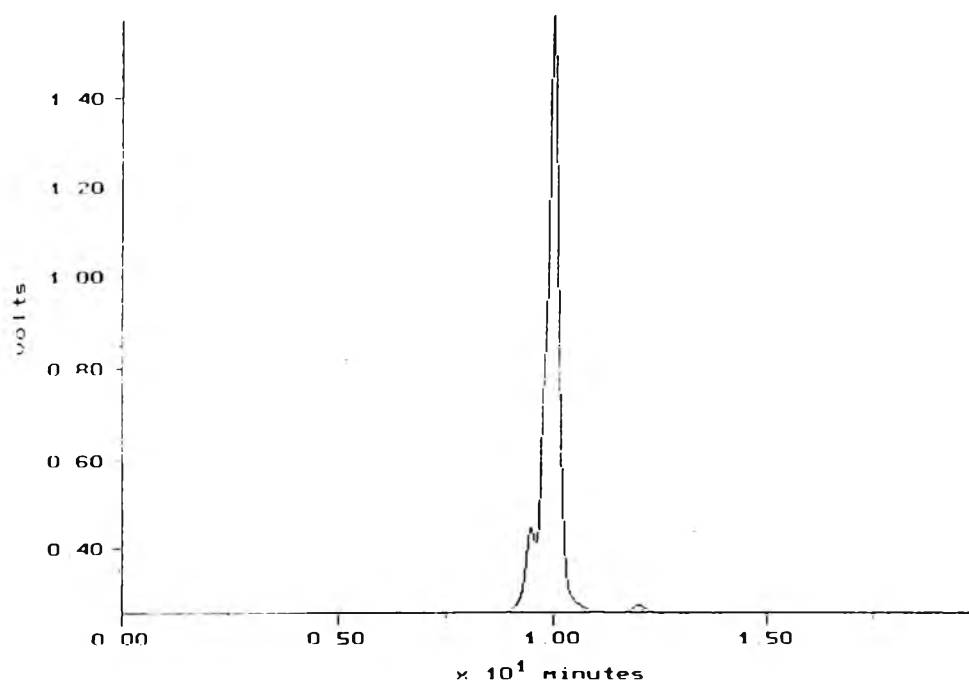


Figure 3.2 The SEC chromatograph of purified B-a.

3.2 Effect of Curing Conditions on Thermal Properties of Polybenzoxazine

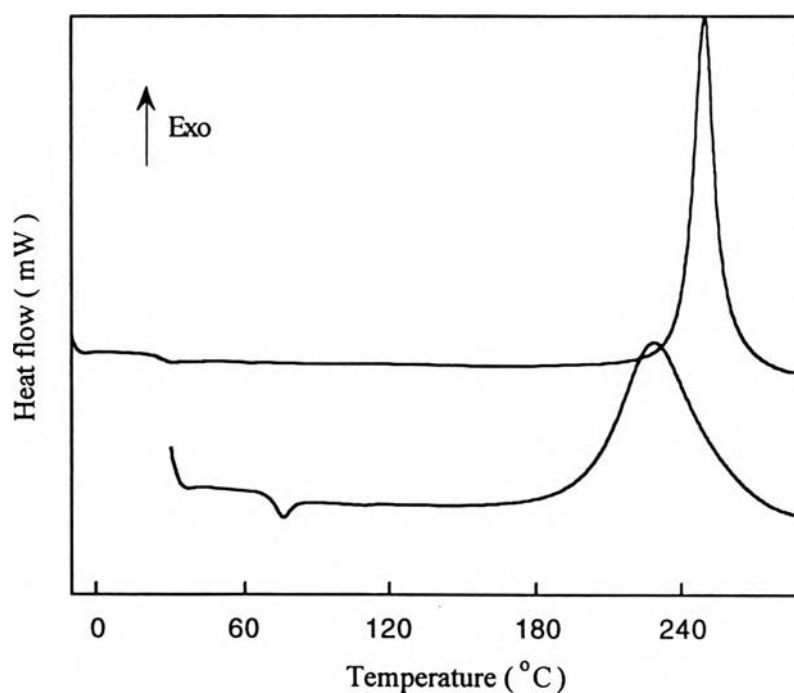


Figure 3.3 DSC thermograms of uncured B-a (top) and B-a isothermally cured at 155 °C for 2 hours (bottom).

Figure 3.3 shows typical DSC thermograms of the uncured and isothermally cured B-a at the curing temperature (T_c) of 155 °C for 2 hours. The T_g appears as an endothermic shift over a temperature interval in the DSC thermogram. In this study, T_g was taken as the midpoint of the step-transition. The residual heat of reaction of the remaining reactants (ΔH_r) appears as an exothermic peak. The heat of polymerization is estimated by drawing a straight line connecting the baseline before and after the peak and integrating the area under the curve. The area of exothermic peak of the uncured sample is the total heat of reaction (ΔH_t). From the value of ΔH_t , ΔH_r , and cure time (t), the fractional conversion or extent of the curing reaction (α) can be calculated as:

$$\alpha = 1 - \left(\frac{\Delta H_r}{\Delta H_t} \right)$$

Figures 3.4 and 3.5 show the DSC thermograms of the materials cured at 155 °C for different times and the materials cured for 3 hours at isothermal T_c at 155, 165, 175, and 185 °C, respectively. From these figures, it was found that T_g increases while ΔH_r decreases with increasing T_c and curing time.

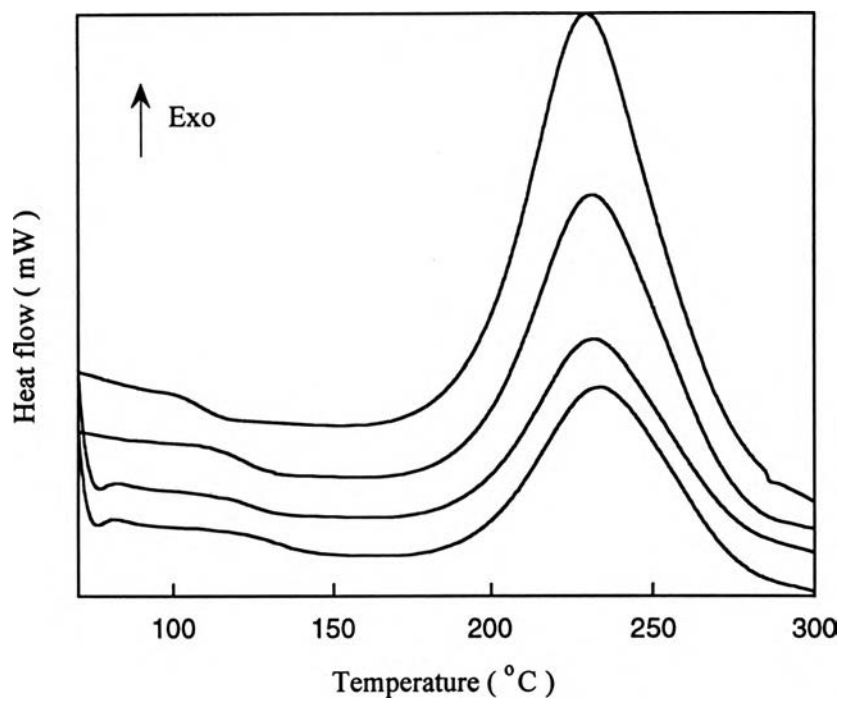


Figure 3.4 DSC thermograms of B-a cured at 155 °C for 3, 4, 5, 6 hours (from top to bottom).

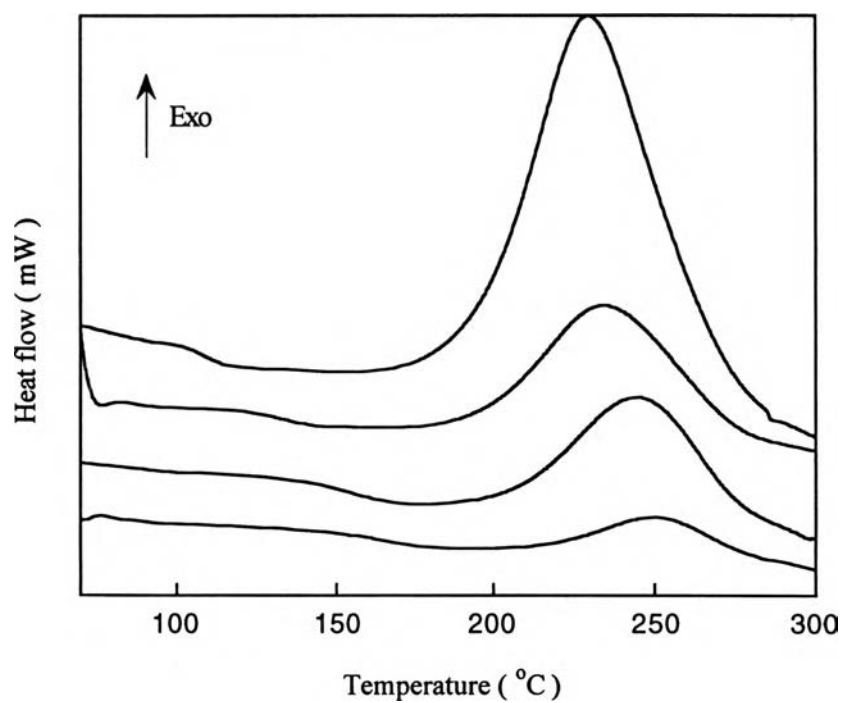


Figure 3.5 DSC thermograms of B-a cured for 3 hours at isothermal curing temperatures of 155, 165, 175, and 185 °C (from top to bottom).

These phenomena are illustrated by the plot of T_g vs. curing time in Figure 3.6 and fractional conversion vs. curing time in Figure 3.7. During curing, the glass transition temperature of the curing system will continuously increase until it approaches the curing temperature. Then the reaction mode will change from chemical reaction control to diffusion control when the viscosity of the reacting system becomes high, and even stop when the T_g equals T_c , and the material vitrifies. Vitrification is found for the materials cured at temperatures lower than the ultimate glass transition temperature ($T_{g\infty}$).

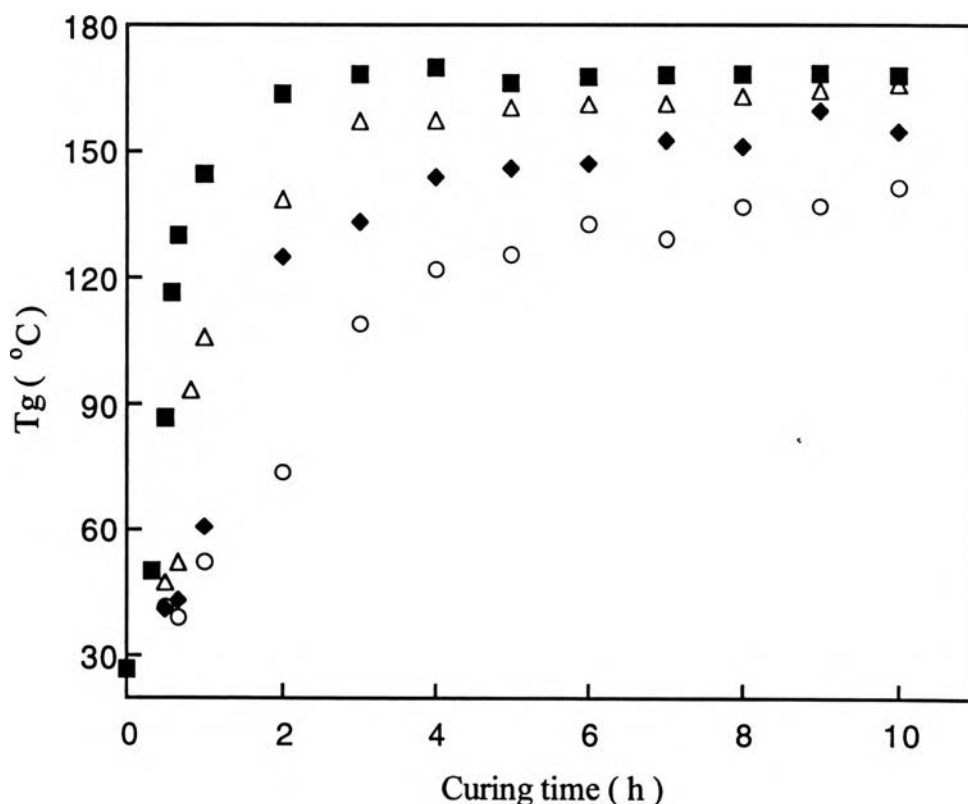


Figure 3.6 Glass transition temperature of B-a cured at $T_c = 155$ (O), 165 (◆), 175 (△), and 185 °C (■).

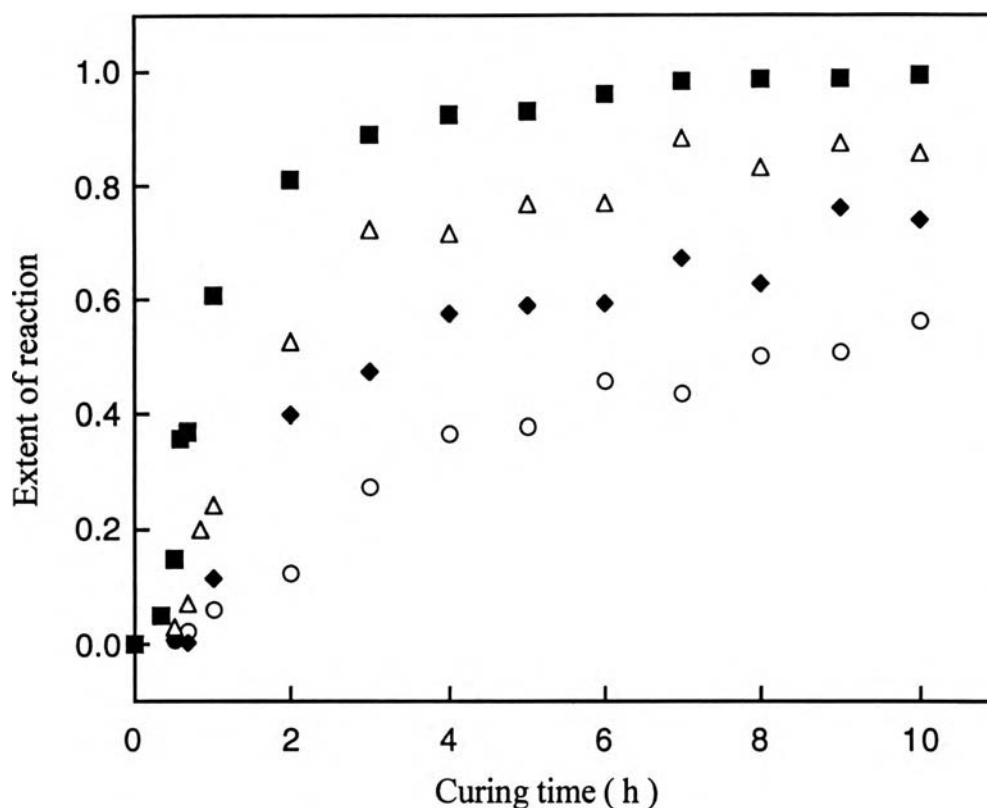


Figure 3.7 Extent of reaction of B-a cured at $T_c = 155$ (O), 165 (◆), 175 (△), and 185 °C (■).

The fractional conversions and T_g 's of isothermally cured B-a at different T_c 's are plotted in Figure 3.8. The $T_{g\infty}$ of B-a is found to be around 170 °C. Unexpectedly, the evolution of the T_g as a function of the fractional conversion shows the opposite trend to epoxy resin studied by Pang and Gillham (1969), and Wisanrakkit and Gillham (1990), and thermosetting polyimide resin investigated by Hale et al. (1991). Gillham and coworkers (1969, 1990) reported that the T_g of an epoxy resin increased very slowly until $0.8 - 0.9$ fractional conversion, after which the T_g increased rapidly. At very high conversion, the reaction leads to an increase in crosslink density which

influences the T_g of the epoxy resin significantly, whereas at low conversion, the reaction leads mostly to the formation of uncrosslinked molecules. This is contrary to what was found with the polybenzoxazine where the main increase in T_g takes place during the early stages of polymerization.

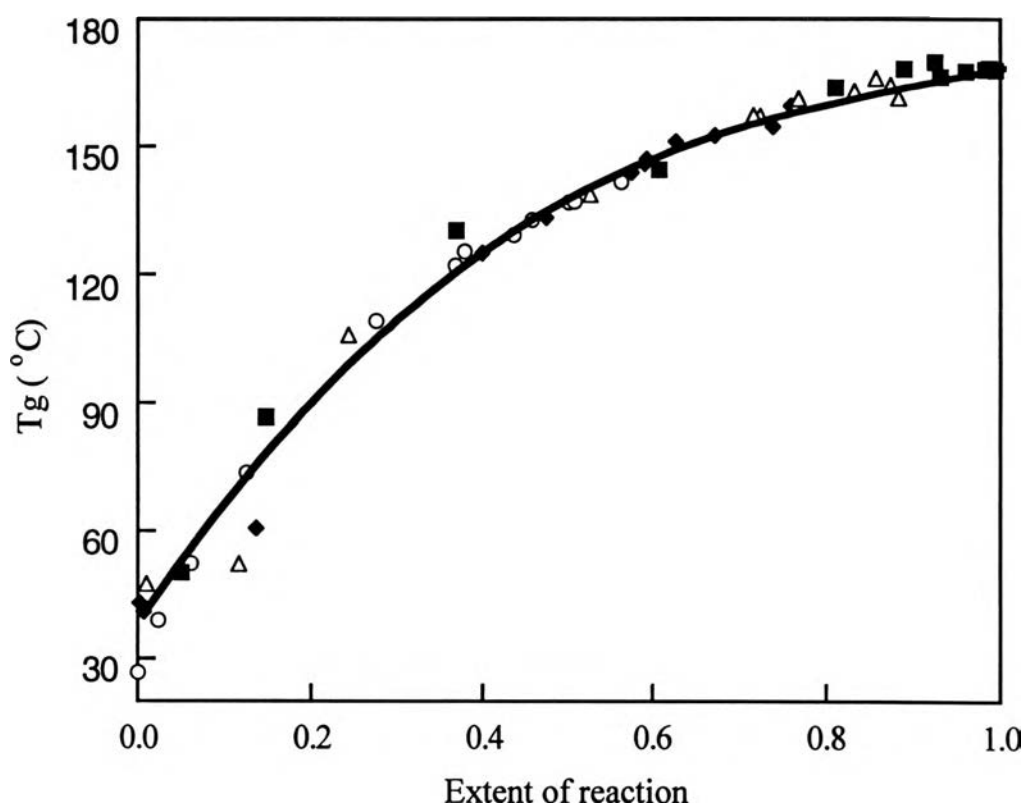


Figure 3.8 Relationship between extent of reaction and glass transition temperature of B-a cured at $T_c = 155$ (O), 165 (◆), 175 (△), and 185 °C (■).

When the normalized glass transition temperature,

$$\frac{T_g^{\text{cured}} - T_g^{\text{uncured}}}{T_{g\infty} - T_g^{\text{uncured}}}$$

is calculated for an arbitrarily set fractional conversion of 0.5, 80% of the glass transition temperature development has already taken place for the polybenzoxazine whereas only 30 % is found for an epoxy resin based on glycidylether of bisphenol-A (Gillham et al. (1990)) and 20% for polyimide resin based on benzophenone tetracarboxylic dianhydride-oxydianiline (Venditti et al. (1994)). This implies that a very high conversion is not necessary for the polybenzoxazine to obtain a T_g that is close to $T_{g\infty}$. This early development of T_g , and thus mechanical and physical properties development, is advantageous from processing point of view. Interestingly, a model epoxy resin that yields one hydroxyl group in every chemical repeat unit upon polymerization exhibits the intermediate situation. For this material, at the fractional conversion of 0.5, 40% of the glass transition temperature development has been observed. This further suggests that hydrogen bonding may indeed be a major parameter for this phenomenon.

The molecular reason for this unusual phenomenon is not known at this time, but it is hypothesized that the very strong inter and intramolecular hydrogen bonding found in polybenzoxazine may be responsible for the rapid T_g increase. As soon as the degree of polymerization exceeds 3, the oligomers possess multifunctional phenolic OH's which can form hydrogen bonding networks. Since no free OH groups are found in the FTIR spectrum of the partially cured benzoxazine resin, all OH's must be participating in hydrogen bonding. A complication arises, however, since intramolecular hydrogen bonding cannot participate in increasing the apparent molecular weight. Hence, the relative ratio of the inter and intramolecular hydrogen bonding becomes an important criterion for the apparent molecular weight development through intermolecular hydrogen bonding. At the present time,

no quantitative data on this ratio is available. However, qualitatively, a very strong intermolecular hydrogen bonded IR band has been observed and thus it is safe to assume that a large number of OH groups are participating as intermolecularly hydrogen bonded groups which were observed by Dunkers et al. (accepted for publication). It is obvious that the apparent molecular weight of the intermolecularly hydrogen bonded molecules develops much faster than the molecular weight based on the covalent bonds alone. It is also important to recognize the stiffening role of the very strongly chelated intramolecular hydrogen bonds, $-O\cdots H^+\cdots N-$. It is for these reasons that the T_g of polybenzoxazine develops quickly at very low fractional conversions of the benzoxazine groups.

3.3 Volumetric Study

By comparing the ρ_{RT} of the amorphous monomer and polymer which are shown in the below table, a volumetric expansion upon curing of 1-2 % was found depending on the curing conditions.

Cure times(h)	Average density at Tc equal to_			
	155°C	165°C	175°C	185°C
0	1.2000	1.2000	1.2000	1.2000
1	1.2002	1.1981	1.1940	1.1857
2	1.1981	1.1873	1.1875	1.1837
3	1.1901	1.1871	1.1828	1.1823
4	1.1886	1.1814	1.1806	1.1827
5	1.1850	1.1824	1.1814	1.1826
6	1.1840	1.1826	1.1771	1.1810

Cure times(h)	Average density at T_c equal to			
	155°C	165°C	175°C	185°C
7	1.1856	1.1823	1.1781	1.1806
8	1.1845	1.1816	1.1789	1.1814
9	1.1855	1.1806	1.1771	1.1822
10	1.1842	1.1834	1.1776	1.1838

In the schematic density diagram shown in Figure 3.9, thermal expansion occurs when the monomer is heated to the curing temperature (T_c), while volumetric shrinkage due to the polymerization reaction takes place during isothermal cure. Thermal shrinkage also occurs in the cooling step which can be divided into shrinkage in the rubbery state ($> T_g$) and glassy state ($< T_g$).

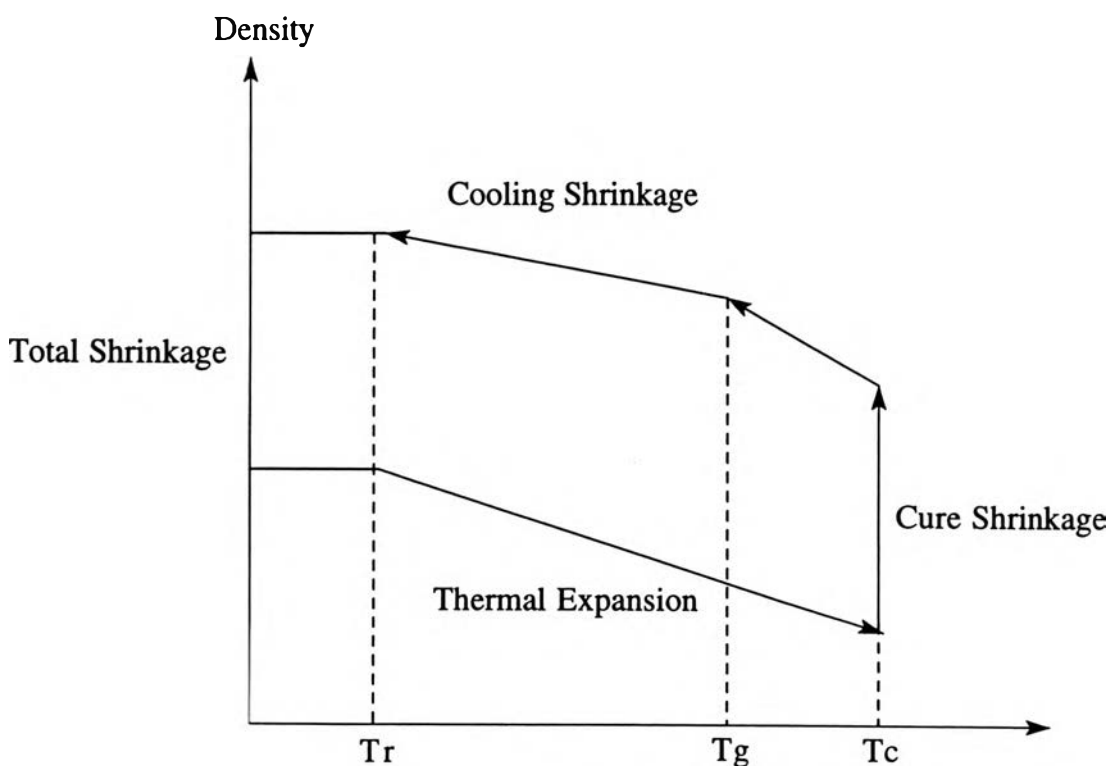


Figure 3.9 Cure diagram of isothermally cured materials.

During the polymerization, monomer molecules move from a Van der Waals distance of separation to a covalent bond distance in the polymer, which significantly influences the volumetric shrinkage. Bailey and coworkers (1973-1990) have studied the volumetric expansion of ring-opening polymerizations. A smaller shrinkage can be found in ring-opening polymerization than in condensation or addition polymerization, and the larger the ring, the smaller the shrinkage. Also, the closer the monomer structure resembles the final polymer, the smaller the shrinkage.

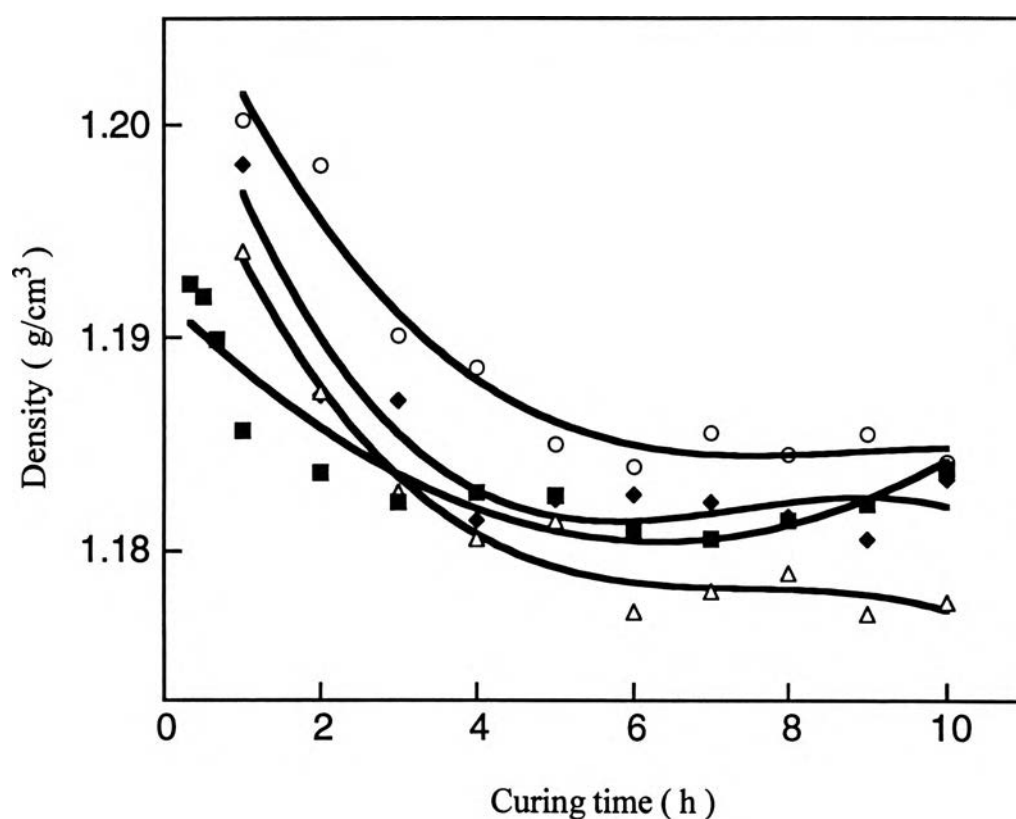


Figure 3.10 Density of B-a cured at $T_c = 155$ (O), 165 (◆), 175 (Δ), and 185 °C (■).

A plot of density vs. curing time is shown in Figure 3.10. Similar trends were observed for samples cured at 155, 165 and 175 °C. The ρ_{RT} decreases as a function of curing time and is nearly constant at the lower

density for long curing times due to the effects of vitrification and diffusion control in decreasing the rate of polymerization. Comparing the ρ_{RT} of the B-a cured for the same time at various T_c 's, it was found that the higher the T_c , the lower the ρ_{RT} due to the increased percent conversion. Gillham and his coworkers (1989) studied extensively the effect of crosslink density on the volume of epoxy resin. They reported that increased crosslink density lead to volumetric expansion. In Wisanrakkit and Gillham's work (1990), the free volume measurement by positron annihilation also supports this statement. It is interesting to note that the ρ_{RT} of the cured B-a at 185 °C shows the opposite trend to the other $T_c < T_{g\infty}$. At this temperature, the ρ_{RT} tends to increase after a prolonged curing time.

Ishida and Allen (in press) reported the density of monomeric and fully cured B-a polybenzoxazine as a function of temperature as well as the volumetric change of B-a benzoxazine under isothermal curing conditions using dilatometer. Based on the room temperature density, zero shrinkage was observed. At the isothermal curing temperature of 140 °C, the material underwent approximately 3% shrinkage upon polymerization until it reached the vitrification point. The greatest cure shrinkage was found at this temperature. Above 140 °C, the cure shrinkage is lower. And above 195 °C, the material cures either with no shrinkage or possibly even some expansion.

The reason why the volumetric expansion of B-a is observed at room temperature despite the isothermal cure shrinkage at 140 °C is the thermal expansion coefficient of the monomer is higher than the polymer. This mitigates the cure shrinkage and shrinkage during cooling. Therefore, a good understanding of the influence of T_c and curing time on each process

shown in Figure 3.9 which contributes to the total shrinkage in the cure mechanism is very important for controlling the volume change of this material.

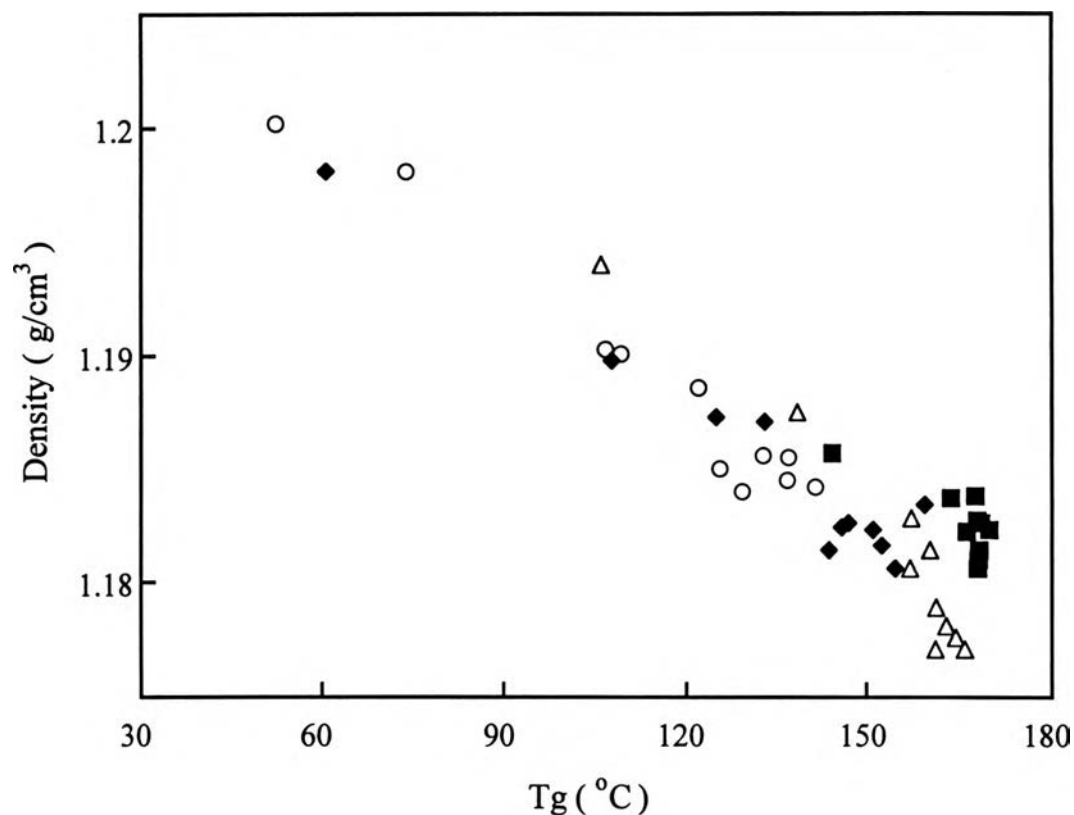


Figure 3.11 Relationship between density of B-a cured at $T_c = 155$ (O), 165 (◆), 175 (△), and 185 °C (■) and glass transition temperature.

A plot of density vs. T_g is shown in Figure 3.11. Most of the data fit on a mild curve except for the material cured at 185 °C. It is possible that the curing reaction at $T_c < T_{g\infty}$ is slightly different from $T_c > T_{g\infty}$. The polymerization preferentially takes place at the ortho position of the phenolic structure. The para position is unavailable since it is occupied by the bond

with the quaternary carbon of bisphenol-A. Although quite unreactive, the meta position is nonetheless available and can react when the condition is favorable. Increasing temperature might provide sufficient condition for the meta position to react. If this reaction takes place, the local structure of the benzoxazine networks would be quite different from that of the ortho-dominated structure. Further study is needed to verify this hypothesis.