A Study on the Volumetric Expansion of Benzoxazine−Based Phenolic Resin

ARTICLE *in* MACROMOLECULES · FEBRUARY 1997

Impact Factor: 5.8 · DOI: 10.1021/ma960539a

2 AUTHORS:

Hatsuo Ishida
Case Western Reserve University
448 PUBLICATIONS **12,896** CITATIONS
SEE PROFILE

Hong Yee Low
Singapore University of Technology and Design
86 PUBLICATIONS **2,071** CITATIONS
SEE PROFILE

A Study on the Volumetric Expansion of Benzoxazine-Based Phenolic Resin

Hatsuo Ishida* and Hong Yee Low

The NSF Center for Molecular and Microstructure of Composites (CMMC), Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106

Received April 8, 1996; Revised Manuscript Received November 26, 1996[⊗]

ABSTRACT: Benzoxazine-based phenolic resin has recently attracted a great deal of attention due to its versatile properties. This paper explores yet another interesting property shown by this class of phenolic resin: volumetric expansion upon polymerization. It is proposed that the volumetric expansion of the benzoxazine resin is mostly due to the consequence of molecular packing influenced by inter- and intramolecular hydrogen bonding. The role of hydrogen bonding on the volumetric expansion has been studied by systematically changing the primary amine used in the benzoxazine monomer synthesis. In comparison to the other known expanding monomer, spiroortho compounds, this resin has been shown to have a high potential for structural/engineering applications. The homopolymers of this resin have a high glass transition temperature (T_g).

Introduction

Shrinkage of a resin occurs during the polymerization of monomers which are transformed into high molecular weight polymers. In a fiber-reinforced composite, this shrinkage imposes some internal pressure onto the fiber so that physical bonding is enhanced.[1,2] The shrinkage could also lead to tension in the matrix depending on the fiber content. However, shrinkage in almost all thermosetting resins is so high that it causes residual stress, warping, premature debonding of the fiber from the matrix, fiber buckling, and delamination in fiber-reinforced composites. Presently, most existing thermosets cure with volumetric shrinkages of 3−15%. An example is the widely used epoxy resin, which undergoes volumetric shrinkage of 2−7% upon curing. Shrinkage of an adhesive can induce residual stresses that are relieved by debonding from the substrate. Residual stresses also result in optical distortion. This will be a concern in using adhesives to join parts such as in an optical telescope. Methyl methacrylate end-capped diglycidyl ether of Bisphenol-A has been widely used as the matrix for dental fillings; however, the shrinkage of this resin upon curing has been a major problem in the dental industry. Due to volumetric shrinkage, problems arise in the molding industry because of nonuniformity in the dimensions of the molded parts. Some thermosetting resins are difficult to mold without using fillers. For example, the molding of a phenolic resin requires fillers such as cellulose flour, wood flour, and, more commonly, mineral fillers to reduce shrinkage.[7] However, these fillers can be abrasive to the mold surface, and the different acidic or basic nature of these fillers can affect the curing rate.

The disadvantages of resin shrinkage and its effect on the final properties and performance of polymers and composites are well documented in the literature. Extensive research has been carried out to reduce the problems of resin shrinkage. Various fillers are incorporated into the matrix and molding conditions are modified to reduce resin shrinkage. Unfortunately, no one has been able to eliminate this problem, but only to reduce it.

In the early 1970s, Bailey et al.[3−6] introduced a series of spiroortho compounds that expand upon curing. Unfortunately, these materials by themselves found few useful applications. Other disadvantages include complicated synthesis procedures and low glass transition temperatures (T_g) of the polymers. Many research groups have tried to incorporate the spiroortho compound as an additive into epoxy resins in an attempt to reduce shrinkage and improve the mechanical properties. A copolymer of bisnorbornenyl spiroorthocarbonate and an epoxy was used by Lim and co-workers[8] as a matrix for a carbon fiber-reinforced composite. They found that the resulting composite had higher impact strength and higher shear strength than that of epoxy−carbon fiber composites. He and co-workers[9,10] also tried to incorporate bisnorbornenyl spiroorthocarbonate into an epoxy resin and found that with a 25% bisnorbornenyl spiroorthocarbonate content, the mixture expanded. They also found that the copolymer with zero shrinkage gave no optical distortion when compared to the copolymers that expand or shrink. However, in the same study, they found that the T_gs and thermal resistance of the copolymers decreased with increasing amounts of bisnorbornenyl spiroorthocarbonate. They concluded that the bisnorbornenyl spiroorthocarbonate by itself has poor mechanical properties, and thus incorporating this compound into epoxy resin causes a decrease in the tensile strengths, elongations at break, and Young's moduli of the copolymers. Shimbo et al.[11,12] also reported that T_gs of the copolymers of spiroorthoester and epoxy decreased with increasing amounts of spiroorthoester, in agreement with He's finding. Shimbo concluded that the reduction in internal stress with an increasing amount of spiroorthoester was not due to the expansion of this material, but rather the reduction in the T_gs of the copolymers. This can be rationalized by Ishida and Nigro's[13] work, where it was found that the gelation of the copolymer occurs after consumption of the majority of the spiroortho compound. Hence, any volumetric expansion from the spiroortho compound prior to gelation cannot be appreciated and thus shrinkage stresses may still be present. Furthermore, the spiroortho compounds were polymerized from a crystalline monomer to an amorphous polymer, with some expansion occurring due to the phase transformation. As a result of the shortcomings of the spiroortho compounds, they have not been used as engineering polymers.

[⊗] Abstract published in *Advance ACS Abstracts,* February 1, 1997.

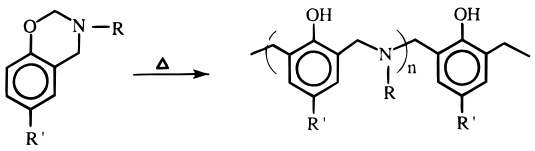
S0024-9297(96)00539-6 CCC: $14.00

Recently a benzoxazine-based phenolic resin was reported by Ishida and Allen[16] to have near-zero volumetric shrinkage upon curing. However, the cause for the expansion or near-zero shrinkage is not well understood. In addition to the near-zero volumetric shrinkage, these resins have been shown to overcome most of the shortcomings of conventional phenolic resins and to have excellent processibility.[15] Thus, this paper will examine the effects of different amines on the volumetric changes upon polymerization of this series of benzoxazine resins.

Experimental Section

Benzoxazine monomers were synthesized according to the procedure of Ning and Ishida.[14] Various benzoxazine monomers were prepared from Bisphenol-A and various primary amines: methylamine, ethylamine, propylamine, isopropylamine, butylamine, *tert*-butylamine, cyclohexylamine, and aniline. The compounds will be referred to as B-m, B-e, B-p, B-ip, B-b, B-t, B-c, and B-a, respectively. The benzoxazine monomer contains an oxazine ring that opens into a phenolic structure upon polymerization:

Scheme 1



R in the structure denotes the radical of amine and R′ the substituent of the phenolic group. In this paper, the difunctional benzoxazines were synthesized using a bifunctional phenol; therefore the monomer contains two oxazine rings that are available for polymerization. Crude reaction products containing the benzoxazine monomer were purified by washing with 3 N NaOH solution at least three times, followed by distilled water, and then drying over sodium sulfate. For B-a, B-c, and B-t, the purified compounds were recrystallized in diethyl ether. The purity of the compounds was determined from ^{1}H-NMR spectra. Pure monomers were used for density measurements.

Purified monomeric materials were used for a stepwise thermal curing from 150 to 195 °C for a total of 4 h. All samples were cured without adding catalyst. Care was taken to ensure that all cured samples were free of bubbles. Density was used to evaluate the shrinkage or expansion of the monomers and polymers. Density measurements were performed according to ASTM D792 (Method A) for all cured polymers. The temperature of the water bath was kept constant at 24 ± 1 °C for all density measurements by water displacement. A 10 mL pycnometer was used to measure the density of the monomers. All monomers were in the amorphous state. The densities of the amorphous monomers and polymers are shown in Table 3.

Molecular modeling was performed on a Silicon Graphics workstation using Sybyl 6.0 software. Charges of the structures were calculated by Pullman's method,[17] where the σ and π orbital contributions are included. Energies of the molecules, bond lengths, and bond angles were evaluated after the molecules were energy minimized. The monofunctional benzoxazine dimer constructed from the X-ray crystal structure by Dunkers and Ishida[18] was used to evaluate the hydrogen bonding. FTIR spectra were taken on a Michelson Bomem FTIR spectrometer.

The T_g of the cured polybenzoxazine was measured using Rheometrics RMS-800 a dynamic mechanical spectrometer with a 2000 g cm force rebalance transducer. This experiment was carried out as temperature sweep from 20 to 200 °C at a heating rate of 2 °C/min, a frequency of 1 Hz, and a strain of 0.05%. Isothermal curing was performed using a parallel plate fixture with a gap of 0.8 mm. The tests were run at a frequency of 1 Hz and a strain of 5%.

Results and Discussion

Volumetric shrinkage of a typical resin occurs during the curing process because molecules move from a van der Waals distance of separation to a covalent distance of separation. Small molecules are sometimes released as byproducts during the polymerization process; for instance, in a condensation polymerization of resole−formaldehyde resin, water molecules are released, thus further reducing the volume in the resulting polymer. When the polymerization reaction is completed, the material is cooled from the curing temperature, which is normally at an elevated temperature, to room temperature, with further thermal shrinkage occurring (Figure 1a). It has been reported that only the shrinkage that occurs when cooling from T_g to room temperature has any significant effect on the material properties.[11,12] An explanation for this is that any volumetric changes, and thus any built-up stresses, can be relaxed above T_g since molecules are readily mobile at these temperatures. However, any stresses caused by cooling from T_g to room temperature cannot be relaxed as molecules are nearly immobile in the glassy state. Since the volumetric relaxation is retarded, the shrinkage will be transformed into residual stress. There are two ways that the volumetric shrinkage can be reduced or reversed: (i) if there is a volumetric expansion during polymerization in such a way as to overcome the shrinkage caused by the difference in the thermal expansion coefficients of the monomer and polymer, as shown in Figure 1b, or (ii) if the thermal expansion coefficient of the polymer is lower than that of the monomer so that the volumetric expansion caused by the thermal expansion coefficient difference overcomes the shrinkage during the isothermal polymerization, as shown in Figure 1c.

According to the polymerization mechanism proposed by Dunkers and Ishida,[18] the oxazine ring opens by breaking a C−O bond of the oxazine ring. During this process a covalent bond is broken and the benzoxazine molecule transforms from a closed-ring structure to a linear open-chain structure as shown in Scheme 1. The open-chain intermediate then reacts with another monomer molecule and breaks a C−H bond that is ortho to the phenolic OH on the aromatic ring of the second molecule. Both O−H and C−ring bonds are formed as a result of polymerization. Thus, a total of two covalent bonds are rearranged (C−O of oxazine and C−ring of Mannich base, $-CH_2-N-CH_2-$); one covalent bond is formed (O−H), and a van der Waals distance is lost when two monomers merge. Data from molecular modeling show that the lengths of the C−O bond of the oxazine ring and the aromatic C−H bond are almost constant for all compounds, regardless of the amine groups. The calculated values are presented in Table 1. The O−H bonds that formed during ring-opening polymerization are shorter than the C−H bond that breaks and their bond lengths are independent of the amine groups as shown in Table 2 from the molecular modeling data. The C−ring bond of the Mannich base, on the other hand, is longer than the C−O bond that breaks upon polymerization, and this is true for all the benzoxazines. The slight increase in the bond length of the linear open-chain structure compared to the closed ring of the monomer may be because the strain is released in the open-chain structure. This rationale was used by Bailey et al.[1−4] for the expansion of the spiroortho compounds. However, in the case of benzoxazine resins, the size of the oxazine ring does not change

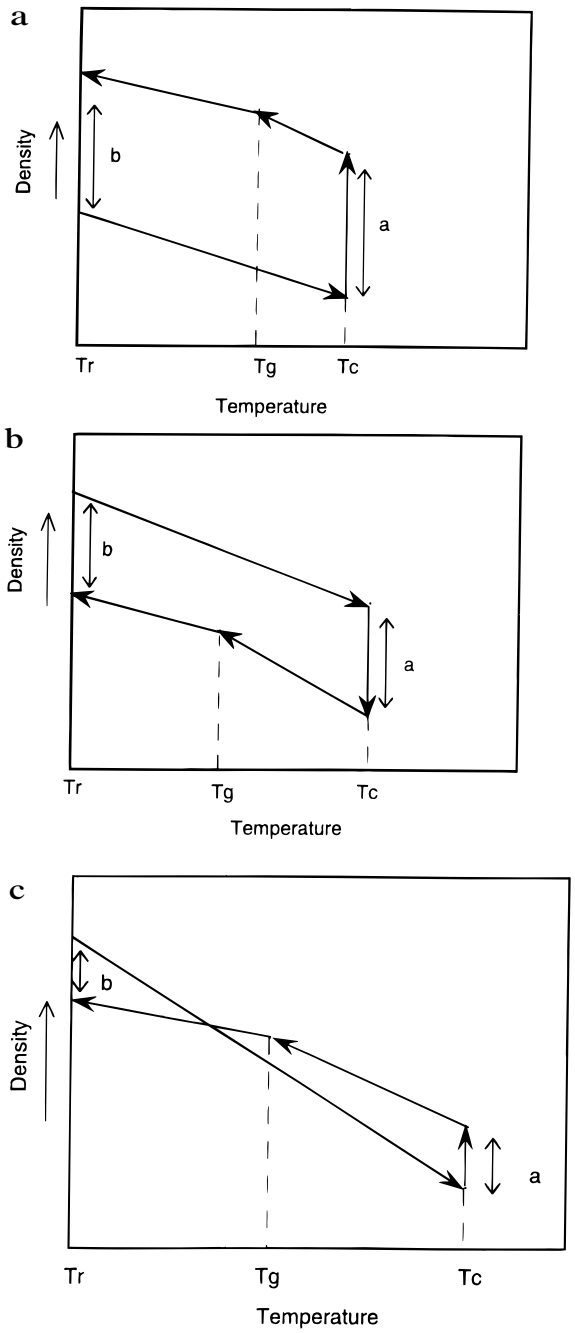


Figure 1. (a) Density changes of a typical shrinking material upon curing: "a" = volumetric shrinkage during curing; "b" = total volumetric shrinkage. T_r = room temperature, T_g = glass transition temperature, and T_c = curing temperature. (b) Density changes of an expanding material upon curing: "a" = volumetric expansion during curing; "b" = total volumetric expansion. (c) Density changes of an expanding monomer with the thermal expansion coefficient of the monomer higher that the polymer "a" = volumetric shrinkage during curing; "b" = net volumetric expansion.

much regardless of the starting compounds. In addition, the benzoxazine ring is a six-membered ring, meaning that the strain energy is almost negligible. Furthermore, the fact that the volumetric expansion is different among the different amine-based benzoxazines indicates that the expansion may not be solely due to the strain that is released in the open-chain structure. It should be mentioned that the comparison is made in this paper between amorphous monomer and amorphous polymer. Thus, the volumetric expansion due to the crystalline-to-amorphous transition is not involved. If this transition is included in the comparison, as is typically done in the spiroortho compound studies, the apparent volumetric expansion of benzoxazine resins would be higher.

Table 1. Calculated Bond Lengths of the Oxazine Ring of the Monomer[a]

amine	C−O	C−H	N−R
methyl	1.396	1.085	1.481
ethyl	1.392	1.084	1.487
n-propyl	1.392	1.084	1.488
isopropyl	1.397	1.085	1.492
butyl	1.392	1.084	1.488
tert-butyl	1.396	1.084	1.497
aniline	1.394	1.083	1.415
cyclohexyl	1.396	1.085	1.492

[a] The C−O and C−H are the bonds that break upon polymerization. R represents the amine. All bond lengths are in angstroms.

Table 2. Calculated Bond Lengths of the Open-Ring Structure of a Dimer[a]

amines	O−H	C−ring	C−H	N−CH_2	N−R
methyl	0.951	1.535	1.101	1.488	1.483
ethyl	0.952	1.536	1.101	1.491	1.487
n-propyl	0.952	1.535	1.101	1.491	1.488
isopropyl	0.951	1.534	1.085	1.494, 1.488	1.494
butyl	0.952	1.536	1.102	1.490	1.488
tert-butyl	0.951	1.536	1.086	1.493	1.499
aniline	0.950	1.538	1.102	1.484	1.416
cyclohexyl	0.948	1.539, 1.544	1.101	1.493, 1.487	1.495

[a] The O−H, C−ring, and the C−H are formed upon polymerization. N−CH_2 and N−R are from the Mannich bridge. R represents the amine. All bond lengths are in angstroms.

Table 3. Room Temperature Densities of the Amorphous Benzoxazine Monomers and Amorphous Polybenzoxazines

amine	density of monomer (g/cm^3)	density of polymer (g/cm^3)	% shrinkage (−) or % expansion (+)
methyl	1.159	1.122	+3.20
ethyl	$1.109 \pm 1 \times 10^{-3}$	$1.104 \pm 2 \times 10^{-3}$	+0.41
n-propyl	$1.076 \pm 1 \times 10^{-3}$	$1.084 \pm 2 \times 10^{-3}$	−0.76
isopropyl	$1.063 \pm 7 \times 10^{-4}$	$1.071 \pm 6 \times 10^{-4}$	−0.72
butyl	$1.067 \pm 1 \times 10^{-3}$	$1.076 \pm 2 \times 10^{-3}$	−0.82
tert-butyl	1.078	1.061	+1.58
aniline	1.200	1.195	−0.40
cyclohexyl	$1.123 \pm 3 \times 10^{-3}$	$1.118 \pm 6 \times 10^{-4}$	+0.43

In order to understand the effects of the amine groups on the volumetric shrinkage or expansion, the benzoxazine compounds are divided into three groups based on the amine structure: (i) the cyclic amines, B-a and B-c; (ii) the aliphatic amines B-m, B-e, B-p, and B-b; and (iii) the steric amines, B-e, B-ip, and B-t.

Cyclic Amines. As shown in Table 3, the density measurements of the amorphous monomers and amorphous polymers indicate that B-a expands about 0.40% and B-c a nearly identical 0.43%. From the results of molecular modeling listed in Tables 1 and 2, the bonds that break and form upon polymerization are slightly shorter for B-a when compared to those of B-c. Therefore, the contribution from the bond length can be eliminated. Dunkers and Ishida[18] found that the polybenzoxazines form both inter- and intramolecular hydrogen bonding. Figure 2 shows the two possible intramolecular hydrogen bonds in the dimer structure of benzoxazine. In Figure 2a, the hydroxyl proton hydrogen bonds with the nitrogen of the Mannich bridge and forms a six-membered ring. On the other hand, Figure 2b shows that the hydroxyl proton hydrogen bonds with an adjacent hydroxyl group of the dimer. It

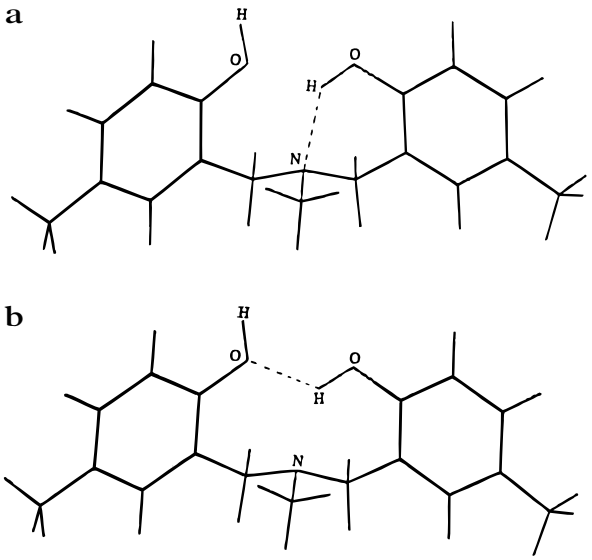


Figure 2. Conformation of the dimer after energy minimization.

can be seen that the latter causes a larger unoccupied volume in the structure. Although the population and stability of the individual hydrogen bonding have not been resolved, both types of hydrogen bonding would cause the molecule to curl, and appear to hinder tight packing.

The strength of this hydrogen bonding is directly dependent on the electronegativity of the amine group that is attached to the nitrogen. For aniline-based benzoxazine, the benzene ring that is attached to the nitrogen atom has delocalized electrons, causing the electron cloud around the nitrogen atom to be lower compared to the cyclohexyl group, where the electrons are localized. Thus, the nitrogen atom of the B-a compound should have weaker hydrogen bonding to the O−H groups compared to B-c. However, in the hydrogen-bonded structure, the nitrogen will have a partial positive charge, and in the case of aniline-based polybenzoxazine, the delocalized electrons in the benzene ring can stabilize the nitrogen and thus the hydrogen bond is more stable in the B-a polybenzoxazine.

The strength of hydrogen bonding of B-a and B-c can be qualitatively evaluated from the FTIR spectra shown in Figure 3c. Hydrogen-bonded hydroxyl groups, from both inter- and intramolecular interactions, appear between 3600 and 2500 cm^{-1}. Ordinary intermolecularly hydrogen-bonded OH groups should appear around 3400 cm^{-1} while the strong intramolecularly hydrogen-bonded OH gives rise to a very broad band and often multiple bands below 3000 cm^{-1}. Obviously, the intermolecular interactions will have a significant effect on the density since the density of a material is a direct consequence of the packing of molecules. Even though the relative intermolecular interactions could not be determined precisely, the OH band around 3400−3300 cm^{-1} of B-a appear to be broader and stronger than that of B-c polybenzoxazine. In spite of the possibly stronger and more stable hydrogen bonding in the B-a polybenzoxazine, the volumetric expansion of the B-a and B-c benzoxazines is comparable. This is probably due to a combined steric effect that compensates for the expected difference in expansion.

Aliphatic Groups. In Table 3, B-m benzoxazine shows the highest volumetric expansion of 3.2%, followed by B-e benzoxazine, which has a volumetric expansion of 0.41%. On the other hand, B-p and B-b

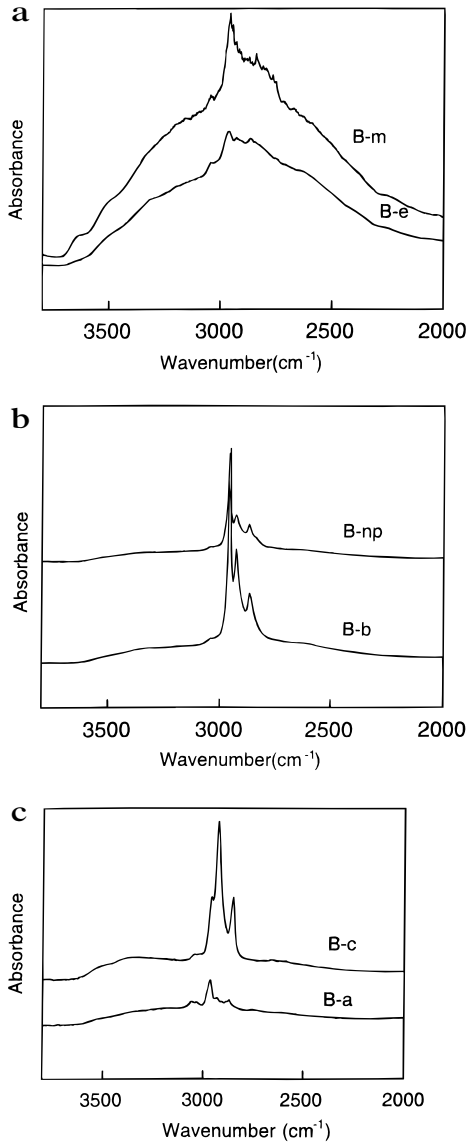


Figure 3. (a) FTIR spectra of B-m and B-e polybenzoxazines. The broad band between 3600 and 2500 cm^{-1} indicates the presence of a hydrogen-bonded OH group. (b) FTIR spectra of the B-p and B-b polybenzoxazines. (c) FTIR spectra of the B-a and B-c polybenzoxazines.

benzoxazines show volumetric shrinkages of 0.72 and 0.82%, respectively, which are still considerably lower than most thermosets. The relationship of volumetric shrinkage versus the number of carbon atoms in the aliphatic group is plotted in Figure 4. Volumetric expansion is found to decrease with increasing length of aliphatic chains in the amine moieties.

The strength of hydrogen bonding and thus the hydrogen bond length is dependent on the electron density of the nitrogen. The higher the electron density on the nitrogen atom, the stronger the hydrogen bond. It appears that there is a drastic decrease in volumetric expansion from methylamine to ethylamine, with the effect of chain length becoming insignificant for chains longer than the propyl group. Since all of these materials are amorphous in their monomeric and polymeric states, the study of intermolecular interactions by molecular modeling is beyond the scope of this paper. Therefore, this study limits itself to the intramolecular interactions from the molecular modeling. The FTIR spectra of the aliphatic amine-based polybenzoxazines are shown in Figure 3a,b. As can be seen, the regions

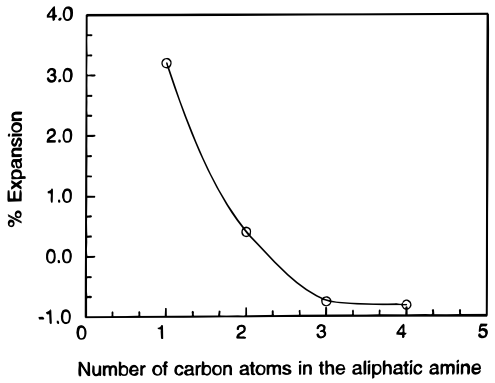


Figure 4. Volumetric expansion as a function of the increasing length of the aliphatic amine. 1 represents the methyl amine-based benzoxazine, 2 represents the ethylamine based-benzoxazine, and so forth.

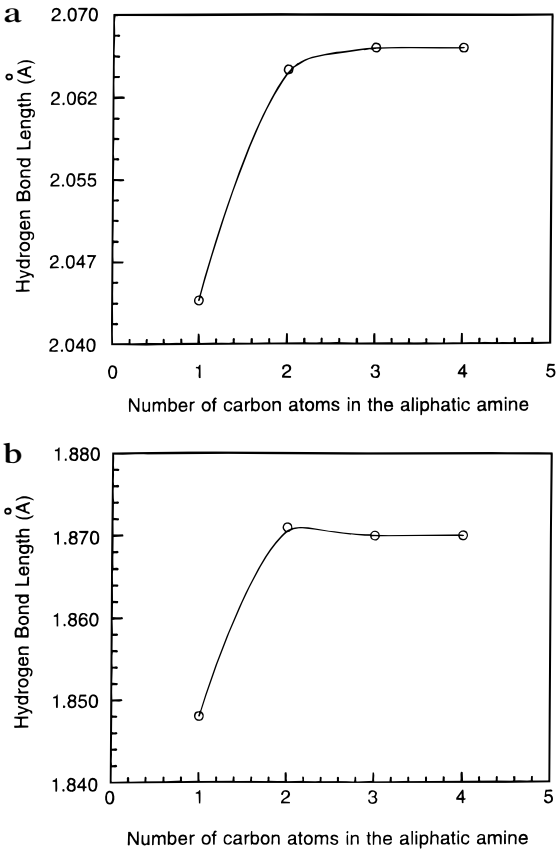


Figure 5. (a) Hydrogen bond lengths between the N and OH as a function of increasing length of aliphatic amine, from methylamine (1) to butylamine (4). (b) Hydrogen bond lengths between the H and OH as a function of increasing carbon in the aliphatic amine, from methylamine (1) to butylamine (4).

of inter- and intramolecular hydrogen-bonded hydroxyl groups of the B-m and B-e are much stronger than that of the B-p and B-b polybenzoxazines.

The relationship between the hydrogen bond length and the length of the aliphatic group of a series of model dimers is plotted in Figure 5a,b. Comparing Figure 4 to Figure 5a, there is an opposite trend in the hydrogen bond length and the percentage volumetric change of the aliphatic amine-based benzoxazines. In Figure 5b, the hydrogen bond length of the H---OH also increases with increasing aliphatic chain, although there is an almost negligible decrease from ethylamine to propylamine. Both Figure 5a and Figure 5b show that there is a dramatic change from the methyl to the ethyl group, and the changes became very small from ethyl to butyl. However, Figure 4 shows that the decrease of volumetric expansion becomes constant after the propyl group. This is because the effect of intermolecular interaction has not been considered in the molecular modeling. It should be mentioned that the above discussion is based on the assumption that both OH---N and H---OH hydrogen bonds exist in all the benzoxazines, which have been observed qualitatively in the FTIR spectra. The hydrogen bond length increases as the number of aliphatic carbons increases, indicating the reduction of the hydrogen bond strength.

Logically, one would expect the density to increase as the hydrogen bonding becomes stronger, which is the case for most organic molecules. The water molecule is an exception to this trend. It is known that the most favorable hydrogen bonding in the ice crystals results in a lower density than the liquid water.[19] The hydrogen bond length calculations and density measurements seem to imply that the polybenzoxazines may behave like the water molecules, although we have considered only intramolecular hydrogen bonding in this paper. It is important to mention that the analysis in this paper is restricted to the intramolecular hydrogen bonding, which tends to force the molecule to curl rather than extend. Such a conformation might be unfavorable for tight packing, leading to a larger volume occupied.

As mentioned earlier, all polybenzoxazines show inter- and intramolecular hydrogen bonding in the FTIR spectra. The aliphatic amine-based polybenzoxazines are no exception. Evidence of intermolecular hydrogen bonding in the aliphatic amine-based polybenzoxazines complicates the explanation. Furthermore, as the aliphatic amine becomes longer, the amine portion of the structure becomes more mobile and can more easily attain the lowest energy of conformation, resulting in a better packing of the polymer chains.

Steric Effect of Amine Groups. The steric effect of the amine group attached to the nitrogen can have a significant effect on the conformations of the polymer chain such that the hydrogen bonding will be affected. The steric effect may be accessed by comparing the B-e, B-ip, and B-t benzoxazines. B-t benzoxazine with the bulkiest amine shows the greatest volumetric expansion, while B-ip shows a slight shrinkage as can be seen in Table 3. The volumetric expansion decreases from B-e to B-ip but increases from B-ip to B-t. In addition to the steric effect from the ethyl to the *tert*-butyl group, there is also an inductive effect from the increasing number of carbon atoms from B-e to B-t, which may explain the increase in shrinkage from B-m to B-ip. However, the steric effect may be stronger when comparing B-ip and B-t, thus causing an increase in expansion.

Isothermal Curing. Isothermal curing at 150 °C, followed by density measurement at room temperature, was carried out for the as-synthesized sample in order to follow the volumetric changes at room temperature as a function of the extent of cure. All benzoxazines show a decrease in density, and thus expansion in volume, as a function of cure time until about 6 or 7 h, when the volume changes level off. Since all samples experienced the same thermal history, the decrease of the density can be explained by the degree of cure. As curing proceeds, more cross-linked chains are formed. A higher cross-link density is believed to result in higher free volume at room temperature.[20] However, in most polymers this increase in the free volume as T_g increases

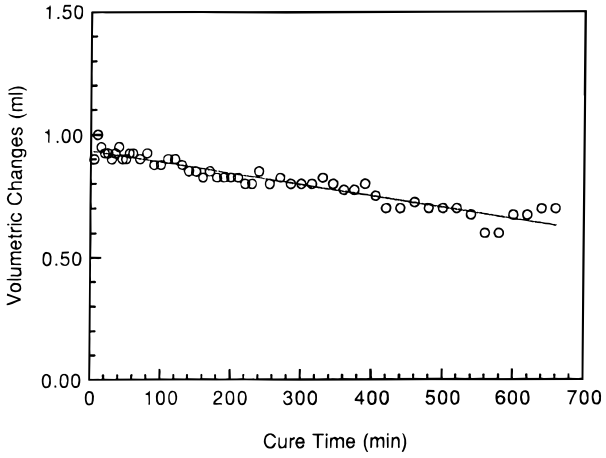


Figure 6. Dilatometry experiment: volumetric changes at 150 °C as a function of curing time for B-e benzoxazine.

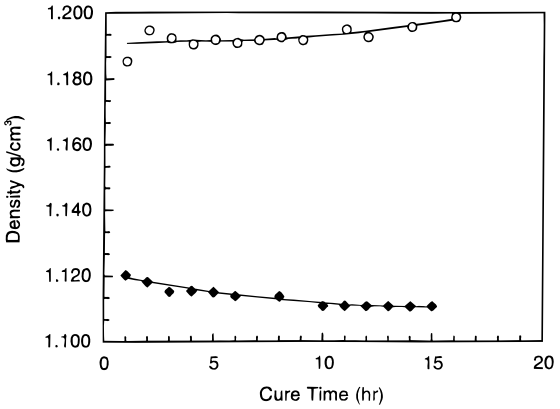


Figure 7. Room temperature density changes of the isothermal curing of as-synthesized (○) B-a and (◆) B-c benzoxazine.

has not been reported to overcome the polymerization shrinkage.

A dilatometric experiment was carried out using a calibrated dilatometer with mercury as the volumetric transfer agent. To eliminate the effects of thermal expansion, the material was cured isothermally at 150 °C. The volumetric changes were recorded at this temperature for a pregelled sample. The volumetric changes of the isothermal curing were followed by a dilatometric experiment with the purified B-e benzoxazine, and the results are shown in Figure 6. The measurements were taken 5 min after the dilatometer containing the sample and mercury was immersed in a 150 °C oil bath for establishing temperature equilibrium. The volumetric changes were recorded *in situ* during the course of curing. It can be seen that there is a volumetric decrease throughout the 16 h of curing. After normalizing the amount of volumetric change to the initial volume, this volumetric decrease is approximately 3%. The small volumetric decrease at 150 °C during curing can be understood as the monomers move from a van der Waals distance to a covalent distance of separation. However, the effect of hydrogen bonding on the volume will become more significant as the cured polymer is cooled down to room temperature.

A comparison of the B-a and B-c polybenzoxazines from the isothermal curing and room temperature measurement also shows that B-c benzoxazine expands slightly more than B-a benzoxazine. A plot of density changes at room temperature as a function of cure time for B-a and B-c polybenzoxazines is shown in Figure 7. In Figure 8, the room temperature densities of the

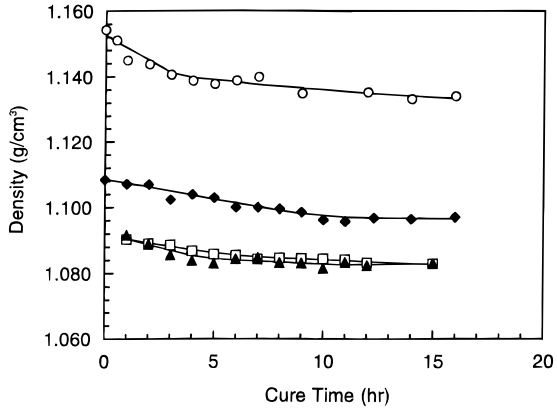


Figure 8. Room temperature density changes as a function of curing time for the as-synthesized aliphatic amine-based benzoxazines: B-m (○), B-e (□), B-p (◆), and B-b (▲).

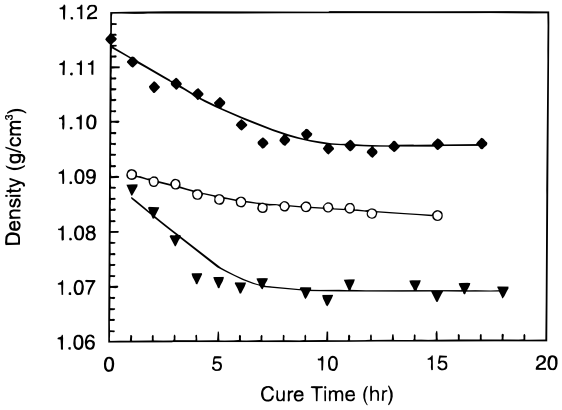


Figure 9. Room temperature density of isothermally cured B-e (○), B-ip (◆), and B-t (▼).

aliphatic amine benzoxazines are plotted as a function of curing time. B-m polybenzoxazine shows the highest decrease in density as a function of isothermal curing. B-e and B-p polybenzoxazines show almost no change in density as curing proceeds, while B-b shows only a slight decrease in density. B-p and B-b benzoxazines show volumetric shrinkage according to the density measurements of purified monomers and stepwise cured polymers. The comparison of B-e, B-ip, and B-t benzoxazines is presented in Figure 9. There is an expansion as a function of cure time, with B-t showing the highest amount of expansion. However, B-ip has a higher volumetric expansion than B-e.

It should be noted that benzoxazines are cured by means of thermal polymerization without using any catalyst and that as-synthesized benzoxazine monomers contain open rings, dimers, and oligomers that may help the ring opening and thus accelerate the polymerization process. Therefore, isothermal curing was also carried out for purified B-m and B-b benzoxazines, and the plots are shown in Figures 10 and 11, respectively. For B-m polybenzoxazine, it was found that the purified form has a lower density than the as-synthesized form. Both the purified and as-synthesized B-m polybenzoxazines show expansion as a function of the curing time. On the other hand, the purified form of B-b polybenzoxazine has a higher density than the as-synthesized form although both show expansion as a function of curing time.

The effect of isothermal curing at different temperatures was determined for purified B-b benzoxazine. The curing temperatures and their durations are presented in Table 4. Different curing times were employed for each curing temperature in order to ensure that all

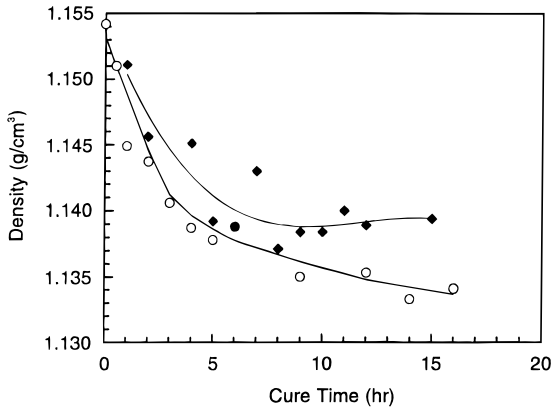


Figure 10. Comparison of the room temperature density changes as a function of curing time for the as-synthesized (○) and purified (◆) B-m polybenzoxazines.

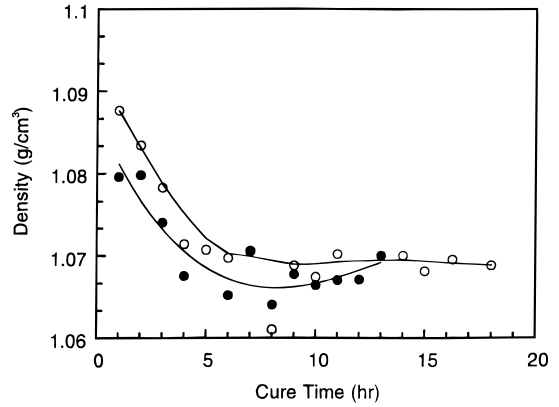


Figure 11. Comparison of the room temperature density changes as a function of curing time for the as-synthesized (○) and purified (●) B-b polybenzoxazines.

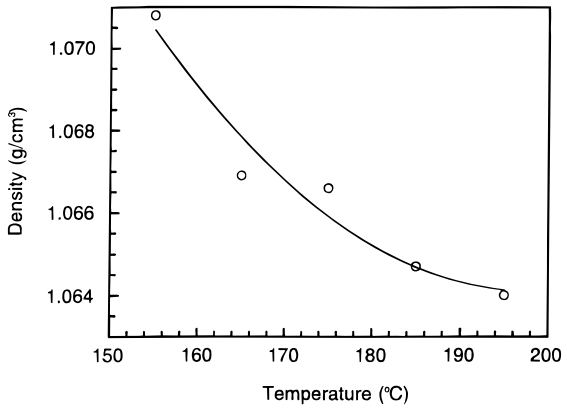


Figure 12. Room temperature density changes as a function of isothermal curing at different temperatures for B-b benzoxazine.

Table 4. Curing Conditions for the B-b Benzoxazines

curing temp (°C)	150	165	175	185	195
curing time (h)	48	24	12	6	3

specimens were cured to the fullest extent at that temperature. The room temperature density as a function of the curing temperature is plotted in Figure 12. There is a systematic decrease in the density as a function of curing temperature. This result is in accordance with other studies of the effects of T_g on the density of isothermally cured thermosets.[20−22] Since the samples were cured isothermally at different temperatures, each of them will have a different T_g. The higher the curing temperature, the higher the resulting T_g until the polymer achieves its ultimate T_g. Hence, this experiment shows that there is a decrease in shrinkage as a function of increasing T_g. Increased T_g is in part a consequence of increased cross-link density, which leads to a higher free volume at room temperature.[21] Hence, the amount of volumetric expansion is associated with the number of oxazine rings that are opened, polymerized, and cross-linked.

Table 5. Gelation Times of the As-Synthesized Benzoxazines at Isothermal Curing (150 °C) and the T_g of the Polybenzoxazines

	polybenzoxazine				
	B-m	B-e	B-ip	B-p	B-b
gelation time (min)	5.9	2.5	7.5	25	
T_g (°C)	180	180	140	130	135

As reported by Ishida and Nigro,[13] the expansion of the spiroortho compounds could not be appreciated if the expansion is completed before gelation occurs. Therefore, isothermal curing utilizing dynamic mechanical spectrometry was performed on the as-synthesized benzoxazines in order to study the gelation time as a function of cure time. Isothermal curing of the as-synthesized monomers was done using parallel plates. The gelation time was taken at the point of crossover between the dynamic storage modulus, G', and dynamic loss modulus, G'', and some representative data are shown in Table 5. It was found that all as-synthesized benzoxazines gelled within half an hour of isothermal curing at 150 °C, except for B-t benzoxazine. B-t benzoxazine did not gel even after 3 h; the experiment had to be stopped because the low viscosity of the material gave a torque lower than the limit of the instrument. The room temperature density of all the polybenzoxazine samples cured under similar conditions, however, continued to show volumetric expansion for about 6 or 7 h.

As mentioned earlier, the polybenzoxazines have properties superior to those of conventional phenolic resin. The T_gs of a few representative materials are shown in Table 5. The T_g decreases as the length of the aliphatic chains becomes longer. Again, this is likely due to the increase in mobility of the amine moiety. Yet, the T_gs are considerably higher relative to many existing polymers. It has been reported that the benzoxazine based on 4,4′-dihydroxybenzophenone gave a T_g as high as 350 °C.[23] This is an important property because in comparison to the only other known expanding monomer, the benzoxazine monomers have a high potential for structural applications. The homopolymers of spiroortho compounds are liquids at room temperature. The polybenzoxazines, on the other hand, have shown mechanical properties of composites comparable to those of PMR-15 polyimide.[23]

Conclusions

The volumetric expansion of benzoxazine resin upon curing is reported to be a consequence of the molecular packing rather than the ring-opening polymerization mechanism. This molecular packing can be a direct consequence of inter- and intramolecular hydrogen bonding, although in this paper only the effect of intramolecular hydrogen bonding is reported. This paper, however, has only investigated the effect of the amine moiety; the effect of the phenolic portion of the benzoxazine molecule on volumetric expansion is yet to be explored. In addition, this class of phenolic resin has been shown to have a high potential for structural or engineering applications.

Acknowledgment. The authors would like to thank the Federal Aviation Administration (FAA) for financial support through the NSF Center for Molecular and Microstructure of Composites (CMMC), which is jointly established by the NSF, the State of Ohio, and EPIC, representing industrial members. The authors would also like to thank Douglas Allen for helpful discussion.

References and Notes

(1) Piggott, M. R.; Pyshnov, T. *Polym. Mater. Sci. Eng.* **1986**, *54*, 18.
(2) Piggott, M. R. *J. Mater. Sci.* **1978**, *13*, 1709.
(3) Bailey, W. J.; Katsuki, H. *ACS Div. Polym. Chem.* **1973**, *14*, 1169.
(4) Bailey, W. J. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1977**, *18*, 17.
(5) Bailey, W. J.; Katsuki, H.; Endo, T. *ACS Div. Polym. Chem.* **1974**, *15* (1), 445.
(6) Bailey, W. J.; Amone, M. J.; Issari, B.; Lin, Y. N.; No, N.; Pan, C. Y.; Saigo, K.; Stansbury, J.; Tan, S. R.; Wu, C.; Yamazaki, N.; Zhou, J. *Polym. Mater. Sci. Eng.* **1986**, *54*, 23.
(7) Knop, A.; Pilato, L. A. *Phenolic Resins*; Springer-Verlag: New York, 1985; p 198.
(8) Lim, T. J.; Piggott, M. R.; Bailey, W. J. *SAMPE Q.* **1984**, 25.
(9) He, P. S.; Zhou, Z. Q.; Pan, C. Y. *J. Mater. Sci. Eng.* **1989**, *24*, 1528.
(10) He, P. S.; Zhou, Z. Q. *J. Mater. Sci.* **1991**, *26*, 3792.
(11) Shimbo, M.; Ochi, M.; Inamura, T.; Inone, M. *J. Mater. Sci.* **1985**, *20*, 2965.
(12) Shimbo, M.; Ochi, M.; Shigeta, Y. *J. Appl. Polym. Sci.* **1981**, *26*, 2265.
(13) Ishida, H.; Nigro, J. In *Polymer Characterization: Physical Property*, Spectroscopy, and Chromatographic Methods; Advances in Chemistry 227; Craver, C. D., and Provder, T., Eds.; American Chemical Society: Washington, DC, 1990; p 259.
(14) Ning, X.; Ishida, H. *J. Polym. Sci., Polym. Chem. Ed.* **1994**, *32*, 1121.
(15) Ishida, H.; Rodriguez, Y. *Polymer* **1995**, *36*, 3151.
(16) Ishida, H.; Allen, D. J. *J. Polym. Sci., Polym. Phys. Ed.* **1996**, *34*, 1019.
(17) Berthod, H.; Pullman, A. *J. Chem. Phys.* **1965**, *62*, 942.
(18) Dunkers, J. P.; Zarate, A.; Ishida, H. *J. Phys. Chem.* **1996**, *100*, 13514.
(19) Hamilton, W.; Ibers, J. A. In *Hydrogen Bonding in Solids*; W. A. Benjamin, Inc.: New York, 1968; p 197.
(20) Gillham, J. K. *Polym. Eng. Sci.* **1986**, *26* (2), 1429.
(21) Wang, X.; Gillham, J. K. *J. Coat. Technol.* **1992**, *64* (807), 37.
(22) Wang, X.; Gillham, J. K. *J. Appl. Polym. Sci.* **1993**, *47*, 425.
(23) Shen, S. B.; Ishida, H. *Polym. Compos.* **1996**, *17*, 710.

MA960539A