

Study on the Volumetric Expansion of Benzoxazine Curing with Different Catalysts

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ABSTRACT: A systematic investigation on the volumetric expansion of four benzoxazine systems, which are benzoxazine, benzoxazine/tertiary amine, benzoxazine/organic acid, and benzoxazine/epoxy resin/tertiary amine, was done. By using gravimetric and dilatometric methods, etc., studies on volumetric shrinkage, isothermal cure shrinkage, and density versus cure time plots were done. The cure reactions of these benzoxazines were carried out at 140 and 160°C. The results show that all benzoxazine systems exhibit apparent volumetric expansion after polymerization, that is, the densities of monomers are larger than are those of polymers at room temperature. But, meanwhile, they exhibit volumetric shrinkage while curing isothermally. The results also show that the higher the cure temperature is, the larger the cure shrinkage of the benzoxazines will be and that the extent of the cure shrinkage of the benzoxazines with the aid of catalysts is larger than is that of thermal polymerization systems. The reason for this is that, accelerated by catalysts, the polymerization rate become faster and the extent of polymerization becomes larger. It is obvious that catalysts can make a notable impact on the cure reaction of benzoxazines. Therefore, the dimension of the volumetric expansion of benzoxazine is associated with its polymerization mechanism, molecular structure, and extent of polymerization. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1107–1113, 2002; DOI 10.1002/app.10267

Key words: benzoxazine; cure shrinkage; volumetric expansion; density

INTRODUCTION

It is well known that thermosetting resins undergo variable volumetric shrinkage during polymerization. For example, the cure shrinkage of epoxy resins, which are widely utilized in the fields of coating, adhesive, lamination, casting, etc., is above 5%.¹ Cure shrinkage can make a notable impact on the performance of polymeric materials, especially of fiber-reinforced compos-

ites and adhesives because high shrinkage in all thermosetting resins can inevitably result in residual stress, warping, premature debonding of the fiber from the matrix, fiber buckling, and delamination in fiber-reinforced composites and debonding from the substrate in adhesives. As a result, the volumetric shrinkage during polymerization of thermosetting resins has attracted a great deal of attention in recent years.^{2–6}

Benzoxazines are a kind of heterocyclic compounds which can polymerize via a ring-opening reaction without yielding any small molecular by-products. It should be noted that this kind of material exhibits not only no shrinkage but also a slight expansion after curing. As a new class of high-performance phenolic resins, benzoxazines,

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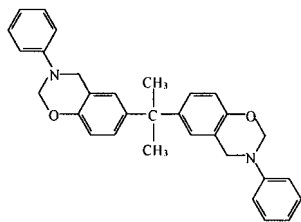
have been used in a wide field of industries, such as in fiber-reinforced laminates, brake shoes of trains, and injection molding.^{7,8} Ishida et al. initially investigated the volumetric expansion of benzoxazines without catalysts during ring-opening polymerization.^{9–11} However, the reason for the expansion or near-zero shrinkage is not well understood. In our previous studies,^{12–14} systematic investigations on the cure shrinkage of three benzoxazine systems with different phenolic portions were done from the point of view of the apparent volumetric shrinkage, isothermal cure shrinkage, and density versus temperature plots and density versus cure time plots. The results showed that these three kinds of benzoxazines display volumetric shrinkage while curing isothermally and apparent volumetric expansion after polymerization and that the dimension of volumetric expansion of polybenzoxazine is associated with its polymerization mechanism, molecular structure, and extent of polymerization.

In the present work, volumetric expansion of four benzoxazine systems with different catalysts was studied in detail using gravimetric and dilatometric methods, etc. The effects of different catalysts on polymerization as well as volumetric expansion of bisphenol A benzoxazine are discussed.

EXPERIMENTAL

Materials

A benzoxazine precursor was synthesized using the suspension method. Its chemical structure is shown below:



This precursor was synthesized from bisphenol A (polycarbonate-grade, Mitsubishi Petrochemical Co. Ltd., Japan), formaldehyde (37–40% in water), and aniline (A.R., Chengdu Chemical Agent Factory, Chengdu, China) in the molar ratio of 1:4:2. A solution of aniline (0.5 mol) was added dropwise to a stirred solution of formaldehyde (1 mol) in distilled water (50 mL) at room tempera-

Table I Curing Profile Utilized During the Molding of Specimens for Measurement of Apparent Volumetric Shrinkage

Parameter	Temperature (°C)				
	140	150	160	170	180
Time (h)	6	2	2	2	6

ture. Then, bisphenol A (0.25 mol) and the dispersing agent were slowly added at 70°C. After 3-h stirring at 90°C, a large quantity of cold distilled water was added quickly. Afterward, the light yellow colored fine powder product was washed with warm distilled water at least five times and then vacuum-dried below 50°C for 24 h before use (yield 80%); the softening point was 75–80°C. The IR spectra were measured with a Nicolet 20SXB FTIR instrument as potassium bromide pellets. IR (KBr, cm⁻¹): 942 (oxazine ring); 1360 (C–N); 1241, 1029 (Ar–O–C); 864 (1,2,4-trisubstituted benzene ring).

Epoxy resin (E44, Wuxi Resin Plant, Wuxi, China), oxalic acid (A.R., Chongqing Chemical Agent Plant, Chongqing, China), and *N,N*-dimethylbenzylamine (A.R., Shanghai Chemical Agent Plant, Shanghai, China) were used without further purification.

Cure Reaction

In this study, there were four kinds of benzoxazine systems including benzoxazine without a catalyst (BOZ), benzoxazine with (0.07% wt) oxalic acid [BOZ/C(1)], benzoxazine with (1% wt) *N,N*-dimethylbenzylamine [BOZ/C(2)], and benzoxazine with (10% wt) epoxy resin and (1% wt) *N,N*-dimethylbenzylamine [BOZ/E-44/C(2)]. First, the reactants and catalysts of these systems were each melted and mixed thoroughly at 130°C and degassed at 140°C in a vacuum oven for 1 h to remove any entrapped air. Second, the materials were cured under normal pressure according to curing schedule 1 as shown in Table I. Finally, the cured materials were naturally cooled to room temperature.

Measurements

The density of a solid monomer and polymer at room temperature was measured according to ASTM D792 using a 10-mL pycnometer calibrated with pure water at 25 ± 1°C. The isother-

Table II Density and Apparent Shrinkage of Different Benzoxazine Systems

System	Composition	Density		Shrinkage (%)
		Monomer	Polymer	
I	BOZ	1.2030	1.1854	-1.48
II	BOZ/C(1)	1.2030	1.1870	-1.37
III	BOZ/C(2)	1.2026	1.1885	-1.19
IV	BOZ/E-44/C(2)	1.2030	1.1867	-1.37
V	E-44/MDA	1.1998	1.1989	-0.075

Testing temperature: 30°C; BOZ: bisphenol A benzoxazine; C(1): oxalic acid; C(2): tertiary amine; E-44: epoxy resin.

mal cure shrinkage that benzoxazine undergoes during its cure was determined using a dilatometer. The method used was a modification of that reported by Parry and Mackay.¹⁵ Silicon oil was used as a volume-transfer agent. The percent shrinkage was calculated by the following equation:

$$S\% = (h_0 - h_t)A\rho_t W^{-1}$$

where S is the volumetric shrinkage at different times; h_0 , the height of oil at thermal equilibration; h_t , the height of oil at different times; A , the volume-transfer coefficient; ρ_t , the density of sample at the designated temperature; and W , the weight of the sample.

FTIR spectra of benzoxazine were examined using a Nicolet 20SXB. The gel point of benzoxazines was determined by the flat-knife method.

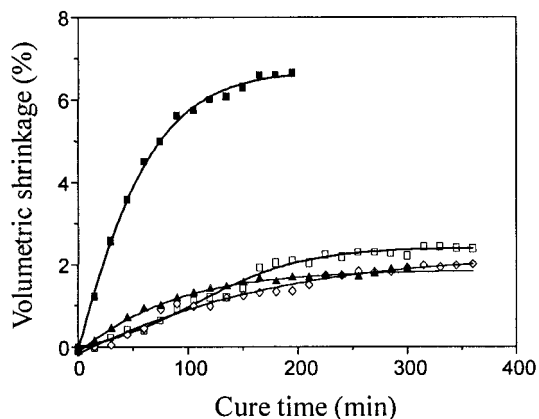


Figure 1 Volumetric shrinkage as a function of time for isothermal cure at 140°C: (▲) BOZ; (◇) BOZ/C(1); (□) BOZ/C(2); (■) BOZ/E-44/C(2).

RESULTS AND DISCUSSION

Apparent Volumetric Shrinkage

The densities of the monomers and polymers of different benzoxazine systems at 30°C were determined according to ASTM D792. The results are shown in Table II. It can be seen from this table that all the volumetric shrinkage values of benzoxazine with different catalysts are negative, that is, all the benzoxazines exhibit volumetric expansion after polymerization, and that the volumetric expansion values of benzoxazines with catalysts are smaller than that of pure benzoxazine (BOZ). It should be noted that the volumetric expansions of all benzoxazine systems are much larger than that of the epoxy resin (E-44/MDA).

Isothermal Cure Shrinkage at 140°C

A dilatometric experiment was carried out at 140°C to obtain the isothermal cure shrinkage of four benzoxazine systems. The gel points of these systems were measured at the corresponding

Table III Gel Time and Total Cure Shrinkage of Different Benzoxazine Systems at 140°C

System	Composition	Gel Time (min)	Cure Shrinkage in 360 min (%)
I	BOZ	>360	1.99
II	BOZ/C(1)	283	2.11
III	BOZ/C(2)	104	2.60
IV	BOZ/E-44/C(2)	193	6.62
V	BOZ/E-44	331	5.44
VI	E-44/C(2)	>360	1.75

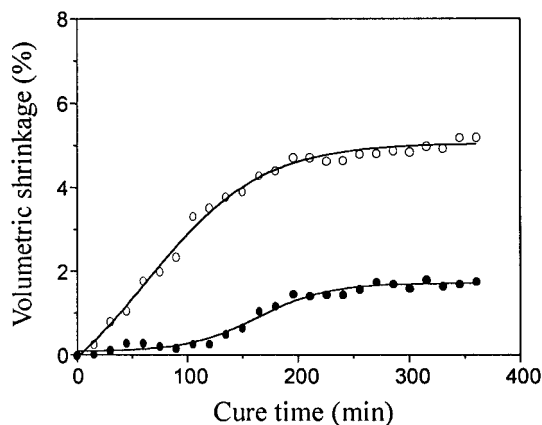


Figure 2 Volumetric shrinkage as a function of time for isothermal cure at 140°C: (○) BOZ/E-44; (●) E-44/C(2).

temperature. The cure shrinkage after gelification was compared with the total cure shrinkage in 6 h. The results are shown in Figure 1 and Table III.

It is clear from Figure 1 and Table III that the insignificant oxalic acid (0.07% wt) can make some impact on the ring-opening polymerization of benzoxazines. As a result, the gel time of system II becomes shorter and the total cure shrinkage is slightly larger than that of pure benzoxazine. According to our previous study on the ring-opening reaction mechanism of benzoxazine, the molecular structure of polybenzoxazine catalyzed by oxalic acid was the same as that of pure polybenzoxazine and the structure of the polymer containing phenolic hydroxyl played a leading role. Therefore, the results in Figure 1 indicate that the similarity of a polymer's structures of these two benzoxazine systems leads to the similarity of volumetric change during polymerization. The ring-opening polymerization of benzoxazines is also influenced by tertiary amine (1% wt). We can see that the gel time of system III is shortened and that the volumetric shrinkage at the gel point is 1.6%, which accounted for 61.5% of the total cure shrinkage (2.60%). This is due to acceleration by active hydrogen of *ortho*-phenoxy and phenolic hydroxyl. Ring-opening polymerization of benzoxazines is catalyzed by benzylamine, which enables the extent of the reaction to improve slightly. It can be noted that the addition of epoxy resin (10% wt) and tertiary amine (1% wt) can make a notable impact on the cure reaction of benzoxazines. As a result, the reaction rate of system IV dramatically increased and the gel

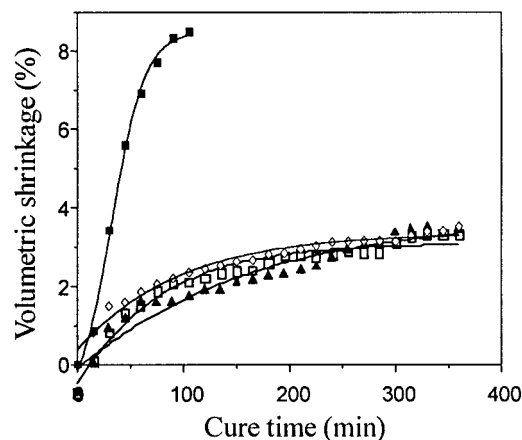


Figure 3 Volumetric shrinkage as a function of time for isothermal cure at 160°C: (▲) BOZ; (◇) BOZ/C(1); (□) BOZ/C(2); (■) BOZ/E-44/C(2).

time is shortened and the cure shrinkage in 195 min is as high as 6.62%, which is greatly larger than that of pure benzoxazine (1.6%).

To realize further the effect of epoxy resin and tertiary amine on the cure shrinkage of benzoxazine, we carried out a cure-shrinkage analysis of two systems including benzoxazine with epoxy resin and epoxy resin with tertiary amine. It can be seen from Figure 2 and Table III that the addition of epoxy resin (10% wt) enables the gel time of benzoxazine to be shortened slightly and the total cure shrinkage in 6 h to increase significantly from 1.99 to 5.44%. Meanwhile, the cure rate of epoxy resin with tertiary amine (1% wt) is so slow that no gellation was found up to 360 min. Thus, as far as the cure reaction of benzoxazine with the epoxy resin (10% wt) and tertiary amine (1% wt) is concerned, the effect of the epoxy resin is significant. Furthermore, the polymerization between benzoxazine and the epoxy resin can still take place without benzylamine.

Table IV Gel Time and Total Cure Shrinkage of Different Benzoxazine Systems at 160°C

System	Composition	Gel Time	Cure Shrinkage in 360 min (%)
I	BOZ	41 min + 23 s	4.23
II	BOZ/C(1)	29 min + 25 s	3.53
III	BOZ/C(2)	27 min + 48 s	4.10
IV	BOZ/E-44/C(2)	49 min + 17 s	8.34 ^a

^a Curing shrinkage in 100 min.

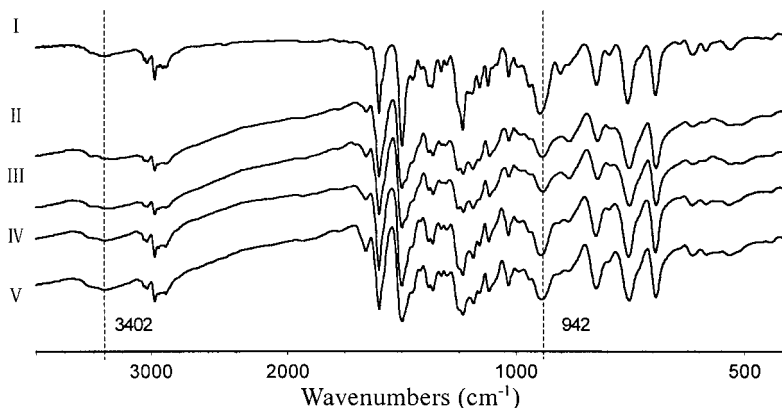


Figure 4 IR spectra of isothermal cure products at 140°C for 6 h: (I) BOZ; (II) BOZ/C(1); (III) BOZ/C(2); (IV) BOZ/E-44/C(2); (V) BOZ/E-44.

Isothermal Cure Shrinkage at 160°C

To gain a clear idea of the cure-shrinkage regularities of the above-mentioned systems, the isothermal cure shrinkage and gel time of these systems at 160°C were measured. The results are shown in Figure 3 and Table IV. In comparison with the isothermal cure shrinkage at 140°C, there is a dramatic shortening in the gel time and a gradual increase in the total cure shrinkage of the preceding three benzoxazine systems. The cure shrinkage after the gel point holds a dominant position, which accounts for 67, 63, and 69% of the total cure shrinkage in 6 h, respectively. It has been reported that the cure shrinkage after the gel point is the main factor which leads to inner stress. Therefore, we can predict that the higher the cure temperature, the larger the cure shrinkage after the gel point, the bigger the inner stress in the cured materials, and the worse the performance of cured materials will be. It can be seen that the gel time at 160°C is shortened by adding benzylamine or oxalic acid, that is, the reaction rate became faster. The total cure shrinkage in 6 h is smaller than that of pure benzoxazine. The probable reason is that the polymerization rate increases significantly with the aid of catalysts so as to form a crosslinking network quickly, which prevents the molecular chains from moving easily and hinders further shrinkage. Therefore, compared with that of pure benzoxazine, the cure shrinkage of benzoxazine with catalysts decreases slightly. As can be seen from Figure 3, the cure shrinkage of benzoxazine with epoxy resin and benzylamine at 160°C increased dramatically from 0 to 8.34% during 45 min. In comparison with the result of benzoxazine

with benzylamine, there is no doubt that epoxy resin has a big influence on the polymerization of benzoxazine.

IR Analysis

Figures 4 and 5 show IR spectra of the isothermal cured products of these systems at 140 and 160°C, respectively, which can be used to analyze the extent of polymerization and the molecular structures of the cured products. According to Figure 4, the molecular structure of II is nearly the same as that of III. Thus, the three-fourths difference of volumetric changes during curing between them should be attributed to the changes of molecular chain packing. In comparison with the structure of pure benzoxazine (I), the characteristic absorption peaks of the oxazine ring neighboring 942 cm^{-1} of II and III are weakened and, meanwhile, the absorption peaks indicating a hydroxyl group were strengthened, which suggested that ring-opening polymerization took place. Interestingly, the circumstances of IV and V are similar to the case of II and III, which demonstrates that there is no effect on the molecular structure of benzoxazine by using benzylamine (1% wt). In other words, only the reaction activity energy decreased and the extent of cure improved. Furthermore, the absorption peak indicating the epoxide ring near 910 cm^{-1} disappeared, which reveals that polymerization between benzoxazine and the epoxy resin occurred. Figure 5 shows that, compared with that of 140°C, there is an increase in the hydroxyl group contribution at 3410 cm^{-1} and a decrease in the oxazine ring contribution at 947 cm^{-1} at 160°C of all benzoxazine systems, which suggests that the extent of polymerization in-

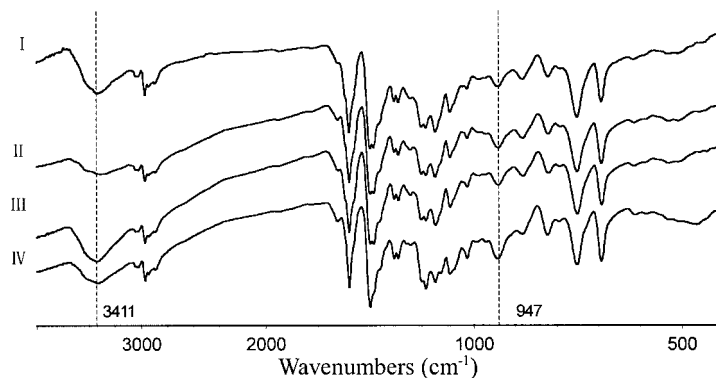


Figure 5 IR spectra of isothermal cure products at 160°C for 6 h: (I) BOZ; (II) BOZ/C(1); (III) BOZ/C(2); (IV) BOZ/E-44/C(2).

creased and that it is the changes of molecular packing that lead to the volumetric changes during curing of I, II, and III.

Densities Versus Cure Time Plots

To analyze the relationship between the volumetric changes at room temperature and the extent of cure, isothermal curing at 160°C, followed by density measurement at room temperature, was carried out for all the above benzoxazine systems. The results are shown in Figures 6 and 7. It is clear from Figure 6 that as the cure time increases all the benzoxazines show a decrease in density, which means that all of them exhibit volumetric expansion and that there are many differences in the dimension of the volumetric expansion of these benzoxazines, where the volumetric decrease of I, II, III, and IV is 0.91, 0.55,

0.42, and 0.39%, respectively. Thus, the sequence of the dimension of the volumetric expansion should be $I > II > III > IV$, which is in accordance with the results of the apparent volumetric shrinkage and isothermal cure shrinkage, that is, the volumetric expansions of benzoxazines with catalysts are smaller than that of pure benzoxazine. As can be seen from Figure 7, the trend of the density change of the epoxy resin with benzylamine is contrary, which indicates that there is a volumetric shrinkage in the cured product of the epoxy resin.

CONCLUSIONS

All benzoxazines with different catalysts exhibit apparent volumetric expansion after polymerization. However, they exhibit volumetric shrinkage while curing isothermally at an elevated temper-

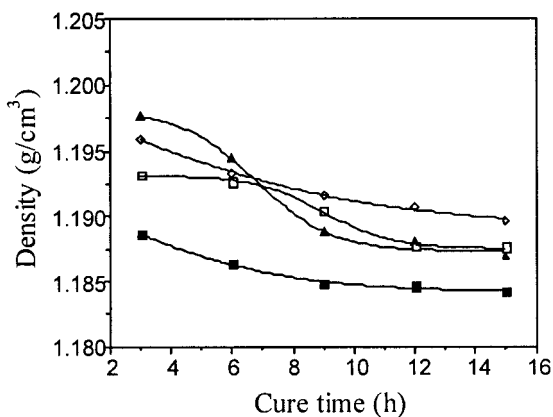


Figure 6 Room-temperature density changes after isothermally curing at 160°C for (▲) BOZ, (◇) BOZ/C(1), (□) BOZ/C(2), and (■) BOZ/E-44/C(2).

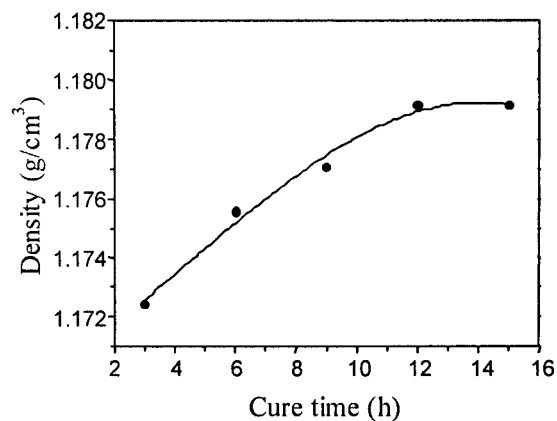


Figure 7 Room-temperature density changes after isothermally curing at 160°C for E-44/C(2).

ature. It is obvious that catalysts can make a notable impact on the cure reaction rate of benzoxazines. Therefore, the dimension of the volumetric expansion of benzoxazine is associated with its polymerization mechanism, the extent of polymerization, and the crosslinking density.

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