Polybenzoxazine and Its Alloys: Some Potential Applications

By

Sarawut Rimdusit, Ph.D.

Polymer Engineering Laboratory, Department of Chemical Engineering,

Faculty of Engineering, Chulalongkorn University

Bangkok 10330, THAILAND

Benzoxazine resins are self-polymerizable crosslinking systems with high thermal and mechanical integrity. The resins are capable of undergoing ring-opening polymerization upon heating without strong acid or base catalysts; therefore, no condensation by-products are released during a fabrication process. A relatively low a-stage viscosity, one of the most useful properties of benzoxazine resins, results in an ability of the resins to accommodate relatively large quantity of filler while still maintaining their good processability as compared to traditional phenolic resins. Moreover, polybenzoxazines possess several outstanding properties such as good dimensional stability, low moisture absorption, and relatively high glass transition temperature even though they have relatively low cross-linking density. One intriguing characteristic of benzoxazine resin is its ability to alloy with various resin systems such as phenolic novolac, epoxy, polyimide, and polyurethane to broaden its range of useful properties. In this work, examples of those useful properties of benzoxazine resins as well as their alloys for some engineering applications will be discussed.

Keywords: Polybenzoxazine, Alloys, Epoxy, Thermomechanical Properties.

1. Introduction

Benzoxazine resins are a novel kind of thermosetting phenolic resin. Their polymerization proceeds without using a curing agent and the resins do not produce by-products during cure [1]. Additionlly, polybenzoxazines have some outstanding properties such as relatively high glass transition temperature, high thermal stability, near-zero volumetric shrinkage, and [1-3] etc. A series of benzoxazine resins can be synthesized using different types of amine groups to yield polybenzoxazine of various property ranges. According to Ishida and Sanders [3], benzoxazine resins with arylamine show improved mechanical properties, including higher crosslink densities and glass transition temperature. From the work by Ishida and Allen about benzoxazine-epoxy systems [2], the great increase of the crosslink density of the alloy systems was found to strongly influence their mechanical and thermal properties. As an interesting example of benzoxazine polymer alloys, this research will examine the effect of the three types of arylamines based benzoxazine resins i.e. aniline, m-toluidine, and 3,5-xylidine on the thermomechanical properties of benzoxazine-epoxy alloys.

2. Experimental

Aniline-based benzoxazine resin (BA-a) was synthesized from bisphenol-A, paraformaldehyde, and aniline at a molar ratio of 1:4:2. The mixture was heated to 110°C in an aluminum pan and was mixed rigorously for about 30 minutes to yield a light yellow solid monomers. The same procedure was also used to synthesize BA-mt or BA-35x by replacing aniline with m-toluidine or 3,5-xylidine.

Curing behaviors of samples were studied using a differential scanning calorimeter (DSC) model 2910 from TA Instruments. The mass of the samples was in the range of 3-5 mg. Each specimen was sealed in an aluminum pan with lid. The heating rate used was 10°C/min from room temperature to 300°C.

Dynamic mechanical analyzer (NATZSH, model DMA242) was used to obtain a storage modulus (E′) and loss modulus (E″) of the polymeric specimens. The dimension of each specimen was about $10 \times 50 \times 2$ mm^3. The specimen was tested using a 3-point bending mode at the frequency of 1 Hz. and heating rate of 2°C/min from room temperature to the temperature beyond the glass transition temperatures (T_g) of each specimen.

3. Results and Discussion

The curing behaviors of the neat arylamine-based benzoxazine monomers are shown in Fig. 1. From the figure it can be observed that BA-a showed only one exothermic peak while BA-mt and BA-35x types benzoxazine resins showed overlapped exothermic peaks. The curing mechanism in the first exothermic peak of BA-35x resin is the same as that of BA-a resin [4], whereas the second shoulder exothermic peak at high temperature corresponds to the side reactions which generate the bisphenolic methylene linkages and possible reaction to the *para* position of the arylamine ring [5]. Fig. 2 exhibits effects of epoxy on curing behaviors of its mixture with BA-35x. The exothermic peak of BA-35x was observed to systematically shift to higher temperature with an addition of epoxy resins. The curing condition of all specimens in this work was determined by DSC to be 150°C/1hr., 170°C/1hr., 190°C/1hr., 200°C/4hr.

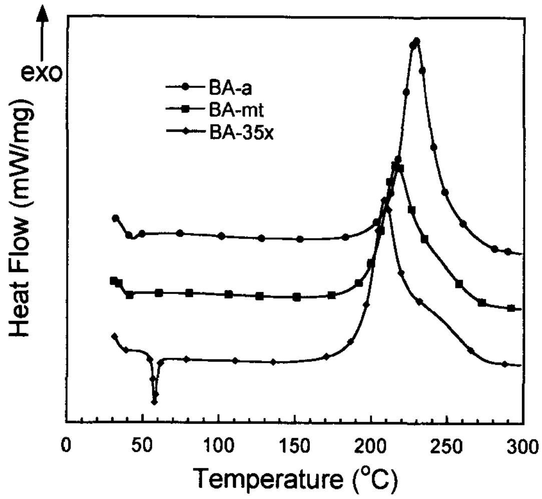

Fig. 1 DSC thermograms of three types of arylamine-based benzoxazine resins.

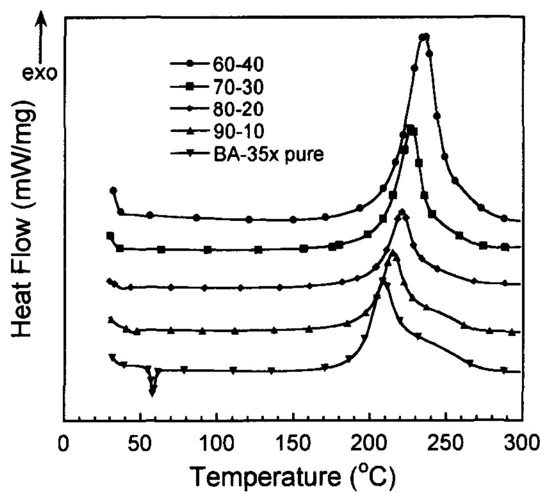

Fig. 2 Curing behaviors of BA-35x alloyed with epoxy resin at various compositions.

Table 1 Glass transition temperature (T_g) and storage modulus (E′) at room temperature of the three arylamine-based benzoxazine resins alloyed with epoxy resin at various epoxy contents.

	BA-a		BA-mt		BA-35x	
	T_g (°C)	E′ (GPa)	T_g (°C)	E′ (GPa)	T_g (°C)	E′ (GPa)
60:40	174	4.76	207	4.43	223	3.81
70:30	180	4.97	209	4.50	230	4.12
80:20	182	5.28	213	4.86	235	4.30
90:10	178	5.60	212	5.09	238	4.60
Pure	172	5.94	210	5.32	241	4.98

The glass transition temperatures (T_g) and storage modulus (E′) of the three arylamine-based benzoxazine resins alloyed with epoxy resin at various epoxy contents are listed in Table 1. Among these alloys, the T_g of BA-35x alloyed with the epoxy resin showed highest values because of amounts of additional cross-links (i.e., methylene linkages) would increase the T_g of the network significantly [5]. However, the values tended to decrease with an addition of the epoxy. On the other hand, T_g maxima were observed in the BA-a/Epoxy and BA-mt/epoxy systems. The complementary properties of greater molecular rigidity of benzoxazine resin and the higher crosslink density of the epoxy resin might attribute to the synergistic behavior in the T_g. Finally, the storage modulus at room temperature of the three arylamine-based benzoxazine resins alloyed with epoxy resin were found to increase systematically with the amount of the benzoxazine fraction as a result of a greater molecular rigidity of the benzoxazine resins.

4. Conclusions

The maxima in glass transition temperature were observed in BA-a and BA-mt alloyed with epoxy whereas BA-35x showed the decreasing trend with an epoxy content. However, all three benzoxazine-epoxy alloys can yield polymer matrices with T_gs of greater than 200°C which are considered as high temperature polymer. The storage modulus at room temperature of the three arylamine-based benzoxazine alloyed with epoxy resin were found to increase with increasing the amount of the benzoxazine fraction.

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