

# Effect of Novel Benzoxazine Reactive Diluent on Processability and Thermomechanical Characteristics of Bi-Functional Polybenzoxazine

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**ABSTRACT:** Effects of a monofunctional benzoxazine diluent (Ph-a) on properties of a bifunctional benzoxazine resin (BA-a) have been investigated. The BA-a/Ph-a mixtures are miscible in nature rendering the properties highly dependent on their compositions. The viscosity of the BA-a resin can be reduced to one third using only about 10% by weight the Ph-a diluent. The addition of the Ph-a resin into the BA-a resin can also lower the liquefying temperature of the resin mixtures whereas the gel point is marginally decreased. The gel point, which depends on the BA-a/Ph-a mixtures and the cure temperature, was determined by the frequency independence of loss tangent in the vicinity of the sol-gel transition. The relaxa-

tion exponent values of the copolymer were found to be 0.24–0.55, which is dependent on the cure temperature. Gel time of the BA-a/Ph-a systems decreases with increasing temperature according to an Arrhenius relation with activation energy of  $60.6 \pm 1.5$  kJ/mol. Flexural moduli of the BA-a/Ph-a polymers also increase with the Ph-a mass fraction, however, with the sacrifice of their flexural strength and glass-transition temperature. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2928–2938, 2007

**Key words:** gelation; thermal properties; modification; curing of polymers; thermosets

## INTRODUCTION

As polymer applications have been diversified, the improvement of their properties particularly by modification of the existing polymers becomes increasingly important. For instance, a diluent has been used in several polymers or resins to formulate solvent-free compounds for coating, adhesive, or composite applications.<sup>1–6</sup> In the composite fabrication process, the resin viscosity is an important variable, affecting the resin flow-out and wetting characteristics. Furthermore, diluted resins are employed in some formulations to achieve easier handling, increase filler loading, and reduce costs. In the past, organic solvents have been used extensively to lower resin viscosity. However, because of recent stricter environmental regulations on the release of volatile organic compounds (VOC), solvent use has become increasingly restrictive.<sup>4</sup>

Generally, there are two classes of diluents. A reactive diluent is the ingredient that actually undergoes chemical reaction with the resin and becomes part of the polymeric structure. The other type is a nonreactive diluent, which can also lower the viscosity of the base resin but does not take part in the polymer structure formation. The class of resin that most widely used as a reactive diluent is epoxy resin. This type of reactive diluent was reported to provide good properties and enhance processing characteristics of the base resin.<sup>1,4–6</sup> Urethane prepolymer as well as unsaturated polyester had also been investigated as reactive diluents of some major polymer constituents.<sup>7,8</sup> In recent years, a novel class of thermosetting resin based on a benzoxazine structure has gained substantial attraction because of some of its intriguing properties.

Benzoxazine resins were reported to provide self-polymerizable crosslinking system 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. Moreover, polybenzoxazines possess several outstanding properties such as good dimensional stability, low moisture absorption, and rela-

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tively high glass-transition temperature even though they have relatively low crosslinking density.<sup>6,9–11</sup>

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 when compared with traditional phenolic resins. Ishida and Rimdusit<sup>10</sup> reported that the use of low melt viscosity benzoxazine resins filled with boron nitride ceramics could improve the composite thermal conductivity with the value as high as 32.5 W/mK at the maximum filler loading of 78.5% by volume. In the system of polybenzoxazine wood, substantial amount of woodflour filler (i.e., up to 70% by volume) was reported to be incorporated in the polybenzoxazine matrix with a significant enhancement in the resulting thermal and mechanical properties of the obtained wood composites.<sup>12</sup>

As some types of bifunctional benzoxazine resins are solid at room temperature, many studies have been done to utilize reactive diluents to lower liquefying temperature as well as to further reduce melt viscosity of the benzoxazine resins. For example, Ishida and Allen<sup>1</sup> reported that an addition of liquid epoxy (EPON825) to a polybenzoxazine greatly increased a crosslink density of the thermosetting matrix and strongly influenced its mechanical properties besides an obvious ability of the epoxy diluent to lower the liquefying temperature of the resin mixtures. Moreover, Rimdusit et al.<sup>5</sup> showed that toughness of polymer alloys of rigid polybenzoxazine and low viscosity flexible epoxy (EPO732) systematically increased with the amount of the epoxy due to an addition of more flexible molecular segments in the polymer hybrids. Although a significant reduction in viscosity and liquefying point was obtained using the epoxy, the resulting benzoxazine-epoxy resin mixtures required higher curing temperature than that of the neat benzoxazine resin. The addition of a small fraction of phenolic novolac resin as an initiator into the benzoxazine-epoxy mixtures was reported to be crucial to help lowering their curing temperature.<sup>6,13</sup>

A liquid monofunctional benzoxazine resin had also been investigated as a reactive diluent of solid benzoxazine resins. The melt viscosity of a bifunctional benzoxazine resin, a bisphenol-A-aniline type (BA-a), was reported to be substantially reduced by the use of a monofunctional benzoxazine resin i.e., 4-cumylphenol-aniline type (C-a).<sup>4</sup> However, the addition of the C-a resin into the solid BA-a resin was reported to lower a crosslink density of the polymer network and led to the decrease in thermal degradation temperature and char yield of the polymer hybrids. Recently, Wang and Ishida<sup>14</sup> investigated a series of monofunctional benzoxazine resins. In their arylamine-based resins, a monofunctional phenol-ani-

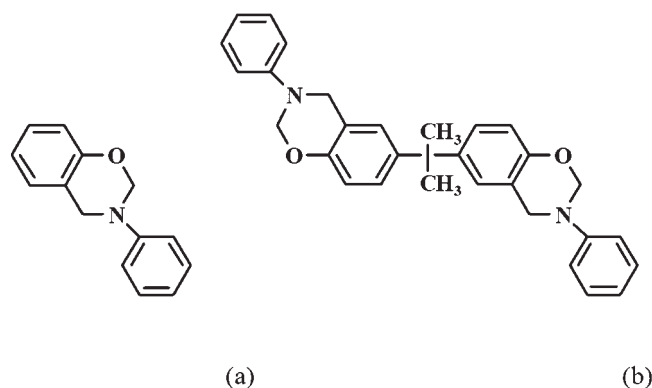
line type benzoxazine (Ph-a) showed superior processability as well as thermal stability to the phenol-to-luidine type (Ph-mt) and the phenol-xylylidine type (Ph-35x) resins. Degradation temperature and char yield of the Ph-a polymer were also reported to exhibit the values even greater than those of its bifunctional counterpart i.e., BA-a polymer. Its  $T_{g,DSC}$  of 142°C is the highest among the three monofunctional resins tested although the value is lower than that of the bifunctional BA-a polymer i.e., 160°C. Finally, curing kinetic analysis of a random copolybenzoxazine of BA-a type and Ph-a type resins has also been reported to exhibit an activation energy of about 50–84 kJ/mol.<sup>15</sup> The obtained activation energy of the copolybenzoxazine is also relatively close to that of the BA-a type resin ( $E = 81$  kJ/mol).<sup>15–18</sup>

In this investigation, the Ph-a benzoxazine resin is examined as a novel reactive diluent of a bifunctional benzoxazine resin i.e., BA-a resin. Since the structure of the Ph-a resin resembles the BA-a resin chemically, a miscible mixture of the Ph-a and the BA-a resins should be expected. The processability, thermal, and mechanical properties of the resulting polymer hybrids are also studied.

## EXPERIMENTAL

### Materials

Monofunctional and bifunctional benzoxazine resins used are phenol-aniline type (Ph-a) and bisphenol-A-aniline type (BA-a). The synthesis procedures are followed those mentioned in Ref. 14. The chemical structures of these resins are shown in Scheme 1. Bisphenol-A was kindly supplied by Thai Polycarbonate Co., Ltd. (TPCC). Formaldehyde was obtained from Merck Co. Phenol and aniline were obtained from Fluka Chemicals Co. The as-synthesized Ph-a resin is a clear yellowish liquid at room temperature while the as-synthesized BA-a benzoxazine resin is a light yellow solid at room temper-



**Scheme 1** (a) The reactive diluent-Ph-a monofunctional benzoxazine monomer structure and (b) the BA-a bifunctional benzoxazine monomer structure.

ature and can be molten to yield a low viscosity resin at about 80°C. The BA-a resin was ground to fine powder and both were kept in a refrigerator prior to use.

### Specimen preparation

BA-a/Ph-a polybenzoxazine specimens were prepared by weighing a desired amount of the resin mixture in an aluminum container. The binary systems to be investigated are BP91, BP82, BP73, BP64, BP55, and BP28. In the nomenclature, B stands for the bifunctional BA-a resin whereas P is the monofunctional Ph-a resin. The numbers after the letters are the mass ratio of the two monomers in the respective order. The two resins were mixed mechanically at 80°C for about 15 min to obtain a homogeneous mixture. The mixture was then poured onto a metal mold and cured in an air-circulating oven using a step heating profile as follows to ensure fully cured condition: 100°C for 45 min, 120°C for 45 min, 160°C for 90 min, and 200°C for 120 min. The densities of the poly(BA-a), the poly(Ph-a), and the BA-a/Ph-a polymer hybrids were determined by a water displacement method, ASTM D792-00 (Method A). The dimension of each specimen is 25 × 60 × 3 mm<sup>3</sup>.

### Rheological property measurement

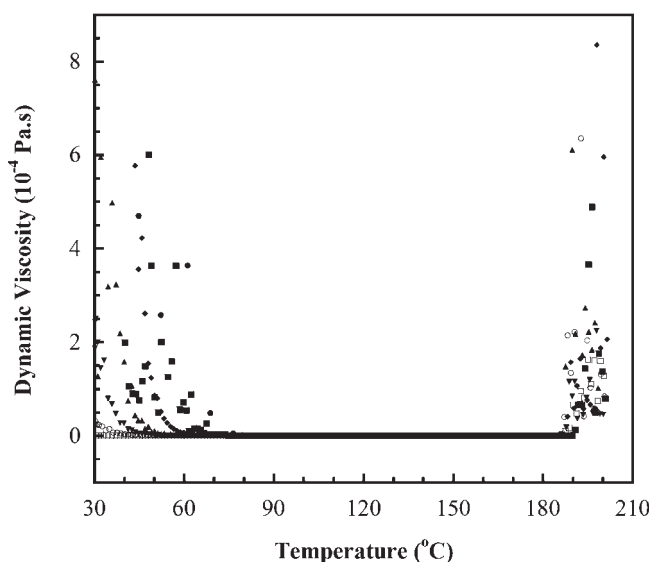
Dynamic shear viscosity measurements were performed on a parallel plate rheometer using HAAKE RheoStress model RS600. Disposable aluminum plates having 20 mm in diameter were preheated for 30 min with the gap zeroed at the testing temperature. The void-free monomer mixture, which was liquefied at 80°C, was then poured onto the lower plate and the gap was set to 0.5 mm. The temperature was immediately equilibrated at the set point for about 180 s and the test was then started.

### Differential scanning calorimetry

The curing behaviors of BA-a/Ph-a resin mixtures were investigated using a differential scanning calorimeter (DSC) model DSC 2910 from TA Instruments. Specimen mass of about 5 mg was sealed in a nonhermetic aluminum pan with lid. The heating rate used was 10°C/min from 30 to 300°C. The experiment was performed under nitrogen purging.

### Thermogravimetric analysis

Thermal decomposition characteristic of each specimen was determined using a thermogravimetric analyzer from Perkin–Elmer (Diamond TG/DTA). The experiment was performed under nitrogen purging with a constant flow of 100 mL/min. Sample mass of 15–20 mg was heated using a linear heating rate of 20°C/min from room temperature to 800°C.



**Figure 1** Processing window of the BA-a/Ph-a resin mixtures at various Ph-a resin using a heating rate of 2°C/min: (●) BA-a resin, (■) BP91, (◆) BP82, (▲) BP73, (▼) BP64, (○) BP55, (□) Ph-a resin.

### Dynamic mechanical analysis

Dynamic mechanical properties of the specimens were obtained using a dynamic viscoelastic analyzer model DMA 242 C from Netzsch Inc. The test was done under a three point bending mode. The strain amplitude used was 30 μm at the frequency of 1 Hz. The specimen was heated at a rate of 2°C/min from 30 to 250°C. The specimen is 52 × 10 × 2.5 mm<sup>3</sup>. Glass-transition temperature was taken from the temperature at the maximum point on the loss modulus curve.

### Bending test

The flexural behaviors of the cured copolymers were determined using a universal testing machine (Instron Instrument, model 5567) at room temperature. The specimens were tested according to ASTM D790-00 (Method I). A crosshead speed of 1.2 mm/min was used. Three specimens from each copolymer composition were tested and the average values were reported.

## RESULTS AND DISCUSSION

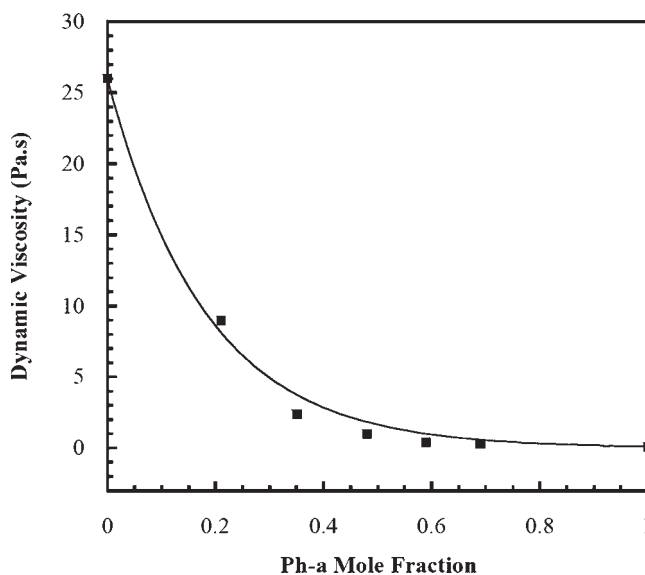
### Chemorheological properties of BA-a/Ph-a resin mixtures

All BA-a/Ph-a resin mixtures are miscible giving homogenous and transparent liquid mixtures. The effect of the Ph-a benzoxazine resin on the chemorheology of the BA-a/Ph-a resin mixture is shown in Figure 1. In the rheograms, the temperature of the resin mixture was ramped from about 30°C up to the temperature

beyond the gel point of each sample using a heating rate of 2°C/min and the dynamic viscosity was recorded. On the left hand side of Figure 1, we can see that the liquefying temperature of the binary mixture as indicated by the lowest temperature that the viscosity rapidly approaches its minimum value significantly decreases with increasing the Ph-a mass fraction. For consistency, the temperature at the viscosity value of 1000 Pa s was used as a liquefying temperature of each resin. On the basis of this convention, the liquefying temperatures of BA-a resin, BP82 and BP64 resins are 73, 58, and 42°C, respectively. This is due to the fact that the Ph-a resin used is liquid while the BA-a resin is solid at room temperature. The addition of the liquid Ph-a in the solid BA-a resin yielded a softer solid at room temperature ranging from BP91 to BP64. With increasing the Ph-a mass fraction beyond 40% by weight i.e., BP64, the resin mixture became highly viscous liquid with decreasing viscosity down to the liquid Ph-a having lowest viscosity at room temperature. In practice, lowering the resin liquefying temperature obviously enables the use of lower processing temperature for a compounding process, which is desirable in various composite applications.

On the right hand side of Figure 1, gel temperature of each resin mixture can also be determined. Interestingly, the gel temperature of each resin ranging from BA-a, BP91, to BP55 shows minor influence by an increase in the Ph-a fraction compared to its effect on the liquefying temperature. In this case, the maximum temperature at which the viscosity was rapidly raised above 1000 Pa s was used as gel temperature of each resin. The gel temperatures of BA-a, BP82, BP64, and Ph-a were determined to be 190, 187, 185, and 185°C, respectively. As a result, the addition of the Ph-a diluent seems to marginally affect the gel temperature of the BP resin mixtures with the value of only few degrees lower than that of the BA-a resin. In general, the opposite trend i.e., an increase in the gel temperature with an addition of a reactive diluent has been reported.<sup>19</sup> The addition of the Ph-a diluent to the BA-a resin was, therefore, found to largely maintain the thermal curing or processing condition of the obtained resin mixtures. Furthermore, all the tested BP resin mixtures can maintain their relatively low viscosity within the temperature range of 80–185°C. This behavior provides sufficiently broad processing window for a compounding process in a composite manufacturing.

Dynamic shear viscosity at 90°C of BA-a/Ph-a resin mixture as a function of Ph-a resin content is exhibited in Figure 2. From the experiment, the mixture viscosity was found to be significantly reduced from that of the neat BA-a benzoxazine resin with increasing mole fraction of the Ph-a diluent. For instance, BP91 (mole fraction of BA-a = 0.79 and Ph-a = 0.21) possesses a melt viscosity measured at 90°C to be about 9 Pa s while that of the BA-a resin compared at the same



**Figure 2** Dynamic viscosity at 90°C of the BA-a/Ph-a resin mixtures at various Ph-a mole fractions: Experimental data (symbol), Predicted data with the Grunberg-Nissan equation (solid line).

temperature is ~ 26 Pa s. The addition of the liquid Ph-a resin of only 10% by weight (0.21 mol fraction) can thus significantly improve processability of the BA-a resin by reducing the a-stage viscosity of the BA-a resin to be about one third. In theory, the lower viscosity of the resin can enhance the ability of the resin to accommodate greater amount of filler and increase filler wettability of the resin during the preparation of the molding compound. Furthermore, we can see that viscosity of the BA-a/Ph-a resin mixture shows a non-linear relationship with the Ph-a mole fraction. A viscosity model of liquid mixture based on Grunberg-Nissan equation<sup>20</sup> was used to predict the correlation between viscosity and composition fraction. The Grunberg-Nissan equation was the most suitable equation for determining the viscosity of nonassociated liquid mixture as discussed by Monnery et al.<sup>21</sup> However, Irving<sup>22</sup> showed that a good agreement was also obtained for some associated liquid mixture. The calculation of liquid viscosity for a binary mixture using this equation is as follows:

$$\ln \eta_m = \sum_{i=1}^c x_i \ln \eta_i + \frac{1}{2} \sum_{i=1}^c \sum_{j=1}^c x_i x_j G_{i,j} \quad (1)$$

where  $G_{i,i} = 0$ . for example, for a binary mixture ( $c = 2$ )

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{1,2} \quad (2)$$

In eqs. (1) and (2),  $\eta_m$  is the mean viscosity of liquid mixture (Pa s);  $\eta$  is the viscosity of pure component  $i$  and  $j$  (Pa s);  $x_i$  and  $x_j$  are the mole fractions of the component  $i$  and  $j$ ;  $G_{i,j}$  is the interaction parameter (Pa s); and  $c$  is the number of components.

Since chemical structures of the BA-a benzoxazine resin and the Ph-a resin are similar, the components in a mixture should not interact exclusively with each other and thus should behave in a similar manner as an individual component.<sup>23</sup> Consequently, it was assumed that the interaction parameter ( $G_{1,2}$ ) in eq. (2) would be small and could be neglected. Thus eq. (2) can be written as:

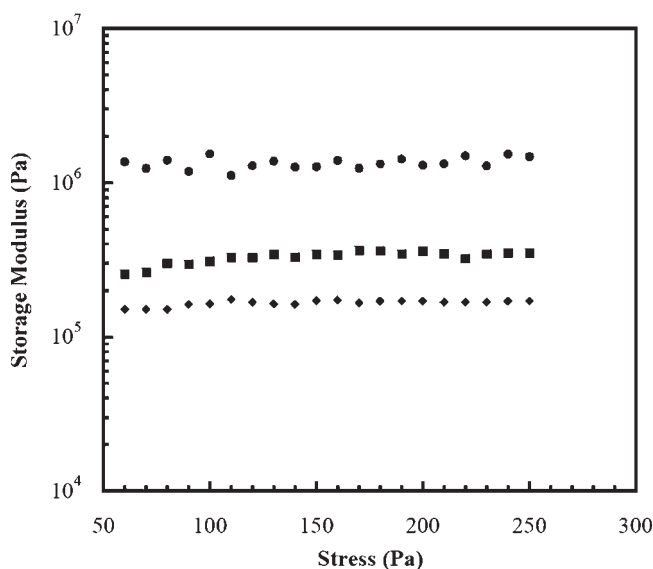
$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 \quad (3)$$

In Figure 2, the calculated viscosity curve by the Grunberg-Nissan equation seems to fit well with the experimental viscosity data thus the present assumption is suitable for the prediction of the liquid viscosity of the BA-a/Ph-a resin mixtures in the entire composition range.

### Investigation of the gel formation

One important aspect of thermosetting polymers is their gelation behavior, especially, the kinetics of gelation as well as gel time. Sol-gel transition, known as the gel point, is one critical phenomenon that is crucial, especially, for the material processing. The linear viscoelastic properties in a dynamic experiment are sensitive to the three-dimensional network formation and can be used to precisely examine the gel point. Measurements of oscillatory shear moduli have frequently been used to continuously monitor viscoelastic properties in chemically crosslinked networks during the gel evolution. An oscillatory experiment is preferable since minimum deformation is applied to the material, particularly the delicate gel material, at the gel point. The frequency independence principle of the loss tangent in the vicinity of the gel point in accordance with Winter-Chambon criterion has been widely used to define gel point of crosslinked polymers.<sup>19,24–27</sup>

In oscillatory shear mode using a rotational controlled stress rheometer, the range of stress that can be applied to the material is needed to be verified because different types of gels are able to sustain different levels of stress. Therefore, the gel must exhibit a linear relationship between stress and strain, i.e., modulus is constant in the whole stress range used. In the investigation to find the suitable stress range, the gel point is obtained using a frequency of 1 rad/s with 2.5% strain. The gelation temperature used was 140°C for each resin composition i.e., BP91, BP73, and BP55. After reaching the gel point, which was defined by the crossover of the storage and loss modulus during an isothermal cure (ASTM D4473), the temperature of each BA-a/Ph-a resin mixture was immediately lowered and equilibrated at 120°C to suppress further gelation process while still maintaining the fluidity of the sol fraction. The stress sweep experiment at the gel



**Figure 3** Stress sweep experiment at the gel points of BP systems: (●) BP91, (■) BP73, (◆) BP55.

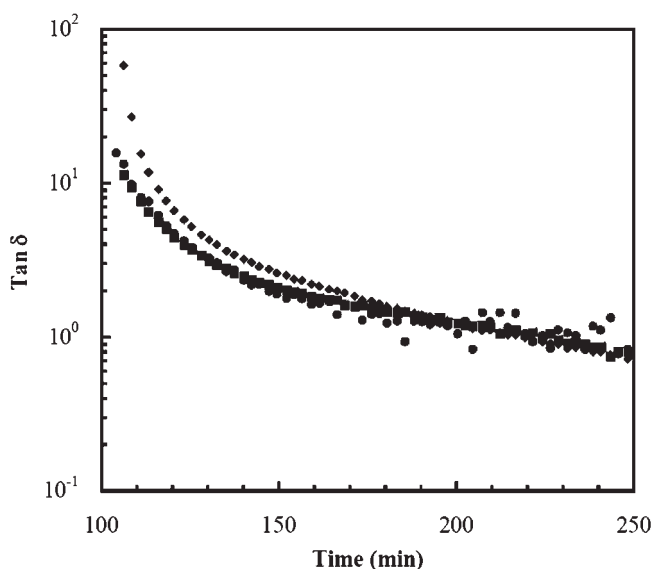
point of the three different compositions of the BA-a/Ph-a resin mixtures was then performed using a frequency of 1 rad/s within the stress range of 60–250 Pa. The results are shown in Figure 3. From the plots, we can observe that all of the BA-a/Ph-a systems show a fairly constant modulus in this stress range. This means that a linear viscoelastic relationship can be obtained in this chemically crosslinked systems in the vicinity of their gel points.

In the rest of our experiments, the minimum constant stress value of 60 Pa will be used for gel point determination to ensure both linear viscoelastic relationship as well as minimum gel network rupturing. The dynamic moduli of a curing system under oscillatory shear, generally, follow the power law at the gel point.<sup>19,28–30</sup> The power law equation at the gel point may be used to examine the gel time and the corresponding value of the relaxation exponent is obtained from eq. (4)

$$\tan \delta = G''/G' = \tan(n\pi/2) \quad (4)$$

when  $n$  is the relaxation exponent.

Figure 4 is a plot of  $\tan \delta$  at different frequencies as a function of heating time of BP91 using the gelation temperature of 140°C. The gel time is obtained from the point where the loss tangent is frequency independent. Experimentally, it is the point where the loss tangents of different frequencies intersect each other. From the plot, the values of  $\tan \delta$  intersect at a time = 198 min corresponding to the gel time,  $t_{gel}$ , of this resin. The gel times for the BA-a/Ph-a systems at different temperatures were also obtained from the  $\tan \delta$  plots similar to that in Figure 4. The relationship of gel time as a function of temperature of the BA-a/Ph-a



**Figure 4** Loss tangent at various frequencies as a function of time for BP91at 140°C: (●) 10 rad/s, (■) 31 rad/s, (◆) 100 rad/s.

systems was presented in Table I. We can see that the gel time of all resin mixture compositions tends to decay exponentially with increasing temperature. This is due to the fact that increasing the processing temperature increases the rate of crosslinking of BA-a/Ph-a systems. Consequently, at higher temperature, the systems reach their gel points more quickly and the gel times are shorter. From the table, the gel time of BP91 ranges from 198 min at 140°C to about 63 min at 170°C. Moreover, at the same temperature, we can observe that the gel time decreases with increasing the Ph-a content, which is likely due to the faster crosslinking rates of the mixtures. For instance, at 140°C, the gel time of BP91 = 198 min, BP73 = 185 min, and BP55 = 182 min. This also implies that the curing conversion of the BP resin can also increase with the Ph-a content compared at the same processing condition.

As mentioned in eq. (4), at the gel point, a power law may be used to examine the corresponding value of the relaxation exponent,  $n$ , for each gelling systems. The relaxation exponent is a specific parameter that is related to the growing clusters in a material near the

**TABLE I**  
Gelation Times of BA-a/Ph-a Systems  
at Different Temperature

Temperature (°C)	Gelation time, $T_{gel}$ (min)		
	BP91	BP73	BP55
140	198	185	182
150	152	147	142
160	94	89	82
170	63	62	58

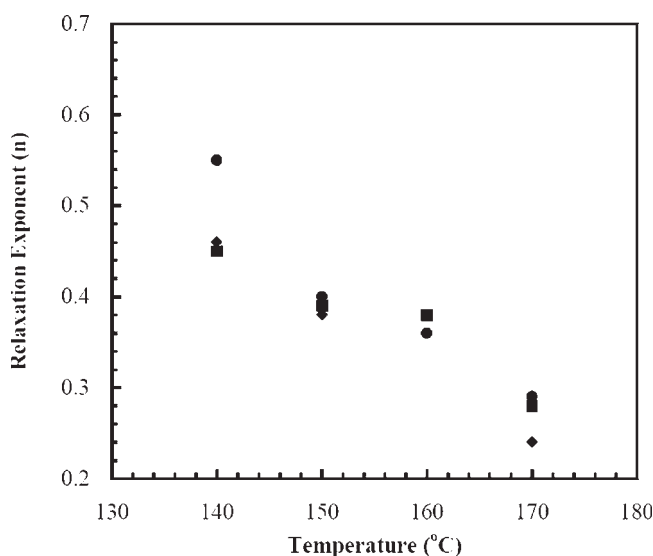
gelation threshold. For the BA-a/Ph-a systems, the relaxation exponent at the gel point was determined from the  $\tan \delta$  plots and by using eq. (4). Figure 5 exhibits the relaxation exponent values of BP91, BP73, and BP55 at different cure temperature. The values were almost unchanged with the resin composition. Moreover, the relaxation exponent tends to decrease with increasing the cure temperature. Recently, the relaxation exponent values of the chemical gel systems have been reported to show a nonuniversal value and vary with the gelling system. The values of the relaxation exponents of the chemical gels were reported to be 0.2–0.7 in PDMS system,<sup>31</sup> 0.5–0.7 in polyurethane system,<sup>32</sup> and 0.68–0.72 in BA-m benzoxazine system<sup>29</sup> etc. In this work, the relaxation exponent values of BA-a/Ph-a systems were found to be 0.24–0.55 depending on the cure temperature. This indicates that the cure temperature shows some effect on the structure of the network clusters formed at the gel point for these BA-a/Ph-a resins.

Furthermore, from the gel times calculated at different temperatures, we can determine apparent activation energies for the BA-a/Ph-a systems. The curing reaction can be represented by a generalized kinetic equation:

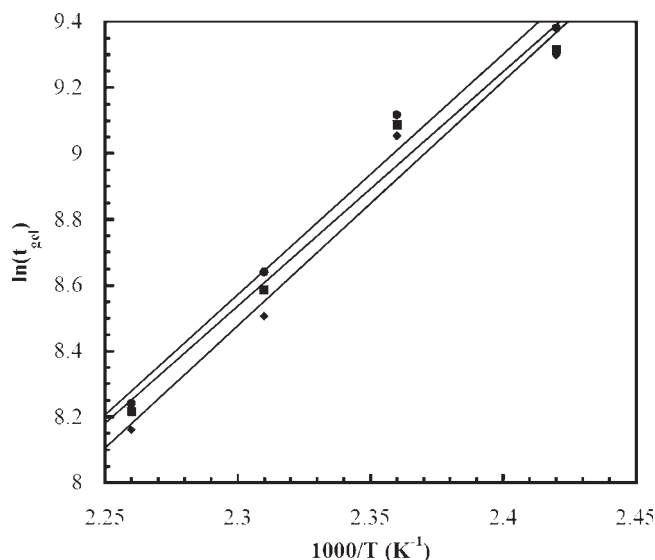
$$\frac{dx}{dt} = k(T) f(x) \quad (5)$$

where  $k(T)$  is the rate constant,  $t$  is the reaction time,  $f(x)$  represents an arbitrary functional form for the curing conversion,  $T$  corresponds to the temperature of the reaction. The rate constant,  $k(T)$ , is temperature dependent according to Arrhenius law shown in eq. (6)

$$k(T) = A \exp(-E/RT) \quad (6)$$



**Figure 5** The relaxation exponent ( $n$ ) from gel point as a function of cure temperature: (●) BP91, (■) BP73, (◆) BP55.



**Figure 6** Plots of gel times as a function of  $1/T$  based on rheological data at various Ph-a mass fractions: (●) BP91, (■) BP73, (◆) BP55.

An integration of eq. (5) from the onset of the cross-linking reaction ( $t = 0$ , and  $x = 0$ ) to the gel point ( $t = t_{\text{gel}}$ , and  $x = x_c$ ) yields

$$\ln(t_{\text{gel}}) = \ln\left(\int_0^{x_c} dx/f(x)\right) - \ln(A) + E/RT \quad (7)$$

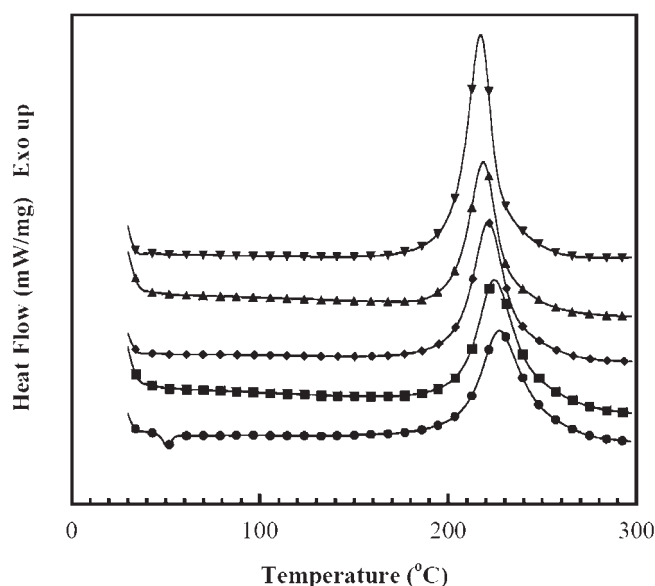
where  $t_{\text{gel}}$  is the gel time,  $A$  is the pre-exponential factor,  $E$  is the activation energy, and  $T$  is temperature in Kelvin.

Thus, the activation energies for gelation can be determined from the slope of the plots between  $\ln(t_{\text{gel}})$  against  $1/T$  as depicted in Figure 6 and the corresponding activation energies are summarized in Table II. We can notice that the activation energy values of BP91, BP73, and BP55 are approximately the same. This means that the Ph-a reactive diluent does not significantly affect the kinetics of the gelation process of the resin mixtures. The apparent activation energy value averaged from the slopes of the plots was determined to be  $60.6 \pm 1.5$  kJ/mol. The value is in the same range as that of epoxy molding com-

**TABLE II**  
Apparent Activation Energy Values Obtained from Rheological Tests for BA-a/Ph-a Systems at Various Ph-a Resin Contents

BP contents	Activation energy (kJ/mol)
BA-a	88 <sup>a</sup>
BP91	61
BP73	59
BP55	62

<sup>a</sup>  $E$ -value of benzoxazine resin (BA-a) from Ref. 29.



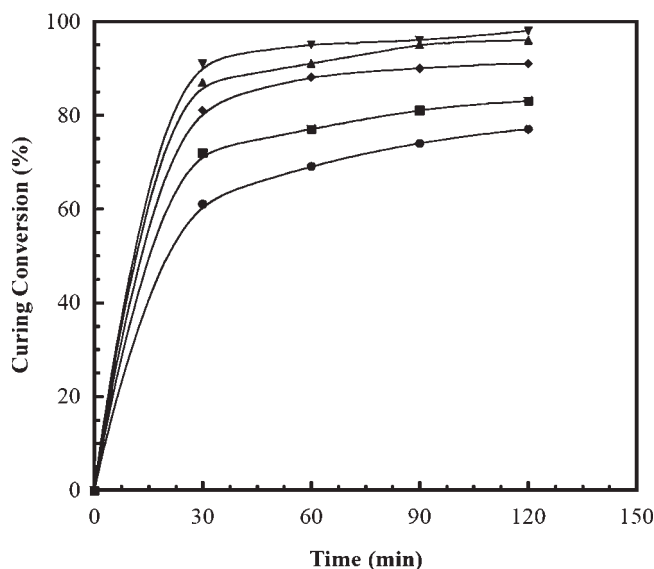
**Figure 7** DSC thermograms of the BA-a/Ph-a resin mixtures at different Ph-a resin contents: (●) BA-a resin, (■) BP82, (◆) BP55, (▲) BP28, (▼) Ph-a resin.

pound, using the same technique to determine the gel point, i.e.,  $E = 61\text{--}73$  kJ/mol.<sup>30,33</sup>

### Curing reaction investigation by calorimetry

The DSC thermograms for the curing reaction of the BA-a resin, the Ph-a diluent, and the BA-a/Ph-a mixtures at various compositions are shown in Figure 7. From the thermograms, we observed only single dominant exothermic peak of the curing reaction in each resin composition. The phenomenon suggests that the reaction to form a network structure of these binary mixtures takes place simultaneously at about the same temperature. In our previous work, the split of the curing exotherms with an addition of a reactive diluent, i.e., in benzoxazine-epoxy resin mixture, has been observed. In these resin systems, the newly formed exothermic peak at higher temperature was attributed to the interaction between the benzoxazine monomer and the epoxy diluent whereas the peak at lower temperature was due to the reaction among the benzoxazine monomers.<sup>13</sup>

On the contrary, the curing peak temperature observed in our BA-a/Ph-a mixtures in Figure 7 is systematically shifted to a slightly lower temperature with increasing the Ph-a diluent. This is due to the fact that the curing peak exotherm of the BA-a resin was determined to be  $228^\circ\text{C}$  while that of the Ph-a diluent was found to be  $217^\circ\text{C}$ . Our Ph-a diluent thus possesses a slightly low curing temperature comparing with the base BA-a resin. The addition of Ph-a diluent into the BA-a resin, therefore, renders a positive effect on curing reaction of the obtained resin mixture by

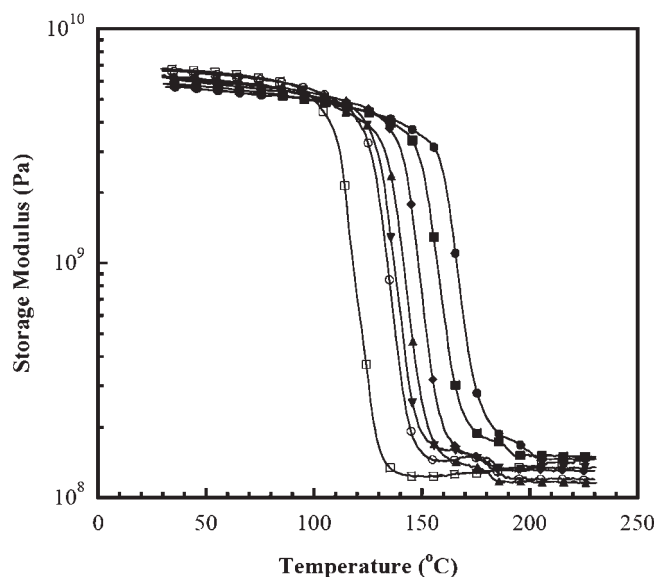


**Figure 8** Conversion-time curve of thermally cured the BA-a/Ph-a mixtures at 180°C: (●) BA-a resin, (■) BP82, (◆) BP55, (▲) BP28, (▼) Ph-a resin.

lowering its curing temperature even though of only marginally. A relationship between curing conversion with curing time of the BA-a/Ph-a resin mixtures at 180°C is illustrated in Figure 8. The trend of each curve is similar to the observed dramatic increase in the degree of conversion at the first 30 min of the curing program. The longer curing time beyond 30 min can increase the degree of conversion of each resin marginally with the maximum achievable conversion depending on the resin composition. From the plot, the curing conversions at 180°C and 120 min of the Ph-a, BP28, BP55, BP82 and BA-a polymers are 98, 96, 91, 83, and 76%, respectively. This result also suggests that our Ph-a reactive diluent renders a faster curing than the BA-a. Its presence in the BA-a can help lowering the curing temperature of the resulting resin mixtures.

### Mechanical property of the polymer hybrids

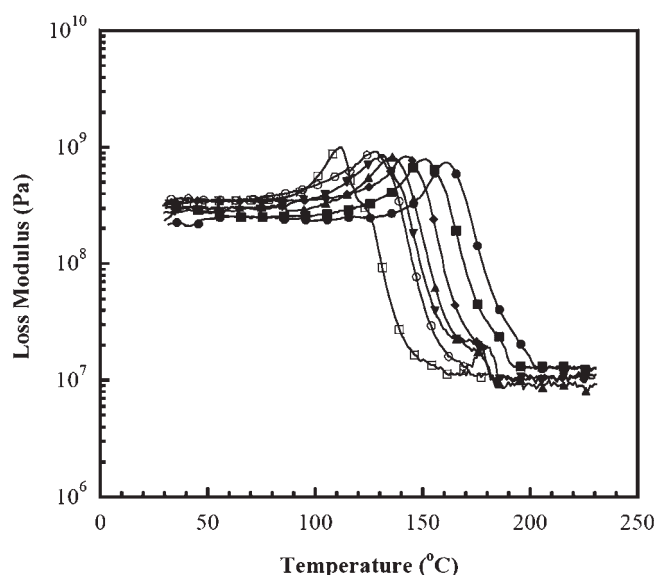
The effect of the Ph-a composition on the dynamic mechanical properties of the BA-a/Ph-a polymers is depicted in Figures 9–11. The storage modulus in the glassy state region reflecting molecular rigidity of the BA-a/Ph-a polymer networks is shown in Figure 9. From this figure, we can clearly see that the storage modulus of the poly(Ph-a) is higher than that of the poly(BA-a). The storage modulus at the room temperature of the poly(Ph-a) exhibits a value of about 6.7 GPa whereas that of the poly(BA-a) is ~ 5.7 GPa. The Ph-a network is thus stiffer molecularly than the BA-a network. Moreover, the storage modulus of the BA-a/Ph-a polymers was found to systematically increase when the Ph-a resin composition increased as a result of the addition of the more rigid molecular



**Figure 9** Storage modulus of the BA-a/Ph-a polymer as a function of temperature at different Ph-a contents: (●) poly(BA-a), (■) BP91, (◆) BP82, (▲) BP73, (▼) BP64, (○) BP55, (□) poly(Ph-a).

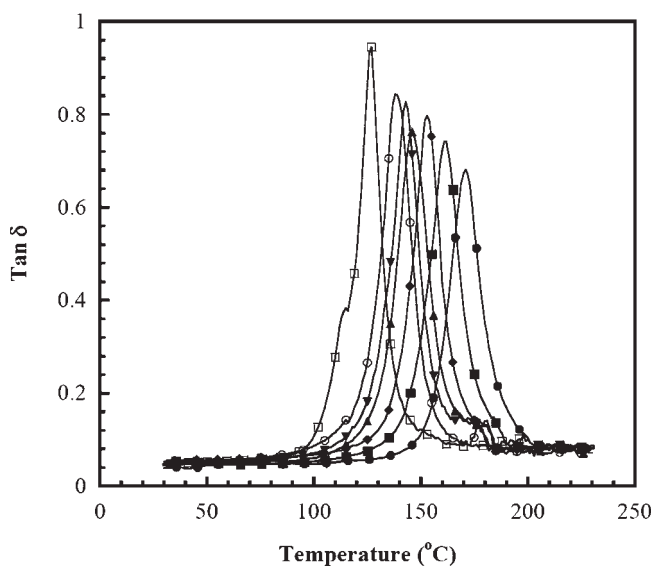
segments of the poly(Ph-a) into the network as discussed above. However, the presence of the Ph-a fraction in the poly(BA-a) network trends to lower the rubbery plateau modulus of the polymer hybrids as seen in Figure 9. This behavior implies that the cross-linked density of the polymer hybrids decreases with an increase of the Ph-a fraction.

The glass transition temperatures ( $T_g$ 's) of the BA-a and Ph-a polymers as well as their copolymers were determined from the loss modulus peak in the dynam-



**Figure 10** Loss modulus of the BA-a/Ph-a polymer as a function of temperature at different Ph-a contents: (●) poly(BA-a), (■) BP91, (◆) BP82, (▲) BP73, (▼) BP64, (○) BP55, (□) poly(Ph-a).

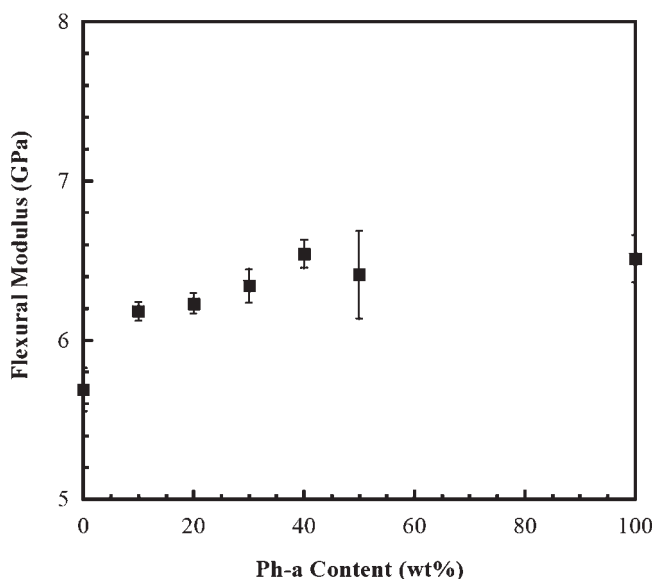




**Figure 11** Tan  $\delta$  of the BA-a/Ph-a polymers as a function of temperature at different Ph-a contents: (●) poly(BA-a), (■) BP91, (◆) BP82, (▲) BP73, (▼) BP64, (○) BP55, (□) poly(Ph-a).

ical mechanical thermograms as seen in Figure 10. The average  $T_{g, DMA}$  of the poly(Ph-a) and poly(BA-a) were reported to be about 115 and 160°C, respectively.<sup>5,9,12,14</sup> In Figure 10, the  $T_g$ s of the BP polymer hybrids were expectedly found to increase with the mass fraction of BA-a polymer. In our study, the  $T_g$ s of poly(BA-a), BP82, BP64, and poly(Ph-a) were determined to be 160, 142, 128, and 111°C, respectively. The  $T_g$  values of both parent polymers are consistent with those reported elsewhere<sup>5,9,12,14</sup> with the  $T_g$ s of their polymer hybrids varied systematically depending on the composition of the BP polymers. The loss modulus curve for each BP composition also reveals only one  $\alpha$ -relaxation peak suggesting the presence of a single phase material in these polymer hybrids. In theory, if the two starting materials have undergone phase separation upon copolymerization, two glass transition peaks could be expected, one for each of the starting homopolymer.

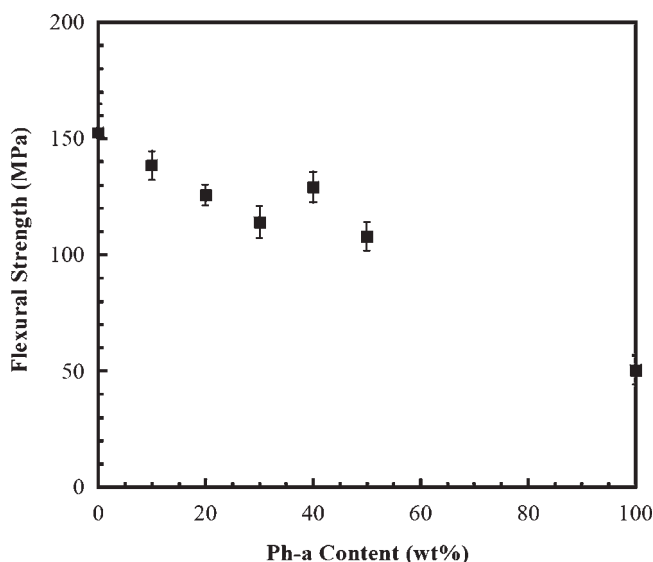
The tan  $\delta$  curve of the BA-a/Ph-a polymers at various Ph-a compositions is also illustrated in Figure 11. Again, only a single tan  $\delta$  peak was observed in each BP polymer which is in good agreement with the loss modulus result in Figure 10. The magnitude of the  $\alpha$ -relaxation from the tan  $\delta$  peak reflects trend in large scale segmental mobility in the polymer network. In the network, a greater separation between crosslinks permits greater mobility of chain segments while the width of the  $\alpha$ -relaxation peak of the tan  $\delta$  curve relates to network homogeneity. From our experiment, the maximum amplitude of the  $\alpha$ -relaxation peak was found to increase with increasing the Ph-a resin composition. This behavior suggests the lower crosslinking density of the BP polymers when the



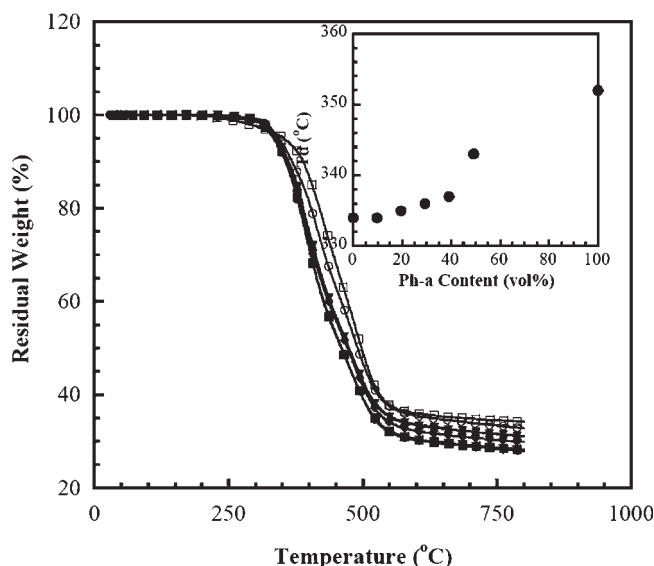
**Figure 12** Flexural modulus of the BA-a/Ph-a polymers as a function of Ph-a compositions.

Ph-a mass fraction increases thus allowing greater segmental mobility in the polymers. The lower degree of crosslinking of the BP polymers with the amount of the Ph-a content was also confirmed by the lower rubbery plateau modulus of the polymer hybrids with increasing the amount of the Ph-a diluent as appeared in Figure 9. Moreover, the widths at half height of the  $\alpha$ -relaxation peaks are about the same for all Ba-a/Ph-a polymers. This implies that the degree of network homogeneity of the two polymers as well as their hybrids is likely to be similar.

Figure 12 shows the flexural moduli of the specimens at different Ph-a contents. From this plot, the



**Figure 13** Flexural strength of the BA-a/Ph-a polymers as a function of Ph-a compositions.



**Figure 14** TGA thermograms of the BA-a/Ph-a polymers at different Ph-a mass fractions: (●) poly(BA-a), (■) BP91, (◆) BP82, (▲) BP73, (▼) BP64, (○) BP55, (□) Poly(Ph-a).

flexural moduli of the samples were found to increase with increasing the Ph-a resin. This correlation is in good agreement with the modulus values obtained from our dynamic mechanical analysis in the previous section. The flexural modulus of the poly(BA-a) was calculated to be  $5.69 \pm 0.14$  GPa, while that of the poly(Ph-a) was  $6.51 \pm 0.15$  GPa. Furthermore, the flexural modulus values of the BA-a/Ph-a polymers at various Ph-a contents ranging from 0 to 50% by weight tends to increase with the poly(Ph-a) mass fraction. For instance, BP55 possesses a flexural modulus value of about  $6.41 \pm 0.28$  GPa, which is also close to that of poly(Ph-a). The phenomenon is attributed to the ability of the Ph-a diluent to easily react to form a crucial part of the BA-a polymer networks as a result of their similarity in chemical nature. In Figure 13, the flexural strength of the poly(Ph-a) was found to be significantly lower than that of the poly(BA-a) i.e., 50 MPa versus 152 MPa of poly(BA-a). Additionally, the flexural strength of the BA-a/Ph-a polymers was observed to decrease with increasing the Ph-a content in the polymer hybrids from 0 to 50% by weight. The lower degree of crosslinking of the poly(Ph-a) comparing with that of poly(BA-a) might be responsible for the observed characteristics. The phenomenon is also understandable as the Ph-a resin has functional groups only half of those of the BA-a resin. Its ability to crosslink is thus inferior to that of the BA-a resin.

#### Thermal degradation behaviors of BA-a/Ph-a polymers

The TGA thermograms of the poly(BA-a), the poly(Ph-a), and the BA-a/Ph-a polymers are shown in

Figure 14. Intriguingly, all specimens exhibit an improvement in their degradation temperature at 5% weight loss and char yield over the poly(BA-a) with an addition of the Ph-a diluent. The degradation temperature at 5% weight loss of the poly(BA-a) was determined to be  $334^\circ\text{C}$  comparing with the value of  $352^\circ\text{C}$  of the poly(Ph-a). In addition, the decomposition temperature of the BA-a/Ph-a polymers was found to gradually increase with increasing the mass fraction of the poly(Ph-a) as shown in the inset of Figure 14. This behavior can be explained by the fact that there is no isopropyl moiety in the poly(Ph-a) structure. Therefore, the less stable, weaker moieties in the poly(Ph-a) structure are eliminated whereas in poly(BA-a), the isopropyl linkages from its bisphenol-A structure has been reported to undergo thermal decomposition at relatively lower temperature.<sup>14,34,35</sup>

The study on a bisphenol-A-based polybenzoxazine exposed to ultraviolet radiation has revealed that the isopropyl linkage is the reactive site of cleavage and oxidation.<sup>36</sup> Moreover, the substituents of poly(Ph-a) are also different from that of poly(BA-a). Poly(BA-a) has only one unblocked ortho position to form the hydroxyl group that is subjected to electrophilic aromatic substitution upon its ring-opening polymerization while the poly(Ph-a) has two unblocked positions, one at the ortho and another at the para position. The study on polybenzoxazine model dimers has also demonstrated that the absence or presence of the substituents has profound effects on thermal decomposition patterns and the char formation of the dimers. Therefore, the absence of isopropyl moiety along with the absence of substituents at both ortho and para positions is likely responsible for the greater thermal stability of the poly(Ph-a).<sup>36,37</sup> Other possibilities, such as fewer short-chain branches in the poly(Ph-a) structure, which can serve as the initiation sites of the degradation process, can also attribute to the improvement of its thermal stability. As a result, the char yield of the BA-a/Ph-a polymers systematically increases from that of the poly(BA-a) with an increase in the Ph-a content.

## CONCLUSIONS

The monofunctional Ph-a resin can effectively serve as a reactive diluent of the bifunctional BA-a resin to further improve the latter processability. The viscosity and liquefying temperature of the BA-a/Ph-a mixtures were found to significantly decrease with the Ph-a mass fraction. The resin mixture renders miscible, homogeneous, and void-free cured specimen with the properties highly dependent on the composition of the resin mixture. The gelation exponent,  $n$ , of the BA-a/Ph-a mixtures is dependent on the cure temperature while the activation energy for the gelation pro-

cess of the BA-a/Ph-a mixtures was found to be constant and independent on the Ph-a mass fraction. The incorporation of the poly(Ph-a) into the poly(BA-a) can improve the stiffness as well as the thermal stability (in terms of degradation temperature at 5% weight loss and char yield) of the specimens whereas the  $T_g$  and flexural strength of the BA-a/Ph-a polymers were found to decrease with the Ph-a mass fraction.

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## References

- Ishida, H.; Allen, D. J. *Polymer* 1996, 37, 4487.
- Park, L. J.; Lee, H. Y.; Han, M.; Hong, S. K. *J Colloid Interface Sci* 2004, 270, 288.
- Takeichi, T.; Guo, Y.; Rimdusit, S. *Polymer* 2005, 46, 4909.
- Huang, M. T.; Ishida, H. *Polym Polym Compos* 1999, 7, 233.
- Rimdusit, S.; Pirstpindvong, S.; Tanthapanichakoon, W.; Damrongsakkul, S. *Polym Eng Sci* 2005, 45, 228.
- Rimdusit, S.; Ishida, H. *Polymer* 2000, 41, 7941.
- Brzozowski, Z. K.; Bratychak, M. M. *React Funct Polym* 1997, 33, 217.
- Takeichi, T.; Guo, Y.; Agag, T. *J Polym Sci Part A: Polym Chem* 2000, 38, 4165.
- Ishida, H.; Allen, D. J. *J Polym Sci Part B: Polym Phys* 1996, 34, 1019.
- Ishida, H.; Rimdusit, S. *Thermochim Acta* 1998, 320, 177.
- Ishida, H. U.S. Pat. 5,543,516 (1996).
- Rimdusit, S.; Tanthapanichakoon, W.; Jubsilp, C. *J Appl Polym Sci* 2006, 99, 1240.
- Rimdusit, S.; Ishida, H. *J Polym Sci Part B: Polym Phys* 2000, 38, 1687.
- Wang, Y. X.; Ishida, H. *J Appl Polym Sci* 2002, 86, 2953.
- Su, Y. C.; Yei, D. R.; Chang, F. C. *J Appl Polym Sci* 2005, 95, 730.
- Ishida, H.; Rodriguez, Y. *Polymer* 1995, 36, 3151.
- Ishida, H.; Rodriguez, Y. *J Appl Polym Sci* 1995, 58, 1751.
- Jubsilp, C.; Damrongsakkul, S.; Takeichi, T.; Rimdusit, S.; *Thermochim Acta* 2006, 447, 131.
- Rimdusit, S.; Ishida, H. *Rheol Acta* 2002, 41, 1.
- Grunberg, L.; Nissan, A. H. *Nature* 1949, 164, 799.
- Monnery, W. D.; Svrcek, W. Y.; Mehrotra, A. K. *Can J Chem Eng* 1995, 73, 3.
- Irving, J. B. *Viscosity of binary liquid mixtures: A survey of mixture equations*, 1977. NEL Report 630.
- Allen, C. A. W.; Watts, K. C.; Ackman, R. G.; Pegg, M. J. *Fuel* 1999, 78, 1319.
- Kjønixsen, A. L.; Nyström, B. *Macromolecules* 1996, 29, 5215.
- Chiou, B. S.; English, R. J.; Khan, S. A. *Macromolecules* 1996, 29, 5368.
- Commereuc, S.; Bonhomme, S.; Verney, V.; Lacoste, J. *Polymer* 2000, 41, 217.
- Meng, J.; Hu, X. C.; Boey, F. Y.; Li, L. *Polymer* 2005, 46, 2766.
- Winter, H. H.; Mours, M. *Adv Polym Sci* 1997, 134, 167.
- Ishida, H.; Allen, D. J. *J Appl Polym Sci* 2001, 79, 406.
- Kwak, G. H.; Park, S. J.; Lee, J. R. *J Appl Polym Sci* 2001, 81, 646.
- Scanlan, J. C.; Winter, H. H. *Macromolecules* 1991, 24, 47.
- Winter, H. H.; Morganeli, P.; Chambon, F. *Macromolecules* 1988, 21, 532.
- Halley, P. J. *J Appl Polym Sci* 1997, 64, 95.
- Ishida, H.; Sanders, D. P. *J Polym Sci Part B: Polym Phys* 2000, 38, 3289.
- Hemvichian, K.; Ishida, H. *Polymer* 2002, 43, 4391.
- Macko, J. A.; Ishida, H. *J Polym Sci Part B: Polym Phys* 2000, 38, 2687.
- Hemvichian, K.; Laobuthee, A.; Chirachanchai, S.; Ishida, H.; *Polym Degrad Stab* 2000, 76, 1.