

Effect of Triphenyl Phosphate Flame Retardant on Properties of Arylamine-Based Polybenzoxazines

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ABSTRACT: Three types of arylamine-based benzoxazine resins modified with both condensed-phase and gas-phase action flame retardant, i.e. triphenyl phosphate (TPP) at various weight ratios were investigated. From rheological study, it was found that the viscosity of benzoxazines/TPP mixtures were significantly lower than that of the neat benzoxazine monomers suggesting flow property enhancement. Furthermore, differential scanning calorimetry results revealed that the onset and the maximum temperatures of the exothermic peak, due to the ring opening polymerization of benzoxazine resins, shifted to lower temperatures with increasing TPP. In addition, all polybenzoxazines possessed relatively high char yield, which increased as the TPP content increased thus enhancing their flame retardancy. The limiting oxygen index values of the flame retarded polybenzoxazines also increased with TPP addition. The maximum flame retardancy of UL94 V-0 class was obtained with an addition of only few percents of TPP in the polybenzoxazines. Flexural strength, flexural modulus, and glass transition temperature of those polybenzoxazines tended to decrease with an addition of TPP mainly due to its plasticizing effect. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

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INTRODUCTION

Benzoxazine resins, a new type of phenolic resins, were developed to overcome the shortcomings of traditional phenolic while retaining their benefits. Benzoxazine resins can be easily synthesized from phenol, formaldehyde, and amine either by employing solution or solventless methods. The polymerization of resins proceeds via ring-opening of oxazine rings by thermal cure. On curing, benzoxazine resins create a phenolic-like structure with inherent flame retardant properties.¹ Polybenzoxazines exhibit the characteristics that found in traditional phenolic such as heat resistance, flame retardance, and good electrical insulation property. Besides, they also exhibit lots of unique characteristics including low melt viscosity, dimensional stability, excellent mechanical properties, as well as low water absorption.² Nowadays, polybenzoxazines are highly attractive from

electronic industries such as printed circuit board or encapsulation materials. However, the flame retardancy of polybenzoxazines is not high enough for the requirements of certain electronic applications thus an attempt to develop the flame retardancy of benzoxazine resins has been investigated.

The well known method to enhance the flame retardancy is the application of flame retardant additives, which mainly have an influence on two modes of actions, i.e. condensed phase and/or gas phase activities.³ The condensed phase effects of flame retardants are majorly related to coating and charring. When the char is formed, it inhibits gaseous products from diffusing to the pyrolysis zone and protects the polymer surface from heat and air.^{2,4,5} Whereas, the gas phase effects are relevant to the mechanism of hydrogen and hydroxyl radical scavengers which contribute to combustion reactions.^{6,7}

In general, the halogenated compounds are widely used to enhance the flame retardancy of polymers. Nevertheless, this kind of additive produces environmental problems because toxic combustion products are released during combustion. Because of the environmental concerns, non-halogenated based flame retardants become increasingly popular alternatives for replacing the halogenated flame retardants. Among the available non-halogenated based flame retardants, phosphorus containing compounds are frequently used as flame retardants. The most of literature on halogen-free retardants are deeply involved with phosphorus-based products. Furthermore, they are predicted to be the biggest growing share of flame retardant market.⁸ That is attributed to the fact that phosphorus flame retardants typically do not generate any toxic gas due to char formation; phosphorus is generally locked into the char.⁸ In addition, not only condensed phase action but also gas phase action occurs during the flame retardancy process, when phosphorus flame retardants are applied.

From the work of Sponton et al.⁹ they reported that incorporating phosphorus can improve fire resistant properties of polybenzoxazine. In their research, copolymerization of aniline-based benzoxazine (BA-a) with various molar ratios of phosphorus containing glycidyls (Gly-P) and silicon-containing epoxy (Gly-Si) were prepared. It was observed that the presence of phosphorus-containing epoxy significantly increased the limiting oxygen index (LOI) values of the resulting polymers even when the phosphorus content was only 1.7%. T_g was also found to increase with the amount of Gly-P while decreased with an addition of Gly-Si. Additionally, the phosphorus-based flame retardants are able to enhance the flammability of other polymeric systems. From the recent research,¹⁰ it was reported that the char yield of unsaturated polyester resin (UPR) could be enhanced when the phosphorus-based compound was added. The residual weight at 800°C of pure UPR was increased from 0.2% to 8.3% (at phosphorus content of 1.3 wt %). In the system of ethylene vinyl acetate copolymer (EVA), the V-2 classification of UL-94 test was obtained when loading 5 wt % of a complex of cyclodextrin nanosponge-phosphorus compounds.¹¹ Beach et al.³ studied the degradation enhancement of polystyrene by flame retardant additives. They reported that the active phosphorous species (such as HPO_2 , PO, PO_2 , and HPO_3 species) from triphenyl phosphate (TPP) could provide high potential for gas-phase action.

In order to enhance the flame retardancy of polybenzoxazine, TPP, phosphorus containing flame retardant, was incorporated because it is typically effective in thermosetting polymers and has an environmentally friendly profile with both condensed phase and gas phase actions. That means TPP can provide both the increase of char residue and the mechanism of radical scavengers. Moreover, TPP can be used as plasticizers. Three types of high temperature arylamine-based benzoxazine resins were modified with TPP, i.e. BA-a, *m*-toluidine based benzoxazine (BA-mt), and 3,5-xylidine based benzoxazine (BA-35x). The important properties were evaluated by the techniques of differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), flexural test, thermogravimetric analysis (TGA), limiting oxygen index (LOI) test, as well as UL-94 test.

EXPERIMENTAL

Materials

Bisphenol-A, polycarbonate grade, was kindly supplied by Thai Polycarbonate Co. (Rayong, Thailand). Para-formaldehyde ($\geq 95\%$ purity) was purchased from Merck & Co. (Hohenbrunn, Germany). A series of arylamines, i.e. aniline (99% purity), *m*-toluidine ($\geq 99\%$ purity), 3,5-xylidine ($\geq 97\%$ purity) from Fluka Chemicals Co. (Buchs, Switzerland). were used as-received. TPP was purchased from Ajax Finechem Co. (Auckland, New Zealand).

Preparation of Arylamine-Based Benzoxazine Resins

BA-a resin was synthesized from bisphenol-A, formaldehyde, and aniline in a molar ratio of 1 : 4 : 2. The monomer synthesis was followed a solvent-less technique. All reactants were mixed and heated to 110°C for about 30 min to yield a light yellow monomer product. The products were dissolved in diethyl ether and washed with 3N NaOH solution and distilled water. The purified products were dried over sodium sulfate. Finally, the solvent was evaporated. As the same procedure, BA-mt and BA-35x were synthesized by replacing aniline with *m*-toluidine and 3,5-xylidine, respectively.

Sample Preparation

The thick sample was prepared by mixing benzoxazine resins with TPP at various weight contents of TPP, i.e. 0, 2, 5, 8, and 10%. The mixtures were heated and mixed until the homogeneous resin mixtures were obtained. The curing step in an air-circulating oven was carried out at 150°C for 1 h, 170° for 1 h, 190°C for 1 h, and 210°C for 2 h. The polybenzoxazines were left to cool down and taken out from molding.

The thin film was prepared for DMA sample. The monomers were mixed with various contents of TPP i.e. 0, 2, 5, 8, and 10% in tetrahydrofuran (THF). The resin solutions were cast onto a glass plate and the cast films were dried at 60 and 100°C for 1 h each to remove THF. The curing step was the same as that of the thick sample. The thickness of the films obtained was about 100 μm .

Characterizations

Chemorheological properties of each mixtures were investigated using a rheometer (Haake Rheo Stress 600, Thermo Electron Cooperation) equipped with parallel plate geometry. The measuring gap was set at 0.5 mm. The processing window was performed under an oscillatory shear mode at a frequency of 1 rad/s. The testing temperature was ramped from room temperature at a heating rate of 2°C/min to a temperature beyond the gel point of each resin and the dynamic viscosity was recorded.

Curing behavior of the benzoxazine monomer with TPP at various weight ratios were examined using a DSC, Rigaku Thermo Plus 2 DSC8230 model. The samples were sealed in aluminum pans by weighing a monomer of approximately 5–10 mg. The calorimetric measurement was performed at a heating rate of 10°C/min and a nitrogen flow of 50 mL/min from room temperature to 300°C.

Thermal stability of flame retarded polybenzoxazines was measured using TGA, Rigaku Thermo Plus 2 TG-DTA TG8120. Mass of samples was in a range 10–15 mg. The sample was heated at

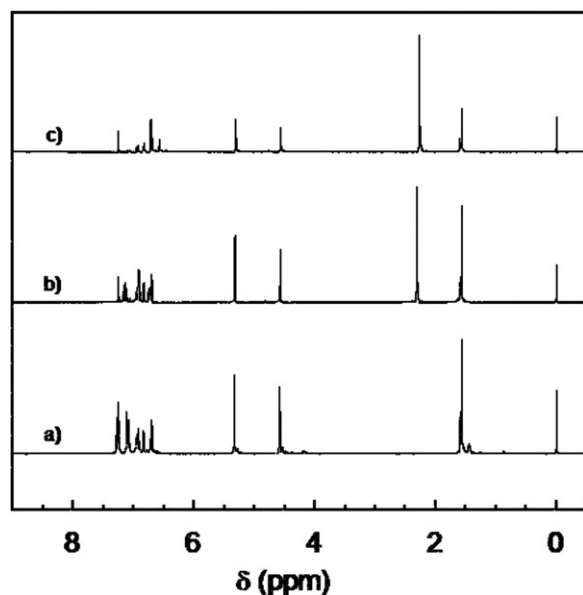


Figure 1. $^1\text{H-NMR}$ spectra of the neat arylamine-based benzoxazine resins: (a) BA-a, (b) BA-mt, and (c) BA-35x.

a heating rate $20^\circ\text{C}/\text{min}$ in argon atmosphere. Degradation temperature was determined at 5% weight loss of the specimen while char residue was recorded at 800°C .

Fire resistance of unmodified and modified polybenzoxazines was evaluated by LOI and UL 94 vertical tests. LOI values were examined using specimen bars ($70\text{ mm} \times 7\text{ mm} \times 3\text{ mm}$) according to ASTM D2863. The test was based on the determination of the lowest volume concentration of oxygen in a gas mixture of nitrogen and oxygen required for ignition and the onset of burning. A UL 94 standard for vertical test was performed using five specimens having a dimension of $120\text{ mm} \times 12\text{ mm} \times 3\text{ mm}$. The specimen was held in a vertical position. The lower end of specimen was contacted by a flame for 10 s to initiate burning. A second ignition was made after self-extinguishing of the flame at the sample for 10 s. The burning process was characterized by the times t_1 and t_2 pertaining to the two burning steps. The parameters t_1 and t_2 denoted the time between removing the methane flame and self-extinguishing of the sample. Moreover, it was also noted whether drips from the sample were released during the burning times t_1 and t_2 . If $t_1 + t_2$ were less than 10 s with no dripping, the specimen would be classified as a V-0 material.

RESULTS AND DISCUSSION

Chemical Structures of Benzoxazine Resins

A series of arylamine based-benzoxazine resins was synthesized from bisphenol-A, paraformaldehyde, and arylamine. The reaction products were purified to eliminate the partially ring-opened oligomers and unreacted reactant. The structure and purity of benzoxazine resins were identified by $^1\text{H-NMR}$. Figure 1 shows the $^1\text{H-NMR}$ spectrum of three types of benzoxazine resins studied in this work. According to Ishida and Sanders,¹² the characteristic protons at approximately 4.57 and 5.32 ppm were assigned to those of $-\text{Ar}-\text{CH}_2-\text{N}-$ and $-\text{O}-\text{CH}_2-\text{N}-$

bonds which are responsible for a formation of a benzoxazine ring. A resonance appearing near 1.57 ppm was associated with the methylene proton of bisphenol-A, whereas the signal in the range 6.5–7.5 ppm was from aromatic protons. BA-mt and BA-35x showed the development of signal at 2.31 and 2.27 ppm, respectively, which are related to methyl protons on the substituted aniline rings ($\text{Ar}-\text{CH}_3$). Nevertheless, the absence of resonance at 3.6 ppm indicated that the opened Mannich base and oligomeric compounds had been removed during the purification procedure.⁴ The spectra suggested that these three types of arylamine-based benzoxazine resins were highly pure.

Chemorheological Behavior of TPP-Modified Polybenzoxazines

Effects of TPP on the viscosity of BA-a were recorded as a function of dynamic viscosity with temperature ($^\circ\text{C}$) as shown in Figure 2. BA-a/TPP mixtures were miscible giving homogenous and transparent liquid mixtures. From the figure, the liquefying temperature was the transition of solid to liquid at low temperature that complex viscosity of resin rapidly approaches its minimum value and the gel temperature was the transition of liquid to solid at high temperature that complex viscosity was rapidly raised. In addition, the temperature range from the liquefying point to the gel point was called processing window which was the range of the lowest viscosity useful for polymer compounding or processing. For consistency in this study, the liquefying temperature of each resin was defined at the viscosity value of 1000 Pa s. Table I shows the rheological data of all benzoxazine resins. The liquefying temperature of BA-a, BA-mt, and BA-35x decreased from 64, 66, and 74 to 55, 56, and 65°C , respectively, with an increasing amount of TPP from 0 to 10 wt %. This was owing to the fact that TPP, a small molecule, became very low viscosity liquid above its melting point thus further lowering the viscosity of the benzoxazine resins. Lowering the resin liquefying temperature obviously enables the use of lower processing temperature of a compounding process, which is desirable in various applications.¹³ In addition, the gel temperature of the resin mixtures were shifted to lower temperature from 183, 180, and 175°C to 162, 161, and 160°C , respectively, with an increasing

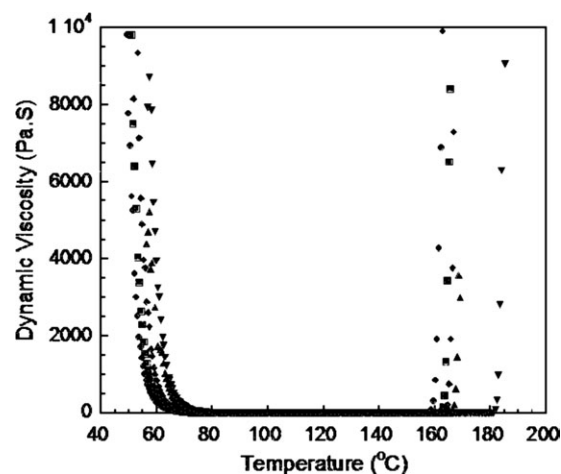


Figure 2. Processing window of BA-a resin at various TPP contents: (∇) 100 : 0, (\blacktriangle) 98 : 2, (\blacklozenge) 95 : 5, (\blacksquare) 92 : 8, and (\bullet) 90 : 10.

Table I. Liquefying and Gel Temperature of Arylamine-Based Polybenzoxazine at Various TPP Contents

| Sample | Resins : TPP | Liquefying temperature (°C) | Gel temperature (°C) |
|--------|--------------|-----------------------------|----------------------|
| BA-a | 100 : 0 | 64 | 183 |
| | 98 : 2 | 63 | 168 |
| | 95 : 5 | 59 | 165 |
| BA-mt | 92 : 8 | 56 | 164 |
| | 90 : 10 | 55 | 162 |
| | 100 : 0 | 66 | 180 |
| BA-35x | 98 : 2 | 64 | 167 |
| | 95 : 5 | 59 | 164 |
| | 92 : 8 | 56 | 164 |
| | 90 : 10 | 56 | 161 |
| | 100 : 0 | 74 | 175 |
| | 98 : 2 | 71 | 164 |
| | 95 : 5 | 69 | 162 |
| | 92 : 8 | 68 | 161 |
| | 90 : 10 | 65 | 160 |

amount of TPP from 0 to 10 wt %. The results from Figure 2 and Table I indicated that TPP additive could be able to accelerate curing reaction of the benzoxazine resins. When TPP additive is applied to all three types of arylamine-based benzoxazine resins, the temperature required for processing is lower.

Figure 3 represents dynamic shear viscosity of benzoxazine resins/TPP mixtures at 100°C. From the results, viscosity of all benzoxazine resins was noticeably reduced with an addition of TPP. BA-35x was observed to be the highest viscosity among the three benzoxazine resins. The complex viscosity were determined to be about 0.82, 1.41, and 3.72 Pa s for BA-a, BA-mt,

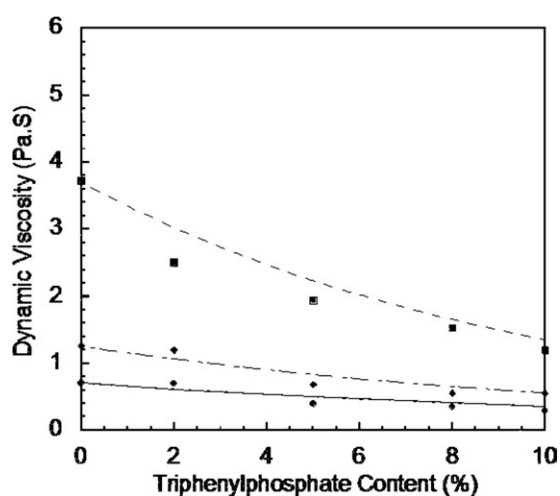


Figure 3. Dynamic viscosity at 100°C of the three types of benzoxazine with TPP resins mixtures at various TPP contents (▲) BA-a, (◆) BA-mt, and (■) BA-35x: Experimental data (symbol), predicted data with the Grunberg–Nissan equation (line) - - - BA-a, BA-mt, and ---- BA-35x.

and BA-35x, respectively, comparing at the same temperature. The viscosity of the benzoxazine resins dramatically decreased with only 2 wt % of TPP flame retardant. However, an increase of the TPP content from 2 to 10 wt % in the benzoxazine–TPP mixtures caused a slight decrease in viscosity of the three mixture systems to 0.29, 0.35, and 1.19 Pa s in BA-a/TPP, BA-mt/TPP, and BA-35x/TPP, respectively. In practice, the lower viscosity of the resin provides enhanced processability and aids filler wetting in molding compound preparation. Besides several equations employed for predicting viscosity correlation of liquid mixtures, the Grunberg–Nissan equation is one of the most widely used.² This equation was also evaluated by Reid et al. and Monnery et al. It was selected as the most suitable equation for computing viscosity of liquid mixtures.^{13–17} This empirical equation is written as:

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

For a binary mixture of component 1 and 2, the equation takes the form:

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \quad (2)$$

where η_m is the mean viscosity of liquid mixture (Pa s), η 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_{ij} is the interaction parameter (Pa s), $G_{ij} = 0$ for $i = j$, which is a function of the component as well as temperature. n is the number of components.¹⁴

G_{ij} is a mild function of temperature. This parameter has been regarded as a measure of the strength of the interaction between the components. It can be determined using:

$$G_{ij}(T) = 1 - [1 - G_{ij}(298.15)] \frac{573 - T}{275} \quad (3)$$

More recently, Isdale et al.¹⁸ proposed a group contribution method to estimate the binary interaction parameter at 298 K. From the theory, G_{ij} at 298.15 K can be calculated from

$$G_{ij} = \sum \Delta_i - \sum \Delta_j + W \quad (4)$$

$\sum \Delta_i$ and $\sum \Delta_j$ were estimated from the contributions at 298.15 K. Parameter W is given as:

$$W = \frac{(0.3161)(N_i - N_j)^2}{N_i + N_j} - (0.1188)(N_i - N_j) \quad (5)$$

If either of the component i or j contains atoms other than carbon and hydrogen, set $W = 0$. N_i and N_j are the number of carbon atoms in component i and j .¹⁷

For these systems, the interaction parameter could be neglected because the benzoxazine resins did not interact with TPP. Thus, the equation can be written as follows:

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 \quad (6)$$

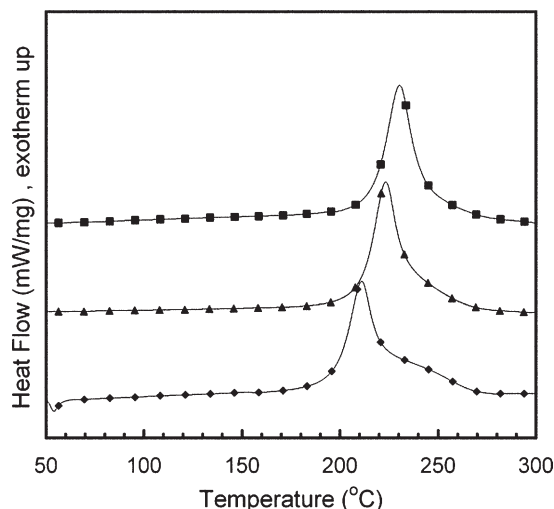


Figure 4. DSC thermograms of neat arylamine-based benzoxazine resins: (■) BA-a, (▲) BA-mt, and (◆) BA-35x.

The curves constructed using Grunberg–Nissan equation was illustrated in Figure 3. The empirical model was found to fit relatively well with the experimental viscosity data thus can be used to predict the viscosity of these TPP-modified benzoxazine resins.

Curing Process Investigation

Polymerization of benzoxazine resins can be completed merely by thermal treatment. From DSC experiment as shown in Figure 4, BA-mt and BA-35x exhibited different curing behaviors from that of BA-a. In the case of BA-mt and BA-35x, two overlapped exothermic curing peaks were observed while BA-a showed only a single dominant exothermic peak. This indicated that the curing reaction of BA-mt and BA-35x possessed at least two curing stages. These results were also in good

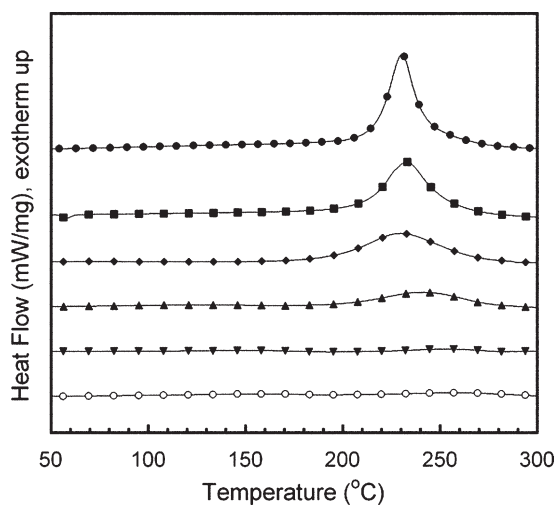


Figure 5. DSC thermograms of neat BA-a at various curing conditions: (●) uncured, (■) 150°C/1 h, (◆) 150°C/1 h + 170°C/1 h, (▲) 150°C/1 h + 170°C/1 h + 190°C/1 h, (▼) 150°C/1 h + 170°C/1 h + 190°C/1 h + 210°C/1 h, and (○) 150°C/1 h + 170°C/1 h + 190°C/1 h + 210°C/2 h.

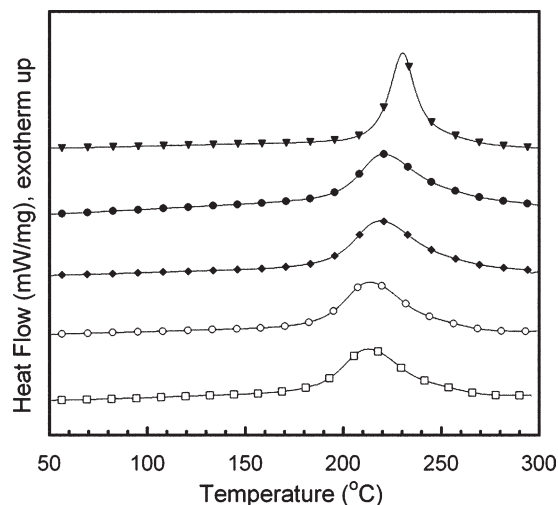


Figure 6. DSC thermograms at various BA-a : TPP ratios: (▼) 100 : 0, (●) 98 : 2, (◆) 95 : 5, (○) 92 : 8, and (□) 90 : 10.

agreement with the report by Ishida and Sanders.¹² The curing process in the main exotherm (first peak) at lower temperature was assigned to the oxazine ring opening reaction. Meanwhile, the small shoulder, at higher temperature beside the main peak, corresponded to the reaction at the *para* position of arylamine ring which generated the biphenolic methylene linkages called arylamine Mannich bridge and methylene-linked structures.

The fully cured condition of the benzoxazine and TPP mixtures was determined from the disappearance of the exothermic heat of reaction under the DSC curve. Figure 5 shows the DSC thermograms of the neat BA-a. From the figure, the area under the exothermic peaks decreased with increasing the curing temperature, using a curing time of 1 h at each temperature or as specified in the figure. The fully cured stage was achieved at 210°C up to 2 h. The degrees of conversion of the polymerized benzoxazine resins after each curing stage were calculated according to the following relationship.

$$\% \text{ conversion} = \left(1 - \frac{H_{\text{rxn}}}{H_0} \right) \times 100 \quad (7)$$

where, H_{rxn} is a heat of reaction of a partially cured specimen.

H_0 is a heat of reaction of an uncured resin.

Both H_{rxn} and H_0 values can be obtained from DSC experiments. The heat of reaction of uncured BA-a was determined to be 282 J/g (0% conversion). The heat of reaction was reduced to 193 J/g (32% conversion), 170 J/g (40% conversion), 89 J/g (68% conversion), 17 J/g (94% conversion), 10 J/g (96% conversion) after curing at 150°C for 1 h, 170°C for 1 h, 190°C for 1 h, 210°C for 1 h, and 210°C for 2 h.

Effects of TPP flame retardant on curing behaviors of BA-a were monitored by a DSC as shown in Figure 6. The investigated weight ratios of the BA-a : TPP were 100 : 0, 98 : 5, 92 : 8, and 90 : 10. As seen in the figure, the exothermic

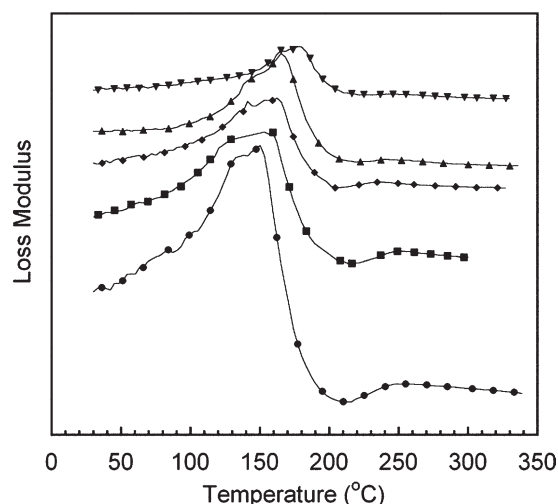


Figure 7. Loss modulus (E'') at various BA-a : TPP ratios: (▼) 100 : 0, (▲) 98 : 2, (◆) 95 : 5, (■) 92 : 8, and (●) 90 : 10.

peak of BA-a was shifted to 221, 218, 214, AND 212°C for 98 : 2, 95 : 5, 92 : 8, and 90 : 10 mass ratios of BA-a : TPP. Moreover, the heat of reaction determined from the area under the main exothermic peak and the second shoulder exothermic peak also decreased with the TPP content. These results were also in good agreement with the chemorheological results. The observed curing acceleration suggested that TPP might act as a Lewis acid catalyst or initiator for polymerization of the benzoxazine resins. Only small amount of TPP, i.e. 2% by weight, was needed to obtain significant curing acceleration. However, the addition of larger amount of TPP in these benzoxazine resins showed marginal shifting of the exothermic peak to lower temperature. The reduction of the area under the peak was also observed with the amount of the TPP possibly due to the dilution effect of the additive.

Glass Transition Temperature Determination

Viscoelastic behavior reflects the combined viscous and elastic responses, under mechanical stress, of materials which are intermediate between liquid and solid in character. Glass transition temperatures are characterized by a change from hard, glass-like material to a rubbery solid.¹⁹ The behavior can be examined directly using DMA.

The plots of the loss modulus (E'') of BA-a at various TPP contents as a function of temperature (°C) are shown in Figure 7.

Table II. Glass Transition Temperature (T_g) of Arylamine-Based Polybenzoxazine at Various TPP Contents

| Benzoxazine : TPP | T_g (°C) | | |
|-------------------|------------|-------|--------|
| | BA-a | BA-mt | BA-35x |
| 100 : 0 | 177 | 220 | 255 |
| 98 : 2 | 166 | 210 | 228 |
| 95 : 5 | 162 | 195 | 210 |
| 92 : 8 | 154 | 192 | 207 |
| 90 : 10 | 151 | 186 | 201 |

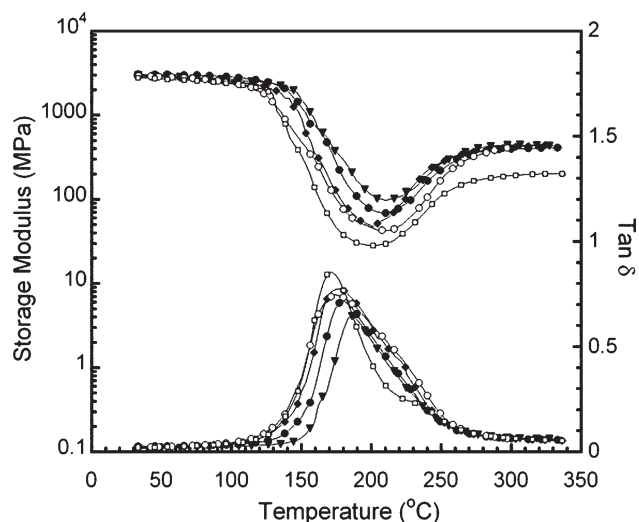


Figure 8. Storage modulus (E') and dissipation factor ($\tan \delta$) of BA-a at various TPP contents (▼) 100 : 0, (●) 98 : 2, (◆) 95 : 5, (○) 92 : 8, and (□) 90 : 10.

The glass transition temperature or T_g was determined from the maximum point on the loss modulus curves. As seen from summarized data in Table II, the neat BA-35x demonstrated the highest T_g at 255°C comparing with those of BA-mt, or BA-a which were found to be 220 and 177°C, respectively. The introduction of aryl-substituted amines was reported to help increase the network crosslink density that occurred at the *para* position of arylamine ring, i.e. arylamine Mannich bridge and methylene linkage formation. The additional crosslinking would clearly increase the T_g of the network.⁹ The T_g s of three types of polybenzoxazines exhibited the same tendency that T_g of BA-a, BA-mt, and BA-35x values decreased to 151, 186, and 201°C, respectively, with an addition of 10% by weight of TPP. The lower T_g of polybenzoxazines with increasing TPP content was because TPP (a low molecular weight additive acting as a plasticizer) gets in between the polymer chains and spaces them apart from each other. That leads to the increased free volume, and the ease of segment mobility. In other word, the polymer chains can move around at lower temperatures resulting in a decrease in T_g .²⁰

Figure 8 exhibits storage modulus (E') and dissipation factor ($\tan \delta$) of BA-a at various TPP contents. The results of polybenzoxazine reveal that the height of the $\tan \delta$ peaks tended to increase with increasing TPP. The addition of TPP made the rubbery plateau region lower than that of the neat polybenzoxazines. In principle, the crosslinked density (v_e) of a polymer network can be estimated from the rubbery plateau modulus (E_r) as presented in eq. (8).^{21,22}

$$v_e = E_r / (3RT_r), \quad (8)$$

where E_r is the storage modulus at $T_g + 30^\circ\text{C}$, T_r is the temperature for E_r in Kelvin unit, R is gas constant ($8.314 \text{ m}^3 \cdot \text{Pa} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$). From the calculation, the crosslink density of polybenzoxazine at 0%, 2%, 5%, 8%, and 10% of TPP were $8,318 \text{ mol/m}^3$, $5,701 \text{ mol/m}^3$, $4,596 \text{ mol/m}^3$, $3,580 \text{ mol/m}^3$, $2,391 \text{ mol/m}^3$,

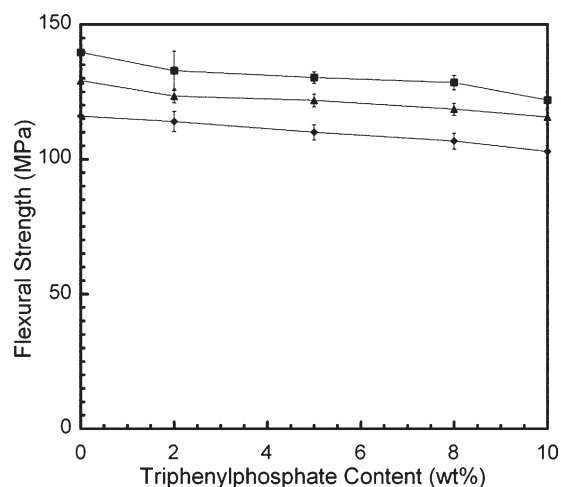


Figure 9. Flexural strength of arylamine-based polybenzoxazines at various TPP contents: (■) BA-a, (▲) BA-mt, and (◆) BA-35x.

respectively. In other words, the crosslink density values tended to decrease with TPP contents. From Figure 8, the increase of height of $\tan \delta$ could associate with higher segmental mobility and more relaxing species.²³ This indicated that the networks of neat polybenzoxazines were denser than those of polybenzoxazines-TPP systems.

Flexural Property Examination

In three-point-bending test, the specimen having standard geometry is supported at its ends. A load is then applied at the center of the specimen under standard conditions. The force is measured and registered during the deformation. From the evaluation, the flexural (bending) strength (proportional to the maximal load-bearing capacity) and the flexural modulus (proportional by the stiffness of material) can be determined.²⁴

Flexural strength represents an ability of materials to absorb maximum force at rupture. This ability concerns with storing and dissipating forces in polymers in the form of movement, rotation, and vibration of molecules, which might be transformed to heat, deformation, or sound, etc.²⁴ The flexural properties of polybenzoxazines at various weight percentage of TPP are shown in Figures 9 and 10. Figure 9 is a plot of the flexural strength (MPa) of the three polybenzoxazines as a function of the TPP content (wt %). In principle, flexural strength of a thermosetting resin is influenced by a number of interrelated parameters including T_g , molecular weight between crosslinks, free volume, chemical structure, network regularity and perfection, and some other contributing factors.²⁵ As seen in Figure 9, the flexural strengths of the neat polybenzoxazines were determined to be 139.6, 129.2, and 116.0 MPa for BA-a, BA-mt, and BA-35x, respectively, i.e. BA-a exhibited the highest flexural strength among the three polybenzoxazines. However, the flexural strengths of BA-a, BA-mt, and BA-35x decreased to 122.0, 115.7, and 102.8 MPa, respectively, with an addition of 10% by weight of TPP. Flexural strengths of the modified polybenzoxazines decreased approximately 11–12% in comparison with those of the neat polybenzoxazines. These were acceptable range for our systems. This result was ascribed to the effect of free

volume of the modified specimens. A higher free volume with increasing TPP contents might lower interactions and enhance the ability of the polymer chain segments to flow under load by such means as rotationally configurational changes.²⁵ In addition, as described previously, TPP tended to disperse only physically, without no chemical bonding, in a polybenzoxazine matrix thus provided no contribution to mechanical performance of the polymer.

The plot of flexural modulus (GPa) of the arylamine-based polybenzoxazines at various weight percents of TPP is shown in Figure 10. As seen in the figure, BA-a possessed the highest flexural modulus value of 5.8 GPa. For BA-mt and BA-35x, those values were found to be about 5.4 and 4.8 GPa, respectively. Furthermore, the flexural modulus values of BA-a, BA-mt, and BA-35x at 10% weight of TPP decreased to 4.3, 4.3, and 3.6 GPa, respectively. The observed phenomena also confirmed that TPP was only physically mixed with the polybenzoxazine matrix to yield a homogeneous mixture. The effect of TPP, as a small molecule, tended to increase free volume of the polymer matrix thus promoting its strain at break. However, the presence of this small molecular weight additive contributed to the lowering of mechanical strength and modulus of the polybenzoxazine matrices.

Thermal Stability Evaluation

Effect of TPP content on degradation temperature at 5% weight loss ($T_{d5\%}$) and char yield of polybenzoxazines are summarized in Table III. The $T_{d5\%}$ s of BA-mt and BA-35x were higher than that of BA-a, i.e. $T_d = 330, 350,$ and 349°C for BA-a, BA-mt, and BA-35x, respectively. Ishida and Sanders¹² reported that the polymerized network structures of BA-mt and BA-35x, contained additional crosslinking structures, i.e. arylamine Mannich bridge and methylene linkage. Moreover, the more rigid networks created by the methylene linkages create kinetic barriers to weight loss as well. Those bond formations therefore contribute to the observed enhancement in T_d of BA-mt and BA-35x comparing with that of BA-a. On the other hand, the char yields of BA-a, BA-mt, and BA-35x were not significantly

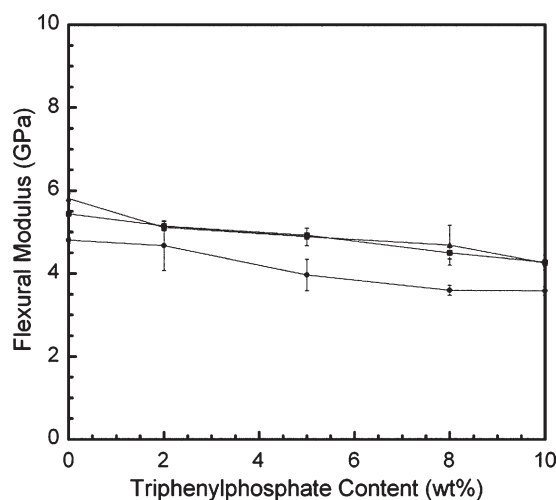


Figure 10. Flexural modulus of arylamine-based polybenzoxazines at various TPP contents: (■) BA-a, (▲) BA-mt, and (◆) BA-35x.

Table III. Degradation Temperatures (T_d) at 5% Weight Loss and Residue Weights (Char Yield) at 800°C of Arylamine-Based Polybenzoxazine at Various TPP Contents

| Benzoxazine : TPP | BA-a | | BA-mt | | BA-35x | |
|-------------------|------------|----------|------------|----------|------------|----------|
| | T_d (°C) | Char (%) | T_d (°C) | Char (%) | T_d (°C) | Char (%) |
| 100 : 0 | 330 | 30.2 | 350 | 31.4 | 349 | 31.0 |
| 98 : 2 | 326 | 33.6 | 343 | 33.8 | 343 | 32.2 |
| 95 : 5 | 312 | 34.8 | 336 | 34.7 | 335 | 33.3 |
| 92 : 8 | 310 | 36.2 | 333 | 37.2 | 328 | 34.7 |
| 90 : 10 | 295 | 37.7 | 330 | 39.3 | 326 | 35.9 |

different with the values in a range of 30–31%. Thus, the additional crosslinking from phenolic Mannich bridges and methylene linkages provided insignificant effect on the char formation of the resulting polybenzoxazine networks.

The $T_{d5\%}$ values tend to decrease with TPP content for all three types of polybenzoxazines. Due to its relatively low boiling point (245°C), under temperature scan, TPP tended to release from the specimen before the thermal degradation of benzoxazine matrix. Meanwhile, the char yields of polybenzoxazines in the presence of TPP were observed to be higher than that of the neat polybenzoxazines. The char yields at 800°C of BA-a, BA-mt, and BA-35x increased from 30.2, 31.4, 31.0 to 37.7, 39.3, and 35.9%, respectively, with 10 wt% of TPP content. Char yield of the material has been correlated with its flame retardancy.^{26,27} Increasing char yield implied the improvement of fire resistance of the sample as it was proposed that char formation would limit production of combustion gases, inhibit combustion gases from diffusing to the pyrolysis zone and protect the polymer surface from heat and air. Thus, it can be concluded

Table IV. Flammability of Three Types of Arylamine Based-Polybenzoxazines at Various TPP Contents (3 mm Thick Sample)

| Sample | Resins : TPP | Total after flame time condition set (s) | UL-94 grade |
|--------|--------------|--|-------------|
| BA-a | 100 : 0 | 100.1 | V-1 |
| | 98 : 2 | 47.1 | V-1 |
| | 95 : 5 | 16.7 | V-0 |
| | 92 : 8 | 8.7 | V-0 |
| | 90 : 10 | 8.3 | V-0 |
| BA-mt | 100 : 0 | >250 | Burning |
| | 98 : 2 | 21.1 | V-0 |
| | 95 : 5 | 13.1 | V-0 |
| | 92 : 8 | 8.7 | V-0 |
| | 90 : 10 | 8.3 | V-0 |
| BA-35x | 100 : 0 | >250 | Burning |
| | 98 : 2 | 139.5 | V-1 |
| | 95 : 5 | 43.43 | V-0 |
| | 92 : 8 | 40.57 | V-0 |
| | 90 : 10 | 17.23 | V-0 |

that fire resistant property of the polybenzoxazines tend to be improved with the TPP addition.

Effect of TPP on Flame Retardancy of Arylamine-Based Polybenzoxazines

UL94 Vertical Test of TPP-Modified Polybenzoxazines. UL94 is the most commonly used standard test for measuring the ignitability and flame-spread of vertical bulk materials exposed to a small flame. Five specimen bars of each fully cured polybenzoxazine suspended vertically over surgical cotton were ignited by a methane burner. Two ignitions of 10 s were applied to the specimen. The flammability of the three types of arylamine-based polybenzoxazines without the TPP additive is summarized in Table IV. It was evident that the neat BA-a provided the shortest total after-flame time (t_1 plus t_2) from five tested specimens where t_1 = the after-flame time after the first ignition and t_2 = the after-flame time after the second ignition.

Meanwhile, BA-mt and BA-35x showed the longer times for self-extinction than BA-a and the flame propagated the tested specimens up to a holding clamp. It was also observed that BA-35x specimens showed a greater fire spread than BA-mt and were severely burnt after the flame test. However, all three polybenzoxazines exhibited no dripping of flaming particles in the UL94 vertical test. The total after flame time of the neat BA-a, BA-mt, and BA-35x were found to be 100.1, >250, and >250 s, respectively thus BA-a was classified as V-1 rating under UL94 test. In the case of BA-mt and BA-35x, both could not pass the vertical rating category. This result indicated that BA-a exhibited the best flame retardancy among the three types of polybenzoxazines used in this study. The flammability of the polybenzoxazines was ranging in the order of BA-a < BA-mt < BA-35x. The phenomenon might be ascribed to the presence of methyl group on the arylamine ring which, upon pyrolysis, produced relatively flammable CH_3 free radicals. In theory, the flammability of a given material is strongly dependent on the concentration of free radicals.²⁸ Wang et al. synthesized polybenzoxazines from different types of bisphenol, i.e. bisphenol-A and bisphenol-F and investigated fire resistance of the polymers.²⁹ They found that the burning time of bisphenol-A based benzoxazine was longer than bisphenol-F based benzoxazine. This was because the structure of bisphenol-A has an addition of two methyl side groups comparing with bisphenol-F. This result was in good agreement with our result which the methyl side groups have effect on the fire resistance of polybenzoxazines.

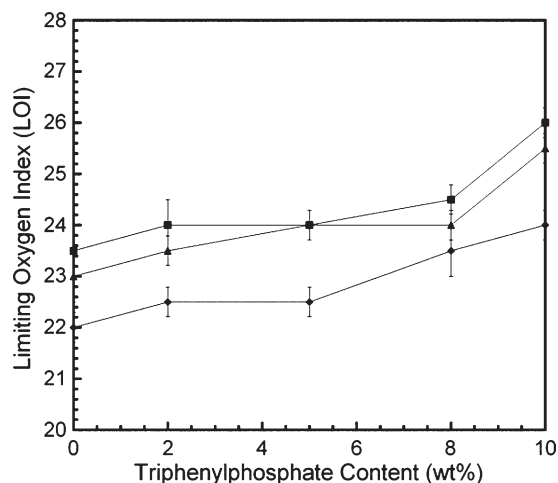


Figure 11. LOI of arylamine-based polybenzoxazines at various TPP contents: (■) BA-a, (▲) BA-mt, and (◆) BA-35x.

For BA-a type polybenzoxazine, the classification of V-0 rating was achieved when at least 5 wt % of TPP was added. The total after-flame time for five specimens of BA-a was reduced substantially from 100.1 to only 16.7 s. The flame was observed to extinguish almost immediately after the removal of the burner. Similar effect of TPP on fire resistant behaviors of BA-mt and BA-35x systems was also observed. UL94 classification of V-0 rating was also achieved with an addition of only 2 wt % and 5 wt % of TPP in BA-mt and BA-35x, respectively. The total after-flame time for five specimens was significantly reduced from >250 s to 21.1 s for BA-mt systems and from >250 s to 43.4 s for BA-35x systems. An addition of TPP flame retardant above those specified levels for each polybenzoxazine provided only a further slight reduction in the burning time. Consequently, maximum fire resistance of V0 category under UL94 test of those arylamine-based polybenzoxazines could be easily obtained with relatively low amount of the TPP flame retardant. This small required amount of TPP would prevent the negative effect on other good properties of the polybenzoxazines.

It had been reported that, during combustion, TPP mainly acted in gas phase as it could vaporize into the gas phase, to yield active radicals, such as $\text{PO}_2\bullet$, $\text{PO}\bullet$ and $\text{HPO}\bullet$. These radicals acted as scavengers of $\text{H}\bullet$ and $\text{OH}\bullet$ radicals and thus resulted in suppression of the combustion process.³⁰ However, TPP was also reported to act in a condensed phase by promoting the formation of char as also observed in our polybenzoxazine systems. In the condensed phase, char formation on the surface inhibited gaseous products from diffusing to the flame as well as shielded the polymer surface from heat and air.⁹ As a result, combustion process was suppressed or even terminated.

Limiting Oxygen Index

The ignitability and fire resistivity of polymers can be characterized by a LOI. The relative flammability is determined by adjusting the concentration of oxygen. The LOI is the lowest oxygen gas concentration which a material can be burnt. Figure 11 presents the LOI values of the three types of arylamine-based polybenzoxazines at various TPP contents. From the figure, BA-

a possessed the highest LOI values of 23.5 while BA-mt and BA-35x showed LOI values of 23.0 and 22.0, respectively. The LOI values were also found to be systematically enhanced by an addition of TPP. The higher LOI values of 26.0, 25.5, and 24.0 with an addition of 10% by weight of TPP were obtained for BA-a, BA-mt, and BA-35x, respectively. The effect of TPP content on the LOI values of polymer has been extensively studied, and usually found that LOI values increased with an addition of TPP content. For example, Mark et al.³¹ found that LOI value of polystyrene increased from 18.8 to 20.7 with an addition of 5% by weight of TPP. Junfeng et al.³² examined the flame retardance of TPP in polybutylene terephthalate (PBT). They reported that LOI value of PBT was significantly increased from 20.9 to 24.6 at 10% by weight of TPP. L. Kyongho et al.³³ also found that LOI values of acrylonitrile-butadiene-styrene were increased by addition of TPP. The higher LOI values confirmed that TPP was an effective flame retardant for our polybenzoxazines. These results were also consistent with those char yield values from the TGA results. The char yield also increased with increasing of TPP content. The char formed during combustion can act as a protective layer for polybenzoxazines, which prevents oxygen diffusion to the surface of the specimen thus more oxygen is needed for its combustion.³⁴

CONCLUSIONS

Among three types of polybenzoxazines, BA-a showed the best fire resistant properties, provided a V-1 rating, while BA-mt and BA-35x did not pass UL-94 vertical test standard. All three polybenzoxazines achieved the highest V-0 rating of UL94 standard with only a small addition of TPP. LOI values of these polybenzoxazines were also enhanced with increasing amount of TPP. TGA results revealed that the degradation temperature at 5% weight loss of the polybenzoxazines decreased with increasing TPP content in the polymers. On the other hand, residual weight at 800°C increased with increasing of TPP. From the DSC experiment, ring opening polymerization of benzoxazine resins was observed to be accelerated by a presence of TPP, a possible Lewis acid catalyst for benzoxazine resins. The glass transition temperature obtained from the peaks of loss moduli of the polybenzoxazines were observed to be reduced with an addition of TPP. In dynamic mechanical property measurement, flexural strength and flexural modulus of all polybenzoxazines were also found to slightly decrease with increasing amount of the TPP. Meanwhile, the flexural strain-at-break was increased with increasing TPP.

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