

# Investigation of Curing and Thermal Behavior of Benzoxazine and Lignin Mixtures

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**ABSTRACT:** This article describes the synthesis and characterization of two types of benzoxazine monomers based on phenol or bisphenol, aniline, and formaldehyde. Their characterization was achieved by Fourier transform infrared,  $^1\text{H}$ -nuclear magnetic resonance, differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Lignin polymer was characterized by infrared, DSC, and TGA. The curing behavior of mixtures of benzoxazine monomers and lignin was investigated by DSC. The mass ratios of benzoxazine monomers/lignin of a series of samples were 100 : 0, 95 : 05, 90 : 10, 85 : 15, 80 : 20, 75 : 25, and 70 : 30. The results indicate that the maximum curing temperatures of the mixtures were lower than that of the pure benzoxazine monomers, and that they decreased with increasing contents of lignin in the mixture. The heat of polymerization ( $\Delta H$ ) of the benzoxazine monomers and

lignin mixtures as a function of the mass ratio and the structure of the benzoxazine monomers shows no definite trend. The samples were cured according to the following conditions: 170°C/2h + 200°C/2h and analyzed by DSC and TGA. In all the samples, the glass transition temperature of the benzoxazines increased upon mixing with increasing amounts of lignin. The changes may be due to the formation of a more compact network structure in the mixtures. The thermal stability of the isothermally cured resins is found to be dependent on the mass ratio of benzoxazine/lignin and structure of the benzoxazine monomers. The more lignin in the mixture, the higher is the char yield in the mixture. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1773–1781, 2012

**Key words:** biopolymers; blends; curing of polymers; thermal properties; thermosets

## INTRODUCTION

There is a need to reduce the use of petrol-based chemicals in the manufacturing of polymers due to rising costs and the depletion of petroleum reserves. This requires the investigation and use of natural and renewable resources that can serve as alternatives to petrol-based chemicals for the polymer industry.

Lignin is a renewable natural resource obtained by several pulping techniques and recently from the ethanol production processes. Lignin is an amorphous polyphenolic material arising from the copolymerization of three phenylpropanoid monomers, namely, coniferyl, sinapyl, and *p*-coumaryl alcohols that lead, respectively, to guaiacyl (G), syringyl (S), and *p*-hydroxyphenyl propane (p-H)-type units. These structures are linked by a multitude of interunit bonds that include several types of ether ( $\alpha$ -O-4,  $\beta$ -O-4, and 4-O-5) and carbon–carbon linkages.<sup>1</sup> The major chemical functional groups presented by lignin

are phenolic and aliphatic alcohol groups and methoxy groups in various amounts, whose contents depend on the botanic origin and the applied extraction processes.<sup>2</sup> With the recent increase in the price of oil-derived synthetic resins for polymeric materials, the availability, low toxicity, and low price of lignin has attracted attention as a substitute for the fossil fuel-based resins. In addition, lignin possesses a chemical structure similar to that of phenols and phenolic resins. This resemblance makes lignin an interesting alternative to phenol compounds in any phenol-based polymers. It can substitute for petrol-based chemical compounds in polymer formulations, dispersant agents, emulsifiers, chelating agents, or adsorbents, and phenolic resins.<sup>3–9</sup>

Phenolic resins are considered to have potential for the application of lignin polymers. They are widely used in industry because of their good heat resistance, electrical insulation, dimensional stability, low flammability, and low smoke generation. However, they have a number of shortcomings, such as poor shelf life, the release of by-products, and the brittleness of the materials produced with them. Water and ammonia compounds can be released due to condensation reactions, and these affect the properties of the cured phenolic resins by the

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formation of microvoids. In addition, curing the resins requires the use of acid or base catalysts, which corrode the processing equipment.

Benzoxazine-derived phenolics are an alternative to traditional phenolics. They are synthesized by ring-opening polymerizations of the aromatic oxazines. They do not produce by-products during polymerization, and strong catalysts are not required.<sup>10</sup> Despite their high performance (e.g., high resistance to heat and water), the crosslinking densities of benzoxazine-based resins are believed to be surprisingly lower than those of ordinary thermosetting resins.<sup>11</sup> For some applications, the improvement in toughness could be useful. This is possible by the incorporation of low glass transition temperature ( $T_g$ ) components that improve the flexural and impact properties.<sup>12</sup> However, another limitation of benzoxazines is their high cure temperatures.

This article describes the synthesis and characterization of two benzoxazine monomers with various structures obtained by reacting phenol or bisphenol, aniline, and formaldehyde. Mixing lignin with varying quantities of benzoxazine monomers was carried out to study the curing temperature and cross-linking density of the benzoxazine-based resins. The effect of the mixture composition and benzoxazine structures on the curing characteristics was investigated by differential scanning calorimetry (DSC). Additionally, the thermal stability of the isothermally cured mixtures was evaluated using thermogravimetric analysis (TGA) under a nitrogen atmosphere.

## EXPERIMENTAL

### Materials

Aniline, formaldehyde (35–40% aqueous solution), paraformaldehyde, phenol, and bisphenol A were purchased from Sigma Aldrich (Shanghai, China) and used as received. All the solvents were used without further purification. The alkaline lignin used as the starting natural material for the mixtures with benzoxazine monomers was supplied by South China University of Technology (Guangzhou, China). This lignin was produced by the alkaline process using sodium hydroxide and  $\text{Na}_2\text{CO}_3$  from rice straw and was made by Shandong QuanMing Paper Making. It was used in its powder form after its purification following the procedure described below.

### Purification of lignin

As was performed in Lin's<sup>13</sup> work, the alkaline lignin used in this work was treated with sulfuric acid (1%) several times and washed extensively with deionized hot water to dissolve the residual sugars until it became impurity free, and the final pH was

neutral. The obtained lignin was air-dried at room temperature to equilibrate the moisture content and stored in plastic bottles before the characterization and use in the mixing preparation.

### Synthesis of benzoxazine monomers

Phenol- and bisphenol-based benzoxazine monomers [Phenol-Aniline-Formaldehyde (PAF) and Bisphenol A-Aniline-Formaldehyde (BAF)] were synthesized by the two following methods to compare and optimize the yield and purity.

#### Method 1

According to Ishida's<sup>14</sup> method, 0.1 M of phenol or 0.05 M of bisphenol-A, 0.2 M of paraformaldehyde, and 0.1 M of aniline were placed in a 250-mL round-bottomed flask, and the mixture was heated to 100°C. After heating for 15 min, the mixture was cooled and dissolved in ethylic ether and washed three times with a 3-N NaOH solution and water. The organic phase was dried with anhydrous  $\text{MgSO}_4$  and filtered, and the solvent was removed at low pressure to obtain a viscous fluid.

#### Method 2

The second method used to prepare the benzoxazine monomers was reported by Brunovska et al.<sup>15</sup>

### Synthesis of 1,3,5-triphenylhexahydro-1,3,5-triazine

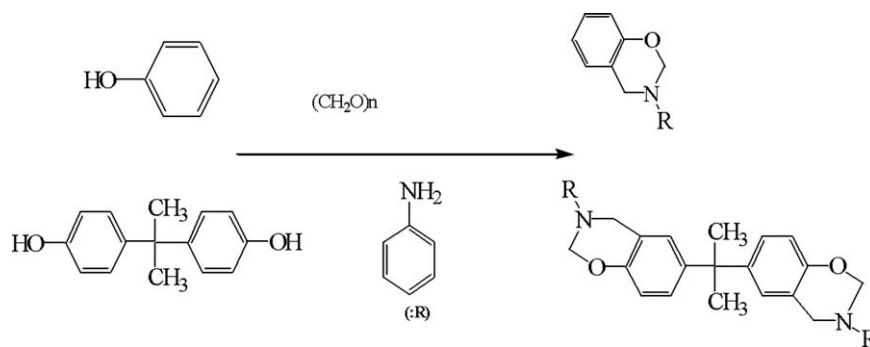
Aniline (1 M) was added to 1 M of paraformaldehyde in a 250-mL two-necked round-bottomed flask with magnetic stirring. The mixture was heated to 100°C and 75 mL of toluene was added under continuous stirring for 2 h. The mixture was then cooled, filtered, and washed several times with small volumes of cold toluene. The product was dried at 60°C.

### Synthesis of benzoxazine derivative

Quantities of 0.016 M of 1,3,5-triphenylhexahydro-1,3,5-triazine, 0.048 M of phenol or 0.024 M of bisphenol-A, and 0.048 M of paraformaldehyde were added in a 50-mL round-bottomed flask at 100°C with magnetic stirring for 1 h. The mixture was cooled, dissolved in ethylic ether, and washed three times with 3 N NaOH and three times with water. The organic phase was dried with anhydrous  $\text{MgSO}_4$ , and the ethylic ether was removed under low pressure.

### Structural characterization of lignin and benzoxazine monomers

The lignin and benzoxazine monomers were characterized by Fourier transform infrared (FTIR)



**Figure 1** Synthesis of benzoxazine monomers by the solventless method.

spectroscopy (Nicolet 5700), using the KBr-pellet method. The acquisition conditions were as follows: spectral width of 4000–400  $\text{cm}^{-1}$ , 32 accumulations, and a 4- $\text{cm}^{-1}$  resolution. The  $^1\text{H}$ -nuclear magnetic resonance ( $^1\text{H}$ -NMR) spectra were recorded on a Bruker 500 MHz NMR Spectrometer. Deuterated chloroform and tetramethylsilane were used as the solvent and internal standard, respectively.

### Curing studies

The thermal analyzer TA MDSC2910 module was used for recording the DSC traces at a heating rate of 10°C  $\text{min}^{-1}$  under a nitrogen atmosphere with a flow rate of 60  $\text{cm}^3 \text{min}^{-1}$ . Approximately  $5 \pm 2$  mg of sample was used in each test. For the curing studies, the samples were prepared by mixing the benzoxazine monomers (PAF or BAF) with lignin in mass ratios of 95 : 5, 90 : 10, 85 : 15, 80 : 20, 75 : 25, and 70 : 30 with the solvent. An accurately weighed mass of lignin was first dissolved in pyridine and stirred for 2–3 h after the benzoxazine monomers (PAF or BAF) were added, and the mixture was further stirred for 30 min before the solvent was evaporated at 80°C under vacuum. All the samples were evaporated again under vacuum at 120°C for 1 h to eliminate any residual solvent before the DSC analysis. The samples are designated as PAF-LIG 5–30 for the mixtures of the phenol-based benzoxazine and lignin and BAF-LIG 5–30 for the mixtures of the bisphenol-based benzoxazine and lignin. The numbers 5–30 in the sample names represent the aforementioned content of lignin mixed with benzoxazine. The DSC scans of the isothermally cured samples at the following conditions: 170°C/2h + 200°C/2h. The DSC scans were also recorded to determine the effect of the network structure on the  $T_g$ .

### Thermal stability

The thermal stability of the samples cured by heating at 170°C for 2h and 200°C for 2 h in an air oven was evaluated by recording the TG/DTG traces

under a nitrogen atmosphere (flow rate of 60  $\text{cm}^3 \text{min}^{-1}$ ). A PerkinElmer Pyris Diamond was used for recording the TG/DTG traces at heating rate of 10°C  $\text{min}^{-1}$ . Sample sizes of  $5 \pm 0.1$  mg in a fine powder form were used in each experiment.

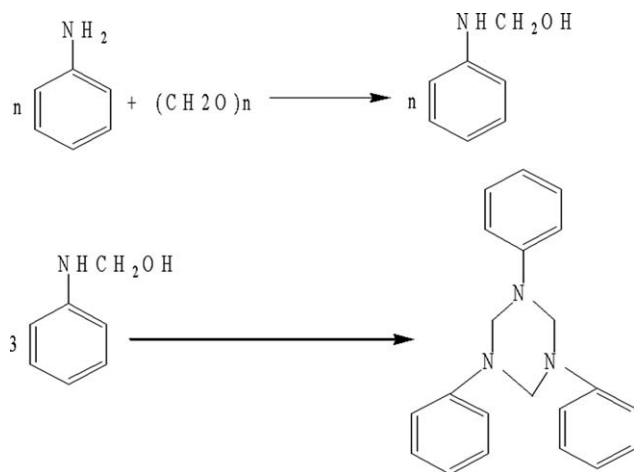
## RESULTS AND DISCUSSION

### Preparation and characterization of benzoxazine monomers

The reaction using phenol or bisphenol-A, aniline and paraformaldehyde in the absence of solvent to synthesize phenol-based benzoxazine (PAF) and bisphenol-based benzoxazine (BAF) monomers as described in Method 1 section, is presented in Figure 1. When bisphenol was used instead of phenol, the high viscosity of the melt impeded mixing. The unreacted starting reagents, including paraformaldehyde and aniline, were observed in the final product. In this case, pure benzoxazine monomers were not obtained because a triazine intermediate was formed and did not transform into the final corresponding benzoxazine. The formation of the triazine intermediate during the preparation of the benzoxazine monomers was also reported by Brunovska et al.<sup>15</sup> and Espinosa et al.<sup>16</sup> The obtained yields were 75% and 18% for phenol-based (PAF) benzoxazine and bisphenol-based benzoxazine (BAF), respectively.

The reaction of aniline and paraformaldehyde leading to 1,3,5-triphenylhexahydro-1,3,5-triazine is presented in Figure 2. Figure 3 shows the  $^1\text{H}$ -NMR spectrum of triazine, which is characterized by the resonance at 4.9 ppm assigned to the methylene protons in the cyclic intermediate. The estimated yield of 1,3,5-triphenylhexahydro-1,3,5-triazine obtained by this reaction was approximately 77%.

Figure 4 displays the reaction of phenol or bisphenol-A, paraformaldehyde, and the triazine intermediate to obtain the benzoxazine monomers as described in Method 2 section. The estimated yields were approximately 75 and 85% for the phenol-based benzoxazine and bisphenol-based benzoxazine, respectively. Thus,

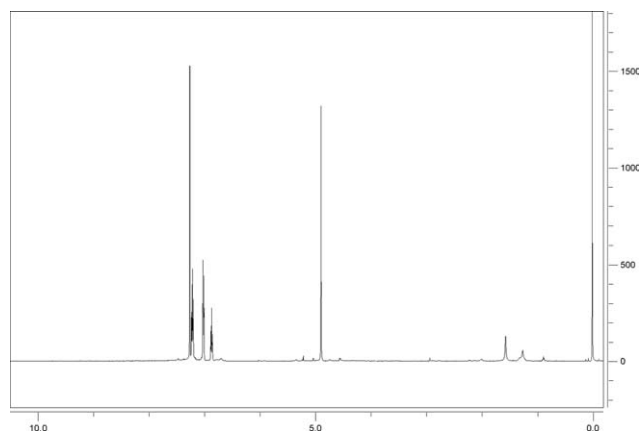


**Figure 2** Reaction of aniline and paraformaldehyde.

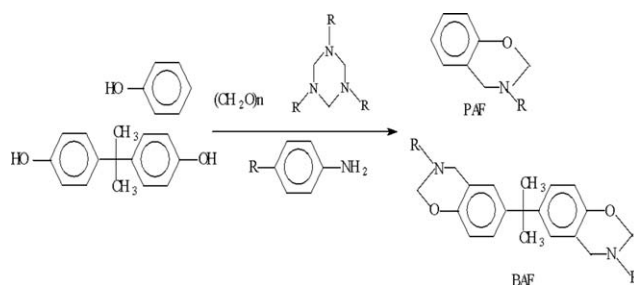
it is possible to obtain benzoxazine monomers with high yield and purity by the solventless method using the active triazine intermediate.

The FTIR spectra of the synthesized phenol-based benzoxazine (PAF) and bisphenol-based benzoxazine (BAF) obtained using Method 2, are shown in Figure 5. The asymmetric stretching of C—O—C ( $1234\text{ cm}^{-1}$ ), the asymmetric stretching of C—N—C ( $1180\text{ cm}^{-1}$ ), and the  $\text{CH}_2$  wagging of oxazine ( $1326\text{ cm}^{-1}$ ) are observed. Additionally, the characteristic absorptions assigned to the trisubstituted benzene ring at  $1510\text{ cm}^{-1}$  and out of plane bending vibrations of C—H at  $940\text{ cm}^{-1}$  are exhibited, indicating that the obtained precursors containing the benzoxazine structure in the backbone were achieved.

$^1\text{H-NMR}$  spectroscopy was performed to confirm the structure of the benzoxazine monomers. The  $^1\text{H-NMR}$  spectra of the synthesized benzoxazine monomers (PAF and BAF from method 2) are shown in Figure 6. The characteristic peaks attributable to the O— $\text{CH}_2$ —N methylene and the Ar— $\text{CH}_2$ —N methylene of the oxazine ring arise as singlets at 4.7 and 5.45 ppm, respectively. The peak from the



**Figure 3**  $^1\text{H-NMR}$  spectrum of the triazine intermediate.



**Figure 4** Synthesis route of the benzoxazine monomers using the triazine intermediate.

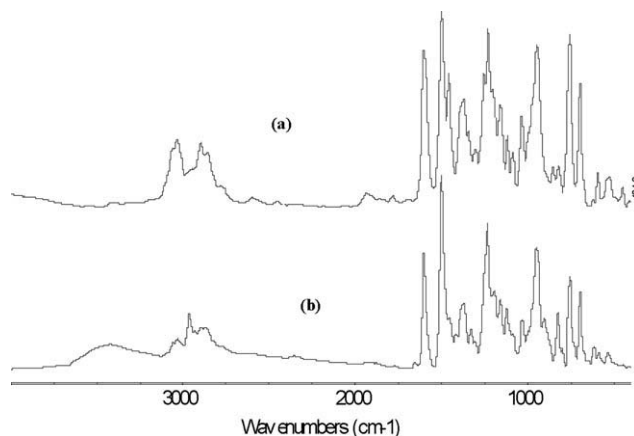
methyl proton of bisphenol-A occurs at 1.58 ppm. The aromatic protons show multiplets in the range of 7–7.45 ppm.

### Characterization of lignin

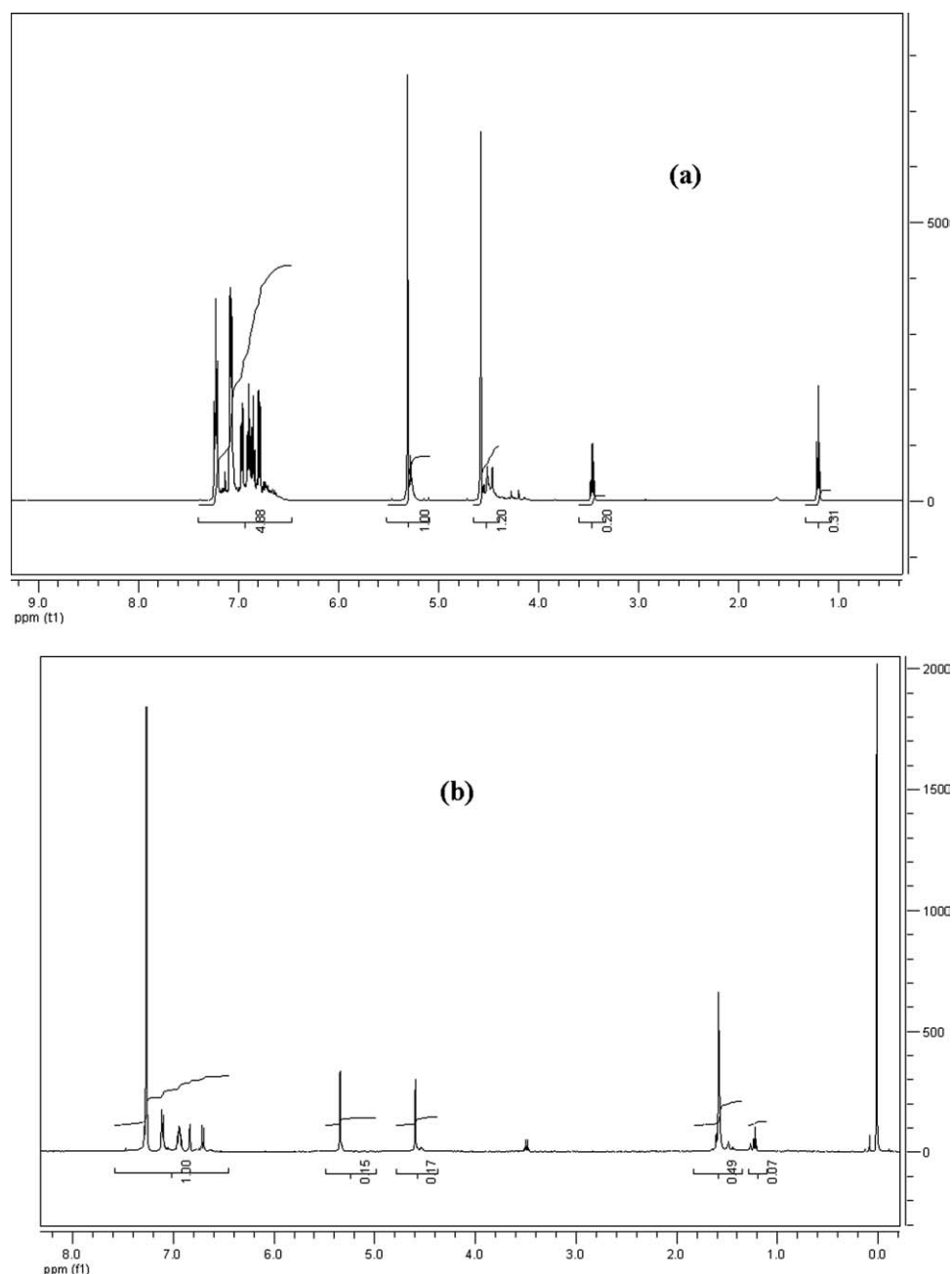
The used alkaline lignin was characterized with detail in our previous work.<sup>17</sup> Its FTIR spectrum is characterized by a broad O—H band at  $3400\text{ cm}^{-1}$ , an intense C—H band at  $2935\text{ cm}^{-1}$ , and another at  $2848\text{ cm}^{-1}$ , which are typical of methoxyl groups. The absorbance band of the carbonyl groups is at  $1717\text{ cm}^{-1}$ . The absorbance bands of phenolic hydroxyl groups are at  $1364$  and  $1328\text{ cm}^{-1}$ . The absorbance of the C—H vibration of the aromatic ring is at  $1615$  and  $1514\text{ cm}^{-1}$ . Two additional bands attributed to methoxyl groups appear at  $1459$  and  $1425\text{ cm}^{-1}$ . The secondary aliphatic hydroxyl group occurs at  $1212\text{ cm}^{-1}$ , and the ether (—O—) group arises at  $1117\text{ cm}^{-1}$ .

### Curing the mixtures of benzoxazine monomers with lignin

The curing behavior of both of the pure benzoxazine monomers (PAF and BAF) and their mixtures with the lignin polymer was investigated by differential



**Figure 5** FTIR spectra of (a) phenol-based benzoxazine and (b) bisphenol-based benzoxazine monomers.



**Figure 6**  $^1\text{H}$ -NMR of (a) phenol-based benzoxazine and (b) bisphenol-based benzoxazine monomers.

scanning calorimetry (DSC). Figure 7 shows the DSC scans of the pure benzoxazine monomers recorded at a heating rate of  $10^\circ\text{C min}^{-1}$ . In these DSC curves, a narrow exothermic peak is observed. The comparison of the curing behavior of BAF and PAF reveals that the maximum curing temperature of BAF ( $261.1^\circ\text{C}$ ) is higher than that of PAF ( $253.6^\circ\text{C}$ ), but the  $\Delta H$  values show an opposing trend ( $\Delta H_{\text{BAF}} = 276.6 \text{ J g}^{-1}$  and  $\Delta H_{\text{PAF}} = 297.6 \text{ J g}^{-1}$ ).

In the DSC scan of lignin alone, no exothermic transition was observed in the temperature range of  $25\text{--}300^\circ\text{C}$ , thereby indicating the absence of a cross-linking reaction occurring in the lignin. However, a

$T_g$  was detected at  $155^\circ\text{C}$ .<sup>17</sup> This value is in the range of those reported in the literature by Goring<sup>18</sup> from 400 to 466 K.

The DSC scans of benzoxazine monomers mixed with varying amounts of lignin are presented in Figure 8. An exothermic transition associated with cross-linking or curing is observed, and some characteristic parameters are labeled as follows:  $T_i$ : Kick-off temperature, at which the curing starts;  $T_{\text{onset}}$ : the temperature at which the released heat is detectable and is obtained by extrapolation of the steepest portion of the curve;  $T_p$ : the temperature of the peak position of the exotherm;  $T_f$ : the final temperature of

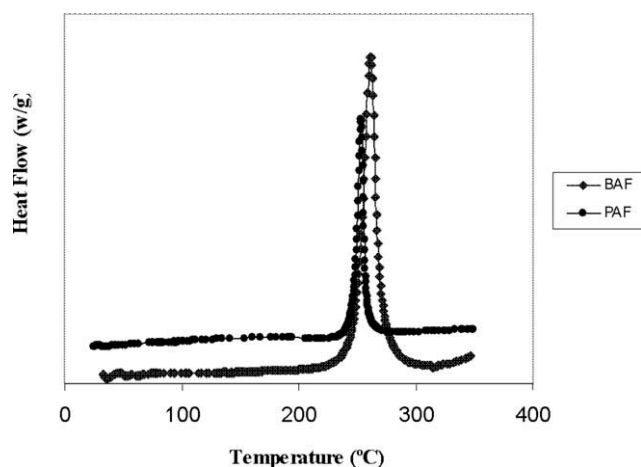


Figure 7 DSC curves of PAF and BAF.

the curing exotherm; and  $\Delta H$ : the heat of curing, calculated by measuring the area under the exothermic peak. The results of the DSC scans are summarized in Table I.

The incorporation of lignin to benzoxazine monomers in different ratios was expected to affect the curing behavior and the thermal stability of the cured network. Therefore, two types of benzoxazine, such as PAF and BAF, with different structures were used to investigate systematically the curing behavior in the presence of varying mass ratios of lignin. The curing temperatures of both benzoxazine monomers ( $T_p$ ) decreased with increasing amounts of lignin. Thus, the curing temperature is dependent on the amount of lignin introduced into the benzoxazines.

It is clear that the addition of the lignin polymer to the benzoxazine monomers activates their polymerization or cross-linking reaction. The typical method for obtaining polybenzoxazines is to polymerize the corresponding monomers at high temperature without catalysts. The catalyzed polymerization of benzoxazines has also been reported. The reactivity of

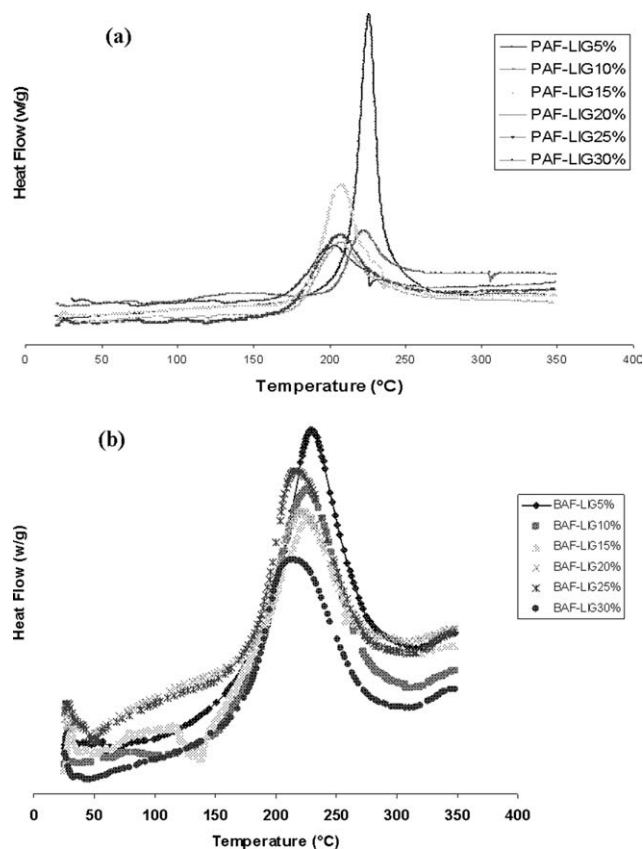


Figure 8 DSC plots of (a) PAF/lignin mixtures and (b) BAF/lignin mixtures.

bisphenol-A-based benzoxazines has been studied using a series of acids, alkalis, and Lewis acids as catalysts.<sup>16,19,20</sup> The presence of phenols with free ortho-positions functioned as initiators in the polymerization of benzoxazine compounds, reported previously by Riess et al.<sup>21</sup> At elevated temperatures, the self-dissociation of the benzoxazine ring could produce a free phenol structure that can act as a catalyst for the polymerization of benzoxazines.<sup>18</sup>

TABLE I  
Results of DSC Scans of Benzoxazine Monomers in the Presence of Lignin

Samples	Mass ratio (PAF/BAF : lignin)	$T_i$ (°C)	$T_{onset}$ (°C)	$T_p$ (°C)	$T_f$ (°C)	$\Delta H$ (J·g <sup>-1</sup> )	$T_g$ (°C)
PAF	100 : 00	227.8	247.0	253.6	277.0	297.6	210
PAF-LIG5	95 : 05	181.7	213.3	225.9	274.6	439.6	214
PAF-LIG10	90 : 10	196.0	204.5	221.0	268.0	187.8	216
PAF-LIG15	85 : 15	161.9	186.8	207.4	265.5	319.4	218
PAF-LIG20	80 : 20	161.4	179.8	207.4	281.5	227.2	218
PAF-LIG25	85 : 25	149.7	175.3	206.7	277.2	224.1	223
PAF-LIG30	70 : 30	133.1	175.1	203.4	264.4	202.0	237
BAF	100 : 00	214.8	248.8	261.1	312.5	276.6	240
BAF-LIG5	95 : 05	111.3	186.2	228.7	300.7	330.5	304
BAF-LIG10	90 : 10	127.3	174.6	225.5	309.3	395.4	309
BAF-LIG15	85 : 15	143.3	168.1	225.3	297.0	283.9	310
BAF-LIG20	80 : 20	141.7	184.2	219.3	298.6	299.6	310
BAF-LIG25	85 : 25	135.8	180.9	215.2	298.6	339.0	310
BAF-LIG30	70 : 30	151.8	175.7	212.4	284.7	303.1	311

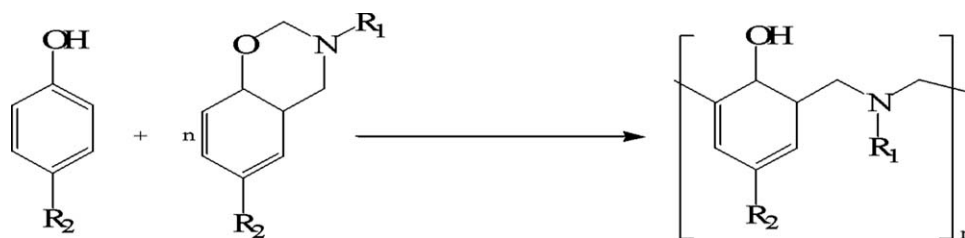


Figure 9 Ring-opening reaction of monofunctional benzoxazine initiated by para-substituted phenol.

A simplified mechanism scheme for the ring-opening reaction of monofunctional benzoxazine initiated by para-substituted phenol is shown below (Fig. 9).

With bifunctional or multifunctional benzoxazine molecules, the resulting product would be a cross-linked network. Lignin is an amorphous polyphenolic material containing different phenolic structures with a free orthoposition, such as coniferyl and *p*-coumaryl alcohols. Therefore, as expected, these phenolic structures could accelerate the ring-opening polymerization of both benzoxazines, which was confirmed by the decrease in the maximum curing temperature, as reported in the results summarized in Table I.

It is clear from Figure 8 that broad exothermic curves are obtained when the content of lignin increases and the molecular weight of the benzoxazine monomer is higher. Also, the maximum curing temperature of BAF-LIG is higher than that of PAF-LIG. Therefore, the curing temperature of the mixture depends on the structure of the phenols and the amount of lignin polymer used in the preparation of the mixtures. The  $\Delta H$  values show no definite trend as a function of the mass ratio.

These results clearly show that cross-linking or ring-opening polymerizations of benzoxazine monomers with lignin are dependent on the structure of the benzoxazine monomers and the mixture composition.

The mixtures of the benzoxazine monomers and lignin were cured isothermally according to the curing conditions mentioned in the experimental section to confirm the success of the curing process and to determine the  $T_g$ . In the DSC scans of the cured samples, no exothermic transition was observed, thereby indicating that the complete polymerization and cross-linking reactions have occurred. However, a shift in the base line was observed in the DSC scans of the cured samples. The  $T_g$  is noted as the midpoint inflexion, and the results are summarized in Table I.

In all the samples, the  $T_g$  of the benzoxazines increased upon mixing with lignin and increased with higher concentrations of lignin. This could be due to the increase in the cross-link density. The maximum value of  $T_g$  was obtained at the mass ratio of PAF-LIG30 and BAF-LIG30. The  $T_g$  was dependent on the rigidity of the polymer backbone and on

the cross-link density. Thus, the more lignin polymer present in the mixture, the more compact is the network structure form and the higher is the  $T_g$  of the mixture. In the pure benzoxazine monomers, the cured BAF had a more compact network structure and rigid backbone than the cured PAF benzoxazine.

### Thermal stability of mixtures

Figure 10 shows the TG/DTG traces of isothermally cured benzoxazine monomers and lignin mixtures (PAF-LIG, 30% and BAF-LIG, 30%). The relative thermal stability of all the cured samples was evaluated by comparing the initial decomposition temperature

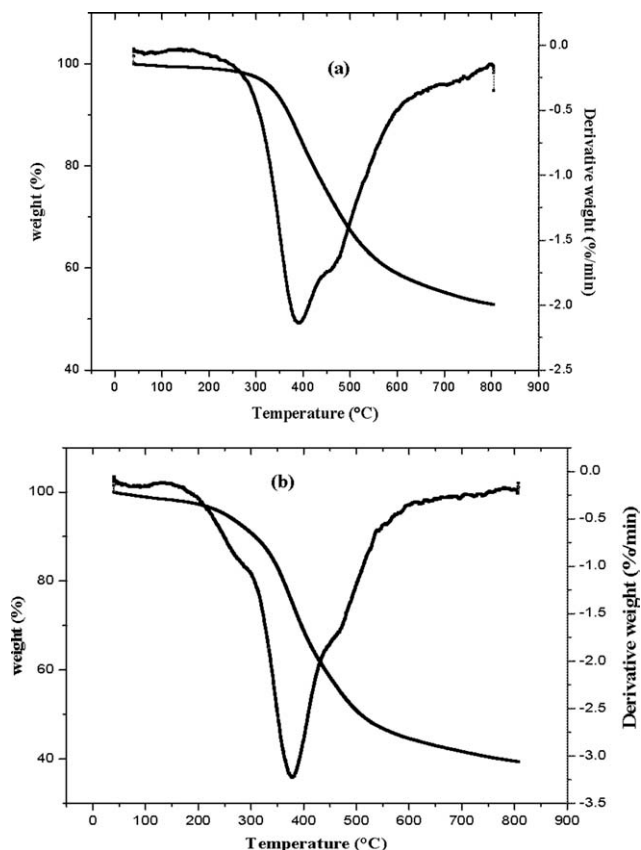


Figure 10 TG/DTG traces of isothermally cured (a) PAF-LIG 30% and (b) BAF-LIG 30%.

TABLE II  
Thermal Behavior of Benzoxazine Monomers in the Presence of Lignin

Samples	Mass ratio (PAF/BAF : lignin)	IDT (°C)	$T_{\max}$ (°C)	FDT (°C)	Char yield at 800°C (%)	LOI (%)
Lignin	00 : 100	345	410	464	39.7	–
PAF	100 : 00	354	384	446	24.3	27.2
PAF-LIG5	95 : 05	340	389	442	43.9	35.1
PAF-LIG10	90 : 10	338	390	441	40.4	33.6
PAF-LIG15	85 : 15	338	391	440	47.3	36.4
PAF-LIG20	80 : 20	339	389	435	54.6	39.3
PAF-LIG25	85 : 25	340	390	436	49.3	37.2
PAF-LIG30	70 : 30	338	394	436	52.9	38.7
BAF	100 : 00	268	299	400	25.7	27.8
BAF-LIG5	95 : 05	325	378	440	32.9	30.7
BAF-LIG10	90 : 10	320	378	439	36.0	31.9
BAF-LIG15	85 : 15	321	377	442	37.5	32.5
BAF-LIG20	80 : 20	318	376	440	40.1	33.5
BAF-LIG25	85 : 25	322	378	445	39.5	33.3
BAF-LIG30	70 : 30	316	375	441	40.8	33.8

(IDT), the temperature of the maximum rate of weight loss ( $T_{\max}$ ), the final decomposition temperature (FDT), and the percentage of the char yield at 800°C. The results of the TG/DTG scans are summarized in Table II.

In comparison to the isothermally cured bisphenol-based benzoxazine monomer, the isothermally cured phenol-based benzoxazine monomer had a higher IDT,  $T_{\max}$ , FDT, and a lower char yield. The same results were reported by Jain et al.<sup>12</sup> and Wang and Ishida<sup>22</sup> when they studied the thermal stability of different benzoxazines. The IDT,  $T_{\max}$ , FDT, and char yield of alkaline lignin were found to be 355°C, 410°C, 464°C, and 39.7%, respectively. It is clear that after heating to 800°C, a sample with a high content of lignin still remains unvolatilized due to the formation of highly condensed aromatic structures. The maximum rate of loss of weight in PAF and BAF occurred at 384°C and 299°C, respectively. Therefore, the introduction of lignin in the benzoxazine resin formulations, especially those with higher thermal stability than the benzoxazine monomers, led to higher decomposition temperatures of the final cured mixtures. This enhanced thermal behavior may suppose a wider temperature range of application for lignin-modified benzoxazine blends. This behavior is very obvious in the case of BAF because of its lower  $T_{\max}$ , whereas in the case of PAF, the changes of  $T_{\max}$  are near 390°C. In all samples, the char yield increased with the addition of lignin in the mixture. The results demonstrate that lignin can be successfully used to improve the thermal stability of benzoxazine resins.

On the other hand, the char yield can be used as a criterion for the evaluation of the limiting oxygen index (LOI) of the resins. In accordance with the Van Krevelen and Hoftyzer equation:  $LOI = 17.5 + 0.4 CR$ , where CR is the char yield, all the formula-

tions based on the benzoxazine monomers and lignin mixtures have LOI values that were calculated based on their char yield and were higher than 28. Based on the LOI values, such materials can be classified as self-extinguishing resins. This is a resin formulation that burns in the presence of a flame, but extinguishes itself within a specified time after the flame is removed.

## CONCLUSIONS

The high yield and purity of two kinds of benzoxazine monomers (PAF and BAF) was achieved by comparing two synthesis methods. The curing behavior of mixtures of benzoxazine monomers and lignin investigated by DSC showed that the maximum curing temperature of the mixtures were lower than that of the pure benzoxazine monomers and decreased with an increase in the amount of introduced lignin to the blend. The heat of polymerization ( $\Delta H$ ) of benzoxazine monomers and lignin mixtures showed no definite trend as a function of the mass ratios and the structure of the benzoxazine monomers. The  $T_g$  of the isothermally cured benzoxazines increased upon mixing with lignin and increased with a higher content of lignin. This could be due to the formation of a more compact network structure. The thermal stability of the isothermally cured resins was also found to be dependent on the mass ratio of benzoxazine/lignin and the structure of the benzoxazine monomers. The effect of lignin on the improvement in the thermal stability of benzoxazines was distinct. The char yield of the mixtures was higher than that of the pure benzoxazine resins.

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