

## REVIEW ARTICLE

# High Performance Polybenzoxazines as a Novel Type of Phenolic Resin

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Polybenzoxazines that can be obtained by the thermally induced ring-opening polymerization of cyclic benzoxazine monomers are expected as a novel type of phenolic resins. Various benzoxazine monomers are easily synthesized from mono- or diamines, mono- or bisphenols, and formaldehyde. Polybenzoxazines have not only the advantageous properties of the traditional phenolic resins such as the high thermal properties, but also other properties that are not found in the traditional phenolic resins such as the molecular design flexibility, and excellent dimensional stability. The disadvantages of the typical polybenzoxazines are high temperature needed for the cure and brittleness of the cured materials. Further enhancement of thermal properties is also expected for the applications in harsh conditions. Herein, we report on our various approaches for performance enhancement of the polybenzoxazine, including the designs of novel monomers, high molecular weight polymeric precursors, polymer alloys, and hybrids with inorganics.

KEY WORDS: Thermoset / Ring-Opening Polymerization / Thermal Properties / Toughness / Polymer Alloy / Organic-Inorganic Hybrid / Nanocomposite /

The traditional phenolic resins possess excellent characteristics such as good heat and chemical resistance, flame retardancy, electrical properties, low water absorption, and low cost due to the inexpensive raw materials and fabricating processes. Therefore, they are widely used in various fields such as structural materials, adhesives, paints and matrix for fiber-reinforced plastics (FRP). Nevertheless, the traditional phenolic resins has many disadvantages including poor shelf life of the precursors, the use of harsh catalyst for polymerization, evolution of volatiles during the cure leading to a large volumetric shrinkage upon cure and formation of voids, and the brittleness of the cured materials. Furthermore, the volatilization of phenol and formaldehyde into the air during the cure process causes some health concern.

A series of polybenzoxazine has been developed as a novel type of phenolic resin.<sup>1</sup> It differs from the traditional phenolics in that the phenolic moieties are connected by a Mannich base bridge [-CH<sub>2</sub>-N(R)-CH<sub>2</sub>-] instead of methylene (-CH<sub>2</sub>-) bridge associated with the traditional phenolics. The structure of a typical benzoxazine monomer (B-a) prepared from bisphenol-A, aniline and formaldehyde along with the structure of its polybenzoxazine (PB-a) are shown in Figure 1. The monomers for polybenzoxazines are easily prepared from phenols, primary amines and formaldehyde. The wide variations of raw materials, phenols and amines, allow tremendous molecular-design flexibility for the cyclic monomers. Polymerization proceeds through the ring-opening of the cyclic monomers only by heat treatment without the need of catalysts and without generating byproducts or volatiles, and thus offering an excellent dimensional stability for the cured product.

Polybenzoxazines provide characteristics found in the traditional phenolic resins such as excellent heat resistance and flame retardance. They also provide characteristics that are not found in the traditional phenolic resins such as excellent dimensional stability, low water absorption and stable low dielectric properties. Various applications as electronic materials, matrix resin for FRP, and adhesives are expected.

However, polybenzoxazines are brittle as is common for thermosets. They also need relatively high temperature (*ca.* 200 °C) for the ring-opening polymerization, although acidic catalysts are effective to lower the cure temperature. As shown in Figure 2, the typical polybenzoxazine, PB-a, has  $T_g$  at *ca.* 160 °C and storage modulus drops considerably at around  $T_g$  due to the low crosslink density. Therefore, further enhancement of the thermal properties is also expected. Another shortcoming is the difficulty to process into thin films from the typical monomers because most monomers are powder and the cured polymers are brittle. Aiming at performance enhancement and lowering the polymerization temperature, various approaches have been developed as will be described below.

## MOLECULAR DESIGN OF BENZOXAZINE MONOMER

One approach for the performance enhancement of polybenzoxazine is the modification of a monomer by introducing crosslinkable units into the benzoxazine moiety. It is known that polybenzoxazines decompose by volatilizing aniline fragments during the thermal degradation.<sup>2</sup> Therefore, the introduction of additional cross-linkable sites into the aniline part

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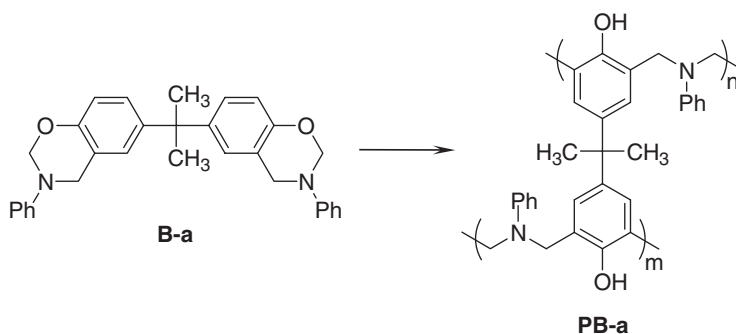


Figure 1. Structures of B-a and PB-a.

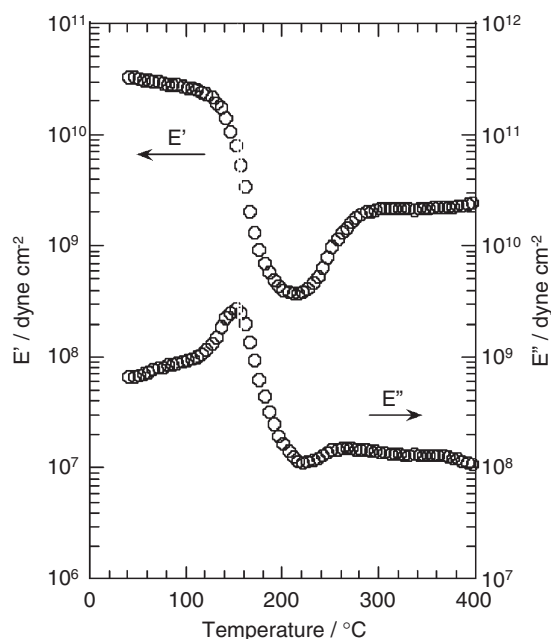


Figure 2. Viscoelastic properties of PB-a.

should be effective for obtaining thermosets with enhanced thermal and mechanical properties. Various crosslinkable groups such as double and triple bonds have been found to be effective. For example, Ishida *et al.* introduced ethynyl<sup>3</sup> and nitrile groups<sup>4</sup> into the benzoxazine structure, which afforded polybenzoxazines with improved thermal properties.

The propargyl group was also studied as a possible crosslink site for benzoxazine.<sup>5</sup> A propargyl ether-based monofunctional benzoxazine (P-appe) and a bifunctional benzoxazine (B-appe) were prepared as shown in Figure 3. Ring-opening polymerization of the oxazine ring and cross-linking of the propargyl ether group occurred at almost the same temperature range. Polybenzoxazines derived from the novel monomers exhibited significantly improved thermal properties than the typical polybenzoxazines. For example, the  $T_g$  of the novel polybenzoxazines increased by *ca.* 100–140 °C than the typical polybenzoxazines as evidenced by the dynamic mechanical analysis (DMA, Figure 4). Moreover, the storage modulus was maintained constant up to 300 °C. Thermogravimetric analysis

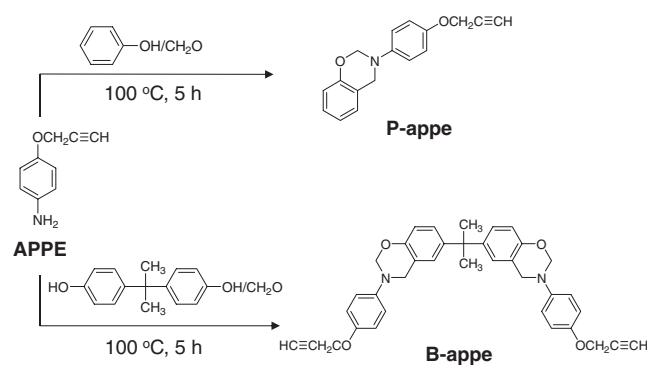


Figure 3. Preparation of P-appe and B-appe.

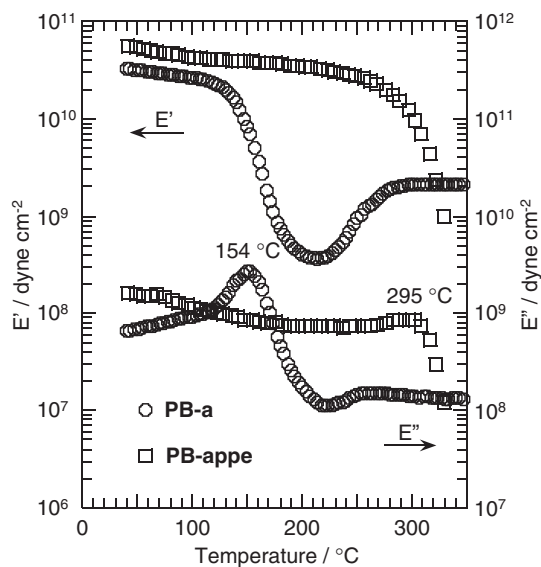


Figure 4. Viscoelastic properties of PB-a and PB-appe.

(TGA) showed that the 5 and 10% weight loss temperatures ( $T_5$  and  $T_{10}$ ) are increased by 20–40 °C, because the aniline moiety is anchored into the network through the reaction of the propargyl groups. The char yield at 800 °C was also increased, indicating that the flame retardance property also increased.

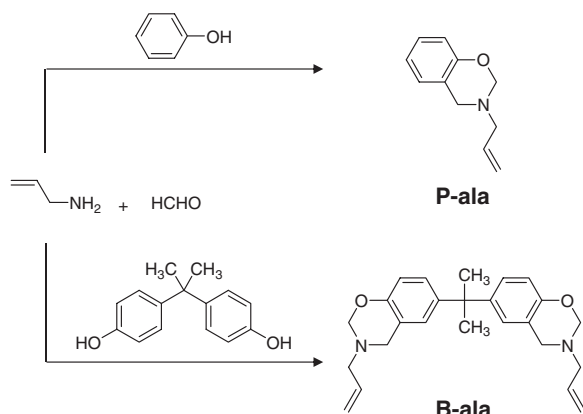


Figure 5. Preparation of P-ala and B-ala.

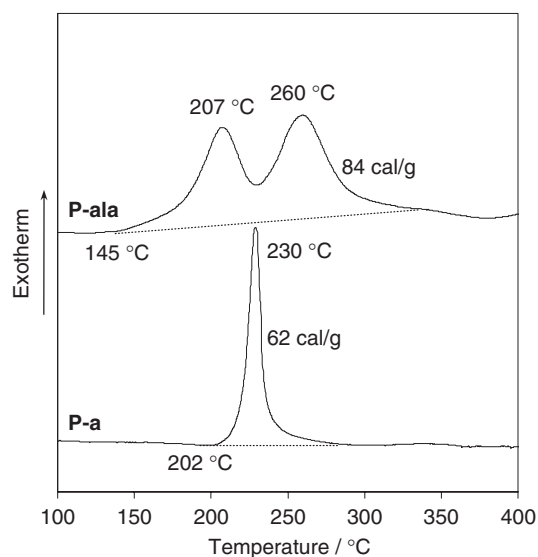


Figure 6. DSC thermograms of P-a and P-ala.

Allyl group is also effective as another cross-linkable site that works at moderate temperature.<sup>6</sup> The allyl-containing monomers, P-ala and B-ala, were prepared from phenol and bisphenol A with allylamine and formaldehyde (Figure 5). DSC thermogram of P-ala showed the presence of two separate exotherms with maxima at 207 and 260 °C, which correspond to the polymerization of the allyl groups and the ring-opening of oxazine, respectively (Figure 6). The obtained thermosets exhibit higher  $T_g$  (ca. 300 °C), maintain their storage moduli at higher temperature as shown in Figure 7, and have better thermal stability than the typical polybenzoxazines without allyl groups.

Another series of allyl-containing monofunctional benzoxazine monomers were prepared by reacting various cresols with allylamine and paraformaldehyde.<sup>7</sup> The obtained monomers were highly sublimable, but high quality films were successfully obtained by using pre-formed oligomers. Thermal properties of the novel polybenzoxazines were investigated, and it was made clear that the *ortho*-position in cresol is more

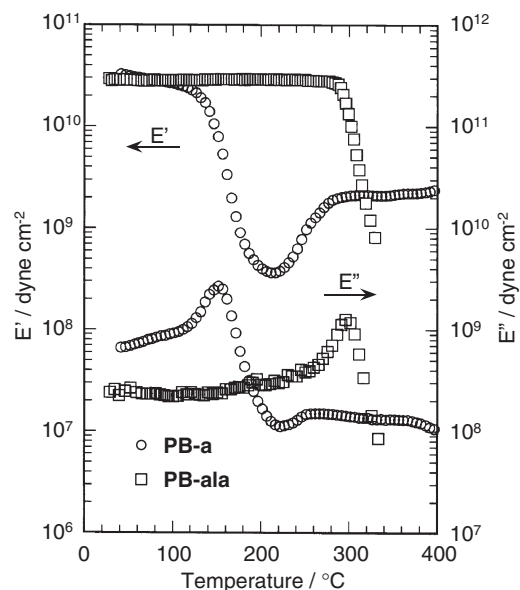


Figure 7. Viscoelastic properties of PB-a and PB-ala.

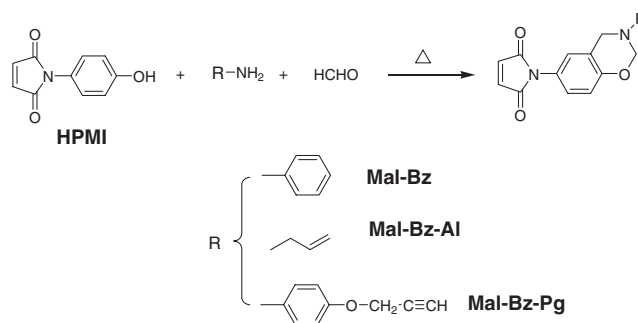


Figure 8. Preparation of maleimidobenzoxazines.

reactive than the *para*-position. Compared with the typical aniline-based benzoxazine, the introduction of the allyl group increased the softening temperature by ca. 70–130 °C and the thermal decomposition temperature by 20–60 °C.

New series of benzoxazine-based monomers containing maleimide groups, namely maleimidobenzoxazines, were prepared from the reaction of hydroxyphenylmaleimide, formalin, and various amines (e.g., aniline, allylamine, and aminophenyl propargyl ether) as shown in Figure 8.<sup>8</sup> The monomers were easily dissolved in many common organic solvents. DSC of the novel monomers showed exotherms at different temperature ranges that corresponded to the polymerization of benzoxazine and maleimide along with other functionalities such as allyl or propargyl (Figure 9). The ring opening polymerization of benzoxazine was occurring in a faster rate than the polymerization of maleimide. However, in the presence of allyl functionality, the cure of maleimide and allyl was occurring faster than benzoxazine. The thermal cure of the monomers at 250 °C afforded a novel network structure that combined polybenzoxazine and polymaleimide. DMA of the thermosets showed that the storage moduli were kept

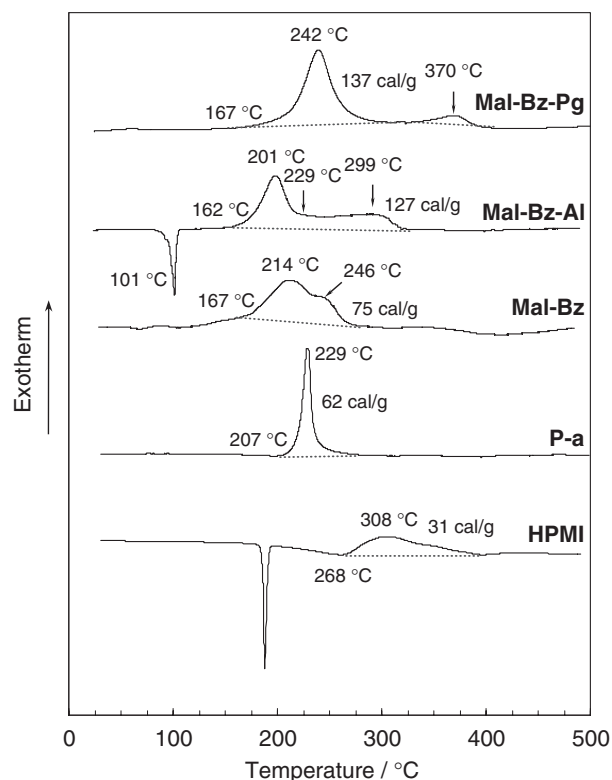


Figure 9. DSC thermograms of maleimidobenzoxazines.

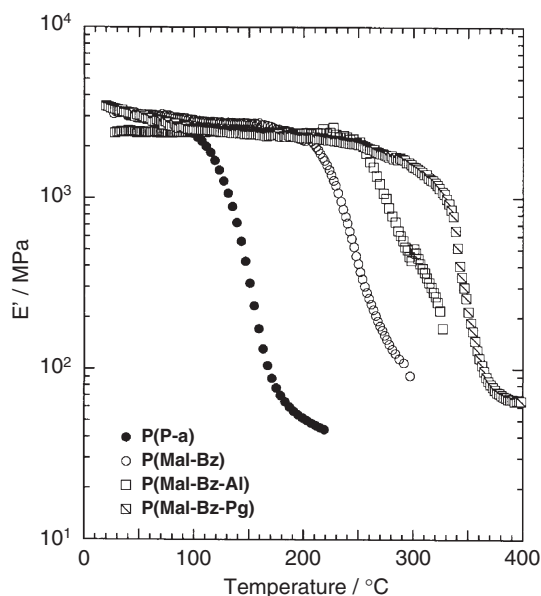


Figure 10. Viscoelastic properties of polybenzoxazines from maleimidobenzoxazines.

constant up to high temperatures, and the  $T_g$ s were as high as 241–335 °C (Figure 10). Furthermore, TGA revealed that the thermosets did not show any weight loss up to about 350 °C, with char yields ranging from 62 to 70% at 800 °C.

Many types of crosslink sites are available that can be incorporated into the benzoxazine structure. Thus, further study

will be continued for getting high performance polybenzoxazine with improved processability.

## HIGH MOLECULAR WEIGHT BENZOXAZINE PRECURSORS

So far, only the low molecular weight cyclic monomers have been studied in detail as the precursors of polybenzoxazines. Though Ishida reported the modification of polyphenol with a monofunctional amine to get a benzoxazine-functional polymer,<sup>9</sup> a high molecular weight polymer containing the cyclic benzoxazine structure as a repeating unit in the main chain has not yet been prepared. This is probably due to the belief that the attempt to form a polymeric benzoxazine precursor would result in gel or insoluble solid because of the ring-opening polymerization of the once-formed cyclic ring during the preparation of the precursors. If it is possible to prepare soluble high molecular weight polybenzoxazine precursors, processing into thin films should become very easy, and the application into the fields for which the low molecular weight cyclic monomer has not used will be realized.

High molecular weight polybenzoxazine precursors containing cyclic benzoxazine groups in the backbone were first prepared from bisphenol A, various diamines, and paraformaldehyde (Figure 11).<sup>10</sup> The yields of various precursors were in the range of 77–87% after purification. The  $M_w$  was in the range of 6,000–8,900 and  $M_n$  was 2,200–2,600, showing that the molecular weight is not so high. But, it should be emphasized that self-standing thin films were easily obtained by casting the precursor solutions. Heat treatment of the precursor films up to 240 °C gave brown transparent polybenzoxazine films. The polybenzoxazine films from the high molecular weight precursors exhibited significantly improved toughness than the typical polybenzoxazine, PB-a, due to the long linear backbone and high crosslink density. The PB-a film of 100  $\mu$ m thickness is very brittle, and we could not bend further than as is shown in Figure 12a. However, all the polybenzoxazine films from high molecular weight precursors showed remarkably improved toughness, and the films were easily bent as shown in Figure 12b.

Tensile properties of the films were examined, and it was found that the tensile strength and the elongation at break of the polybenzoxazines from the high molecular weight precursors were much higher than that of PB-a (Table I). PB-mda films have higher modulus than that of PB-a, probably because PB-mda has high content of rigid aromatics. PB-eda also showed high modulus because of the rigidity due to the short aliphatic chain. PB-hda with longer flexible methylene chain showed lower modulus but higher elongation at break. The  $T_g$  values of the polybenzoxazines from the high molecular weight precursors were as high as 238–260 °C, much higher than the  $T_g$  of the typical PB-a (171 °C) (Figure 13). The significant increase in  $T_g$  indicates the beneficial effect of the linear long backbone and the high crosslink density. The decrease of storage modulus above  $T_g$  was also considerably suppressed. Thermal stability of the polybenzoxazines depended on the aromatic content. The

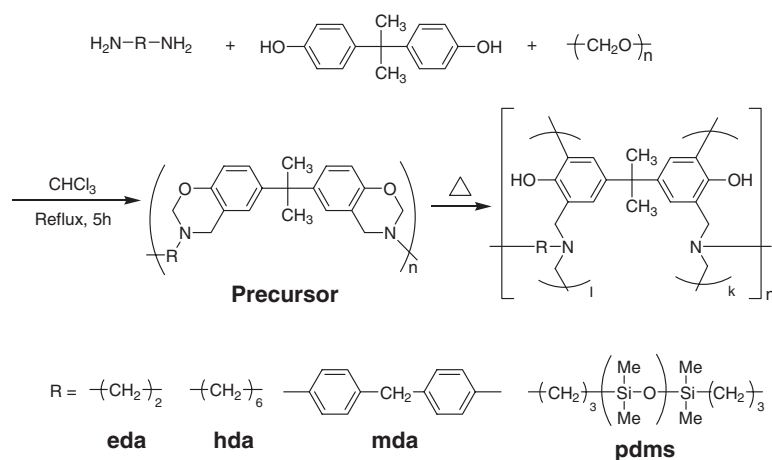


Figure 11. Preparation of polymeric benzoxazine precursors.

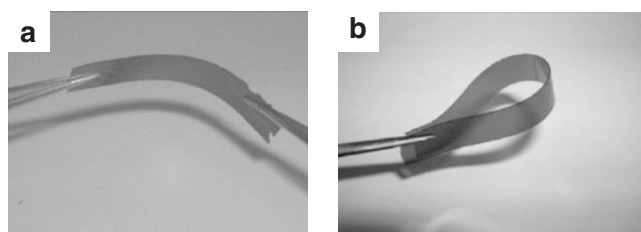


Figure 12. Appearance of polybenzoxazine films. a) PB-a, b) PB-mda.

Table I. Tensile properties of PB-a, PB-eda, PB-hda, and PB-mda films

	Tensile modulus	Tensile strength	Elongation at break
	GPa	MPa	%
PB-a	3.3	37	1.6
PB-eda	3.3	58	2.4
PB-hda	2.0	65	4.1
PB-mda	3.5	87	4.1

precursor with low aromatic content showed somewhat lower thermal stability. But, the thermal stability of PB-mda was higher than that of PB-a due to the high aromatic content.

High molecular weight precursors, namely AB-type polybenzoxazine precursors, were also synthesized from aminophenols and formaldehyde (Figure 14).<sup>11</sup> The precursors also gave self-standing thin films when their solutions were cast on glass plates and dried. Upon a gradual thermal cure up to 250 °C, they afforded polybenzoxazine films, having  $T_g$  as high as 260–300 °C. TGA results indicated that the onset of decomposition and the char yield of the thermosets were higher than those of the typical polybenzoxazine.

## POLYMER ALLOY

Performance of polybenzoxazines can be improved, to a great extent, by alloying with various polymers or precursors, offering high degree of flexibility in tailoring materials with variation in properties. Alloying with epoxy and/or phenolic resin has been one of the well studied example.<sup>12</sup> Polybenzox-

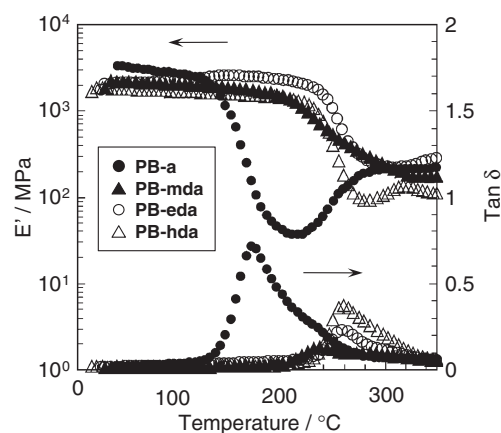


Figure 13. Viscoelastic analysis of PB-a, PB-mda, PB-eda, and PB-hda films.

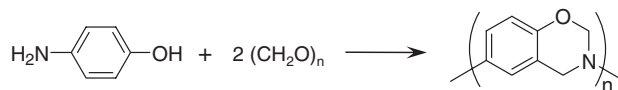


Figure 14. Preparation of an AB-type polybenzoxazine precursor.

azine reacts with epoxy through its phenolic OH, and the traditional phenolic resin works as an acid catalyst for the ring-opening polymerization of benzoxazine. Addition of the low viscous epoxy resin is also advantageous in processing.

Toughness of the brittle polybenzoxazine can be remarkably improved by alloying with elastomers like liquid rubber and polyurethane. By alloying with high temperature polymers like polyimide, the thermal and physical properties of polybenzoxazines can be significantly improved. Some examples will be shown below.

### Alloying with Liquid Rubber

The addition of a liquid rubber such as an amine- and a carboxy-terminated butadiene acrylonitrile (ATBN and CTBN) is an effective method to enhance the toughness of brittle

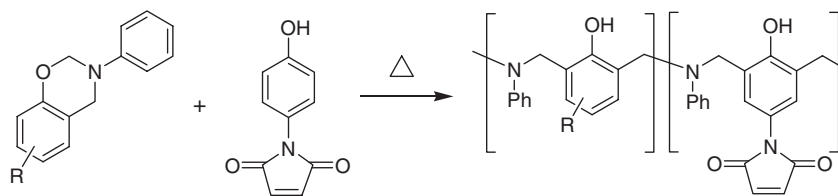


Figure 15. Possible reaction between benzoxazine and HPMI.

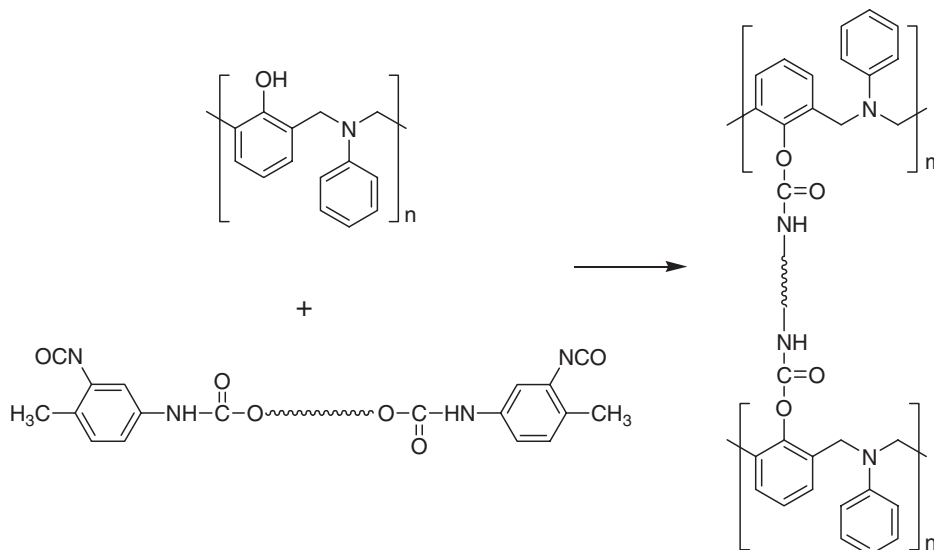


Figure 16. Possible reaction between polybenzoxazine and PU prepolymer.

materials like epoxy and bismaleimide. For polybenzoxazine, ATBN is reported to be more effective than CTBN on the toughness improvement.<sup>13</sup>

The performance of the ATBN-modified polybenzoxazines can be further improved by the addition of hydroxyphenylmaleimide (HPMI).<sup>14</sup> HPMI is activated by its OH group and copolymerize with benzoxazine (Figure 15). The blend with HPMI effectively lowers the cure temperature of B-a as large as 40–60 °C. The maleimide double bond in HPMI further crosslinks to give a cured resin having improved properties such as higher  $T_g$ , tensile modulus and thermal stabilities. Thus, the combination of HPMI and ATBN was effective to lower the ring-opening temperature, to enhance  $T_g$ , toughness, and degradation temperature at the same time.

#### Alloying with Polyurethane

Polyurethane (PU) is one of the most important functional polymers that are being used in various applications, but the poor thermal properties limit its applications. There are many studies to enhance the thermal properties of PU. Alloying with an aromatic polymer such as polyimide has been studied, and proved to be effective for enhancing the thermal properties of PU.<sup>15–17</sup> Alloying of PU with polybenzoxazine can be considered as a novel polymer alloy of PU and phenolic resin, in which improvement of both the thermal properties of PU and the toughness of polybenzoxazine can be achieved.

The blend of an NCO-terminated PU prepolymer and a benzoxazine monomer was thermally treated at 190–200 °C to give yellow transparent films.<sup>18,19</sup> The network structure is formed by the reaction of the NCO functionality with the phenolic OH that was formed through the ring-opening polymerization of the benzoxazine (Figure 16). Films became a plastic or an elastomer depending on the ratio of the benzoxazine and the PU prepolymer. Only one  $T_g$  was observed, and the  $T_g$  value increased with the increase of the benzoxazine content. By the introduction of PU, the toughness of benzoxazine was improved. On the other hand, the thermal stability of the PU was improved by the addition of a small amount of the benzoxazine.

#### Alloying with Polyimide or Poly(imide-siloxane)

A series of polyimide is one of the most important thermally stable polymers. Wide variations of the monomers and the precursors make polyimide a suitable candidate to be used as one component of a polymer alloy.

Polymer alloys of a polybenzoxazine and a polyimide was prepared by blending B-a as a benzoxazine monomer with a poly(amide acid), PAA, as a precursor of polyimide, followed by film casting and thermal treatment for the ring-opening polymerization of the benzoxazine and imidization.<sup>20</sup> Various types of PAA were prepared as shown in Figure 17. It was observed that the onset temperature of the exotherm due to the

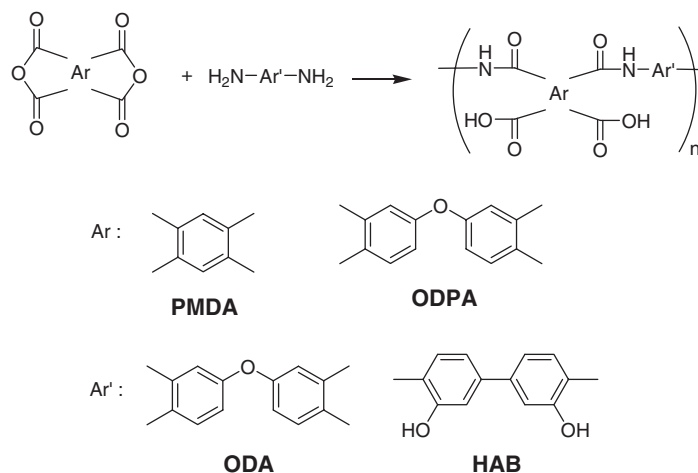


Figure 17. Preparation of various poly(amide acid)s.

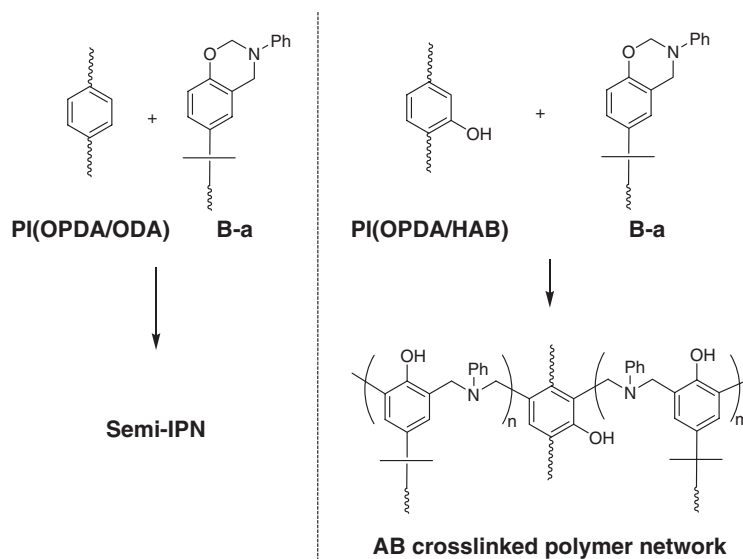


Figure 18. Structure of polymer alloys obtained from polyimide and benzoxazine.

ring-opening polymerization decreased as large as *ca.* 80 °C by blending B-a with a PAA because of the catalytic effect of the carboxylic group in the PAA. The resulting alloy films are considered to form a semi-interpenetrating polymer network (semi-IPN) consisting of a linear polyimide and a crosslinked polybenzoxazine or to form an AB co-crosslinked polymer network by the copolymerization of benzoxazine with polyimide containing a pendent phenolic hydroxyl group (Figure 18). The semi-IPN films gave two  $T_g$ 's, while the AB-co-crosslinked films gave only one  $T_g$ . Both types of polymer alloys were effective to improve the brittleness of a polybenzoxazine and to increase the  $T_g$  and the thermal degradation temperature. The semi-IPN formation was especially effective for toughening the polybenzoxazine, while the AB-co-crosslinked polymer network was effective for increasing  $T_g$ .

For further enhancing the toughness of the brittle PB-a, various poly(imide-siloxane)s were examined.<sup>21</sup> Soluble poly-

(imide-siloxane)s were prepared using 6FDA as a dianhydride. A poly(imide-siloxane) with hydroxyl group, PISi(OH), and a poly(imide-siloxane) without hydroxyl group, PISi, were prepared, as shown in Figure 19. Poly(imide-siloxane)s and B-a were dissolved in various weight ratios, cast onto glass plates followed by thermal treatment, affording yellow opaque films. When PISi was used, a semi-IPN type polymer alloy is considered to be formed, and two  $T_g$ 's were observed at *ca.* 230 and *ca.* 300 °C, suggesting phase separation between PB-a and PISi. On the other hand, when PISi(OH) was used, an AB co-crosslinked polymer network is considered to be formed, and only one  $T_g$  was observed at *ca.* 300 °C. In both cases,  $T_g$  due to the PB-a increased. Another  $T_g$  due to the PDMS component was found at *ca.* -60 °C. As the content of the poly(imide-siloxane) increased, the elongation at break increased, implying its effectiveness for the toughening of the PB-a. There is a tendency that the blend with PISi gave higher elongation at

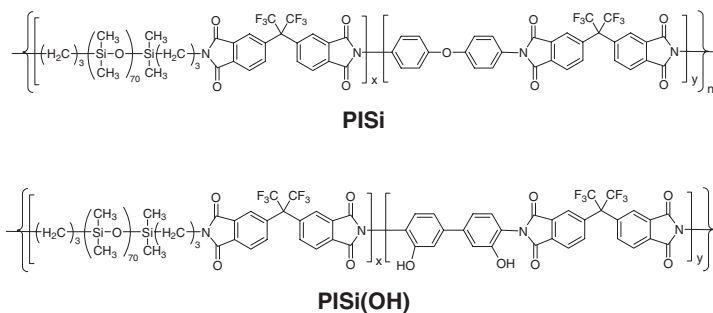


Figure 19. Structure of poly(imide-siloxane) with and without phenolic groups.

break than with PISi(OH), and was suggested to be more effective for toughening. In both cases, the thermal decomposition temperature also increased with the increase of the poly(imide-siloxane) content. Thus, both the toughness and the thermal properties of the PB-a were enhanced by the introduction of poly(imide-siloxane)s.

The effect of the preparation method was examined by preparing polymer alloys of a polyimide and a polybenzoxazine by two different methods: from the combination of B-a with a soluble polyimide (PI) or with its precursor, a poly(amide acid) (PAA), that was synthesized from oxydianiline (ODA) and bisphenol A di(phthalic anhydride) ether (BPADA).<sup>22</sup> Both of the polymer alloy films from PI/B-a and from PAA/B-a are considered to form semi-IPNs consisting of the linear PI and the PB-a network, in which two components are well miscible as confirmed by the transparency and the existence of only one  $T_g$ . Both of the blending methods significantly improved the thermal and the physical properties as well as the toughness of PB-a. Interestingly, however, in the polymer alloy films from PI/B-a, the PI component dissolved completely, while in the alloy films from PAA/B-a, the PI component did not dissolve. Also, the films from PI/B-a were much more flexible than the films from PAA/B-a. These differences indicate the formation of some kind of chemical linkage that leads to a cross-linking between the linear PI and the PB-a when prepared from PAA/B-a.

#### Alloying with Bismaleimide

Another type of polymer alloy was prepared by mixing a typical benzoxazine monomer, such as P-a and B-a, and a typical bismaleimide, 4,4-bismaleimidodiphenyl methane (BMI), followed by a thermal cure.<sup>23</sup> IR and DSC analyses of the cure stage indicated the thermal reaction between the hydroxyl group of the polybenzoxazine and the double bond of BMI, forming an AB co-crosslinked structure as supported by the model reaction of phenol and *N*-phenylmaleimide. DMA of the polymer alloys showed only one  $T_g$ , also suggesting the formation of the AB co-crosslinked structure. Interestingly,  $T_g$  of the polymer alloys shifted to higher temperature by the increase of the BMI content, and were even higher than those of each resin due to the formation of the AB-co-crosslinking (Figure 20). The thermal stability also increased with the increase of the BMI content.

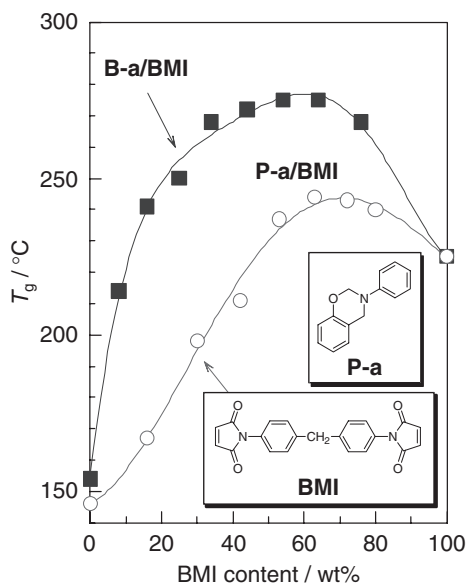


Figure 20. Influence of BMI content on  $T_g$  (from  $E''$  determined by DMA) of P-a/BMI and B-a/BMI alloys.

## ORGANIC-INORGANIC HYBRIDS

Another approach is based on the inclusion of inorganic materials such as organically modified layered clays and metal oxide nanoparticles by the sol-gel process. This approach was successful in obtaining polybenzoxazine hybrids with improved thermal and mechanical properties.

#### Preparation of Hybrids by the Inclusion of Layered Clay

Polymer-clay hybrid is a new class of composite materials, in which a clay as a layered silicate is dispersed in a polymeric matrix in nanoscale size.<sup>24</sup> Recently, we have successfully prepared several types of polybenzoxazine/clay hybrids, in which the inclusion of an organically modified-montmorillonite (OMMT) into a polybenzoxazine matrix led to a dramatic improvement of its properties.<sup>25,26</sup> Polybenzoxazine/clay hybrids were prepared by two different methods; a melt method and a solvent method. X-Ray diffraction (XRD) measurements of the hybrids showed that the blending method and the kind of solvent play crucial roles for the dispersion of OMMT in the



polybenzoxazine matrix. In the melt method and in the solvent method using NMP as a solvent, a complete exfoliation of clay nanolayers into the polybenzoxazine matrix was achieved, and red-brown transparent films were obtained. Interestingly, the inclusion of any type of OMMT significantly lowered the curing exotherm of the benzoxazines, suggesting a catalytic effect of the onium ions of the clay surface and/or the silanol groups at the edge of the clay on the ring-opening polymerization of the benzoxazines. The hybrids exhibited higher  $T_g$  values (for 25–30 °C) and increased storage moduli than the pristine resins. Dynamic and isothermal TGA clearly showed the improvement of the thermal stability by the inclusion of the clay. The effect of the clay was most significant at around 2–5 wt % of inclusion for the improvement of various properties.

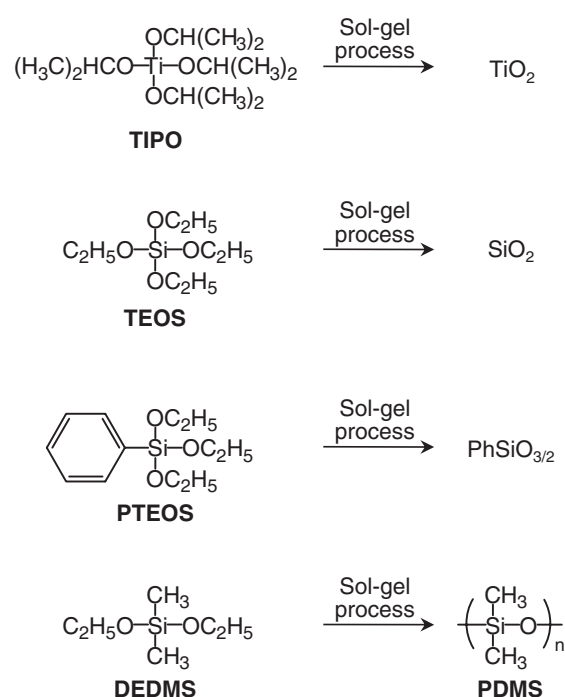
The effect of OMMT inclusion was also examined in the epoxy/polybenzoxazine<sup>27,28</sup> and the polyurethane/polybenzoxazine<sup>29</sup> alloys. In both cases, lowering of the cure temperature and the enhancement of the thermo-mechanical properties were achieved.

Polybenzoxazine-clay hybrids were also prepared using a synthetic mica.<sup>30</sup> The storage moduli of the hybrids were much enhanced because of the reinforcing effect of the mica nanolayers that have large aspect ratio. The hybrids also showed an improved thermal and thermoxidative stability with higher char yield.

### Preparation of Hybrid by *in situ* Formation of Metal Oxide by Sol-gel Process

The sol-gel process is a common and a convenient technique to develop a homogeneous and high purity metal oxide (Figure 21). Therefore, it is convenient to grow an inorganic ceramic network within a polymer matrix through the sol-gel process, thus producing organic-inorganic hybrids even at molecular level. Various types of organic-inorganic hybrids have been prepared by the sol-gel process.

Polybenzoxazine/SiO<sub>2</sub> hybrids were prepared by blending various content of tetraethoxysilane (TEOS) with B-a using THF followed by the curing up to 240 °C for 1 h.<sup>31</sup> Polybenzoxazine/TiO<sub>2</sub> hybrids were similarly prepared by using titanium isopropoxide (TIPO).<sup>32</sup> The hybrid films were optically transparent with loading of SiO<sub>2</sub> or TiO<sub>2</sub> up to 10–20%, and the transparency decreased at higher loading. In the hybrid blends of B-a and TEOS or TIPO, the onset and the maximum of the exotherm due to the ring-opening of the oxazine ring was shifted to lower temperature at small loading of the metal oxide precursor. This implies that the acidity of the residual Si-OH and Ti-OH group in SiO<sub>2</sub> or TiO<sub>2</sub> network is high enough to initiate the ring-opening polymerization of B-a. The morphology of the hybrids was studied by TEM, indicating that the inorganic domains are homogeneously dispersed into the organic matrix in a nanoscale. The viscoelastic analyses revealed that the inclusion of silica or titania shifted the  $T_g$  to higher temperature in comparison with the neat resin. The temperatures at 5 and 10% decomposition, and also the char yield of PB-a considerably increased by the inclusion of small

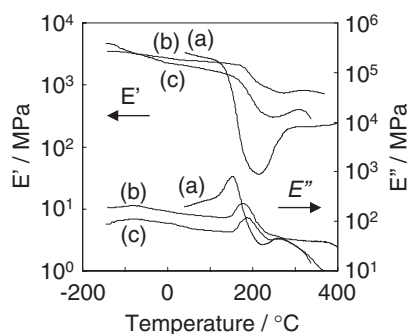


**Figure 21.** Preparation of TiO<sub>2</sub>, SiO<sub>2</sub>, PhSiO<sub>3/2</sub>, and PDMS through sol-gel process from TIPO, TEOS, PTEOS, and DEDMS, respectively.

amount of silica or titania, demonstrating that the metal oxide dispersed into the matrix acts as a thermal insulator to protect the polybenzoxazine network.

Polysilsesquioxane (RSiO<sub>3/2</sub>) was also introduced into polybenzoxazine, PB-a, by using the sol-gel process of trifunctional alkoxy silane.<sup>33</sup> The introduced PhSiO<sub>3/2</sub> (Figure 21) showed higher compatibility with PB-a than SiO<sub>2</sub> due to the enhanced interaction between the organic and the inorganic phases through the  $\pi$ - $\pi$  interaction. Resulting hybrid showed improved thermal and mechanical properties.

Polydimethylsiloxane (PDMS) is an inorganic polymer that shows not only flexibility but also unique properties such as good thermal and oxidative stability, low surface energy, high hydrophobicity, and high gas permeability. Polybenzoxazine/PDMS hybrids were successfully prepared by blending a benzoxazine monomer and diethoxydimethylsilane (DEDMS), followed by the thermal cure that induce the ring-opening polymerization of the benzoxazine and the sol-gel process of DEDMS (Figure 21).<sup>34</sup> The introduction of PDMS improved the tensile strength and the elongation at break of the pristine PBa, because of the toughening effect of the PDMS. Surprisingly, in spite of the introduction of the flexible PDMS with low  $T_g$ ,  $T_g$  of the polybenzoxazine component shifted to higher temperature (Figure 22). The decrease of the storage modulus above  $T_g$  was also suppressed by the hybridization with PDMS. These results suggest that the *in situ* formed PDMS behaves as a plasticizer for the polymerization of benzoxazine accompanied with the increase of the crosslink density. Moreover, the decomposition temperature and the weight residue at 850 °C increased with increasing the PDMS content.



**Figure 22.** DMA of pristine PB-a (a), and PB-a/PDMS hybrids at 7 (b) and 13 wt % (c) of PDMS contents.

## CONCLUSION

In this article, recent studies on the development of the polybenzoxazine as a novel type of phenolic resin were reviewed. The designing of novel monomers and high molecular weight precursors are a promising approach to obtain polybenzoxazines for specific applications taking advantage of the wide selection of mono- and diamines and also mono- and bisphenols. Polymer alloys or organic-inorganic hybrids are also promising approaches to design polybenzoxazine-based materials with required performance. Among the various approaches, the introduction of crosslink sites into a benzoxazine monomer is especially effective to enhance the thermal properties such as  $T_g$ . A problem is the brittleness of the cured materials. The final cure temperature also tends to increase. The approach using high molecular weight precursors is effective to give tough films with enhanced thermal and physical properties, though the final cure temperature is slightly increased. The approach of preparing polymer alloys is effective to design polymers with necessary performance. The alloys with elastomers are effective to give tough films, and interestingly, with enhanced thermal properties because of the increased crosslink density due to the plasticizing effect of the elastomers. Some polymers act as catalyst and lower the initial cure temperature of benzoxazine. The approach of organic-inorganic hybrids is effective to lower the final cure temperature and to enhance the thermal properties. The introduction of the hard inorganics increases the modulus but lowers the toughness. An exception is the introduction of flexible PDMS, in which case tough films are obtained without sacrificing the thermal properties.

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