

Chapter 2

Polybenzoxazine Alloys

Abstract Polybenzoxazine is a class of high-performance materials possesses many intriguing characteristics. The ability of alloying with other minor components is one of the crucial properties for this novel kind of thermosetting, i.e., the properties of the rendered alloys and blends could be tailor-made to meet the requirements of any application. In this chapter, the reviews of the polybenzoxazine alloys in the aspects of some important characteristics (such as thermal and mechanical properties) were dedicated.

Keywords Polybenzoxazine • Alloys • Blends • Tailor-made properties

2.1 Introduction

Polybenzoxazine (PBZ), a novel class of high-performance phenolic resin, have attracted great attention as versatile materials for structural and engineering applications because they possess good flame retardance, and thermal properties of phenolic resins, including their high mechanical properties, with good sound and noise absorbance. This class of thermosetting polymer could be synthesized from phenol (or substituted phenols), aldehyde (such as formaldehyde, acid aldehyde, or pyromucic aldehyde), and amine groups. Even though these resin types were firstly produced in 1940s by Holly and Cope [1], the capability of polybenzoxazine has become well known recently in 1990s [2]. The novel polymers can be synthesized via either solvent or solventless technology. Additionally, the curing of the resins involves ring-opening polymerization with no need of any catalyst or curing agent for producing, and there is no by-product during curing, which leads to no void in the products. In addition, polybenzoxazines render near-zero volumetric shrinkage or expansion upon cure, high processability due to low melt viscosity before polymerization, low water uptake, high char yield, and low coefficient of thermal

expansion. Moreover, the polymers render low dielectric constant and dissipation loss, high mechanical performance and great molecular design flexibility [3–15]. Interestingly, the polymers possess a crucial property, i.e., the ability to be alloyed with many chemicals such as epoxy, polyurethane. This interesting property leads to the modification of mechanical and thermal properties of the rendered alloys. That means the drawback of the polybenzoxazine, i.e., its brittleness, could be managed by alloying with other polymers [3–15]. In this chapter, this review article is dedicated to the polybenzoxazine alloys and blends.

2.2 Benzoxazine/Epoxy Copolymers

Although polybenzoxazines (PBZ) possess high glass-transition temperature and modulus, it is reported that the crosslink density of PBZ is rather lower than that of other thermosetting polymers with the same properties. The reason is attributed to the fact that hydrogen bonding could be sufficient to hinder the chain mobility and induce the rigidity as observed in the glassy state [12]. Ishida and Allen studied the copolymerization between PBZ and diglycidyl ether of bisphenol-A (DGEBA), the most commonly used epoxy resin in the copolymer, could lead to higher crosslink network [13]. That also has an effect on the higher glass-transition temperature (T_g) than the parent polymers as reported by Rimdusit et al. [16, 17]. The authors proposed that the reaction between benzoxazine and epoxy were composed of two reactions, i.e., the first reaction is the polymerization reaction between the monomers of benzoxazine, and the second one is the reaction between epoxide group on the epoxy and the phenyl group on polybenzoxazine. Furthermore, it was reported that the reaction between epoxide group and phenyl group was expected to proceed after ring-opening polymerization of phenolic hydroxyl group in benzoxazine monomers occurred [11, 17, 18]; the proposed reaction is presented in Fig. 2.1 [9].

Additionally, the DMA results reveal the synergistic behavior of glass-transition temperature as shown in Fig. 2.2. It could be noticed that the copolymer at the epoxy content beyond 45 wt% presents the significant decrease of T_g with the system containing equal amount of both two components. This could be attributed to the fact that the stoichiometric ratio of components was approached; the excess small molecular weight epoxy could not be unreacted and remain in the network formed. This could hinder network formation and act as a plasticizer in the fully polymerized network as discussed by Rimdusit et al. [17].

2.3 Benzoxazine/Epoxy/Phenolic Ternary System

The ternary system of benzoxazine, epoxy, and phenolic resins was developed by Rimdusit and Ishida [19]. It was reported that the properties of the mixtures depends on the mass ratios of the starting materials. Interestingly, the synergistic

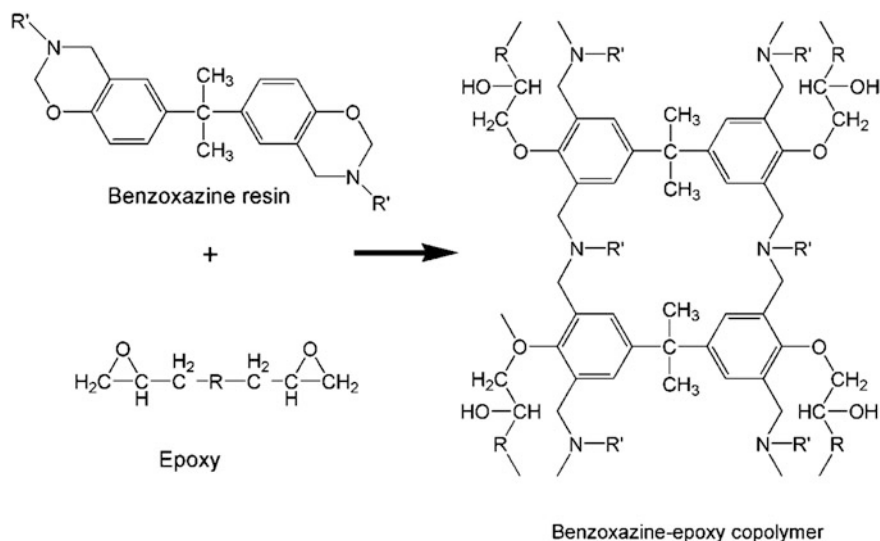
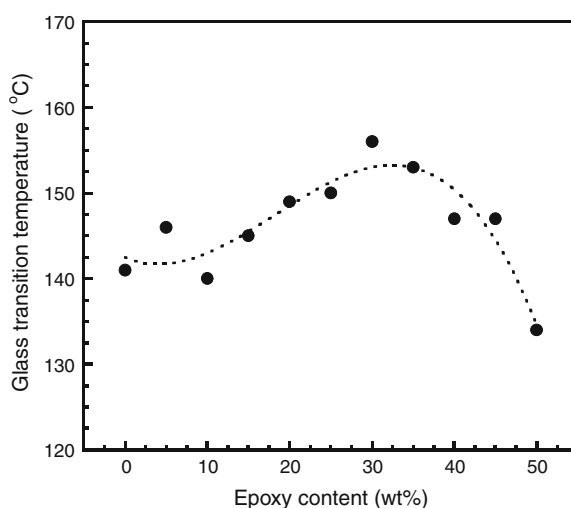


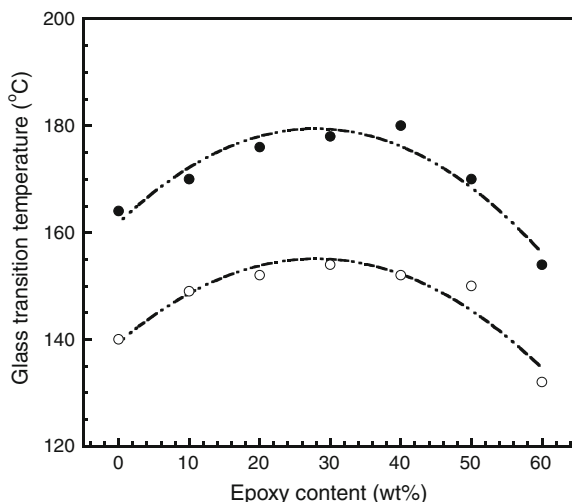
Fig. 2.1 Proposed reaction between benzoxazine monomer and epoxy

Fig. 2.2 Relationships between epoxy content and glass-transition temperature in benzoxazine-epoxy binary system



behavior of glass-transition temperature (T_g) is obtained. The relationships between the epoxy content and glass-transition temperature of the mixture with six blending ratios of benzoxazine/epoxy/phenolic resin (3/6/1; 4/5/1; 5/4/1; 6/3/1, 7/2/1, and 8/1/1) from DSC and DMA are exhibited in Fig. 2.3. It could be noticed that the highest glass-transition temperature observed from DMA is 180 °C, when the weight ratio of is 5/4/1 [13, 18]. The authors noted that the epoxy acted as diluents in the ternary system and increase the crosslink density and flexibility

Fig. 2.3 Relationships between the epoxy content and glass-transition temperature in the ternary system: (black circle) DMA values, (white circle) DSC values



compared with parent materials. Additionally, it was reported that the small amount of added phenolic resin could improve the crosslink density and the glass-transition temperature of benzoxazine/epoxy copolymer. The amount of phenolic resin in the range of 6–10 wt% was needed to obtain the highest T_g . Moreover, the synergistic behavior of glass-transition temperature was contributed to the rigidity from benzoxazine molecules and the increase of crosslink density from epoxy. It was reported that the small amount of phenolic resin leads to the decrease in the curing temperature of the ternary system in comparison with curing reaction of only benzoxazine/epoxy binary system.

2.4 Poly(Benzoxazine-Urethane) Alloys

The poly(benzoxazine-urethane) alloys were synthesized from urethane prepolymer and monofunctional or bifunctional benzoxazine resins. For example, the synthesis of the alloy using 3-phenyl-3,4-dihydro-2H-1,3-benzoxazine (Cm-type monofunctional benzoxazine resin) and urethane prepolymer (derived from polyethylene adipate polyol with molecular weight of 1000 Da and 2,4-tolylene diisocyanate at molar ratio of 1:2) are shown in Fig. 2.4 [20]. It was reported that during polymerization, there could be intermolecular reaction between hydroxyl groups (OH-) of benzoxazine monomer and isocyanate groups (NCO-) of urethane prepolymer. The cured poly(benzoxazine-urethane) alloys films were transparent, indicating good compatibility between two components. This is confirmed by the only one glass-transition temperature, suggesting no phase separation in the alloys. Furthermore, the authors reported that the decomposition temperature of the alloys were higher than that of pure polyurethane. That means even small amount of

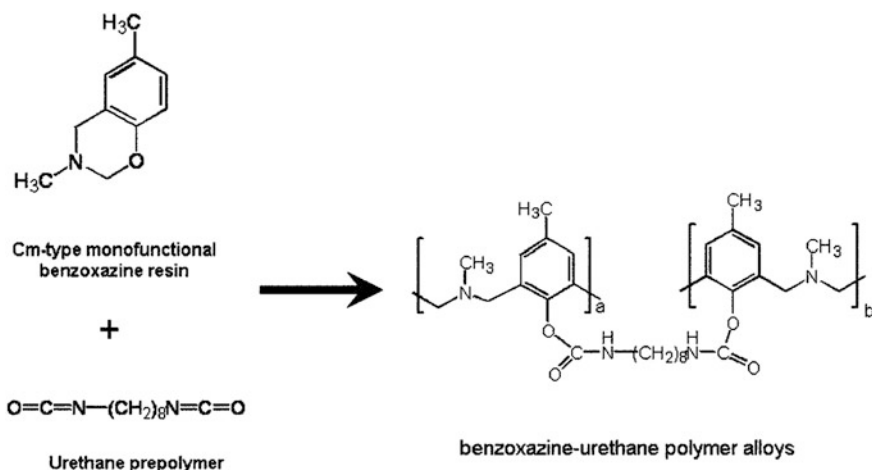


Fig. 2.4 Proposed reaction of Cm-type benzoxazine resin and urethane prepolymer

benzoxazine added in the polyurethane could increase the thermal stability of the polyurethane.

The alloys between BA-a (bifunctional benzoxazine) resin and urethane prepolymer (prepared from isophorone diisocyanate and polyether polyol with molecular weight of 2000 Da at the molar ratio of 2:1) was studied by Rimdusit et al. [21]. The authors reported that the enhancement of the glass-transition temperature (T_g) of the alloys also observed as seen in Fig. 2.5. It could be noticed that one glass-transition temperature is observed for the alloy synthesized from urethane prepolymer and either monofunctional or bifunctional benzoxazine resins. That exhibits high miscibility between the starting polymeric components because of the copolymer reaction [19, 21, 22].

The T_g of the alloys are noticeably higher than those of the parent resins, e.g., the alloy at 30 wt% of PU renders the glass-transition temperature of approximately 220 °C, while those of pure PU and PBZ are reported to be about −70 and 165 °C, respectively [11, 16–18, 23]. The effects of polyol molecular weight on the properties of poly(benzoxazine-urethane) alloys were investigated using various molecular weights, e.g., 1,000, 2,000, 3,000, and 5,000 [24]. The flexural strength values of the poly(benzoxazine-urethane) at different molecular weights of polyol are presented in Fig. 2.6. It could be seen that the strength of the binary systems did not reveal a linear relationship with the PU content but exhibited the synergistic behavior with the maximum values at the BA-a:PU ratio of 90:10. It was reported that there was no significant effect of polyol molecular weight on the glass-transition temperature (T_g) of the alloys. The synergy of T_g of polybenzoxazine has been reported in various alloy systems as the polybenzoxazine renders relatively low crosslink density in comparison with epoxy of the same type of bisphenol as starting material. The research related to the model of benzoxazine dimer and trimer structures has revealed the intermolecular and intramolecular

Fig. 2.5 DSC thermograms of the poly(benzoxazine-urethane) alloys at various BA-a:PU ratios: (black circle) 100:0, (white circle) 90:10, (black square) 80:20, (white square) 70:30

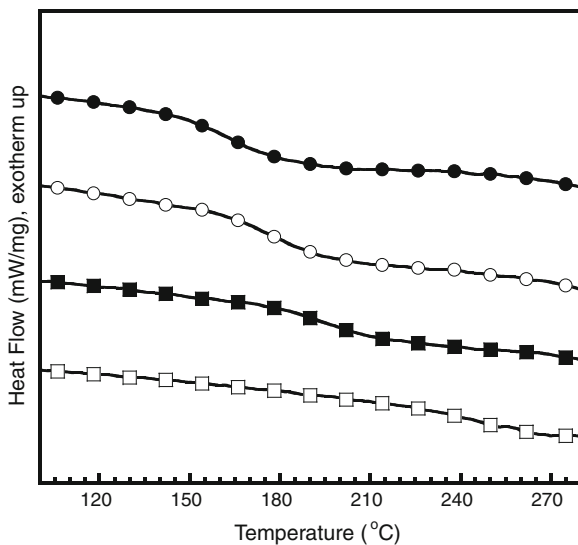
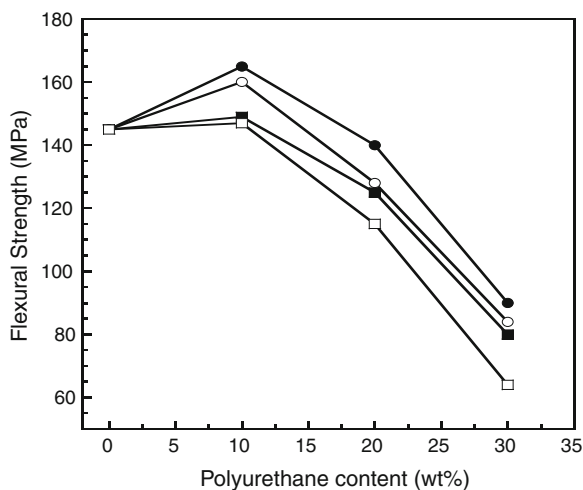
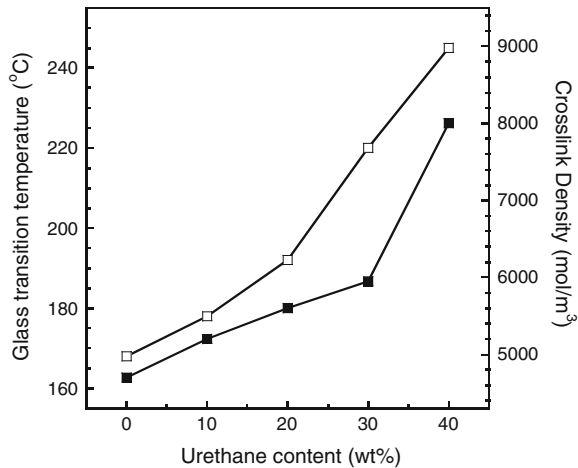


Fig. 2.6 Relationship between average values of flexural strength and urethane content at different polyol molecular weights: (black circle) 1000, (white circle) 2000, (black square) 3000, (white square) 5000



hydrogen bonding, hindering the network formation to obtain high crosslink density [12]. The addition of second polymer to form the alloy could increase the crosslink density of poly(BA-a) alloyed with PU elastomer. Figure 2.7 presents the effects of polyurethane contents on the glass-transition temperature and the crosslink density of the alloys of benzoxazine and polyurethane synthesized from the polyol at a molecular weight of 2000 with toluene diisocyanate (TDI) [16]. In the figure, the crosslink density of the copolymer networks, ρ_x , can be approximately calculated from the equilibrium value of shear storage modulus in the rubbery region (G_e') which equal to $E_e'/3$ as presented in Eq. (2.1)

Fig. 2.7 Relationships of urethane content on glass-transition temperature and crosslink density of poly(benzoxazine-urethane) alloy: (white square) glass-transition temperature, (black square) crosslink density



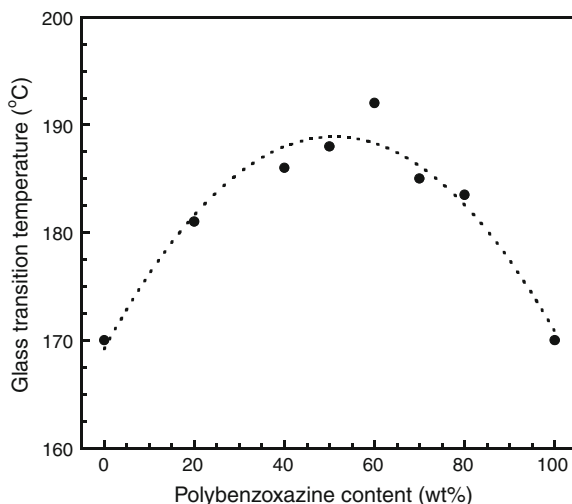
$$\log \left[\frac{E'_e}{3} \right] = 7.0 + 293(\rho_x) \quad (2.1)$$

where E'_e is an equilibrium value of tensile storage modulus at rubbery plateau in the unit of dyne/cm^2 . ρ_x is a value of crosslink density, being the amount of mole of network chains per unit volume of the polymers.

2.5 Polybenzoxazine/Poly(N-Vinyl-2-Pyrrolidone) Alloy

Su et al. [25] prepared the alloys between BA-a-type polybenzoxazine (PBZ) and poly(N-vinyl-2-pyrrolidone) (PVP); the thermal properties and hydrogen bonding of the alloys were determined. The authors reported that only one glass-transition temperature (T_g) was observed for all PVP contents, exhibiting complete miscibility in the PBZ/PVP alloy. The synergism of glass-transition temperature was reported as shown in Fig. 2.8. The highest value of glass-transition temperature could be found at the weight ratio of 50:50. Furthermore, the researchers reveal that the hydrogen bonding in polybenzoxazine/poly(N-vinyl-2-pyrrolidone) alloy could occur due to the interaction between the carbonyl group of poly(N-vinyl-2-pyrrolidone) and hydroxyl group of polybenzoxazine. This interaction could be sufficient to induce rigidity and impede the molecular mobility in the alloys, leading to the T_g synergism.

Fig. 2.8 Synergism of glass-transition temperature in the PBZ/PVP alloy

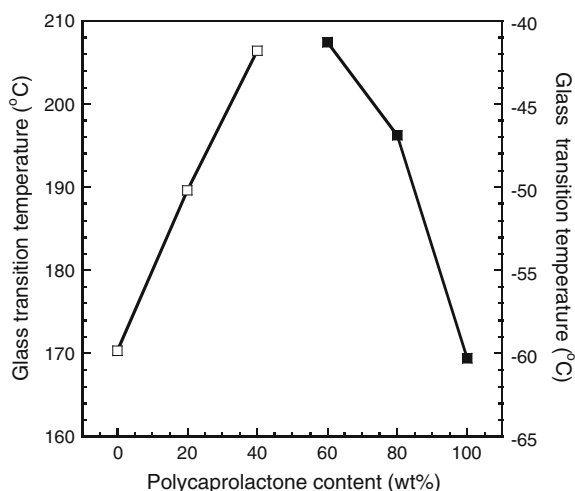


2.6 Polybenzoxazine/Poly(ϵ -Caprolactone) Blends

As a nature of phenolic materials, polybenzoxazines tend to be brittle. This characteristic limits the applications of this material. Thus, the flexural and impact properties of the polymers are expected to enhance when incorporating a component rendering a low glass transition (T_g). Huang and Yang [26] prepared the blends between bisphenol-A/methylamine-based benzoxazine resin (BA-m) and poly(ϵ -caprolactone) (PCL) via solution blending method. The miscibility and thermal behaviors of the blends were studied. They reported that the synergistic behavior of glass-transition temperature (T_g) was found in low content of PCL. As presented in Fig. 2.9, the T_g value of the blends is as high as ca. 206 °C, while those of poly(BA-m) and PCL are ca. 170 and –60 °C, respectively. This could be attributed to the fact that higher polymerization conversion occurred when PCL was presented as observed in the Fourier transform infrared spectroscopy (FTIR) results. The FTIR spectra revealed intermolecular hydrogen bonding between the hydroxyl groups of PBZ and the carbonyl groups of PCL during polymerization. This could lead to the improvement of T_g and the miscibility of poly(BA-m) and PCL. This can be implied that the addition of poly(ϵ -caprolactone) into polybenzoxazine could enhance the properties of the polybenzoxazine at high temperature. The enhancement of flexural properties of the polybenzoxazine/poly(ϵ -caprolactone) blends was reported by Ishida and Lee [27], while the phase separation was discussed by Zheng et al. [28].

Despite many outstanding characteristics of polybenzoxazine as previously mentioned, pure polybenzoxazine is not suitable for coating such as its brittleness. There has been an attempt to modify the properties of polybenzoxazine, i.e., the preparation of benzoxazine monomer with additional functional group, the synthesis of benzoxazine-based composites and alloys, and incorporation of

Fig. 2.9 Glass-transition temperature of polybenzoxazine/poly(ϵ -caprolactone) blends at various PCL contents: (*white square*) low content, (*black square*) high content



benzoxazine in polymer chain. Recently, there has been a study on the system of sunflower oil-modified polyester (SOMP) prepared via the ring-opening polymerization of ϵ -caprolactone [29]. Stannous octoate and partial glycerides were used as catalyst and initiator, respectively. The mole ratio of monomer by initiator was various to control the chain length of polycaprolactone and shorten the reaction time. The hydroxyl functional benzoxazine monomer was prepared by combining with SOMP. The FTIR results revealed the urethane linkage between the hydroxyl functional benzoxazine monomer (HFBa) and SOMP. The rendered alloys possess low brittleness. The thermal properties of the cured alloys and pure polymers are presented as shown in Table 2.1.

From Table 2.1, it reveals that the degradation temperature of cured HFBa was lower than cured SOMP-HFBa because of the highly cleavable Mannich bridges of HFBa. However, it could be noticed that after removing the volatile portion, the remained char yield is rather high.

Table 2.1 Thermal characteristics of the cured alloys and pure polymers (adapted from Taşdelen-Yücedağ et al. [29])

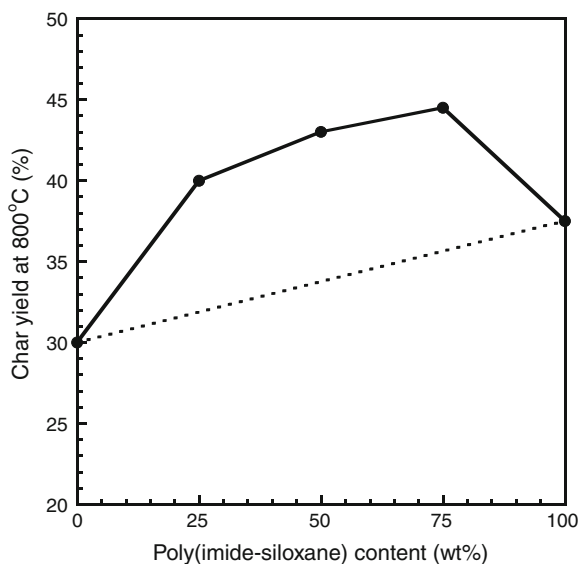
Sample	Degradation temperature at 5% weight loss (°C)	Char yield at 538 °C (%)
Pure SOMP-HFBa	304	1.1
SOMP-HFBa/HFBa (1/8 mol ratio)	291	26.6
SOMP-HFBa/HFBa (1/10 mol ratio)	274	26.4
Pure HFBa	270	28.8

2.7 Polybenzoxazine/Poly(Imide-Siloxane) Alloys

Ardhyananta et al. [30] reported the improvement of thermal stability, mechanical property, flame resistance, and flexibility of bisphenol-A/aniline-based polybenzoxazine (poly(BA-a)) by alloying with polydimethylsiloxane (PDMS) since PDMS is one of the most important silicones that have inorganic main chain, showing both high flexibility and many intriguing properties, e.g., good oxidative stability, low surface energy, high hydrophobicity, high gas permeability, and good biocompatibility [31]. The alloys at 7 and 13 wt% of PDMS revealed higher thermal stability, i.e., the degradation temperatures at 10 %weight loss are 352 and 368 °C, respectively. These values are greater than that of pure polybenzoxazine (326 °C). It was reported that the glass-transition temperature determined from E'' peak of DMA results presented two values. The higher T_g was in the range of 176–185 °C, while the lower T_g was in the range of 63–72 °C. These T_g values correspond to those of poly(BA-a) and PDMS components, respectively. This behavior revealed the phase separation of the alloy in microscale. In addition, the char yield at 850 °C of the alloys increased with increasing PDMS content. The values of residual weight were in the range of 40–46 %, presenting the enhancement of the flame retardancy. In addition, they reported that the obtained alloy film render higher tensile strength and elongation at break than neat poly(BA-a) due to the toughening effect of PDMS. Recently, the effect of pendant groups of polysiloxane, e.g., PDMS, PMPS, and PDPS on thermal properties have been reported by Ardhyanant et al. [31]. The phenyl group of polysiloxanes as PMPS and PDPS improved their compatibility with poly(BA-a). The alloying could enhance the glass-transition temperature because of high crosslink density by plasticizing effect of polysiloxanes. Moreover, poly(BA-a)/PDMS alloy exhibited the optimum improvement of decomposition temperature, while poly(BA-a)/PDPS presented the most effectiveness of flame retardancy. That means the thermal properties of the polybenzoxazine/poly(imide-siloxane) alloys depends on the types of polysiloxanes.

In order to enhance the miscibility of the alloy between poly(BA-a) and polysiloxanes, the polybenzoxazine alloying with PDMS-containing polyimide as poly(imide-siloxane) with hydroxyl functional group (PI-Si(OH)) was developed by Takeichi et al. [32]. The researcher reported that only one glass-transition temperature was observed at ca. 300 °C because crosslinked polymer networks were formed. It is worthy to note that in case of poly(BA-a) alloyed with poly(imide-siloxane) without hydroxyl functional group (PISi), the synergy of char yield was reported at certain content of PISi as presented in Fig. 2.10 [33]. The phenomenon could be due to a large amount of aromatic ring in the blends with some chemical interaction between poly(BA-a) and PISi.

Fig. 2.10 Char yield of the polybenzoxazine/poly(imide-siloxane) alloys



2.8 Polybenzoxazine/Polyimide Blends

Takeichi et al. [34] prepared the polymeric blends using a bifunctional benzoxazine resin, 6,6'-(1-methylethylidene)bis(3,4-dihydro-3-2H-1,3-benzoxazine) (BA-a) and a polyamic acid (PAA, intermediate compound to synthesize polyimide) or soluble polyimide (PI) derived from bisphenol-A di(phthalic anhydride) ether (BPADA) and oxydianiline (ODA). The results of loss modulus (E'') and loss tangent ($\tan\delta$) exhibited only one glass-transition temperature (T_g) in both systems of poly(BA-a)/PAA and poly(BA-a)/PI. That means these blending systems were miscible. The T_g s was shifted to higher temperature when increasing the content of imide. In comparison at the same ratio, the T_g s of poly(BA-a)/PAA alloys were slightly higher than that of poly(BA-a)/PI alloys. For example, at 30 wt% of poly(BA-a), the T_g of poly(BA-a)/PI alloys is 205 °C, while that of poly(BA-a)/PAA is higher than 215 °C. That indicates the formation of crosslinked structure in the alloys of poly(BA-a)/PAA. In aspect of thermal stability of poly(BA-a)/PI alloys and poly(BA-a)/PAA alloys, the value of decomposition temperature increased with the increase of imide content. In addition, the synergism of char yield was observed as shown in Fig. 2.11. It was presented that an interpenetrating polymer network (IPN) structure occurred in the systems. The PAA was imidized in situ with the polymerization of BA-a. This leads to the formation of aromatic ester group (AR-COOR). The proposed reaction between PAA and BA-a is presented in Fig. 2.12. The researchers explained that the combination of poly(BA-a) and PAA contains IPN structure, while that of poly(BA-a) and PI are supposed to be pure semi-IPN structures.

Fig. 2.11 Synergism of char yield in the polybenzoxazine/polyimide blends

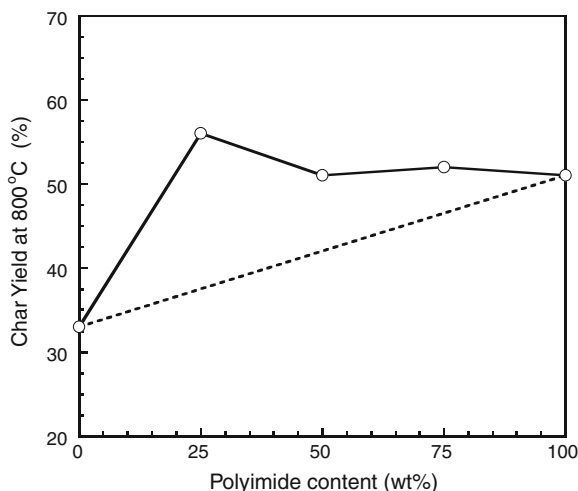
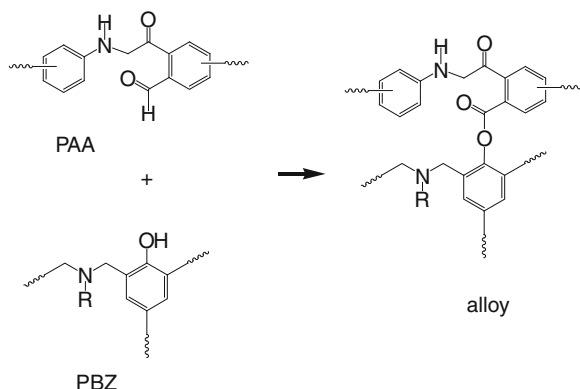


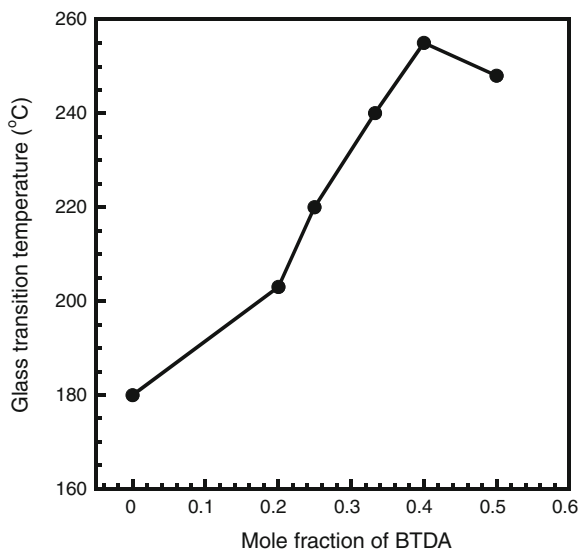
Fig. 2.12 Proposed reaction between PAA and PBZ



2.9 Polybenzoxazine/Dianhydride Copolymer

As previously mentioned in the section of the polybenzoxazine/polyimide blends, Takeichi et al. [34] reported that the chemical bonding between carboxylic acid of poly(amic acid) to generate aromatic ester group (Ar-COOR). Thus, the chemical bonding could be expected in the system of poly(BA-a) copolymerized with dianhydride (BTDA). In general, BTDA is applied as comonomer for high tensile strength polyimide fiber, films, and foams to render outstanding mechanical and electrical performances including excellent heat insulation and fire retardancy. Recently, the copolymers prepared from bisphenol-A/aniline-type benzoxazine resin (BA-a) and BTDA in N-methyl pyrrolidone (NMP) solvent were studied by Rimdusit and Jubsilp [35] and Jubsilp et al. [36]. From their works, the results from FTIR spectra showed that the chemical interaction between hydroxyl groups

Fig. 2.13 Glass-transition temperature of the polybenzoxazine–dianhydride copolymer at various BTDA mole fractions

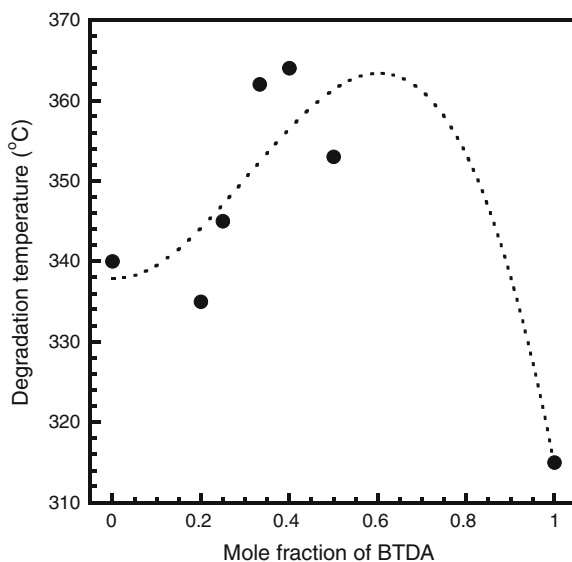


of poly(BA-a) and anhydride groups of dianhydride occur to generate ester linkages at the spectrum of 1730 cm^{-1} , similar to the peak found in the benzoxazine containing polyester studied by Tuzun et al. [37].

When the poly(BA-a) was incorporated with dianhydride, the ester linkages (the functional group with structural flexibility) were formed. That is able to make the rigid poly(BA-a) flexible. Furthermore, the transparency of copolymer indicates that there is no phase separation in the binary system. This physical appearance of fully cured copolymer is in agreement with the DSC results, which presents the single glass-transition temperature (T_g). It is worthy to note that the synergism of (T_g) was observed in the poly(BA-a) modified with BDTA, i.e., the T_g value of the BA-a:BDTA copolymer at the weight ratio of 60:40 (mole fraction of BDTA = 0.4) was reported to be $255\text{ }^{\circ}\text{C}$. This value is significantly higher than that of unmodified poly(BA-a), i.e., $173\text{ }^{\circ}\text{C}$ as presented in Fig. 2.13. The T_g improvement of poly(BA-a) is attributed to the increase in crosslink density of the copolymers determined by dynamic mechanical analysis (DMA). Additionally, the degradation temperatures of the copolymer were remarkably higher than those of the parent components as exhibited in Fig. 2.14. The residual weight or char yield of the copolymer at $800\text{ }^{\circ}\text{C}$ was as high as ca. 61 %, much higher than that of pure poly(PBA-a). Thus, the obtained copolymer possesses high mechanical properties with excellent fire retardancy.

Recently, there was an investigation on the effects of aromatic tetracarboxylic dianhydrides on the thermomechanical properties of poly(BA-a)-dianhydride copolymer [38]. Three different tetracarboxylic dianhydrides were determined, i.e., pyromellitic dianhydride (PMDA), 3,3',4,4' biphenyltetracarboxylic dianhydride (s-BPDA), or 3,3',4,4' benzophenonetetracarboxylic BTDA. The authors discussed that the rendered copolymer of poly(BA-a) and three types of dianhydride

Fig. 2.14 Degradation temperature of the polybenzoxazine–dianhydride copolymer at various BTDA mole fractions



could be potential candidates for high-performance materials with excellent mechanical integrity for high temperature applications. The glass-transition temperatures (T_g) of the copolymers were reported to be in the order of poly(BA-a):PMDA > poly(BA-a):s-BPDA > poly(BA-a):BTDA. The difference of the glass transition is relevant to the rigidity of dianhydride components. All types of dianhydride render significantly higher T_g than that of neat poly(BA-a) due to the improved crosslink density. Moreover, the decomposition temperature at 10 % weight loss of neat poly(BA-a) was 361 °C, while those of the copolymers increased in the order of poly(BA-a):PMDA (426 °C) > poly(BA-a):s-BPDA (422 °C) > poly(BA-a):BTDA (410 °C). This thermal stability could be related to the aromatic skeleton of the acid dianhydride component, i.e., phenylene unit > biphenyl unit > benzophenone unit [37].

2.10 Polybenzoxazine/Lignin Alloys

The curing and thermal behaviors of polybenzoxazine alloyed with lignin were investigated by Noru-Eddine et al. [39]. Two types of polybenzoxazines were determined, i.e., phenol-based benzoxazine (Pa) and bisphenol-A-based benzoxazine (Ba). The DSC results reveal the initial temperature (T_i), final temperature (T_f), peak curing temperature (T_p), heat of enthalpy of curing (ΔH), and glass-transition temperature (T_g) of the alloys as shown in Table 2.2. The results revealed that the maximum curing temperatures of the mixtures were less than that of neat benzoxazine monomer. The heat of polymerization of the mixture between

Table 2.2 DSC results of the polybenzoxazine/lignin alloys at various lignin contents (adapted from Noru-Eddine et al. [39])

Mpiass ratio of benzoxazine and lignin	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)	T_g (°C)
Pa-type polybenzoxazine	228	254	277	298	210
Pa:lignin = 95:5	182	226	274	440	214
Pa:lignin = 90:10	196	221	268	188	216
Pa:lignin = 85:15	162	207	266	319	218
Pa:lignin = 80:20	161	207	282	227	218
Pa:lignin = 75:25	150	207	277	224	223
Pa:lignin = 70:30	133	203	264	202	237
Ba-type polybenzoxazine	215	261	313	277	240
Ba:lignin = 95:5	111	229	301	330	304
Ba:lignin = 90:10	127	226	309	395	309
Ba:lignin = 85:15	143	256	297	284	310
Ba:lignin = 80:20	142	219	299	300	310
Ba:lignin = 75:25	136	215	299	339	310
Ba:lignin = 70:30	152	212	285	303	311

benzoxazine monomer and lignin had no relationship with the mass content. The increase in the lignin content leads to the increase in T_g . This could be attributed to the increase in crosslink density. In general, the value of T_g is related to the mobility of the polymer backbone and the crosslink density. Therefore, the lignin polymer could make network structure denser and the mobility of the backbone lower than the neat polybenzoxazine. Recently, Emranul Haque et al. [40] prepared and studied the polymer alloys of bisphenol-A-based polybenzoxazine and lignin by mixing two components and following with thermal curing. It was revealed that lignin accelerates the polymerization of benzoxazine. At the lignin content up to 2 wt%, the alloy is transparent. In case of higher content, the phase separation was observed. In aspect of thermal stability at lignin content of 10 wt%, the highest onset of decomposition temperature was observed. Moreover, it was reported that the char yield of the alloy film was increased with increased the lignin content. That indicates the higher flame retardancy of the alloy film than the neat polybenzoxazine.

2.11 Potential Applications of Polybenzoxazine Blends and Alloys

The wide applications of polybenzoxazine blends and alloys are in many areas, i.e. for fabricating molded and casted stuffs, as bonding particles, for ion exchange uses, for lamination and impregnation process, in manufacturing composites including electrical components, etc., because of the ability to be alloys with various kinds of resins or polymers. The property is able to broaden the range of applications of the polymer [8, 41, 42]. At present, the benzoxazine resins are

commercially produced as the component in prepreg composites due to their excellent toughness and stability at high temperature, significantly low shrinkage enhancing equipment surface quality, and drastically long out-life. In addition, liquid form of benzoxazine resin can be applied in the process of vacuum-assisted resin transfer molding (VARTM) and resin transfer molding (RTM) because of their excellent characteristics, e.g., easiness to process in VARTM and RTM, wide processing window, long storage time in room temperature. Another application of this resin is as film adhesive for composite bonding and high temperature composites. Moreover, benzoxazine resins are a good chemical to substitute phenolic resins attributed to nontoxicity before and upon cure and great fire resistant characteristics, high glass-transition temperature. Therefore, the familiar uses of the polybenzoxazine are such as the prepreg for aircraft interior parts that must meet the fire, smoke, and toxicity (FST) regulations. Recently, benzoxazine has been developed and favorably introduced for the applications in the halogen-free printed circuit board (PCB) manufacturing due to their many outstanding characteristics [43].

Furthermore, recently, the polybenzoxazine alloyed with poly(benzimidazole) has been developed for the purpose of highly durable polymer electrolyte membranes at high temperature (over 100 °C) [44]. The casting method is applied to the solution of a poly[2,2'-(*m*-phenylene)-5-5'-bibenzimidazole] and di-functional benzoxazine monomer, HFa benzoxazine, in *N,N*-dimethylacetamide before stepwise heating. The rendered films are potential to be produced in large scale by roll-to-roll coating. The products provide the thermal and mechanical stability.

References

1. Holly FW, Cope AC (1944) Condensation products of aldehydes and ketones with *o*-Aminobenzyl alcohol and *o*-Hydroxybenzylamine. *J Am Chem Soc* 66:1875–1879
2. Liu J, Ishida H (1996) A new class of phenolic resins with ring-opening polymerization. The polymeric materials encyclopedia. In: Salamone JC (ed), CRC Press, Florida, pp 484–494
3. Nair CPN (2004) Advances in addition-cure phenolic resins. *Prog Polym Sci* 29:401–498
4. Ghosh NN, Kiskan B, Yagci Y (2007) New high performance thermosetting resins: synthesis and properties. *Prog Polym Sci* 32:1344–1391
5. Yagci Y, Kiskan B, Ghosh NN (2009) Recent advancement on polybenzoxazine—a newly developed high performance thermoset. *J Polym Sci Part A: Polym Chem* 47:5565–5576
6. Endo T, Sudo A (2009) Development and application of novel ring-opening polymerizations to functional networked polymers. *J Polym Sci: Part A: Polym Chem* 47:4847–4858
7. Kumar KSS, Nair CPR (2010) Polybenzoxazines: chemistry and properties, iSmithers Rapra Publishing, England
8. Ishida H (1996) Process for preparation of benzoxazine compounds in solventless systems. US Patent 5,543,516
9. Ning X, Ishida H (1994) Phenolic materials via ring-opening polymerization: synthesis and characterization of bisphenol-A based benzoxazines and their polymers. *J Polym Sci Part B: Polym Phys* 32:921–927
10. Shen SB, Ishida H (1996) Development and characterization of high-performance polybenzoxazine composites. *Polym Compos* 17:710–719

11. Shen SB, Ishida H (1999) Dynamic mechanical and thermal characterization of high-performance polybenzoxazines. *J Polym Sci Part B: Polym Phys* 37:3257–3268
12. Ishida H, Allen DJ (1996) Physical and mechanical characterization of near-zero shrinkage polybenzoxazines. *J Polym Sci Part B: Polym Phys* 34:1019–1030
13. Ishida H, Low HY (1997) A study on the volumetric expansion of benzoxazine-based phenolic resin. *Macromolecules* 30:1099–1106
14. Wang YX, Ishida H (2002) Development of low-viscosity benzoxazine resins and their polymers. *J Appl Polym Sci* 86:2953–2966
15. Ishida H, Rodriquez Y (1995) Curing kinetics of a new benzoxazine-based phenolic resin by differential scanning calorimetry. *Polymer* 36:3151–3158
16. Rimdusit S, Bangsen W, Kasemsiri P (2011) Chemorheology and thermomechanical characteristics of benzoxazine-urethane copolymers. *J Appl Polym Sci* 132:13669–3678
17. Rimdusit S, Kunopast P, Dueramae I (2011) Thermomechanical properties of arylamine-based benzoxazine resins alloyed with epoxy resin. *Polym Eng Sci* 51:1797–1807
18. Kumar KSS, Nair CPR, Ninan KN (2009) Investigations on the cure chemistry and polymer properties of benzoxazine–cyanate ester blends. *Eur Polym J* 45:494–502
19. Rimdusit S, Ishida H (2000) Development of new class of electronic packaging materials based on ternary systems of benzoxazine, epoxy, and phenolic resins. *Polymer* 41:7941–7949
20. Takeichi T, Guo Y, Agag T (2000) Synthesis and characterization of poly(urethane-benzoxazine) films as novel type of polyurethane/phenolic resin composites. *J Polym Sci-A* 38:4165–4176
21. Rimdusit S, Pirstpindvong S, Tanthapanichakoon W, Damrongsakkul S (2005) Toughening of polybenzoxazine by alloying with urethane prepolymer and flexible epoxy: a comparative study. *Polym Eng Sci* 45(3):288–296
22. Takeichi T, Guo Y (2001) Preparation and properties of poly(urethane-benzoxazine)s based on monofunctional benzoxazine monomer. *Polymer* J 33(5):437–443
23. Rimdusit S, Ishida H (2000) Synergism and multiple mechanical relaxations observed in ternary systems based on benzoxazine, epoxy, and phenolic resins. *J Polym Sci Pol Phys* 38:1687–1698
24. Rimdusit S, Mongkhonsi T, Kamonchaivanich P, Sujirot K, Tiptipakorn S (2008) Effects of polyol molecular weight on properties of benzoxazine-urethane polymer alloys. *Polym Eng Sci* 48:2238–2246
25. Su YC, Kuo SW, Yei DR, Xu H, Chang FC (2003) Thermal properties and hydrogen bonding in polymer blend of polybenzoxazine/poly(N-vinyl-2-pyrrolidone). *Polymer* 44:2187–2191
26. Huang JM, Yang SJ (2005) Studying the miscibility and thermal behavior of polybenzoxazine/poly(3-caprolactone) blends using DSC, DMA, and solid state ¹³C NMR spectroscopy. *Polymer* 46:8068–8078
27. Ishida H, Lee YH (2001) Synergism observed in polybenzoxazine and poly(ϵ -caprolactone) blends by dynamic mechanical and thermogravimetric analysis. *Polymer* 42(16):6971–6979
28. Zheng S, Lu H, Guo Q (2004) Thermosetting blends of polybenzoxazine and poly(ϵ -caprolactone): phase behavior and intermolecular specific interactions. *Macromol Chem Phys* 205(11):1547–1558
29. Taşdelen-Yücedağ Ç, Erciyes AT (2013) Preparation of oil-modified polycaprolactone and its further modification with benzoxazine for coating purposes. *Prog Org Coat* 76:137–146
30. Ardhyananta H, Wahid MH, Sasak M, Agag T, Kawauchi T, Ismail H, Takeichi T (2008) Performance enhancement of polybenzoxazine by hybridization with polysiloxane. *Polymer* 49:4585–4591
31. Ardhyananta H, Kawauchi T, Ismail H, Takeichi T (2009) Effect of pendant group of polysiloxanes on the thermal and mechanical properties of polybenzoxazine hybrids. *Polymer* 50:5959–5969
32. Takeichi T, Agag T, Zeidam R (2001) Preparation and properties of polybenzoxazine/poly(imide-siloxane) alloys: In situ ring-opening polymerization of benzoxazine in the presence of soluble poly(imide-siloxane). *J Polym Sci Pol Chem* 39:2633–2641

33. Tiptipakorn S, Damrongsakkul S, Ando S, Hemvichian K, Rimdusit S (2007) Thermal degradation behaviors of polybenzoxazine and silicon-containing polyimide blends. *Polym Degrad Stabil* 92(7):1265–1278
34. Takeichi T, Guo Y, Rimdusit S (2005) Performance improvement of polybenzoxazine by alloying with polyimide: effect of preparation method on the properties. *Polymer* 46:4909–4916
35. Rimdusit S, Jubsilp C (2007) Polymer from anhydride modified polybenzoxazine. Thailand Patent pending. Issue Number 5543516
36. Jubsilp C, Takeichi T, Rimdusit S (2010) Property enhancement of polybenzoxazine modified with dianhydride. *Polym Degrad Stabil* 96(6):1047–1053
37. Tuzun A, Kiskan B, Alemdar N, Erciyes AT, Yagci Y (2010) Benzoxazine containing polyester thermosets with improved adhesion and flexibility. *J Polym Sci Polym Chem* 48:4279–4284
38. Jubsilp C, Ramsiri B, Rimdusit S (2012) Effects of aromatic carboxylic dianhydrides on thermomechanical properties of polybenzoxazine-dianhydride copolymers. *Polym Eng Sci* 52(8):1640–1648
39. Nour-Eddine EM, Yuan Q, Huang F (2012) Investigation of curing and thermal behavior of benzoxazine and lignin mixtures. *J Appl Polym Sci* 125:1773–1781
40. Emranul Haque HM, Islam Z, Kawauchi T, Takeichi T (2012) Preparation and properties of polybenzoxazine/lignin alloy. *Adv Mater Process Technol* 217–219:571–577
41. Ishida H (1999) Composition for forming high thermal conductivity polybenzoxazine-based material and method. US Patent 5900447
42. Ishida H, Rimdusit S (2001) Ternary systems of benzoxazine, epoxy, and phenolic resins. US Patent 6207786
43. Chen LC (2010) Halogen-free varnish and prepreg thereof. US patent 7842401
44. Kim SK, Kim KH, Park JO, Kim K, Ko T, Choi SW, Pak C, Chang H, Lee JC (2013) Highly durable polymer electrolyte membranes at elevated temperature: Cross-linked copolymer structure consisting of poly(benzoxazine) and poly(benzimidazole). *J Power Sour* 226:346–353

Alloys and Composites of Polybenzoxazines

Properties and Applications

Rimdusit, S.; Jubsilp, C.; Tiptipakorn, S.

2013, IX, 159 p., Hardcover

ISBN: 978-981-4451-75-8