

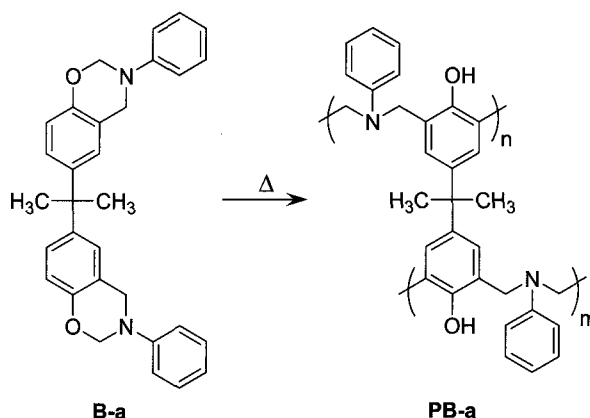
Preparation of High Molecular Weight Polybenzoxazine Prepolymers Containing Siloxane Unites and Properties of Their Thermosets

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Introduction

The traditional phenolic resins possess excellent characteristics such as good heat and chemical resistance, flame retardancy, and low cost due to the inexpensive raw materials and fabricating processes. Nevertheless, the traditional phenolic resins have some shortcomings as their brittleness, use of harsh catalyst for polymerization that corrode the equipments, presence of voids due to volatile by-products, and large volumetric shrinkage upon cure. The use of aqueous phenol also results in pollution of waste water which causes environmental and health threats. During the decade, benzoxazine-derived phenolic resins, namely polybenzoxazine, have been expected as a novel type of phenolic resins.¹ Chemical structures of a typical benzoxazine monomer,



Scheme 1. Thermal ring-opening polymerization of B-a.

6,6'-(1-methylethylidene)bis(3,4-dihydro-3-phenyl-2H-1,3-benzoxazine) (B-a), and its thermoset (PB-a) are shown in Scheme 1. The polymerization process proceeds through ring-opening of benzoxazine by heat treatment without using harsh catalysts and without generating by-products. Polybenzoxazine resin provides not only the advantageous properties of traditional phenolic resins but also other characteristics that are not present in the traditional phenolic resins such as excellent dimensional stability, low water absorption and good dielectric properties. Therefore, the application of polybenzoxazine as electronic materials, matrix for FRP and high performance adhesives is expected.

However, the shortcoming of polybenzoxazines is lack of flexibility as is common for thermosets, which limits their application. So far, some efforts that can be classified into two approaches have been done to improve the toughness of polybenzoxazines. First approach is alloying with flexible polymers such as polydimethylsiloxane (PDMS).²⁻⁴ For instance, PB-a/PDMS alloy with 13 wt% PDMS content was achieved by combining two types of reactions in-situ; the ring-opening polymerization of B-a and the sol-gel process of diethoxydimethylsilane.² The tensile strength and elongation at break of the obtained PB-a/PDMS alloy films were higher than the pristine PB-a film because of the toughening effect of PDMS. However, at ca. 25 wt% PDMS content, macroscopic phase separation occurred and the film became brittle.

Second approach is molecular design of the benzoxazine monomer such as high-molecular-weight polybenzoxazine prepolymers.⁵ Recently, we succeeded in the preparation of high-molecular-weight polybenzoxazine prepolymers from aromatic or aliphatic diamine and bisphenol-A with paraformaldehyde.⁵ The toughness of the crosslinked polybenzoxazine films from the high-molecular-weight prepolymers was greatly enhanced compared with the PB-a film.

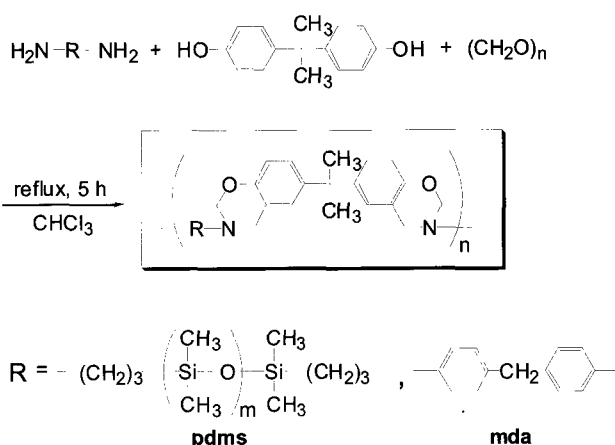
We report here the preparation of a novel type of high-molecular-weight polybenzoxazine prepolymers having polysiloxane unit through step-wise benzoxazine ring formation by the reaction of bisphenol-A and α,ω -bis(aminopropyl)polydimethylsiloxane (pdms) (Scheme 2). Influences of molecular-weight and content of pdms on thermal and mechanical properties of the thermosets were

investigated. Furthermore, methylenedianiline (mda) was used as a co-diamine for high-molecular-weight prepolymers.

Results and Discussion

Preparation of polybenzoxazine prepolymers. Polybenzoxazine prepolymers were prepared by reacting bisphenol-A, pdms (molecular weight = 248, 850 and 1622) and paraformaldehyde in CHCl_3 under reflux for 5 h (Scheme 2). The formulation for the preparation is shown in Table 1. The sample codes are abbreviated using the molecular weight of pdms such as B-pdms(248). The prepolymers were purified firstly by filtration to remove any formed insoluble gel, followed by washing the prepolymer solution in chloroform by aqueous NaHCO_3 solution to remove any residual unreacted phenolic compounds and paraformaldehyde. After evaporating the solvent at low temperature, powder was obtained having color ranging from colorless to pale yellow. The yields, viscosities and molecular weights of the prepolymers are shown in Table 2. The yield was ca. 80% after purification. The number average molecular weight (M_n) was 3,000~4,200 and the weight average molecular weight (M_w) was 5,700~9,800. This range of molecular weight was high enough to give easily free standing and flexible film by casting the prepolymer solutions.

In the same way, the B-mda/pdms prepolymers were prepared easily by using mda as the copolymer component (runs 4, 5 in Table 2).



Scheme 2. Preparation of siloxane-containing prepolymers, B-pdms and B-mda/pdms.

Table 1. Formulation for the preparation of siloxane-containing polybenzoxazine prepolymers.

Code	pdms		Siloxane content / %	mda		Bisphenol-A	
	Molecular weight of pdms	Feed / g (mmol)		Feed / g (mmol)	Feed / g (mmol)		
B-pdms(248)	248	4.97 (20.0)	25	-	4.57 (20.0)		
B-pdms(850)	850	5.00 (5.9)	65	-	1.34 (5.9)		
B-pdms(1622)	1622	6.57 (4.1)	79 ^a	-	0.93 (4.1)		
B-mda/pdms(850)	850	2.91 (3.5)	25	2.94 (14.8)	4.16 (18.3)		
B-mda/pdms(1622)	1622	2.69 (1.7)	25	3.22 (16.2)	4.01 (17.9)		

Formation of polybenzoxazine prepolymer films and cured films.

The siloxane-containing prepolymers were dissolved in dioxane and cast on glass plates. The free standing films were obtained by removing the solvent at 50 °C for 24 h. Brown transparent polybenzoxazine films were obtained by heat treatment with up to 240 °C to progress the ring-opening polymerization of the benzoxazine-ring (Scheme 3).

Table 2. Synthesis of siloxane-containing polybenzoxazine prepolymers

Run	Code	Yield / %	$\eta_{\text{red}}^a / \text{dL g}^{-1}$	$M_n (M_w)^b$
1	B-pdms(248)	75	0.06	3,000 (5,700)
2	B-pdms(850)	75	0.08	4,200 (9,800)
3	B-pdms(1622)	79	0.08	4,200 (8,900)
4	B-mda/pdms(850)	78	0.12	3,500 (10,000)
5	B-mda/pdms(1622)	83	0.15	3,600 (11,000)

^a The viscosity was measured in dioxane (0.5 g/dL) at 30 °C.

^b Determined by GPC (polystyrene standards).

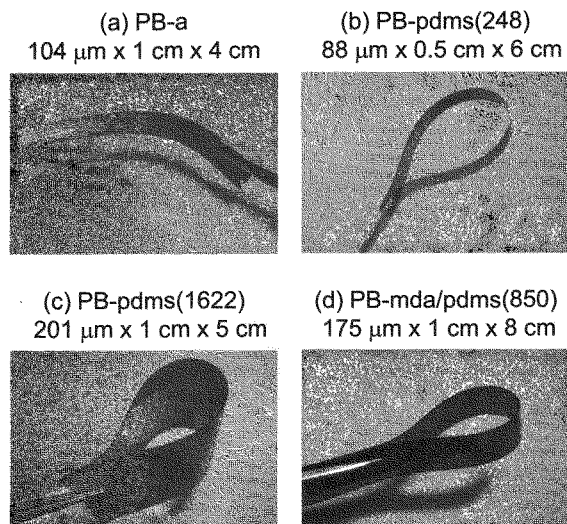
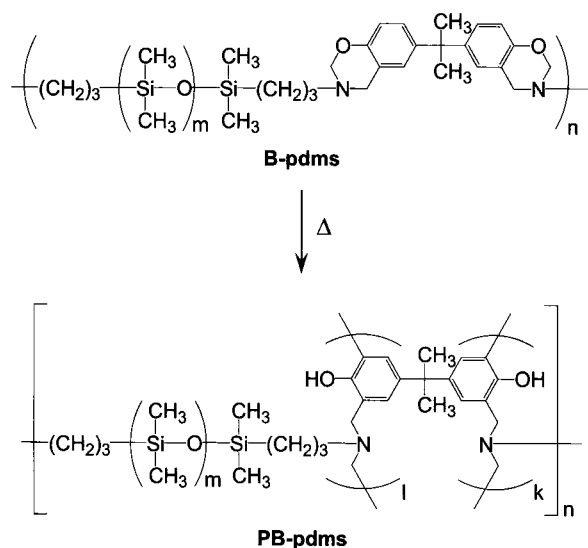


Figure 1. Appearance of pristine PB-a (a) and

Scheme 3. Thermal ring-opening polymerization of

The appearances of the cured polybenzoxazine films are shown in Figure 1. The PB-a film of 104 μm thickness is very brittle, and we could not bend further as shown in Figure 1a. In contrast, the PB-pdms films had remarkably improved toughness, and even the thick films are easy to bend (Figures 1b,c). The PB-mda/pdms film also shows high flexibility (Figure 1d).

Tensile properties of siloxane-containing polybenzoxazine films. The tensile properties of the siloxane-containing polybenzoxazine films were measured (Figure 2). The typical polybenzoxazine film, PB-a, shows high modulus, but the poor toughness made film easy to break at low elongation. On the other hand, tensile strength and elongation at break of PB-pdms(248) film increased, because of the flexible siloxane backbone. Interestingly, in spite of the introduction of siloxane component, tensile modulus did not decrease so much. By using high-molecular-weight pdms (pdms(850) and pdms(1622)), the elongation at break increased a lot. These results clearly indicate that the siloxane component acts as the toughener. However, the modulus and strength of the PB-pdms(850) and PB-pdms(1622) significantly decreased. The drawback was overcome by copolymerizing pdms with mda, and the cured polymer films showed much improved tensile modulus and strength than the PB-pdms films. The copolymer films also revealed improved tensile strength and elongation at break in comparison PB-a without sacrificing the modulus so much (Figure 2).

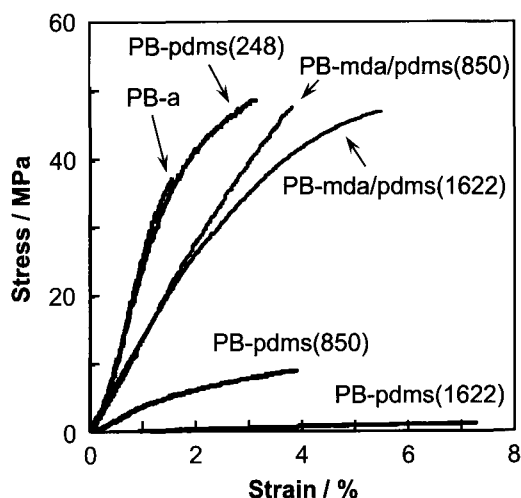


Figure 2. Stress-strain curves of PB-a, PB-pdms and

Thermal properties of siloxane-containing polybenzoxazine films. Viscoelastic analysis of the siloxane-containing polybenzoxazine films were examined. The storage modulus (E') at room temperature and T_g s determined from the maxima of loss modulus (E'') and $\tan \delta$ are summarized in Table 3. The E' value at room temperature decreased by the introduction of pdms. The tendency is in good agreement with the results from the tensile test mentioned above. Surprisingly, in spite of the introduction of siloxane component that have low T_g , the T_g of PB-pdms(248) was 238 °C from $\tan \delta$ which was higher than that of PB-a (171 °C), indicating the beneficial effect of linear long backbone which restricted the movement of polymer chain. Furthermore, the decrease of E' above T_g was

suppressed, suggesting that crosslink density of polybenzoxazine component increased, which also contributes to the increase of T_g , probably due to the plasticizing effect of the introduced pdms(248) during the curing.

Moreover, the significant increase in T_g was achieved for the PB-mda/pdms films; the T_g s of PB-mda/pdms(850) and PB-mda/pdms(1622) were 283 °C and 276 °C, respectively. It should be noted that the T_g s of PB-mda/pdms are higher than those of PB-a ($T_g = 171$ °C) and PB-mda ($T_g = 238$ °C). The decrease of E' above T_g was also considerably suppressed.

Table 3. DMA results of pristine PB-a and siloxane-containing polybenzoxazines.

Code	E' at r.t. / GPa	T_g of siloxane / °C		T_g of polybenzoxazine / °C	
		E''	$\tan \delta$	E''	$\tan \delta$
PB-a	3.4	-	-	153	171
PB-pdms(248)	0.5	-	-	225	238
PB-pdms(850)	0.1	-107	-99	-	140
PB-pdms(1622)	0.09	-110	-98	-	-
PB-mda/pdms(850)	1.1	-	-	279	283
PB-mda/pdms(1622)	1.3	-	-	272	276

Thermal stability of siloxane-containing polybenzoxazine was investigated by TGA under argon. As the results, the $T_{-5\%}$ for PB-pdms and PB-mda/pdms are higher (324~384 °C) than PB-a (308 °C), because the polysiloxanes possess high thermal stability. Moreover, the PB-mda/pdms films showed higher char yield at 850 °C than PB-a and PB-pdms films due to the high aromatic content.

Conclusion

Siloxane-containing polybenzoxazine prepolymers with high molecular weight were prepared from bisphenol-A, diaminopolysiloxane, and paraformaldehyde. Free standing prepolymer films with high transparency were easily obtained by casting the prepolymer solutions on glass plates. Heat treatment of the prepolymer films up to 240 °C gave brown transparent siloxane-containing polybenzoxazine films. The novel polybenzoxazine films exhibited significantly improved toughness due to the polysiloxane component and long linear backbone. The polysiloxane component also acted as a plasticizer, and the crosslink density of polybenzoxazine component increased, affording the PB-pdms(248) film having higher T_g than the typical polybenzoxazine PB-a film. Moreover, the siloxane-containing polybenzoxazines revealed higher degradation temperature than PB-a as evidenced by TGA. The novel siloxane-containing polybenzoxazines developed in this study can be good candidates for the matrix resin of advanced composite materials and high-temperature adhesives.

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