

High-performance polymer alloys of polybenzoxazine and bismaleimide

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Abstract

Two series of high-performance polymer alloys were prepared by mixing typical benzoxazine monomers, 3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine (P-a) or 6,6-(1-methylethyliden)-bis-(3,4-dihydro-3-phenyl-2*H*-1,3-benzoxazine) (B-a), with a typical bismaleimide, 4,4-bismaleimido-diphenyl methane by various ratios followed by thermal treatment up to 240 °C. DSC and IR of the alloys were examined to follow the curing reaction. These analyses showed that the obtained polymer alloys are AB co-cross-linked polymer networks through the formation of ether linkage between the hydroxyl group of polybenzoxazine and the double bond of bismaleimide. Viscoelastic analysis and softening temperature measurement revealed that the polymer alloys have much higher glass transition temperatures than those of each homopolymer. The thermal stability also increased with the increase of bismaleimide content as evidenced by TGA.

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1. Introduction

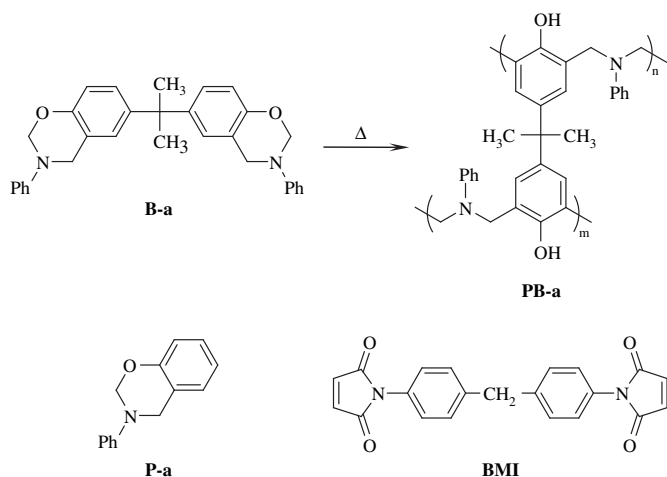
Polybenzoxazines have been developed as a novel type of phenolic resins that can be afforded by the ring-opening polymerization of benzoxazine monomers [1,2]. Chemical structures of typical benzoxazine monomers, 3-phenyl-3,4-dihydro-2*H*-1,3-benzoxazine (P-a) and 6,6-(1-methylethyliden)-bis-(3,4-dihydro-3-phenyl-2*H*-1,3-benzoxazine) (B-a), and polymer of B-a (PB-a) are shown in Scheme 1. They have not only the characteristics of traditional phenolic resins such as good flame retardancy and chemical resistance, but also unique characteristics that are not found in the traditional phenolic resins such as molecular design flexibility, low moisture absorption, near-zero shrinkage upon polymerization, and low dielectric constant [2–6]. Furthermore, benzoxazines can be polymerized simply through heating without the need of strong acid catalyst, and without producing harmful byproducts during the cure process. Therefore, polybenzoxazines overcome the disadvantages of the traditional phenolic resins

without sacrificing the advantages of the resins. However, it is reported that glass transition temperature (T_g) of PB-a is ca. 150 °C which is not high enough for the use in a harsh condition [7]. The approaches for improving the thermal properties of polybenzoxazine can be classified into two ways. One is the modification of the monomer structure [8–12] and the other is the alloys or hybrids with highly thermally stable materials, such as polyimide [13,14], multiwalled carbon nanotube [15], titania [16], silsesquioxane [17], and clay [18,19].

Bismaleimides, such as 1,1'-(methylenedi-4,1-phenylene)-bismaleimide (BMI, Scheme 1), offer excellent thermo-mechanical properties and withstand high stress at high temperatures at which typical phenol and epoxy resins as well as most high-performance plastics are no longer satisfactory. Thus, the maleimide structure has long been incorporated into many polymeric systems because it often yields thermally stable polymers with a high T_g and improved heat distortion temperature due to the rigid imide ring [20–22]. Recently, it was reported that incorporation of the maleimide group into benzoxazine monomer effectively improved the thermal property of its thermoset [23–25]. In this paper, we report thermal property enhancement of polybenzoxazine by alloying with

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Scheme 1. Chemical structure of B-a, PB-a, P-a and BMI.

BMI. The polymer alloys of polybenzoxazine and BMI resin were prepared by mixing benzoxazine and BMI monomers followed by curing. The curing behavior of the alloys and the effects of BMI content on thermal properties of the alloys are investigated.

2. Experimental

2.1. Materials

P-a and B-a were kindly supplied by Shikoku chemicals Co., Tokyo, Japan, and purified by washing with 3 N NaOH aq. BMI and *N*-phenylmaleimide were purchased from Tokyo Kasei, Tokyo, Japan. Phenol and dichlorodimethylsilane were used as-received from Kishida Chemicals Co., Japan.

2.2. Measurements

IR spectra were obtained with JASCO spectrophotometer model FT/IR-420. NMR spectra were recorded on a Varian Mercury 300 (300 MHz for ^1H and 75 MHz for ^{13}C NMR) instrument. Differential scanning calorimetry (DSC) was conducted using Rigaku Thermo Plus 2 DSC8230 at a heating rate of $10\text{ }^\circ\text{C}/\text{min}$ under nitrogen. Thermogravimetric analysis (TGA) was performed with Rigaku Thermo Plus 2 TG-DTA TG8120 at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ under argon. Dynamic viscoelastic measurements were conducted on ORIENTEC automatic dynamic viscoelastomer Rheovibron model DDV-01FP at 35 Hz at a heating rate of $4\text{ }^\circ\text{C}/\text{min}$.

The softening curves (i.e., penetration depth *versus* scanning temperature) were measured by the penetration method under a constant indentation load for rising temperature scanning with the heating rate of $5\text{ }^\circ\text{C}/\text{min}$. A constant load during the penetration test was applied on a Vickers indenter made by silicon carbide through a load train using a mechanical lever. The penetration depth as a function of temperature was continuously detected by an electro-optical extensometer (Model 200X, Zimmer) with a precision of $0.5\text{ }\mu\text{m}$ by monitoring

the gap made by a pair of silicon nitride tabs mounted at sample stage and indenter.

2.3. Preparation of benzoxazine/BMI polymer alloy

Benzoxazine and BMI monomers were mixed at various weight ratios in chloroform and stirred for 30 min. The blend solutions were cast on glass plates that were pre-treated with dichlorodimethylsilane, dried at $50\text{ }^\circ\text{C}$ for 4 h, and then thermally treated at 100, 120, 160, 200, $240\text{ }^\circ\text{C}$ for 1 h each to obtain the alloy films.

2.4. Model reaction of phenol and *N*-phenylmaleimide

Thermal reaction of phenol and *N*-phenylmaleimide was carried out as the model reaction between polybenzoxazine and bismaleimide. To phenol (9.411 g, 0.1 mol) was added *N*-phenylmaleimide (1.732 g, 0.01 mol) at room temperature and the mixture was refluxed at $170\text{--}180\text{ }^\circ\text{C}$ for 8 h. Then, the unreacted phenol was removed by distillation. The crude product was purified by recrystallization from chloroform to obtain the reaction product as a white powder (0.67 g, 25.1% yield). Mp: $202\text{--}204\text{ }^\circ\text{C}$. Elem. Anal. Calcd for $\text{C}_{16}\text{H}_{13}\text{NO}_3$: C, 71.90; H, 4.90; N, 5.24; O, 17.96. Found: C, 71.22; H, 5.03; N, 5.18; O, 18.57.

3. Results and discussion

3.1. Preparation of benzoxazine/BMI polymer alloy

Polymer alloys were prepared by blending BMI and benzoxazine followed by heat treatment. The blends of benzoxazine and BMI after drying at $50\text{ }^\circ\text{C}$ for 4 h were yellow opaque. However, all the blend films became transparent after curing at $160\text{ }^\circ\text{C}$ that is higher than the melting point of BMI. The color of the films after curing up to $240\text{ }^\circ\text{C}$ was dark red at high benzoxazine content and became brown with the increase of BMI content. In addition, the alloy films obtained by casting on glass plates without surface treatment by dichlorodimethylsilane were difficult to peel off glass because of the very strong adhesive property and also high hydrophilicity of polybenzoxazine.

The obtained alloy films had improved toughness than the neat benzoxazine films and the toughness of alloy films increased with the increase of BMI content. The tendency of toughening by alloying with BMI was more remarkable in the case of monofunctional P-a than that of difunctional B-a.

3.2. Curing behavior of benzoxazine/BMI polymer alloy

The curing behavior of benzoxazine and BMI was investigated by DSC and IR measurements. Fig. 1 shows the DSC curves of blends of P-a and BMI with various blend ratios after removal of solvent at $50\text{ }^\circ\text{C}$ for 4 h. Pristine P-a showed a sharp exothermic peak corresponding to the ring-opening polymerization of P-a, starting at ca. $198\text{ }^\circ\text{C}$ with peak maximum at $222\text{ }^\circ\text{C}$ and 57 cal/g as exothermic heat, while the

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