Polymer Alloys of Polyimide and Polybenzoxazine: Synthesis and Characterization

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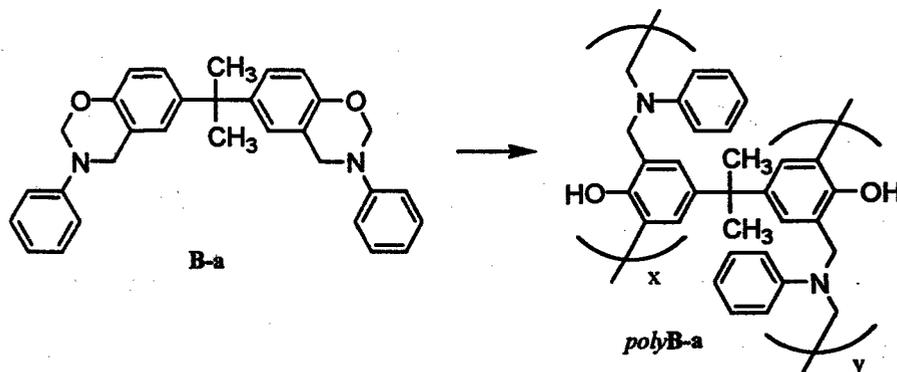*School of Materials Science, Toyohashi University of Technology,*
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Introduction

Recently developed polybenzoxazines are new members in the family of phenolic resins, which are derived from the ring-opening polymerization of corresponding benzoxazine monomers. These novel types of phenolic resins have not only the characteristics of traditional phenolic resins such as excellent thermal properties and flame retardance, but also unique characteristics such as molecular design flexibility, low moisture absorption, near-zero shrinkage upon polymerization, low melt viscosities, and low dielectric constant [1-6]. Furthermore, benzoxazines are able to polymerize simply through heating without strong acid catalyst, and without producing harmful byproducts during the cure process. Thus, polybenzoxazines overcome the shortcomings of the traditional phenolic resins without sacrificing the advantages of those resins, which leads to a novel and promising candidate for high performance thermosetting resins. Structures of a typical bifunctional benzoxazine monomer, 6,6'- (1-methyl-ethylidene)bis(3,4-dihydro-3-2H-1,3-benzoxazine) (B-a) and the polymer, polyB-a, are shown in Scheme 1.

The thermally initiated polymerization of benzoxazine monomers, however, needs a temperature as high as more than 200°C, which could be a shortcoming in its processability. The glass transition temperature (Tg) of polyB-a is ca. 150°C, which is considered to be not high enough for applications in a harsh condition [7]. We carried out a series of studies on structure-modified benzoxazines [8] and polybenzoxazine-based alloys and composites [9-15]. In this study, we prepared a series of polymer alloys of polybenzoxazine and polyimide (PI). We used a soluble PI, which enable us to blend B-a with not only its precursor poly(amide acid) (PAA) but also PI. The effect of the preparation method, either PAA/B-a or PI/B-a, on the properties of the polymer alloys were investigated.
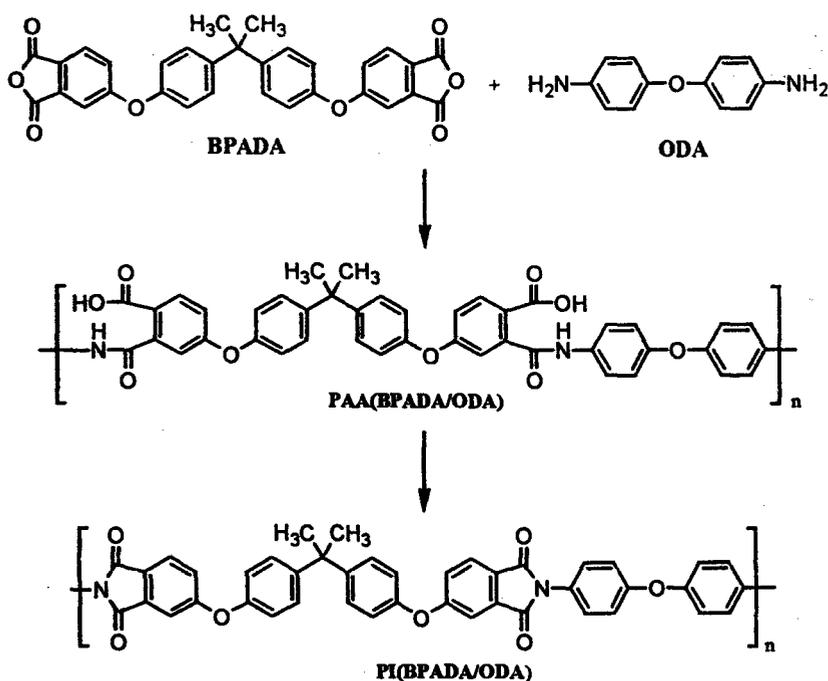

Scheme 1. Structures of B-a and polyB-a

Experimental
Synthesis of PAA and PI

The synthesis of the PAA, as shown in **Scheme 2**, was conducted by the solution polymerization of BPADA and ODA using NMP. The viscosity of the synthesized PAA was 2.03 dL/g (0.5 g/dL in NMP). The imidization was carried out by refluxing in toluene. Grayish PI pellets were obtained in ca. 96% yield. The viscosity of the obtained PI was 1.97 dL/g (0.5 g/dL in NMP).

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Scheme 2.   Preparation of PAA(BPADA/ODA) and PI(BPADA/ODA).

Results and discussion

Preparation of polymer alloy films from PI/B-a and PAA/B-a

Polymer alloy films of PI/B-a were prepared by blending PI with B-a in NMP, followed by thermal treatment at 150°C, 200°C and 240°C for 1 h each. The same procedure was employed for the preparation of PAA/B-a films, using PAA instead of PI. All the films prepared from both PI/B-a and PAA/B-a were deep wine color and transparent at any ratio. The thickness of the polymer alloy films obtained from both PI/B-a and PAA/B-a was in the range of 0.1 - 0.3 mm, and latter was apparently more brittle than the former. On the whole, the films from both PI/B-a and PAA/B-a were much more tough than that from polyB-a.

The curing behaviors of B-a were investigated by DSC. Fig. 1 and 2 show the DSC profiles of PI/B-a=50/
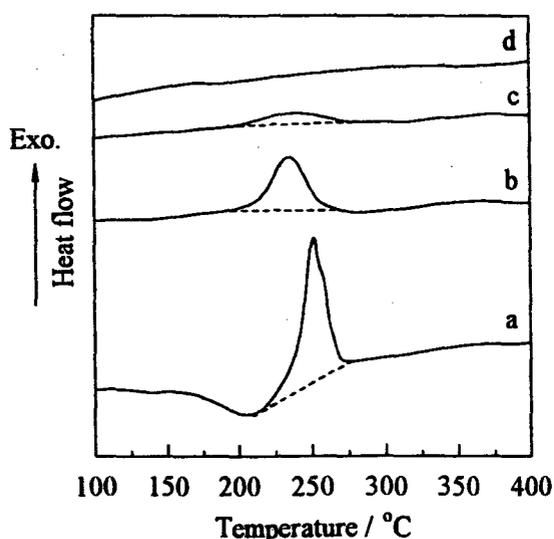

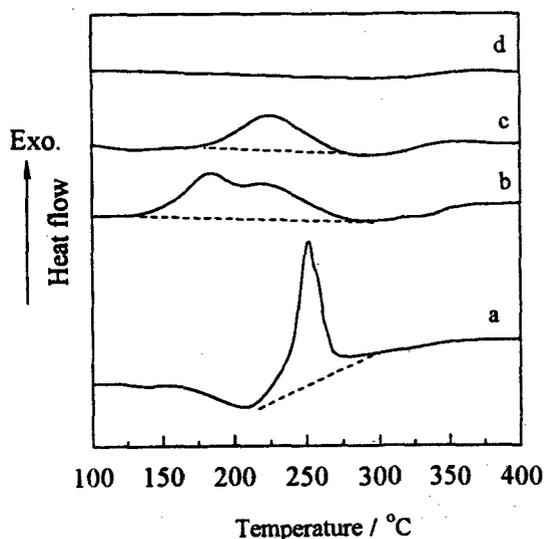Figure 1.   DSC of B-a (a), and of PI/B-a=50/50 before curing (b) and after cured at 150 °C (c) and 240 °C (d).

Figure 2.   DSC of B-a (a), and of PAA/B-a=50/50 before curing (b) and after cured at 150 °C (c) and 240 °C (d).

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50 and PAA/B-a=50/50 after each cure cycle. From the exothermic peak due to the ring-opening polymerization of B-a in **Fig. 1**, the temperature necessary for curing **PI/B-a** was the same as that for **B-a**. The exothermic amount for curing of **PI/B-a** decreased gradually as the temperature increased, and disappeared after 240°C/2h cure. In the presence of **PAA**, however, the onset curing temperature of **B-a** lowered significantly by ca. 50°C. This can be ascribed to the catalytic effect of the carboxylic groups in the backbone of **PAA**. IR measurements of **PI/B-a** and **PAA/B-a** also confirmed the progress of the reaction from the disappearance of the characteristic absorptions of **B-a** and appearance of new absorptions, which indicates that the Mannich bridge linkage and phenolic hydroxyl groups were produced by the ring-opening polymerization of **B-a** at elevated temperature.

The solubility of polymer alloy films from **PI/B-a** and **PAA/B-a** after curing at 240°C for 2 h was examined by immersing in NMP over 3 days. The percentages of dissolved part (PDP) were calculated from the original and the residual weight of the samples. The pristine **PI** dissolved completely in NMP, while polyB-a after curing at 240°C/2 h was insoluble. As expected, the polymer alloys based on **PI/B-a** dissolved partially making NMP yellow, with the values of PDP exactly corresponding to the content of **PI**. Therefore, it is conclusive that the structure of the polymer alloy based on **PI/B-a** is a semi-IPN without any strong bond between the two components. The polymer alloys based on **PAA/B-a**, however, exhibited near-zero PDP values, keeping NMP colorless. This means that the **PI** component became insoluble by thermally imidizing **PAA** in **PAA/B-a** at 240°C/2 h. This also suggests the cross-linkages between the two components. It is in support with the formation of AB cross-linked polymer from blends of **PAA** and polyB-a.

Dynamic mechanical analysis (DMA) of polymer alloy films

The viscoelastic properties of polymer alloy films were measured, and the results of the storage modulus (E') and of the loss modulus (E") and tan δ are illustrated in **Fig. 3** and **Fig. 4** for **PI/B-a**. The E' value of polyB-a was higher than that of **PI** by ca. two fold. Therefore, the modulus of **PI** was enhanced by alloying with **B-a**. From **Fig. 4**, it is clear that all the polymer alloys have only one glass transition temperature (Tg) from both the E" and tan δ maxima. And the Tg shifted to higher temperature as **PI** content increased. Although most of the simi-IPN systems tend to phase separate and show two Tgs, the appearance of only one Tg in all films with any
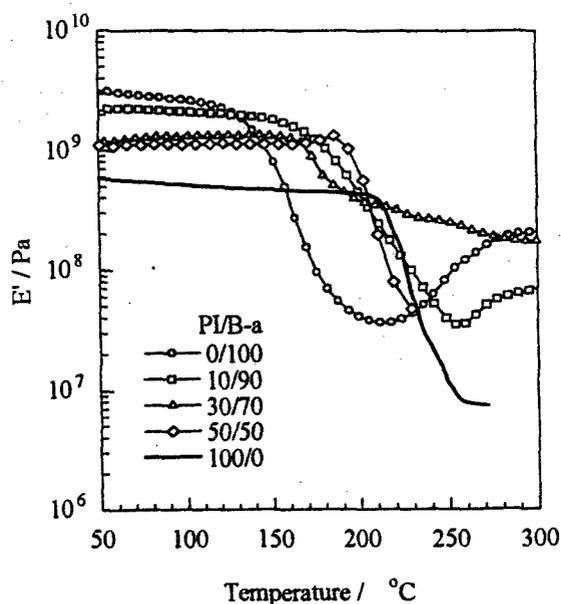

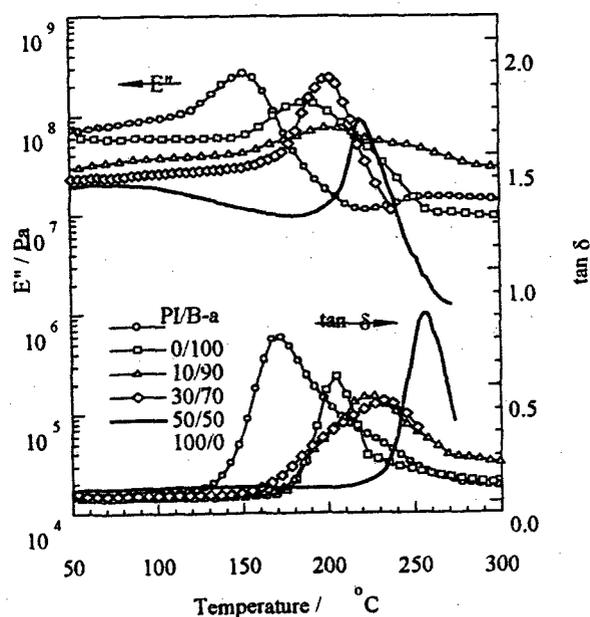Figure 3. Storage modulus of PI/B-a films with various ratios.

Figure 4. Loss modulus and tan d of PI/B-a with various ratios.

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ratio of PI/B-a show that the two components in this study are well miscible. The polymer alloy films from PAA/B-a also showed one Tg. The Tg of the polymer alloys from PAA/B-a was slightly higher than that of PI/B-a in the same ratio, which is also another important evidence indicating the formation of AB cross-linking copolymer from PAA/B-a.

Tensile properties of polymer alloy films

Tensile properties of the polymer alloy films were measured. The films from PAA/B-a failed in this measurement because of the brittleness. The results for PI/B-a films are shown in the form of stress-strain curves in Fig. 5. As the content of B-a increased, the modulus of the polymer alloy films increased. On the other hand, the elongation at break decreased with the increase of B-a content. This is due to the cross-linkage of polyB-a, which contributed stiffness to the polymer alloy films. Inversely, the elongation of polyB-a increased with the addition of PI. Namely, linear-structured PI improved the toughness of polyB-a, which is considered as a result of well-balanced semi-IPN from PI/B-a.

Thermal stabilities of polymer alloy films

The thermal stabilities of polymer alloy films from PI/B-a and PAA/B-a were investigated by TGA. The results in case of PI/B-a are shown in Fig. 6 as an example. The initial decomposition temperatures of the polymer alloys increased obviously with the content of PI due to higher thermal stability of PI than that of polyB-a. For the polymer alloys based on PAA/B-a, the same results were obtained.
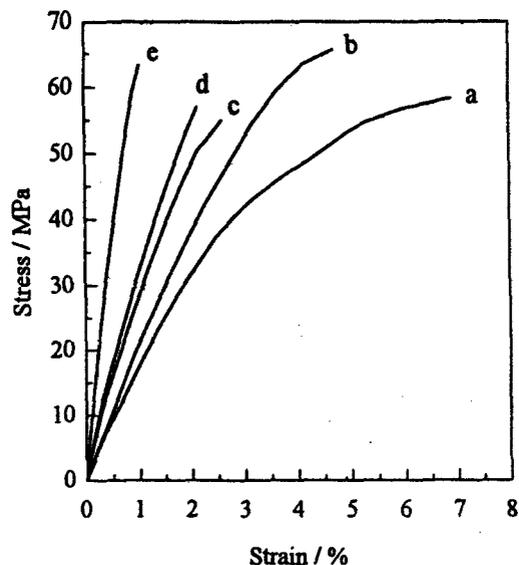

Figure 5. Tensile properties of PI/B-a films with the ratio of (a) 100/0, (b) 50/50, (c) 30/70, (d) 10/90, and 0/100.
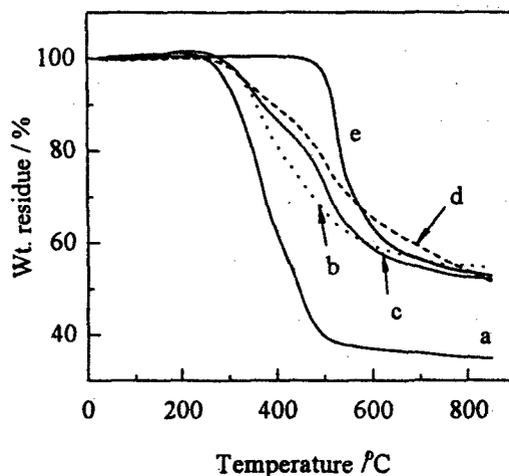

Figure 6. TGA of PI/B-a films with the ratio of (a) 0/100, (b) 10/90, (c) 30/70, (d) 50/50, and (e) 100/0.

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