Preparation of Imide-modified Benzoxazines and Characterization of Cured Films

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We synthesized novel monofunctional and bifunctional benzoxazines having imide groups. Brown-colored transparent films were obtained by curing the benzoxazines up to 240 °C. Monofunctional benzoxazine gave brittle film, but bifunctional benzoxazine gave tough film. Viscoelastic analysis revealed that glass transition temperature of the polybenzoxazine film obtained from the bifunctional benzoxazine was 289 °C, about 90 °C higher than that of a typical polybenzoxazine. Thermogravimetric analyses revealed that the introduction of imide groups was also effective to improve the thermal stability of polybenzoxazines.

Keywords: benzoxazine, phenolic resin, imide group, curing

1. Introduction
Polybenzoxazine is a series of novel phenolic resin obtained by the ring-opening polymerization of cyclic monomer, benzoxazine [1]. Synthesis of a typical bifunctional benzoxazine monomer (B-a) and polymer of B-a (PB-a) is shown in Scheme 1.

\begin{center}
\begin{align*}
\text{bisphenol-A} + 2\text{ aniline} + 4\text{ formaldehyde} & \rightarrow \text{B-a} \\
\text{B-a} & \rightarrow \text{PB-a}
\end{align*}
\end{center}

Scheme 1. Synthesis of B-a and PB-a.

Polybenzoxazines have good thermal properties like phenolic resin, and also have excellent dimensional stability, low water absorption, low dielectric constant, and requiring no catalyst for the ring-opening polymerization. Therefore, polybenzoxazine is expected as a novel thermoset that can overcome the disadvantages of the traditional phenolic resins [2-7]. However, typical polybenzoxazine like PB-a has disadvantages that glass transition temperature ($T_g$) is not high enough and cured films are brittle. Therefore, improvement of thermal properties and toughness are required.

As the methods of improving thermal properties of polybenzoxazines, introduction of rigid cyclic structure, introduction of cross-linkable groups, and addition of inorganic fillers are well known. By these methods, thermal properties were improved, but often became even more brittle. To enhance toughness, alloying with elastomers [8] and the use of high molecular weight benzoxazines [9-11] are representative methods. Interestingly, these toughening methods often improve also thermal properties by increasing the crosslink
density of polybenzoxazine [1].

Polyimide (PI) is a series of most important high temperature polymer because of the superior properties, such as thermal stability, toughness, and mechanical properties. Since there are wide variety of raw materials, the molecular design flexibility is very high. Thus, PI has been widely used as a component of high performance polymer alloys. Previously, we reported that PI/benzoxazine alloy films prepared by heat treating a mixture of linear PI and B-a gave films with improved toughness and thermal properties [12]. It was also reported that introduction of maleimide group into benzoxazine enhanced thermal properties [13-15]. In this paper, we prepared novel monofunctional and bifunctional benzoxazines containing imide groups aiming to improve the toughness and thermal properties.

2. Experimental

2.1. Materials

4,4’-(Hexafluoroisopropylidene) diphthalic anhydride (6FDA) was purchased from Tokyo Kasei Kogyo (Tokyo, Japan) and was used after sublimation. p-Aminophenol, phthalic anhydride, aniline, N-methyl-2-pyrrolidone (NMP), N,N-dimethylacetamide (DMAc), xylene, and toluene were obtained from Wako Pure Chemical Industries (Osaka, Japan), and were used without further purification. Paraformaldehyde was obtained from Kishida Chemicals (Osaka, Japan) and was used as received.

2.2. Synthesis of p-HPPI

In a 200 ml three-necked flask, p-aminophenol (1.64 g, 15.0 mmol) was dissolved in NMP (34.7 g) and then a solution of phthalic anhydride (2.22 g, 15.0 mmol) in toluene (50 g) was added. A Dean-Stark tube was attached to the flask and then the mixture was stirred at 180 °C for 3h. After the reaction, the mixture was condensed into a small portion under reduced pressure and then poured into a large amount of water. White precipitate was collected by filtration and dried under vacuum to give p-HPPI as a white powder (3.27 g, 91 % yield).

IR (ATR, cm⁻¹): 3409 (O-H), 1709 (C=O), 1396 (C-N)

1H NMR (DMSO-d₆, r.t., 400 MHz, ppm):
δ= 9.8 (OH, H, s), 7.85-7.97 (CH₂, 4H, m), 6.86-7.20 (CH, 4H, d)

2.3. Synthesis of p-BP(6FDA)

Into a 100 ml round flask, DMAc (37.5 g), p-aminophenol (2.18 g, 20.0 mmol) and 6FDA (4.44 g, 10.0 mmol) were added, and the mixture was stirred at 200 °C for 15 h. The reaction mixture was poured into large amount of a mixture of methanol:water (1:1). The precipitate was collected by filtration, washed with methanol, and dried under vacuum to give p-BP(6FDA) as a yellow powder (5.14 g, 82 % yield).

IR (ATR, cm⁻¹): 3409 (O-H), 1717 (C=O).

1H NMR (DMSO-d₆, r.t., 400 MHz, ppm):
δ= 9.8 (OH, H, s), 7.72-8.14 (CH, 3H, d), 6.88-7.20 (CH, 4H, d).

2.4. Synthesis of monofunctional benzoxazine

Into a 100 ml round flask, xylene (22.2 g), p-HPPI (2.39 g, 10.0 mmol), aniline (0.93 g, 10.0 mmol) and paraformaldehyde (0.600 g, 20.0 mmol) were added and the mixture refluxed for 5h. The reaction mixture was poured into a large amount of hexane. Yellow precipitate was collected by filtration, and dried under vacuum. The precipitate was then dissolved in chloroform. The solution was washed with 5 wt% NaHCO₃ aqueous and with water, and then dried with magnesium sulfate. Removal of solvent by evaporation and drying under vacuum afforded p-IB as a yellow powder (1.57 g, 44 %).

IR (ATR, cm⁻¹): 3409 (O-H), 1233 (C-O-C), 1030 (C-O-C), 942 (trisubstituted Ar)

1H NMR (DMSO-d₆, r.t., 400 MHz, ppm):
δ= 7.88 (CH, 4H, m), 6.40-7.40 (CH, 8H, m), 5.45 (CH₂, 2H, s), 4.65 (CH₂, 2H, s)

2.5. Synthesis of bifunctional benzoxazine

Into a 100 ml round flask, xylene (10.5 g), p-BP(6FDA) (1.25 g, 2.00 mmol), aniline (0.37 g, 4.00 mmol) and paraformaldehyde (0.24 g, 8.00 mmol) were added and the mixture was refluxed for 7h. The reaction mixture was poured into a large amount of hexane, and the precipitate was collected by filtration and dried. Then, the precipitate was dissolved in chloroform. The solution was washed with 5wt% NaHCO₃ aqueous and with water, and then dried with magnesium sulfate. Removal of solvent by evaporation and drying under vacuum afforded p-bisIB(6FDA) as a yellow powder (0.96 g, 56 %).

IR (ATR, cm⁻¹): 1031 (C-O-C), 941 (trisubstituted Ar)

1H NMR (DMSO-d₆, r.t., 400 MHz, ppm):
δ= 8.20-7.60 (CH, 3H, d), 6.40-7.40 (CH, 8H, m), 5.50 (CH₂, 2H, s), 4.70 (CH₂, 2H, s)
2.6. Measurements

$^1$H NMR spectra were recorded on a Varian Mercury 300 (300 MHz for $^1$H) in DMSO-$d_6$ at room temperature. IR spectra was obtained with a JASCO spectrophotometer model FT/IR-420. Differential scanning calorimetry (DSC) was conducted using a Rigaku Thermo Plus 2 DSC8230. Samples (ca. 5 mg) were heated from 300 °C at a heating rate of 10 °C min$^{-1}$ under nitrogen. Thermogravimetric analysis (TGA) was performed with a Rigaku Thermo Plus 2 TG-DTA TG8120. Samples (ca.5 mg) were heated up to 850 °C at a heating rate of 5 °C min$^{-1}$ under argon. Dynamic viscoelastic measurements were conducted on an ORIENTEC automatic dynamic viscoelatomer Rheovibron model DDV-01FP at 35 Hz at a heating rate of 4 °C min$^{-1}$.

3. Results and discussion

3.1. Synthesis of $p$-IB

The imide-modified phenol, $p$-HPPI, was synthesized from $p$-aminophenol and phthalic anhydride. The structure of the $p$-HPPI was confirmed by FT-IR and $^1$H NMR. Monofunctional benzoxazine, $p$-IB was synthesized from $p$-HPPI according to Scheme 2. Fig. 1 shows FT-IR spectra of $p$-HPPI and $p$-IB. The characteristic absorption due to the OH stretching vibration (3409 cm$^{-1}$) of $p$-HPPI disappeared in the spectrum of $p$-IB. Instead, C-O-C symmetric stretching of the oxazine ring (1030 cm$^{-1}$), the asymmetric stretching (1233 cm$^{-1}$), and trisubstituted benzene vibration (942 cm$^{-1}$) were observed, indicating the formation of $p$-IB.

3.2. Synthesis of $p$-bisIB(6FDA)

Imide containing bifunctional phenol, $p$-BP(6FDA) was synthesized from $p$-aminophenol and 6FDA. The chemical structure of $p$-BP(6FDA) was confirmed by FT-IR and $^1$H NMR. Bifunctional benzoxazine having imide group, $p$-bisIB(6FDA), was prepared from $p$-BP(6FDA) (Scheme 3). Fig. 3 shows FT-IR spectra of $p$-BP(6FDA) and $p$-bisIB(6FDA). The characteristic absorption of the imide structure (C=O) was observed at 1717 cm$^{-1}$ in the both spectra. Absorption band due to the OH stretching, which was observed at 3484 cm$^{-1}$ in the spectrum of $p$-BP(6FDA), disappeared for $p$-bisIB(6FDA). Characteristic absorption bands corresponding to the C-O-C symmetric stretching of the oxazine ring (1031 cm$^{-1}$) and trisubstituted benzene
vibration (942 cm⁻¹) were clearly observed in the spectrum of p-bisIB(6FDA).

Scheme 3. Synthesis of p-bisIB(6FDA) from p-BP(6FDA).

Fig. 3. FT-IR spectra of p-BP(6FDA) (a) and p-bisIB(6FDA) (b)

Fig. 4. ¹H NMR spectra of p-BP(6FDA) (a) and p-bisIB(6FDA) (b).

¹H NMR spectra of p-BP(6FDA) and p-bisIB(6FDA) are shown in Fig. 4. The OH proton signal (9.8 ppm) disappeared in the spectrum of p-bisIB(6FDA). Also, the characteristic signals assigned to methylene (O-CH₂-N) and methylene (Ar-CH₂-N) of oxazine-ring were observed at 5.45 and 4.65 ppm, respectively. These IR and NMR analyses confirmed the formation of p-bisIB(6FDA).

Fig. 5. Curing behaviors of p-IB (a) and p-bisIB(6FDA) (b) monitored by DSC.

3.3. Polymerization behavior of the benzoazines

The benzoazines having imide groups were heat-treated at 60, 100, 140, 180, 220 and 240 °C
for 1h each, and samples after each treatment were taken to measure DSC. The DSC results of monofunctional and bifunctional benzoxazines are shown in Fig. 5. Before curing, onset temperature of polymerization was found at 169 ºC for p-IB and at 188 ºC for p-bisIB(6FDA), which are almost same as B-a (192 ºC).

In both cases, amount of exotherm did not decrease up to the heat treatment at 140 ºC, and started to decrease at 180 ºC. The exotherm disappeared completely by the thermal cure at 240 ºC, indicating that the temperature is needed to complete the ring-opening polymerization.

3.4. Preparation of polybenzoxazine films

The benzoxazines were dissolved in THF, cast onto silane-treated glass plates, and heat treated at 60, 100, 140, 180, 220 and 240 ºC for 1 h each, affording brown transparent polybenzoxazine films. The polybenzoxazine film from p-IB was too much brittle to be peeled off from the glass plate. Since the para position of p-IB is substituted with a phthaloyl group, a linear polybenzoxazine might be obtained by the polymerization. In general, the degree of polymerization of the polybenzoxazine is not so high, which is considered to be the cause that the film is brittle.

On the other hand, from p-bisIB(6FDA), a self-standing film was obtained (Fig. 6). The presence of the rigid phthalamide and hexafluoroisopropylidene groups improved mechanical properties. However, the film was still hard and not flexible. Introduction of flexible groups such as ether, sulfide and sulfone should improve the toughness of polybenzoxazine films.

3.5. Viscoelastic analysis of polybenzoxazine films

Fig. 7 shows DMA results of Pp-bisIB(6FDA) and PB-a films cured at 240 ºC. Storage modulus at room temperature (E’), T_g form E” and tan δ of the typical bifunctional polybenzoxazine (PB-a) were determined to be 2.3 GPa, 193 ºC, and 188 ºC, respectively. On the other hand, the values were 2.8 GPa, 226 ºC, and 289 ºC for the imide containing polybenzoxazine, Pp-bisIB(6FDA). It was clearly shown that T_g was enhanced by the introduction of imide groups.

3.6. Thermogravimetric analysis of the polybenzoxazines

Thermal stability of Pp-IB and Pp-bisIB (6FDA) were investigated by TGA. The TGA profiles are shown Fig. 8. For PB-a, T_5, T_10, and char yield were estimated to be 280 ºC, 322 ºC, and 28 %, respectively. For the monofunctional benzoxazine with imide group, Pp-IB, the values were 286 ºC, 322 ºC and 32 %, respectively, and slightly increased as compared with PB-a.

On the other hand, Pp-bisIB(6FDA) revealed that T_5 and T_10 are 317 ºC, 382 ºC, respectively, with a char yield of 47 %, which has higher heat resistance and flame retardance than PB-a and Pp-IB. Increased crosslink density based on the bifunctional
polybenzoxazine structure and introduction of thermally stable CF₃ groups are the reason for the improved thermal stability.

Pyrolysis of polybenzoxazine consisting of bisphenol A as a raw material have been reported to be classified into three stages, decomposition of amine moiety at under 300 ºC, decomposition of the Schiff base between 300 ~ 400 ºC, and degradation of the phenol moiety above 400 ºC [16]. Amine content of PB-a, p-IB and Pp-bisIB(6FDA) are almost same, thus, weight loss at 300 ºC hardly changed. Then, significant weight loss for PB-a and Pp-IB were observed at around 400 ºC, whereas the weight loss for Pp-bisIB(6FDA) was low at the temperature.

Char yield of Pp-bisIB(6FDA) is 20% higher than that of PB-a, which is derived from the introduction of imide ring and increasing of aromatic ring ratio. By comparison with Pp-IB, it is considered that the crosslinking density that is improved by bifunctionality influenced the thermal stability. From these results, the introduction of the imide group into the bifunctional benzoxazine is effective to enhance the chemical heat resistance. By using amine or diamine compounds having a crosslinkable functional group as the amine component, it is possible to anchor the amine structure into network structure, which can be expected to further improve the heat resistance.

4. Conclusion
We synthesized monofunctional and bifunctional benzoxazines that contain aromatic imide group. The benzoxazines polymerized by the heat treatment higher than 180 ºC, and polymerization was completed by heat treatment at 240 ºC. Cured film of the monofunctional benzoxazine was very brittle, but brown transparent good film was obtained from the bifunctional monomer. Both DMA and TGA indicated that the imide-containing polybenzoxazines had improved thermal properties including glass transition temperature and degradation temperature. The enhancement of the thermal properties can be attributed to introducing a rigid imide group bound to the aromatic ring to benzoxazine.

5. References
[1] H. Ishida, T. Agag, editor. “Handbook of benzoxazine resins”, Elsevier, Amsterdam (2011).
[2] J. Liu, H. Ishida, In: Salamone JC, editor. “The polymeric materials encyclopedia”, Florida: CRC Press (1996) p. 484.
[3] T. Takeichi, T. Kawauchi, T. Agag, Polym. J., 40 (2008) 1121.
[4] T. Takeichi and T. Agag, High Perform. Polym., 18 (2006) 777.
[5] N.N. Ghosh, B. Kiskan, Y. Yagci, Prog. Polym. Sci., 32 (2007) 1344.
[6] T. Takeichi, T. Kawauchi, T. Agag, Polym. J., 40 (2008) 1121.
[7] Y. Yagci, B. Kiskan, N.N. Ghosh, J. Polym. Sci., Part A: Polym. Chem., 47 (2009) 5565.
[8] S. Rimdusit, S. Tiptipakorn, C. Jubsilp, and T. Takeichi, React. Funct. Polym., 73 (2013) 369.
[9] T. Takeichi, T. Kano, T. Agag, Polymer, 46 (2005) 12172.
[10] T. Takeichi, T. Kano, T. Agag, T. Kwauchi, N. Furukawa, J. Polym. Sci. Part A: Polym. Chem., 48 (2010) 5945.
[11] T. Agag and T. Takeichi, J. Polym. Sci.: Part A: Polym. Chem., 45 (2007) 1878.
[12] T. Takeichi, Y. Guo, S. Rimdusit, Polymer, 46 (2005) 4909.
[13] T. Agag and T. Takeichi, J. Polym. Sci.: Part A: Polym. Chem., 44 (2006) 1424.
[14] H. Ishida, S. Ohba, Polymer 46 (2005) 5588.
[15] T. Agag and T. Takeichi, High Perform. Polym., 13 (2001) S327.
[16] T. Takeichi, Y. Guo, S. Rimdusit, Polymer, 46 (2005) 4909.