

Synthesis and characterization of novel benzoxazine oligomer and polymer alloy with thermoplastic polyimide

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Abstract: Recently, a series of high molecular weight benzoxazine has been studied and reported as a novel heat-resistant thermosetting resin. In this study, a new series of benzoxazine oligomer was synthesized from 2,2-bis[4-aminophenoxyphenyl]propane, 4,4'-isopropylidenediphenol and paraformaldehyde and the average molecular weight (M_w) of oligomer was more than 2,000. The benzoxazine structure in oligomer backbone was confirmed by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and two-dimensional NMR ($^{13}\text{C-}^1\text{H COSY}$) measurement. Self-standing film was obtained from the oligomer solution in 1,4-dioxane through solution cast method. The oligomer showed exothermic reactivity at the temperature range of $220^\circ\text{C} \sim 280^\circ\text{C}$, which was based on crosslinking reaction accompanying benzoxazine ring-opening. Further, the glass transition temperature increased from 140°C to 240°C after final curing at 240°C due to the progress of crosslinking reaction while maintaining film-forming property. Furthermore, a novel polymer alloy which was derived from composition of both the benzoxazine oligomer and a thermoplastic aromatic polyimide was prepared and thermal properties were characterized.

Keywords: Benzoxazine, Oligomer, Self-standing Film, Thermosetting, Heat-resistant, Polymer Alloy

1. Introduction

3,4-dihydrobenzoxazine structure (abbreviated as benzoxazine) are heterocyclic compounds synthesized by reaction of the corresponding phenols, primary amines, and formaldehyde. They were discovered as Mannich reaction products from these reactants^{(1),(2)}. Bi-functional benzoxazines are also prepared from corresponding bisphenols, which are well known as high performance thermosetting resins. In general, the thermally induced reaction of bi-functional benzoxazine gives the corresponding network polymer having phenolic and tertiary amino moiety as a bridging group $-\text{CH}_2\text{-NR-CH}_2-$. Therefore, sometimes benzoxazine compounds are called a new type of phenolic

resins with hetero component. In the last two decades, various bi-functional benzoxazines have been reported as a novel thermosetting resin with ring-opening reactivity, which has superior properties

such as low resin shrinkage, low moisture absorption, good heat-resistance and high glass transition temperature (T_g)^{(3) - (5)}. In recent years, various application technologies have been developed for benzoxazines such as high-grade encapsulant for semiconductor device, matrix resin and adhesive for advanced composite materials (ACM)^{(6) - (10)}. Furthermore, several composite resins such as polymer alloys have been developed to cover the shortcomings as brittleness and generation of volatile components at nearly 300 °C, while taking advantage of benzoxazines⁽¹¹⁾. However, it is difficult to overcome this shortcoming without drastically changing the whole resin system. Recently, Takeichi *et al.* have reported that high molecular weight benzoxazines ($M_w > 2,000$) derived from diamines, bisphenols and paraformaldehyde, gave flexible colored transparent flexible film and exhibit good thermal and mechanical properties even after thermal curing⁽¹²⁾.

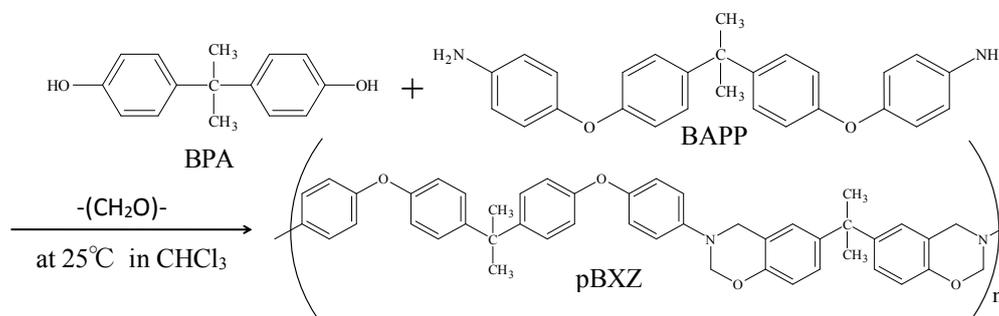
In this study, a new series of high molecular weight benzoxazine (benzoxazine oligomer) were synthesized from 2,2-bis[4-aminophenoxyphenyl] propane, 4,4'-isopropylidenediphenol and paraformaldehyde. The structure of synthesized benzoxazine oligomer was analyzed by NMR measurement. The thermal reactivity and viscoelastic properties of the oligomer were studied in detail. In addition, novel polymer alloys derived from the benzoxazine oligomer and a thermoplastic polyimide were prepared and studied for design of new composite materials with practical values, such as good thermal and mechanical properties.

2. Experimental

2.1. Syntheses of benzoxazine oligomer

Benzoxazine oligomer (abbreviated as pBXZ) was prepared from 2,2-bis[4-aminophenoxyphenyl]propane (0.05mol, abbreviated as BAPP), 4,4'-isopropylidenediphenol (0.05mol, abbreviated as BPA) and paraformaldehyde (0.20mol, $-(CH_2O)-$, abbreviated as PFA) and chloroform (177g, $CHCl_3$) was used as solvent as shown in scheme 1. The whole reaction was carried out in a four-necked round-bottomed separable flask equipped with a thermocouple, a mechanical stirrer, and a condenser. The reaction temperature was kept at $50 \pm 2^\circ C$ for 10 hours. The reaction mixture was then evaporated to remove and the residue was dissolved in 100mL of 1,4-dioxane. The solution was washed by blender apparatus as follows, twice with 1N $NaHCO_3$ aqueous solution (200mL), twice with distilled water (200mL), once with 2-propanol (200mL). The precipitated solid was filtrated and dried under vacuum, then, pBXZ was obtained as pale yellow powder.

2.2. Preparation of uncured pBXZ film and post-reaction pBXZ film



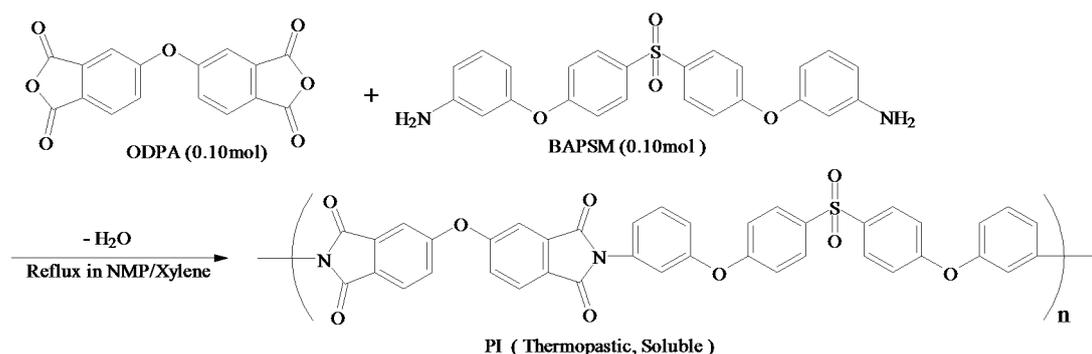
2.2. Preparation of uncured pBXZ film and post-reaction pBXZ film

The pBXZ solution dissolved in 1,4-dioxane (concentration: 30 wt%) was cast on glass plate and the

solvent was removed by stepwise heat treatment at 100 °C and 140 °C for 1h. The thickness of the resultant yellow pBXZ film was controlled to a level of $50 \pm 5 \mu\text{m}$ (uncured pBXZ). Post-reaction BXZ film was given by the stepwise heat treatment of the pBXZ film at 180 °C, 200 °C, and 240 °C for 1h each (cured pBXZ).

2.3. Syntheses of thermoplastic aromatic polyimide

4,4'-Oxydiphthalic dianhydride (ODPA, 0.10mol) was added into a solution of 4,4'-bis[3-aminophenoxyphenyl]sulfone (BAPSM, 0.10mol) in N-methyl-2-pyrrolidone (NMP, 108.2~110.0g) and reacted at room temperature for 3-5 h to produce polyamic acid. Then, for solution imidization of the polyamic acid, the reaction system was heated at 180-190 °C in NMP/xylene mixed solvent with distilled water azeotropically for 5h. Fully imidized aromatic polyimide was synthesized this way, and viscous polyimide solutions were obtained (concentration: $25 \pm 1 \text{wt}\%$).



Scheme 3. Synthesis of thermoplastic aromatic polyimide (PI).

2.4. Preparation of polymer alloy film

The polymer alloy from pBXZ and PI dissolved in NMP (concentration: 30 wt%) and stirred for over 12 hours (overnight), was cast on glass plate and the NMP was removed by stepwise heat treatment at 100, 140 and 180 °C for 1h. The thickness of the resultant pale brown film was controlled to a level of $50 \pm 5 \mu\text{m}$. Polymer alloy films were obtained by the stepwise heat treatment of the pBXZ film at 200 °C and 240 °C for 1h each.

2.5. Instrumental Analysis

The structures of uncured pBXZ were analyzed by $^1\text{H-NMR}$, $^{13}\text{C-NMR}$ and two-dimensional NMR ($^{13}\text{C-}^1\text{H COSY}$) measurements. Average molecular weights were measured by size exclusion chromatography (SEC). The reactivity of pBXZ was measured by differential scanning calorimetry (DSC) and 5% weight-loss temperature was measured by thermogravimetric analysis (TGA). The glass transition temperature (T_g) and thermo-mechanical properties were analyzed by Dynamic viscoelastic measurement.

3. Results and Discussion

3.1. Synthesis of thermosetting oligomer pBXZ

The oligomerization reaction was followed by SEC, because all components of the reaction mixture should have different hydrodynamic volumes. After the oligomerization reaction of 1 hour, two major peaks could be distinguished in the chromatogram. After the reaction of 10 hours, the peak at the retention time of 12.8–15.2 min presumably represented the pBXZ and the trace peak at a longer retention time of 15.7–15.9 min corresponded to the main raw materials of low molecular weights as shown in Figure 1. The average molecular weight (Mw) was approximately 2,100.

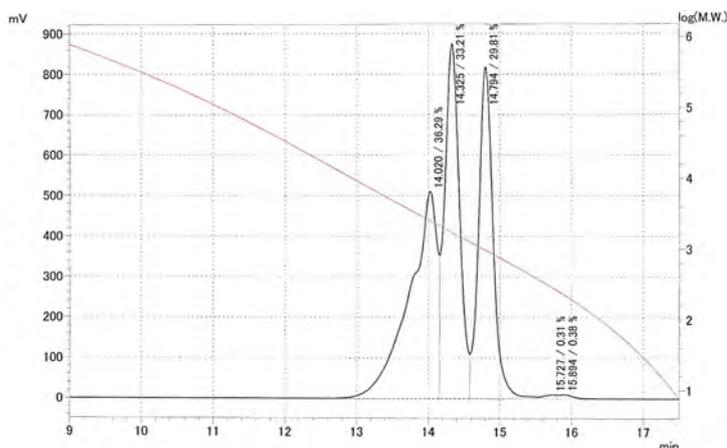


Figure 1. SEC chromatogram of the oligomerization reaction mixture.

The NMR (^{13}C - ^1H COSY) spectrum of uncured BXZ was shown in Figure 2. Two singlet resonances at 4.5 ppm ((a) Ar-CH₂-N) and 5.2 ppm ((b) O-CH₂-N) were assigned to the methylene bridge of the oxazine ring. The resonances at 1.5–1.60 ppm were assigned to the protons of the isopropyl group in main chain. The resonances at 6.7–7.2 ppm were assigned to the protons of the aromatic rings (Figure 2). In addition, the resonances at 4.8–4.9 ppm were probably suggested to come from the methylene units in uncycled intermediate products. Therefore, the ratio of oxazine ring was estimated from integration ratio of ^1H -NMR by comparison with aromatic or methyl protons as internal references, such as following equations ((A) or (B)):

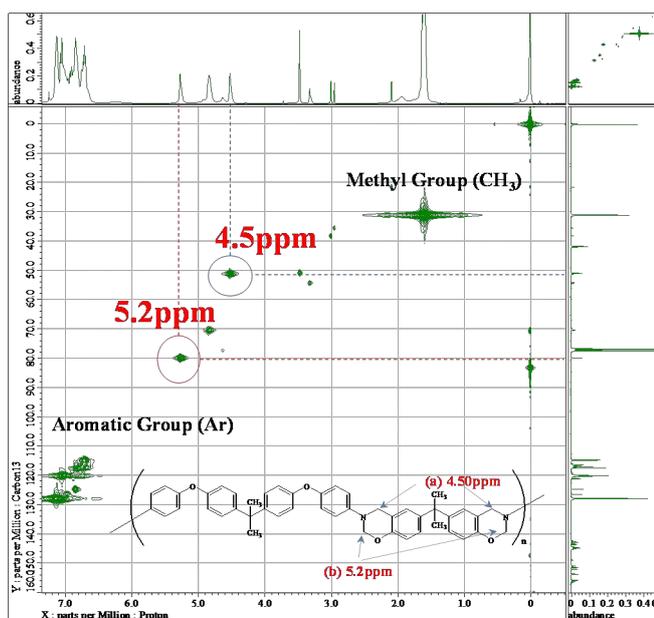


Figure 2. ^{13}C - ^1H COSY spectrum of the reaction products (the abscissa shows ^1H -NMR and the ordinate shows ^{13}C -NMR).

protons as internal references, such as following equations ((A) or (B)):

$$\text{Ratio of benzoxazine ring (} R_f \text{; Methyl Protons) (\%)} = (I_{(a)+(b)} / I_{\text{Me}}) / (8/12) \times 100 \quad (\text{A})$$

$$\text{Ratio of benzoxazine ring (} R_f \text{; Aromatic Protons) (\%)} = (I_{(a)+(b)} / I_{\text{Ar}}) / (8/22) \times 100 \quad (\text{B})$$

where $I_{(a)+(b)}$ is integration ratio of sum of protons (a) and (b), I_{Ar} is integration ratio of aromatic

protons of 6.7-7.2 ppm, and I_{Me} is integration ratio methyl protonsof 1.5-1.60 ppm.

The 1H -NMR spectra of samples was collected and analyzed at hourly intervals throughthe reaction for 10 hours. The intensity of the resonances assigned to the oxazine ring gradually increased with passage of reaction time (Figure 3).The characteristic ^{13}C -NMR signals of methylene for oxazine ring appearedapproximatelyat 51.2ppm ((a) Ar-CH₂-N) and 80.1ppm ((b) O-CH₂-N) and a correlation with the corresponding methylene protonswasaccepted.

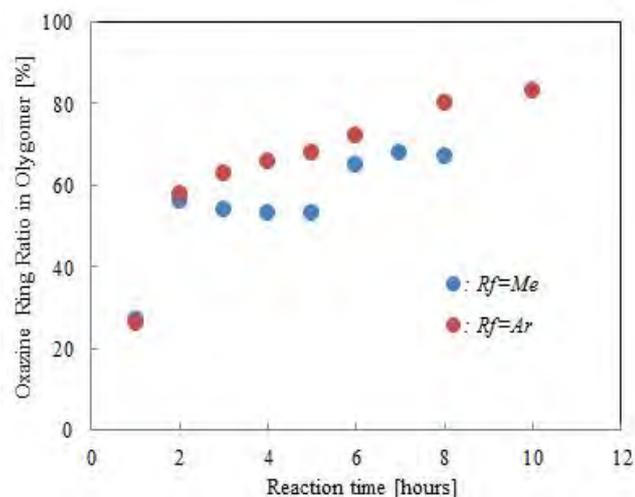


Figure3. The ratio of oxazine ring structure dependence on reaction time.

3.2. Thermal reactivity and viscoelastic behavior of pBXZ

The uncured pBXZ exhibited an exothermal peak at 264-270 °C of DSC profile, which was assigned to thecrosslinking reaction involving oxazine ring opening (see Figure 4).Further, theactivation energy (E_a) of the reaction was approximately 46.1kJ/mol as the results of the kinetics of the chemical process from the DSC curves at different heating rate.

The dynamic viscoelastic properties of the uncured pBXZ and the cured pBXZ at 240°C were shown in Figure 5 and 6, respectively. The T_g of the cured pBXZ (~250 °C) was extremelyhigher than that of the uncured pBXZ (~106 °C) because the movement of molecular chain was restricted by crosslinking of pBXZ.

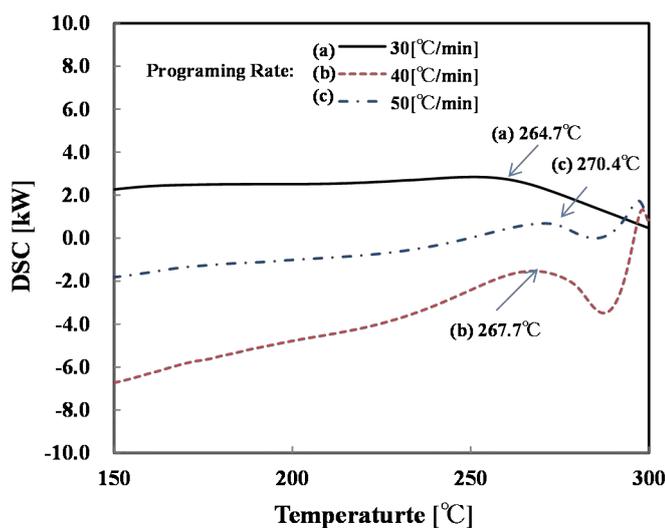


Figure 4. DSC curves for pBXZdependence on different heating rates: 30, 40, 50°C/min.

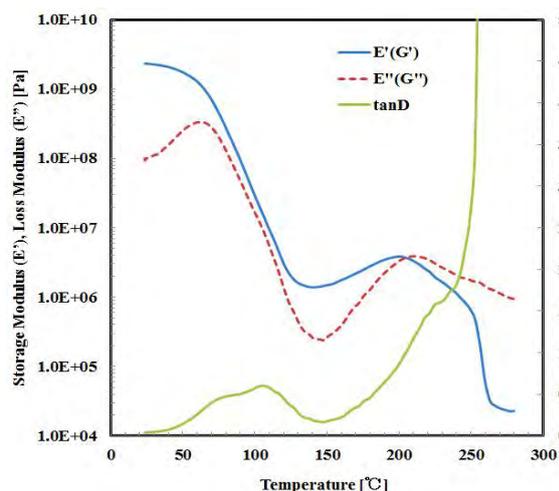


Figure 5. The dynamic viscoelastic analysis of the uncured pBXZ.

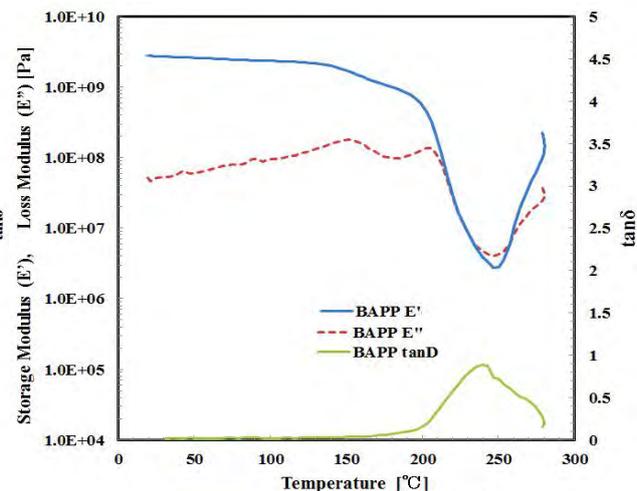


Figure 6. The dynamic viscoelastic analysis of the cured pBXZ at 240°C.

3.3. Properties of polymer alloys from pBXZ and PI

The dynamic mechanical properties the polymer alloys composed of PI/pBXZ=20/80 and PI/pBXZ=50/50 at 240 °C were shown in Figure 7. The Tg of the polymer alloys were gradually lowered with increasing of pBXZ component due to their compatibility in the significant amount. However, the storage modulus in the elastomeric state were maintained higher level compared with PI, because the component of cured pBXZ was crosslinked and restricted the movement of whole compositions. In addition, the flexibility of the polymer alloy films from pBXZ and PI was much improved compared with pristine pBXZ (Figure 8).

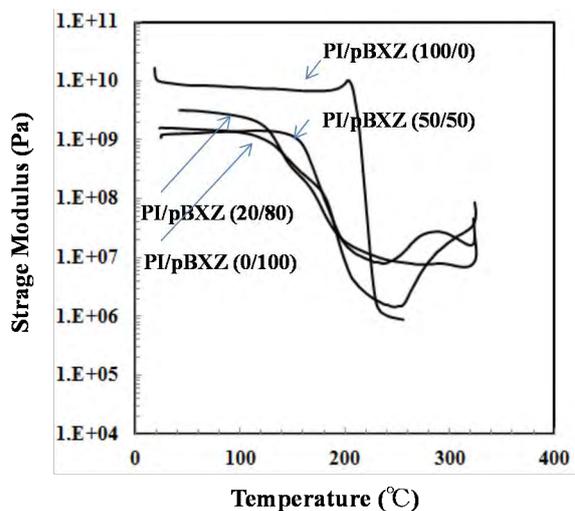


Figure 7. The dynamic viscoelastic analysis of cured pBXZ, PI and polymer alloys.



Figure 8. Appearance of the cured polymer alloy film with flexibility (PI/pBXZ=20/80).

4. Conclusion

A new class of benzoxazine oligomer was successfully synthesized from 2,2-bis[4-aminophenoxyphenyl] propane, 4,4-isoprpylidenediphenol and paraformaldehyde with high molecular weight (Mw) of over 2,000. The benzoxazine structure was effectively introduced into the oligomer backbone. The self-standing film was obtained from the oligomer solution through solution

cast method. The oligomer showed exothermic reactivity at the temperature range of 260 °C ~270 °C due to the crosslinking reaction. Then, the glass transition temperature was remarkably increased from 110 °C to 240 °C. Furthermore, a series of novel polymer alloys were derived from composition of both pBXZ and PI.

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