

High Thermal Stability of Arylamine-based Polybenzoxazine by Copolymerization with Aromatic Tetracarboxylic Dianhydride

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Introduction

Since polymeric material applications have diversified, the improvement of the properties of new polymer products, particularly by modification of the existing polymers, continues to be essential. Recently, benzoxazine resins have been widely studied in the applications required thermosetting characteristics because these resins have high mechanical properties, relatively high thermal stability, as well as excellent electrical properties. One of the outstanding properties of the resin is its ability to alloy with other polymers that provides the resin with even broader range for high temperature applications such as dianhydride-modified bisphenol-A/aniline based polybenzoxazine systems. Therefore, in this work, thermal stability of dianhydride-modified polybenzoxazine based on bisphenol-A/3,5-xylylene systems was studied.

Experimental

Materials used in this study are bisphenol-A-3,5-xylylene based benzoxazine resin (BA-35x), 3,3',4,4'-benzophenone tetracarboxylic dianhydride (BTDA) and methyl- pyrrolidone (NMP) as a solvent. The BA-35x based on bisphenol-A, paraformaldehyde and 3,5-xylylene was synthesized according to the patented solventless technology [1] as shown in Fig. 1.

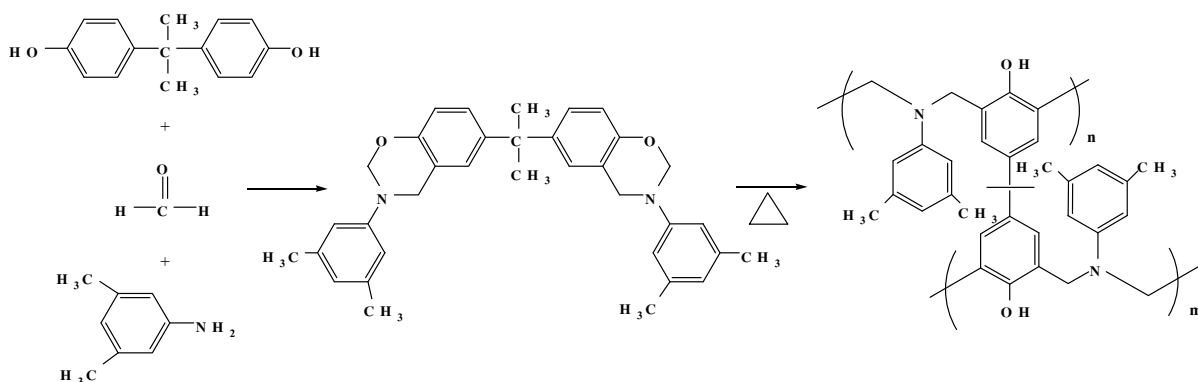


Fig. 1 Polymerization reaction of Bisphenol-A/3,5-xylylene based benzoxazine monomer.

Each resin component was first measured at the desirable mole ratios. The monomer mixture to be investigated was BA-35x:BTDA ranging from 1:0.25 to 1:1. The mixture was dissolved in NMP solvent and stirred at 80°C until a homogeneous solution was obtained. Then, the obtained liquid mixture was cast on dichlorodimethylsilane-treated glass plate. The NMP solvent was then removed by drying the sample in a vacuum oven at 60°C for 2h before undergoing a step cure in a conventional oven. The sample was then cured sequentially at 170°C to 230°C for 7 h to ensure a fully cure stage of the mixture.

Results and Discussion

Chemical structure of BA-35x type benzoxazine monomer

Bisphenol-A and 3,5-xylylidine based-bifunctional benzoxazine monomer (BA-35x) was synthesized from bisphenol-A, *para*-formaldehyde, and 3,5-xylylidine and then the synthesized BA-35x monomer was purified to eliminate the partially ring-opened oligomer compounds and unreacted reactant. The spectra for the BA-35x monomer displayed approximately 4.57 and 5.32 ppm which are attributed to methylene protons of (Ar-CH₂-N) and (O-CH₂-N) of oxazine ring, respectively. The aromatic protons displayed at range 6.5–7.1 ppm as a multiplet and the methyl proton of bisphenol-A appeared near 1.57 ppm. In addition, the methyl protons on the substituted aniline ring (Ar-CH₃) also showed at 2.27 ppm.

Thermomechanical property of BA-35x/BTDA copolymers

Fig. 2 and Fig. 3 is a plot of storage modulus and loss modulus curves as a function of temperature in the range of 25°C–400°C for poly(BA-35x) modified with various BTDA contents from 0.25 to 1 mole.

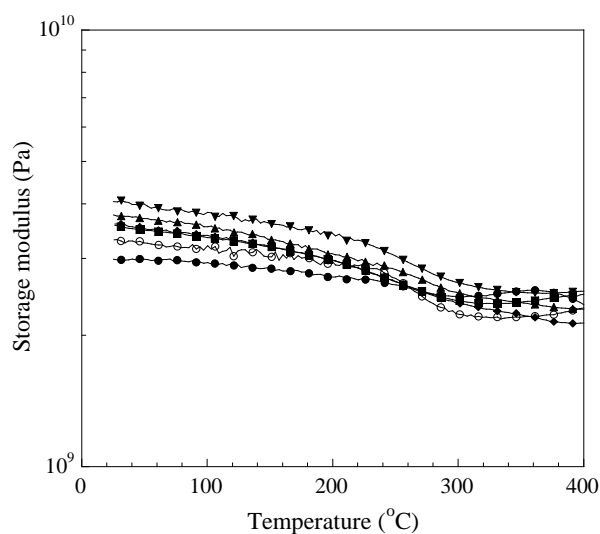


Fig. 2 Storage modulus of BA-35x/BTDA copolymers at various mole ratio of BA-35x/BTDA: (●) 1:0, (■) 1:0.5, (◆) 1:0.33, (▲) 1:0.5, (▲) 1:0.67, (○) 1:1

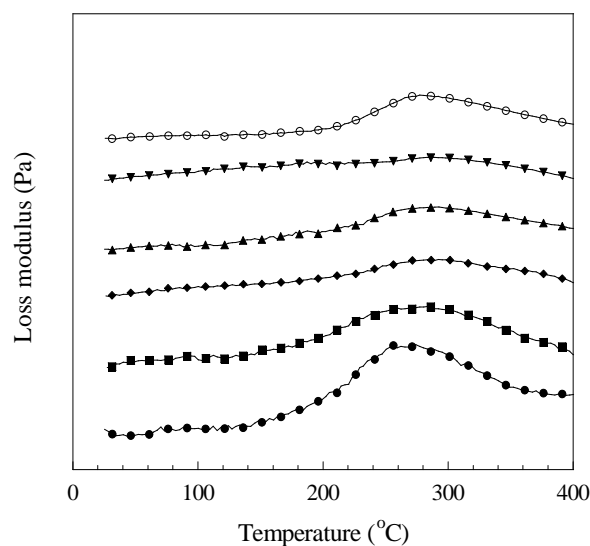


Fig. 3 Loss modulus of BA-35x/BTDA copolymers at various mole ratio of BA-35x/BTDA: (●) 1:0, (■) 1:0.5, (◆) 1:0.33, (▲) 1:0.5, (▲) 1:0.67, (○) 1:1

From Fig.2, three areas including the glassy state, the transition region, and the rubbery plateau of BA-35x/BTDA copolymers at various BTDA compositions were obtained. Ordinarily, the storage modulus of the copolymers decreased with increasing temperature. At room temperature, the storage modulus in a glassy state of the copolymer systems was found to increase with increasing BTDA mole ratio up to 0.67 mole and then decreased. We can see that the storage moduli of the BA-35x/BTDA copolymers were enhanced from 3.57 GPa for BTDA

= 0.25 mole to 4.05 GPa for BTDA = 0.67 mole which are higher than that of PMR-15 type polyimide (2.50 GPa) [2] and s-BPDA/ODA type polyimide (3.00 GPa) [3]. Furthermore, the glass transition temperature (T_g) of the BTDA-modified poly(BA-35x) copolymers was observed from loss modulus curve at peak position as depicted in Fig. 3. We can clearly see that the T_g s of the copolymers are higher than that of the neat poly(BA-35x) and the values increased with increasing BTDA contents up to 0.67 mole and then also slightly decreased. The T_g of the neat poly(BA-35x) is 260°C. The addition of 0.25, 0.33, 0.50 and 0.67 mole of BTDA into the poly(BA-35x) shifted the T_g to 270°C, 285°C, 290°C and 310°C, respectively. Specifically, the poly(BA-35x) hybrid films prepared from a mole ratio between BA-35x:BTDA = 1:0.67 exhibited the highest T_g of 310°C that is substantially higher than that of the neat poly(BA-35x), i.e. 260°C and closes to that of PETI-330 based on BPDA from UBE industries, Ltd., i.e. T_g = 330°C [4].

Thermal stability of BA-35x/BTDA copolymers

The poly(BA-35x) hybrid films clearly showed improved thermal stabilities, i.e. degradation temperature at 10% weight loss (T_{d10}) and char yield as compared to the neat poly(BA-35x) listed in Table 1. We can see that the incorporation BTDA into the poly(BA-35x) can help enhance T_{d10} and char yield at 800°C of all hybrid films, i.e. 378-398°C and 54-57%, respectively, which significantly increased compared to those of the neat poly(BA-35), i.e. T_{d10} = 362°C and char yield at 800°C of 49%. The ester linkage formation between hydroxyl group and anhydride group of the BTDA was expected for the enhanced thermal stabilities of these poly(BA-35x) hybrid films.

Table 1 Thermal stability of BA-35x/BTDA copolymers at various BTDA contents.

| BA-35x:BTDA (Mole ratio) | T_d at 10% weight loss (°C) | Char yield at 800°C (%) |
|-----------------------------|----------------------------------|----------------------------|
| Poly(BA-35x) | 362 | 49 |
| BA-35x:BTDA = 1:0.25 | 378 | 54 |
| BA-35x:BTDA = 1:0.33 | 389 | 57 |
| BA-35x:BTDA = 1:0.50 | 383 | 57 |
| BA-35x:BTDA = 1:0.67 | 387 | 55 |
| BA-35x:BTDA = 1:1.00 | 398 | 57 |
| BTDA | 317 | 2.5 [5] |

IR spectra of BA-35x/BTDA copolymers

To confirm the formation of ester linkage in BA-35x/BTDA copolymers, the characteristic absorption bands of the ester groups near 1735 cm^{-1} (C=O stretch) and 1100 cm^{-1} (C-O stretch) were observed in the FTIR spectra of the cured copolymer, while the characteristic absorption of the anhydride groups at 1860 and 1780 cm^{-1} did not appear in the spectra, indicating that the reaction formation is complete [4,5] as illustrated in Fig. 4. Furthermore, the characteristic vibration bands of the copolymer were also observed at 3670-3100 cm^{-1} (O-H stretch in phenol and carboxylic acid), 1370 cm^{-1} (Isopropyl group) and 740 cm^{-1} (CH out-of-plane deformation in *m*-disubst benzenes). Therefore, it is possible that ester linkage, a covalent bond, formed between hydroxyl groups of poly(BA-35x) and anhydride groups of BTDA (Fig. 5) as similarly observed our previous works [5-7].

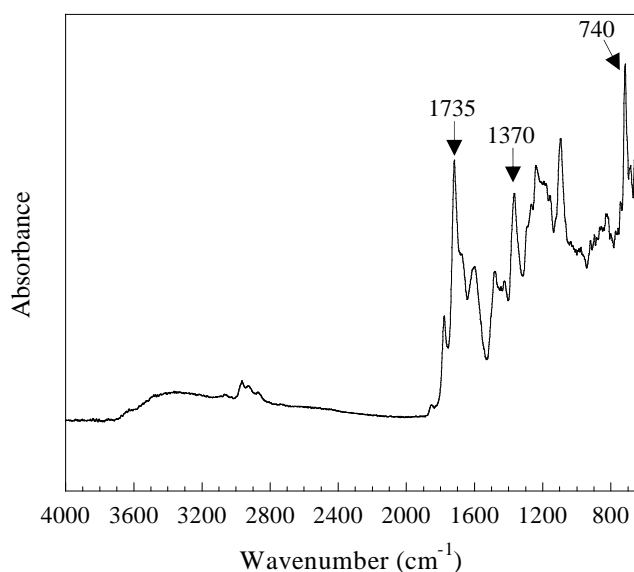


Fig. 4 IR spectrum of BA-35x/BTDA (1:0.67) copolymer

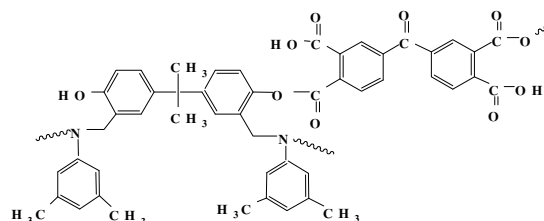


Fig. 5 Possible chemical structure of BA-35x/BTDA copolymer

Conclusions

A series of a novel BA-35x/BTDA copolymers were prepared by blending the BA-35x type benzoxazine monomer and BTDA, followed by thermal curing. The thermal properties, i.e. glass transition and degradation temperatures of poly(BA-35x) were enhanced significantly by blending with BTDA due to ester group formation in the copolymer structures. Furthermore, viscoelastic measurement displayed that the presence of BTDA can also help improve modulus of the poly(BA-35x). Therefore, polybenzoxazine modified with dianhydride should be effective for applications that require high thermal stability and high mechanical characteristics.

Acknowledgements

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