

Property Enhancement of Polybenzoxazine Modified with Maleic Anhydride

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Abstract

One seemingly shortcoming of polybenzoxazine is its relatively high rigidity. Therefore, various efforts have been attempted to toughen polybenzoxazine such as by alloying with more flexible monomers or polymers e.g. urethane elastomers or flexible epoxy. The alloying of polybenzoxazine with those resins or polymers has been reported to show synergy in some properties thus economically provide a novel class of resin systems with superior performance.⁽¹⁻⁴⁾ In this work, polybenzoxazine alloys were prepared from bisphenol-A-aniline based benzoxazine resin (BA-a) and maleic anhydride (MA) in N, NDimethylformamide (DMF) solvent. The miscible monomer mixture was easily transformed into transparent polymer alloys by thermal cure. Fourier transform infrared spectroscopy showed that the chemical interaction between hydroxyl groups of poly(BA-a) and the carbonyl group of MA occurred and generated ester linkages, resulting in a more flexibility in poly(BA-a):MA alloys. The thermomechanical properties of poly(BA-a):MA alloys and the neat poly(BA-a) were characterized by dynamic mechanical analysis (DMA). The result revealed that storage modulus (E') at room temperature of the polymeric alloy films exhibited a value of 3.91 GPa at poly(BA-a):MA of 1:1 mole ratio. The value is significantly higher than that of the neat poly(BA-a) i.e. 2.57 GPa. Interestingly, glass transition temperature (T_g) of the monoanhydride-modified poly(BA-a), obtained from the maximum peak of the loss modulus, increased with an increase in MA content. The maximum value of 200°C was obtained in poly(BA-a):MA=1:1 and is higher than that of the neat poly(BA-a) i.e. 178°C. Moreover, only single T_g was observed in these alloy systems, indicating no phase separation in poly(BA-a):MA samples. From thermogravimetric analysis, it was found that the incorporation of MA in poly(BA-a) could raise its degradation temperature as well as the char content. The modification is highly simple and of practical use for polybenzoxazines which are currently commercialized for applications such as aerospace composites, or electronic packaging materials.

Keywords : Polybenzoxazine, Anhydride, Alloy, Thermomechanical Properties

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Introduction

Polybenzoxazine is a newly developed addition polymerized phenolic systems, having a wide range of interesting properties and potential to overcome several shortcomings of conventional novolac and resole type phenolic resin. For example, hexamethylenetetramine (hexamine) is used as a curing agent.⁽⁵⁾ In the curing process of novolac-hexamine, volatiles such as water or ammonia compounds, etc. Moreover, benzoxazine resin can be easily synthesized from bisphenol-A, formaldehyde and amine by employing solution or solventless methods.⁽⁶⁾ The polymerization of benzoxazine resin proceeds via ring opening of oxazine rings by thermal cure. In addition, they do not require catalysts for polymerization or provide a self-polymerizable cross-link system⁽⁷⁻⁹⁾, do not produce by-product upon curing and there is no corrosion of processing equipment. At present,

there are many companies in the world which have been produced benzoxazine for trading including multiplicity requirements of individual applications i.e. Shikoku Chemicals Corporation, Huntsman Company and Henkel Corporation.

There are many ways to develop the performance of polybenzoxazine into two methods. Firstly, the modification of the structure of benzoxazine monomers However, disadvantages of the modification of the molecular structure of the benzoxazine resins to obtain high performance polymer include difficulty of the resin preparation, the purification process, and the high cost of raw materials used. And the other is the blends or composites with other high-temperature polymers like polyimide⁽¹⁰⁻¹¹⁾, dianhydrides.⁽¹²⁻¹³⁾ In this work, we demonstrate an ability of benzoxazine resin to react with maleic anhydride (MA) to yield novel high performance thermosetting copolymers. The modification is very simple and highly practical for industrial use.

Materials and Methods

Materials

BA-a type benzoxazine resin based on bisphenol-A, formaldehyde, and aniline was synthesized according to the patented solventless technology.⁽²⁰⁾ The BA-a resin is a yellow clear solid at room temperature. Bisphenol-A (polycarbonated grade) was supplied by Thai Polycarbonate Co., Ltd. (TPCC). Paraformaldehyde (AR grade) and aniline (AR grade) were purchased from Merck Co. and Panreac Quimica SA, respectively. Anhydride used in this work was maleic anhydride (MA) purchased from Sigma Aldrich Co. Dimethylformamide (DMF; AR grade) solvent was purchased from Fisher Scientific UK Ltd. All chemicals were used as-received.

Synthesis of Benzoxazine Monomers

Benzoxazine monomer (BA-a) was synthesized from bisphenol-A, Paraformaldehyde and aniline at a molar ratio of 1:4:2. The mixture was heated at 110°C in an aluminium pan for 30 minutes to yield a light yellow solid monomer. The resin was then ground in to fine powder and was stored in refrigerator for future use.

Preparation of BA-a:MA Copolymer Films

Benzoxazine monomer (BA-a) was blended with various amounts of maleic anhydride (MA) i.e. BA-a:MA = 1:1, 1.5:1, 2:1, 3:1 and 4:1 mole ratios, in dimethylformamide (DMF) and stirred at 80°C until clear homogenous mixture was obtained. The solution was cast on Teflon sheet and dried at room temperature for 24 hours. Addition drying was carried out at 80°C for 24 hours in a vacuum oven followed by thermal curing at 150°C for 1h, 170°C for 1h, at 190°C, 210°C, 230°C for 2 hours and 240°C for 1 hour to guarantee complete curing of the mixtures.

Characterizations of the Samples

Fourier transform infrared spectra of fully cured samples were acquired at room temperature using a Spectrum GX FTIR spectrometer from Perkin Elmer with an attenuated total reflection (ATR) accessory. In the case of a BA-a resin and maleic anhydride, a small amount of maleic anhydride powder was cast as thin film on a potassium bromide (KBr) window. All spectra were

taken with 64 scan at a resolution of 4 cm⁻¹ and in a spectra range of 4000-400 cm⁻¹.

Dynamic mechanical analysis (DMA) was conducted on NETZSCH, model DMA242 in the tensile geometry at 1 Hz with a strain value of 0.1% and at heating rate of 2°C min⁻¹ from 30 to 300°C under constant nitrogen flow of 80 mL/min. using the sample size of 0.7 mm × 10 mm × 0.1 mm.

Degradation temperature (T_d) and char yield of all samples were acquired using a Diamond TG/DTG from Perkin Elmer. The testing temperature program was ramped at a heating rate of 20°C/min from 30 to 850°C under nitrogen purging with a constant flow of 50 ml/min. The sample mass used was measured to be approximately 8-15 mg. The T_ds and char yields of the samples were reported at their 10% weight loss and at 800°C, respectively.

Results and Discussion

Network Formation by Thermal Cure of PBA-a:MA Copolymers

The IR spectrum of BA-a, MA, PBA-a and PBA-a:MA =1:1 mole ratio are show in Figure 1. From the figure, the BA-a resin (Figure 1(a)) was characterized by the band at 1232 cm⁻¹ from the aromatic ether C-O-C stretching model of an oxazine ring whereas the band around 947 cm⁻¹, and 1497 cm⁻¹ were attributed to the tri-substituted benzene ring. For the MA materials, the IR spectrum, in Figure 1(b), revealed carbonyl characteristic absorption peaks in anhydride at 1780 and 1860 cm⁻¹.⁽¹²⁻¹⁴⁾

After thermal cure, these bands completely disappeared indicating a complete loss of the oxazine ring in the BA-a resin. In addition, new absorption peaks at 878 cm⁻¹ and 1488 cm⁻¹ of the tetra-substituted aromatic ring were observed suggesting the ring opening reaction to take place ortho to the phenolic moiety as display in Figure 1(c) Furthermore, an indication of ring opening reaction of the BA-a resin upon thermal treatment could also be observed from the appearance of a broad peak about 3300 cm⁻¹ which was assigned to the phenolic hydroxyl group formation.

The chemical transformation of BA-a:MA at 1:1 mole ratio upon thermal curing were investigated and the resulting spectra are shown in

Figure 2(d). The new absorption bands of PBA-a:MA copolymer were observed. The phenomenon was ascribed to the appearance of carbonyl stretching bands of ester linkage. From the PBA-a:MA spectra in Figure 1, we can see that the anhydride carbonyl stretching bands of MA at 1860 and 1780 cm^{-1} completely disappeared. It was suggested that the reaction between the phenolic hydroxyl group of PBAa and the anhydride group of MA to form ester carbonyl linkage as evidenced by observed peak in the spectrum at 1750-1730 cm^{-1} of its C=O stretching band.⁽¹²⁻¹⁴⁾

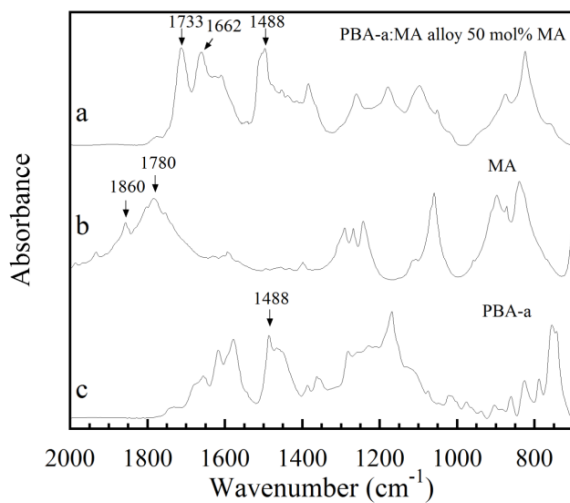


Figure 1. IR spectra : (a) BA-a:MA = 1:1 mole ratio, (b) MAa and (c) PBA-a

Dynamic Mechanical Properties of PBA-a:MA Copolymers

The storage modulus that provides the material stiffness of the PBA-a:MA copolymer samples at glassy state region reflecting their molecular rigidity is depicted in Figure 2. From this figure, we can clearly see that the storage modulus of the PBA-a:MA copolymers was higher than that of the neat PBA-a and the values increased with the MA contents. The room temperature modulus at 25°C of the copolymers exhibited the values in the range of 3.27-3.91 GPa. whereas that of the neat PBA-a was about 2.57 GPa.

All PBA-a:MA copolymers sample are homogeneous and transparent, implying that no phase separation. The PBA-a:MA copolymer samples were subjected to thermal analysis by examining T_g characteristic. From an inset of Figure 3, the T_g of PBA-a determined from the maximum of loss modulus curve in DMA experiment was about 178°C and the value was

found to be substantially enhanced by blending with the MA. All of the fully cured PBAa:MA copolymer samples showed only single T_g ranging from 180 to 200°C. This characteristic confirmed a presence of a single phase material in these copolymers. Additionally the copolymer of PBA-a:MA at a mole ratio of 1:1 exhibited a maximum value in T_g . Moreover, the chemical interaction between hydroxyl groups of PBA-a and anhydride groups of MA occur to generated ester linkage as depicted in FTIR spectra results in further T_g improvement of the copolymers.

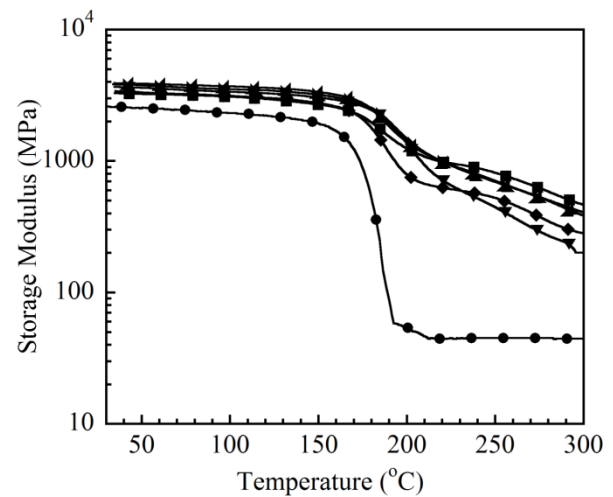


Figure 2. Storage modulus of PBA-a:MA copolymers as a function of temperature : (●) PBA-a, (■) PBA-a:MA = 4:1, (◆) PBA-a:MA = 3:1, (▼) PBA-a:MA = 2:1, (▲) PBA-a:MA = 1.5:1, (▲) PBA-a:MA = 1:1

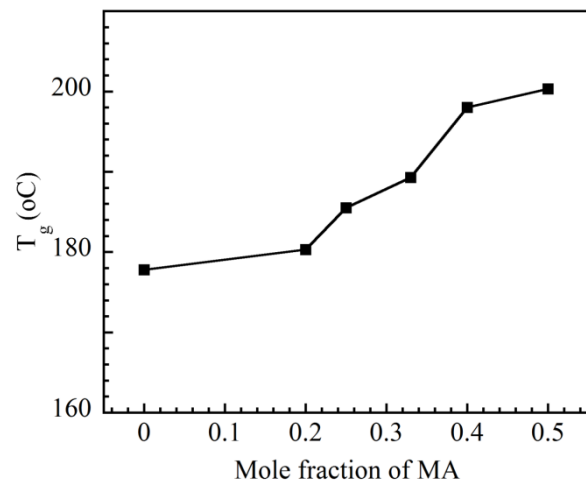


Figure 3. Glass transition temperature of PBA-a:MA copolymer at various MA fractions.

Thermal Stability of PBA-a:MA Copolymers

Thermal stability of the neat BA-a and PBA-a:MA copolymers was investigated by

thermogravimetric analysis (TGA). Figure 4 compares TGA thermograms of the PBA-a and its copolymers in nitrogen atmosphere. From the figure, we can see that the degradation temperature (T_d) at 10% weight loss of the copolymer was shifted to a higher value than that of the neat PBA-a. The maximum T_d of 361°C belonged to the copolymer sample of PBAa:MA copolymer at mole ratio 1:1 while the T_d of the neat PBA-a was measured to be about 347°C. The formation of an addition ester linkage between the carbonyl group in the MA and hydroxyl group of the neat PBA-a was found to effectively improve the degradation temperature of the resulting PBA-a:MA copolymers.

Another interesting feature in the TGA thermograms is an amount of residual at 800°C of all samples shown in Figure 4. A remarkable improvement of char yield was clearly observed in the copolymers i.e. the char yields of all copolymers showed the values significantly greater than that of neat PBA-a. In particular, the cured copolymer sample of PBA-a:MA at the mole ratio of 1:1 provided a value as high as 40% which is much greater than that of the neat PBA-a, i.e. 27%. The high char yield of these PBA-a copolymers due to their higher aromatic content in the molecular structure. In principle, the greater the char yield, the higher the flam retardancy of the polymer. Therefore, these copolymers tended to provide a sample with potentially substantial improvement in their flam retardancy which was highly useful in some applications such as aviation, automotive and electronic industries.

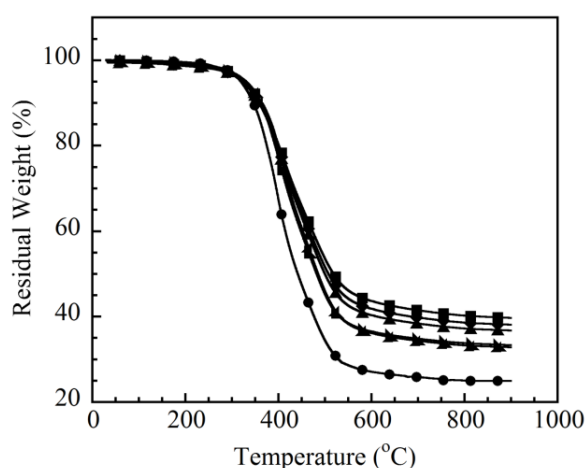


Figure 4. TGA thermograms of BA-a:MA copolymer as a function of temperature : (●) PBA-a, (■) PBA-a:MA = 4:1, (◆) PBA-a:MA = 3:1, (▼) PBA-a:MA = 2:1, (▲) PBA-a:MA = 1.5:1, (▲) PBA-a:MA = 1:1

Conclusions

The copolymers of bisphenol-A-aniline based polybenzoxazine (PBA-a) modified with maleic anhydride (MA) showed significant enhancement in their mechanical and thermal properties compared to those of the neat PBA-a. The obtained network structures were due to reaction between the hydroxyl group of PBA-a and the anhydride group of MA as revealed by FTIR. The obtained copolymers exhibited excellent mechanical and high thermal properties. The thermal decomposition temperature and weight residue at 800°C also remarkably increased with an incorporation of the MA. Therefore, the PBA-a modified with the MA should be considered as good potential candidates for applications such as aerospace composites, or electronic packaging materials.

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