Preparation and Characterization of Liquid Rubber-modified Polybenzoxazine

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Alloying polybenzoxazine with liquid rubber was studied in order to overcome its brittleness. We used three kinds of liquid rubber having different functional groups at the chain-end, which are amino, carboxyl and methoxyl groups, namely ATBN, CTBN and ETBN, respectively, to examine the effect of liquid rubber terminal groups on the polymerization of a typical benzoxazine monomer, F-a, and the compatibility with the polybenzoxazine, PF-a. DSC analysis revealed that ATBN and CTBN were effective modifier for lowering the onset temperature of the ring-opening polymerization of F-a. PFa/ATBN hybrid films exhibited high homogeneity throughout wide range of weight ratios of ATBN due to acid-base interaction between the phenolic groups of PF-a and the amino terminal groups of ATBN as confirmed by SEM. Viscoelastic measurement of the hybrids revealed improvement in toughness for the hybrids having low content of ATBN. Moreover, increase of the glass transition temperature of the polybenzoxazine was observed by the hybridization with ATBN. Thermogravimetric analyses revealed that the addition of liquid rubber also enhanced the thermal stability of the polybenzoxazine.

KEYWORDS: Polybenzoxazine / Liquid rubber / Rubber modification / Ring-opening polymerization / ATBN

1. Introduction

Polybenzoxazine has been developed to overcome the shortcomings of the traditional phenolic resins. It is synthesized through the ring-opening polymerization of benzoxazine monomer, which is easily prepared from phenols, primary amines and formaldehyde. Wide variation of raw materials allows tremendous flexibility in molecular design and versatile performance as well as the balance between thermal and mechanical performance [1-10]. The ring-opening polymerization proceeds through thermal treatment without the need of catalyst and without the generation of volatiles, thus maintaining the dimensional stability. The structures of a typical benzoxazine monomer, bis(3-phenyl-3,4-dihydro-2H-1,3-benzoxazinyl)isopropanol (abbreviated as F-a) and its polymer, PF-a, are shown in Scheme 1.

Despite of its great advantages, polybenzoxazines also share the drawbacks associated with phenolic resins such as brittleness and high temperature required for polymerization. Many efforts have been carried out to improve thermal and mechanical properties of polybenzoxazine, for instance, by alloying with high performance polymers such as epoxy resin [11].
polyurethane [12], polyimide [13], and poly(imide-siloxane) [14].

Liquid rubber has been known as a toughener commonly used in epoxy resins. It is an appropriate choice of modifier for polybenzoxazine, because its low viscosity provides easy handling and the polarity can be adjusted by changing the ratio of polybutadiene and acrylonitrile content. It has been previously reported that the incorporation of reactive liquid rubbers such as amine-terminated poly(butadiene-acrylonitrile) (ATBN) and carboxy-terminated poly(butadiene-acrylonitrile) (CTBN) as modifiers improved toughness [9, 10, 15], however, glass transition temperature (Tg) of the modified polybenzoxazine was found to decrease with the increasing content of liquid rubber [9]. In this study, we investigated the influence of the terminal groups of ATBN, CTBN and ester-terminated poly(butadiene-acrylonitrile) (ETBN) on the ring-opening polymerization of F-a and their compatibility. The liquid rubber structures are shown in Figure 1. The thermal and mechanical properties of the obtained polybenzoxazine/liquid rubber hybrids were also examined.

Figure 1. Chemical structures of ATBN, CTBN, and ETBN.

2. Experimental

2.1. Materials

F-a was kindly donated by Shikoku Chemicals Co. and was used after purification by washing with using 3 N NaOH solution and water. ATBN (code. 1300 × 16 Hycar) and CTBN (code. 1300 x 8 Hycar) were kindly supplied by UBE Co. ATBN has a molecular weight of 3600 with 18% acrylonitrile content, while CTBN has a molecular weight of 3550 with 18% of acrylonitrile content. Tetrahydrofuran (THF) from Wako Pure Chemical (Japan) was used as received. Diazomethane in diethyl ether was generated from N-methyl-N-(p-tolylsulfonyl)nitrosamide (Diazald, from Tokyo Kasei) just before use. ETBN was prepared through the methylation of CTBN with diazomethane.

2.2. Preparation of PF-a Film

F-a (1.5 g, 3.45 mmol) was dissolved in 5 ml THF. The light yellow solution was then cast on a glass plate pre-treated with dichlorodimethylsilane. The cast film was then heated in an air oven at 60, 100, 150, 200, 240 °C for 1h each to obtain PF-a with thickness in the range of 0.1 mm.

2.3. Preparation of PF-a/liquid rubber hybrid films

The hybrid films were prepared by blending F-a and the liquid rubbers in various ratios followed by curing. A typical procedure is described below. F-a (1.46 g, 3.37 mmol) was dissolved in THF (2 mL) and stirred at room temperature. ATBN (0.037 g) was dissolved in THF (3mL), and filtrated with cotton absorber. The THF solution of ATBN was introduced into the F-a solution to afford transparent yellow solution. The mixture was then cast on a pre-treated glass plate and heated in an air oven at 50, 100, 150, 200, 240 °C for 1h each to obtain PF-a/ATBN film containing 2.5 wt% of ATBN with thickness in the range of 0.1 mm.

2.4. Measurements

IR spectra were obtained using a Jasco FT/IR-420 spectrometer. Scanning electron microscopic observation was performed using a Hitachi S-4800 at an accelerating voltage of 10 kV. Differential scanning calorimetry (DSC) was carried out using a Thermo Plus 2 DSC8230 calorimeter (Rigaku) at a heating rate of 10 °C/min under nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed using a Rigaku Thermo Plus 2TG-DTA TG8120 at a heating rate of 5 °C/min under argon atmosphere. Dynamic viscoelastic measurements were conducted using an Orientec Automatic Dynamic Viscoelastomer Rheovibron model DDV-01FP at 35 Hz at a heating rate of 4 °C/min. Tensile properties were recorded using an Imada Seisaku-sho Model SV-3 at a crosshead speed of 1 mm/min using films of about 2 cm long. The tensile properties of each variable were determined from the average value of 10 tests.

3. Results and discussion

3.1. Effect of liquid rubber terminal groups on the
ring-opening polymerization of F-a

First of all, influence of the liquid rubbers on the ring-opening polymerization of F-a was investigated by DSC. The DSC thermograms of F-a after solvent removal at 60 °C for 12 h are shown in Figure 2a. The onset of ring-opening polymerization of F-a appears at 225 °C with its maximum centered at 247 °C. These values decrease to 210 and 239 °C, respectively, in the presence of 5 wt% of ATBN (Figure 2b).

![DSC thermograms of F-a (a), F-a/ATBN (b), F-a/CTBN (b), and F-a/ETBN blends with a liquid rubber content of 5 wt%.

Similarly, CTBN also exhibited lowering effect on the ring-opening polymerization. Figure 2c shows that, in the presence of 5 wt% of CTBN, the onset and the maximum temperatures lower to 216 and 237 °C, respectively. It is known that acids and bases act as catalyst for ring-opening polymerization of benzoxazines. The DSC results clearly indicate that the terminal groups of ATBN and CTBN act as the catalyst. As opposed to ATBN and CTBN, no temperature shift was observed in the cure temperature of F-a in the presence of ETBN (Figure 2d). The ester terminal group doesn’t impose any effect on the ring opening polymerization.

3.2. Effect of liquid rubber terminal groups on the morphology of the cured hybrid films

In order to investigate the influence of the liquid rubber terminal groups on the miscibility, PF-a/liquid rubber hybrids were prepared at various liquid rubber contents. THF solutions of F-a/liquid rubber blends were cast on a glass plate and then cured at 60 °C, 100 °C, 150 °C, 200 °C, and 240 °C for 1 h each to afford self-standing homogeneous films. Figure 3 shows photographs of the obtained films. PF-a/liquid rubber hybrids afforded films ranging from orange to dark wine in color. From the Figure it is evident that PF-a/ ATBN hybrids exhibit homogeneity and consistency. PF-a/CTBN hybrids show the same degree of consistency only at 5 wt% of CTBN content. At 10 wt% of CTBN, voids and bubbles appear in some areas causing the surface to be uneven. It is possible that esterification between the carboxylic terminal groups of CTBN and the phenolic moiety of polybenzoxazine might occur, which is supported by the fact that voids are generated at the temperature around 200 °C, at which the ring-opening polymerization begins to occur very rapidly. PF-a/ETBN hybrids exhibit even lower compatibility as bubbles appear in lower weight ratio. At higher content of ETBN it grows more severe.

![Comparison in the appearance of hybrid films with the incorporation of different kinds of liquid rubber.

Since ATBN showed the best miscibility with PF-a among the liquid rubbers, further study was carried out by using ATBN. As shown in Figure 4, the PFa/ATBN blends with various ATBN contents gave flexible homogeneous films of dark wine color. It is apparent that the increase in ATBN content significantly improved the flexibility of the hybrid film.
Another interesting phenomenon observed in this system is the change in film transparency at different content of ATBN. Pristine PFa gives a transparent film of orange color. With the incorporation of ATBN from 2.5 to 20 wt%, the hybrid films grow opaque. At higher content of ATBN, however, the films turn transparent.

Figure 4. Photographs of PF-a film (a) and PF-a/ATBN hybrid films at 2.5 (b), 5.0 (c ), 10 (d), 15 (e), 20 (f), 40 (g), 60 (h ), and 80 wt% (i) of ATBN content.

Quantitative analysis of film transparency was carried out using UV-vis analysis. As shown in Figure 5a, pristine PFa film showed the highest transparency of 82% at 800 nm. The incorporation of ATBN seems to bring about considerable decrease in transparency up to a certain extent; an increase of ATBN content from 2.5 to 20% wt% of ATBN decreased the film transparency from 13% to 0.26% at 800 nm (Figure 5 inset). Further ATBN loading, however, gradually turned the film into transparent again; an increase in ATBN content from 40 to 80 wt% resulted in increased transparency from 2.5 to 68% at 800 nm. This result concurs with visual comparison, in which the corresponding hybrid films appears opaque up to a certain extent but then turns transparent at high content of ATBN.

Figure 6. SEM images of fracture surfaces for PF-a film (a), PF-a/ATBN at 2.5 (b), 5.0 (c), 7.5 (d), 10 (e), 15 (f), 20 (g), 40 (h), 60 (i), and 80 wt% (j) of ATBN, PF-a/CTBN at 5 wt% of CTBN (k), and PF-a/ETBN at 5 wt% of ETBN (l) hybrid films. Bar 10 µm.

Opaqueness exhibited by hybrid films was caused by phase separated morphology as revealed by SEM observations. Figure 6 shows the SEM images of fracture surfaces of PF-a/ATBN hybrid films with various ATBN content. Even at 2.5 wt% ATBN, the hybrid exhibited spherical rubber domains dispersed in continuous polybenzoxazine matrix (b). Interestingly, hybrid film containing 40 wt% of ATBN revealed vague phase separated morphology (h), and no distinguishable phase separation appeared on the hybrids containing 60 to 80
wt% of ATBN (i and j). This is possibly due to phase interchange where ATBN becomes the continuous phase. In addition strong acid-base interaction between phenol and amine terminal group and hydrogen bonding may have promoted the compatibility between two phases.

Similar phase-separated structures in micro scale were also observed in PF-a/CTBN and PF-a/ETBN hybrid films at 5 wt% of the liquid rubber (k and l). However, further increase of the rubber contents led to severe macroscopic phase separations. This result also implies the effect of the acid-base interaction between ATBN and PF-a on the miscibility.

Rubber domain size distribution for various weight ratios of PF-a/ATBN hybrids was estimated. At 10 wt% of ATBN, the rubber domain size exhibited narrow distribution ranging from 0.9 to 1.2 \( \mu \text{m} \). However, hybrids having 15 and 20 wt% of ATBN showed wider distribution of 1.6 ± 0.8 and 2.9 ± 0.8 \( \mu \text{m} \), respectively. This result might have been caused by particle aggregation in the matrix which would greatly affect the mechanical properties of the hybrids.

3.3. Influence of terminal groups on the tensile properties of PF-a/liquid rubber hybrids

The effect of terminal groups on the mechanical properties of the hybrids was examined. Here, all specimens were cured up to 180 °C for 12 h instead of 240 °C to keep them homogeneous and bubble free, especially for PF-a/CTBN hybrid. With the addition of 5 wt% of ATBN, the tensile strength (\( \sigma_\text{b} \)) of pristine PF-a increased from 50.5 to 61.2 MPa and its elongation at break (\( \varepsilon_\text{b} \)) from 1.6 to 2.2. With the same amount, CTBN gave lower tensile strength value, 51.4 MPa. It seems that the terminal groups affects more on the tensile strength than it does on the elongation at break as both ATBN and CTBN gave similar value of 2.2 %.

3.4. Tensile properties of PF-a/ATBN hybrids

In this section, unlike the previous one, all the specimens of PF-a/ATBN hybrids were cured to 240 °C since bubble free films can be prepared even at elevated temperature. The stress-strain curves are shown in Figure 7. The tensile strength of unmodified PF-a (81.8 MPa) increased to 87.1 and 83.2 MPa with the addition of 2.5 and 5 wt% of ATBN, respectively. The elongation at break also increased from 3.1% (unmodified PF-a) to 3.8 to and 4.4% with the addition of 2.5 and 7.5 wt% of ATBN, respectively. At 60 and 80 wt% of ATBN, as rubber became the major component and dominated most of the hybrid properties, materials exhibited rubbery properties; elongation at break increased significantly to 8.1 and 11.3% but tensile modulus (\( E \)) for corresponding hybrids dropped to 0.4 and 0.2 GPa, respectively.

3.5. Influence of terminal groups on the viscoelastic properties of PF-a/liquid rubber hybrids

It is notable that hybrids containing 15 and 20 wt% of ATBN exhibited poor tensile properties compared to other concentration. The tensile strength dropped from 69.4 MPa at 10 wt% of ATBN to 38.2 and 21 MPa at 15 and 20 wt% of ATBN, respectively. In addition, the elongation at break is also considerably lower than those having less content of the liquid rubber. In the previous section, it was revealed the corresponding ATBN content have poor particle-size distribution which gave rise to uneven stress distribution and became a point of failure in the material. A study by Deanin and Manion stated that two phase structure and control of dispersed particles size are essential factors in attaining the optimum toughness of a material. The optimum size of rubber particles is between 1- 10 \( \mu \text{m} \) and compatibility between two phases must be achieved in order to form a strong interphase which allows the modulation of property gradient and successful stress transfer across it [16].

3.5. Influence of terminal groups on the viscoelastic properties of PF-a/ATBN and
PF-a/CTBN hybrids with 5 wt% of the liquid rubber were investigated by DMA. Apparently, the terminal group didn’t impose much effect on the $T_g$ of the hybrid as peak of $E''$ only shifts very slightly. At the 5 wt% of the liquid rubber, PF-a/ATBN hybrid showed $T_g$ at 175.2 whereas the CTBN at 172.3 °C. From the above result, we have come to understand that the compatibility between PF-a and ATBN contributes to its fine morphology and in turn to the mechanical performance of the hybrids, extensive study of which will be given in the next section.

3.6. Viscoelastic properties of PF-a/ATBN hybrids

The viscoelastic results of unmodified PF-a and PFa/ATBN hybrids are shown in Figure 8 and are summarized in Table 1. As opposed to previous study by Jang and Seo [9], $T_g$ of PF-a increased with the addition of ATBN. The $T_g$'s obtained from values corresponding to the maximum of loss modulus shifted to higher temperature with the increasing content of ATBN. The $T_g$ of unmodified PF-a increased from 189 °C to 191 and 228 °C by the addition of 10 and 20 wt% of ATBN, respectively.

In order to elucidate the $T_g$ improvement, we estimated crosslink density ($N$) derived from $T_g$ as obtained from the storage modulus ($E'$) with the following equation:

$$ N = \frac{E'}{3RT} $$

The result is summarized in Table 1. The increase in $T_g$ indicates the beneficial effect of high crosslink density which restricted the movement of polymer chains [5]. The PF-a/ATBN hybrid with 20 wt% of ATBN demonstrated how the drop in storage modulus corresponding to the surpassing of polymer glass transition temperature is considerably suppressed compared to minimum of pristine PF-a and PF-a/ATBN with 10 wt% of ATBN. The improved crosslink density of the hybrid must have prevented the drop in storage modulus due to the restriction of polymer chain movement.

![Figure 8. DMA results of pristine PF-a and PF-a/ATBN hybrids at various ATBN contents.](image)

![Figure 9. TGA curves of pristine PF-a (a), PF-a/ATBN hybrids at 10 (b), 20 (c), 60 wt% (d) of ATBN content. and pristine ATBN (e) under argon atmosphere at heating rate of 5 °C/min.](image)

3.7. Thermal stability of PF-a/ATBN hybrids

The thermal stability of PF-a and PF-a/ATBN hybrids was evaluated using TGA under N$_2$ atmosphere and the profiles are shown in Figure 9. The TGA results
for PF-a/ ATBN, PF-a/CTBN and PF-a/ETBN hybrids are also summarized in Table 2. Modification has apparently improved the thermal stability of the hybrids as shown by the increasing trend in decomposition temperature with the increase in ATBN content.

The 5% weight loss temperature (T_{5%}) of pristine PF-a was determined to be 295 °C. In the presence of 2.5 wt% of ATBN, the T_{5%} was observed at higher temperature of 302 °C. Unexpectedly, the hybrids exhibited higher decomposition temperature than pristine PF-a. The modification didn’t seem to increase the thermal flame retardance of the hybrids though. In particular, the char yield decrease from 53% for unmodified PF-a to 51, 42 and 30% with the incorporation of 5, 10 and 20 wt% of ATBN.

4. Conclusion

The presence of liquid rubber having functional terminal groups even in small amount imposed a pronounced effect on the ring-opening polymerization of F-a as revealed by DSC study, with ATBN being the best modifier compared to CTBN and ETBN. We have successfully prepared homogeneous PF-a/ATBN hybrid films in wide range of the ATBN content and studied the morphology. We found that the hybrid exhibited phase separated morphology in micro scale, which led to enhanced tensile and viscoelastic properties. Moreover, the incorporation of ATBN increased the crosslink density of PF-a and increased the T_{g} of the hybrids as both parameters shared similar trend. Thus we can conclude that ATBN is a key compound in improving the cure behavior as well as thermal and mechanical properties of PF-a.

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