Preparation of Polybenzoxazine/Ionic Liquid Hybrids

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We successfully prepared a novel hybrid of polybenzoxazine (PBa) and ionic liquids (ILs), such as 1-butyl-3-methylimidazolium trifluoromethanesulfonate ($BMICF_3SO_3$) by the polymerization of benzoxazine in the presence of IL. The obtained hybrid film at 20 wt % $BMICF_3SO_3$ content had higher tensile strength and elongation at break than those of the pristine PBa film without sacrificing the modulus. The hybrid also showed high T_g and degradation temperature evidenced by DMA and TGA.

Polybenzoxazines are expected to be a novel type of phenolic resin that can be obtained by the thermally induced ring-opening polymerization of cyclic benzoxazine monomers.[1] Chemical structures of a typical benzoxazine monomer, 6,6′-(1-methylethane-1,1-diyl)bis(3,4-dihydro-3-phenyl-2*H*-1,3-benzoxazine) (Ba), and its thermoset (PBa) are shown in Figure 1. Polybenzoxazines have not only the advantageous properties of traditional phenolic resins such as high thermal properties, but also other properties that are not found in traditional phenolic resins such as molecular design flexibility, low moisture absorption, and no by-product release upon curing.[1] However, polybenzoxazines are brittle as is common for thermosets, which limits its application. In order to achieve toughness improvement, hybridization with elastomers like liquid rubber,[2] polyurethane,[3] poly(imide-siloxane),[4] and polydimethylsiloxane[5] were reported. Since the hybrids are prepared by the in situ polymerization of Ba in the presence of elastomer, the elastomer component requires high thermal stability during cure of Ba.

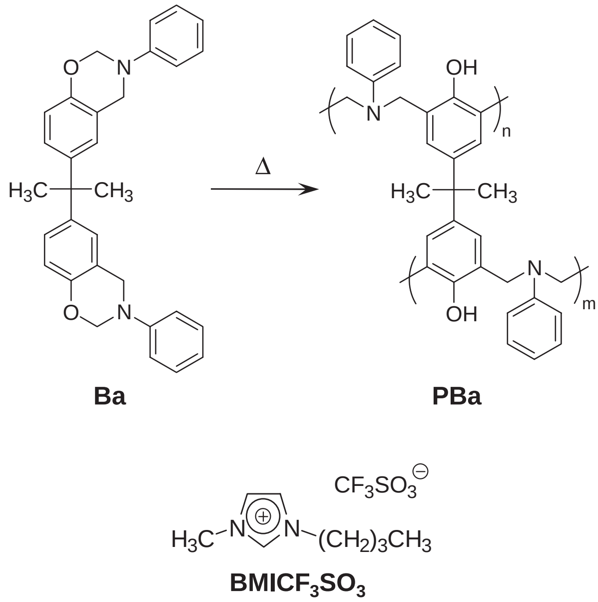

Figure 1. Chemical structures of Ba, PBa, and ionic liquid.

Recently, ionic liquids (ILs), molten salts at room temperature, have widely been used as recyclable solvents alternative to traditional organic solvents for organic syntheses due to their non-volatility and high thermal stability.[6] We expected that ILs can be used to toughen PBa owing to their high thermal stability. Herein, we report on the preparation of PBa/IL hybrids by the in situ polymerization of Ba in the presence of IL. The mechanical and thermal properties of the hybrids were also investigated.

We used 1-butyl-3-methylimidazolium trifluoromethanesulfonate ($BMICF_3SO_3$) as the IL for hybridization with PBa (Figure 1).[7] Ba, $BMICF_3SO_3$, and *p*-toluenesulfonic acid (PTS) as the catalyst for the ring-opening polymerization of Ba were mixed at various ratios in *N*,*N*-dimethylformamide (DMF). The solutions were cast on glass plates followed by thermal curing up to 220 °C.[8,9] Homogeneous PBa/$BMICF_3SO_3$ hybrid films were obtained from 20 to 80 wt % of $BMICF_3SO_3$ content (Figure 2). The pristine PBa film of 100 μm thickness is very brittle, and we could not bend more than as is shown in Figure 2a. However, the hybrid film at 20 wt % $BMICF_3SO_3$ [PBa/$BMICF_3SO_3$ (20 wt %)] showed remarkably improved toughness, and even the 150 μm thick film is easy to bend (Figure 2b). Flexibility further increased with the increase of the IL content (Figure 2c). Homogeneous self-standing PBa/$BMICF_3SO_3$ hybrid films could be obtained up to 80 wt % $BMICF_3SO_3$ content (Figure 2d). The mixture at 90 wt % $BMICF_3SO_3$ content became highly viscous solution after curing, and could not be obtained as a solid film.

The tensile properties of the hybrid films were examined. Figure 3 shows stress–strain curves of the pristine PBa and PBa/$BMICF_3SO_3$ (20 wt %) films. Pristine PBa film prepared by curing up to 220 °C in the presence of PTS possesses high

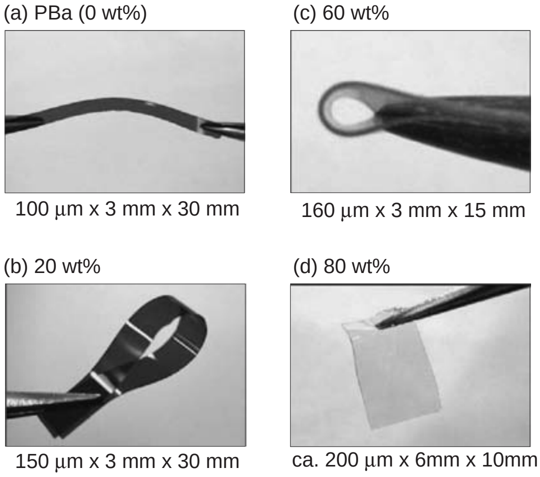
(a) PBa (0 wt%)
100 μm x 3 mm x 30 mm
(c) 60 wt%
160 μm x 3 mm x 15 mm
(b) 20 wt%
150 μm x 3 mm x 30 mm
(d) 80 wt%
ca. 200 μm x 6mm x 10mm

Figure 2. Photographs of pristine PBa (a) and PBa/$BMICF_3SO_3$ hybrids at 20 (b), 60 (c), and 80 wt % (d) IL content.

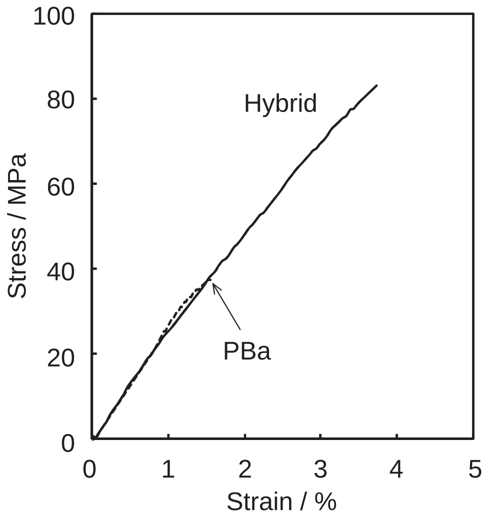

Figure 3. Stress–strain curves of pristine PBa (dotted line) and PBa/$BMICF_3SO_3$ hybrid at 20 wt % IL content (solid line) films.

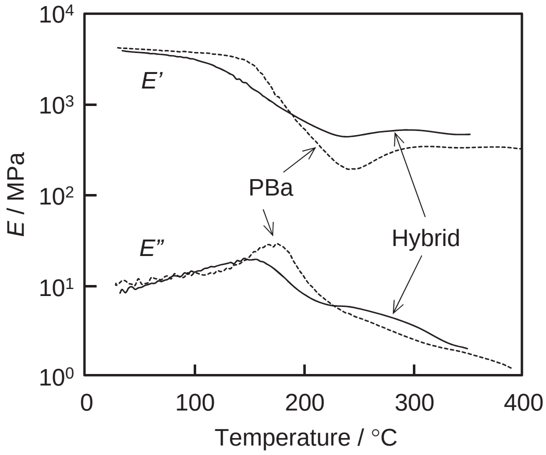

Figure 4. DMA results of pristine PBa (dotted line) and PBa/$BMICF_3SO_3$ hybrid at 20 wt % IL content (solid line) films.

tensile modulus ($E = 2.7$ GPa), but low tensile strength ($s_b = 37$ MPa) and elongation at break ($e_b = 1.5\%$), corresponding to the brittleness of the film. By introducing $BMICF_3SO_3$ into the PBa matrix, the tensile strength and elongation at break increases ($s_b = 83$ MPa, $e_b = 3.7\%$ at 20 wt % IL), clearly showing that the IL acts as a toughener. Interestingly, in spite of the addition of IL, tensile modulus did not decrease ($E = 2.8$ GPa).

Viscoelastic properties of PBa/$BMICF_3SO_3$ (20 wt %) was investigated by dynamic mechanical analysis (DMA). The storage modulus (E') and loss modulus (E'') are plotted in Figure 4. Glass-transition temperatures (T_gs) of the films were determined by the maxima of E''. The T_g of the pristine PBa film was 175 °C, while the T_g of PBa/$BMICF_3SO_3$ (20 wt %) film decreased to 154 °C by the addition of the IL. It is worth noting that the hybrid maintained relatively high T_g even by the addition of IL at 20 wt %.

Generally, addition of an elastomer, such as liquid rubber and polyurethane, into a network polymer causes significant decrease of the modulus and T_g.[2,3] Surprisingly, the storage modulus at room temperature (E'_{rt}) of the pristine PBa and the hybrid were almost the same [PBa: $E'_{rt} = 4.1$ GPa, PBa/$BMICF_3SO_3$ (20 wt %): $E'_{rt} = 3.9$ GPa] in spite of the addition of IL, and the tendency is in good agreement with the results from the tensile test mentioned above. The decrease of E' above T_g was also suppressed by the hybridization, which suggests that crosslink density of PBa was increased by the addition of IL. Thus, the increase of crosslink density brought about the minimum decrease of T_g and higher storage modulus above T_g.

The solvent resistivity of PBa/$BMICF_3SO_3$ (20 wt %) hybrid film was examined in hexane, tetrahydrofuran (THF), acetone, and DMF (Table S1 in Supporting Information).[9] While most of the IL was eluted in polar solvents like acetone and DMF, the hybrid film showed high resistivity in less polar solvents like hexane and THF.

The thermal stability of the hybrid was investigated by thermogravimetric analysis (TGA). The 5% weight loss temperature (T_5) of the hybrid ($T_5 = 294$ °C) was almost the same as that of pristine PBa ($T_5 = 301$ °C), indicating that the thermal stability was maintained after the addition of $BMICF_3SO_3$ (Figure S2 in Supporting Information).[9]

In conclusion, we have successfully prepared hybrids of PBa and $BMICF_3SO_3$ by the ring-opening polymerization of Ba in the presence of the IL. Because of the toughening effect of IL, the hybrid had higher tensile strength and elongation at break than the pristine PBa without sacrificing the modulus and thermal stability owing to the increased crosslink density of PBa by the hybridization. Moreover, the self-standing hybrids could be obtained up to 80 wt % of the IL content. Such hybrid films can be applicable for advanced electrochemical devices as ion gels.[6d]

References and Notes

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7 We examined the thermal stability of imidazolium salts, such as $BMICF_3SO_3$, 1-butyl-3-methylimidazolium hexafluorophosphate ($BMIPF_6$), and 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide (BMITFSI) by TGA in air. Among them, $BMICF_3SO_3$ revealed the highest degradation temperature (Figure S1 in Supporting Information).[9] Furthermore, in the case of $BMICF_3SO_3$, changes of weight and chemical structure were not observed after thermal treatment at 220 °C for 1 h, as evidenced by TGA and IR, respectively. Hence, $BMICF_3SO_3$ was mainly used as the IL component for the hybridization.
8 The completion of ring-opening polymerization of Ba was confirmed by DSC measurement. After curing at 220 °C for 1 h, pristine PBa and PBa/$BMICF_3SO_3$ hybrid films did not show an exothermic peak corresponding to the ring-opening polymerization.
9 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

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