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Viscoelasticity and fracture toughness of blended epoxy resins containing two monomers with different molecular weights

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Abstract In the present work, we investigated the thermo-viscoelasticity and fracture toughness of various cured blends of two epoxy monomers with different molecular weights: 380 (Epikote 828) and 900 (Epikote 1001). The blended resins were easily prepared, and miscibility (no phase separation) in the blended resins was expected. The composition of the blended epoxy resins ranged from 0 to 100% by weight of the Epikote 1001. The measured damping factor and dynamic loss modulus in the glass-transition confirmed that each blended resin had a single phase, i.e., they were miscible. The fracture toughness at room temperature increased modestly with the Epikote 1001 content over the whole range (0–100 wt%). We found that below the glass-transition temperature, the macromolecular modifications enabled tailoring of the fracture toughness while maintaining the glassy bending modulus and with little change in the glass-transition temperature.

Introduction

Epoxy resins now comprise one of the most important and largest materials groups in the industrial field. Initially used as adhesives and tooling and potting compounds, epoxy resins are now also extensively used in aeronautical, electronic, fusion reactor, automotive, and structural applications. However, these highly crosslinked systems are usually brittle.

Several methods have been developed for toughening epoxy resins. Incorporating rubber into the epoxy network is a commonly used method [1–3]. Second-phase dispersion of a rigid filler into the epoxy network can also be used to toughen epoxy resin [4–6]. For example, the addition of spherical silica particles (silica-particulate-filled epoxy composites) improves the fracture toughness of epoxy resins, accompanied by increases in strength, modulus, and thermal performance [7, 8].

Another approach is to use polymer blending. Polymer blends have become one of the most interesting means to obtain new materials with specific properties rather than synthesis of new polymer. Some properties can be combined by blending different polymers together and can even be improved compared to those of the individual components [9]. Blending with high-modulus and high-glass-transition-temperature thermoplastics at low contents can improve fracture toughness without sacrificing the mechanical properties of the epoxy resins [10–12]. Additionally, a polymer blend can consist of two different epoxy monomers. One advantage of such a blend is that solvent resistance is maintained due to the fully crosslinked epoxy mixture obtained after curing, which overcomes one of the weak points of modifications with rubbers or thermoplastics. Another advantage is related to the maintenance or even an increase in the small-strain mechanical properties of these dual-crosslinked networks [13]. Furthermore, blends of two epoxy monomers retain their original density, so they are lighter than epoxies reinforced by fillers. It is known that not all desirable properties, such as high toughness, high modulus, excellent adhesion, good solvent resistance, low density, and high thermal performance, can be obtained with any single method. Each method has specific advantages and disadvantages offering tailorability of material properties.

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The mechanical properties of the cured blend of two epoxy monomers are still scarcely obtained. Only a few investigations of these properties have been reported. Sawa et al. [14] investigated the fracture toughness of a cured blend of two epoxy monomers with different numbers of epoxy groups for cryogenic temperature application. They added diglycidil ether of bisphenol-A (DGEBA) to tetraglycidil meta-xylene diamine (TGMXDA) within the range of 0–100 wt%. Zubeldia et al. [13] investigated the fracture toughness of a cured blend of two epoxy monomers with different molecular weights. They added Rutapox 0199 (DGEBA with an epoxy-equivalent weight of 2,800 g/equiv, and an average molecular weight of 5,600) to DER 332 (DGEBA with an epoxy-equivalent weight of 175 g/equiv, and an average molecular weight of 350) at low contents (0–30 wt%). They found that an increase in fracture toughness is a result of two factors: phase separation and an increase in the overall molecular weight between crosslinks, which maintains and even increases the elastic modulus. The phase separation occurs through curing for monomers with molecular weights of 3,800 but not 1,800.

In the present work, we investigated cured blends of two epoxy monomers with different molecular weights: 380 and 900. Blended resins were easily prepared, and miscibility (no phase separation) in the blended resins was expected. Our objective was to investigate the effects of the macromolecular modifications on the mechanical properties of miscible blended epoxy resins, especially thermoviscoelasticity and fracture toughness. We previously investigated blended epoxy resins with low contents (0–30 wt%) of higher-molecular weight epoxy monomer [15]. Those resins were prepared and examined using dynamic mechanical thermal analysis, and fracture testing was done using the three-point bending mode. We have now extended our previous study by extending the content range up to 100 wt%.

Specimens

Materials

Two epoxy monomers with different molecular weights, Epikote 828 (JER 828) and Epikote 1001 (JER 1001), were obtained from Japan Epoxy Resins Co. Ltd. Both are produced from DGEBA and epichlorohydrin. Epikote 828 is a liquid epoxy with a viscosity of 13 Pa s at 298 K, an epoxy-equivalent weight of 190 g/equiv, and an average molecular weight of 380. Epikote 1001 is a solid epoxy with (a viscosity of 6×10^{-3} Pa s at 298 K, an epoxy-equivalent weight of 475 g/equiv, and an average molecular weight of 900.

The curing agent, methyl-tetrahydro-phthalic anhydride (HN-2200), was obtained from Hitachi Chemical Co. Ltd. The accelerator, 2,4,6-tris(dimethylaminomethyl) phenol (Daitocurar HD-Acc43), was obtained from Daito Sangyo Co. Ltd.

Preparation

Samples were made from mixtures of Epikote 828 and Epikote 1001 at weight ratios of 100/0, 95/5, 90/10, 80/20, 70/30, 50/50, 30/70, 10/90, 5/95, and 0/100. In this article, the symbol ϕ is used to represent the Epikote 1001 content by weight. Epikote 1001 was dissolved in Epikote 828 by heating at 383 K for 80 min, with continuous stirring in the last 10 min. The curing agent and accelerator, both heated to 383 K, were then added to the mixture in stoichiometric quantities by continuous stirring for 10 min at 383 K. The complete mixture was then degassed at 383 K in a vacuum oven.

After the degassing process, the complete mixture was poured into a preheated mold. The mold ($5 \times 200 \times 300$ mm^3) was made of an aluminum alloy coated with a Teflon sheet. The curing process for every complete mixture was carried out in two steps: precuring at 353 K for 3 h and postcuring at 443 K for 15 h. The mixture was then allowed to cool down naturally in the oven to room temperature. The specimens were machined from the cured plates to the size required for each test with a diamond saw.

Experiments

Dynamic mechanical thermal analysis

Dynamic mechanical thermal analysis (DMTA) was performed using a dynamic mechanical analyzer (Tritec 2000, Triton Technology Ltd.) operating in single-cantilever-bending mode. The test specimens were approximately 3.6 mm thick, 5.2 mm wide, and 30 mm long. Storage modulus, E', loss modulus, E'', and damping factor, tan δ, were recorded at each 0.5 K for a heating rate of 2 K/min from 273 to 453 K at a frequency of 1 Hz. Liquid nitrogen was used for precise temperature control. The span was set at 12.5 mm, and the amplitude of deflection was set at 15 μm.

Fracture toughness test

Three-point bending tests for measuring mode I fracture toughness were performed at room temperature using a universal testing machine (8501, Instron) in accordance with ASTM standard D5045–90. The specimens were rectangular bars, 90 mm long, 20 mm wide, and 5 mm thick. A slot-notch was cut in them with a saw, and a sharp crack was initiated with a razor blade. The slot-notch was 9 mm deep, and the sharp crack was approximately 1 mm deep. The crack length of each specimen was measured after testing by observing the fracture surface with an optical microscope. The span was set at 80 mm, and the deflection rate at the loading point was set at 2.0 μm/s.

Since the load–deformation curve of each specimen was linear until brittle breaking occurred, meaning that the stress field near the crack tip was small-scale yielding, we were able to apply linear elastic fracture mechanics to the experimental results to determine the fracture toughness. The critical-stress-intensity factor, K_{IC}, was determined using [16]

$$K_{IC} = \frac{SP_Q}{BW^{3/2}} f(\alpha), \tag{1}$$

where

$$f(\alpha) = \frac{3\alpha^{1/2}\left\{1.99 - \alpha(1-\alpha)(2.15 - 3.93\alpha + 2.7\alpha^2)\right\}}{2(1+2\alpha)(1-\alpha)^{3/2}}$$

and

$$\alpha = \frac{a}{W}.$$

The P_Q is the maximum load at fracture, and S, B, W, and a are the span length, thickness, width, and crack length of the specimen, respectively. The average value of K_{IC} for each blended epoxy resin was determined using at least six results.

Results and discussion

Damping factor

Figure 1 shows the damping factor, tan δ, of the samples measured from 273 to 453 K at a frequency of 1 Hz using the dynamic mechanical analyzer. All the samples had a single phase, i.e., they were miscible, because they had a single sharp peak of tan δ at the glass transition.

The glass-transition temperature, T_g, defined as the temperature at the maximum value of tan δ, is plotted in Fig. 2 for every blended resin. For neat Epikote 828, it was 401.3 K; for neat Epikote 1001, it was 395.6 K. As the content of Epikote 1001 in the blend, ϕ, was increased from 0 to 30 wt%, the glass-transition temperature dropped rapidly from 401.3 to 386.4 K. For ϕ from 30 to 70 wt%, the glass-transition temperature was approximately constant at about 387.0 K. With a further increase in ϕ, the glass-transition temperature gradually increased from 387.0 to 395.6 K.

Figure 3 plots the maximum value of tan δ for the blended epoxy resins. Those with ϕ from 30 to 70 wt% had higher maximum values of tan δ than neat Epikote 828 and neat Epikote 1001.

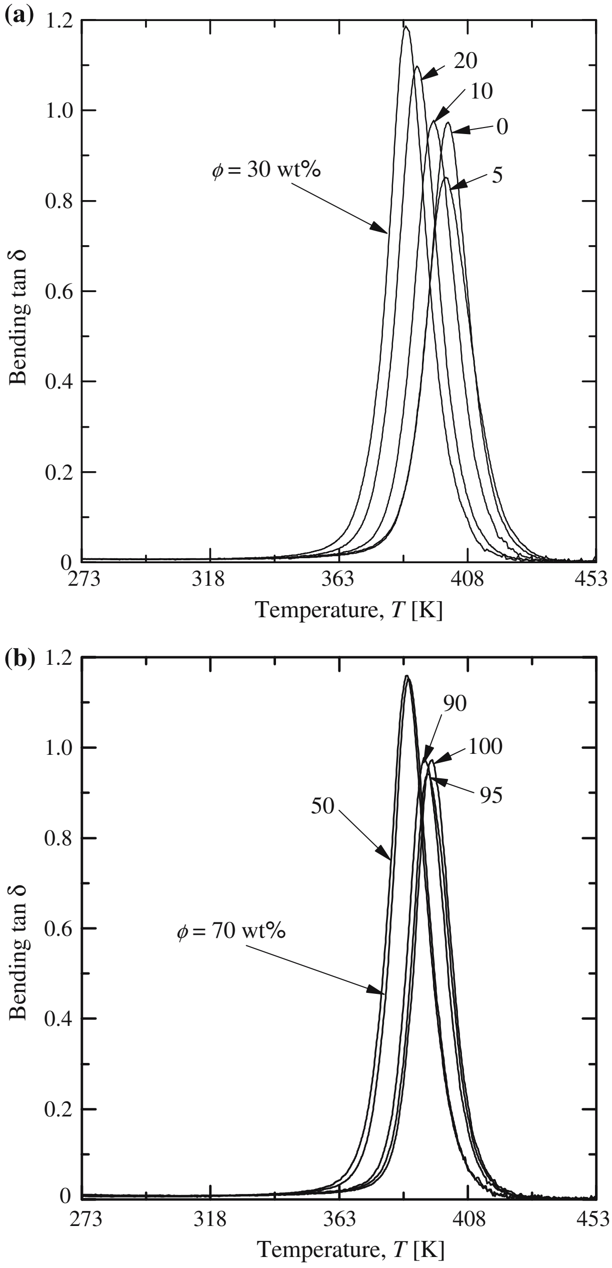

Fig. 1 Temperature dependence of damping factor for blended epoxy resins at 1 Hz: (**a**) 0 wt% ≤ ϕ ≤ 30 wt% and (**b**) 50 wt% ≤ ϕ ≤ 100 wt%

From this tan δ characterization, we obtain that the modified resins (blended resins with ϕ from 30 to 70 wt%) had lower glass-transition temperatures and higher maximum values of the damping factor compared with neat Epikote 828 and neat Epikote 1001. A decrease in the glass-transition temperature and an increase in the maximum value of the damping factor are indications of molecular mixing in blended epoxy resins [17–19]. It is

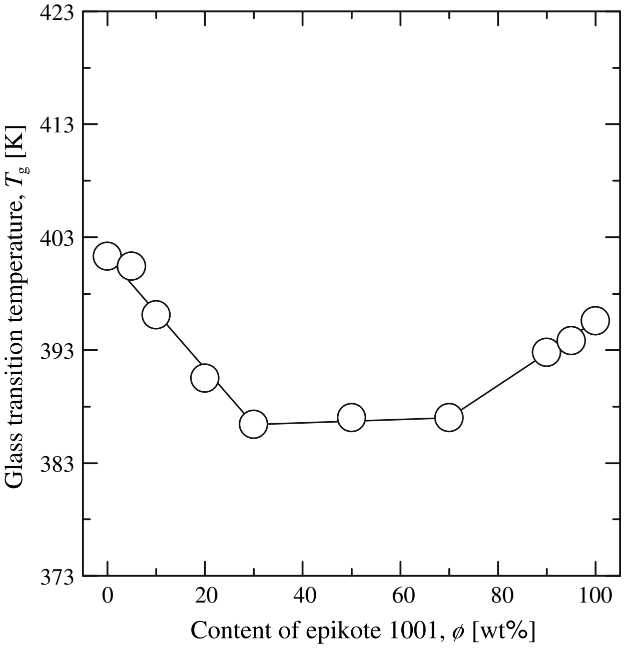

Fig. 2 Glass-transition temperature of blended epoxy resins

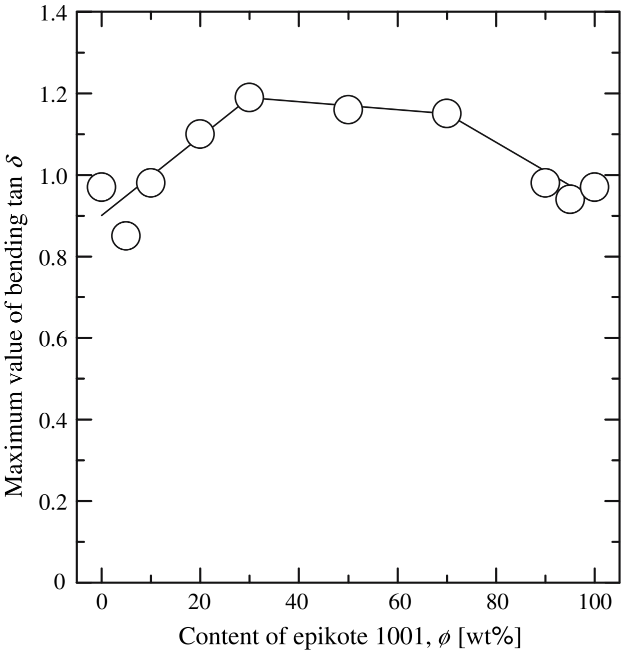

Fig. 3 Maximum value of damping factor for blended epoxy resins

possible that these blended resins had greater disorder or more free volume, which would lower the glass-transition temperature [20].

Storage and loss moduli

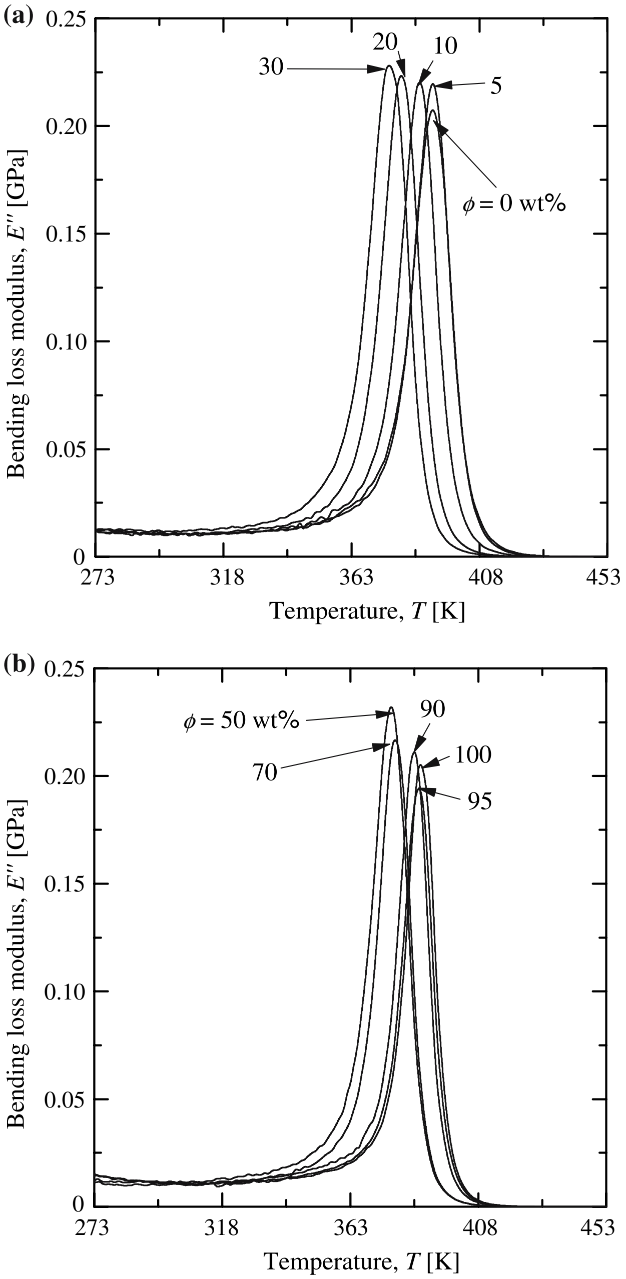

Fig. 4 Temperature dependence of dynamic loss modulus for blended epoxy resins at 1 Hz: (**a**) 0 wt% $\le \phi \le$ 30 wt% and (**b**) 50 wt% $\le \phi \le$ 100 wt%

The temperature dependence of the bending loss moduli, E'', at 1 Hz for the blended epoxy resins is shown in Fig. 4. It can be observed clearly that each blended epoxy resin exhibited a single distinct peak of loss modulus. Furthermore, the modified Epikote 828 and 1001 blends exhibited peak values of loss moduli at lower temperatures than both neat Epikote 828 and neat Epikote 1001. These results are consistent with those for tan δ.

Figure 5 plots the temperature dependence of the bending storage moduli, E', at 1 Hz for the blended epoxy resins. The storage moduli of the resins in the glassy region (298 K) and rubbery region (453 K) demonstrated different

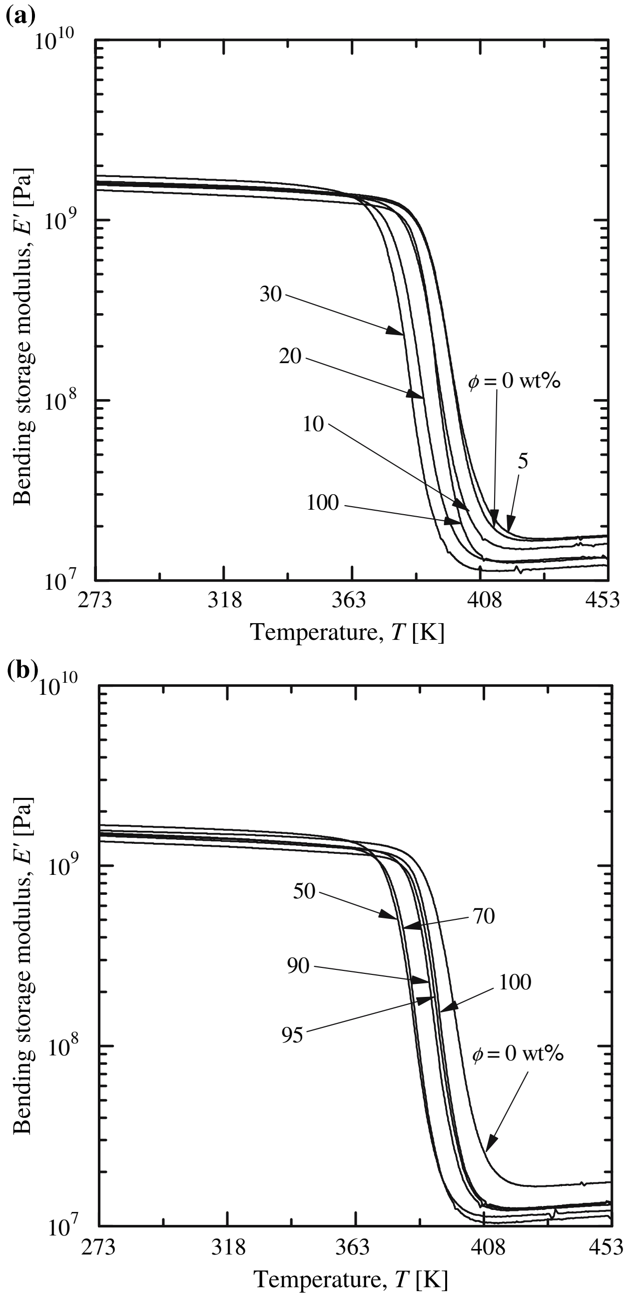

Fig. 5 Temperature dependence of dynamic storage modulus for blended epoxy resins at 1 Hz: (**a**) 0 wt% $\le \phi \le$ 30 wt% and (**b**) 50 wt% $\le \phi \le$ 100 wt%

trends, as shown in Fig. 6. The variation in the storage moduli in the glassy region ranged from 1.3 to 1.7 GPa, while the blend with ϕ of 30 wt% showed the highest modulus. In the rubbery region, the storage modulus dropped rapidly from 17.5 to 12.0 MPa as ϕ was increased from 0 to 30 wt%. An increase in ϕ from 30 to 70 wt% caused a slight decrease, from 12.0 to 10.8 MPa. The storage modulus then gradually increased from 10.8 to 13 MPa as ϕ was increased from 70 to 100 wt%. As reported by Ogata et al. [21], these different trends for the storage moduli in glassy and rubbery regions can be explained by the fractional free volume.

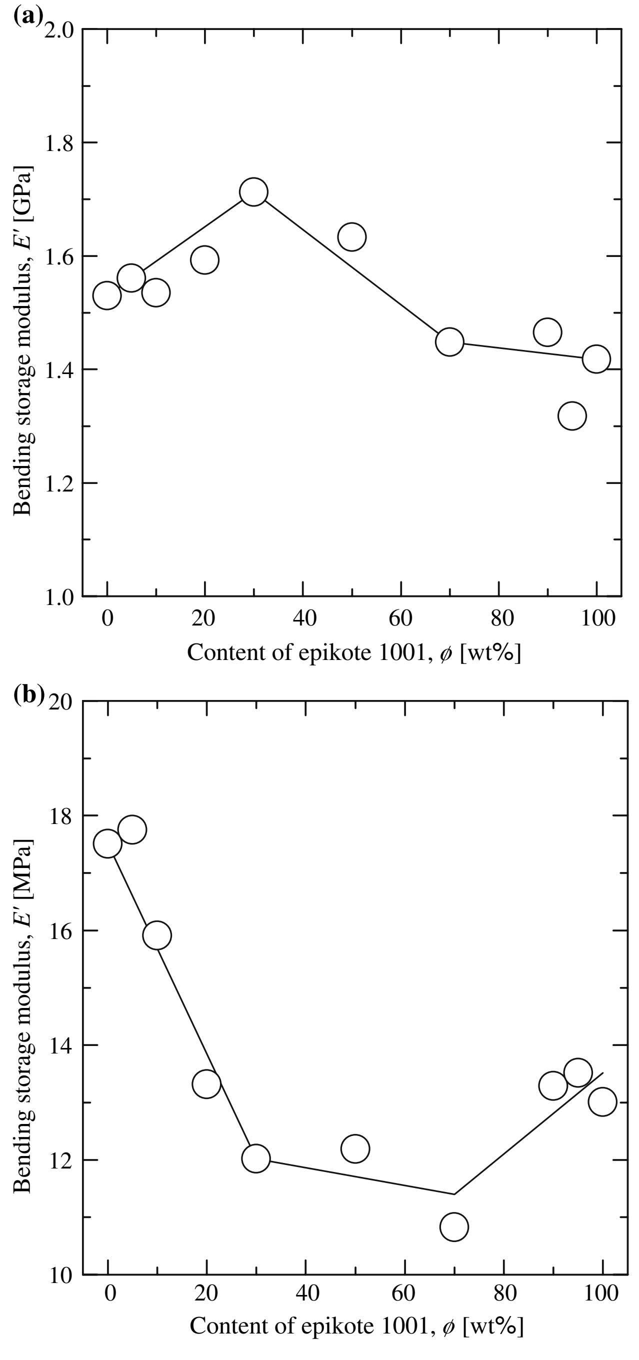

Fig. 6 Storage modulus of blended epoxy resins at 1 Hz: (**a**) 298 K (glassy region) and (**b**) 453 K (rubbery region)

Fracture toughness

The fracture toughness, K_{IC}, at room temperature for each specimen is shown in Fig. 7. The error bars indicate the standard deviation. The K_{IC} for the neat Epikote 828 was

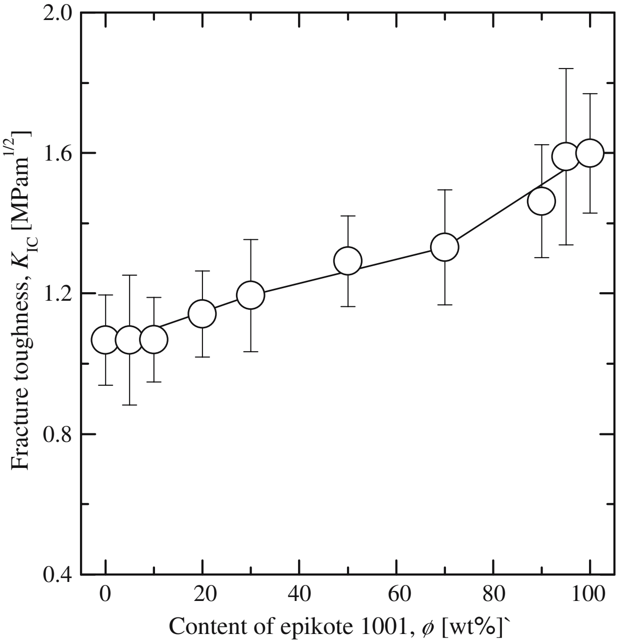

Fig. 7 Fracture toughness of blended epoxy resins at 298 K

1.06 MPam$^{1/2}$, which is typical of a brittle thermosetting polymer [22, 23]. This value is lower than the 1.59 MPam$^{1/2}$ of the neat Epikote 1001. This agrees well with the results of Pearson and Yee [24] who found that epoxy resin cured from a high molecular weight monomer has higher toughness than that cured from a low molecular weight monomer. Figure 7 also shows that the K_{IC} increased with the content of Epikote 1001 over the whole content range (0–100 wt% Epikote 1001). On the contrary, it was reported that toughening is not expected in miscible systems [25, 26].

Tailoring mechanical properties

The effects of the compositions of the blended resins on fracture toughness and thermo-viscoelastic properties are summarized in Fig. 8. The values of the properties were normalized by the mechanical property of the unmodified Epikote 828 resin ($\phi = 0$ wt%). The normalized glass-transition temperature was calculated using K/K as the unit.

Fig. 8 Normalized properties of blended epoxy resins: (**a**) fracture toughness; (**b**) dynamic storage modulus; and (**c**) glass-transition temperature

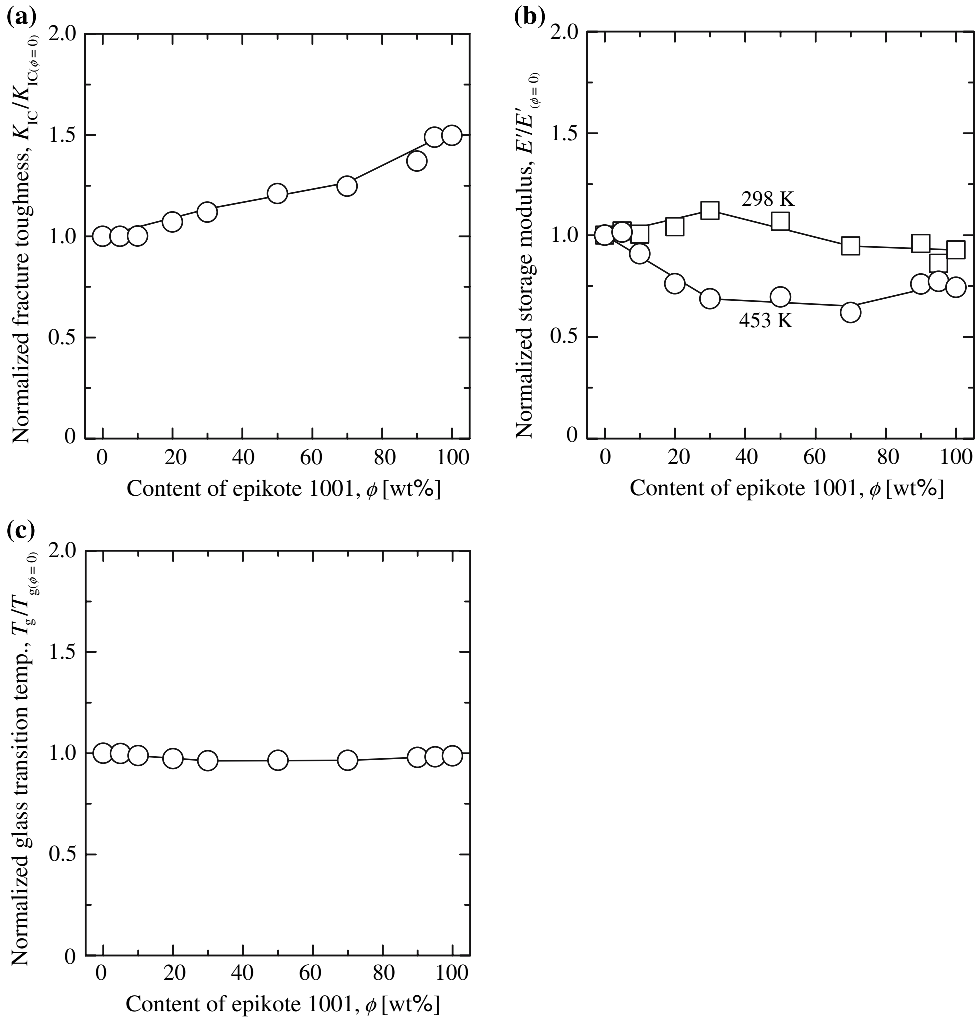

Figure 8 shows that adding Epikote 1001 up to 30 wt% increased the fracture toughness about 12%, increased the glassy bending modulus about 12%, reduced the rubbery bending modulus about 31%, and reduced the glass-transition temperature about 4%. When the Epikote 1001 content was increased to 50 wt%, the fracture toughness increase was about 21% while the glassy bending modulus was maintained. The fracture toughness increase reached 50% when the Epikote 1001 content was increased from 50 to 100 wt%. This further increase in fracture toughness was accompanied by a decrease in the glassy bending modulus of about 7%, a decrease in the rubbery bending modulus of about 26%, and a decrease in glass-transition temperature of about 1%.

As mentioned above, these macromolecular modifications enable independent tailoring of the fracture toughness while maintaining the glassy bending modulus and with little change in the glass-transition temperature. Although the rubbery bending modulus decreased by as much as 38%, this would not affect the use of epoxy resin in applications. This is because the use of epoxy resins in applications is usually below their glass-transition temperatures, which are little changed, so there is no need to consider the rubbery modulus. Furthermore, this blending provides other benefits such as maintaining good solvent resistance, which overcomes one of the weak points of modification with rubbers or thermoplastics, and also maintaining the density thus lighter than particulate-filled epoxy composites.

Conclusion

The effects of macromolecular modifications on the mechanical properties of blended epoxy resins, especially their thermo-viscoelasticity and fracture toughness, were investigated. The results for the damping factor and dynamic loss modulus in the glass-transition showed that every blended epoxy resin had a single phase, i.e., they were miscible. The fracture toughness at room temperature increased modestly with the Epikote 1001 content over the whole range (0–100 wt%). We found that below the glass-transition temperature, the macromolecular modifications enabled tailoring of the fracture toughness while maintaining the glassy bending modulus and with little change in the glass-transition temperature.

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