Polysiloxane Modified Epoxy Networks. IV. Catalytic Effect on Fracture Behaviors of Jointed Interpenetrating Polymer Networks

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ABSTRACT: Jointed interpenetrating polymer networks of epoxy resin and poly(dimethylsiloxane) (PDMS) are synthesized using PDMS-α,ω-diol as the reactive modifier. We attempt to control the reaction rate and the morphology of the rubber domains by using the acid as the catalyst. According to the scanning electron microscopy results, the morphologies of the acid catalyzed specimens do not show strain-induced crystallization during the fracture mode due to the homogeneity of the molecule structure. The tensile strengths and moduli decrease when the reaction rate is increased. However, the acid contents have no effect on the fracture energy. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2352–2357, 2002

Key words: poly(dimethylsiloxane); epoxy; toughness; acid catalyst; interpenetrating polymer network

INTRODUCTION

Epoxy resins are one of the most important engineering polymeric materials that possess high elastic moduli and high glass-transition temperatures. However, their low crack growth resistance further restricts applications. Much work has been carried out to modify the epoxy structure in order to improve its fracture toughness, flexibility, impact strength, and mechanical properties. The most successful modification thus far has been achieved by introducing reactive carboxyl-terminated butadiene acrylonitrile copolymer (i.e., the rubber domain) into the epoxy matrix.[1,2]

It is known that the toughness and flexibility of the modified epoxy largely depend on the elastomer structures, the contents of the elastomer in the epoxy matrix, and the morphology of the phase separation.[3–7] It is also believed that formation of the plastic zone during crack growth is the major contribution to the fracture toughness. However, without an appropriate rubber domain the toughening effect is usually not observed.

In our previous study[8] we synthesized a series of jointed interpenetrating polymer networks (jointed-IPNs) by incorporating reactive poly(dimethylsiloxane) (PDMS)-α,ω-diol into the epoxy system. Although there were no rubber domains appearing in the system, the experimental results showed significant improvement of the fracture energy. We also observed a very special strain-induced crystallization pattern in the fracture mode. Unfortunately, the toughening mechanism was not very clear.

Table I   Formulation of Jointed IPN

Sample	Epoxy	SF-8427	MDA	Capric Acid	TDI	T-12	Dehydran-1208
SF-40	100	40	26.2	—	6.43	0.04	5.18
CAP-1	100	40	26.2	2.62	6.43	0.04	5.26
CAP-2	100	40	26.2	5.24	6.43	0.04	5.34
CAP-3	100	40	26.2	7.86	6.43	0.04	5.42
CAP-4	100	40	26.2	10.48	6.43	0.04	5.50

All values are in parts per hundred parts of epoxy resin.

Herein we attempted to control the morphology of the jointed-IPN by changing the reaction rate. We are convinced that the siloxane modifier can cause phase separation within an epoxy matrix because of thermodynamic incompatibility and a large difference in the solubility parameters. However, increasing the reaction rate should cause the siloxane modifier to have less chance of precipitating during the curing process. The resulting materials were examined by dynamic mechanical analysis (DMA), tensile tests, and fracture toughness tests. The morphologies of the materials are also evaluated.

EXPERIMENTAL

Materials and Synthesis

The epoxy resin used in this study was the diglycidyl ether of bisphenol A (DGEBA, Epon 828) with an equivalent weight of 187 g mol^{-1}. The bifunctional modifier PDMS {HO—(CH$_2$)$_n$—[Si(CH$_3$)$_2$O]$_m$—(CH$_2$)$_n$—OH} was employed and purchased from Dow Chemical Company (SF-8427). The molecular weight was determined using a Waters M-410 GPC, which was calibrated with standard polystyrene. The resulting value of the number-average molecular weight was 2130 g mol^{-1}. By comparing the NMR results we were able to identify the structure of this polymer with n,m values of 32 and 17, respectively. The epoxy resin and modifiers were dried at 100°C under a vacuum for 8 h before use. The chain extender tolylene-2,4-diisocyanate (TDI, Aldrich) and hardener 4,4′-methylene dianiline (MDA, R.D.H.) were used as received.

In order to synthesize the isocyanate-terminated epoxy/siloxane graft copolymer, fixed amounts of TDI and tin catalyst (di-n-butyltin dilaurate, T-12) were added to the DGEBA (NCO/OH = 2). The temperature was maintained at 35°C for 5 h under nitrogen to allow the ure-

thane reaction between TDI and the secondary hydroxyl group of DGEBA to occur (monitored by FTIR). Then 40% polysiloxane modifiers (parts per hundred parts of epoxy) were mixed with this mixture at 65°C for 12 h to ensure complete reaction. The procedures for this are described in detail elsewhere.[8] To synthesize the jointed interpenetrating siloxane/epoxy networks, fixed amounts of MDA were melted at 120°C and mixed with the graft copolymer and 3 wt % silicon antifoaming agent (Dehydran 1208, Henkel). After degassing for 10 min, the mixture was poured into a hot mold (120°C) and precured for 2 h, and subsequent step curing was performed at 160°C for another 3 h. This specimen was designated SF-40. In order to increase the reaction rate, various amounts of capric acid were also added to the SF-40 mixtures before curing, which were termed the CAP system.

The basic formulations for the jointed-IPNs are listed in Table I.

Testing Methods

The measurements of the mechanical properties were conducted on a universal testing machine (Hung Ta Instrument Co., Taiwan). The tensile strengths were measured according to ASTM D 638 with a crosshead speed of 5 cm/min. The fracture energy (G_{IC}) was measured by using a compact tension specimen.[8,9]

The dynamic mechanical properties were measured on a DMA instrument (Perkin–Elmer DMA-7e). These measurements were carried out in a temperature range of −150 to 250°C at a heating rate of 10°C/min and a frequency of 1 Hz. The morphology of the samples was examined by scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

As described in our previous article,[8] the SF-40 specimen showed an unusual strain-induced crys-
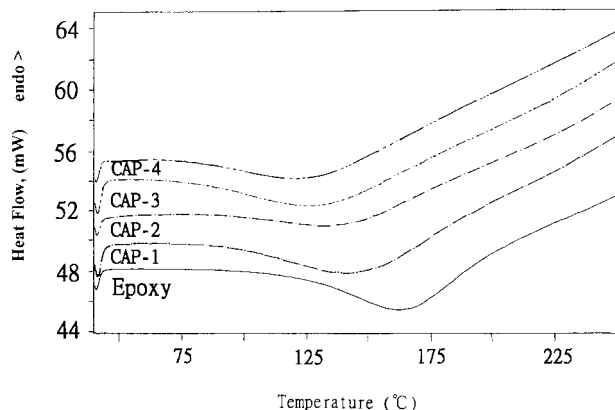
Figure 1 DSC curves of the reaction exotherms of epoxy resins with MDA and various amounts of capric acid.

Figure 2 DSC curves of the reaction exotherms of epoxy resins with different addition sequences of MDA and capric acid.

tallization in the fracture mode. We also concluded that the crystallization was formed by the orientation of the long polyolefin chain of the siloxane modifier during slow rate deformation. The purpose of this work is to further prove the above-mentioned mechanism. Addition of acid catalyst to the amine cured epoxy systems has three major effects. First, increasing the reaction rate might decrease the possibility of phase separation, which might also restrict the aggregation of the long polyolefin chain of the siloxane modifier. Second, the homogeneity of the jointed-IPN structures might decrease the mechanical properties slightly. Third, the fracture energy of the specimens might decrease according to the catalyst contents because of the degree of phase domain restriction.

The exotherms in the differential scanning calorimetry (DSC) traces showed that the reaction temperature decreased from 170 to 125°C according to the acid contents (Fig. 1). It is interesting to note that the addition sequence of the acid catalyst and amine curing agent may significantly influence the reaction rate. As seen in Figure 2, adding acid prior to the amine curing agent further decreased the maximum reaction exotherm temperature to 110°C. Its pot life is reduced to about 2 min, which is too short for the processing. The reason for this difference is that, while adding acid prior to the amine curing agent, the acidic accelerators donate a hydrogen atom to the oxygen on the epoxy ring, causing the ring opening. The terminal carbon atom then exhibits a slight charge, which is readily attacked by the electron pair of the primary or secondary amines. The mechanism is illustrated in Scheme 1. How-
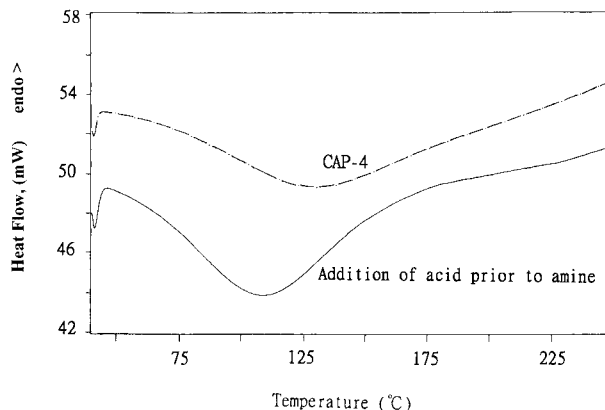
ever, if the acid was added in the base circumstance, part of the amine curing agent would transform to an ammonium salt, which might decrease the reaction rate.

The effects of a variation in the acid/amine ratio on the tensile strength and modulus are illustrated in Figure 3 and listed in Table II. The maximum tensile strength decreased slightly according to the acid contents. This result may possibly occur because the monofunctional capric acid served as a plasticizer that may increase the flexibility of the epoxy main chain in the higher deformation. Although the modulus of the CAP systems also decreased according to the acid contents, the systems show higher modulus than the SF-40 specimen. This result indicates that the increasing of the reaction rate due to the inclusion of the acid might decrease the phase separation; the structure is therefore more compact. However, increasing the reaction rate also inhibited the alignment of the epoxy main chains; the modulus was therefore decreased as the acid increased.

The G_{IC} measurements were conducted on the compact-tension specimen ($40 \times 20 \times 10$ mm
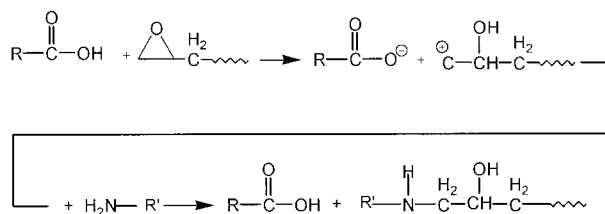
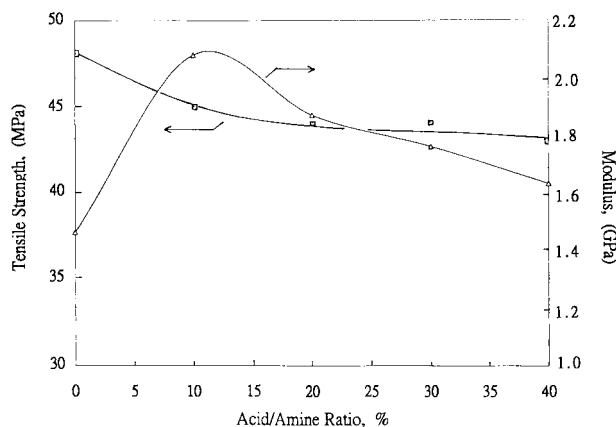**Scheme 1** The reaction of epoxy and amine with acid as the catalyst.

Figure 3 The tensile strength and modulus versus the acid/amine ratio plots for the polysiloxane modified epoxy networks.

Figure 4 The fracture energy versus the acid/amine ratio plots for the CAP system.

dimensions). A precrack initiated by a razor blade before the test is a critical step in these fracture measurements. These slow strain rate fractures were tested at a crosshead speed of 0.5 cm/min. The magnitude of the G_{IC} was calculated by the following equation[9]:

$$G_{IC} = [Y^2(a/w) \times P^2 \times a]/(E \times W^2 \times b^2) \quad (1)$$

where

$$Y(a/w) = 29.6 - 186(a/w) + 656(a/w)^2$$
$$- 1017(a/w)^3 + 639(a/w)^4$$

and a, b, w, and E are the crack length, thickness, and width, and the Young's modulus of the specimen, respectively; and P is the force required to fracture the sample. A more accurate value of a could be obtained by a modified method that was described elsewhere.[8] Variations in the fracture energy of siloxane modified epoxy resins with dif-
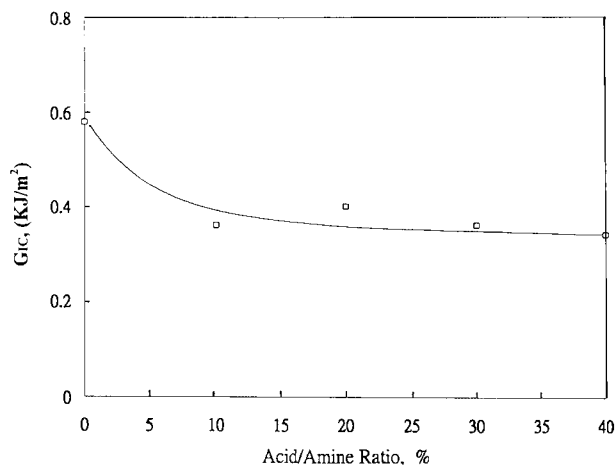
ferent acid/amine ratios are plotted in Figure 4 and listed in column 4 of Table II. All the jointed-IPN samples are clear and transparent. In the rubber and rigid particulate plastic filler toughening mechanism it is believed that appropriate separated domains make a major contribution to the improvement in the fracture energy. However, without any rubber domains, the fracture energy of the SF-40 specimen showed a significant improvement of the fracture energy of up to 250%. We concluded that *in situ* crystallization that formed during strain played a major role in the toughening effect.[8] The SEM details of this stress-whitened region [Fig. 5(a)] show that the white spots are composed of tree leaf type crystals.

In contrast to the SF-40, the CAP specimens show no strain-induced crystallization region in the fracture surface [Fig. 5(b)]. Actually, there was no rubber domain found in CAP systems. By increasing the reaction rate, the aggregation of

Table II   Mechanical and Thermal Properties of Jointed IPN

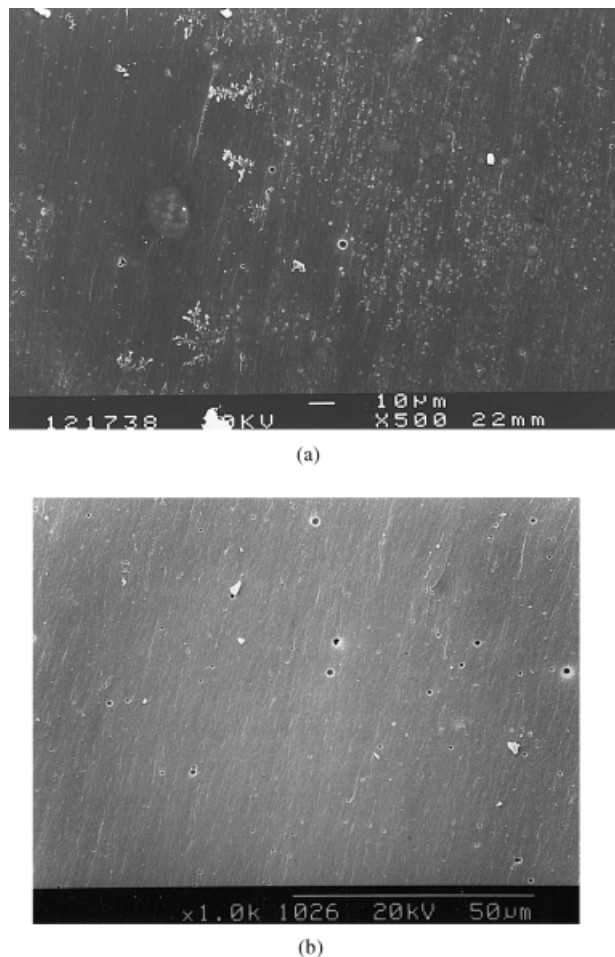| Sample	Max. Stress (MPa)	Modulus (GPa)	Fracture Energy (kJ/m²)	T_g (°C)			Plastic Zone 2γ (μm)
				T_g(I)	T_g(II)	T_g(III)	
Epoxy	77	2.35	0.17	167	−75	—	8.3
SF-40	48	1.46	0.58	150	−78	—	46.1
CAP-1	45	2.08	0.36	156	−74	—	46.2
CAP-2	44	1.87	0.40	141	−77	—	47.7
CAP-3	44	1.76	0.36	141	−78	−144	41.7
CAP-4	43	1.63	0.34	136	−83	−145	36.6

Figure 5 SEM micrographs of (a) SF-40 and (b) CAP-4.

the modifier would be further inhibited by the epoxy main chains. Therefore, the polyolefin chain has less chance to crystallize during deformation. Because there is no rubber domain observed (or the rubber domain is extremely small), we therefore believed that the CAP system should have no toughening effect. It is surprising to find that the acid content has no effect on the fracture energy and the values remained about 62% of the controlled specimen (SF-40, Fig. 4). This value is about twice as the pure epoxy network.

Although the specimens showed no appropriate rubber domain, the fracture toughness still improved slightly. This is in contrast to the conventional toughening mechanism. Bascom et al.[10] and Pearson and Yee[11,12] proposed that the cavitation and plastic shear yielding of the matrix in front of the crack tip play the most important role in the energy dissipation. In 1993 Lozzeri and Bucknall[13] proposed that when the size of the

rubber particle is smaller than 0.25 μm, it will show no toughening effect. Because there is no visual rubber domain seen in our systems by SEM measurement, the cavitation mechanism should only have a minor effect. The theoretical plane strain plastic zone size can be calculated by the Irwin equation[14]:

$$2\gamma = (2/6\pi)(K_{IC}/\sigma_y)^2 \qquad (2)$$

where K_{IC} is the critical stress intensity factor and σ_y is the yield stress of the specimen. Because the G_{IC} values are obtained from compact tension specimens in this study, the K_{IC} values can be calculated using the following equation:

$$G_{IC} = (1 - \nu^2)K_{IC}^2/E \qquad (3)$$

where E is the Young's modulus and ν is Poisson's coefficient. The ν value is taken as 0.35 for epoxy resins.[10] The predicted plastic zone sizes are listed in column 8 of Table II. All values are significantly higher than that of the pure epoxy resin. In comparing the calculated plastic zone results, we are able to conclude that the partial phase separation and large plastic shear yielding are essential to the enhancement of the fracture energy.

The tan δ versus temperature plot is presented in Figure 6 and the corresponding glass-transition temperature (T_g) values are listed in columns 5–7 of Table II. For pure DGEBA, the high T_g [T_g(I)] and low T_g [T_g(II)] appear at 167 and $-75°C$, respectively. An extension to the dynamic mechanical plots of epoxy cured with MDA was made by Murayama and Beli, who noted that the low-temperature transition was related to the
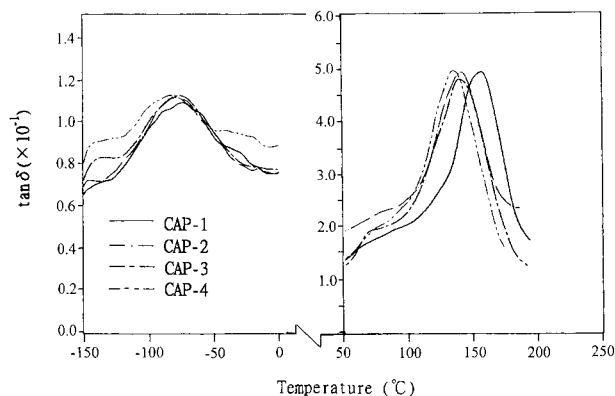

Figure 6 The tan δ versus temperature plots for the CAP system.

diglycidyl ether portion of the molecule and the high-temperature transition was influenced by substituents on the central carbon bridge of the bisphenol portion of the molecule.[15] Because the phase separation of the modifier in the epoxy matrix is further restricted with an increase in the reaction rate, the T_g(I) and T_g(II) values of the CAP systems continuously shifted to lower temperature with an increase in the acid content. PDMS main chains show a damping peak at around $-145\ °C$ [T_g(III)]. A shoulder instead of a sharp damping peak was observed in the CAP systems. Both results indicate the partial compatibility between the epoxy resin and the siloxane main chain. This result is in agreement with the SEM and fracture energy results.

CONCLUSION

The effects of varying the morphologies of siloxane modified epoxy resins by changing the reaction rate via addition of acid catalyst were discussed. The following conclusions were made:

1. Adding acid as a catalyst would further inhibit the aggregation of the modifier by increasing the curing rate. The tensile strengths wer decreased due to the plasticizer effect of the monofunctional capric acid. The moduli increased compared to the one without acid catalyst because of the homogeneity of the chemical structure.
2. In contrast to the one without acid as the catalyst, the specimens showed no strain-induced crystallization region in the fracture surface.
3. The contents of the acid catalyst have no effect on the fracture energy.

4. The cavitation of the rubber domain on the siloxane modified epoxy resin makes a minor contribution to the fracture toughness.

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