

Polysiloxane modified epoxy networks (III) strain-induced crystallization of jointed interpenetrating polymer networks in fracture mode

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Jointed interpenetrating polymer networks (jointed-IPN) of epoxy resin and polydimethylsiloxane (PDMS) were synthesized using polydimethylsiloxane- α,ω -diol as the reactive modifier. Since this modifier is fully compatible with the epoxy resins, no phase separation (rubber domain) occurred in the final cured samples. The tree-leaf-type crystals, due to the strain-induced crystallization, were observed in both tensile as well as fracture samples. Although there is no appropriate rubber domain, the experimental results indicate that strain-induced crystallization and the crosslinking density effects of PDMS modified epoxy resins could improve the fracture energy significantly. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polydimethylsiloxane; strain-induced crystallization; epoxy)

INTRODUCTION

Epoxy resins are important engineering polymeric materials that possessing high elastic moduli and glass transition temperatures. Many papers have been carried out to modify the epoxy structure, in order to improve its fracture toughness, flexibility, impact strength and mechanical properties. So far, the most successful modification has been achieved by introducing reactive carboxyl-terminated butadiene acrylonitrile copolymer (CTBN) 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 phase separation^{3–7}.

Polymeric blends of epoxy resins and polysiloxane usually exhibit two separate T_g values due to their thermodynamic incompatibility. However, owing to its superior flexibility and thermal stability, polysiloxane is always regarded as one of the best candidates to modify the mechanical properties of the epoxy resins. Several methods such as functional group capped polysiloxane⁸, polysiloxane block copolymer⁹, and graft interpenetrating polymer networks (graft-IPN)¹⁰ have been proposed to improve the compatibility. However, the positive free energy of the polymer pair results in a significant phase separation, prior to the network formation. In our previous studies, we observed that incorporation a third component (viz. Polypropylene glycol) into the polysiloxane–epoxy graft-IPN system, by varying the polysiloxane–polyurethane ratio, can improve the phase separation significantly¹¹.

In the present study, we attempted to graft the epoxy resin matrix using different molecular weights of polydimethylsiloxane- α,ω -diol as the reactive reagents. The

graft copolymers were then crosslinked with MDA (4,4'-methylene dianiline). The resulting materials were examined by dynamic mechanical analysis and scanning electron microscopy. The fracture behaviours and mechanical properties are also investigated.

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 modifiers, viz. polydimethylsiloxane- α,ω -diol, HO-(CH₂)_n-[Si(CH₃)₂O]_m-(CH₂)_n-OH, employed were two samples purchased from Dow Chemical Company, designated as BY-16005 and SF-8427, respectively. The molecular weights of these samples were determined using a Waters M-410 GPC, calibrated with standard polystyrene. All measurements were carried out at 30°C with THF as eluent. The resulting values of M_n were 1100 and 2130 g mol⁻¹, respectively. By comparing the NMR results, we were able to identify the structure of these two polymers, with n values of 7, 32 and m values of 12, 17, respectively. The epoxy resin and modifiers were dried at 100°C under vacuum for 8 h before the measurements. The chain extender TDI (Toluylene-2,4-diisocyanate, Aldrich) and hardner MDA (R.D.H.) were used as received.

To prepare graft copolymers, fixed amounts of TDI and Tin catalyst (T-12) were added to DGEBA (NCO/OH = 2). The temperature was maintained at 35°C for 5 h under nitrogen, to allow the urethane reaction between TDI and secondary hydroxyl group of DGEBA to occur. Varying amount of polysiloxane modifier was then mixed with this mixture at 65°C for 12 h to ensure complete reaction. Since excess amounts of TDI was used, the unreacted NCO groups

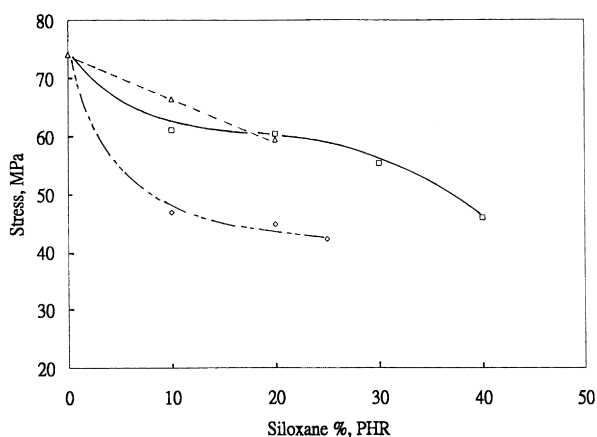
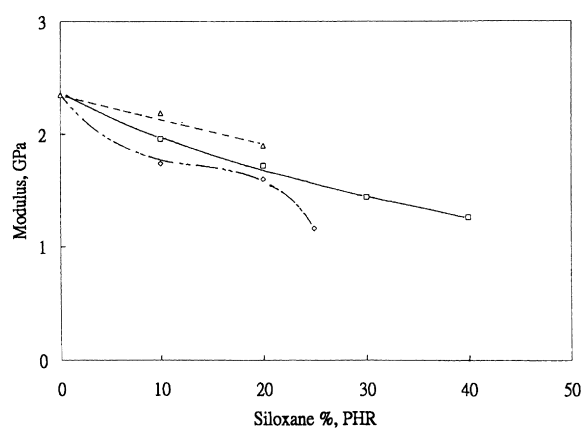
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Table 1 Formulation of joint IPN

Sample	Epoxy	SF-8427	BY-16005	MDA	T-12	TDI	Dehydran-1208
A	100	—	—	26.2	—	—	3.79
B-10	100	10	—	26.2	—	—	4.09
B-20	100	20	—	26.2	—	—	4.39
SF-10	100	10	—	26.2	0.010	6.43	4.28
SF-20	100	20	—	26.2	0.020	6.43	4.58
SF-30	100	30	—	26.2	0.030	6.43	4.88
SF-40	100	40	—	26.2	0.040	6.43	5.18
BY-10	100	—	10	26.2	0.010	6.43	4.28
BY-20	100	—	20	26.2	0.020	6.43	4.58
BY-25	100	—	25	26.2	0.025	6.43	4.73

Table 2 Mechanical and thermal properties of jointed-IPNs

Sample	Max. stress (MPa)	Modulus (GPa)	Fracture energy (KJ m ⁻²)	T _g (°C)		
				T _g (I)	T _g (II)	T _g (III)
A	74.0	2.35	0.17	167	- 67	—
B-10	66.4	2.19	0.20	128	- 79	- 125
B-20	59.5	1.90	0.21	151	- 83	- 127
SF-10	61.1	1.96	0.30	162	- 80	- 125
SF-20	60.5	1.72	0.34	157	- 78	- 130
SF-30	55.4	1.44	0.46	149	- 78	- 132
SF-40	45.9	1.26	0.58	151	- 78	—
BY-10	46.8	1.74	0.25	167	- 67	- 130
BY-20	44.8	1.60	0.36	167	- 77	- 133
BY-25	42.2	1.16	0.27	163	- 81	- 126

**Figure 1** Tensile strength versus modifier-epoxy ratio plots for: polyblend (Δ); SF-8427 jointed-IPN (\square); and BY-16005 jointed-IPN (\diamond)**Figure 2** Modulus versus modifier-epoxy ratio plots for: polyblend (Δ); SF-8427 jointed-IPN (\square); and BY-16005 jointed-IPN (\diamond)

remaining in the mixture were expected to react with MDA. Therefore, the mixture was first reacted with dry ethanol, before MDA was added.

To synthesize the jointed interpenetrating siloxane/epoxy networks, various amounts of MDA were melted at 120°C, and mixed with the graft copolymer and 3 wt% of silicon antifoaming agent (Dehydran 1208, Henkel, Germany). After degassing for 10 min, the mixture was poured into a hot mould (120°C) and cured for 2 h, with subsequent step-curing at 160°C for another 3 h. The basic formulations for jointed-IPN networks are listed in Table 1, in terms of parts per hundred parts of epoxy resin (PHR).

For comparison, polyblends of epoxy resin and SF-8427

were also prepared by mixing the epoxy resin, modifier and MDA together and curing under identical conditions. These specimen showed excellent compatibility at any ratio before curing. However, significant phase separation (modifiers floating on the surface of the samples) was observed for the modifier-epoxy ratio larger than 0.2 in the final cured stage, due to the thermodynamic incompatibility. The formulations of these polyblends are also listed in Table 1.

Testing methods

Measurements of all the mechanical properties were conducted on a universal testing machine (Hung Ta

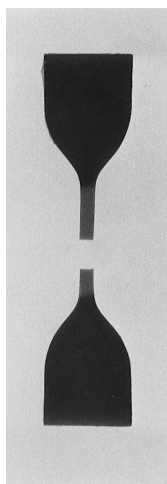


Figure 3 Stress-whitened zone of SF-40 specimens in tensile mode

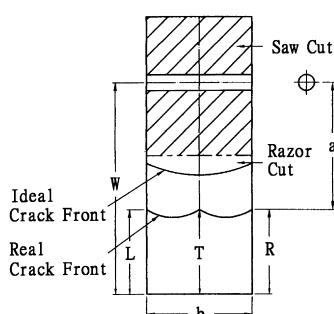


Figure 4 Fracture surface of compact tension specimens

Instrument Co., Taiwan). The tensile strengths were measured according to ASTM D-638 with a crosshead speed of 5 cm min^{-1} . The fracture energy G_{IC} was measured by using compact tension specimen.

The dynamic mechanical properties were measured on a Dynamic Mechanical analyzer (Perkin-Elmer DMA-7e). These measurements were carried out in the temperature range of -150 – 250°C , with a heating rate of $10^\circ\text{C min}^{-1}$ and frequency of 1 Hz . The morphology of the samples was examined by scanning electron microscopy.

RESULTS AND DISCUSSION

Since the polydimethylsiloxane- α,ω -diol contains two reactive -COH groups on its both ends, it is frequently used as the siloxane modifier in the aliphatic and aromatic polymeric systems^{12,13}. However, these polymers usually contain $-(\text{CH}_2)_3\text{OH}$ attached to the polysiloxane main-chain, which have only limited compatibility with the conventional polymers. The resulting modified samples are therefore translucent or opaque. The compatibility between silicone modifier and polymers can be significantly improved by increasing the length of chain [i.e. $(\text{CH}_2)_n$]. The modifier BY-16005 has n value of 7, and is compatible with the epoxy resin below the siloxane-epoxy ratio (w/w) of less than 0.3. As for SF-8427, it has n value of 32, and is, therefore, fully compatible with the epoxy resins in any ratio. The cured jointed-IPN specimens were clear and transparent. However, the cured polyblends are opaque. The effects of variation in the siloxane ratio on tensile strength and modulus are illustrated in Figures 1 and 2, and also

listed in Table 2. The siloxane structures are more flexible than those of epoxy main-chains. Therefore, the modulus and tensile strength progressively decrease with increasing contents of the siloxane modifiers. With the same volume content of modifier, the BY-16005 system exhibits lower stress and modulus than the SF-8427 system, due to the higher percentage of siloxane contents in the structure. It is interesting to note that in the SF-8427 systems, with siloxane contents around 40%, a very significant stress-whitened zone in the necked region was observed before breaking the specimen, as can be seen in Figure 3. Pearson and Yee also observed a similar phenomena in CTBN modified epoxy resin¹⁴. They suggested that cavitation of the separated rubber domains during the increase in hydrostatic tensile component of stress contributes to stress-whitening. However, no rubber domains are present in the jointed-IPN systems. Therefore, cavitation effect should not be responsible for the observed stress-whitening. Evidence for the possible reason will be presented from the SEM micrographs, latter in this paper. Since the cured epoxy resins possess rigid and highly crosslinked structure, it is impossible for the epoxy main-chain to significantly orient along the stretching direction, with such a small deformation (around 6%). As has been mentioned previously, the siloxane modifiers are the triblock copolymers of polyolefin and PDMS. Wherein PDMS has three distinctive transition regions (-38 , -68 and -120°C) which, respectively, correspond to crystalline melting, cold crystallization and main-chain transition¹⁵⁻¹⁸. These temperatures are far below the testing conditions in this study. Besides, J.E. Mark *et al.*^{19,20}, who have focused on the stress-strain isotherm measurements of PDMS networks in the past 20 years, have concluded that the up turn in the reduced force is due to the non-Gaussian distribution of PDMS chain at high elongation, instead of strain-induced crystallization. Therefore, it is reasonable to predict that orientation and crystallization of the polyolefin chains during stretching are the main reasons for the observed phenomena of stress-whitening. We have also observed that SF-8427 crystallizes at 12°C , which further confirms the above prediction.

The fracture energy (G_{IC}) measurements were conducted on the compact-tension specimen of dimensions $40 \times 20 \times 10 \text{ mm}$. A pre-crack, 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^{-1} . The magnitude of G_{IC} was calculated by the following equation²¹.

$$G_{IC} = (Y_{(a/w)}^2 \times P^2 \times a) / (EW^2b^2)$$

Where $Y_{(a/w)} = 29.6 - 186(a/w) + 656(a/w)^2 - 1017(a/w)^3 + 639(a/w)^4$; a , b , w and E are the crack length, thickness, width and Young's modulus of the specimen, respectively. P is the force required to fracture the sample. The reading of crack length ' a ' significantly influences the measured results. The deviation in G_{IC} , calculated for every 12 samples, was found to be as high as 30% when ' a ' was taken as an average value. As can be seen from Figure 4, a modified method was chosen to estimate the magnitude of ' a ' more accurately, which reduced the deviation in G_{IC} values to about 10%. Readings corresponding to the right edge (R), left edge (L) and tip (T) of the crack front were recorded. The crack length was then calculated according to the average values of these three reading by the following

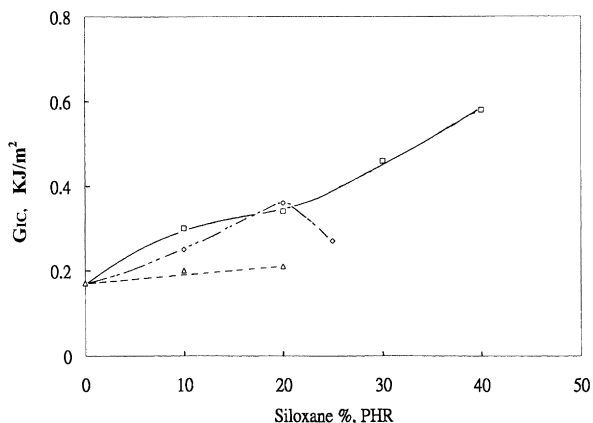


Figure 5 Fracture energy versus modifier-epoxy ratio plots for: polyblend (Δ); SF-8427 jointed-IPN (□); and BY-16005 jointed-IPN (◇)

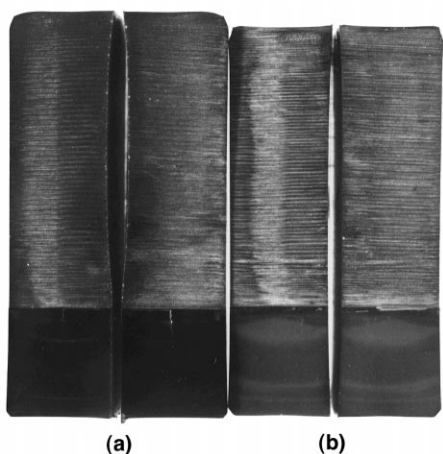


Figure 6 Photographs of the fracture surface of (a) the neat epoxy resin; and (b) the SF-40 specimen

equation.

$$a = W - (L + 2T + R)/4$$

Variations in the fracture energy of siloxane modified epoxy resins are plotted in Figure 5 and also listed in column 4 of Table 2. Although all the jointed-IPN samples are clear and transparent, existence of separated domains which was composed of modifier and epoxy resin still observed from the SEM micrographs of the fracture surface (treated in liquid N₂) of the BY-16005 systems. For the SF-8427 jointed IPN systems, no rubber domain was observed. In the rubber and rigid particulate plastic filler toughening mechanism, it is believed that appropriate separated domains have a major contribution to the improvement in fracture energy. As observed in this study, the polyblends exhibited no toughening effect, due to the weak interfacial bonding between DGEBA and polysiloxane. The BY-16005 system showed a maximum value at the siloxane-epoxy ratio of 0.2, which is consistent with the theory. It was, however, surprising to find that without any rubber domains, the fracture energy of the SF-8427 system increased progressively with increasing the content of siloxane modifiers. The fracture energy increased by up to 250% for the siloxane-epoxy ratio of 0.4.

The fracture surfaces of the specimen displayed several distinct and visually observable regions: viz. the saw cut, the razor cut, initiated crack, the stress-whitened zone, and fast-crack zone. In Figure 6, photographs of the fracture surface

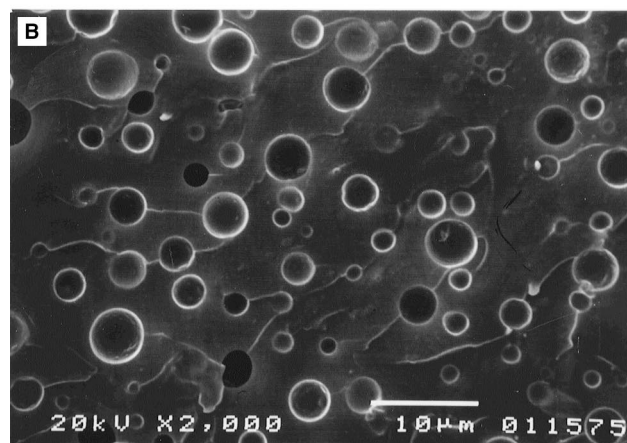
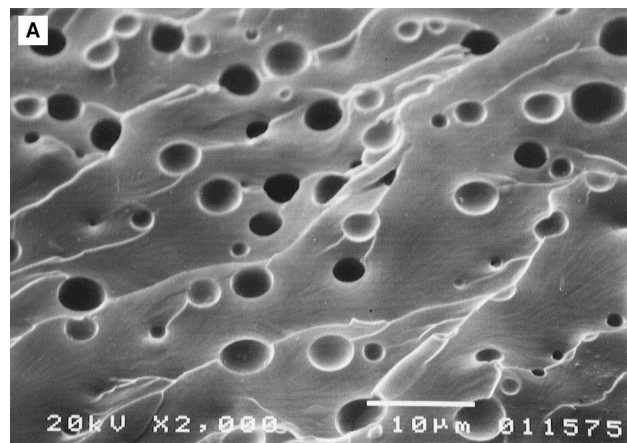


Figure 7 SEM micrographs of polyblend: (A) B-10; and (B) B-20

of the epoxy and SF-8427 jointed-IPN are presented. As can be seen, stress-whitened zone can be observed even visually for the IPN system. The SEM micrographs of the fracture surfaces of the neat epoxy resin, on the other hand, showed smooth and glassy surface. The tiny rubber domains (around 3 μm) were dispersed in the polymer matrix for the polyblends (Figure 7). Very significant separated domains were observed in the BY-16005 jointed-IPN systems, the size of which increased according to the modifier content (Figure 8). In contrast to the spherical rubber domains of the polyblend system, the fracture surface is clear and flat. It is believed that the domain composed of modifier and the epoxy resin. The amine cured SF-8427 siloxane modified jointed-IPN are shown as a function of siloxane content in Figure 9. As the SF-8427 siloxane content increases, white spots gradually appear in the stress-whitened zone. The SEM details of this stress-whitened region (Figure 10) show that the white spots are composed of tree-leaf-type crystal. In contrast, the fast fracture region still remains mirror smooth surface. In the conventional rubber modified epoxy resins, the stress-whitened region is always attributed to cavitation between rubber particles and matrix or crazing^{5,6}. Combined with the tensile results, it is believed that these crystals are formed due to strain-induced crystallization during the slow rate deformation. To our knowledge, this is the first time that strain-induced crystallization of epoxy resins is observed in the fracture mode. In order to evaluate the properties of these crystal, the stretched samples were reheated in a programmed oven. It was observed that the

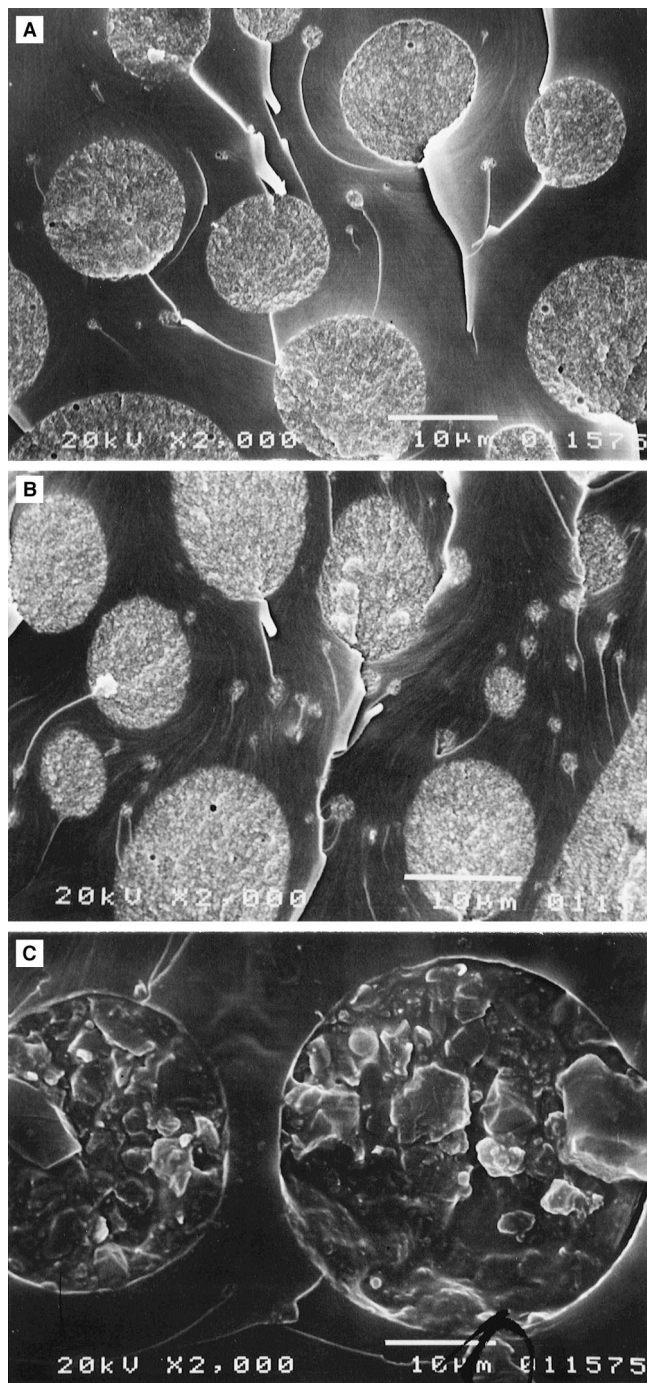


Figure 8 SEM micrographs of BY-16005 jointed-IPN: (A) BY-10; (B) BY-20; and (C)BY-25

stress-whitened region turned clear at around 120°C, which is close to the glass transition temperature of cured specimen. Since orientation of the polyolefin chains along the stretching direction is frozen in the partially deformed epoxy network chains, relaxation of these polyolefin chain is, therefore, inhibited unless the epoxy main-chains have enough energy to translate. The SEM micrographs of the fracture surface of the SF-8427 specimen in tensile mode were also studied (Figure 11). As can be seen, the slow crack growth regions show shallow cigar-shaped cavities, which initiate from one nucleus and terminate on other. The voids in these micrographs are the air bubbles trapped in the sample. Since the polyolefin chain aligned along the stretching direction, the white spots instead of the tree-leaf

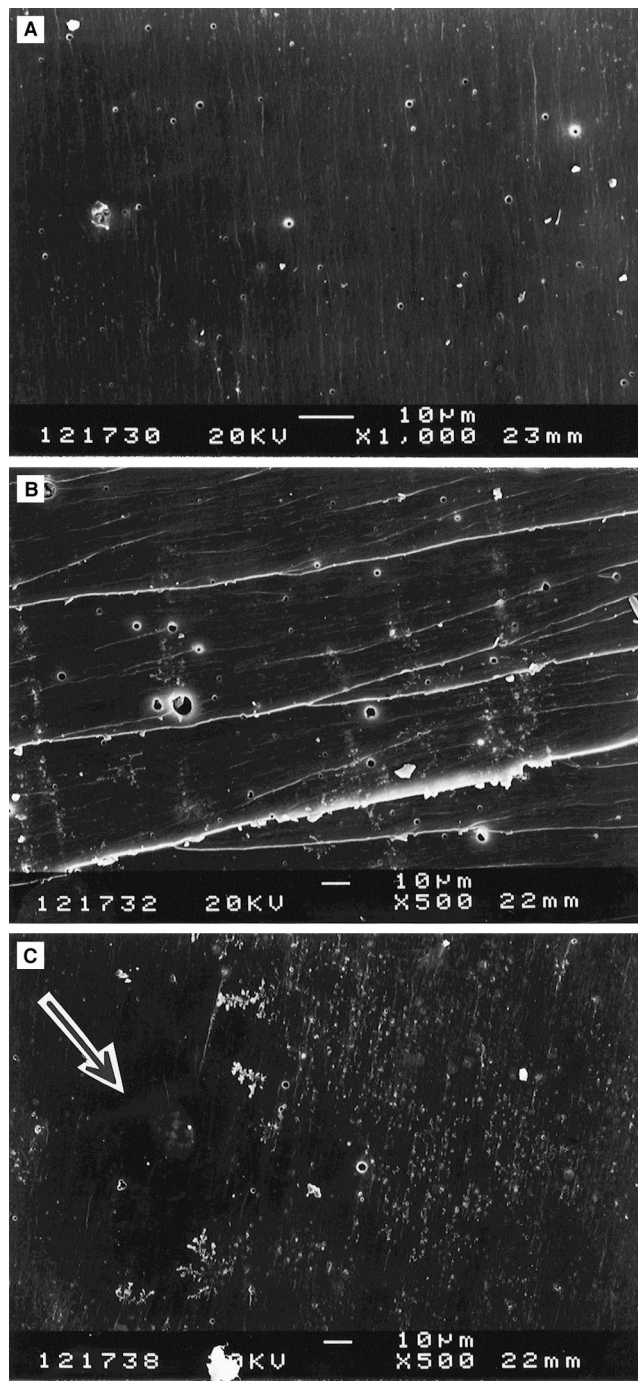


Figure 9 SEM micrographs of SF-8427 jointed-IPN: (A) SF-20; (B) SF-30; and (C) SF-40, arrow indicates the fast crack region

pattern crystal observed in this tensile fracture surface which is perpendicular to the stretching direction. Although it is not clear why the formation of the crystals improves the fracture energy, the following three reasons may attribute to the toughening effects: (1) the deformations of the polyolefin chain dissipate energy into heat due to viscoelastic property; (2) crystallization of the polyolefin chains further releases heat; and (3) the crystallization of the polyolefin may increase the plastic yield zone. The detail evaluation is now in progress.

The $\tan \delta$ versus temperature plots are presented in Figures 12–14 and the corresponding T_g values are listed in columns 5, 6 and 7 of Table 2. For pure DGEBA, the high T_g [assigned as $T_g(I)$] and low T_g [assigned as $T_g(II)$] appear at

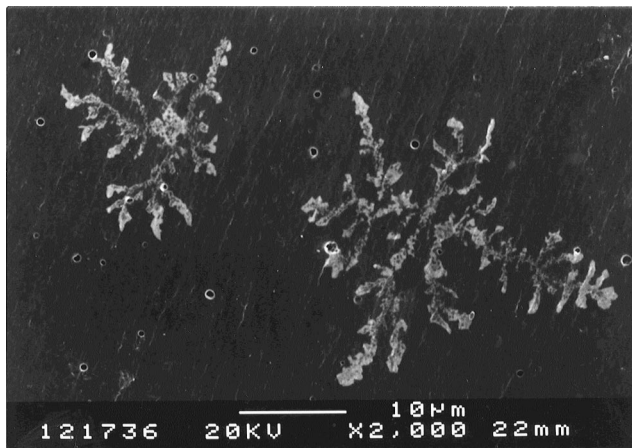


Figure 10 Magnification of the stress-whitened region of SF-40

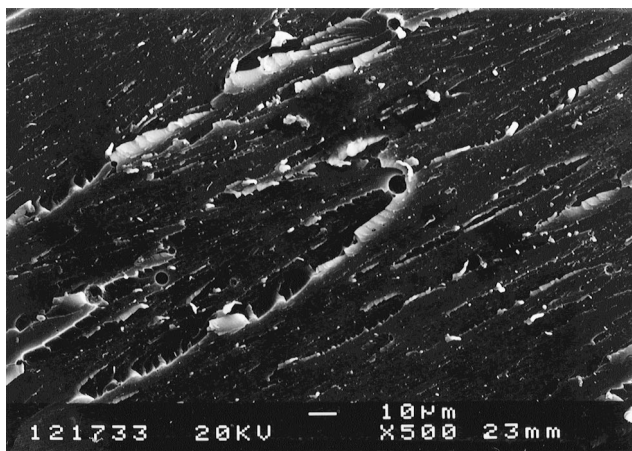


Figure 11 SEM micrographs of SF-8427 jointed-IPN (SF-40) in the fracture surface of the tensile specimen

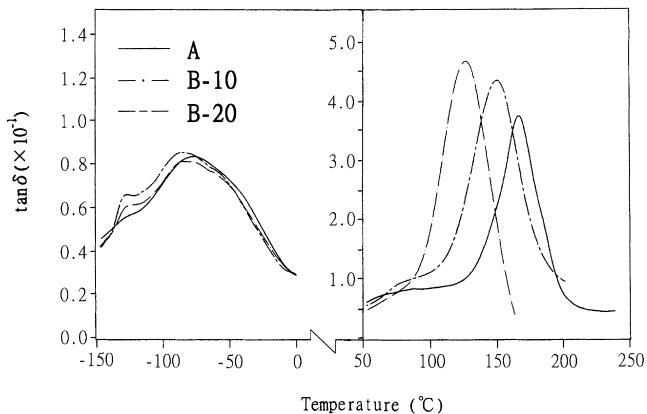


Figure 12 Tan δ versus temperature plots for the polyblends

167 and -67°C , respectively. In the polyblends of 10% modifier, the $T_g(\text{I})$ shifted to low temperature (128°C) and a new T_g [assigned as $T_g(\text{III})$] was observed at low temperature (-125°C), which is attributed to the transition of siloxane chains. As the siloxane content further increased, $T_g(\text{I})$ shifted to higher temperature (151°C). This result suggests a significant phase separation. Due to the compatibility between the siloxane chains and bisphenol portion of the epoxy molecules, the $T_g(\text{I})$ values of the

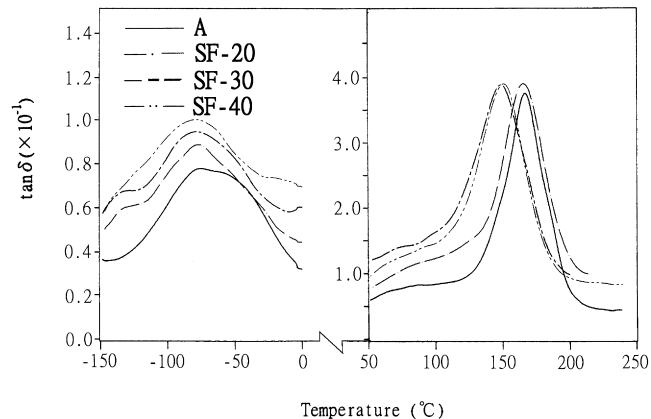


Figure 13 Tan δ versus temperature plots for the SF-8427 jointed-IPN

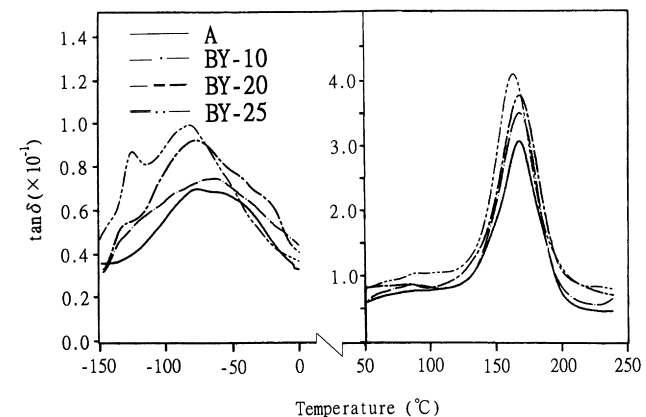


Figure 14 Tan δ versus temperature plots for the BY-16005 jointed-IPN

SF-8427 jointed-IPN systems shifted to lower temperature continuously, with increase in the siloxane content. Since the existence of separated domains was observed from the SEM micrographs in the BY-16005 jointed-IPN systems, the $T_g(\text{I})$ values accordingly remained constant, same as the neat epoxy resins. For the $T_g(\text{II})$ region of these three kinds of sample, it is worth to point out that the damping peak intensity increased and the temperature decreased according to the content of the modifiers. This results suggest that with the aid of the long olefin chain, the siloxane chains have an excellent compatibility with the diglycidyl ether portion of the epoxy molecules.

CONCLUSION

We have shown here that it is possible to prepare homogeneous siloxane-epoxy jointed-IPN systems by carefully choosing appropriate polydimethylsiloxane- α,ω -diol as the reactive modifier. These IPN systems show no rubber domains. Although it is against the theory of rubber toughened mechanism, the most important contribution of this study is that we have been able to demonstrate that strain-induced crystallization during deformation can improve the fracture energy significantly.

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