Toughened Interpenetrating Polymer Network Materials Based on Unsaturated Polyester and Epoxy

MU-SHIH LIN, CHIA-CHENG LIU, CHEN-TZE LEE

Department of Applied Chemistry, National Chiao-Tung University, Hsinchu, Taiwan 30050

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ABSTRACT: Simultaneous interpenetrating polymer networks (IPNs) based on epoxy (diglycidyl ether of bisphenol A) and unsaturated polyester (UP) were prepared by using *m*-xylenediamine and benzoyl peroxide as curing agents. A single glass transition temperature for each IPN was observed with differential scanning calorimetry, which suggests good compatibility of epoxy and UP. This compatibility was further confirmed by the single damping peak of the rheometric dynamic spectroscopy. Curing behaviors were studied with dynamic differential scanning calorimetry, and the curing rates were measured with a Brookfield RTV viscometer. It was noted that an interlock between the two growing networks did exist and led to a retarded viscosity increase. However, the hydroxyl end groups in UP catalyzed the curing reaction of epoxy; in some IPNs where the hydroxyl concentration was high enough, such catalytic effect predominated the network interlock effect, leading to fast viscosity increases. In addition, the entanglement of the two interlocked networks played an important role in cracking energy absorption and reflected in a toughness improvement. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 585–592, 1999

Key words: IPN; toughness improvement; curing behaviors; compatibility

INTRODUCTION

Both epoxy resin and unsaturated polyester (UP) are commodity thermosetting polymers and are widely used commercially. UP is a relatively hard and brittle material with a low cost and is applied mainly in glass fiber-reinforced plastics. Epoxy resin, although a stronger material used largely in composites, coatings, adhesives, electronics, etc., still lacks of good toughness. Many attempts have been made to toughen the epoxy resin. The incorporation liquid rubbers is a possibility.^{1–5} However, the reduction of $T_{g^{*}}$ modulus, and tensile strength is the drawback. Thermoplastic modification via blending or the addition to a thermoset is another possibility.^{6–12} In recent

Correspondence to: M.-S. Lin.

Journal of Applied Polymer Science, Vol. 72, 585–592 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/040585-08 years, blending of two thermosets *via* interpenetrating polymer networks (IPNs) have been extensively studied.^{13–21} Several studies on IPNs revealed an improved mechanical properties.^{22–24} In our previous article,^{25,26} we reported the chemorheology and kinetic study on epoxy/UP IPNs. In another article, we reported an enhanced cracking energy-absorbing capability of epoxy/ acrylic IPNs.²² Our present study on the mechanical properties of epoxy/UP IPNs found that the entanglement of the two interlocked networks exhibited an improved toughness. In this article, we would like to report such a result.

EXPERIMENTAL

Diglycidyl ether of bisphenol A (DGEBA; Epikote 815) liquid epoxy resin with an EEW of 190 was obtained from Shell Chemical Co. *m*-xylenedi-



Figure 1 Dynamic DSC thermograms showing exothermic peaks for various IPN compositions. DGEBA/UP = (A) 0/100, (B) 25/75, (C) 50/50, (D) 75/25, and (E) 100/0.

amine (MXDA) was purchased from ICI and was used directly as a curing agent for DGEBA. A stoichiometric balance of DGEBA and MXDA was maintained for all compositions. General purpose UP (157 BQTC) with a number-average molecular weight of 2000 was obtained from Young-Shun Industrial Co. (Taiwan), which was made from phthalic anhydride, propylene glycol, maleic anhydride, and 35% of styrene monomer. Benzoyl peroxide (BPO) was recrystallized from 95% eth-



Figure 2 Viscosity increases for various compositions during IPN formation at 70°C. DGEBA/UP = (A) 0/100, (B) 25/75, (C) 50/50, (D) 75/25, and (E) 100/0.



Figure 3 Plots of gel fractions against % epoxy for various compositions.

anol before use. BPO (1 phr; based on UP) was used as the curing agent for UP. Samples of various weight ratios of UP/DGEBA in 100/0, 75/25, 50/50, 25/75, and 0/100, including MXDA and BPO, were poured into Teflon molds. They were precured at 60°C for 4 h and postcured at 120°C for another 6 h. Dynamic differential scanning calorimeter (DSC) thermograms were obtained with a Seiko 5200 model DSC, with a heating rate of 10° min⁻¹ in a nitrogen atmosphere. Gel fractions were measured with a Soxhlet extractor, using acetone as co-solvent after 24 h's continuous extraction. Dynamic mechanical properties were investigated with a Rheometric II dynamic rheometric spectroscopy, with 31.4 rad s^{-1} and 0.2% strain, and temperature sweeping from -100° to 200°C. Tensile elongation was tested according to ASTM 0638, whereas impact resis-



Figure 4 DSC thermograms for the epoxy/UP IPNs. Compositions are indicated on each thermogram.



Figure 5 RDS curves showing tan δ versus temperature for various compositions. DGEBA/UP = (A) 0/100, (B) 25/75, (C) 50/50, (D) 75/25, and (E) 100/0.

tance was performed with an instrumented falling-type impact tester. Scanning electron microscopic (SEM) photographs were obtained from the fractured surfaces of tested impact samples.

RESULTS AND DISCUSSIONS

The curing behavior of thermosetting polymers can be studied with a dynamic DSC thermogram.²⁷ Figure 1 shows the results of this DGEBA/UP IPNs curing behavior. It is noted that all of the IPNs in 75/25, 50/50, and 25/75 of DGEBA/UP (curves B, C, and D) indicated exothermic peaks at higher and broader temperature ranges than the two respective pure DGEBA and UP. It can be inferred that the entanglement of the two growing networks provided sterically hindered environment and restrained chain mobilities for the curing reactions. An increase of temperature would compensate such a network interlock effect.²⁷ Figure 2 plots the viscosity changes during IPN formation at 70°C for various DGEBA/UP ratios. Curve A is the viscosity change for the pure UP cured by BPO, and curve E is that of pure DGEBA cured by MXDA. Both curves show relatively rapid curing rates. When the two components were blended and cured simultaneously, delayed viscosity increases were generally observed as reported for other IPN sys-



Figure 6 RDS curves showing storage modulus versus temperature for various compositions. DGEBA/UP = (A) 0/100, (B) 25/75, (C) 50/50, (D) 75/25, and (E) 100/0.

tems.²⁶⁻²⁸ In other words, both curves B and C should have showed slower viscosity increases than both A and E curves, because of the network



Figure 7 RDS curves showing loss modulus *versus* temperature for various compositions. DGEBA/UP = (A) 0/100, (B) 25/75, (C) 50/50, (D) 75/25, and (E) 100/0.



Figure 8 Plots of elongation at break and tan δ against % epoxy content for various compositions.

interlock effect. However, present studies indicate quite different curing behavior. Curve B (DGEBA/UP = 25/75) and curve C (UP/DGEBA= 50/50) clearly show curing rates intermediate between the two respective components (curves A and E), presumably because the hydroxyl end groups of the UP catalyzed the curing reaction of DGEBA; and this catalytic effect predominated the effect of network interlock. This catalytic effect of OH on the curing of epoxide by amine has been reported in the literature.^{26,29} This catalytic effect depends on the OH concentration, because it is included in the rate expression.²⁶ Curve D (DGEBA/UP = 75/25) appears showing a normal delayed curing rate because much less OH concentration is present in this composition. The steric hindrance of the network interlock has been known to make the curing reactions more difficult and reflecting in lower gel fractions.^{27,28} Figure 3 shows this result. Figure 4 shows the glass transition temperature (T_g) of each IPN composition. The uncured portions of DGEBA and UP would probably act as plasticizers and hence lowers the T_g of each IPN material. It is noted that the lower gel fraction (and higher uncured

portions) that an IPN has, the lower T_g and damping temperature the IPN indicates. Figure 5 shows the RDS curves of damping peaks (tan δ) versus temperature for various IPNs. The damping peaks of IPNs (curves B, C, and D) occur at a lower temperature because they have less crosslinking with more uncured epoxy and/or UP as plasticizers. The molecular interaction of the closely interlocked networks resulted in a slower molecular relaxation and exhibited a broader α -transition in the RDS curves. Similar broadening was reported in our previous article on the fully and semi-IPNs based on epoxy and acrylics.²⁷ Han and coworkers,³⁰ in their study of compatible polyurethane (PU)/poly(methyl methacrylate) (PMMA) IPNs, also reported a broadened T_{o} . This broadening is associated with an enhancement of tensile strength.

Figure 6 shows storage modulus *versus* temperature for various IPNs. In general, a higher crosslinked material would show higher storage modulus. Compositions B, C, and D exhibit lower moduli because they have less gel fractions due to network interlock during cure reaction. Composition B shows the lowest modulus because it has



Figure 9 Plots of tensile stress at break *versus* % epoxy content for various compositions.

the DGEBA/UP equivalent ratio near 1 and hence has the largest extent of network interlock. Figure 7 shows the loss modulus curves. Again, compositions B, C, and D indicate higher E'' near the transition temperature. Figure 8 shows the correlation of tan δ and elongation versus composition. Compositions B, C, and D contain more uncured portions of low molecular DGEBA and/or UP, and indicate the higher tan δ and elongation. It is also noted that composition B has the highest tan δ and elongation because it contains the largest extent of network interlock and hence the lowest gel fraction.

Figure 9 plots the tensile stress at break versus composition. Physical entanglements between the two respective UP and epoxy networks seem to enhance the tensile stress at break, as reflected in IPN compositions B, C, and D. Compared with Figure 8, it is also noted that composition B shows the highest tensile stress and elongation at break. The equivalent ratio of epoxy/UP for composition B (DGEBA/UP = 25/75, w/w) is much closer to 1 than the other IPNs. In other words, composition B would contain much more chain entanglements and, this larger extent of chain entanglement is associated with a broadened T_g and an enhance-

ment of the tensile strength as reported by Han and coworkers.³⁰ The large extent of chain entanglement between the two respective epoxy and UP networks in composition B is also reflected in lower gel fraction as previously described (Figure 3). The large amounts of uncured DGEBA and/or UP molecules would act as plasticizers, leading to not only lower T_g (Figure 4), but also larger elon-



Figure 10 Plots of tan δ values and cracking energy *versus* % epoxy content for various compositions.



Figure 11 SEM photomicrographs of fracture surfaces for various compositions. DGEBA/UP = (A) 100/0, (B) 75/25, (C) 50/50, (D) 25/75, and (E) 0/100.

gation (Figure 8). It seems that an IPN material with higher tan δ value would show a higher stress at break. Because tan $\delta = E''/E'$, a higher

tan δ means a higher loss modulus, which would turn more mechanical energy into heat *via* molecular relaxation. In the IPN materials, the two



(E)

Figure 11 (Continued from previous page)

networks are closely interlocked; the cracking energy would be dissipated simultaneously by both the networks via molecular interactions and relaxations, a synergestic cracking energy-absorbing capability is observed, which is indicated in Figure 10. Similar results were found in other IPN systems.^{31,32} Akay and Cracknell,²⁴ in their study of PU/PMMA IPN materials, find that energy dissipation is closely related to molecular relaxation. The entanglement of the interlocked networks topology represents a means of molecular interaction. This molecular interaction resulted in a broader transition, as previously described. Material with higher tan δ and/or broader transition would show better energy dissipation. The entanglement of the interlocked networks seems to show a significant toughness improvement. This result is consistent with the findings of Akay and Cracknell.24 Galli and coworkers³¹ and Xiao and coworkers,³² in their studies of epoxy/PMMA and PU/silicone IPN materials, concluded that the energy dissipation is proportional to the number of internal surfaces newly produced (i.e., shear banding yield mechanism). Figure 11 shows the SEM photomicrographs of fractured surfaces of samples. Obviously newly sheared internal surfaces with uniform distribution can be clearly found from the SEM photographs. This result is fairly consistent with data in Figure 10, especially in view of composition C, which shows the highest shear banding yield with the highest impact resistance.

CONCLUSIONS

Network interlock in IPN materials of DGEBA/UP were evidenced from the dynamic DSC thermograms and viscosity increase curves during IPN formation. This network interlock showed a measurable effect on the cracking energy absorption capability, and reflecting in a toughness improvement of IPN materials.

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REFERENCES

- Sultan, J. N.; McGarry, F. J. Polym Eng Sci 1973, 13, 29.
- 2. Viscouti, S.; Marchessault, R. H. Macromolecules 1974, 7, 913.
- Manzione, L. T.; Gillham, J. K. J Appl Poym Sci 1981, 26, 907 & 889.
- 4. Kim, D. H.; Kim, S. C. Polym Engl Sci 1991, 31, 289.
- Verchere, D.; Pascault, J. P.; Sautereau, H.; Moschiar, S. M.; Riccardi, C. C.; Williams, R. J. J. J Appl Polym Sci 1991, 43, 293.
- 6. Rose, J. B. Polymer 1974, 15, 456.
- Bucknall, C. B.; Partridge, I. K. Polymer 1983, 24, 639.
- 8. Bucknall, C. B.; Gilbert, A. H. Polymer 1989, 30, 213.
- 9. Pearson, R. A.; Yee, A. F. Polymer 1993, 34, 3658.
- Pearson, R. A.; Yee, A. F. J Appl Polym Sci 1993, 48, 1051.
- 11. Iijima, T.; Sato, K.; Fukuda, W.; Tomoi, M. J Appl Sci 1993, 48, 1859.
- Raghava, R. S. J Polym Sci, Polym Phys 1987, 25, 1017.
- Sperling, L. H. Interpenetrating Polymers and Related Materials; Plenum Press: New York, 1981.
- Nishi, S.; Kotoka, T. Macromolecules 1985, 18, 1519.
- Siegfried, D. L.; Thomas, D. A.; Sperling, L. H. Polym Eng Sci 1981, 21, 39.
- Hourston, D. J.; Satguunathan, R. J Appl Polym Sci 1984, 29, 2969.
- Chang, M. C. O.; Thomas, D. A.; Sperling, L. H. J Appl Polym Sci 1987, 34, 409.

- Fox, R. B.; Bitner, J. L.; Hinkley, J. H.; Carter, W. Polym Eng Sci 1985, 25, 157.
- 19. Chen, H.; Chen, J. M. J Appl Polym Sci 1993, 50, 495.
- Hourston, D. J.; Zia, Y. J Appl Polym Sci 1983, 28, 3745.
- 21. Kim, S. C.; Sperling, L. H. IPNs Around the World. John Wiley & Sons: New York, 1997.
- 22. Lin, M. S.; Lee, S. T. Polymer 1997, 38, 53.
- Hsieh, K. H.; Liao, D. S.; Chen, C. Y.; Chiu, W. Y. In IPNs Around the World; Kim, S. C., Sperling, L. H. Eds.; John Wiley & Sons: New York, 1997; pp. 139–153.
- Akay, M.; Cracknell, J. G. J Appl Polym Sci 1994, 52, 663.
- 25. Lin, M. S.; Chang, R. J. J Appl Polym Sci 1992, 46, 815.

- Lin, M. S.; Chang, R. J.; Yang, T.; Shih, Y. F. J Appl Polym Sci 1995, 55, 1607.
- 27. Lin, M. S.; Lee, S. T. Polymer 1995, 36, 4567.
- Wang, M. W.; Lee, C. T.; Lin, M. S. Polym Int 1997, 44, 503.
- Ohashi, K.; Hasegawa, K.; Fukuda, A.; Uede, K. J Appl Polym Sci 1992, 44, 419.
- Han, X.; Chen, B.; Guo, F. In IPNs Around the World; Kim, S. K., Sperling, L. H. Eds.; John Wiley & Sons: New York, 1997; pp. 241–257.
- Galli, P.; Danesi, S.; Simonazzi, T. Polym Eng Sci 1984, 24, 544.
- 32. Xiao, H.; Ping, Z. H.; Xie, J.; Yu, T. Y. J Polym Sci Polym Chem Ed, 1990, 28, 585.