Pergamon

PII: S0014-3057(96)00214-5

Eur. Polym. J. Vol. 33, No. 6, pp. 903–906, 1997
© 1997 Elsevier Science Ltd. All rights reserved
Printed in Great Britain
0014-3057/97 $17.00 + 0.00

POLYSILOXANE MODIFIED EPOXY POLYMER NETWORKS—I. GRAFT INTERPENETRATING POLYMERIC NETWORKS

PO-HOU SUNG* and CHIEN-YANG LIN
Department of Chemistry, Fu-Jen Catholic University, Hsinchung, Taipei, Taiwan, Republic of China

(Received 23 January 1996; accepted in final form 25 April 1996)

Abstract—Graft interpenetrating polymeric networks of epoxy resin and polydimethylsiloxane (PDMS) were synthesized using 3-aminopropyltrimethoxysilane (γ-APS) as coupling agent. The dynamic mechanical analysis shows partially mutual compatibility between these two thermodynamically immiscible polymers. Due to the inappropriate domain size and the poor cohesive properties between epoxy resin and PDMS domain, the fracture energy (G_{IC}) decreased drastically at low PDMS content (5%). While the PDMS domain size increased according to the PDMS contents, the fracture energy was then improved. This experimental result indicates that PDMS with an appropriate domain size can be used as a toughness modifier for polyfunctional epoxy resins. © 1997 Elsevier Science Ltd

INTRODUCTION

Epoxy resins are important engineering polymeric materials possessing high elastic modulus and glass transition temperature. Many papers have dealt with modification of the epoxy structure to improve its fracture toughness, flexibility, impact strength and mechanical properties. The most successful example of modification is 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 depends on the elastomer structures, the contents of the elastomer in the epoxy matrix and the morphology of phase separation [3, 4].

Polysiloxane, owing to its flexibility and thermal stability, is one of the best candidates to be used to modify the mechanical properties of epoxy resin. However, the thermodynamical immiscibility between epoxy and polysiloxanes restricts this. In order to improve the compatibility, several modified polysiloxanes such as functional group capped polysiloxane [5] and polysiloxane block copolymer [6] have been used to improve the fracture toughness.

In this study, we attempted to crosslink the epoxy resin matrix using γ-APS (3-aminopropyltrimethoxysilane) and MDA (4,4′-methylene dianiline). The alkoxy groups in γ-APS were then reacted with PDMS (hydroxyl terminated polydimethylsiloxane) simultaneously. The resulting graft interpenetrating polymer networks (graft-IPN) were examined by dynamic mechanical analysis, scanning electron microscopy and tensile testing. The fracture behaviors are also discussed.

EXPERIMENTAL

Sample preparation

The epoxy resin was the diglycidyl ether of bisphenol A (DGEBA, BE-188) which was generously provided by Chang Chun Plastic Corporation, Taiwan. This product is related to the Epon 828. The hardener MDA (Merck), γ-APS (Aldrich), PDMS ($M_w = 1500$–2000, United Technologies, Inc.) and tin octoate (50% in PDMS, United Technologies Inc.) were used as received. Water should be involved in the reaction of PDMS and γ-APS, therefore no drying procedure was conducted for the reagents.

The graft IPN of epoxy and PDMS were prepared by adding a fixed amount of MDA into epoxy resin at 120°C. After the temperature cooled down to 60°C, varying amounts of PDMS, γ-APS (the stoichiometric equivalent based on OH group of PDMS and OR group of γ-APS), and tin octoate (as catalyst) were thoroughly blended with the epoxy and MDA mixture. The temperature was maintained at 80°C for 15 min to allow partial condensation reaction between γ-APS and PDMS to occur. The mixture was then degassed for 5 min to remove bubbles and CH_3OH (side product of the reaction of PDMS and γ-APS). After pouring into a hot mold (60°C) and cured for 3 hr, the specimens were then step cured at 125°C for 2 hr and 160°C for another 3 hr. The basic formulations for graft IPN are listed in Table 1.

Testing methods

All 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 three point bending flexural properties of specimens were determined according to ASTM D-790. The load was recorded until 30% deflection was reached. The size of the specimen was 8 cm × 2.54 cm × 0.25 cm. The fracture energy G_{IC} was measured using compact-tension specimens [7].

A differential scanning calorimeter (Du Pont 9900) was used to measure the reaction temperature between epoxy and curing agents as well as the glass transition temperature

---

*To whom all correspondence should be addressed.

(T_g) of a specimen. The measurements were carried out from 25 to 200°C under N_2 gas with a heating rate of 10°C/min. The dynamic mechanical properties were measured on a Rheometric Dynamic Analyzer (RDA II). The measurements were made at temperatures in the range of −125 to 200°C with a heating rate of 8°C/min and a frequency of 1 Hz. The morphology of the samples was examined by scanning-electron microscopy.

Table 1. Formulation of graft IPN

Sample	Epon 828	PDMS	γ-APS	MDA
Blank	100	0	0	26.2
A	100	3	0.15	26.2
B	100	5	0.25	26.2
C	100	10	0.50	26.2
D	100	15	0.75	26.2
E	100	20	1.00	26.2
F	100	25	1.25	26.2

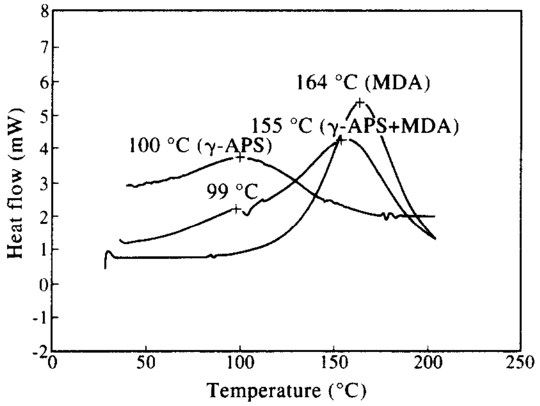

Fig. 1. DSC curves of the reaction exotherms of epoxy resins with γ-APS and MDA.

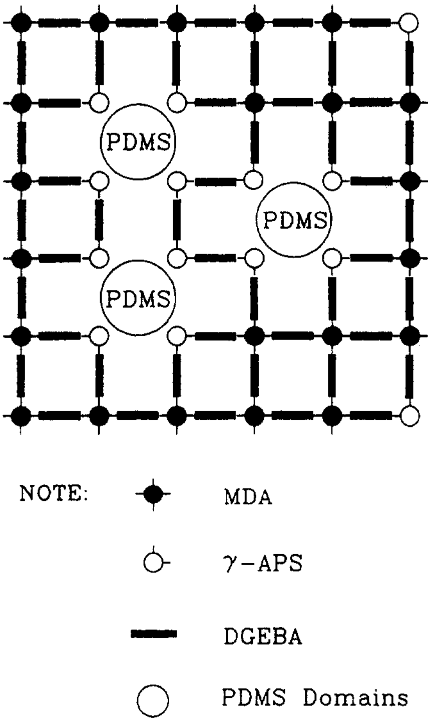

Fig. 2. The structure of graft IPN of epoxy resins and PDMS. (The IPN is not crystalline.)

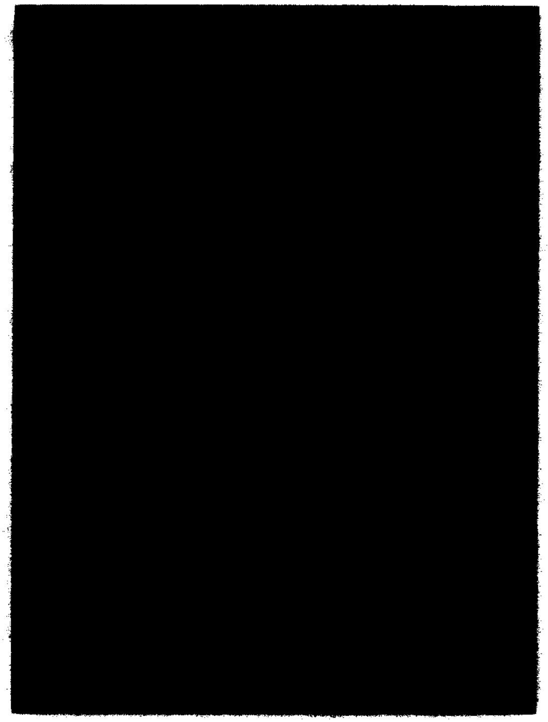

Fig. 3. SEM micrograph of epoxy resin.

RESULTS AND DISCUSSION

The chemical modification of epoxy resins was done in two stages in the same reaction mixture. In the first stage, amino groups of γ-APS were reacted with the epoxide groups of epoxy resins. Exotherms in DSC traces showed that reactions occurred between epoxy resins and both γ-APS and MDA. As shown in Fig. 1, the maximum reaction temperature of epoxy resins with γ-APS and MDA are 100° and 164°C, respectively. In the mixture (including γ-APS and MDA), both of the reaction exotherms shifted slightly to the lower temperature. As the amino group is also a catalyst in the system, the mutual catalytic effect is expected. At the same time, the alkoxy groups of γ-APS were reacted with the hydroxy groups of PDMS through a condensation reaction which was accelerated during degassing. In the second stage, the curing agent MDA was reacted with the remaining epoxide groups. The structure of such a graft IPN is shown in Fig. 2.

Thermodynamic incompatibility of polysiloxane with epoxy resin favors complete phase separation. It is important to improve the compatibility to enhance mechanical properties. Figure 3 is the scanning-electron micrograph of the fracture surface of the pure epoxy resin. It showed a smooth and glassy surface. Figure 4 is the SEM of the graft IPN. It was found that the PDMS domain size increased from 6 to 20 μm according to the PDMS content. It is interesting to note that the PDMS did not rise up to the top layer of the viscous epoxy resin during sample preparation. Instead, it spread over the whole specimen. Without γ-APS, or in inappropriate curing condition, a significant phase separation will be observed immediately. The fixation of the PDMS is therefore due to the chemical linkage between PDMS and γ-APS.

DSC curves for DGEBA and the graft IPNs are given in Fig. 5. The glass transition temperature showed no significant difference. Plots of tan δ vs temperature for DGEBA and the graft IPNs are shown in Fig. 6. Incorporation of PDMS in the DGEBA slightly decrease the high T_g. It also showed that the low T_g increased and the damping area broadened according to the PDMS content. PDMS has three distinctive transition regions (−38, −68, −129°C) corresponding to crystalline melting [8, 9], cold crystallization [8] and the main chain transition region [8–11]. For the PDMS/epoxy graft IPNs, the PDMS T_g apparently merged with the transition region of the diglycidyl ether portion of the epoxy matrix (−65°C) [12]. If the PDMS network was an essentially isolated domain, its T_g should be at a lower temperature. However, no such transition region was observed. The broadened behavior of the damping area on the low T_g region may be attributed to the partial compatibility between PDMS and soft segments of the epoxy resin.

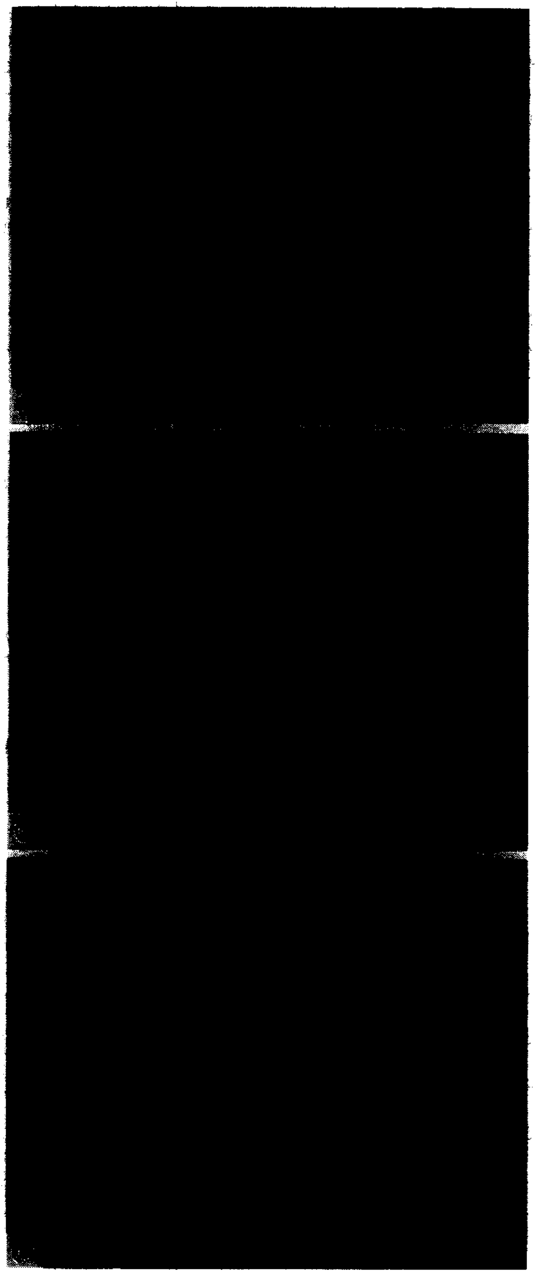

Fig. 4. SEM micrograph of the graft IPN. (a) 5% PDMS (b) 15% PDMS (c) 25% PDMS.

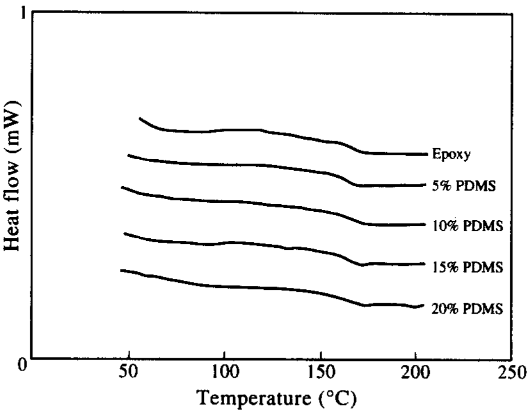

Fig. 5. DSC traces of DGEBA and graft IPNs.

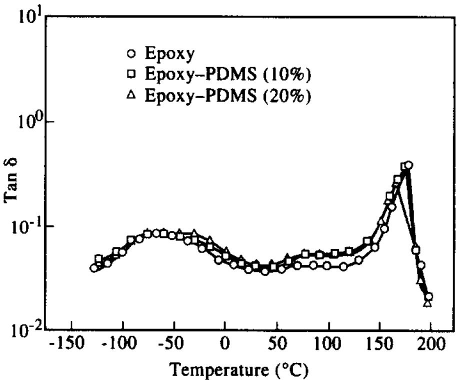

Fig. 6. Loss tangent as a function of temperature.

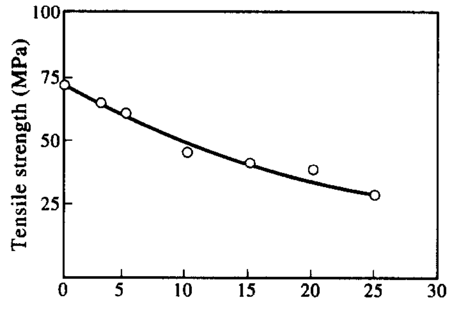

Fig. 7. Tensile strength of graft IPNs.

In the conventional IPN samples, a maximum tensile strength will be reached according to the

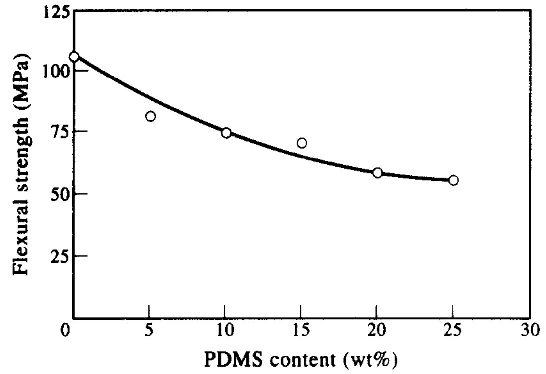

Fig. 8. Flexural strength of graft IPNs.

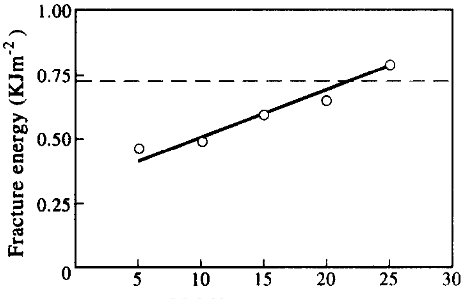

Fig. 9. Fracture energy of graft IPNs.

contents of the second component [13, 14]. However, no such phenomenon was observed in our study. Figures 7 and 8 are the tensile and flexural strength of the PDMS/epoxy graft IPN system. As shown, the mechanical properties decrease along with the PDMS contents. From the micrograph, it is believed that there is no strong interfacial boundary between the PDMS domain and the matrix due to phase separation. As a result, the PDMS greatly decreased the crosslinking density of the matrix, the tensile strength then decreased.

The G_{IC} measurement was conducted according to the compact-tension specimens and calculated by the following equation [7]

$$G_{IC} = \frac{Y^2(a/w)P^2a}{Ew^2b^2},$$

where $Y(a/w) = 29.6 - 186(a/w) + 656(a/w)^2 - 1017(a/w)^3 + 639(a/w)^4$. a, b and E are crack length, thickness and modulus of the specimens; P is the force to fracture. A sharp precrack was made with a razor blade before the test. These slow strain rate fractures were tested at a crosshead speed of 0.5 cm/min. The fracture energy G_{IC} of PDMS/epoxy graft IPNs is shown in Fig. 9. The value decreased drastically with 5% PDMS content. It is probably due to the inappropriate PDMS domain size (6 μm) and the poor cohesive properties between epoxy and PDMS domain. Further increasing the PDMS contents increases the domain size, thus improving the fracture energy. The cavitation mechanism [15] of heterogeneous morphology is usually used to interpret the toughening behavior. Although the PDMS/epoxy graft IPNs did show a poor cohesive strength between PDMS and epoxy resins, the propagation of a crack was stopped by the rubber phase, and the energy dissipated by the rubber deformation or along the weak interfacial boundary between the rubber phase and matrix is probably the main contribution to the improvement of the fracture toughness.

CONCLUSION

We have shown that it is possible to prepare PDMS/epoxy graft IPN by using γ-APS as the coupling agent. Although the poor cohesive properties do not favor the toughening mechanism, it was found that PDMS can be used as a toughness modifier for polyfunctional epoxy resins. In order to improve the cohesive properties, a third component is introduced into the system. The results will be presented elsewhere.

Acknowledgements—The authors are grateful to Dr T. W. Lai (Asia Chemical Co.) for assistance in carrying out the dynamic mechanical analysis.

REFERENCES

1. Sperling, L. H., *Interpenetrating Polymer Networks and Related Materials*, Plenum Press, New York, 1981.
2. Bruins, P. S., *Epoxy Resin Technology*, Interscience, New York, 1968.
3. Sultan, J. N. and McGarry, F. J., *Polym. Eng. Sci*, 1973, **13**, 29.
4. Nakamura, Y., Tabata, H., Suzuki, H., Ito, K., Okubu, M. and Matsumoto, T., *J. Appl. Polym. Sci.*, 1986, **32**, 4865.
5. Tong, J., Bai, R., Zou, Y., Pan, C. and Ichimura, S., *J. Appl. Polym. Sci.*, 1994, **52**, 1373.
6. Kochergin, Y. S., Kobzeva, T. I., Storozhuk, I. P. and Kulik, T. A., *Kompoz. Polit. Mater.*, 1988, **36**, 41.
7. Ting, R. T. and Cottington, R. L., *J. Appl. Polym. Sci.*, 1980, **25**, 1815.
8. Ebdon, J. R., Hourston, D. J. and Klein, P. G., *Polymer*, 1984, **25**, 1633.
9. Fisher, D. J., *J. Appl. Polym. Sci.*, 1961, **5**, 436.
10. Cowie, J. M. G., *Polym. Eng. Sci.*, 1979, **19**, 709.
11. Xiao, H., Ping, Z. H., Xie, J. W. and Yu, T. Y., *J. Polym. Sci. Polym. Chem.*, 1990, **28**, 585.
12. Murayama, T. and Beli, J. P., *J. Polym. Sci., Part A-2*, 1970, **8**, 437.
13. Frisch, K. C., Klempner, D., Migdal, S., Frisch, H. L. and Ghiradella, H., *Polym. Eng. Sci.*, 1975, **15**, 339.
14. Sung, P. H. and Wu, W. G., *Eur. Polym. J.*, 1994, **8**, 905.
15. Bascom, W. D., Ting, R. Y., Moulton, R. J., Riew, C. K. and Siebert, A. R. *J. Mater. Sci.*, 1981, **16**, 2657.