Study on modification of epoxy resins with acrylate liquid rubber containing pendant epoxy groups

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Epoxy resins are a class of versatile thermosetting polymers with high strength, low creep, low cure shrinkage, and excellent chemical resistance. Nowadays, they are widely used in fiber reinforced resin matrix composites, structural adhesives, and surface coating materials. Unfortunately, the inherent toughness of cross-linked epoxy resins is relatively low. It is therefore desirable to enhance toughness without adversely affecting the other useful properties of this polymer [1, 2]. Modification with reactive liquid rubbers is one of the most frequent methods to toughen the rigid polymer. In this method, the rubber modifier is initially dissolved into the matrix. Then the rubber phase separates as discrete particulate phase due to the decreasing of solubility between rubber and cross-linked epoxy resins caused by the increase in molecular weight of the epoxy resins [3]. Reactive liquid rubbers, such as carboxyl-terminated butadiene and acrylonitrile copolymer liquid rubber (CTBN), amine-terminated butadiene and acrylonitrile copolymer liquid rubber (ATBN), or hydroxyl-terminated polybutadiene (HTPB) liquid rubber, have been proved as effective toughening modifier for epoxy resins [4–6]. However, the main deficiency of these rubbers is the high unsaturation in their molecular structure and the traces of free carcinogenic acrylonitrile. Moreover, for the ambient temperature curing epoxy resins–aliphatic amine system, the reaction between terminated carboxyl group and epoxy resins need be catalyzed additionally [7]. So, liquid rubbers possessing saturated structure and higher reactive, such as carboxyl terminated poly(2-ethylhexyl acrylate), amine randomized poly(2-ethylhexyl acrylate), copolymer of *n*-butyl acrylate and glycidylmethacrylate and copolymer of *n*-butyl acrylate, glycidylmethacrylate and styrene, etc., have been as alternatives to CTBN and ATBN [8–12].

In our previous works, a novel acrylate liquid rubber containing pendant epoxy groups had been synthesized by copolymerization of ethyl acrylate, butyl acrylate, and glycidylacrylate by solution polymerization [13]. In the present paper, the acrylate liquid rubber was used to toughen the bisphenol A diglycidyl ether epoxy resins with triethanolamine as hardener. The toughening efficiency and phase morphology were investigated by mechanical properties testing and Scanning Electron Microscope.

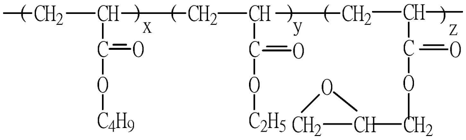

Figure 1 Molecular formula of acrylate liquid rubber containing pendant epoxy group.

The acrylate liquid rubber was synthesized by copolymerization of ethyl acrylate, butyl acrylate, and glycidylacrylate by solution polymerization. The M_n of the rubber is about 6300 and the content of epoxy group is 1.2 m mol/g, and its molecular formula is presented in Fig. 1.

Process of modification is described as follows. Epoxy resin and liquid rubber (3–20 phr) were first mixed together and heated at approximately 80 °C for 20 min in oil bath, then the mixture were degassed in a vacuum oven for 20 min. Once the mixture had cooled to approximately 40 °C, the hardener of 12 phr was added with vigorous stirring for 5 min. After that, the mixture was casted into a polytetrafluoroethylene (PTFE) mold, and reacted at 80 °C for 2 hr, at 100 °C for 2 hr, and at 120 °C for 2 hr, respectively. The post-cured treatment was carried out at 140 °C for 2 hr in the oven equipped with temperature controller.

The toughness properties of epoxy resins, such as impact strength and fracture toughness (G_{IC}), were measured according to Izod unnotched impact test method (GB/T2571-1995 of China) and double cantalever beam test [14], respectively. Impact fractured surface of modified epoxy resins samples was sputter coated with gold and examined using a Scanning Electron Microscope (AMRAY Model-1000B). Glass transition temperature (T_g) was determined via Differential Scanning Calorimetry

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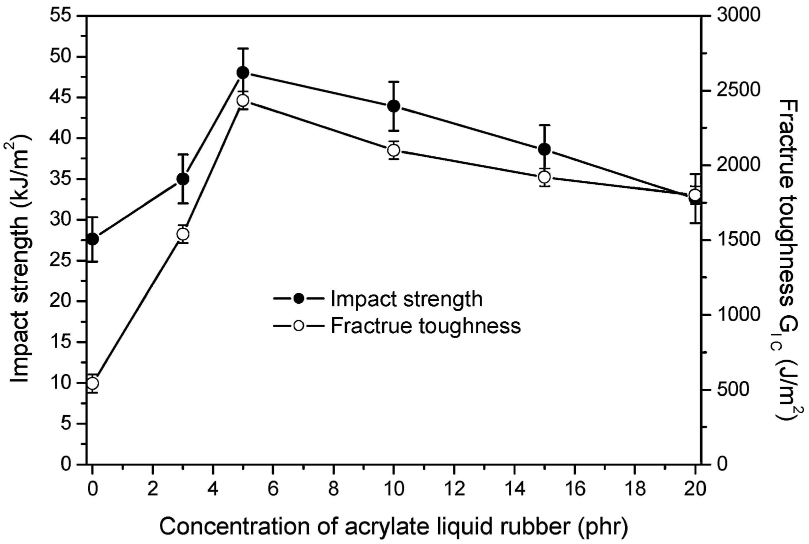

Figure 2 Dependence of impact strength and fracture toughness for modified epoxy resin samples on concentration of liquid rubber.

(MDSC2910, TA Instrument) with a scanning rate of 15 K/min.

The toughening efficiency was firstly investigated and the dependence of impact strength and fracture toughness G_{IC} for modified epoxy resins samples on concentration of liquid rubber is shown in Fig. 2.

As can be seen from Fig. 2, impact strength and fracture toughness G_{IC} of the modified epoxy resins samples are higher than that of the unmodified epoxy resin samples. The value passes through a maximum when the concentration of acrylate liquid rubber is 5 phr. The modified epoxy resins containing 5 phr rubber shows maximum impact strength of 48.0 kJ/m^2 and maximum G_{IC} of 2480 J/m, which are about 63 and 350% higher than that of the unmodified epoxy resins sample, respectively. It indicated this acrylate liquid rubber containing pendant epoxy group is effective to reduce the brittleness of epoxy resin–triethanolamine curing system. This can be attributed to the different phase morphology of the unmodified and modified epoxy resins samples. The SEM photographs for the fracture surfaces of unmodified and modified epoxy networks are presented in Fig. 3.

For the case of unmodified epoxy resins, smooth glassy fractured surface with cracks in different planes can be seen in the SEM photograph of fractured surface. The brittle fracture may explain its low impact strength. On the contrary, image of fractured surface for modified epoxy resins with 5 phr acrylate liquid rubber shows discrete distribution of rubber globular in the connected epoxy resin phase. Due to inherent epoxy group of this novel liquid rubber, good adhesion can exist between rubber globular particles with connected epoxy resins phase. So the rubber globular particles dispersed in the connected epoxy resins phase can act as centers for dissipation of mechanical energy by cavitations and shear yielding [15]. It can be proved by the existence of cavitations of rubber particles and corresponding stress whitened zone around rubber particles as described in Fig. 3. This two-phase

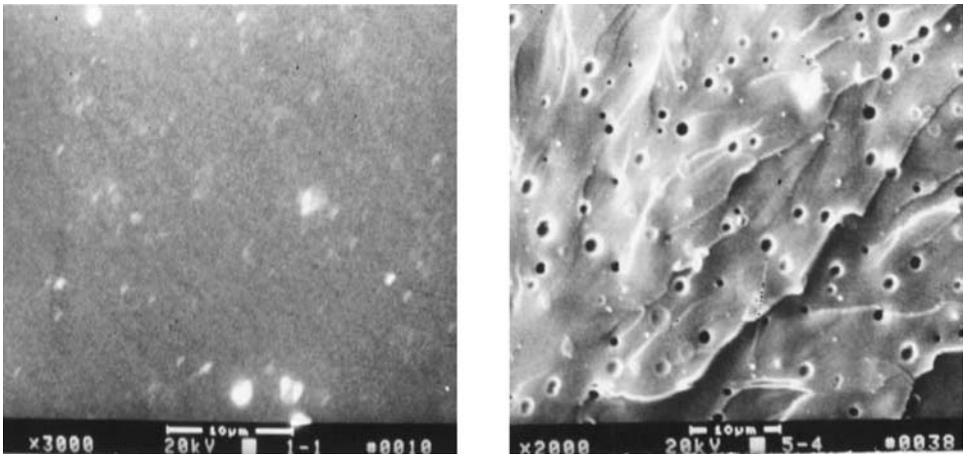

Figure 3 SEM photographs of fracture surfaces of parent resin and rubber modified epoxy resin (*left*: unmodified epoxy; *right*: 5 phr liquid rubber modified epoxy).

TABLE I Mechanical properties and T_g of epoxy resins modified with liquid rubber

Concentration of rubber (phr)	0	5	10	15	20
Tensile strength (MPa)	69.3	63.8	54.3	51.2	51.3
Tensile modulus (GPa)	2.7	2.6	2.4	2.3	2.3
Elongation at break (%)	3.6	5.1	3.8	3.1	3.0
Flexural strength (MPa)	121.7	110.0	101.8	92.5	78.5
T_g (°C)	78.4	71.1	70.1	70.4	69.8

Note. T_g: glass transition temperature.

structure can be considered to enhance the shear yielding at the crack tip through changing in stress state in the region around rubber particles. So this can be considered as the most important reason for the high impact strength and fracture toughness (G_{IC}) of the modified epoxy resins samples.

Besides the toughness of modified epoxy resins, the flexural strength, tensile properties, and thermal properties of unmodified and modified epoxy resins were also investigated and the results were listed in Table I.

It is clear that the tensile strength, tensile modulus, flexural strength, and glass transition temperature of the modified networks decrease with the increasing concentration of acrylate liquid rubber. One reason is that the presence of rubber particles with low modulus and T_g dispersed in the connected epoxy resins phase, the other is that the "soften effect" of connected epoxy resins phase due to unavoidable dissolution of some amount of rubber. This result is in accordance with the effect as described in others modified epoxy networks with liquid rubber [7, 11]. But the interesting result is that the improvement in elongation at break, impact strength and fracture toughness (G_{IC}), is achieved without significant loss in mechanical and thermal properties of the modified epoxy resins with the appropriate concentration of 5 phr acrylate liquid rubber. This may be attributed to the uniform two-phase structured as presented in Fig. 3. In conclusion, the above results demonstrate that the acrylate liquid rubber containing pendant epoxy groups is effective to enhance the toughness of epoxy resin–triethanolamine curing system without significant reduction of mechanical and thermal properties.

Acknowledgments

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References

1. R. A. PEARSON and A. F. YEE, *J. Mater. Sci.* **21** (1986) 2475.
2. Y. HUANG, A. J. KINLOCH, R. J. BERTSCH and A. R. SEIBERT, in "Toughened Plastics I, Science and Engineering", edited by C. K. Riew and A. J. Kinloch (American Chemical Society, Washington, DC, 1993), p. 189.
3. D. VERCHERE, H. SAUTEREAU, J. P. PASCAULT, S. M. MOSCHAIR, C. C. RICCARDI and R. J. J. WILLIAMS, *J. Appl. Polym. Sci.* **41** (1990) 467.
4. C. W. WISE, W. D. COOK and A. A. GOODWIN, *Polymer* **41** (2000) 4625.
5. N. CHIKHI, S. FELLAHI and M. BAKER, *Eur. Polym. J.* **38** (2002) 251.
6. A. OZTURK, C. KAYNAK and T. TINCER, *ibid.*, **37** (2001) 2353.
7. D. RATNA and G. P. SIMON, *Polymer* **42** (2001) 7739.
8. D. RATNA, A. K. BANTHIA and P. C. DEB, *J. Appl. Polym. Sci.* **78** (2000) 716.
9. S. KAR and A. K. BANTHIA, *Pigm. Res. Tech.* **32** (2003) 69.
10. D. RATNA and A. K. BANTHIA, *Polym. Int.* (2000) 281.
11. T. IIJIMA, M. TOMOI, A. SUZUKI and H. KAKIUCHI, *Eur. Polym. J.* **27** (1991) 851.
12. T. IIJIMA, T. HORIBA and M. TOMOI, *ibid.*, **27** (1991) 1231.
13. J. KONG, R. NING, Z. BAI and Y. TANG, *Chin. J. Aero. Mater.* **6** (2003) 48.
14. S. M. WIEDERHORN, *J. Appl. Phys.* **39** (1968) 1569.
15. D. V. ERCHERE, J. P. PASCAULT, H. SAUTEREAU, S. M. MOSCHAIR, C. C. RICCARDI and R. J. J. WILLIAMS, *J. Appl. Polym. Sci.* **42** (1991) 701.

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