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Synergic Effect of Acrylate Liquid Rubber and Bisphenol A on Toughness of Epoxy Resins

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Summary

The synergic effect of acrylate liquid rubber with pendant epoxy group and bisphenol A on the toughness of epoxy resins was presented in this paper. The addition of bisphenol A enhances the impact strength and elongation at break of epoxy resin and actually increases the ductibility of epoxy resin matrix. Much higher toughness efficiency can be achieved for the ALR modified epoxy resins by the incorporation of bisphenol A at the same time. The synergic promotion effect of acrylate liquid rubber and bisphenol A on the toughness efficiency of epoxy resins is attributed to the two-phase morphology and high ductibility of matrix, and the resultant large stress white zones and high shear yielding during the fracture process.

Keywords

Epoxy Resin; Acrylate Liquid Rubber; Toughness; Synergic Effect

Introduction

Epoxy resins are one type of thermoset resins combining many attractive properties, such as high mechanical properties, and excellent dimensional, thermal and environmental stabilities. Up to now, epoxy resins are widely applied as matrix of coatings, adhesives and composites. However, due to the high cross-linking and inherent low toughness of epoxy resin, it is desirable to enhance their toughness without adverse influence on others useful properties, i.e., high thermal stabilities and low cure shrinkage [1,2]. Many types of modifiers were employed to improve the mechanical and thermal properties of epoxy resins, such as reactive liquid rubbers [3-5], hyperbranched blockcopolyethers [6], amine terminated poly(arylene ether ketone)s [7], triblock copolymers [8], thermoplastics [9], and carbon nanotubes or silicate-based nanofillers [10-12].

Modification with reactive liquid rubbers is one of the most effective strategies to toughen epoxy resins. In this strategy, the liquid rubbers are initially dissolved into epoxy resins, and then the rubber separates as discrete particulate phase due to the decreased solubility of rubber in matrix that is caused by the increase of molecular weight of the cross-linked epoxy resins [13]. Many reactive liquid rubbers, such as carboxyl-terminated butadiene and acrylonitrile copolymer (CTBN), amine-terminated butadiene and acrylonitrile copolymer (ATBN), carboxyl-terminated polybutadiene (CTPB), and hydroxyl terminated polybutadiene (HTPB), have been employed as effective toughening modifiers for epoxy resins [3-4,14-18]. However, the main deficiency of these liquid rubbers is the high unsaturation in their molecular structure and the trace of free carcinogenic acrylonitrile for CTBN liquid rubber. Moreover, for epoxy resins-aliphatic amine system cured at ambient temperature, the reaction between terminated carboxyl group of liquid rubber and epoxy group of matrix often need to be catalyzed and reacted in advance, which complicates matters considerably [19]. So reactive liquid rubbers possessing both saturated structure and high reactive group, such as amine randomized poly (2-ethylhexyl acrylate), copolymers of n-butyl acrylate and glycidylmethacrylate and copolymers of n-butyl acrylate, glycidylmethacrylate and styrene, have shown unique properties and potential applications [5,20-24].

In our previous work [25], the acrylate liquid rubber with pendant epoxy group was synthesized by the copolymerization of ethyl acrylate, butyl acrylate and glycidylacrylate. It was employed to toughen the epoxy resins with triethanolamine as hardener, and the content of liquid rubber and morphology were studied. As we know that the morphology of discrete rubber phase, interface interaction between discrete rubber phase and epoxy resin matrix, and ductility of matrix will influence on the toughness efficiency of reactive rubber modified epoxy resins. Thus the further investigation on interface interaction and matrix ductility will be useful for well comprehension of toughness mechanism of epoxy resins and tailoring the properties. Due to the special molecular structure of as-prepared acrylate liquid rubber containing pendant epoxy group, the interface interaction between discrete rubber phase and epoxy resin matrix can be adjusted by the epoxy group's content of acrylate liquid rubber. Additionally, the ductility of epoxy resin matrix can be enhanced by the extended chain reaction using bisphenol A. Consequently, the synergic effect of acrylate liquid rubber with pendant epoxy group and bisphenol A on the toughness efficiency of epoxy resins was studied in this paper.

Experiments

Materials

The acrylate liquid rubber (ALR) was synthesized by the copolymerization of ethyl acrylate, butyl acrylate and glycidylacrylate in solution. Its molecular weight (M_w) is about 6400g/mol and content of epoxy group is 0.4~1.6mmol/g. Here, the molecular weight of acrylate liquid rubber was determined using multi-angle laser light scattering (LLS) instrument (DAWN®) and refractive index instrument (Optilab rEX) (Wyatt Technology Co., St. Barbara, USA). HPLC grade tetrahydrofuran was used as flow phase. Content of epoxy group was determined via hydrochloric acid-acetone titration method. Bisphenol A diglycidyl ether epoxy resins (CYD-128) and the hardener of triethanolamine were all purchased from Yueyang Petroleum Chemical Plant of China. Bisphenol A (Analytic grade) was commercially available from Shanghai Chemical Reagent Ltd of China. The molecular structure schemes of the above four materials are all illustrated in Figure 1.

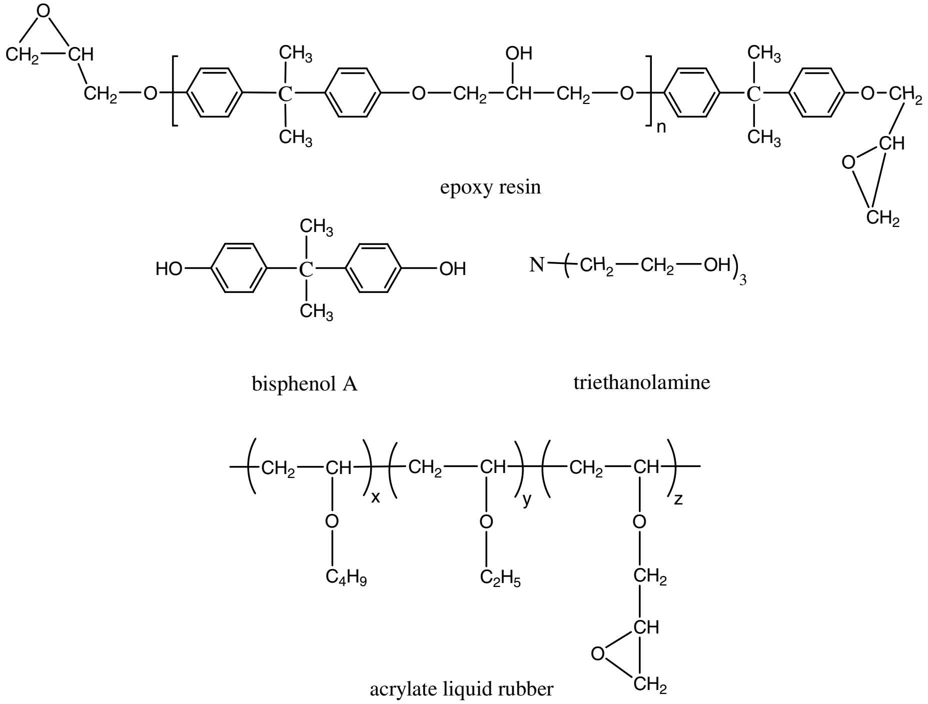

Figure 1. Molecular formula of epoxy resin, bisphenol A, hardener and acrylate liquid rubber containing pendant epoxy group

Preparation

Epoxy resin and bisphenol A were mixed uniformly at 120°C in advance. Then the mixture of epoxy resin/bisphenol A and liquid rubber were mixed together and heated to 80°C for 20min in oil bath, then the mixture were degassed in a vacuum oven for 20min. Once the mixture was cooling to 40°C, the hardener of 12phr was added under vigorous stirring. Then the mixture was casting into a polytetrafluoroethylene mould. After being degassed in a vacuum oven at 40°C, the system was heated and kept at 80°C for 2h, at 100°C for 2h, and at 120°C for 2h step by step. The post-cured treatment was conducted at 140°C for 2h in the oven equipped with a temperature controller.

Measurement

The impact strength was measured using standard Izod impact test method (GB/2568-1995). Tensile properties including tensile strength and elongation at break were determined via the standard testing method (GB/T2571-1995). Bending strength was measured using the standard testing method (GB/T2570-1995). The fracture toughness (G_{IC}) was determined via the double cantalever beam test method [26]. The fractured surfaces of samples were observed using scanning electron microscope (Amray Model-1000B). All the samples were coated with 5nm Au before observation.

Results and Discussion

The mechanical properties of epoxy resins modified by 5phr ALR with different content of epoxy group (epoxy/ALR system) were measured. The dependence of impact strength of epoxy/ALR system on content of epoxy group of ALR is presented in Figure 2. Compared with the native epoxy resins, the epoxy/ALR system possesses much higher impact strength and G_{IC} properties. The toughness efficiency is increased with the increase of content of epoxy group of ALR. The maximum value of impact strength and G_{IC} can be achieved when the content of epoxy groups of ALR is 1.2mmol/g. SEM images for the fracture surfaces of epoxy/ALR system are presented in Figure 3. For the ALR with high content of epoxy groups, the obvious shear yielding and stress white zones can be found on the fracture surface. It can be attributed to the high interface interaction of globular discrete phase and the epoxy resins matrix due to the reaction between the epoxy groups on rubber and matrix catalyzed by triethanolamine during the curing process. The results demonstrate that the high interface interaction between discrete phase and matrix can be helpful to enhance the toughness efficiency for epoxy/ALR system. It is interest that either impact strength or G_{IC} decrease at the content epoxy groups of 1.6mmol/g. This may be attributed to the high solubility of liquid rubber in epoxy, thus resulting in the small size of globular discrete phase.

On the other hand, the ductibility of epoxy resins matrix can be enhanced by the extended chain reaction using bisphenol A. Since the phenolhydroxide of bisphenol A can be reacted with epoxy groups catalyzed by triethanolamine at 120°C. As shown as in Table 1, the addition of bisphenol A enhances the impact strength and elongation at break of epoxy resin, which actually increases the ductibility of epoxy resin matrix.

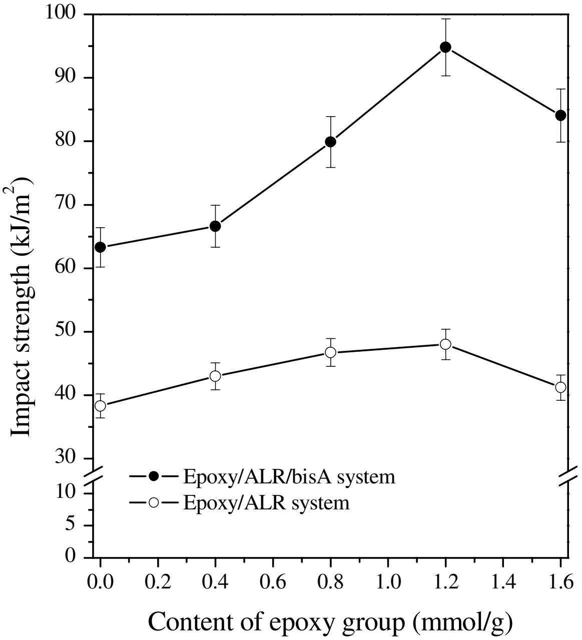

Figure 2. Dependence of impact strength for epoxy/ALR and epoxy/ALR/bisA systems on content of epoxy group of ALR

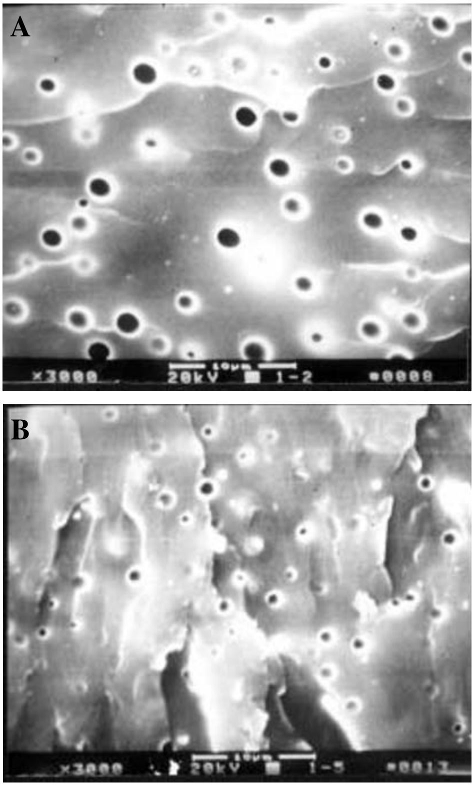

Figure 3. SEM images of fracture surfaces of epoxy/ALR system. A: modified by ALR with 0.4 mmol/g epoxy group, B: modified by ALR with 1.2 mmol/g epoxy group

Table 1. Mechanical properties of native epoxy resins and epoxy/bisA system

Resins	Bending strength (MPa)	Tensile strength (MPa)	Elongation at break (%)	Impact strength (kJ/m^2)	G_{IC} (kJ/m^2)
Native epoxy resins	121.7	69.3	3.6	27.6	0.54
Epoxy/ bisphenol A	102.3	57.1	4.8	47.2	1.6

Furthermore, the synergic effect of acrylate liquid rubber and bisphenol A on toughening efficiency of epoxy resins was investigated. As can be seen from Figure 2, the cured epoxy/ALR/bisA system containing 5phr of ALR and 24phr of bisphenol A shows high impact strength compared with that of epoxy resins modified only with ALR. The highest impact strength of epoxy/ALR/bisA system is 94.0kJ/m^2, while the impact strength of epoxy/ALR system is 48.0kJ/m^2. It demonstrates that much higher toughness efficiency can be achieved for the epoxy/ALR/bisA system by the incorporation of bisphenol A.

The plots of G_{IC} of epoxy/ALR system and epoxy/ALR/bisA system against content of epoxy groups of ALR are presented in Figure 4. It shows higher increase in fracture toughness of epoxy/ALR/bisA system than that of epoxy/ALR system. The

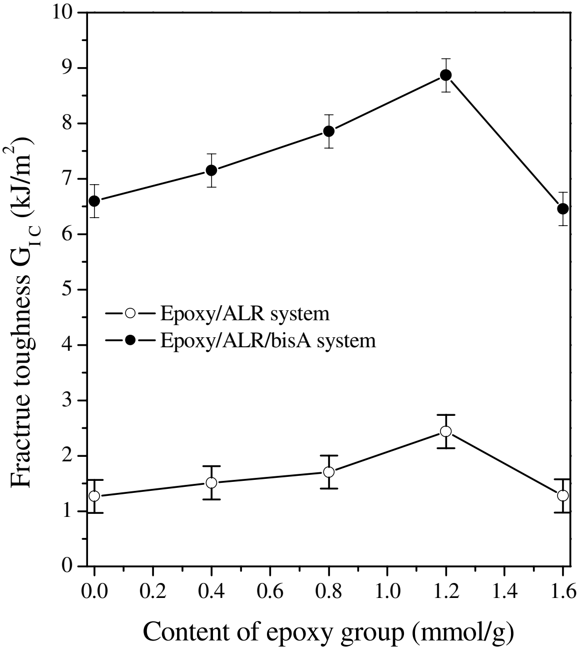

Figure 4. Dependence of G_{IC} for epoxy/ALR and epoxy/ALR/bisA systems on content of epoxy group of ALR

value passes through a maximum when the content of epoxy groups of ALR is 1.2mmol/g. The maximum of G_{IC} of epoxy/ALR/bisA system is about 8.9kJ/m^2, which are about 266% higher than that of epoxy/ALR system (2.43kJ/m^2). It further demonstrates the synergic promotion effect of acrylate liquid rubber and bisphenol A on toughening efficiency of epoxy resins.

The enhanced toughness efficiency in both impact strength and G_{IC} can be explained by the phase morphology of modified epoxy resins. SEM images for the fracture surfaces of epoxy/ALR/bisA system are presented in Figure 5. In the case of unmodified epoxy resins, smooth glassy fracture surface with cracks in different planes can be observed in Figure 5A. The brittle fracture model may explain its low impact strength to some degree. In contrast, the fracture surface of epoxy/ALR/bisA system shows discrete globular rubber in epoxy resin matrix in Figure 5B. The globular rubber particles dispersed in the matrix phase can act as centers for dissipation of mechanical energy by cavitations and shear yielding during the fracture process [27]. It can be confirmed by the existence of cavitations in rubber particles and the according stress white zone around rubber particles in Figure 5B. Due to the increased ductility of the matrix, it is interesting that special stress white zones are found on the fracture surface of epoxy/ALR/bisA system as presented in Figure 5C and D. There exist large stress white zone and high plastic deformation near the crack tip prior to failure of fracture surface for epoxy/ALR/bisA system. The two-phase morphology and resultant large stress white zones and high shear yielding are the important reasons for the enhanced impact strength and G_{IC} of the epoxy/ALR/bisA system.

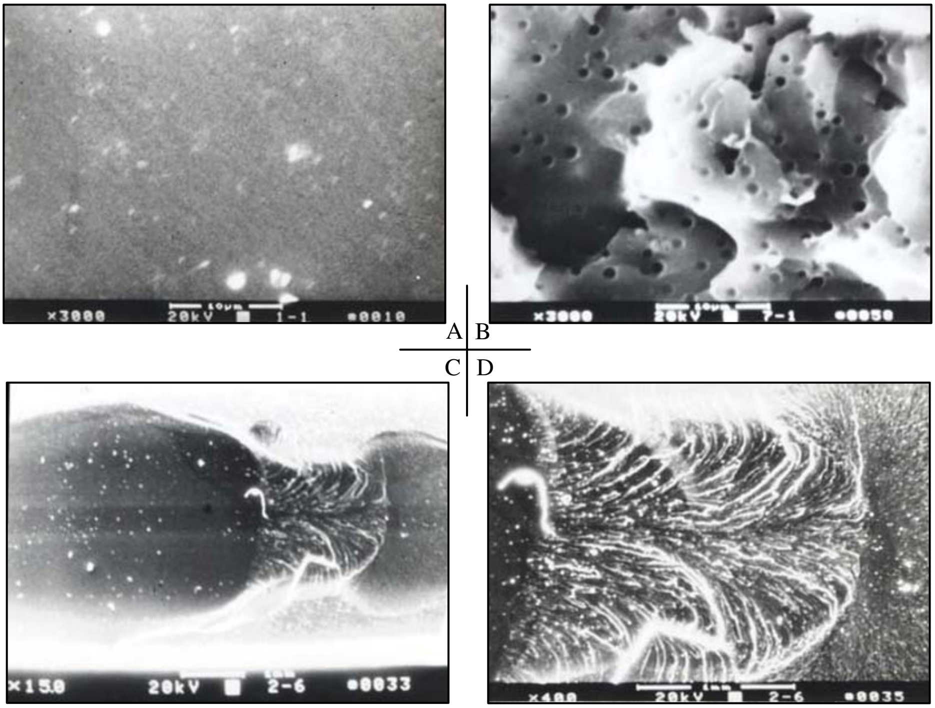

Figure 5. SEM images of fracture surfaces epoxy/ALR/bisA system. A: unmodified epoxy; B: epoxy/ALR/bisA system, C: stress white zone, D: stress white zone

Conclusions

The interface interaction is controlled by the content of epoxy group of employed ALR and the high interface interaction between discrete phase and matrix can enhance the toughness property for epoxy/ALR system. The addition of bisphenol A enhances the impact strength and elongation at break of epoxy resin and actually increases the ductibility of epoxy resin matrix. Much higher toughness efficiency can be achieved for the ALR modified epoxy resins by the incorporation of bisphenol A. The synergic promotion effect of acrylate liquid rubber and bisphenol A on the toughness efficiency of epoxy resins can be attributed to the two-phase morphology and the resultant large stress white zones and high shear yielding during the fracture process.

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References

1. Thomas R, Durix S, Sinturel C, Omonov T, Goossens S, Groeninckx G, Moldenaers P, Thomas S (2007) Polymer 48:695
2. Kaynak C, Ozturk A, Tincer T (2002) Polym Int 51:749
3. Thomas R, Durix S, Sinturel C, Omonov T, Goossens S, Groeninckx G, Moldenaers P, Thomas S (2007) Polymer 48:695
4. Chikihi N, Fellahi S, Baker M (2002) Eur Polym J 38:251-264

5. Ratna D, Banthia AK (2007) Polym Eng Sci 47:26
6. Frohlicha J, Kautza H, Thomanna R, Freyb H, Mulhaupt R (2004) Polymer 45:2155
7. Yıldız E, Özarslan Ö, İnan TY, Kuyulu A, Güngör A (2007) Polym Bull 58:503
8. Hydro RM, Pearson RA (2007) J Polym Sci, Part B: Polym Phys 45:1470
9. Goossens S, Goderis B, Groeninckx G (2006) Macromolecules 39:2953
10. Brunner AJ, Necola A, Rees M, Gasser P, Kornmann X, Thomann R, Barbezat M (2006) Eng Fract Mech 73:2336
11. Rosso P, Ye L, Friedrich K, Sprenger S (2006) J Appl Polym Sci 100:1849
12. Moniruzzaman M, Du FM, Romero N, Winey KI (2006) Polymer 47:293
13. Verchere D, Sautereau H, Pascault JP, Moschair SM, Riccardi CC, Williams RJJ (1990) J Appl Polym Sci 41:467
14. Devi A, Srivastava D (2007) Mater Sci Eng A 458:336
15. Shukla SK, Srivastava D (2007) J Mater Sci 42:3215
16. Wise CW, Cook WD, Goodwin AA (2000) Polymer 41:4625
17. Chikhi N, Fellahi S, Baker M (2002) Eur Polym J 38:251
18. Ozturk A, Kaynak C, Tincer T (1986) Eur Polym J 37:2353
19. Ratna D, Simon GP (2001) Polymer 42:7739
20. Ratna D, Banthia AK, Deb PC (2000) J Appl Polym Sci 78:716
21. Kar S, Banthia AK (2003) Pigm Res Tech 32:69
22. Ratna D, Banthia AK (2000) Polym Int 49:281
23. Iijima T, Tomoi M, Suzuki A, Kakiuchi H (1991) Eur Polym J 27:851
24. Iijima T, Horiba T, Tomoi M (1991) Eur Polym J 27:1231
25. Kong J, Ning RC, Tang YS (2006) J Mater Sci 41:1639
26. Wiederhorn SM (1968) J Appl Phys 39:1569
27. Erchere DV, Pascault JP, Sautereau H, Moschair SM, Riccardi CC, Williams RJJ (1991) J Appl Polym Sci 42:701