

Modification of Epoxy by a Liquid Elastomer and Solid Rubber Particles

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Summary

This work covers studies on epoxy resin systems modified with two different rubber phases. The first modification was the use of recycled car tire rubber particles; while in the second one a silicon based liquid elastomer (Tegomer) was mixed with the epoxy resin matrix. In the third method epoxy resin was modified with both solid rubber particles and liquid elastomer together.

Mechanical tests showed that these modifications resulted in no significant improvements in the mechanical performance of the epoxy resin system. Fractographic studies indicated that poor interfacial adhesion was occurred between the epoxy matrix and the solid rubber particles, while liquid elastomer resulted in formation of round rubbery domains and some plastic deformation lines in the epoxy matrix. For better improvements interfacial phenomenon will be explored.

Introduction

The commonly known approaches for toughening brittle epoxies include chemical modification of a given rigid epoxy backbone to a more flexible backbone structure, increase of epoxy monomer molecular weight, lowering of the crosslink density of the cured resin and finally incorporation of dispersed toughener phases in the cured epoxy matrix.

Among these methods, toughening via dispersed toughener phases has been shown to be the most effective and can provide an order of magnitude toughness improvement. However, only the highly toughenable epoxies modified with rubber tougheners are known to produce such an important toughening effect. These highly toughenable ductile epoxies exhibit rather low glass transition temperatures and low crosslinking densities. Thus, they are not suitable for high temperature applications and researches are focused on toughness improvements of highly crosslinked densities. The cause for such a disappointing result is largely attributed to the high crosslinking densities of epoxy. This reduces the local molecular mobility of the resin. As a result, crack pinning and crack bridging types of toughening mechanisms which are relatively low in energy absorption are dominant. Some researches indicate that the high crosslink density brittle epoxies can undergo shear yielding–banding as long as the stress state favors such mechanisms. Therefore it seems to be possible to toughen high crosslink

density epoxy polymer via shear yielding–banding mechanisms, the toughener phase can change the crack tip stress state from one that favors brittle fracture to one that undergoes shear yielding.

In order to toughen epoxies effectively, the fundamental physics of toughening must be understood. All possible operative toughening mechanisms and their relative effectiveness in toughened epoxies must be known. Using reactive liquid rubbers such as carboxyl terminated or amine terminated butadiene acrylonitrile (CTBN or ATBN) copolymer, or hydroxyl terminated polybutadiene (HTPB) is one alternative for the toughening mechanism [1-11]. By this application, the liquid rubber is miscible with the epoxy resin at first. The phase separation occurs during curing where CTBN, ATBN or HTPB forms a dispersed phase of domains having diameters of a few microns.

In these studies [1-11], CTBN, ATBN or HTPB liquid rubbers were used for DGEBA (diglycidyl ether of bisphenol A) type epoxy resin. They concluded that high toughness value of liquid rubber modified epoxy systems were due to an increase in the plastic zone size. The rubber domains induced the plastic flow which is recognized as the shear banding of the matrix around particles. These researchers also showed that, for significant plastic shear banding to operate under constrained conditions, cavitation of the toughener phase is essential, via internal rubber domain cavitation, debonding at the interface, or crazing mechanisms. In other words, there is a sequence of toughening events. This is simply; cavitation occurs first, followed by shear banding.

As an alternative to the use of reactive liquid elastomers for the rubber modification of epoxy resins, some researchers [12-19] used solid rubber particles for instance recycled car tire particles. The advantage of this method is the control of particle size and volume fraction. Compatibility of the epoxy resin with the rubber particle can be achieved by some surface treatment techniques. In selecting rubber tougheners, the type of rubber, size and dispersion of the rubber particles are very important depending on the application. The use of soluble rubbers to toughen epoxies can bring lowering the T_g , difficulty in morphology control and poor reproducibility of the product performance. These disadvantages are not desirable in many applications. Studies with solid rubber particle modified epoxy systems shows that the highly crosslinked brittle epoxies can undergo shear yielding around the propagated crack tip. The major toughening mechanisms for these systems are found to be the cavitation of the rubber particles, followed by the formation of a shear yielded zone around the propagated crack. If this rather small scale yielding can be extended, an increase in fracture toughness can be observed.

The study of the effect of rubber particle dispersion in epoxy toughening brings a concept concerning approaches for toughening optimization. The dispersion of the rubber particles can influence the toughening mechanisms. Moreover, if combinations of certain mechanisms coexist during the toughening process, a synergistic toughening effect can be obtained. Beside the use of one toughener phase, there are some investigations which study the effect of using several phase on toughening mechanism. The combination of hard zirconia with rubber particles were used in order to toughen epoxy systems by Low [3]. The hard zirconia improved the toughness value by crack pinning or particle fracture. Another mechanism is the deflection of the crack front due to the generation of a larger crack tip opening displacement. The resulting fracture toughness shows that there is a synergistic effect of using both zirconia and rubber.

Bagheri and Williams [5] used a reactive liquid elastomer (CTBN) together with surface treated recycled solid rubber particles in a DGEBA type epoxy resin. They showed that while the recycled rubber particles improved fracture toughness value, by less than 20%, the CTBN introduction increased the value by about 200%. The reason for this difference lies in crack deflection, particle cavitation and shear yielding mechanisms. The results also revealed synergistic toughening when both modification phases were introduced. The toughening mechanism is the plastic zone branching caused by interaction of the stress field of particles with that of the crack tip. The stress field associated with rubber particles enhanced cavitation of neighboring CTBN domains and stretched the shear deformation from the crack tip towards the large particles. Plastic zone branching mechanism enlarged the effective damage zone size and increased the resistance to crack growth.

A similar synergistic effect was observed by Boynton and Lee [4] when CTBN and solid rubber particles were used together. They observed no significant improvements in toughness when they used liquid elastomer and rubber particles separately. However, they concluded that when liquid and solid rubber particles were used together, the fracture toughness increased synergistically resulting from the crack deflection and localized shear yielding.

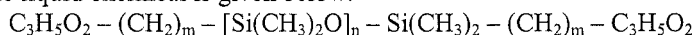
The objective of present study was to investigate the performance of the DGEBA type epoxy resin when modified with a liquid elastomer (Tegomer) and solid recycled car tire rubber particles, first separately for each and then together.

Materials, Specimen Preparation and Testing

The materials used to prepare samples to be tested were the epoxy resin system (with crosslinking agent and accelerator), granulated recycled tire rubber particles, and a liquid elastomer (Tegomer).

Diglycidyl ether of bisphenol A – DGEBA (Ciba–Geigy/LY556) was used as epoxy resin, while *methyl tetra hydro phthalic anhydride* (Ciba–Geigy/HY917) and *tertiary amine* (Ciba–Geigy/DY062) were used as hardener and accelerator, respectively. The ratio of epoxy, hardener and accelerator in the final slurry mixture to compose the matrix was 10:9:0,2 by weight, respectively.

The liquid elastomer used to modify epoxy was α , ω – glycidylorganofunctional polydimethyl siloxane (Goldschmidt/Tegomer E – Si 2330). The structure of this water white liquid chemical is given below:



Solid rubber particles used as a second epoxy modifier were prepared by grinding recycled car tyres (Lassa) cryogenically down to a particle size below 180 μm .

Solid rubber particles were mixed with the matrix slurry in composition of 5% by volume with respect to the amount of the mixture. Liquid elastomer material Tegomer was mixed with three different concentrations; 2.5, 5.0 and 7.5 % by volume. Besides the use of solid rubber particles and liquid elastomer separately, one set of samples were also prepared using these two together. In this set, the concentration of solid rubber particles was the same (5% v) and that of liquid Tegomer was 2% by volume.

After mixing the liquid elastomer and solid rubber particles in the slurry of epoxy system (resin+hardener+accelerator) mechanically, the mixture was poured into the test specimen moulds. The moulds which were made of PTFE (polytetrafluoroethylene), were then put in an oven at a temperature of 90°C for 1 hour

in order to prevent bubble formation and better mixing. After 1 hour, they were put in another oven at a temperature of 140°C for 3 hours for curing.

Tensile tests were performed according to ASTM D638 M-91a standard with the specimen dimensions of M-III type in this standard. Tensile tests were performed using a Lloyd screw-driven universal testing machine with a loading rate of 10 mm/min. Charpy impact tests were performed according to ASTM D256-91a standard with unnotched specimens by using a pendulum impact tester of Coesfeld Material Test. Plane-strain fracture toughness tests were performed according to ASTM D5045-91a standard with single edge notched bend specimens again by using Lloyd universal testing machine. All these tests were conducted for four sets of specimens;

- Neat epoxy specimens
- Epoxy specimens modified with 5%(v) solid rubber particles
- Epoxy specimens modified with three different concentrations (2.5, 5.0, 7.5 % (v)) of liquid elastomer (Tegomer)
- Epoxy specimens modified with 5%(v) solid rubber particles and 2%(v) liquid elastomer

For each test and each specimen sets, at least six specimens were tested, and the specimen designation used in this study is indicated in detail in Table 1. The final part of the experimental work consists of fractographic studies of the fracture toughness test specimens under a scanning electron microscope Jeol JSM-6400.³ Before SEM examination fracture surfaces were cleaned using an ultrasonic cleaner and sputtered with gold.

Table 1. Specimen designation used

E	Neat epoxy matrix
ER	Epoxy modified with 5%v solid rubber particles
ET2.5	Epoxy modified with 2.5%v liquid elastomer (Tegomer)
ET5.0	Epoxy modified with 5.0%v liquid elastomer (Tegomer)
ET7.5	Epoxy modified with 7.5%v liquid elastomer (Tegomer)
ERT	Epoxy modified with 5%v solid rubber particles and 2%v liquid elastomer

Results and Discussion

Results obtained from the tension tests are tabulated in Table 2 as elastic modulus (E), tensile strength (σ_{TS}) and elongation at break (ϵ_f) values. Young's modulus which is the ratio of stress to strain in the linear elastic region of the curve is known to be related to the stiffness of the polymer. The results obtained from Charpy impact (a_n) and plane-strain fracture toughness (K_{IC}) tests are tabulated in Table 3. These tables indicate that addition of solid rubber particles had no improvements in these mechanical properties. On the other hand, modification with liquid elastomer (Tegomer) led to slight increases. It was also observed that there was no significant synergistic effect of using solid rubber particles and liquid elastomer together.

The main reason of having no improvement in solid rubber modification can be explained by the incompatibility of the particles with the epoxy resin matrix. Hydrophobic rubber particles do not make a good interlocking with the matrix which is mostly hydrophilic. SEM fractographs in Figure 1 show the poor interfacial bonding achieved between the solid rubber particles and epoxy matrix. Of course there are other reasons cited in the literature such as size, distribution etc. of the particles.

Table 2. Tensile test results

Specimen Designation	Elastic Modulus E (GPa)	Tensile Strength σ_{TS} (MPa)	Strain at Break ε_f (%)
E	2.99 ± 0.02	73.8 ± 2.2	3.1 ± 0.1
ER	2.86 ± 0.02	52.8 ± 2.1	2.7 ± 0.1
ET2.5	2.81 ± 0.05	62.6 ± 1.5	3.3 ± 0.1
ET5.0	3.22 ± 0.01	70.4 ± 3.2	2.9 ± 0.3
ET7.5	3.31 ± 0.02	68.2 ± 2.5	2.8 ± 0.2
ERT	2.80 ± 0.07	56.7 ± 6.0	2.4 ± 0.5

Table 3. Charpy impact and plane-strain fracture toughness test results

Specimen Designation	Impact Toughness a_n (kJ/m ²)	Fracture Toughness K_{IC} (MPa√m)
E	8.88 ± 0.65	0.61 ± 0.01
ER	4.73 ± 0.86	0.53 ± 0.02
ET2.5	8.66 ± 0.72	0.29 ± 0.01
ET5.0	8.79 ± 0.52	0.48 ± 0.08
ET7.5	8.39 ± 0.81	0.32 ± 0.03
ERT	8.49 ± 0.21	0.42 ± 0.05

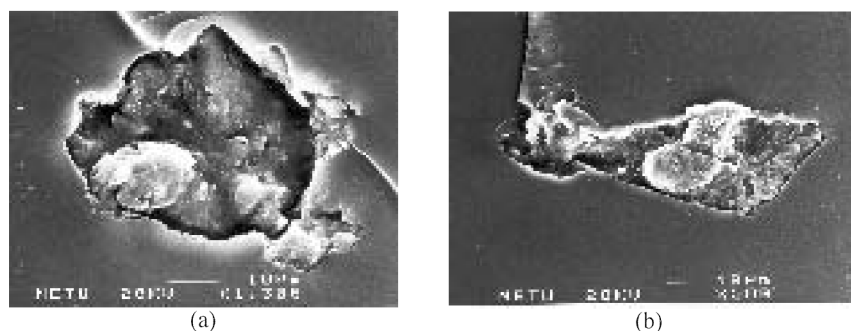
**Figure 1.** (a) and (b) very weak interfacial adhesion between the solid rubber particles and epoxy matrix

Figure 2 shows that when epoxy was modified with liquid elastomer, there were two main morphological changes. The first one was the formation of round shaped rubber domains, and the second one was the deformation lines observed which may be considered as some kind of plasticity obtained in the structure. These microstructural changes (rubber domains and deformation lines) due to the addition of liquid elastomer led to slight improvements in the mechanical performance of the epoxy matrix as compared to the addition of solid rubber particles. Among the three different liquid elastomer concentrations used, 5%(v) resulted in better results.

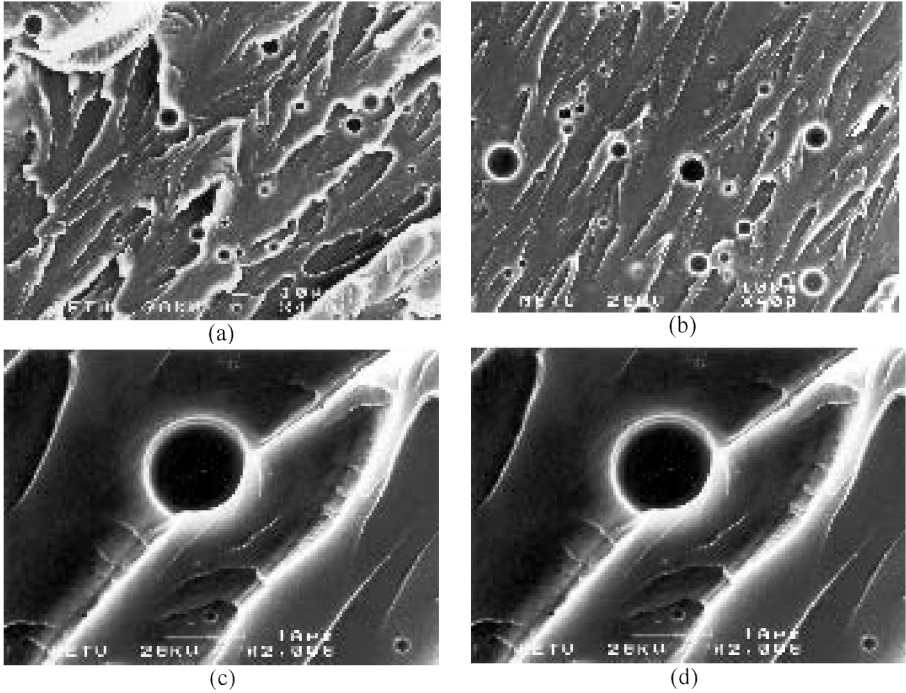


Figure 2. Round shaped rubber domains and plastic deformation lines formed due to the modification of epoxy with liquid elastomer (Tegomer), (a) and (b) general views, (c) and (d) closer views

Figure 3 indicates that when both solid rubber particles and liquid elastomer was added to the epoxy matrix together, similar morphological changes were obtained as in the previous cases; weak interfacial adhesion between the solid rubber particles and the epoxy matrix, and the formation of rubber domains and plastic deformation lines. These changes did not lead to significant synergistic improvement in the mechanical properties of the samples.

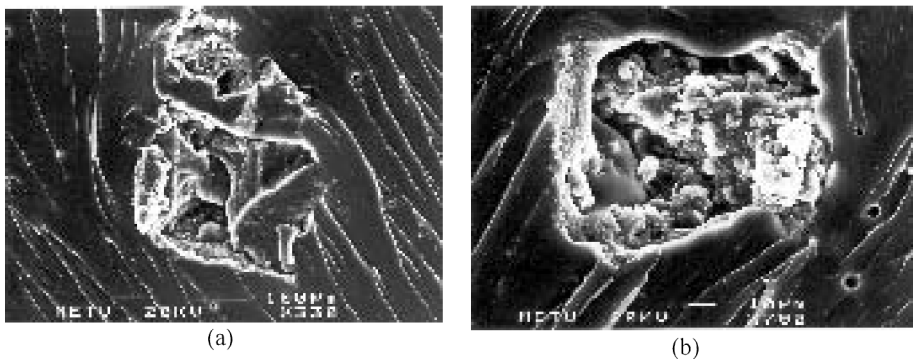


Figure 3. (a) and (b) SEM fractographs of epoxy modified with solid rubber particles and liquid elastomer (Tegomer) together

In the previous studies [12-16] including the works of Saglam, Celikbilek, Akovali and Kaynak [17,18,19], it was shown that if surfaces of rubber particles were modified with an efficient surface treatment techniques (e.g. plasma methods, use of silane coupling agents, etc.), better interfacial adhesion could be obtained between the rubber particles and epoxy matrix leading to improved mechanical performances of the samples. Therefore, this work will be continued with further interfacial exploration.

Conclusion

- When epoxy was modified with solid rubber particles there were no improvements in the mechanical performance of the samples due to mainly very poor interfacial adhesion between the rubber particles and epoxy matrix.
- When epoxy was modified with liquid elastomer (Tegomer), slight increases were observed in the mechanical behaviour of the samples which should be mainly due to the formation of round rubber domains and plastic deformation lines.
- When epoxy was modified with both solid rubber particles and liquid elastomer, no significant synergistic effect was observed in the mechanical performance of the samples.
- Therefore, it may concluded that in order to use car tyre rubber particles as filler or toughening agent, better interfacial adhesion should be achieved for instance by using certain surface treatment techniques on the surfaces of rubber particles. This will be performed in the second stage of this work.

References

1. Bagheri R., Perason RA (1995), *J App Polym Sci* 58:427
2. Bascom WD, Cottington RL, Jones RL, Peyser P (1975) *J App Polym Sci* 19:2425
3. Low IM (1990) *J Mater Sci*, 25:2144
4. Boynton MJ, Lee A (1997) *J App Polym Sci* 66:271
5. Bagheri R, Williams MA; Pearson RA (1997) *Polym Eng Sci* 37:2
6. Douglas SK, Beaumont PWR, Ashby MF (1980) *J Mater Sci* 15:1109
7. Sue HJ, Yee AF (1989) *J Mater Sci* 24:1447
8. Ozturk A, Kaynak C, Tincer T (2001) *Eur Polym J* 37:2353
9. Kaynak C, Ozturk A, Tincer T (2002) *Polym Int* 51:749
10. Arikan A, Kaynak C, Tincer T (2002) *Polym Composites*, 23:790
11. Kaynak C, Arikan A, Tincer T (2003) *Polymer* 44:2429
12. Yee AF, Pearson RA (1986) *J Mater Sci* 21:2462
13. Yee AF, Pearson RA (1986) *J Mater Sci* 21:2475
14. Yee AF, Pearson RA (1989) *J Mater Sci* 24:2571
15. Yee AF, Pearson RA (1991) *J Mater Sci* 26:3828
16. Parker DS, Sue HJ, Huang J, Yee AF (1990) *Polymer* 31:2267
17. Kaynak C, Saglam ES, Akovali G (2001) *Polymer* 42:4393
18. Saglam ES, Kaynak C, Akovali G, Yetmez M, Akkas N (2001) *Polym Eng Sci* 41:514
19. Kaynak C, Celikbilek C, Akovali G (2003) *Eur Polym J* 39:1125