

Recent advances in the anionic photocurable Epoxy/thiol-ene systems

Abstract

This review discusses the characteristics of the epoxy/thiol-ene systems such as high reactivity and the improvement of toughness of the obtained polyether-polythioether co-network. This review also examines the applications of this system in the preparation of glass-fiber reinforced epoxy resins (GFREC), shape memory materials (SMP), foamed epoxy polymers and self-healing polymers.

Keywords: epoxy resins, thiol-ene, toughness, foamed epoxy polymers, self-healing, shape memory, glass-fiber epoxy composites

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Introduction

Epoxy resins are highly utilized in the industrial sector due to several advantages including superior mechanical properties, chemical and heat resistance, low shrinkage, high adhesivity and low toxicity.¹ However, one of the main drawbacks is the inherent fragility due to the high level of crosslinking in these materials. Because of this aspect, several methods to improve their toughness have been reported.^{2,3} Our research group focused on improving the toughness of photocurable epoxy resins by concurrently polymerizing them with a thiol-ene system.^{4,5} Thiol-ene photopolymerization has recently been classified as “click” chemistry because virtually any kind of thiol can react very rapidly under mild conditions, with any unsaturated compound, even in the presence of oxygen, to produce polythioethers.⁶ Recent investigations by our group have demonstrated that simultaneous anionic polymerization of an epoxy resin and a thiol-ene system result in the formation of homogeneous polymeric materials with improved toughness.⁷ This result is due to the flexible polythioethers that originate during thiol-ene photopolymerization. The epoxy/thiol-ene system was composed of an epoxy resin such as the diglycidyl ether of bisphenol A (DGEBA), and the thiol-ene system, The thiol-ene system included a curing agent of the tertiary amine type, such as N¹, N¹, N⁶, N⁶ tetraallyl hexane-1,6-diamine (ALA4) and a radical photoinitiator like dimethoxyphenyl acetophenone (DMPA) (Figure 1). The formulations were subjected to a simultaneous dual photo-thermal cure at 85°C and a 40mW/cm², while varying the molar concentration of the thiol-ene system in the epoxy resin. This epoxy/thiol-ene system was demonstrated to be highly reactive achieving full conversion in less than 10 minutes.⁸ This reactivity can be described to the presence of several initiating species such as the tertiary amine, thiolate, and thioethers groups. They are all basic species that are able to react with the oxirane groups promoting their anionic ring opening polymerization (Figure 2). It can be seen that the tertiary amine attacks the epoxide groups which undergo Hoffman intramolecular rearrangement to produce vinyl alkoxide responsible for the initiation of the anionic ring opening polymerization of the oxirane groups. The tertiary amines are also able to undergo acid-base reaction with the thiol groups to produce thiolates. These species are basic enough to anionically attack the epoxide groups. At the same time the thiol groups can react with the double bonds of the curing agent to produce

polythioethers. When the concentration of the polythioethers is significant, they can also attack the residual epoxy groups to achieve full conversion of the epoxide groups depending on curing conditions.

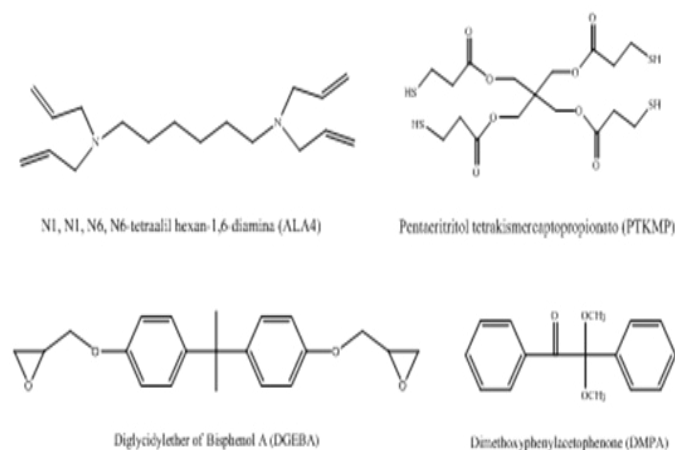


Figure 1 Components of the photocurable epoxy/thiol-ene system.

Discussion

We have taken advantage of the properties of these epoxy/thiol-ene systems to prepare glass-fiber reinforced epoxy composites (GFREC), shape memory materials (SMP), foamed epoxy resins and self healing epoxy systems.

Glass-Fiber Reinforced Epoxy Composites (GFREC)

Regarding the glass-fiber composites, our photocurable glass-fiber/epoxy formulations using the thiol-ene system as initiator were completely cured in 400 seconds despite the fact that the inner layers of the composite were unlikely to be reached by the UV irradiation.⁹ The optical pyrometry results indicated that the heat released during the photopolymerization helped to achieve full conversion of the epoxy groups. The modulus of these glass-fiber reinforced composites were as high as 24500MPa when the glass fiber content was 70 % (Figure 3). According to DMA analysis the T_g of the composites were 110°C. The flexural resistance displayed by the GFREC was 1045MPa when a trifunctional thiol was used in comparison with a

value of 1232MPa for the tetrafunctional thiol, as a result of the higher degree of crosslinking achieved. Therefore this method could be a more economic and efficient option to cure GFREC instead of the thermal curing method.

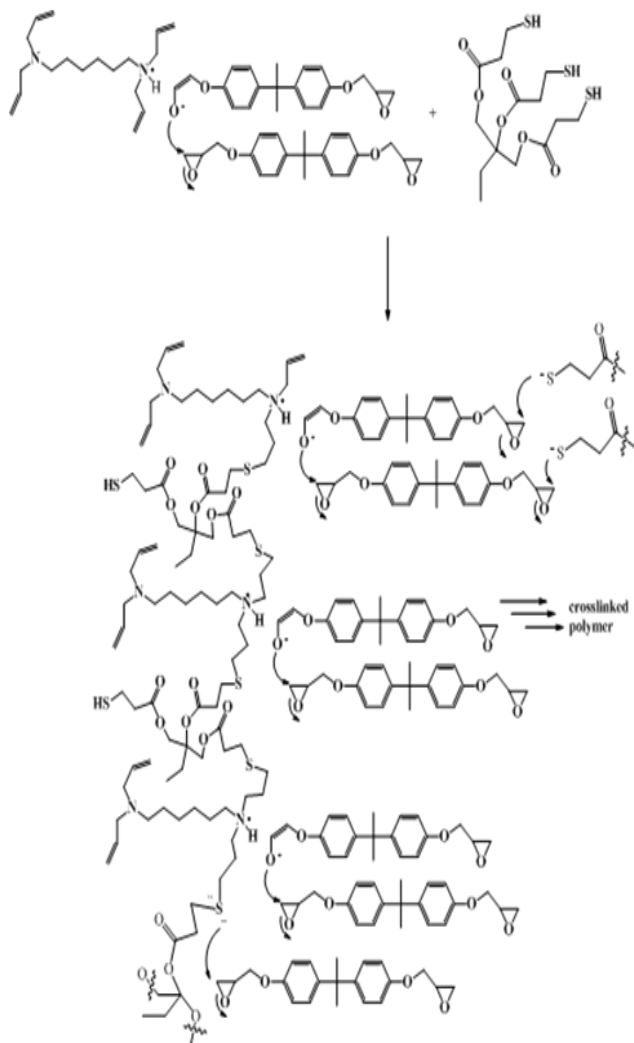


Figure 2 Proposed Mechanism for the photocurable anionic epoxy/thiol-ene systems. Reproduced with permission of Springer, Scheme 5 of reference 5.

Shape Memory Materials (SMP)

The presence of the flexible polythioethers in the co-network with the polyethers derived from the epoxy resin, resulted in a material with shape memory properties.¹⁰ The polythioethers derived from the thiol-ene system were in the “soft-phase” which induced this shape memory phenomenon. It was found that the polymer obtained by adding 10mol% of the thiol-ene system to the epoxy resin was deformed when heated above the T_g (87°C) and the form preserved by cooling at 4°C. The polymer was recovered in its original form in 13 seconds when heated above its T_g (Figure 4). It is worth mentioning that the storage modulus of these materials were as high as 3500MPa. When the concentration of the thiol-ene system was augmented to 20mol% the polymer recovered the original shape in 27 seconds because of the increased amount of the flexible polythioethers, reducing in this way the stress in the hard phase of the co-network, which is the driving force to recover the original form of the deformed polymer. The

polymer was cured with 10mol% of the thiol-ene system at 85°C and 40mW/cm² of UV light intensity, during 400s. The polymers were deformed: A) when heated at 90°C and the form preserved by cooling the polymer at 4°C. The original form was recovered B) when the sample was heated at 90°C.

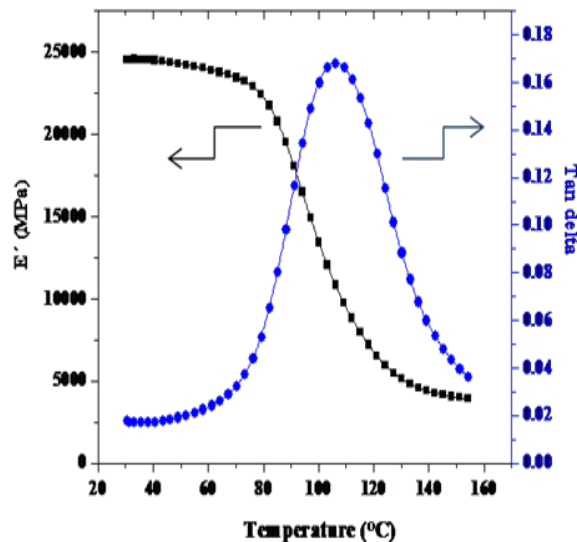


Figure 3 Storage modulus and tan delta of the prepared GFREC with 68% of glass fiber. Reproduced with permission of Springer, Figure 6 of reference 9.

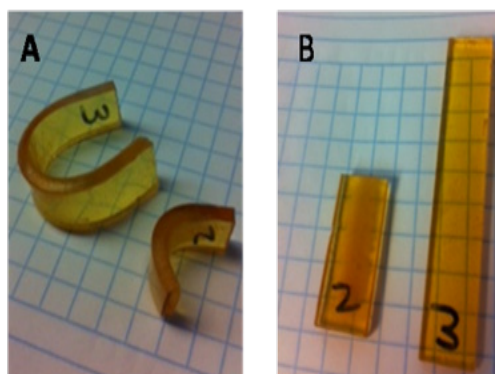


Figure 4 Photographs of the polymers derived from the epoxy/thiol-ene system.

Self-healing epoxy polymer

Self-healing properties are highly desirable in a material whether it is ceramic, metal or polymer. Both extrinsic and intrinsic methods have been tested.¹¹ One of the intrinsic approaches to achieving self-healing properties is by introducing functional groups in the polymer that can undergo dynamic Exchange reactions between reversible covalent bonds. Several photochemical reactions have been used such as the Diels-Alder reaction, cycloaddition reaction [2+2], cycloadditions [4+4], exchange reaction of siloxanes segments, and disulfide exchange to name a few examples.¹² In our epoxy/thiol-ene systems, given that a tetrafunctional thiol was used, it was thought that disulfide bonds could be introduced in the polymer if the tetrafunctional thiol was partially oxidized, generating an oligomer with both thiol and disulfide bonds.¹³ This way, the thiol groups could react with the double bonds of the curing agent inducing the anionic polymerization of the epoxy resin and at the same time introducing disulfide bonds in the resulting polymer. The best method to obtain the

desired thiol-disulfide oligomer was by oxidizing the PTKMP with iodobenzenediacetate in a 1:1 stoichiometry relationship.

An oligomer with a molecular weight of 1837 daltons was obtained. The number of functional groups of this oligomer was determined by ^1H NMR which found 8 thiol groups and 4 disulfide bonds in the chemical structure (Figure 5). When the formulation that included DGEBA, ALA4 and the oxidized oligomer was photopolymerized, in the same conditions described above for the conventional epoxy/thiol-ene system, a rigid polymer with a T_g of 73°C was obtained. The test specimens with a 2mm thickness were cut in half and then heated at different temperatures until the two pieces were joined into one piece. It was determined that the Polymer was completely healed in 10 minutes when heated at 80°C or for 500 minutes at room temperature (Figure 6). Further, it was determined through DMA that the healed specimen retained the mechanical properties in comparison with the control specimen. It is important to note that it was possible to get the self-healing epoxy polymers derived from the epoxy resins DGEBA, despite the rigidity of the specimen that displayed a T_g of 73°C .

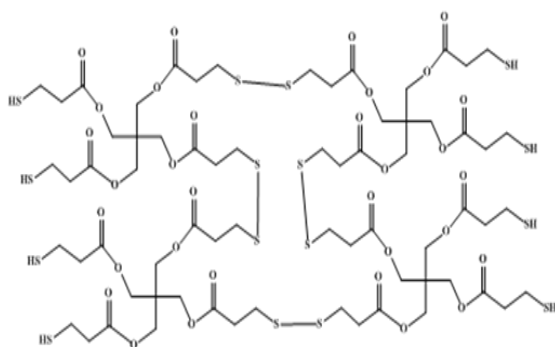


Figure 5 Chemical structure of the obtained thiol-disulfide oligomer responsible for the self healing properties in the polymer derived from the epoxy/thiol-ene system.

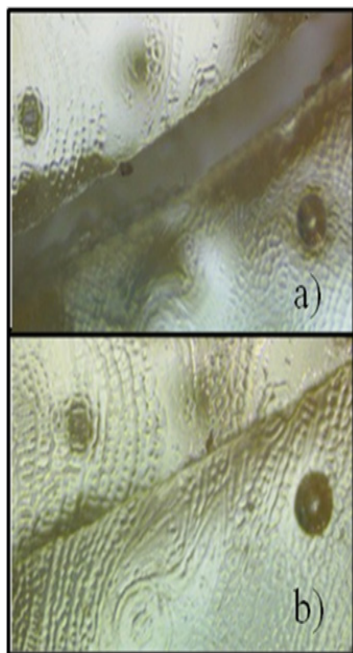


Figure 6 Photographs of the self-healing process of the test specimen derived from the anionic epoxy /thiol-ene system, (A) after the specimen was cut in half, (B) after the self-healing process at 70°C .

Epoxy foams

Another direct application of the anionic epoxy/thiol-ene system is the preparation of epoxy foams, just by adding a chemical foaming agent. Though several foaming agents were tested, only the benzenesulfonyl hydrazide (BSH) was able to produce the epoxy foams. The foaming process was influenced by the concentration of the thiol-ene system (20-40mol%) in the epoxy formulation. At a higher concentration of the thiol-ene system there was a dilution effect reducing the viscosity of the epoxy resin, producing epoxy foams with smaller pore size. The density of the epoxy foams was in the range of 366Kg/m^3 , 788Kg/m^3 . Figure 7 shows a photograph of the foamed test specimens with different concentrations of the thiol-ene system. The specimen with 20mol% of the thiol-ene systems showed bigger pore size while the specimen with 40 mol% of the thiol-ene system displayed a more smaller and more uniform pore sizes.

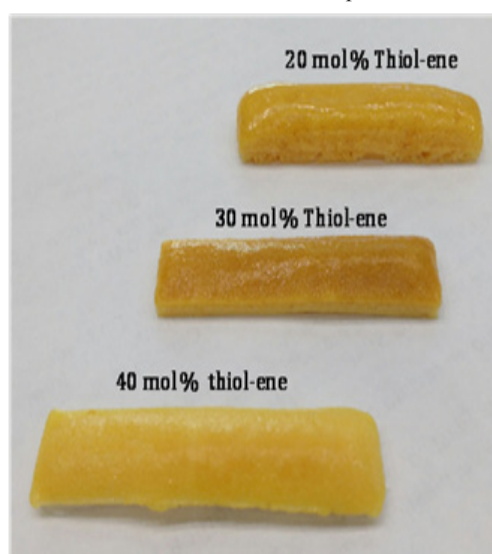


Figure 7 Photographs of the foam test specimens derived from the formulation with DGEBA using concentrations of the thiol-ene system in the range of 20mol%-40mol%.

Conclusion

This paper demonstrated the versatility of the photocurable anionic epoxy/thiol-ene. The high reactivity and the excellent mechanical properties of the derived polymers, allowed us to utilize this process in different applications such as GFREC, SMP, self-healing epoxy polymers and epoxy foams.

Acknowledgements

None.

Conflict of interest

The author declares no conflict of interest.

References

1. May CA. *Epoxy Resins: Chemistry and Technology 2nd ed.* New York, USA: Marcel Dekker Inc; 1988.
2. Ahmad BH, Bakar A, Azlina M, et al. Manufacture of epoxy resin/liquid rubber blends. Thomas C editor. *Micro and Nanostructured Epoxy/Rubber Blends*. Singapore: Wiley-VCH; 2014. p. 73–81.

3. Sprenger S. Epoxy Resins modified with elastomers and Surface modified silica nanoparticles. *Polymer*. 2013;54(18):4709–4797.
4. Acosta Ortiz R, Puente Urbina BA, Cabello Valdez LV, et al. The effect of introducing a cationic system into a Thiol-Ene Photopolymerizable Formulation. *Journal of Polymer Science Part A: Polymer Chemistry*. 2007;45(21):4829–4843.
5. Acosta Ortiz R, Garcia Valdez AE, Navarro Tovar AG, et al. Development of an hybrid epoxy-amine/thiol-ene photocurable system. *Journal of Polymer Research*. 2014;21:504.
6. Hoyle CE, Bowman CN. Thiol-ene click chemistry. *Angewandte Chemie International Edition*. 2010;49(9):1540–1573.
7. Acosta Ortiz R, Garcia Valdez AE. Synthesis, reactivity and mechanical properties of photocurable epoxy-thiol-ene systems. Marcus L Cain editor. *Epoxy resins: Synthesis, Applications and Recent Developments*. New Jersey, USA: Nova Publishers; 2016.
8. Acosta Ortiz R, Garcia Valdez AE, Sangermano M, et al. Comparison of the performance of two bi functional curing agents for the photopolymerization of epoxy resins and the study of the mechanical properties of the obtained polymers. *Macromol Symp*. 2015;358(1):35–40.
9. Acosta Ortiz R, Garcia Valdez AE, Garcia Padilla EE, et al. Development of a photocurable glass-fiber reinforced epoxy-amine/thiol-ene composite. *Journal of Polymer Research*. 2016;23:30.
10. Berlanga Duarte ML, Acosta Ortiz R, Garcia Valdez AE, et al. Preparation and study of epoxy shape memory polymers. Proceedings of the Macromex 2014 meeting, Puerto Vallarta, Mexico; 2014.
11. Yang Y, Urban M. Chemical and physical aspects of self-healing materials. *Progr Polym Sci*. 2015. p. 49–50.
12. Yoon JA, Kamada J, Koynov K, et al. Self-healing polymer film based on thiol-disulfide exchange reactions and self-healing kinetics measured using atomic force microscopy. *Macromolecules*. 2012;45(1):142–149.
13. indawi.com/journals/amse/2016/8245972/