

Synergistic Effect of Hydroxyl-containing Acrylates in Epoxide-Acrylate Hybrid Photopolymerizations

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Abstract

Epoxide-acrylate hybrid systems promise to reduce sensitivity of the photopolymerization to oxygen and moisture. An hydroxyl-containing acrylate was paired with a diepoxide to promote the faster Activated Monomer (AM) mechanism, resulting in increased epoxide conversion. Conversion profiles and physical properties were obtained using real-time Raman spectroscopy and dynamic mechanical analysis, respectively. As the acrylate concentration was increased from 50 to 80wt%, the epoxide conversion increased from 55 to 85%, indicating that the hydroxyl-containing acrylate facilitated the AM mechanism. Similarly, the glass transition temperature of the hybrid polymers decreased from 175 to 150°C, with little or no indication of phase separation.

Introduction

Hybrid photopolymerizations, which contain two functional groups polymerized by independent reaction mechanisms, have arisen in recent years. For example, free-radical and cationic photopolymerization systems like epoxide-acrylate¹⁻³ and acrylate-vinyl ether^{4,5} hybrid systems have been reported. This study focuses on epoxide/acrylate hybrid systems, which have been shown to mitigate oxygen inhibition⁵⁻⁷ and moisture problems⁸ that plague free-radical and cationic polymerizations, respectively. In addition, acrylates act as plasticizers, reducing the glass transition temperature (T_g) and decreasing the brittleness of the resulting polymer compared to the neat epoxide polymer.

Despite the advantages of epoxy-acrylate hybrid resins, low conversions and slow curing rates of the epoxides continue to be problematic since the acrylate polymer forms first, limiting development of the epoxide chains.⁹ Propagation of the cationically polymerizable monomers, such as epoxides, proceeds through the active chain end (ACE) mechanism;¹⁰ however, the presence of a proton donor in the system, such as an alcohol, can facilitate a secondary reaction pathway, namely the activated monomer (AM) mechanism.¹¹ In this chain transfer reaction, cationic active centers react with a proton donor to form a diol (i.e., activated monomer), which may participate in further chain transfer reactions, and to regenerate the initiating proton.¹² In this study, hydroxyl-containing meth/acrylates were used to facilitate the faster AM mechanism in order to increase epoxide conversion and rate of polymerization and to lower the T_g compared to the neat epoxide polymer without inducing phase separation in the hybrid polymer.

Experimental

Materials

Epoxide-acrylate hybrid formulations were made by varying the weight percent of 2-hydroxyethyl methacrylate (HEMA, BASF) or 2-hydroxyethyl acrylate (HEA, BASF) and 3,4-epoxycyclohexane carboxylate (EEC, Union Carbide). 2,2-Dimethoxy-2-phenyl-acetophenone (DMPA, Aldrich) was used

to initiate the free-radical (meth/acrylate) reaction, while diaryliodonium hexafluoroantimonate (DAI, Sartomer) was used to initiate the cationic (epoxide) ring opening. All materials were used as received; the structures are shown in Figure 1.

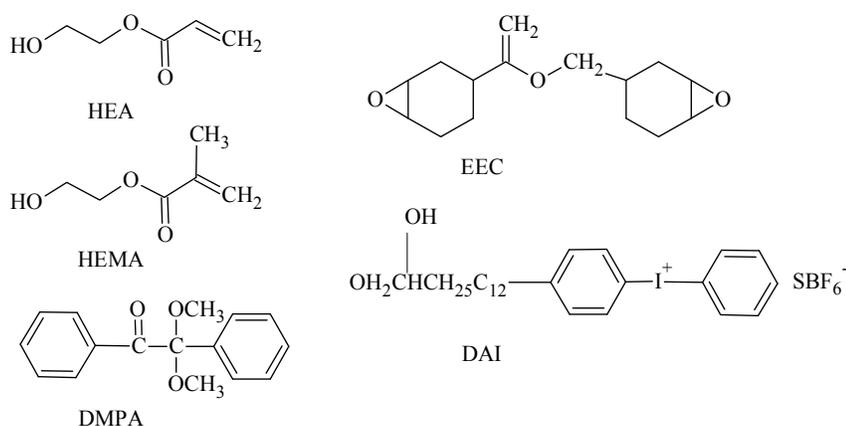


Figure 1. Molecular structures of material used in this study

Methods

Raman spectroscopy was used to monitor the rate and conversion of epoxide and meth/acrylate moieties in real time. A 785-nm near-infrared laser was used to induce the Raman scattering effect, and the Mark II holographic fiber-coupled stretch probehead (Kaiser Optical Systems, Inc.) attached to the HoloLab 5000R modular research Raman spectrograph was used to obtain spectra of the hybrid formulations during photopolymerization. The exposure time for spectra was 200 ms. Samples were cured isothermally at 30°C in 1-mm ID quartz capillary tubes using an Acticure® Ultraviolet/Visible Spot Cure System (EFOS, 250-450nm band pass filter) with an effective irradiance of 100 mW/cm². The effective irradiance was measured using a radiometer (EFOS, R5000). The conversion (α) of each reactive moiety was calculated from the collected Raman spectra using:

$$\alpha = 1 - \frac{A_{rxn}(t)}{A_{rxn}(0)} \quad 1$$

where $A_{rxn}(t)$ is the peak area of the reactive band at a given time, t , in the reaction and $A_{rxn}(0)$ is the peak area of the reactive band before the reaction begins. The reactive bands representing the meth/acrylate C=C double bond and epoxide ring are located at 1640 and 790 cm⁻¹, respectively. Since the spectral baselines were constant throughout the experiment, a reference band was not needed.

A dynamic mechanical analyzer (DMA, Q800, TA) was used to measure the glass transition temperature, which was identified as the temperature corresponding to the maximum of the tan delta (δ) peak, for the hybrid polymer samples. Polymer samples were obtained by sandwiching the epoxy-acrylate hybrid formulations between two glass plates (separated by 150 μ m glass cover slips) and then illuminating for 15 min using the EFOS, 250-450 nm band pass filter curing system with an effective irradiance of 100 mW/cm². The polymerized samples were also conveyed through a Fusion UV system (BF9H2) with a belt speed of 2 ft/min to allow for complete cure. The cured polymer was then placed in an oven at 150°C for 2 hours to ensure full reaction before physical and mechanical properties were obtained.

Result and Discussion

In this study, the synergistic effect of hydroxyl-containing meth/acrylates on the kinetic and physical properties of a commonly used cycloaliphatic diepoxide was studied for photopolymerized epoxy-acrylate hybrid formulations. The meth/acrylate monomer composition in the hybrid formulations was varied from 0 to 100wt% in the presence of a dual photoinitiator system containing 0.5wt% DAI and 0.17 wt% of DMPA. Raman spectroscopy was used to measure the meth/acrylate and epoxide conversions during the hybrid photopolymerizations, while dynamic mechanical analysis provided a measure of the T_g and phase separation for the resulting hybrid polymers.

Free-radical Photopolymerization in Epoxide-Acrylate Hybrid Formulations

Both HEA and HEMA polymerized readily when exposed to UV irradiation in the presence of the dual photoinitiator system (representative HEMA data are shown in Figure 2). The high conversion and rate of polymerization for these hydroxyl-containing monomers are facilitated by hydrogen bonding, which mitigates termination reactions due to reduced polymer radical mobility.¹³ In addition, the presence of the acid produced during the decomposition of cationic photoinitiator (DAI) can increase the rates a result of electrostatic interactions.¹⁴ As expected, the conversion and rate of the neat methacrylate HEMA were lower than the neat acrylate HEA,¹⁵ however, HEMA conversion and rate were enhanced in the hybrid formulations.

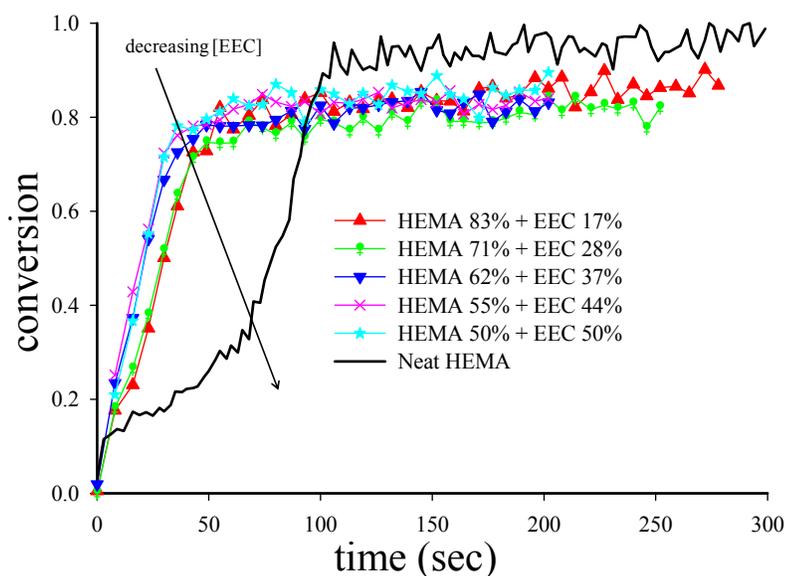


Figure 2: Acrylate C=C conversion for hybrid formulations of EEC-HEMA with 0.5wt% DAI and 0.17wt% DMPA at 30°C and with an effective irradiance of 100 mW/cm².

Cationic Ring-opening Photopolymerization in Epoxide-Acrylate Hybrid Formulations

The conversion of EEC increased dramatically from 15% in the neat epoxide to over 55% in the hybrid formulations (representative data for EEC-HEMA hybrid formulations are shown in Figure 3). The rate of epoxide polymerization also increased with increasing meth/acrylate content. These results demonstrate that epoxy rate and conversion can be increased by taking advantage of the hydroxyl group

in the meth/acrylates to facilitate the faster AM mechanism. In addition, the meth/acrylates may also serve as diluents for the epoxide photopolymerization, but this contribution is small compared to the impact of the hydroxyl groups (studies not shown).

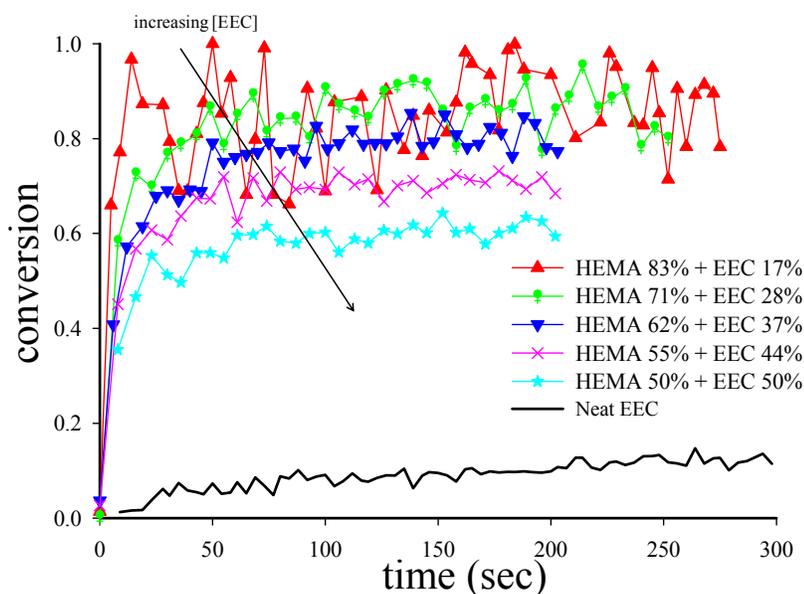


Figure 3: Epoxide ring conversion for hybrid formulations of EEC-HEMA with 0.5wt% DAI and 0.17wt% DMPA at 30°C and with an effective irradiance of 100 mW/cm².

Physical Properties of Epoxide-Acrylate Hybrid Photopolymers

As EEC concentration increased, the T_g of the hybrid polymers increased from 210°C for the neat epoxide to 150°C in the formulation with 83% HEMA and to 50°C with 83% HEA (representative data for EEC-HEMA hybrid formulations are shown in Figure 4). As the meth/acrylate content increased, the left-hand shoulder of the $\tan \delta$ peak disappeared, indicating reduced phase separation as the EEC and meth/acrylate polymer domains were covalently connected through the hydroxyl group via the AM mechanism. Thus, low toughness of epoxides can be reduced by judiciously incorporating hydroxyl-containing meth/acrylates with the desired flexibility.

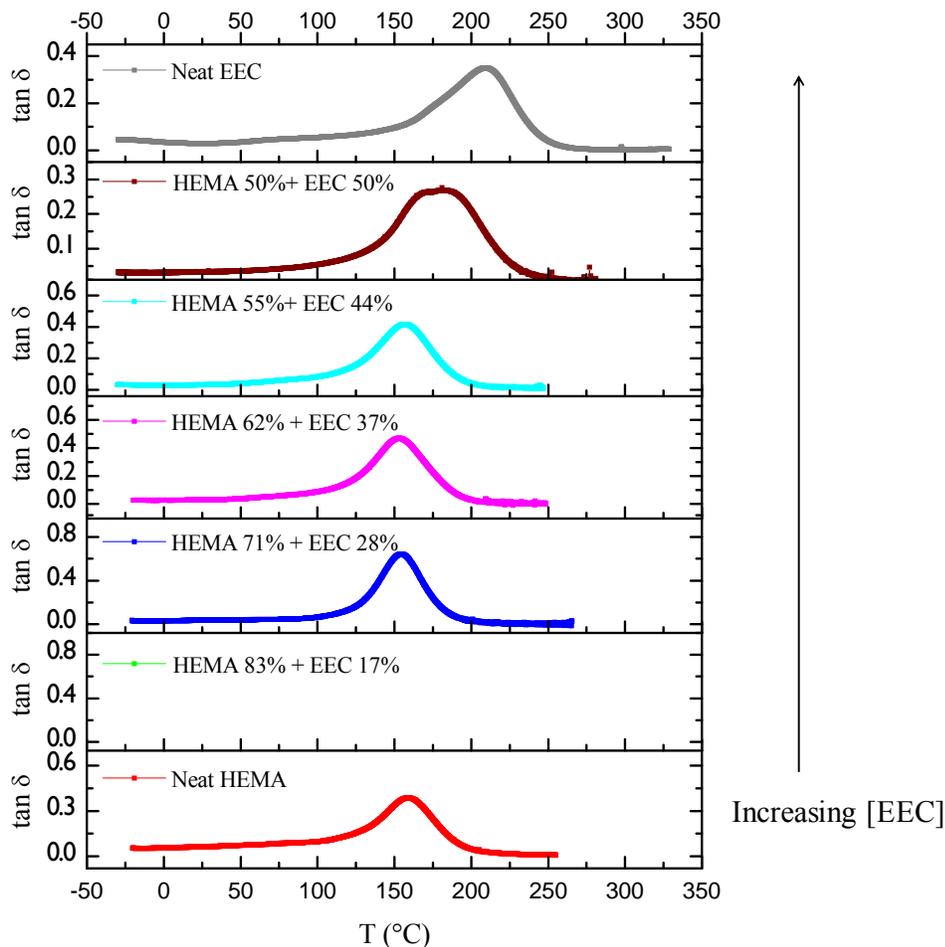


Figure 4: $\tan \delta$ plots, obtained by DMA, of EEC-HEMA polymers. Hybrid formulations were photopolymerized with 0.5wt% DAI and 0.17wt% DMPA at 30°C for 15 min using an effective irradiance of 100 mW/cm², and the resulting polymers were heat treated at 150°C for 2 hours.

Conclusion

Epoxide conversion and rate of polymerization in epoxide-acrylate hybrid monomer systems were shown to increase through the introduction of a hydroxyl group on the meth/acrylate monomer, taking advantage of the faster AM mechanism. In addition, this covalent bond linking the epoxide network to the meth/acrylate polymer chains resulted in little or no phase separation and a reduction of the T_g for the hybrid polymer compared to the neat epoxide.

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References

1. Decker, C. UV-Radiation Curing of Acrylate/Epoxy Systems. *Polymer*. 2001;42:5531-5541.
2. Oxman, J.D.; Jacobs, D.W.; Trom, M.C.; Sipani, V.; Ficek, B.; Scranton, A.B. Evaluation of Initiator Systems for Controlled and Sequentially Curable Free-radical/cationic Hybrid Photopolymerizations. *Journal of Polymer Science Part A: Polymer Chemistry*. 2005;43:1747-1756.
3. He, Y. Photopolymerization Kinetics of Cycloaliphatic Epoxy-Acrylate Hybrid Monomer. *Polymer International*. 2007;56:1292-1297.
4. Rajaraman, S.K.; Mowers, W.A.; Crivello, J.V. Interaction of Epoxy and Vinyl Ethers during Photoinitiated Cationic Polymerization. *J Polymer Science Part A*. 1999;37:4007-4018.
5. Lin, Y.; Stansbury, J.W. Kinetics studies of hybrid structure formation by controlled photopolymerization. *Polymer*. 2003;44:4781-4789.
6. Studer, K. Overcoming Oxygen Inhibition in UV-curing of Acrylate Coatings by Carbon dioxide Inerting: Part II. *Progress in Organic Coatings*. 2003;48:101-111.
7. Cai, Y.; Jessop, J.L.P. Decreased Oxygen Inhibition in Photopolymerized Acrylate/Epoxy Hybrid Polymer Coatings as Demonstrated by Raman Spectroscopy. *Polymer*. 2006;47:6560-6566.
8. Crivello, J.V. Photoinitiated Cationic Photopolymerization. *Annual review of materials science*. 1983;13:173-190.
9. Decker, C. Photoinitiated Crosslinking Polymerization. *Progress in Polymer Science*. 1996;21:593-650.
10. Bednarek M, Kubisa P, Penczek S. Coexistence of Activated Monomer and Active Chain End Mechanisms in Cationic Copolymerization of Tetrahydrofuran with Ethylene oxide. *Macromolecules*. 1999;32:5257-5263.
11. Brzezinska, K.; Szymanski, R.; Kubisa, P.; Penczek, S. Activated Monomer Mechanism in Cationic Polymerization, 1. Ethylene Oxide, Formulation of Mechanism. *Die Makromolekulare Chemie, Rapid Communications*. 1986;7:1-4.
12. Ghosh, N.; Palmese, G. Electron-Beam Curing of Epoxy Resins: Effect of Alcohols on Cationic Polymerization. *Bulletine of Material Science*. 2005;28:603-607.
13. Lee, T.Y. The Effect of Monomer Structure on Oxygen Inhibition of (Meth)Acrylates Photopolymerization. *Polymer*. 2004;45:6155.
14. Kabanov, V.A.; Topchiev, D.A.; Karaputadze, T.M.; Mkrtchian, L.A. Kinetics and Mechanism of Radical Polymerization of Weak Unsaturated Acids in Aqueous Solutions. *European Polymer Journal*. 1975;11:153-159.
15. Kilambi, H. Deconvoluting the Impact of Intermolecular and Intramolecular Interactions on the Polymerization Kinetics of Ultrarapid Mono(Meth)Acrylates. *Macromolecules*. 2007;40:47-54.