Enhancing Kinetics and Tuning Physical Properties via Grafted Networks of Epoxide/Acrylate Hybrid Photopolymerizations

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Abstract

Hybrid systems of epoxides, which undergo cationic polymerization, and acrylates, which undergo free-radical polymerization, have been shown to reduce oxygen sensitivity during photopolymerization. However, slow reaction and low conversion of the epoxides, as well as phase separation of the two polymer networks, remain problematic. These problems are mitigated by inducing the activated monomer mechanism through use of hydroxyl-containing acrylates. The amount of hydroxyl-containing acrylate provides control of the epoxide kinetics and the overall network homogeneity.

Introduction

Hybrid systems containing epoxide and acrylate reactive functional groups hold great promise for addressing long-standing challenges that plague the photopolymerization industry. Issues such as light penetration, oxygen inhibition, and shrinkage stress continue to limit photopolymerization applications in some areas, as well as result in increased processing costs.[1] The synergy between the two orthogonal reaction mechanisms (*i.e.*, free-radical polymerization for the acrylate moiety and cationic ring-opening polymerization for the epoxide moiety) provides targeted solutions to these issues. For example, earlier research with epoxide/acrylate hybrid monomers (*i.e.*, the epoxide and acrylate reactive functional groups are on the same monomer) has shown reduced oxygen sensitivity in systems that contain both cationic and free-radical photoinitiators.[2] Increased epoxide conversion at the surface of the curing films prevented oxygen diffusion into the films, thereby enabling higher acrylate conversions throughout the remainder of the films and eliminating surface tackiness.

In order for hybrid systems to be more widely applicable, hybrid monomer mixtures (*i.e.*, the epoxide and acrylate reactive functional groups are on different monomers) must also be considered. However, photopolymerization of 3,4-epoxycyclohexane carboxylate (EEC), which is commonly used in the photopolymerization industry, is typically slow with low conversions and results in brittle polymers.[3] Exploiting the activated monomer (AM) mechanism in these cationic systems offers a way to address these disadvantages, increase the ability to tailor the polymer properties, and control phase separation between the acrylate and epoxide polymer domains.

Traditional propagation in cationic ring-opening systems proceeds through the active chain end (ACE) mechanism.[4] If hydroxyl groups are present (*e.g.*, water or alcohols), then chain transfer can occur through the AM mechanism.[5] For cyclic ethers such as EEC, the propagation rate constant for the AM mechanism can be approximately five times higher than that of the ACE mechanism.[6] Previous studies have shown that increasing the hydroxyl concentration in EEC improves polymerization kinetics (polymerization rate and conversion) and systematically lowers the glass transition temperature (T_g).[3]

In this study, the beneficial impact of hydroxylated acrylates is demonstrated in formulations with the cycloaliphatic epoxide EEC. The effect of hydroxyl content on epoxide reaction rate and conversion was determined using Raman spectroscopy, while changes in polymer T_g and network homogeneity were determined using dynamic mechanical analysis (DMA). These results can be used as guiding principles to ameliorate key weaknesses of cationic ring-opening polymerization outcomes, enabling the exploitation of epoxide/acrylate hybrid monomer mixtures for photopolymerization applications.

Experimental

Materials

Epoxide/acrylate hybrid formulations were made with 3,4-epoxycyclohexane carboxylate (EEC, Sigma Aldrich) by varying the content of acrylate from 0 to 100 wt% in increments of 10 wt%. The AM mechanism was promoted through 2-hydroxyethyl acrylate (HEA, Sigma Aldrich), while the non-hydroxyl-containing ethylene glycol methyl ether acrylate (EGMEA, Sigma Aldrich) served as a control.   Formulations contained 0.5 wt% of the photoacid generator 4-(2-hydroxyl-1-tetradecyloxy)-phenyl] phenyliodonium hexafluoroantimonate (DAI, Polyset) and 0.2 wt% of the α-cleavable free-radical photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, Sigma Aldrich). All materials were used as received (Figure 1).
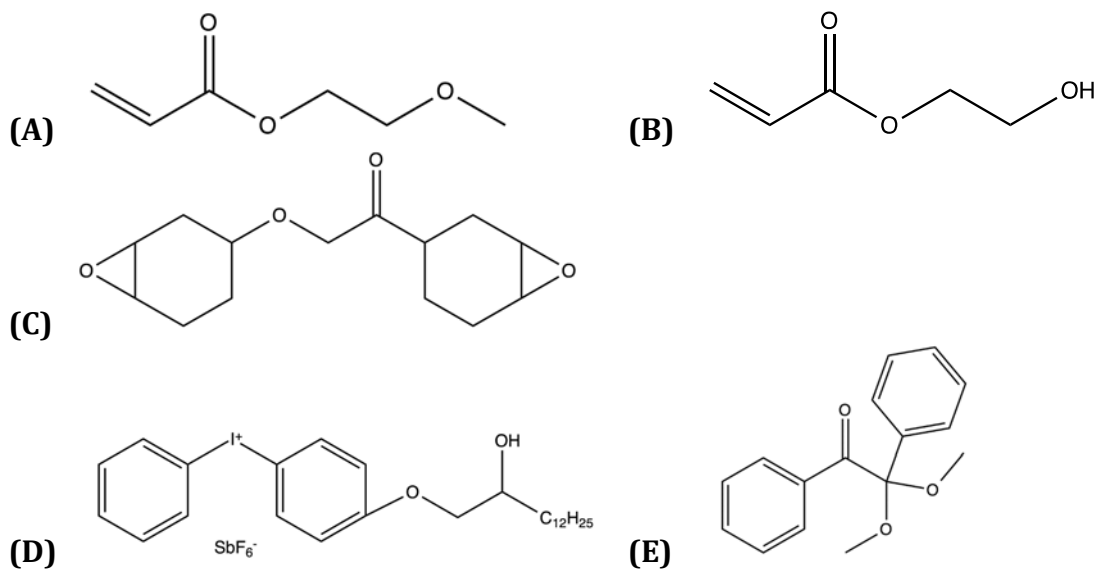

Figure 1. Monomers used in this study: (A) EGMEA, (B) HEA, and (C) EEC; photoinitiators used in this study: (D) DAI and (E) DMPA.

Methods

Kinetic studies using Raman spectroscopy

Real-time Raman spectroscopy was used to measure conversion of epoxide and acrylate moieties during photopolymerization. Epoxide/acrylate hybrid formulations were cured at ambient temperature in 1-mm ID quartz capillary tubes using an Acticure® Ultraviolet/Visible Spot Cure System (EFOS, 250-450 nm band pass filter) with an effective irradiance of 140 mW/cm^2 as measured by a radiometer (OmniCure, Model No. R2000). Raman spectra were gathered before and during the photopolymerization using a holographic probehead (Mark II, Kaiser Optical Systems, Inc.) with a single-mode excitation fiber delivering ~220 mW of 785-nm near-infrared laser intensity to the sample through a 10× non-contact sampling objective. The probehead was connected to a modular research Raman spectrograph (HoloLab 5000R, Kaiser Optical Systems, Inc.). Spectra were collected continuously for 5 min with an exposure time of 250 ms. The conversion (α) of each reactive moiety was calculated separately using from the collected Raman spectra using Equation 1:

$$\alpha = 1 - \frac{I_{rxn}(t)}{I_{rxn}(0)} \qquad (1)$$

where $I_{rxn}(t)$ is the peak intensity of the reactive band at a given time, t, in the reaction and $I_{rxn}(0)$ is the peak intensity of the reactive band before the reaction at time zero. The reactive bands representing the acrylate C=C double bond and epoxide ring are located at 1640 and 790 cm^{-1}, respectively.[7] Since the spectral baselines were constant throughout the experiments containing HEA and EGMEA, a reference band was not needed. Because the lower concentrations have small peak intensities, which introduce noise in the conversion data, the data presented were smoothed using a 5-point moving average in Microsoft Excel.

Physical property studies using dynamic mechanical analysis

Polymer films were tested using dynamic mechanical analysis (DMA) to obtain the glass transition temperature (T_g), full width at half maximum (FWHM) of the tan δ peak, and the cross-link density. Molds consisting of two silanized (Rain-X treated) glass slides sandwiched with 300 μm glass cover slip spacers were used to prepare the epoxide/acrylate hybrid films. Formulations in the glass molds were irradiated using an Omnicure® S1000 Ultraviolet/Visible Spot Cure System (Excelitas, 250-450 nm band pass filter) with an adjustable collimating lens attachment (Lumen Dynamics, Model No. 810-00041) and an effective irradiance of 140 mW/cm^2 as measured by a radiometer (Versaprobe Pro, Con-Trol Cure). Samples were irradiated immediately before testing to minimize dark cure (*i.e.*, continued polymerization after the initiating light source is removed) of the epoxide, with the exception of neat EEC. Neat EEC only formed a usable film approximately 5 h post-illumination. After removal from the molds, samples were cut to approximately 6.25 mm × 25 mm and tested in a dynamic mechanical analyzer (Q800, TA Instruments) equipped with a film tension clamp. A mono-frequency strain, temperature ramp sequence was used to collect storage modulus and T_g values as a function of temperature. Temperature was increased at a rate of 3°C/min over a broad temperature range at a constant oscillating frequency of 1 Hz and a sinusoidal strain of 0.05%. The temperature ramp was repeated twice for each sample since annealing occurs at elevated temperatures in the first cycle. All DMA data were reported from the second temperature ramp.

Results and Discussion

Due to chain transfer via the AM mechanism, hybrid monomer systems containing hydroxylated acrylates pose a unique opportunity to improve EEC kinetics and to tune hybrid polymer properties. The following results demonstrate the influence of [OH] on polymer conversion and tan δ profiles by considering a series of hybrid monomer formulations with increasing amounts of non-hydroxyl-containing vs. hydroxyl-containing acrylate.

Effect of hydroxyl concentration on epoxide kinetics

Increasing the [OH] in the hybrid monomer mixtures resulted in faster epoxide polymerization rates and higher conversions (Figure 2), as has been described in systems with water[7] and alcohol[3] present. Under the conditions of this study, the conversion of neat EEC is ~10% after 5 min of illumination. As the concentration of the control acrylate (EGMEA) increased, EEC conversion decreased to a point at which it was negligible. Since the free-radical reaction is much faster, the acrylate polymerized first, impeding formation of the epoxide network. However, as the concentration of the hydroxylated acrylate (HEA) increased, EEC conversion was equal to or greater than the neat EEC value. When the EEC conversion exceeded the neat EEC value, a minimum [OH] was present in order for the AM mechanism to dominate – here, in formulations with 40 wt% or less EEC. The AM mechanism, enabled by the OH on the acrylate, facilitates ring-opening of the epoxide and mobility of the cationic active center even when trapped amidst the acrylate polymer chains.
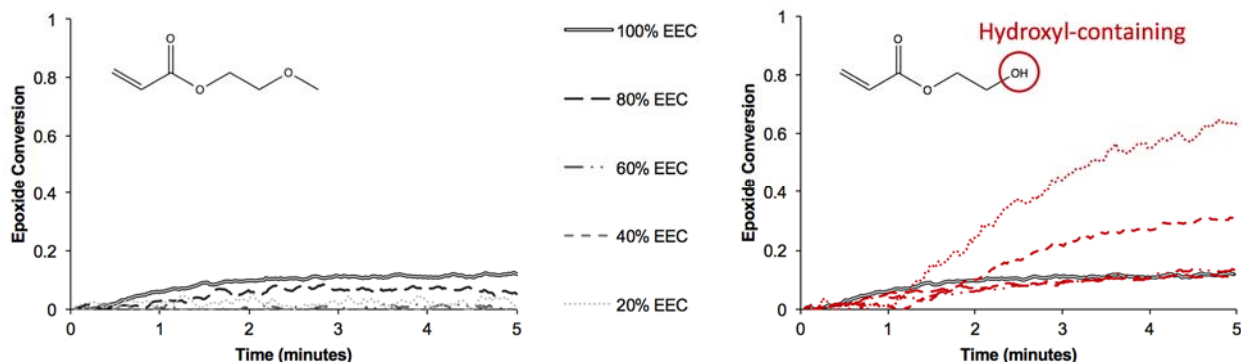

Figure 2. Hybrid formulations containing HEA (right) exhibit faster rates of polymerization and higher epoxide conversions above a minimum threshold hydroxyl concentration (≤ 40 wt% epoxide) compared to equivalent formulations with the EGMEA control (left). Conversion data were obtained via Raman spectroscopy.

In order to confirm that this phenomena was not solely due to viscosity effects, formulations with equivalent viscosity and epoxide content were compared (Figure 3). The conversion of both the control (EGMEA) and hydroxylated (HEA) acrylates was over 95%. However, EEC conversion in the presence of the hydroxylated acrylate was 60%, while the EEC conversion in the presence of the control acrylate was less than 5%. Thus, the increase in epoxide polymerization rate and conversion is due to the presence of the hydroxyl group and not simply a dilution effect.
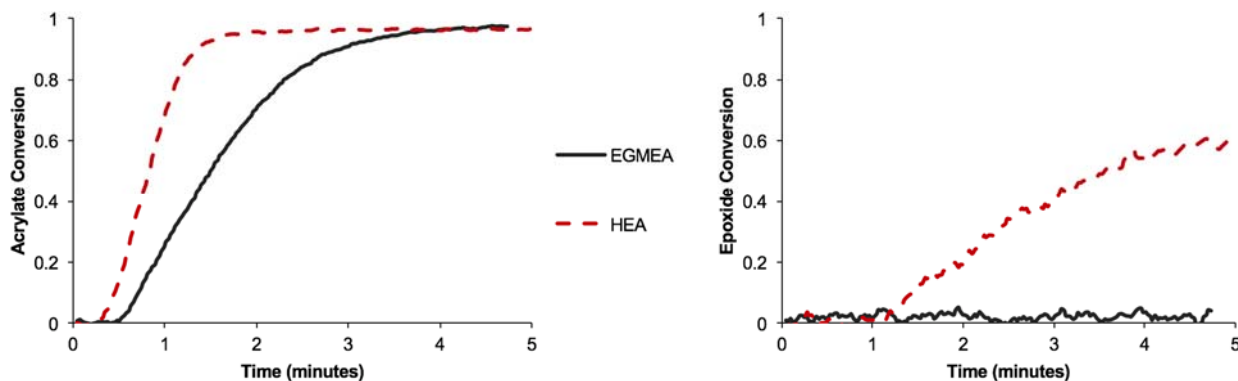
Figure 3. At equivalent viscosity and epoxide content, hybrid formulations containing the hyrdroxylated acrylate (HEA) exhibit faster rates of polymerization and higher epoxide conversions when compared to equivalent formulations with the non-hydroxylated acrylate control (EGMEA). Data are shown for hybrid formulations with 20 wt% epoxide content and initial viscosities of 3-13 cSt (as estimated by the Refutas equation[8]). Conversion data were obtained via Raman spectroscopy.

Effect of hydroxyl concentration on polymer properties

In hybrid monomer systems with the control acrylate, a semi-interpenetrating network[9] results because the monofunctional acrylate forms linear polymer chains entangled in the cross-linked network formed by the difunctional EEC. Most polymer interpenetrating networks tend to phase separate,[9] resulting in more heterogeneous physical properties. However, in hybrid monomer systems with hydroxyl-containing acrylates, the acrylate chains are covalently bonded to the epoxide network through the AM mechanism to produce a grafted polymer network.[10] This linking of the polymer domains should be manifested in changes in the polymer properties. Indeed, the network heterogeneity, as measured qualitatively by the full width half maximum (FWHM) of the tan δ peak, decreases with increasing [OH] (Figure 4). The network
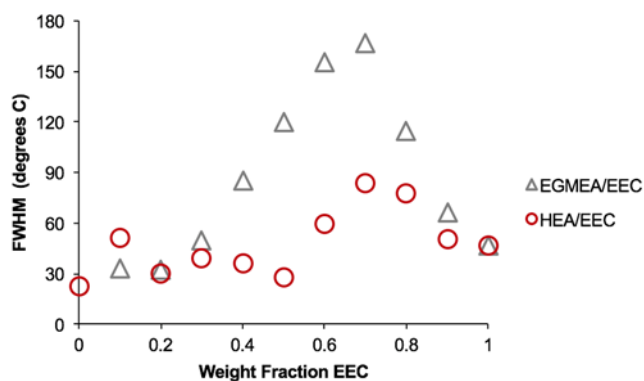

Figure 4. Hybrid formulations containing the hyrdroxylated acrylate (HEA/EEC) exhibit lower FWHM and thus less network heterogeneity when compared to analogous formulations with the non-hydroxylated acrylate control (EGMEA/EEC). The FWHM was calculated using the peak of the tan δ curve from the second DMA cycle.

heterogeneity is similar to that of the neat acrylate up to 50 wt% EEC with the hydroxylated acrylate (HEA), as compared to 30 wt% with the control acrylate (EGMEA). In addition, when network heterogeneity peaks (with formulations containing 70 wt% EEC), the FWHM is 50% less for the hydroxylated formulations than for the non-hydroxylated formulations. Thus, the AM mechanism appears useful in reducing phase separation of the polymer domains. However, even with the hydroxyl present, the T_g of the hybrid polymers increases non-linearly between the neat acrylate and EEC T_g's as EEC content is increased (Figure 5). Hence, the AM mechanism does not impede ability to tune T_g through alteration of the epoxide:acrylate.
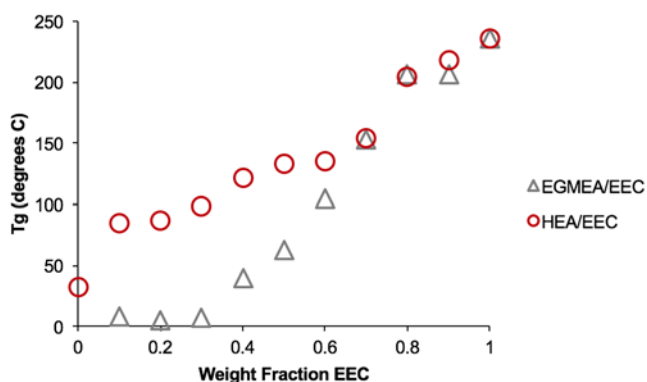

Figure 5. Regardless of hydroxyl concentration, the T_g of hybrid polymers may be tuned between the acrylate and epoxide T_g based on the epoxide content. The T_g was taken as the temperature corresponding to the peak of the tan δ curve from the second DMA cycle.

Conclusions

Epoxide monomers provide opportunities to mitigate light penetration, oxygen inhibition, and shrinkage stress when incorporated in photopolymerizable hybrid monomer systems with acrylates. If hydroxylated acrylates are present in these formulations, the AM mechanism is triggered and can be exploited to increase epoxide reaction rate and final conversion. This study confirms that these improvements in epoxide kinetics are due to the presence of the hydroxyl groups and are not simple viscosity effects. When the AM mechanism is present, the polymer structure is changed such that the acrylate chains are grafted to the EEC network via the pendant hydroxyl groups.   This structural change does provide a means to reduce network heterogeneities by increasing the difficulty of phase separation between the two polymer domains. However, this structural change does not compromise the ability to tune hybrid polymer T_g by varying the relative concentrations of acrylate and epoxide monomers.

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