# Combining oxiranes and oxetanes to enhance kinetics and improve physical properties

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## Abstract.

Cycloaliphatic epoxides (oxiranes) typically polymerize more slowly than acrylates and tend to be brittle. However, cationic active centers are long-lived, resulting in significant dark cure. Here, oxetane addition to formulations is correlated to improvements in polymerization kinetics and polymer properties during dark cure. Raman spectra yielded conversions; DMA provided $T_g$ and crosslink density. Increasing oxetane concentrations improved epoxide conversion and drastically lowered $T_g$ of the resulting polymers, thereby increasing the application range for cycloaliphatic epoxides.

## Introduction.

Cationic photopolymerizations offer unique advantages for many applications. For example, these systems are not inhibited by oxygen and are essentially non-terminating, leading to very long active-center lifetimes (hours or even weeks). In contrast, free radicals generally have propagating lifetimes on the order of seconds due to rapid radical-radical termination reactions or oxygen quenching reactions, both of which quickly consume the free-radical active centers. As a consequence of the long-lived active centers, cationic polymerization may proceed long after the irradiation has ceased, leading to dark cure or post-illumination polymerization. This dark cure results in further property development over the course of hours or days and is due to the active centers lasting long enough to be controlled by diffusion and being able to travel further away from the areas that were initially irradiated, both deeper into the coating and into areas that were never irradiated.[1]

The use of oxetanes in conjunction with epoxides (also known as oxiranes) has the potential to decrease chain transfer during polymerization and enhance physical properties. During ring-opening polymerization, the ring in the growing polymer chain is opened, while the attacking molecule remains intact, so the competition between the monomer and polymer is governed primarily by the nucleophilicity of the oxygen atom in cyclic and linear structures.[2] Because epoxides and linear ethers have very similar $pK_a$ values (see Figure 1), the active centers have almost equal affinity for both the unreacted monomer functional groups and the polymer chains.[3] Thus, competition between the monomer and polymer chains is a large problem in epoxide systems, and chain transfer to polymer is typical in cationic ring-opening polymerizations containing epoxides. Intramolecular reaction leads to cyclic monomers, while intermolecular reaction leads to segmental exchange, or "scrambling."[4] Both of these chain transfer reactions lead to broadening of the molecular weight distribution, which is not favorable. This research examines the effects of combining oxetanes and epoxides on the reactivity of each monomer, the overall reaction kinetics, and the final physical properties of the polymer films, while reducing illumination time and exploiting dark cure in these systems.

pKₐ = 2.0      2.1      3.6    3.7

Ring Strain (kJ/mol) = 107    23    5    --    114
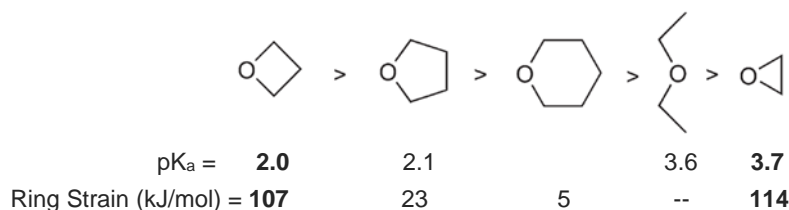
**Figure 1.** Relative nucleophilicities and ring strain of cyclic and linear ethers.

## Experimental.

### Materials.

To determine the effect of viscosity and oxetane structure and functionality on the conversion of an industrially relevant difunctional epoxide, a series of formulations was made containing varying mole percentages of the epoxide and four oxetanes (see Figure 2). The comonomer formulations contained 0.5 mol% diaryliodonium hexafluoroantimonate (IFA, Polyset) in mixtures of the highly viscous 3,4-epoxy-cyclohexylmethanyl 3,4- epoxy-cyclohexanecarboxylate (EEC, Sigma Aldrich) and one of the four oxetanes. The oxetane side groups were a hydroxyl group (OXA), a phenyl group (POX), a branched carbon chain (EHOX), or another oxetane (DOX). With respect to functionality, POX and EHOX are monofunctional oxetanes, DOX is difunctional, and OXA has an intermediate functionality, since it contains one cyclic ether as well as a hydroxyl group that is able to react with a cationic active center through a chain transfer reaction.
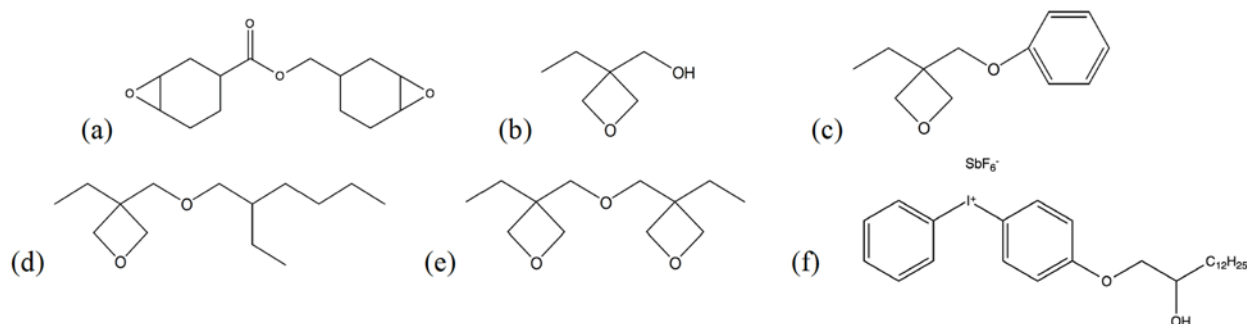


**Figure 2.** Chemical structures for the monomers 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (EEC, a); 3-ethyl-3-hydroxymethyl oxetane (OXA, b); 3-ethyl-3-phenoxymethyl oxetane (POX, c); 3-ethyl-3-[(2-ethylhexyloxy)methyl] oxetane (EHOX. d); 3-ethyl-3 (3-ethyloxetane-3-yl) methoxy methyl oxetane (DOX. e); and the diaryliodonium hexafluoroantimonate photoinitiator (IFA, f).

### Methods.

*Formulations and experimental variables.*

Experiments were performed to determine effects of various formulation factors, including oxetane concentration, liquid monomer viscosity, and comonomer functionality. The oxetane concentration ranged from 0 mol% (i.e., 100% EEC) to 60 mol% (i.e., 40 mol% EEC) in increments of 20 mol%. Because oxetanes have significantly different viscosities and plasticizing ability in EEC, equal viscosity formulations of 200 cP and 300 cP were also compared for each of the oxetanes in EEC.

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***Raman Spectroscopy.***

Raman spectroscopy was used to monitor simultaneously epoxide and oxetane conversion both during UV illumination and at specific time intervals after the light had been shuttered (dark cure).[5] Samples were injected into 1mm-ID quartz capillary tubes and illuminated with a mercury arc lamp fitted with a 250-450nm filter (Acticure® Ultraviolet/Visible Spot Cure system, EXFO Photonic Solutions Inc.) for 10 minutes at an effective irradiance of 710 mW/cm$^2$, measured with a radiometer (R2000, Omnicure, wavelength range 250nm – 1μm). Real-time Raman spectra were acquired using a holographic probe head (Mark II, Kaiser Optical Systems Inc.) with a single-mode excitation fiber delivering ~220 mW of 785-nm near-infrared laser intensity to the quartz capillary tubes. The spectra were collected with a 1-s exposure time and 3 accumulations. Additionally, spectra were taken at various time points after illumination had ceased in order to measure any conversion increases and therefore determine how each formulation affected dark cure over the course of hours and days. Dark cure was followed for up to 4 hours after illumination ceased in 5-15 minute increments. Conversions taken 24-72 hours after illumination did not exceed an additional 5% conversion from the 4-hour measurements for any formulation.

Conversion was calculated from the Raman spectra using Equation 1. The epoxide reaction peak was measured at 790 cm$^{-1}$, the oxetane reaction peak at 1150 cm$^{-1}$, and the reference peak for both monomers at 1450 cm$^{-1}$. This stable reference peak is used to eliminate error due to baseline changes. In Equation 1, $I(t)$ denotes the peak intensity at time $t$, and $I(0)$ represents the initial peak intensity. The subscripts denote whether the measurement is of the reaction peak intensity (rxn) or the reference peak intensity (ref).

$$\textbf{Equation 1.} \quad \frac{\text{Fractional}}{\text{Conversion}} = 1 - \frac{I(t)_{rxn}/I(t)_{ref}}{I(0)_{rxn}/I(0)_{ref}}$$

***Dynamic Mechanical Analysis.***

Dynamic mechanical analysis (DMA) was used to compare the glass transition temperature ($T_g$) and network homogeneity of neat EEC to formulations containing both epoxide and oxetane. The procedure has been described previously.[6] DMA films were made by injecting the formulations between two microscope slides (separated by two cover slips) and photopolymerizing under a belt-driven Fusion curing system fitted with an H bulb with an effective irradiance of 180 mW/cm$^2$, as measured with the radiometer. The films were passed at 8 ft/min under the lamp three times for each side. The resulting films were 0.30 mm in thickness and were cut into rectangles measuring approximately 20 x 5 mm. Each film was allowed to dark cure for multiple weeks in order to ensure a final room-temperature conversion before testing. As noted above, conversion increases were < 5% during this period of extended dark storage. Films were tested using the film tension clamp in the DMA (Q800, TA Instruments). Frequency sweep/temperature ramps for each film ranged from >30°C under the neat oxetane $T_g$ (see Table 1) to 250°C (i.e., 50°C above the neat epoxide $T_g$) at a sinusoidal strain of 0.05% applied at a frequency of 1 Hz. Each film underwent two thermal cycles to determine if annealing was present and how it affected the $T_g$.

|  | $T_g$ | Viscosity at 25°C |
|---|---|---|
| **EEC** | 197°C | 550 cP |
| **EHOX** | -60°C | 5.0 cP |
| **POX** | 1°C | 14 cP |
| **OXA** | 46°C | 22 cP |
| **DOX** | 51°C | 13 cP |

**Table 1.** Comparison of glass transition temperatures and viscosities for neat monomers.

# Results and Discussion

## Impact of Dark Cure on Kinetic Results

The epoxide EEC generally shows low conversions in neat formulations (less than 10% during the first 10 minutes of illumination, less than 40% final conversion after 4 hours). Long illumination times are not required to get full property development or to speed up the reaction, as the conversion profile is similar between a sample illuminated for 4 hours and one illuminated for 10 minutes and allowed to dark cure for 4 hours (Figure 3). Thus, once the cationic active centers have been generated, there is no need to continue illumination, and reduced energy costs are realized.  However, a large proportion of monomer conversion and property development can occur in the time following illumination, and the impact of dark cure must be considered.

The neat oxetanes have long induction periods (on the order of minutes). Combining EEC with any of the oxetanes decreased the oxetane induction period and increased the conversion for both monomers in each formulation. The enhancement in oxetane reactivity stems from the epoxide functional groups acting as reactive sites for the initiation of the oxetane functional groups.[7,8] For example, in the difunctional EEC/monofunctional POX formulation series, increasing the proportion of oxetane results in increased epoxide conversion (see Figure 4) – both at the end of the illumination period (values along the y axis) and during dark cure.  The impact of the epoxide on the kinetics of the oxetanes is more complex (see Figure 5).  For the neat monomer formulation, the reaction proceeds more slowly, with only 10% oxetane conversion occurring during illumination and a final oxetane conversion approaching 30% after 3 hours of dark cure.  Compared to the neat oxetane, the epoxide/oxetane mixtures have higher oxetane conversions during illumination (> 15%), as well as faster polymerization and a reduced induction period (not shown in Figure 5), and final oxetane conversions are achieved much more rapidly in the dark (i.e., within 1 hour of shuttering the light).
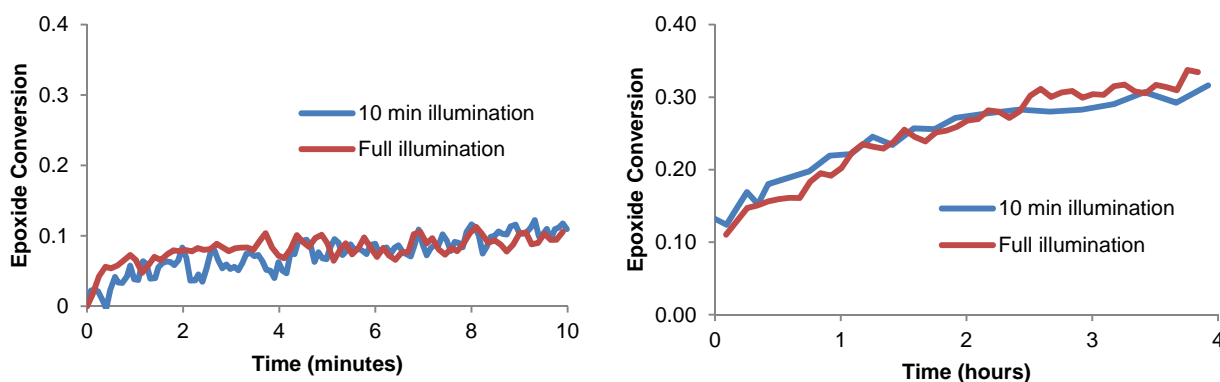


**Figure 3.** EEC conversion as a function of time: (a) during the first 10 minutes of illumination and (b) during the subsequent 4 hours. The red line shows conversion for a sample that was illuminated during the entire period. The blue line shows conversion for a sample that was illuminated only for the first 10 minutes and then allowed to dark cure for the remaining 4 hours. The formulations contained 0.5 mol% of the photoinitiator IFA.
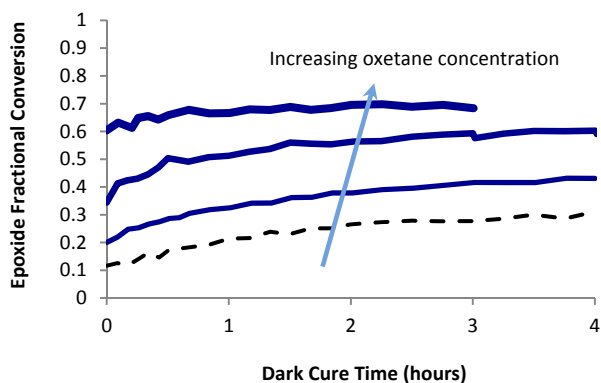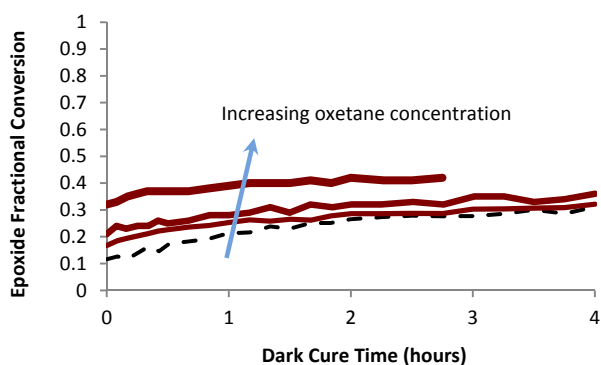
**Figure 4.** Epoxide conversion over time for EEC and POX post-illumination. Conversions immediately after illumination lie on the y-axis. The dashed line represents neat EEC (with 0.5 mol% photoinitiator).
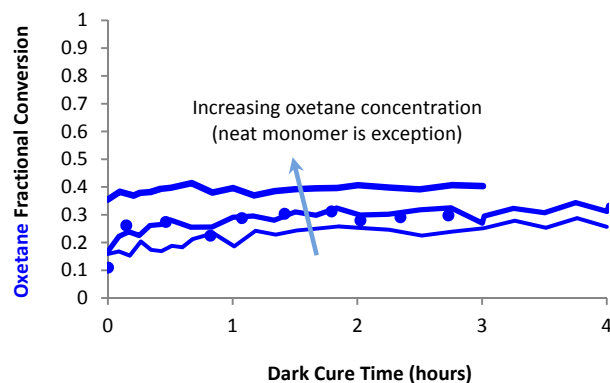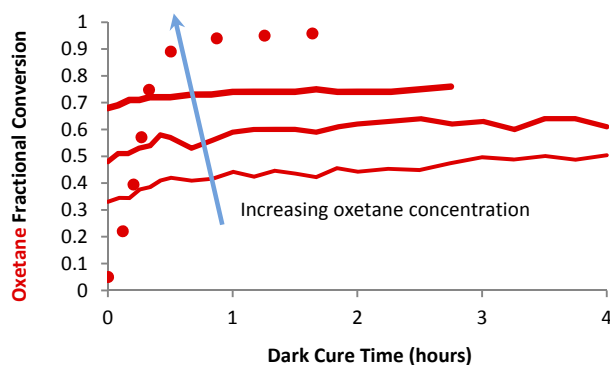


**Figure 5.** Oxetane conversion over time for EEC and POX post-illumination. Conversions immediately after illumination lie on the y-axis. The dotted line represents neat POX (with 0.5 mol% photoinitiator).

The other three oxetanes behave similarly (i.e., increased epoxide conversions result from increased proportions of oxetane in the formulation) to varying degrees. DOX, the difunctional oxetane, does not greatly enhance the epoxide conversion, although the dark-cure conversion of the oxetane greatly benefits from the presence of the epoxide (see Figures 6 and 7). Neat DOX formulations achieve only 5% conversion by the end of the illumination period but show very high dark-cure conversion. Shorter illumination times at lower intensities result in longer induction periods, but as soon as the reaction reaches a threshold conversion, high conversions are obtained quickly. In contrast to neat DOX, a 40:60 EEC:DOX formulation reaches almost 70% oxetane conversion during the same 10 minute illumination period, and less conversion increases are seen post-illumination. DOX does not enhance epoxide conversion as much as the other oxetanes because the initial formulations are highly viscous and a heavily crosslinked network is formed upon illumination of the two difunctional monomers, which traps the active centers and limits reactive diffusion. The functionality of the oxetane monomer, therefore, must be considered when choosing the comonomer for polymerization with EEC. Monofunctional oxetanes enhance the kinetics and conversion of EEC to a higher degree than difunctional oxetanes, reducing the need to illuminate for long periods of time and to wait for physical property development post-illumination.



**Figure 6.** Epoxide conversion over time for EEC and DOX post-illumination. Conversions immediately after illumination lie on the y-axis. The dashed line represents neat EEC (with 0.5 mol% photoinitiator).



**Figure 7.** Oxetane conversion over time for EEC and DOX post-illumination. Conversions immediately after illumination lie on the y-axis. The dotted line represents neat DOX (with 0.5 mol% photoinitiator).

**Impact of Oxetane Addition on $T_g$.**

Two thermal cycles were necessary for most formulations due to the long-lived nature of cationic active centers.[9] The addition of oxetanes has the potential to greatly reduce the $T_g$ of a copolymer film by up to 100°C, resulting in films that are much less brittle than neat EEC. The second thermal cycle resulted in $T_g$ increases of 5°C for EEC, demonstrating that some reaction occurs during the first cycle, which incorporates additional monomer into the polymer matrix. The amount of annealing in the copolymer that occurs during the first thermal cycle depends on both the epoxide-oxetane formation ratio and the oxetane monomer structure. For example, as the amount of POX is increased, the change in $T_g$ from the first to second thermal cycle decreases (see Figure 8). As the amount of POX is increased, the formulation viscosity decreases, and higher conversions are attained for both EEC and POX prior to DMA measurements (see Figures 4 and 5); therefore, less annealing is possible due to these advanced network restrictions. Even less annealing is observed for the EEC/DOX system since both monomers are difunctional.

Additionally, formulation viscosity affects the $T_g$ but the extent depends on the comonomer. Equal viscosity formulations result in similar $T_g$ changes from the first to second cycle, but the $T_g$ values for formulations with the same viscosity can vary up to 20°C for the different oxetane comonomers. For example, in comparing 200 cP formulations of EEC/POX and EEC/DOX, both $\Delta T_g$'s were 6°C; however, the $T_g$ for the first cycle of EEC/POX was 124°C, while EEC/DOX was 145°C. In these equimolar and equal viscosity studies on the physical properties of polymer films, monofunctional oxetanes are better able to lower viscosity and decrease the $T_g$ of EEC, since difunctional oxetane monomers create a highly crosslinked network upon polymerization, causing them to be less effective in lowering the $T_g$.
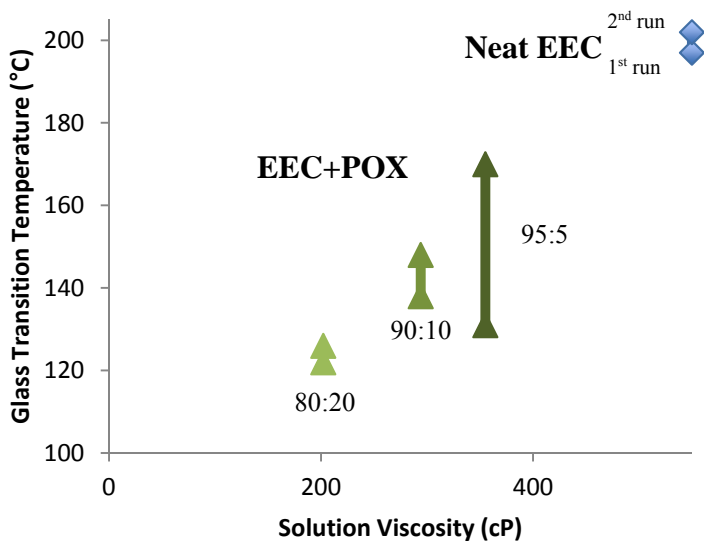


**Figure 8.** $T_g$ for first and second thermal cycle for EEC:POX formulations, 80:20, 90:10, and 95:5 (left to right), plotted as a function of solution viscosity. For each formulation, the first thermal cycle has a lower $T_g$ than second cycle (first on top, second on bottom).

## Conclusions

Once cationic active centers are produced, continued illumination is not beneficial – reaction time and ultimate conversions after dark cure are similar to those after full illumination periods. In fact, most EEC conversion and its corresponding polymer property development can occur during this dark cure period, which results in lower energy requirements. However, the time required to reach these ultimate properties in EEC is still long (on the order of hours).

Combining epoxides and oxetanes greatly increases kinetics for both monomers, lowering illumination time and dark cure needed to reach final polymer properties. In the series of comonomer formulations examined here, increasing the proportion of oxetane in the formulation resulted in acceleration of the EEC polymerization and lowering of the final polymer $T_g$. Monofunctional oxetanes were more effective than multifunctional oxetanes in realizing these benefits due to lower initial viscosities and less restricted network formation.

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