

Photoinitiated cationic polymerization of sustainable epoxy and oxetane thermosets

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Abstract

A group of sustainable materials are proposed and produced from multifunctional epoxides and oxetanes obtained from renewable sources. Monomers are photopolymerized using diaryliodonium salts designed and synthesized by our group as initiator. A detailed investigation of the network formation of epoxidized linseed oil revealed that crosslinks is markedly dependent to the thickness and viscosity of substrate. Copolymerization studies of difunctional oxetane showed that limonene dioxide was effective in increasing the reaction rates and shorten the inherent induction period, also known as “kick-start” effect. Such oxetane thermoset can achieve desirable curing rates and Tg compared to petroleum based epoxy used in applications such as large scale surface coatings.

Introduction

UV irradiation curing technology has been widely employed in the coatings, printing inks, adhesives and imaging industries. One of the major interests of our research group is to study UV photoinitiated cationic polymerizations in thin-films for the preparation of thermosets using sustainable monomers from renewable sources, such as vegetable oils and terpenes. The development of a wide range of diaryliodonium cationic photoinitiators allows us to simply dissolve these photoinitiators into reactive substrate and crosslinked polymers in-situ under UV irradiation.¹ The reaction is rapid, neat and energy efficient without using of volatile organic solvent. Compared with the radical initiators, cationic photoinitiators are less likely to be inhibited by air hence can be applied into a broader range of substrates such as epoxides, oxetanes, vinyl ethers, acrylates without developing tacky surface layers from the oxygen inhibitions for crosslinking.

Epoxy resins are known to be a group of thermosets that receive wide spectrum of applications. Most epoxy resins are produced these days based on the reaction between bisphenol-A and epichlorohydrin in industry.² Therefore, in efforts to relieve growing concerns environmental impacts and unpredicted future of crude oil price, researchers studied the development of sustainable epoxy resins from renewable sources. For example, vegetable oils, which are glycerol triesters of fatty acids, are abundant in natural plants and offer means of starting materials for sustainable epoxy monomers from renewable biosources. By taking advantage of the olefinic double bonds contained in the fatty acid residues of vegetable oils, a variety efforts have been done to develop epoxy thermosets from vegetable oils.³⁻⁵ These bio-sources epoxy materials show excellent flexibility and water resistance due to the long aliphatic chains presented in the structures of triglycerides, making them especially promising as UV curable coatings. However, due to the high viscosity and nucleophilic sites present on the epoxidized vegetable oil structure, the photocuring kinetics are slow and the UV cured network formation tends to be incomplete and inhomogeneous typically across the film thickness. Thus, it becomes especially important to fundamentally understand the formation of network structures when undergoes photoinitiated cationic polymerization.

In this report, we investigated structure-property-relationships of epoxidized linseed oil (ELO) that has been crosslinked by photo-initiated cationic polymerization under UV irradiation. First, we have studied the relationship between “macroscopic” film thickness and UV irradiation dose. This is important to gain understanding on the UV curing discrepancy between the film surfaces that are closest to the UV irradiation (a.k.a. “front end”) and furthest from the irradiation (a.k.a. “back end”). Then, we have performed a variety of thermal and spectroscopic characterizations to elucidate how the network structures are formed in both front- and back-ends of films during UV curing and can be further manipulated during post-thermal treatments.

Apart from epoxides, another big group of reactive substrates that draw our interests is oxetanes, which contains highly strained ring structure as functional group and can undergo facile cationic ring-opening polymerization. Compared to most commercial epoxides, oxetanes are known to be less toxic and volatile, which makes them to be attractive for uses in three-dimensional imaging applications and dental composites etc.⁶ However, oxetanes usually manifest a relatively stagnant polymerization behavior by having a long induction period as shown in previous studies for photo-initiated cationic polymerizations. However, the photocuring delay issues from the induction period could be greatly suppressed by performing copolymerization with a number of highly reactive epoxides, known as “kick-starting” agents for the photo-initiated cationic polymerization.^{6,7} Among many kick starting agents that have been investigated, limonene dioxide (LDO) is of our particular interest because it is prepared from terpene-based sustainable biosources. In addition, the low viscosity of LDO offers the advantage of high mobility of monomers to complete the network formation fast during UV irradiation. In this paper, thermo/mechanical test done on the copolymer of bis{[1-ethyl(3-oxetanyl)]methyl} ether (DOX) and LDO shows the great potential of “kick-starting” effect to further raise the T_g of photocured oxetane thermosets to a level higher than 100 °C by expediting the oxetane network formation during the UV curing at room temperature.

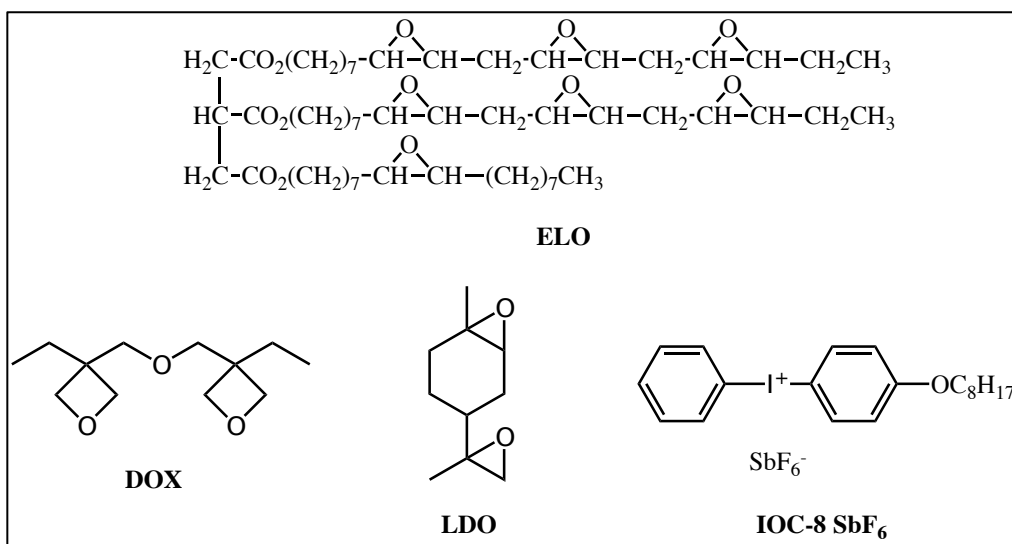


Figure 1. Chemical structures of epoxy and oxetane monomers and cationic photo-initiator used in the study.

Materials

Epoxidized linseed oil (ELO) was obtained from Witco Inc. and Limonene dioxide (LDO) was purchased from Arkema, Inc. Bis{[1-ethyl(3-oxetanyl)]methyl} ether (DOX) was received as gifts from

the Toagosei Chemical Company, Nagoya, Japan. Both of LDO and DOX were purified by fractional distillation before use. The photoinitiator, (4-n-octyloxyphenyl)-phenyliodonium hexafluoroantimonate (IOC-8 SbF₆) was synthesized and purified as described¹. Figure 1 summarizes the chemical structures of all the monomers and photoinitiators used in the study.

Sample preparation

LDO was blended with DOX at varying concentrations (0-30 wt%), followed by the addition of 2 wt% IOC-8 SbF₆. The photo-curable mixture was spread on the glass substrate using draw blade, and exposed to UV irradiation using conveyor belt curing system (Fusion System Inc.) equipped with 300 W mercury lamp.

Characterization

For thickness-irradiation measurement studies, photo-curable mixture containing 2 wt% IOC-8 SbF₆ photo-initiator and ELO was evenly spread on a glass substrate, and placed in UV ozone cleaner equipped with ozone free mercury lamp for a period ranging from 30 s to 10 min. The resulting UV-cured film was transferred to another glass substrate and was submerged in THF to leach out the residual unreacted monomer. After drying, the thickness of the films was measured, and the accumulative irradiation was measured by Control Cure Radiometer (UV Process Supply, Chicago, IL).

Dynamic mechanical analysis (DMA) was recorded on TA Q800 DMA equipped with a tension film, multi-frequency strain mode using a preload force of 0.1 N and 10 μ m amplitude. The ramp rate was kept at of 2 $^{\circ}$ C/min, ranging from -40 $^{\circ}$ C to 180 $^{\circ}$ C. The sample was run for the second time immediately after the first scan.

Results and Discussion

Thickness vs Irradiation studies

Thickness vs. irradiation correlation studies of photo-cationic cross-linking of ELO were performed to understand the effect of accumulated irradiation time on the thickness of the cured thermosets. Figure 2a gives a schematic representation describing the process flow of the experiment, and the scattered plot of measured thickness with respect to different accumulative irradiation are depicted in Figure 2b. A linear correlation was observed between film thickness and accumulative irradiation under the range used for this study. With 2600 mJ/cm² of accumulative UV irradiation, which takes about 10 minutes for our apparatus, the film thickness went to about 600 μ m. The information gained in these studies would aid in an effective design of UV-cure process for targeting a broad range of applications.

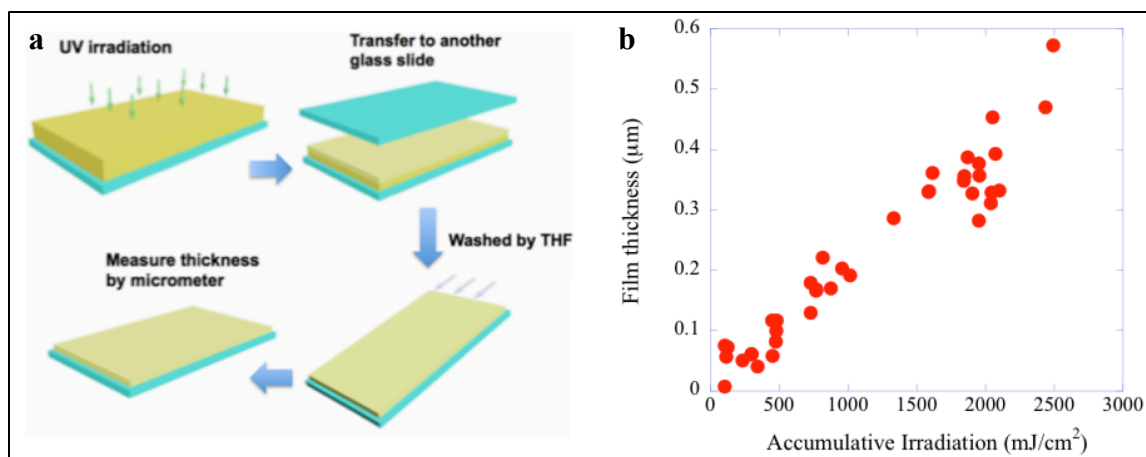


Figure 2. Thickness vs. irradiation correlation studies of photo-cationic cross-linking of ELO a) process flow of the experiment b) scattered plot of measured thickness with respect to different accumulative irradiation.

DOX/LDO thermal/mechanical properties

Figure 3 shows a temperature dependence of tan delta of the photo-cured DOX/LDO copolymer (80/20 weight ratio). Figures 3a and 3b show the first and second DMA scans, respectively. The first DMA scan revealed the presence of two glass transition temperatures occurring at low and high temperatures, which could be attributed to the existence of two different network domains. The lower glass transition peak disappeared after the second scan with an appearance of a single, broad tan delta peak at a higher temperature. This could be explained by the fact that the residual oxetane and epoxide groups after the first scan undergoes thermal cross-linking, thereby resulting in a homogenous network formation.

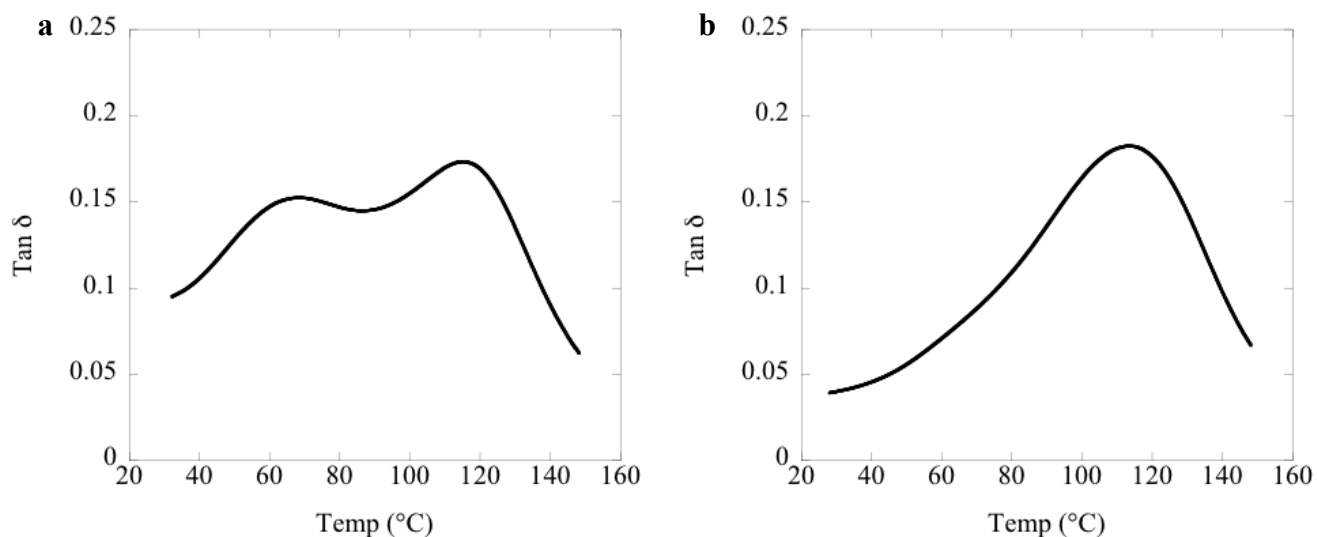


Figure 3. $\text{Tan } \delta$ vs temperature plots of photocured DOX/LDO copolymer (80/20) a) first DMA scan b) second DMA scan

Conclusions

We have successfully developed group of sustainable epoxy thermosets and established a fundamental understanding of the structure-property relationship. A linear correlation was observed between the film thickness and accumulative UV irradiation of epoxidized linseed oil (ELO). We have also investigated the properties resulting from the kick-start effect of DOX/LDO copolymer network. Thermal-mechanical studies of DOX/LDO showed two glass transition temperatures after the first scan, and a broad, single relaxation peak was formed after the second scan, which indicated thermal curing of the unreacted oxetane and epoxy functional groups. With both high-speed curing and good mechanical strength, the “kick-started” oxetane system may replace petroleum-based epoxides and find its uses in many commercial photocurable applications.

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