

Ultraviolet Curing Kinetics of Cycloaliphatic Epoxide with Real-Time Fourier Transform Infrared Spectroscopy

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Received 10 April 2002; accepted 16 January 2003

ABSTRACT: The photo-induced curing kinetics of cycloaliphatic epoxide coatings were investigated with real-time Fourier transform infrared spectroscopy with an optical fiber ultraviolet curing system. The consumption of epoxy group as a function of time was obtained by monitoring of the oxirane absorbance in the 789–746-cm⁻¹ region. The effect of the type of epoxide, hydroxyl equivalent weight, ratio of oxirane to hydroxyl groups (*R*), photoinitiator, and exposure time on the curing reaction was investigated. In general, the rate of curing was dependent on the hydroxyl

equivalent weight, *R*, type of epoxide, and photoinitiator. For formulations without polyol, both initiator concentration and exposure time had minimal effects on the curing reaction. However, for formulations with polyol, the curing a reaction was dependent on the initiator concentration. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 2485–2499, 2003

Key words: chain; coatings; kinetics; IR spectroscopy; epoxides; polyethers

INTRODUCTION

Ultraviolet (UV)-curable coatings offer the advantages of fast cure response, high-energy efficiency, and low volatile organic contents.¹ As the pressure to reduce volatile organic contents continues to mount, the advantages of UV coatings are becoming more attractive. There are two classes of UV-curable coatings, free radical and cationic. In comparison with free-radical UV curing, cationic-initiated UV curing technology offers the advantages of insensitivity to oxygen and lower film shrinkage.² The cationic-initiated UV-curable coatings are also particularly useful in a variety of applications, including paper coatings, wood coatings, plastic substrate coatings, lithographic and screen printing inks, and decorative metal varnishes.³

Epoxides are one of the most important and widely used classes of resins in the field of cationic UV-curable coatings. The three major types of epoxides used are glycidyl ether, epoxidized seed oil (soybean or linseed oil), and cycloaliphatic epoxide. Of the three, cycloaliphatic epoxides are the most widely used because of their fast cure response. In addition to the fast cure response, cycloaliphatic epoxides provide a number of other important advantages in coating applications, including excellent adhesion to a wide variety of substrates, flexibility, good color sta-

bility, excellent gloss, low potential for skin irritation, low shrinkage, good weathering, and good electrical properties.^{4,5}

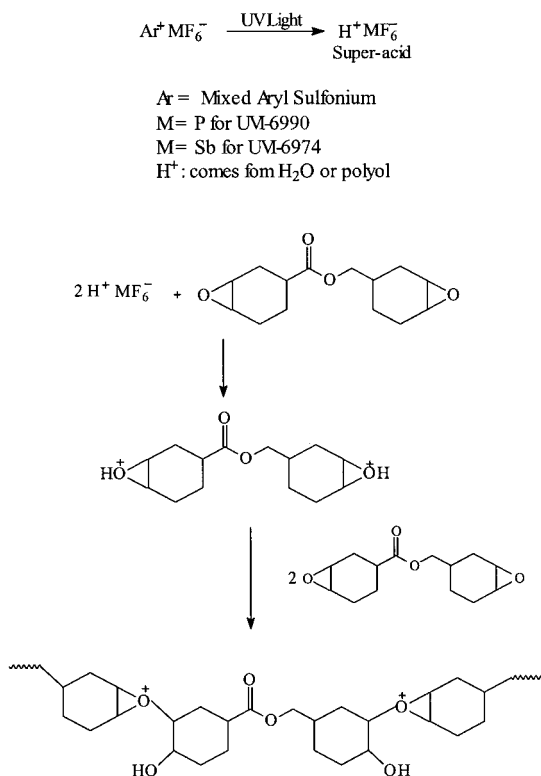
The homopolymer of cycloaliphatic epoxide, shown in Scheme 1, is usually too brittle to be used as a coating. Typically, flexible crosslinkers, such as difunctional and trifunctional polyols (especially ϵ -caprolactone derived polyols), are added into the formulations to improve the toughness and impact resistance.⁶ The superacid-catalyzed crosslinking reaction is shown in Scheme 2. The superacid-catalyzed UV curing reaction of cycloaliphatic epoxide and polyol consists of four steps (Scheme 3): initiation, propagation, chain transfer, and termination. The initiation step involves two reactions: the formation of superacid and the addition of the superacid to the monomer molecules to produce the chain-initiating species (M_1^+), and the subsequent propagation of successive epoxide molecules to the chain-initiated species (M_1^+). If there are nucleophiles present, such as water or alcohol, both a chain transfer and a termination reaction can occur.⁷

The cationic-photoinitiated polymerization occurs not only during short exposure but also after UV exposure. Dark cure is due to the long-lived initiating species or living cationic species.⁶ The dark-cure process was found to represent a significant part of the overall process.⁶ The dark-cure process can improve coating properties such as adhesion and hardness.⁸

A reliable method for the evaluation of a photo-induced curing is very important with respect to the determination of extent of cure and final coatings properties. Cationic UV curing reactions are faster

Part of the work for this article was done at the Polymers and Coatings Department, North Dakota State University, Fargo, ND 58105.

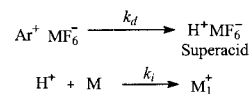
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Scheme 1 Photolytically initiated homopolymerization of cycloaliphatic epoxide.

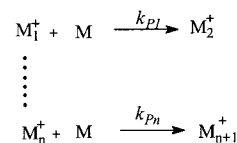
than most monitoring methods. Therefore, it is difficult to find a facile method to quantify the rate of polymerization. Several discrete and time-resolved methods have been used for the study of UV-curable systems, including dilatometry,^{9,10} Fourier transform infrared (FTIR) spectroscopy,^{11,12} time-resolved Ra-

Initiation



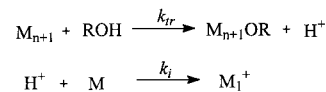
k_d : Rate constant of initiator dissociation
 k_i : Rate constant of initiation step

Homopolymerization Propagation



k_{pi} : Rate constant of propagation

Chain transfer



k_{tr} : Rate constant of chain transfer reaction

Termination

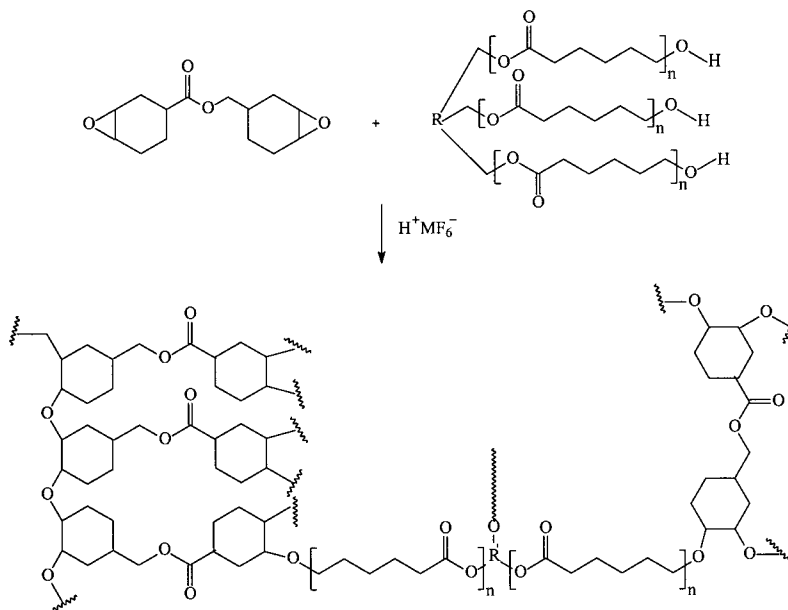


k_t : Rate constant of termination

Scheme 3 Sequence of the steps of the UV curing reaction.

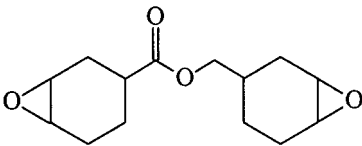
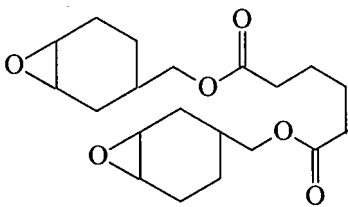
man spectroscopy,¹³ and differential photocalorimetry (or photo-differential scanning calorimetry).^{14,15}

A relatively new technique, real-time FTIR spectroscopy, was proposed by Decker and Moussa.^{6,16-20} Unlike other techniques, this method allows the curing



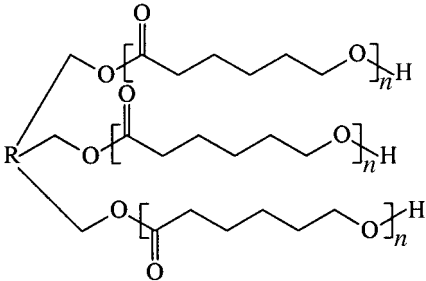
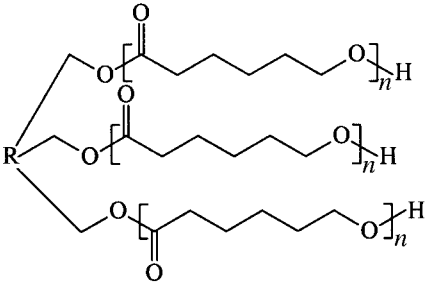
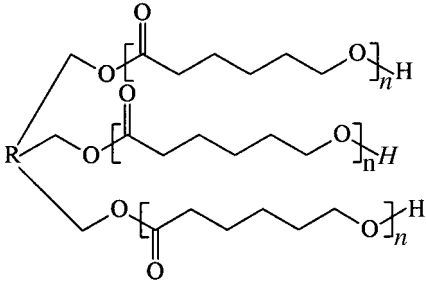
Scheme 2 Step-growth crosslinking reaction of cycloaliphatic epoxide with polyol.

TABLE I
Structures and Typical Properties of the Cycloaliphatic Epoxides

	UVR-6110	UVR-6128
Structure		
Epoxide equivalent weight	3,4-Epoxyhexanoic acid 131-143 (MW-262-286)	Bis-(3,4-epoxycyclohexyl) Adipate 190-210 (MW-380-420)
Viscosity at 25°C (cP)	350-450	550-750

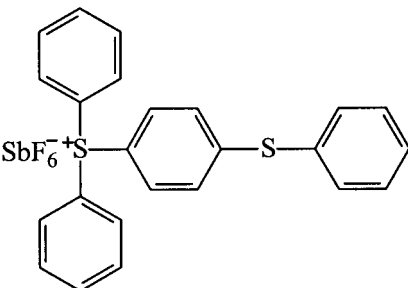
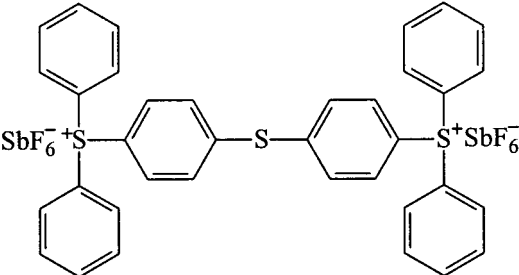
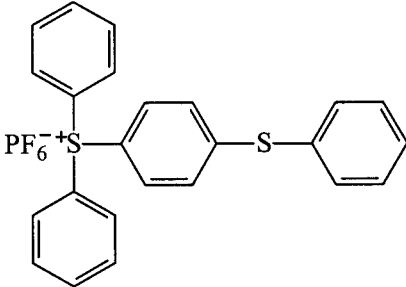
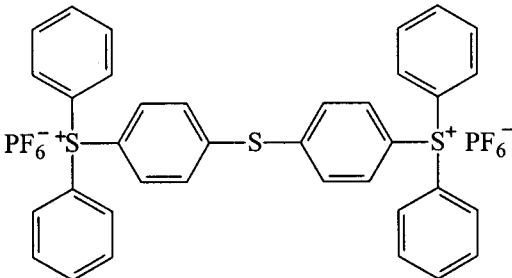
MW = molecular weight.

TABLE II
Structures and Typical Properties of Polyols

	Structure	Hydroxyl equivalent weight	Viscosity at 25°C (cP)
TONE 0301		98-103 (MW = 294-309)	2250
TONE 0305		174-188 (MW = 522-564)	2050
TONE 0310		289-312 (MW = 867-936)	2700

MW = molecular weight.

TABLE III
Structures and Typical Properties of the Photoinitiators

	Structure
UVI-6974	
	
	Mixed triarylsulfonium hexafluoroantimonate salts
UVI-6990	
	
	Mixed triarylsulfonium hexafluorophosphate salts

reaction to be monitored continuously and rapidly at the molecular level. It provides a fingerprint of the chemical structure changes of the formulation components during UV irradiation and even in the dark-cure process. The application of the real-time FTIR spectroscopy to the study of the UV curing reaction offers many advantages. First, the conversion versus time curves can be directly recorded, which allows the determination of both the rate of polymerization and the conversion of the monomer as a function of time. Second, real-time FTIR is a sensitive and nondestructive method that provides good reproducibility.

Although the UV curing of cycloaliphatic epoxide has been studied, most of the studies have been limited to the performance tests, such as by the measurement of the adhesion, solvent resistance, hardness, and impact resistance of the cured coatings.^{21,22} The UV curing kinetics of 3,4-epoxycyclohexylmethyl-3',4'-epoxycyclohexane carboxylate was also studied by Decker and Moussa,²³ but their study was limited to the effect of film thickness and exposure time on the curing reaction without polyol. Crivello et al.²⁴ did studies on the effect of polyols on photoinitiated cationic polymerization; however, only a narrow polyol

TABLE IV
Formulations^a for the Study of the Effect of the Polyol Equivalent Weight and *R* on the Curing Reaction

	UVR-6110 (g)	Polyol (g)			<i>R</i> value
		TONE 0301	TONE 0305	TONE 0310	
A1	69.87	25.63	—	—	2.0
A2	76.74	18.76	—	—	3.0
A3	80.70	14.80	—	—	4.0
A4	85.10	10.40	—	—	6.0
A5	87.48	8.02	—	—	8.0
A6	91.31	4.19	—	—	16.0
A7	93.36	2.14	—	—	32.0
A8	95.50	—	—	—	∞
B1	57.51	—	37.99	—	2.0
B2	66.30	—	29.20	—	3.0
B3	71.79	—	23.71	—	4.0
B4	78.27	—	17.23	—	6.0
B5	81.96	—	13.54	—	8.0
B6	88.22	—	7.28	—	16.0
B7	91.71	—	3.79	—	32.0
C1	45.55	—	—	49.95	2.0
C2	55.17	—	—	40.33	3.0
C3	61.68	—	—	33.82	4.0
C4	69.93	—	—	25.56	6.0
C5	74.95	—	—	20.55	8.0
C6	83.99	—	—	11.51	16.0
C7	89.37	—	—	6.13	32.0

^a The photoinitiator UVI-6974 (4.0 g) was used, and 0.5 g of Silwet L-7604 was used for all of the formulations.

concentration range was investigated. Thus far, no systematic UV curing kinetic study of cycloaliphatic epoxide with polyol has been reported. The focus of this study was to investigate the kinetics of the cationic UV curing reaction of cycloaliphatic epoxide both with and without polyols with real-time FTIR spectroscopy.

EXPERIMENTAL

Materials

Two cycloaliphatic epoxides, 3,4-epoxycyclohexylmethyl-3,4-epoxycyclohexane carboxylate (UVR-6110) and bis(3,4-epoxycyclohexyl) adipate (UVR-6128); three polyols, ϵ -caprolactone triols (TONE 0301, TONE 0305, and TONE 0310); and two photoinitiator

TABLE V
Formulations^a for the Study of the Effect of the Type of Epoxide on the Curing Reaction

	Epoxide (g)		TONE 0305 (g)	<i>R</i>
	UVR-6110	UVR-6128		
D1	—	73.37	22.13	3.0
D2	66.30	—	29.20	3.0
E1	95.50	—	—	∞
E2	—	95.50	—	∞

^a The photoinitiator UVI-6974 (4.0 g) was used, and 0.5 g of Silwet L-7604 was used for all of the formulations.

TABLE VI
Formulations^a for the Study of the Effect of the type of Photoinitiator and Concentration on the Curing Reaction

	UVR-6110 (g)	Polyol (g)		Photoinitiator (g)		<i>R</i>
		TONE 0301	TONE 0305	UVI-6974	UVI-6990	
F1	95.5	—	—	4.0	—	∞
F2	97.5	—	—	2.0	—	∞
F3	98.5	—	—	1.0	—	∞
F4	99.0	—	—	0.5	—	∞
G1	95.5	—	—	—	4.0	∞
G2	97.5	—	—	—	2.0	∞
G3	98.5	—	—	—	1.0	∞
G4	99.0	—	—	—	0.5	∞
H1	71.79	—	23.71	2.0	—	4.0
H2	71.79	—	23.71	4.0	—	4.0
I1	80.70	14.80	—	4.0	—	4.0
I2	80.70	14.80	—	—	4.0	4.0

^a Silwet L-7604 (0.5 g) was used for all of the formulations.

systems, triarylsulfonium hexafluoroantimonate salts (UVI-6974) and triarylsulfonium hexafluorophosphate salts (UVI-6990), were supplied by Union Carbide Chemicals and Plastics Co., Inc. The wetting agent (Silwet L-7604) was provided by Witco Corp. All of the materials were used as received.

Formulations

A typical formulation consisted of cycloaliphatic epoxide resin, polyol, cationic photoinitiator, and the Silwet L-7604 wetting agent. The cycloaliphatic epoxide, polyols, and photoinitiators used in this study are shown in Tables I–III, respectively. For a typical formulation, the desired amount of polyol was added to cycloaliphatic diepoxide [ratio of oxirane to hydroxyl groups (*R*) = 2.0–∞] with 4.0 wt % photoinitiator and 0.5 wt % Silwet L-7604. The mixture was thoroughly mixed on a roller mill for 10 h. The coating was then cast onto a KBr crystal for the kinetic studies. The formulations for the studies of the effect of polyol equivalent weight, *R*, epoxide type, photoinitiator type and concentration, and exposure time on the curing reaction are shown in Tables IV–VII, respectively.

TABLE VII
Formulations^a for the Studies of the Effect of Exposure Time on the Curing Reaction

	UVR-6110 (g)	Polyol (g)		<i>R</i>
		TONE 0301	TONE 0310	
D1	61.68	—	33.82	4.0
D2	69.87	25.63	—	2.0
E1	95.5	—	—	∞

^a The photoinitiator UVI-6974 (4.0 g) was used, and 0.5 g of Silwet L-7604 was used 0.5 g for all of the formulations.

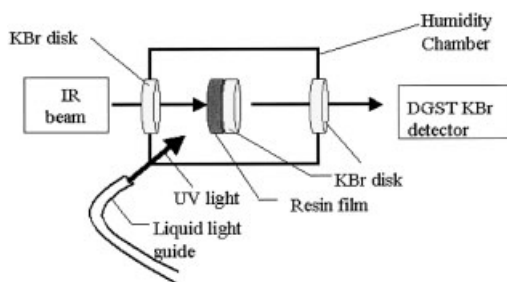


Figure 1 Real-time FTIR experimental setup.

Real-time FTIR spectroscopic measurements

Real-time FTIR spectroscopic measurements were performed on a Nicolet Magna-IR 850 spectrometer equipped with a LESCO Super Spot MK II UV curing system (Waltham, MA). The experimental setup is shown in Figure 1. The relative humidity was controlled by a humidity chamber with the aid of a $\text{LiI} \cdot 3\text{H}_2\text{O}$ constant humidity solution.²⁵ The humidity chamber was fitted into the FTIR spectrometer sample chamber. The UV radiation from a 100-W direct-current mercury vapor short-arc lamp was introduced into the humidity chamber through a flexible optical fiber. The end of the optical fiber was positioned at a distance of 5 cm from the KBr crystal to ensure that the entire crystal was irradiated by the UV light. A UVX digital radiometer was used to measure the radiation intensity, and the intensity was 10.8 mW/cm^2 . The coating was coated on the KBr crystal. Data acquisitions and spectra calculations were performed with

Omnic FTIR software (Nicolet). UV curing was conducted at $23 \pm 2^\circ\text{C}$ and 20% relative humidity. Spectra were collected at a resolution of 4 cm^{-1} and at the rate of 2 spectra/s. In all the cases, triplicate experiments were performed to verify reproducibility.

RESULTS AND DISCUSSION

The objective of this study was to investigate the curing kinetics, especially the dark-cure process, of photoinitiated cycloaliphatic epoxide coatings. A series of cationic UV-curable cycloaliphatic epoxide coatings was formulated with caprolactone polyols as cross-linkers and triarylsulfonium salts as photoinitiators. We carried out the kinetics study by monitoring the consumption of epoxy group as a function of time with real-time FTIR spectroscopy with an optical fiber UV curing system. The effect of the type of epoxide, hydroxyl equivalent weight of polyol, photoinitiator, and exposure time on the curing process was investigated. In addition, R was investigated. R is defined by the following equation:

$$R = \frac{\text{g of epoxy/EEW}}{\text{g of polyol/OH EW}} \quad (1)$$

where EEW and OH EW represent epoxide equivalent weight and hydroxyl equivalent weight, respectively.²⁶

By simultaneously irradiating the coating film with UV light and recording the IR spectra in real time, we monitored the changes in the monomer undergoing

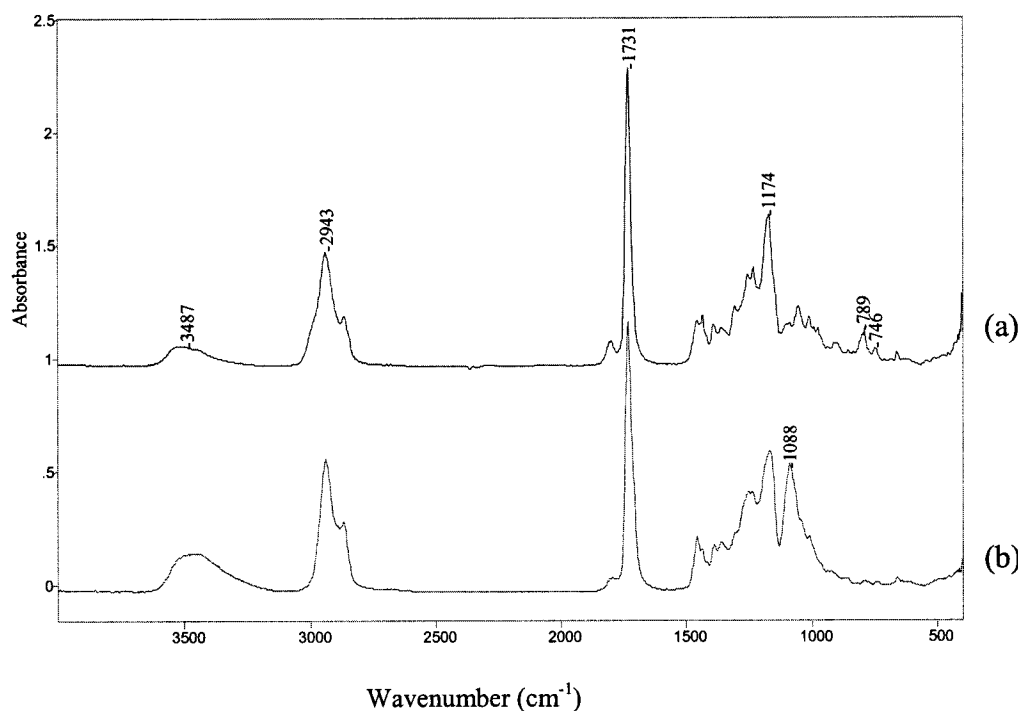


Figure 2 FTIR spectra of UVR-6110/TONE 0310 ($R = 3.0$)/UVI-6974 (4.0 wt %) (a) before and (b) after UV curing.

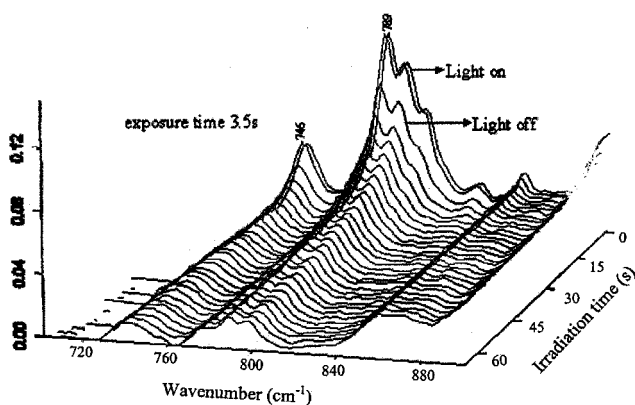


Figure 3 Three-dimensional FTIR spectra of the cationic UV curing reaction of UVR-6110/TONE 0310 ($R = 3.0$)/UVI-6974 (4.0 wt %).

photopolymerization as a function of time. Figure 2 shows the spectra of UVR-6110/TONE 0310 ($R = 3.0$)/UVI-6974 (4.0 wt %) before and after UV exposure. The antisymmetric and symmetric epoxy ring deformation at 789 and 746 cm^{-1} disappeared after UV exposure, and a new band at 1088 cm^{-1} appeared. The 1088- cm^{-1} band was attributed to the C—O—C stretching formed on photopolymerization. Theoretically, both the 789–746 and 1088- cm^{-1} bands could be used to monitor the UV curing reaction. However, the 1088- cm^{-1} band was partially overlapped with the C—O—C stretching of the ester groups (1174 cm^{-1}). Therefore, the epoxide absorption bands in the 789–746- cm^{-1} region were used to characterize the curing reaction (ether formation). A three-dimensional spectral profile of the UV curing reaction of this formulation in the 789–746- cm^{-1} region is shown in Figure 3. The data clearly shows a rapid decrease in the epoxy band even after the UV-radiation pulse, indicating that dark cure existed in the cycloaliphatic epoxide photopolymerization process. Moreover, over 80% of the consumption of the epoxy groups occurred in the dark-cure process. The conversion of the epoxy groups at any time can be calculated by the following equation:

Conversion (%) =

$$\frac{[A_{(789\text{cm}^{-1}+746\text{cm}^{-1})}]_0 - [A_{(789\text{cm}^{-1}+746\text{cm}^{-1})}]_t}{[A_{(789\text{cm}^{-1}+746\text{cm}^{-1})}]_0} \times 100 \quad (2)$$

where $[A_{(789\text{ cm}^{-1}+746\text{ cm}^{-1})}]_0$ and $[A_{(789\text{ cm}^{-1}+746\text{ cm}^{-1})}]_t$ represent the peak area under the 789 and 746- cm^{-1} bands at the beginning of the reaction and at time t , respectively. The actual rate of polymerization (R_p) at time t can be calculated by the following equation:

$$R_p = [M]_0 \frac{[A_{(789\text{ cm}^{-1}+746\text{ cm}^{-1})}]_{t1} - [A_{(789\text{ cm}^{-1}+746\text{ cm}^{-1})}]_{t2}}{t_2 - t_1} \quad (3)$$

where $[M]_0$ is the original concentration of epoxy groups.

It is known that photopolymerization develops at the same rate for thin films with minimal stratification; however, as film thickness increases, the rate of polymerization drops concurrently because of a UV filtering effect of the top layer.²³ For the systems studied, when the film thickness was less than 3 μm , the effect of film thickness was minimal in the early stage and negligible on the overall conversion, as shown in Figure 4.

Figures 5 and 6 show the effect of types of epoxide on the curing reaction of formulations with and without polyol, respectively. The formulations with UVR-6128 had a higher overall conversion than those with UVR-6110. This result was attributed to the flexibility of the polymer chain afforded by UVR-6128 in comparison with UVR-6110. The higher flexibility of the polymer chain increased the mobility of both the monomer and the growing polymer chain. Unlike free-radical polymerization, where increased mobility lowers the overall conversion because of the increased rate of termination,²⁷ in cationic UV curing systems, increased mobility leads to an increase in overall con-

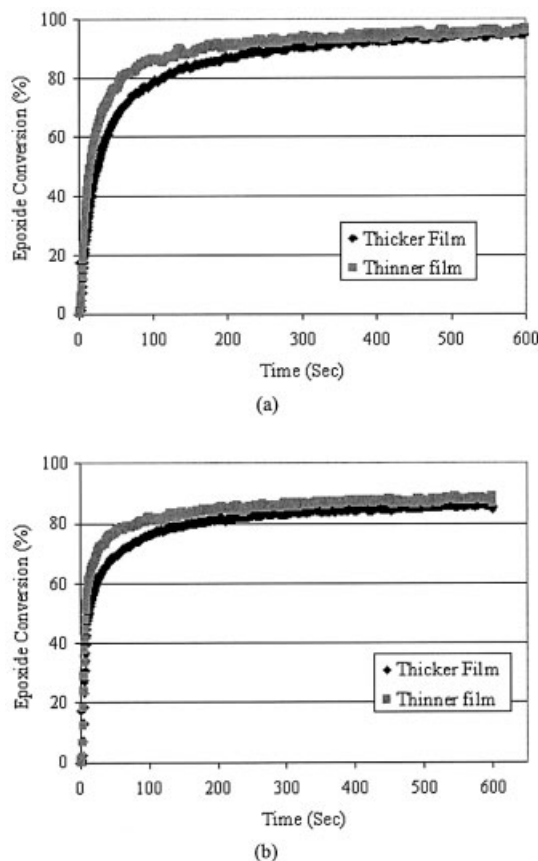


Figure 4 Effect of the film thickness on the curing reaction: (a) UVR-6128/UVI-6974 (4.0 wt %; without polyol) formulation with a 3.5-s exposure and (b) UVR-6110/TONE 0305 ($R = 4.0$)/UVI-6974 (4.0 wt %) with a 3.5-s exposure.

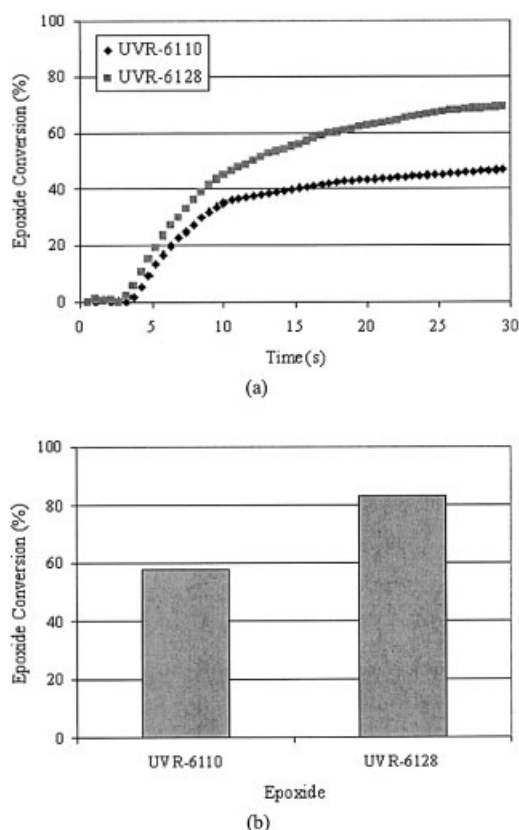


Figure 5 Effect of the type of epoxide on the epoxide conversion for UVI-6974 (4.0 wt %)/epoxide/TONE 0304 ($R = 3.0$) formulations at 20% relative humidity with an exposure time of 3.5 s: (a) $t = 0$ –30 s and (b) overall conversion at $t = 600$ s.

version. This effect has been attributed to a delay in the gelation and vitrification processes. The glass-transition temperature (T_g) of the formed network has a well-known effect on the overall conversion.²⁴ Figures 5 and 6 show that the curing rate passed through a maximum and then rapidly decreased. The slope at each point was proportional to the curing speed. The decrease of the curing rate was due to gelation. When gelation occurred, the curing rate was diffusion-controlled. However, when the T_g of the formed network approached the temperature of the curing reaction, vitrification occurred. At this point, even diffusion of the monomer was impeded, and the polymerization was stopped. For formulations with more flexible polymer chains, the onset of both gelation and vitrification were delayed; thus, overall conversion was enhanced.

The effect of the hydroxyl equivalent weight on the curing reaction is shown in Figures 7 and 8. At the same relative humidity and R , the formulation with TONE 0310 had the highest curing speed and overall conversion. In contrast, the formulation with TONE 0301 had the lowest curing speed and overall conversion. Generally, crosslink density and flexibility were

dependent on the hydroxyl equivalent weight of polyol. TONE 0301 had the lowest hydroxyl equivalent weight, and TONE 0310 had the highest hydroxyl equivalent weight. As a consequence, at the same R , formulations with TONE 0301 had the highest crosslink density and lowest chain flexibility. In contrast, formulations with TONE 0310 had the lowest crosslink density and highest chain flexibility. Crosslink density and flexibility of the network also had a significant effect on the mobility of the monomer and the growing polymer chain. Lower crosslink density and higher chain flexibility led to a higher mobility in both the monomer and growing polymer chain, which resulted in a higher curing speed and overall conversion.²⁴

In addition to flexibility and crosslink density, the effect of hydroxyl equivalent weight on the curing reaction was more pronounced at the lower R ($R = 2.0$) than that at the higher R ($R = 4.0$). At $R = 2.0$, the overall conversion for the formulation with TONE 0301 at 600 s after UV radiation was only 18%, but for the formulation with TONE 0310, the overall conversion was 83%. As shown in Table VIII, at $R = 2.0$, the

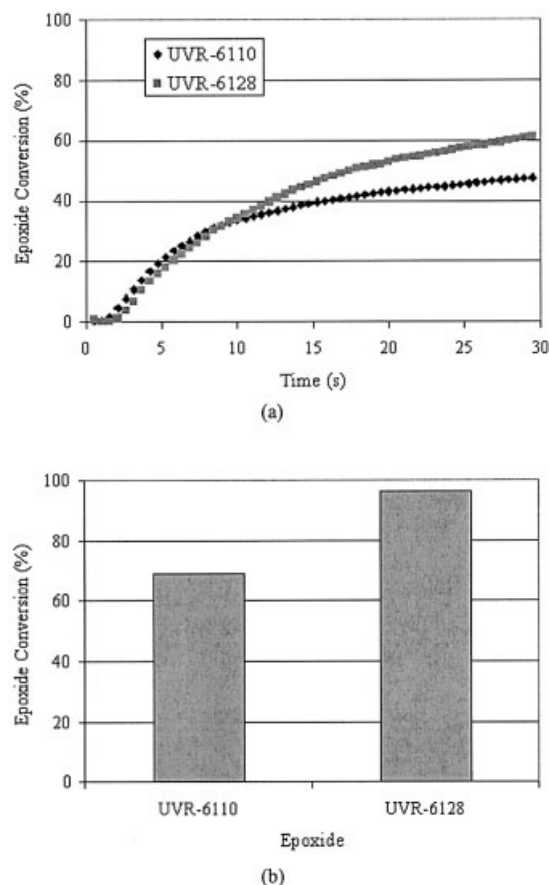


Figure 6 Effect of the type of epoxide on the epoxide conversion for UVI-6974 (4.0 wt %)/epoxide (without polyols) at 20% relative humidity with an exposure time of 3.5 s: (a) $t = 0$ –30 s and (b) overall conversion at $t = 600$ s.

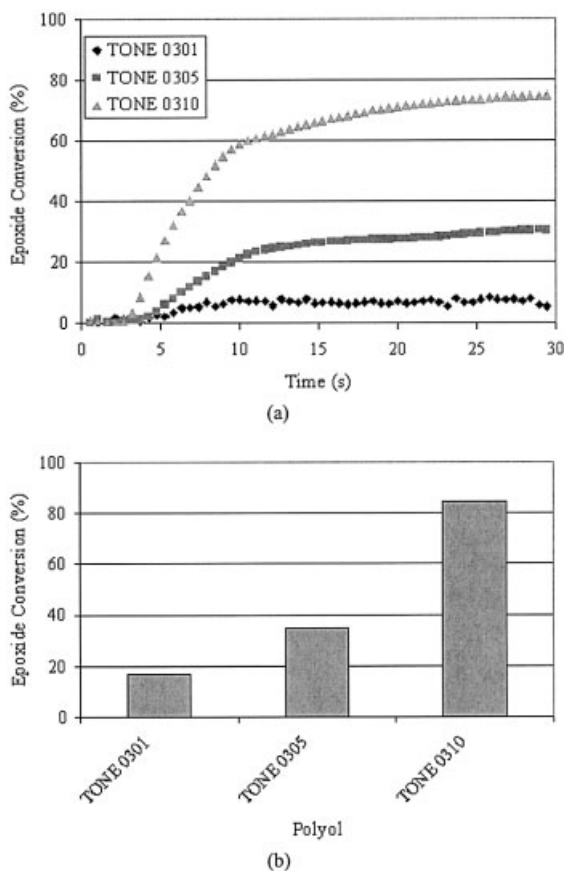


Figure 7 Effect of the hydroxyl equivalent weight on the epoxide conversion for UVR-6110 (4.0 wt %)/polyol ($R = 2.0$)/UVI-6974 (4.0 wt %) at 20% relative humidity with an exposure time of 3.5 s: (a) $t = 0-30$ s and (b) overall conversion at $t = 600$ s.

difference in water content among the three formulations was quite substantial. For example, at 20% relative humidity, the water content was 0.64 wt % for the TONE 0301 formulation and 0.37 wt % for the TONE 0310 formulation. Because the overall conversion for TONE 0301 formulation was quite low, we propose that most of the activated chain ends (ACEs) were terminated by water in the early stages of the reaction. In contrast, termination of the ACEs for the TONE 0310 formulation was not apparent. In this case, water appeared to facilitate the proton transfer, which increased the curing speed and overall conversion. As previously mentioned, the crosslink density and chain flexibility also had effects on the curing speed and overall conversion. At $R = 4.0$, the range of water content for the three formulation was 0.13 wt %. In this case, the chain flexibility, and not the water content, was the primary factor affecting the cure speed and overall conversion.

Figure 9 shows the effect of R on the curing process of the UVR-6110/TONE 0301 formulation with the UVI-6974 photoinitiator. The curing speed and the

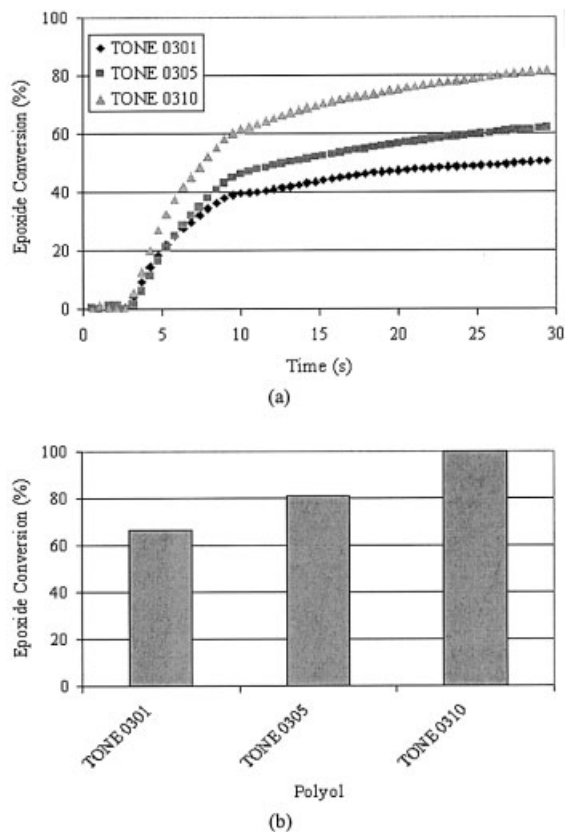


Figure 8 Effect of the hydroxyl equivalent weight on the epoxide conversion for UVR-6110 (4.0 wt %)/polyol ($R = 4.0$)/UVI-6974 (4.0 wt %) at 20% relative humidity with an exposure time of 3.5 s: (a) $t = 0-30$ s and (b) overall conversion at $t = 600$ s.

overall conversion pass through a maximum when the R values varied from 2.0 to infinity ($\infty =$ no polyol). This phenomenon resulted from the different propagation mechanisms. Without polyol, the propagating chain end was the epoxide oxonium ion (M_n^+) and

TABLE VIII
Water Content (%)

	Relative humidity (%)		
	16	20	30
UVR-6110/TONE 0301 ($R = 2$)/UVI-6974 (4.0 wt %)	0.48	0.64	1.06
UVR-6110/TONE 0301 ($R = 4$)/UVI-6974 (4.0 wt %)	0.38	0.46	0.83
UVR-6110/TONE 0305 ($R = 2$)/UVI-6974 (4.0 wt %)	0.35	0.51	0.86
UVR-6110/TONE 0305 ($R = 4$)/UVI-6974 (4.0 wt %)	0.30	0.39	0.76
UVR-6110/TONE 0310 ($R = 2$)/UVI-6974 (4.0 wt %)	0.31	0.37	0.74
UVR-6110/TONE 0310 ($R = 4$)/UVI-6974 (4.0 wt %)	0.26	0.33	0.65
UVR-6110/UVI-6974 (4.0 wt %)	0.23	0.28	0.51

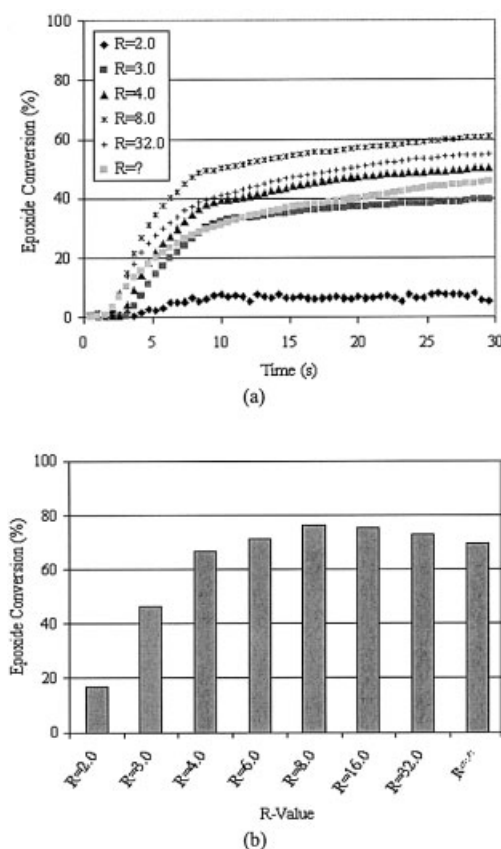
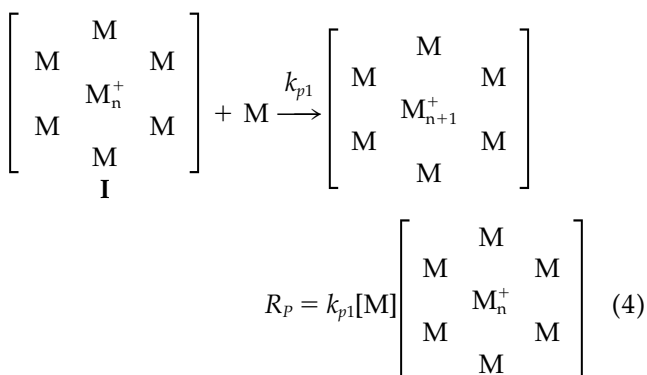
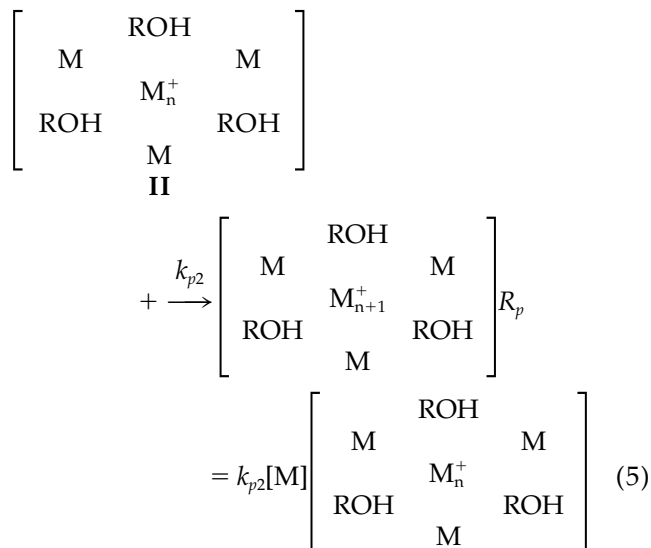


Figure 9 Effect of R on the epoxide conversion for UVR-6110/TONE 0301/UVI-6974 (4.0 wt %) at 20% relative humidity with an exposure time of 3.5 s: (a) $t = 0\text{--}30$ s and (b) overall conversion at $t = 600$ s.

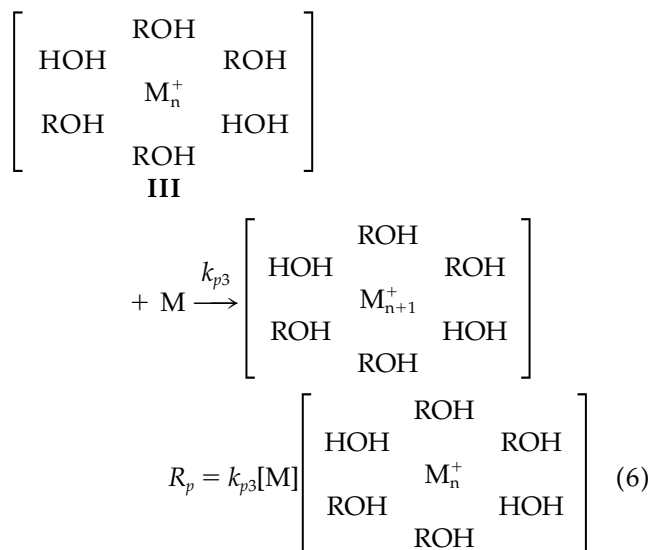
was highly solvated by monomer molecules, as shown in eq. (4):²⁸



where M is the monomer, M_{n+1}^+ is the growing polymer chain, and k_{p1} is the rate constant of homopolymerization. Polymerization took place through the active chain-end mechanism.²⁹ When a small amount of polyol ($R > 8$) was added to the formulation, the oxonium ion was solvated by both monomer and polyol because of the higher basicity and nucleophilicity of polyol, as shown in eq. (5).²⁸



In this case, polyols facilitated the proton transfer. Thus, the curing rate or overall conversion increased with increasing polyol concentration. When the polyol concentration was higher ($R < 8$), the oxonium ion could be solvated by only the polyol. In this case, propagation occurred through an activated monomer mechanism,³⁰ followed by the reaction with polyol via a condensation reaction, which led to cation termination and the release of a proton. The termination of the cations lowered the reaction rate and overall conversion with respect to the consumption of oxirane:

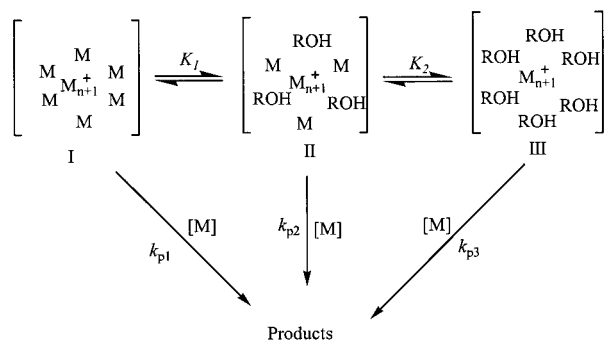


The overall reaction is shown in Scheme 4. The rate of epoxy conversion (R_r) is given by the following equation:

$$R_r = k_{p1}[\text{I}][\text{M}] + k_{p2}[\text{II}][\text{M}] + k_{p3}[\text{III}][\text{M}] \quad (7)$$

where k_p is the propagation rate for each reaction.

With increasing polyol concentration, **II** dominated, and $k_{p2} > k_{p1}$. As a consequence, the overall epoxide



M: monomer and N: polyol or H₂O

$$K_{p1} < K_{p2} \gg K_{p3}$$

Scheme 4 Possible propagation reactions.

conversion increased with increasing polyol concentration. However, with further increasing polyol concentration, both I and II decreased. Although III increased, because $k_{p2} \gg k_{p3}$, the overall epoxide conversion decreased. Therefore, a maximum was observed as the polyol concentration reached the optimum.

Figures 10 and 11 show the effect of R on the curing

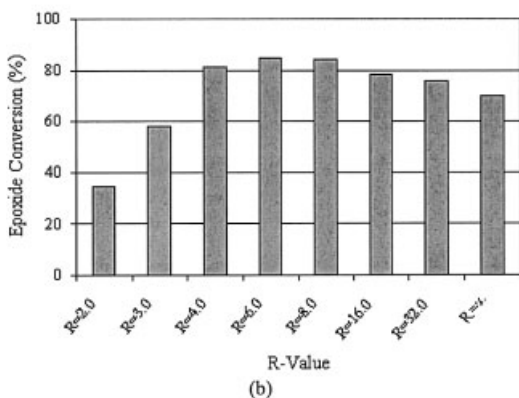
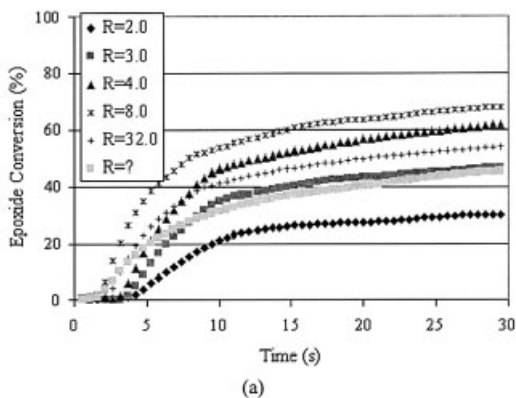


Figure 10 Effect of R on the epoxide conversion for UVR-6110/TONE 0305/UVI-6974 (4.0 wt %) at 20% relative humidity with an exposure time of 3.5 s: (a) $t = 0-30$ s and (b) overall conversion at $t = 600$ s.

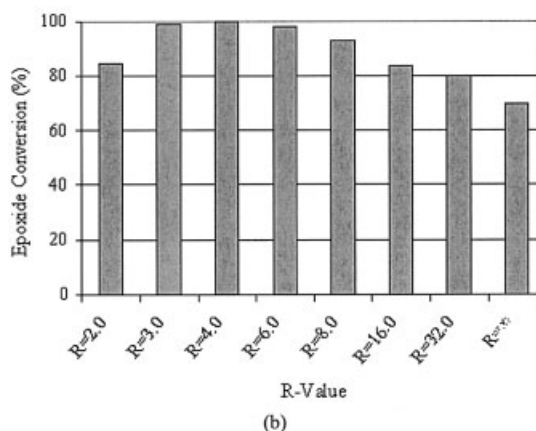
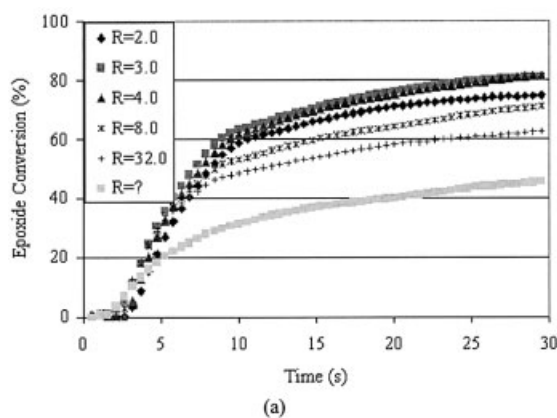


Figure 11 Effect of R on the epoxide conversion for UVR-6110/TONE 0310/UVI-6974 (4.0 wt %) at 20% relative humidity with an exposure time of 3.5 s: (a) $t = 0-30$ s and (b) overall conversion at $t = 600$ s.

reaction when TONE 0305 and 0310 were added to the formulations, respectively. Similar data were obtained. However, when TONE 0305 or TONE 0310 was added to the formulations, the optimum R occurred at 6.0 or 4.0, respectively. It is probable that the optimum value was also a function of water content. At same R, water content in the formulation was dependent on the hydroxyl equivalent weight of the polyol. The higher the hydroxyl equivalent was, the lower the water content was. Water had a similar effect on the reaction as polyol. The lower the water content was, the lower the optimum R was.

Figures 9–11 also show that there was a retardation in the beginning of the UV curing reaction. The induction period existed for all of the UV curing reactions studied, even for the reaction without polyol. For formulations with polyols, the higher the polyol concentration was, the longer the induction period was. We propose that retardation of the curing reaction was due to the competition of the formation of M_{n+1}^+ and the termination of M_n^+ . If the formation of M_{n+1}^+ was faster than the termination of M_n^+ , after the induction period cations were produced in sufficient quantity for an observed change in the epoxy concentration.

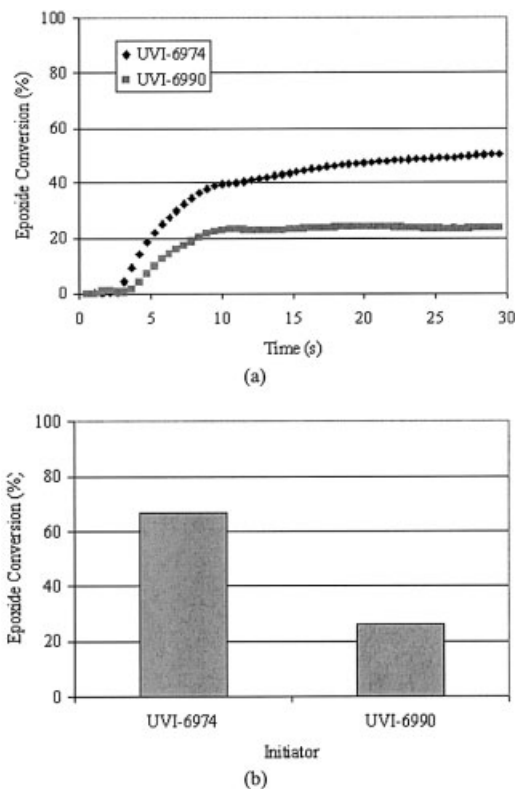


Figure 12 Effect of the type of initiator on the epoxide conversion for UVR-6110/TONE 0301/initiator (4.0 wt %) at 20% relative humidity with an exposure time of 3.5 s: (a) $t = 0$ –30 s and (b) overall conversion at $t = 600$ s.

The effect of the type of photoinitiator on the curing reaction is shown in Figure 12. Figures 13–15 show the effect of the photoinitiator concentration on the curing reaction. As previously reported, the antimonate salt (UVR-6974) was faster curing than the phosphate salt (UVR-6990).³¹ It was surprising that for formulations without polyol (Figs. 13 and 14), the photoinitiator concentration had a minimal effect on the curing reaction at 20% relative humidity. For example, when the photoinitiator concentration increased from 0.5 to 4.0 wt %, the corresponding overall conversion at 600 s was minimally increased (Figs. 13 and 14). However, if polyols were added to the formulations, the curing speed was dependent on the photoinitiator concentration (Fig. 15). The overall conversion at 600 s after UV exposure was doubled when the photoinitiator concentration was varied from 2.0 to 4.0 wt %.

It is well known that the cation radicals formed during UV exposure can only generate superacid in the presence of hydrogen donors.³² Cation radicals are known to react with water or other hydroxyl-containing compounds in a complex way to produce a proton.³³ Therefore, both water and polyols function as hydrogen donors. For formulation without polyols, water is the only hydrogen donor. At 20% relative humidity, the water content in the formulation was

too low (<0.3 wt %) to facilitate homopolymerization. We postulated that the diacrylsulfonium radical cations formed during UV exposure were in excess of the hydrogen donor concentration. For low-relative-humidity conditions, the number of protons formed in the photoinitiation step was controlled by the water concentration in the formulation. However, when polyols were added to the formulation, there were sufficient hydrogen donors to react with diacrylsulfonium cation radicals to produce the protons. In this case, the number of protons that formed was dependent on the concentration of the photoinitiator. The higher the photoinitiator concentration was, the higher the curing speed or overall conversion was.

Similar to photoinitiator concentration, exposure time also showed a minimal effect on the curing reaction for formulations without polyol (Fig. 16). The overall conversion at 600 s was 63% for 1 s of exposure, 71% for 3.5 s of exposure, and 73% for 200 s of exposure. For 1 s of exposure, the number of diacrylsulfonium cation radicals formed was small in comparison to the water concentration. Obviously, as exposure time increased, the concentration of diacrylsulfonium radical cations increased, and as a

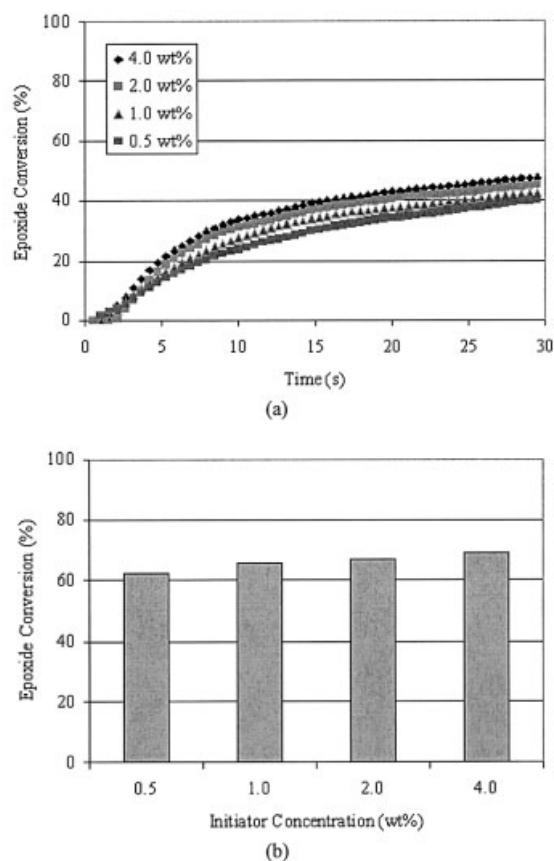


Figure 13 Effect of the initiator concentration on the epoxide conversion for UVR-6110/UVI-6974 (without polyol) at 20% relative humidity with an exposure time of 3.5 s: (a) $t = 0$ –30 s and (b) overall conversion at $t = 600$ s.

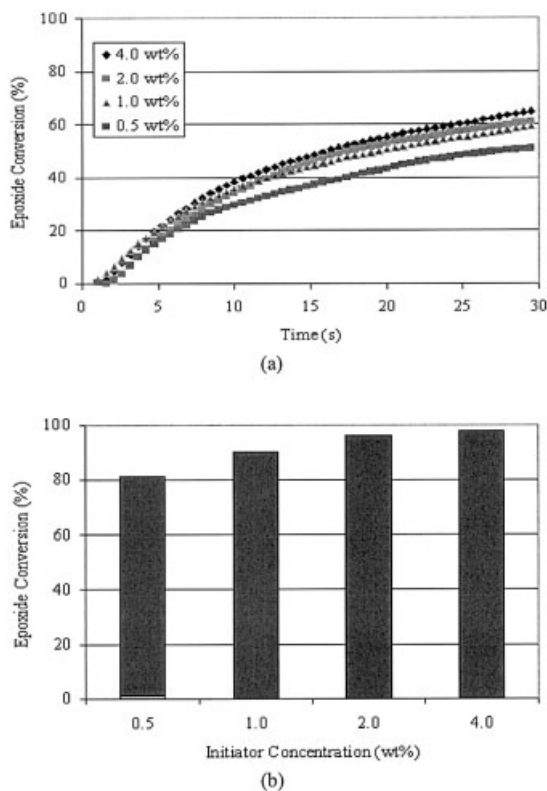


Figure 14 Effect of the initiator concentration on the epoxide conversion for UVR-6128/UVI-6974 (without polyol) at 20% relative humidity with an exposure time of 3.5 s: (a) $t = 0$ –30 s and (b) overall conversion at $t = 600$ s.

consequence, the number of protons produced also increased. When the exposure time increased to 3.5 s, it was evident that the concentration of diarylsulfonium cation radicals formed was greater than the water concentration. In this case, the number of protons formed was limited by the water concentration, and a further increase in the exposure time had little effect on the curing reaction.

Figures 17 and 18 show the effect of exposure time on the UV curing reactions of formulations with polyol. The effect of exposure time on the curing reaction depended on both the hydroxyl equivalent weight of polyol and R . For formulations with high hydroxyl equivalent weight polyols and high R values (Fig. 17), the effect of exposure time on the curing reaction showed a similar trend as the formulation without polyol. However, for formulations with low hydroxyl equivalent weight polyols and low R values (Fig. 18), the curing speed was a function of exposure time. The overall conversion was only 18% at 3.5 s of exposure; however, the curing speed was a function of exposure time. In this case, hydrogen donors were not limiting the speed of reaction as a consequence of the sufficient ROH ($R=H$ or R) concentration. Thus, under these conditions, the formation of superacid was dependent on the exposure time. When the exposure

time was very short, such as 3.5 s, the chain-initiation species were predominately terminated by competitive nucleophiles because of the excess of water and polyol. This assumption was corroborated by the long induction times.

In this study, a synergistic effect between water and polyol was revealed, and the effect of relative humidity without polyol was observed. Decker and coworkers²⁰ reported that the conversion of cycloaliphatic epoxide without polyol was dependent on photoinitiator concentration and curing time. However, the effect of relative humidity was not reported. In this study, it was apparent that water was the salient feature for the formulation without polyol. Previous researchers have postulated that polyol (hydroxyl group) accelerates the curing reactions via a proton-transfer mechanism.²⁴ From our data, it was clear that the proton-transfer effect was only part of the model. The hydrophilicity of the formulation and ambient relative humidity also had to be taken into account. The role of water in the UV-initiated cationically cured coatings was complex. Like polyol, water could participate in the formation of the superacid and termination of the propagating ACEs. In addition, we postulated that at low concentration, water participated in

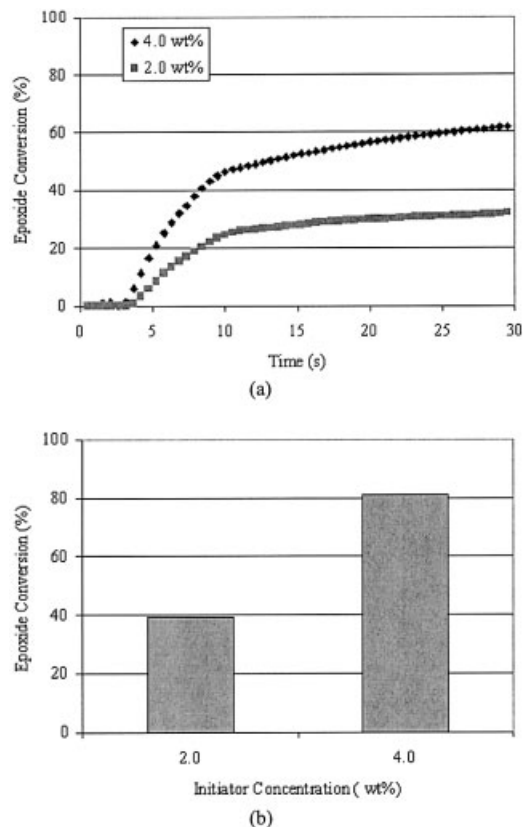


Figure 15 Effect of the initiator concentration on the epoxide conversion for UVR-6110/TONE 0305 ($R = 4.0$)/UVI-6974 at 20% relative humidity with an exposure time of 3.5 s: (a) $t = 0$ –30 s and (b) overall conversion at $t = 600$ s.

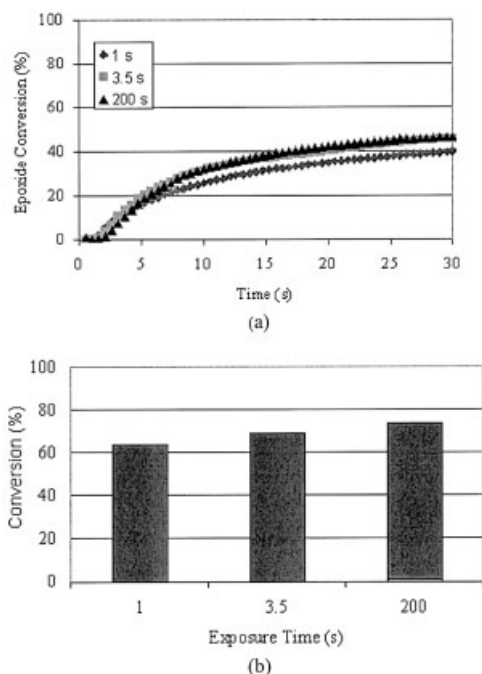


Figure 16 Effect of the exposure time on the epoxide conversion for UVR-6110/UVI-6974 (4.0 wt %, without polyol) at 20% relative humidity with an exposure time of 3.5 s: (a) $t = 0$ –30 s and (b) overall conversion at $t = 600$ s.

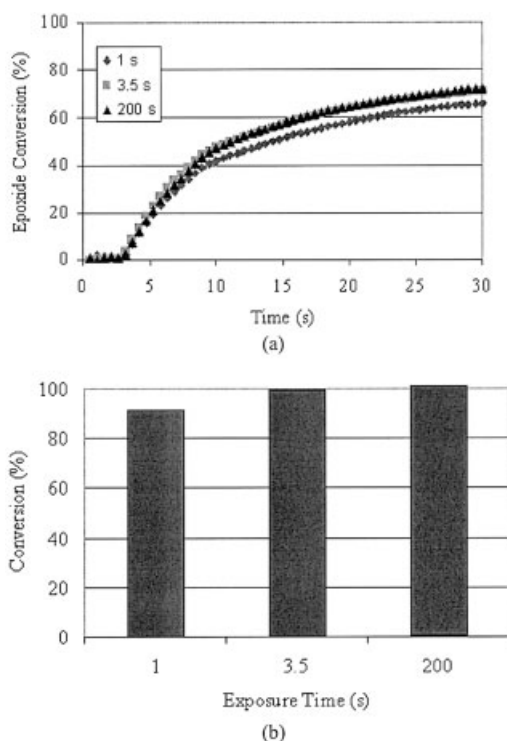


Figure 17 Effect of the exposure time on the epoxide conversion for UVR-6110/UVI-6974 (4.0 wt %)/TONE 0310 ($R = 4.0$) at 20% relative humidity with an exposure time of 3.5 s: (a) $t = 0$ –30 s and (b) overall conversion at $t = 600$ s.

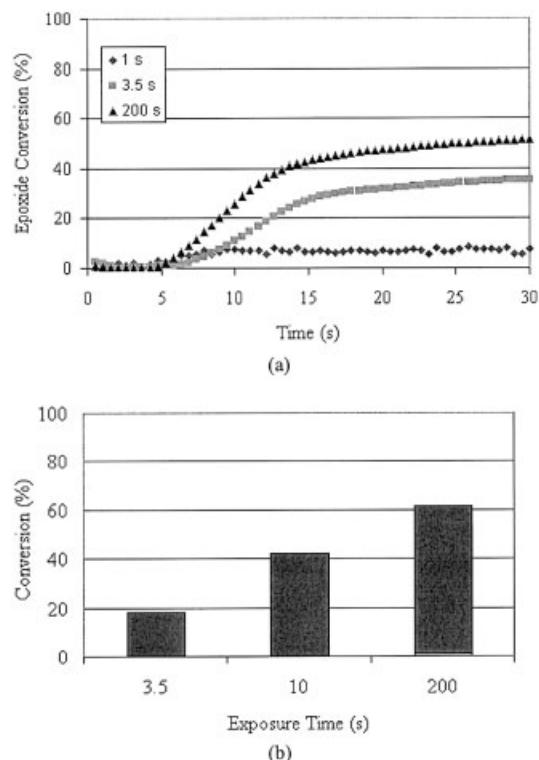


Figure 18 Effect of the exposure time on the epoxide conversion for UVR-6110/UVI-6974 (4.0 wt %)/TONE 0301 ($R = 2.0$) at 20% relative humidity with an exposure time of 3.5 s: (a) $t = 0$ –30 s and (b) overall conversion at $t = 600$ s.

the stabilization of the activated monomer (AM) or ACEs [eqs. (1)–(3) and Scheme 4] and facilitated proton transfer. However, if the formulation was saturated with water, a leveling effect of acid strength was observed, followed by hydrolysis of the AM or ACEs, which resulted in the termination of cure. A more in-depth investigation of the effect of water is currently underway.

CONCLUSIONS

Real-time FTIR was demonstrated as a sensitive, reliable, and easy-to-use analytical technique for the monitoring of cationic UV-curable reactions of cycloaliphatic epoxides. The IR data showed that curing depended on a complex relationship between hydroxyl equivalent weight and R . Polyols accelerated the curing reaction through stabilization of the AM or ACEs and facilitated proton transfer. However, polyol also lowered the homopolymerization reaction via cation termination. We postulated that water and polyol had a synergistic effect on the overall conversion and kinetics of curing. The effect of initiator concentration and exposure time on the curing reaction was also dependent on relative humidity and polyol concentration. Exposure time only had a significant effect on formulations with low hydroxyl equivalent weights

and low R values. For formulations without polyol, both the initiator concentration and exposure time had minimal effects on the curing reaction.

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