

Photopolymerization Kinetics of an Epoxy-based Resin for Stereolithography

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ABSTRACT: Curing reactions of photoactivated epoxy resins are assuming an increasing relevance in many industrial applications, such as coatings, printing, and adhesives. Besides these processes, stereolithography (SL) makes use of photoactivated resins in a laser-induced polymerization for 3D building. The kinetic behavior of photocuring is a key point for full comprehension of the cure conditions occurring in the small zone irradiated by the laser beam during the building process. Furthermore, the kinetic analysis is very important to determine the cure time needed for part building in a stereolithographic equipment. The mechanisms involved in a cationic photopolymerization are complex compared with radical photopolymerization. In this paper the photoinitiated polymerization of a commercially available epoxy-based resin for stereolithography (SL5170)

was studied by means of differential scanning calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR). Substantial information about the SL5170 chemical composition and curing mechanism was determined through FTIR analysis. The polymerization rate and the maximum degree of reaction were determined directly from experimental DSC curves. Kinetic characterization of epoxy photopolymerization was carried out as a function of the temperature and irradiation intensity and experimental results were compared with an original mathematical model. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 3484–3491, 2004

Key words: differential scanning calorimetry; cationic polymerization; kinetics; modeling

INTRODUCTION

In recent years the growing interest in cationic photopolymerization is related to the development of very efficient photoinitiators and to the distinct advantages of this method of radiation curing. As a result, UV-initiated cationic photopolymerization is finding application in a wide variety of areas, including coatings, inks, adhesives, and electronics. Besides these processes, stereolithography (SL) makes use of laser-induced cationic polymerization for 3D building. Stereolithography is the most diffused rapid prototyping process for the fabrication of solid objects starting from three-dimensional CAD models. In this process a laser beam draws cross sections of the model onto the surface of photocurable liquid resin. The major steps of the process include the CAD design, interface with the software equipment, and the stereolithography build process.¹ The kinetic behavior of photocurable resins is the first step for a proper modeling of the heat transfer phenomena occurring in the small zone irradiated by the laser beam and therefore for the correct setting of part building parameters. The first photopolymer systems used for SL were based on acrylate

monomers, which polymerize through a free-radical mechanism. Acrylate-based SL photopolymers are generally characterized by high reactivity, even if not fully cured surfaces may arise from oxygen inhibition, and the polymerization is accompanied by a significant shrinkage. On the other hand, cationic photopolymerization is not influenced by the presence of oxygen and cure shrinkage is quite limited.¹ For this reason, cationic photoactivated monomers are nowadays used in commercial SL equipment. Further, cationic photopolymers show a continued curing, usually called dark reaction,² even after the light source has been removed. Increase of green strength due to the dark reaction, even at room temperature, may be substantial for a cationic system, and particularly beneficial for SL.¹ In acrylate-based resins the dark reaction is negligible, and the green strength does not substantially change once the part has been laser cured. Despite the advantages of cationic photopolymerization discussed above, nearly all the research in UV-initiated polymerization has focused on free radical reactions. This fact may be largely attributed to the lack of suitable UV-sensitive cationic photoinitiators until recently.³ Moreover, cationic polymerization kinetics are complex and strongly affected by resin formulation. Therefore, a simple, coherent, kinetic expression of general validity is not available for cationic photopolymerization.⁴

In this paper the photoinitiated polymerization of a commercially available stereolithographic epoxy-

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based resin was studied by means of modified differential scanning calorimetry (DSC) and by Fourier transform infrared spectroscopy (FTIR). Kinetic characterization of epoxy photopolymerization was carried out as a function of temperature and irradiation intensity, and experimental results were compared with an original mathematical model derived from the one proposed by Nelson et al.⁵ FTIR analysis were carried out to support the DSC data, providing further insight into the reaction mechanisms of the resin.

EXPERIMENTAL

The resin studied was SL5170 by Ciba. As reported in the material safety data sheet, the resin is actually composed of a mixture of butandiol glycidylether and bis(epoxycyclohexyl)-methyl carboxylate at 24 wt % and 60 wt %, respectively. The remaining weight fraction is a mixture of a photoinitiator, a photosensitizer, and a divinyl ether monomer. The presence of a divinyl ether monomer is typical of cationic formulations⁶ and is confirmed by FTIR analysis reported under Results and Discussion. The cure of the SL5170 resin was carried out in a differential scanning calorimeter Perkin–Elmer DSC-7, modified for irradiation of the sample using transparent quartz windows. The light source, produced by a 300-W Xenon lamp Cermax LX 300, was limited to a wavelength interval of 325 ± 4 nm using a monochromator, to simulate the narrow irradiation band of a He-Cd laser beam of the SL apparatus. The beam was focused on the sample using a system of lenses and a mirror. Small size samples (0.9–1.1 mg) were tested, to achieve isothermal conditions and a uniform degree of cure through sample thickness.⁷ Further, given the strong dependence of reaction kinetics on the sample thickness,⁸ a sample thickness was chosen corresponding to the thickness of a single layer built during the stereolithography process. Isothermal scans were run at 30°C at different irradiation intensities (1.44, 1.92, 2.48, 3.20, 3.44, and $4.33 \mu\text{W}/\text{mm}^2$). The beam intensity was adjusted through optical filters. Isothermal scans were also run at different temperatures, 30, 40, 50, 60, and 70°C, at an irradiation intensity of $2.48 \mu\text{W}/\text{mm}^2$. A maximum temperature of 70°C was chosen, corresponding to the glass transition temperature of a fully cured resin, as reported in the technical data sheet. At each temperature and irradiation intensity, the cure was monitored until no exothermal signal was detected, and the reaction can be considered complete. The DSC measurements were used for determination of the advancement of polymerization by assuming that the heat evolved at each time is proportional to the overall extent of reaction, given by the fraction of reactive groups consumed. Following this approach, the degree of reaction, α , was defined as:⁷

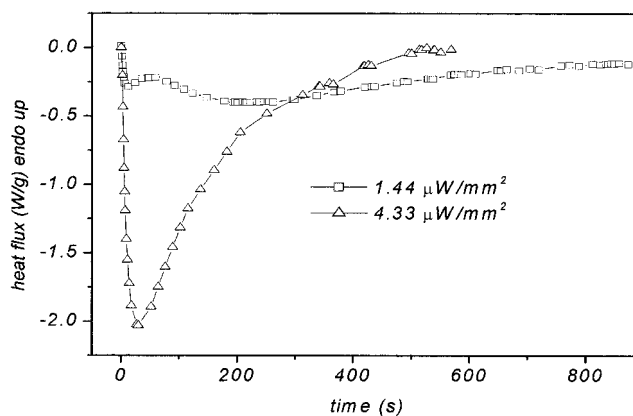


Figure 1 Experimental heat flux versus time at 30°C and 1.44 (\square) and 4.33 (\triangle) $\mu\text{W}/\text{mm}^2$.

$$\alpha = H(t)/H_{\max} \quad (1)$$

where $H(t)$ is the partial heat of reaction developed during a DSC experiment and H_{\max} is the maximum heat of reaction measured combining irradiation and heating as explained below. The rate of reaction, $d\alpha/dt$, was obtained from the heat flow dH/dt as:

$$d\alpha/dt = 1/H_{\max}(dH/dt) \quad (2)$$

For each DSC scan, the final degree of reaction, α_m , was obtained as the ratio between the total heat developed at the end of the scan, H_{iso} , and H_{\max} :

$$\alpha_m = H_{\text{iso}}/H_{\max} \quad (3)$$

A Perkin–Elmer 2000 FTIR spectrometer was used to characterize the SL5170 composition and reaction mechanism. A preliminary FTIR analysis was performed on a thin layer of uncured sample, using a NaCl support. The same sample was then irradiated for 10 s and up to complete polymerization with an irradiation intensity of $3.44 \mu\text{W}/\text{mm}^2$. After each polymerization step, the sample on the support was placed in the FTIR instrument, and its characteristic peaks were determined.

RESULTS AND DISCUSSION

Effect of light intensity

Two representative DSC thermograms obtained at different irradiation intensities during photopolymerization of SL5170 at 30°C are shown in Figure 1. At the lower intensity, two distinct reaction peaks can be observed, becoming more intense and moving to lower times as the incident light increases. The same behavior was previously observed for divinylether resins.⁵ The time needed for each peak to reach its maximum and the maximum height of the peaks are

TABLE I
Characteristic Values of Reaction Peaks for SL5170 at Different Irradiation Intensities

| Light intensity ($\mu\text{W}/\text{mm}^2$) | 1 st Peak time (s) | 1 st Peak height (s^{-1}) | 2 nd Peak time (s) | 2 nd Peak height (s^{-1}) | α_m |
|---|-------------------------------|---|-------------------------------|---|------------|
| 1.44 | 11 | 6.97E-4 | 221 | 9.74E-4 | 0.63 |
| 1.92 | 13 | 8.25E-4 | 164 | 13.84E-4 | 0.66 |
| 2.48 | 10 | 11.81E-4 | 110 | 19.51E-4 | 0.73 |
| 3.20 | 9 | 13.37E-4 | 94 | 24.54E-4 | 0.77 |
| 3.44 | 9 | 19.18E-4 | 71 | 33.40E-4 | 0.86 |
| 4.33 | — | — | — | — | 0.87 |

reported in Table I, as a function of light intensity. At $4.33 \mu\text{W}/\text{mm}^2$ the second peak overlaps on the first, which is no longer observed.

The final degree of reaction α_m is also reported as a function of irradiation intensity in Table I. To obtain the value of H_{max} , an SL5170 sample was photopolymerized at 70°C and $4.33 \mu\text{W}/\text{mm}^2$ and then heated in dark conditions up to 250°C at $10^\circ\text{C}/\text{min}$. The isothermal heat of photopolymerization was calculated to be 367 J/g . The sample heated in dark condition then showed a residual reactivity of 43 J/g . This residual reactivity can be attributed either to the presence of acid catalyst produced by the former exposition to UV light or to active centers developed during isothermal curing and entrapped in the polymer. In both cases, the reaction can continue once the glass transition temperature is exceeded.⁷ This is confirmed by observing that the onset of residual reactivity is at 75°C , just 5°C above the isothermal test temperature. The maximum heat of reaction was taken as the sum of these two contributions, $H_{\text{max}} = 410 \text{ J/g}$. As can be observed in Table I, the maximum degree of reaction increases with the light intensity. This behavior, previously observed for other photoreactive thermosetting acrylic systems⁷ and divinyl ether resins,⁵ is attributed to the delay of vitrification at higher values of α when light intensity increases. In fact, the rate of reaction acts as a driving force for the rate of volume

change. When the light intensity and, consequently, the reaction rate increases, the rate of volume shrinkage cannot follow the rate of chemical conversion, thus leading to an excess of free volume, which is responsible for a delayed transition to the glassy state of the resin.⁷

Effect of temperature

Two representative DSC isothermal scans on SL5170 at different temperatures and at a light intensity of $2.48 \mu\text{W}/\text{mm}^2$ are shown in Figure 2. With this light intensity, at each temperature two distinct peaks can be observed. As reported in Table II, α_m increases with temperature. When the glass transition temperature of the sample reaches the isothermal cure temperature, vitrification of the system determines the end of the reaction.⁷ As the cure temperature increases, vitrification is delayed, and a higher degree of reaction can be obtained. As also shown in Figure 2, both peaks are shifted and their intensities increase with increasing temperature. These observations indicate that an increase of the temperature and of the light intensity lead to an increase of the rate of reaction rate. Therefore, the overall rate of reaction, besides the kinetic effects related to the light intensity and temperature,^{9,10} is affected by diffusion when vitrification occurs^{7,11,12} and by bulk viscoelastic effects determining an increase of α_m with the light intensity.^{7,13}

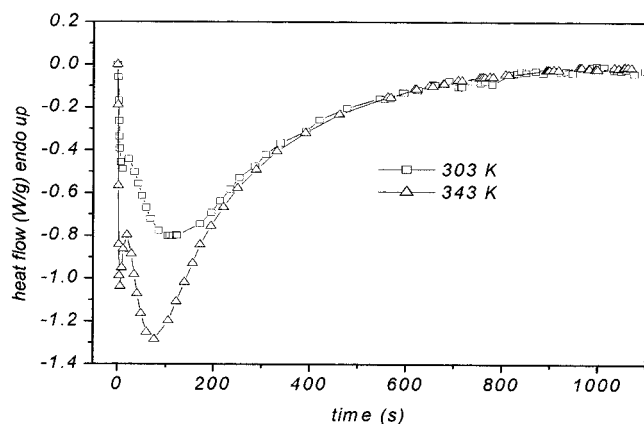


Figure 2 Experimental heat flux at $2.48 \mu\text{W}/\text{mm}^2$ at 30°C (\square) and 70°C (\triangle).

FTIR analysis

The two peaks observed in the experimental DSC curves of Figures 1 and 2 can be attributed to the

TABLE II
Degree of Reaction as a Function of Photopolymerization Temperature

| Temperature (K) | α_m |
|-----------------|------------|
| 303 | 0.73 |
| 313 | 0.76 |
| 323 | 0.77 |
| 333 | 0.79 |
| 343 | 0.81 |

reaction of two distinct species in the SL5170. The presence of different reactive groups in the SL5170 stereolithography resin is confirmed from the FTIR spectrum of the uncured sample, as reported in Figure 3. A wide peak is present at $1,637\text{ cm}^{-1}$, which is a typical value for vinyl ether monomers.^{14,15} Vinyl ether resins are much more reactive than epoxy resins and are typically added as reactive diluents in cationic formulations.⁶ On the other hand, in Figure 3 the presence of epoxy-cyclohexane resin is evidenced by the peak attributed to the oxirane ring fused to cyclohexane at 810 cm^{-1} .¹⁶ The characteristic peaks of the glycidyl ether monomer epoxy groups are also observed at 911 cm^{-1} and 856 cm^{-1} .^{15,17}

A better insight into the reaction mechanisms of SL5170 was obtained through the comparison between uncured, 10-s cured, and fully cured samples. The photopolymerization of mixtures of vinyl ether and cycloepoxy resins was studied through real-time infrared spectroscopy (RTIR) by Rajaraman et al.¹⁸ The authors found that, even if the reaction kinetic of the cycloepoxy can be influenced by the presence of the vinyl ether resin, copolymerization is not observed for such mixtures. In Figures 3 and 4, a comparison between the uncured and 10-s cured sample is shown. After 10 s of irradiation the vinyl ether resin was almost completely reacted, as evidenced in Figure 3 by the disappearance of the peak at $1,637\text{ cm}^{-1}$, while the presence of unreacted epoxy rings is evidenced in Figure 4 by the peaks at 811 cm^{-1} and 911 cm^{-1} for both mono- and disubstituted epoxies. This confirms the hypothesis that vinyl ether resins react rapidly and that unsaturations are almost completely consumed when the reaction of epoxy bonds is activated. Furthermore the monosubstituted glycidyl ether resin is less reactive than the disubstituted cycloepoxy.¹⁹ This is evidenced in the comparison between the uncured and the fully cured sample, reported in Figure 4. When all of the cycloepoxy resin has reacted, as evi-

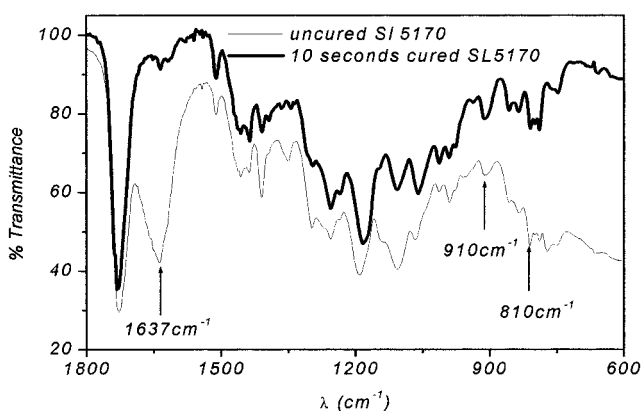


Figure 3 FTIR spectra and characteristic peaks of uncured (—) and 10-s cured (---) SL5170 sample.

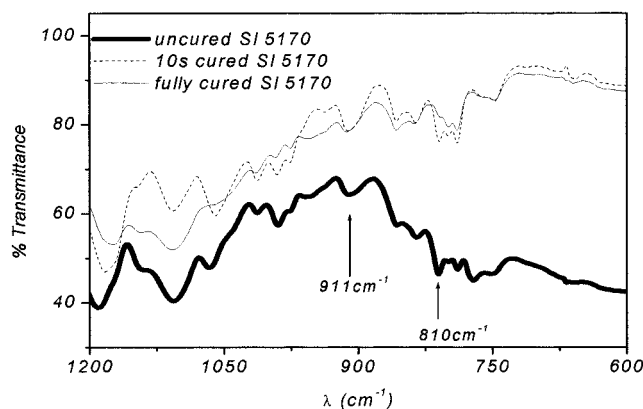


Figure 4 Comparison between FTIR spectra of uncured (—), 10-s cured (---), and fully cured (···) SL5170 samples in the wavelength interval $1,500\text{--}500\text{ cm}^{-1}$.

denced by the disappearance of the characteristic peak at 810 cm^{-1} , a high fraction of epoxy groups in the glycidyl ether is still present, as evidenced by the peak at 911 cm^{-1} . In the time scales of the DSC experiments, the reaction of the glycidyl ether is very weak, and its contribution to the total heat flux is probably negligible.²⁰

The observations performed on FTIR spectra are a clear confirmation of a double-mechanism of reaction. A resin exposure of a few seconds irradiation leads to complete reaction of the vinyl ether groups. The reaction of the cycloepoxy resin is sluggish and is completed in a time of two orders of magnitude higher. The two mechanisms proceed independently and no interaction can be observed between the two reactions. On the other hand, in the time scales of DSC experiments, it is assumed that the reaction of the glycidyl ether resin is not observed.

Kinetic modeling

SL epoxy-based photopolymers for UV curing are generally formulated from reactive liquid monomers and cationic photoinitiators (onium salts), effective in the wavelength between 225 and 275 nm. Since the laser of the SL apparatus emits at 325 nm, formulations for stereolithography include photosensitizers, to expand the spectral region of absorbance up to this wavelength. Photosensitizers are capable of initiating polymerization in the near UV or visible light as a result of a direct interaction between an excited state of the photosensitizer and the initiator.⁴ In the cationic photopolymerizations, during the photosensitization, an electron is transferred from an excited state photosensitizer molecule to the initiator. According to the approach proposed by Nelson,⁵ the rate of monomer consumption is given by:

$$R_p = \frac{d[M]}{dt} = -k_p[M][M^+] \quad (4)$$

TABLE III
Kinetic Constants of Eqs. (6) and (7) at Different Light Intensities for the First Peak Reaction

| Light intensity ($\mu\text{W}/\text{mm}^2$) | $[P_0] \times k_p$ (s^{-1}) | k_t (s^{-1}) | k_i^* (s^{-1}) | $\alpha_{m,ve}$ |
|--|--|---------------------------|-----------------------------|-----------------|
| 1.44 | 0.00199 | 0.154 | 0.0815 | 0.0128 |
| 1.92 | 0.00239 | 0.182 | 0.0887 | 0.0130 |
| 2.48 | 0.00394 | 0.293 | 0.0983 | 0.0134 |
| 3.2 | 0.00561 | 0.357 | 0.102 | 0.0156 |
| 3.44 | 0.00669 | 0.401 | 0.117 | 0.0165 |

In eq. (4) $[M]$ and $[M^+]$ are the unreacted monomer and active center concentration, respectively, and k_p is the propagation constant. The expression for $[M^+]$ can be obtained by analytical integration of the equation proposed by Nelson:⁵

$$\frac{d[M^+]}{dt} = k_i^*[P]_0 \exp(-k_i^*t) - k_t[M^+] \quad (5)$$

In eq. (5) k_t is the termination constant, $k_i^* = k_i[I]$, $= k_i[I]$, where k_i is the initiation constant and $[I]$ is the initiator concentration. $[P]_0$ is the initial photosensitizer concentration. The unreacted monomer concentration $[M]$ can be expressed as a function of the degree of cure α by $[M] = [M]_0(1 - \alpha)$, being $[M]_0$ the initial monomer concentration. The active center concentration $[M^+]$ can be determined by analytical integration of eq. (5). By substituting the value obtained for $[M^+]$ in eq. (4), the following expression can be obtained for the rate of conversion:

$$\frac{d\alpha}{dt} = [P]_0 \frac{k_p k_i^*}{k_t - k_i^*} (e^{-k_i^*t} - e^{-k_t t}) (1 - \alpha) \quad (6)$$

With the initial condition $\alpha = 0$ for $t = 0$, eq. (6) can be analytically integrated in isothermal conditions to obtain the degree of cure as a function of time:

$$\log(1 - \alpha) = -k_2 - k_1 \left(\frac{1}{k_t} e^{-k_t t} - \frac{1}{k_i^*} e^{-k_i^* t} \right) \quad (7)$$

where

TABLE IV
Kinetic Constants of Eqs. (6) and (7) at Different Light Intensities for the Second Peak Reaction

| Light intensity ($\mu\text{W}/\text{mm}^2$) | $[P_0] \times k_p$ (s^{-1}) | k_t (s^{-1}) | k_i^* (s^{-1}) | $\alpha_{m,ve}$ |
|--|--|---------------------------|-----------------------------|-----------------|
| 1.44 | 0.00482 | 0.00496 | 0.00232 | 0.62 |
| 1.92 | 0.00826 | 0.00777 | 0.00272 | 0.65 |
| 2.48 | 0.0135 | 0.0107 | 0.00328 | 0.72 |
| 3.2 | 0.0197 | 0.0141 | 0.00347 | 0.75 |
| 3.44 | 0.0297 | 0.0164 | 0.00373 | 0.84 |

TABLE V
Kinetic Constants of Eqs. (6) and (7) at Different Scan Temperatures for the First Peak Reaction

| Temperature (K) | $[P_0] \times k_p$ (s^{-1}) | k_t (s^{-1}) | k_i^* (s^{-1}) | $\alpha_{m,ve}$ |
|-----------------|--|---------------------------|-----------------------------|-----------------|
| 303 | 0.00394 | 0.293 | 0.0983 | 0.0134 |
| 313 | 0.00625 | 0.422 | 0.115 | 0.0147 |
| 323 | 0.00755 | 0.488 | 0.121 | 0.0153 |
| 333 | 0.00843 | 0.521 | 0.124 | 0.0161 |
| 343 | 0.0118 | 0.606 | 0.132 | 0.0193 |

$$k_1 = \frac{[P]_0 k_p k_i^*}{k_t - k_i^*} \quad (8)$$

and

$$k_2 = k_1 \frac{k_t - k_i^*}{k_i^*} = \frac{[P]_0 k_p}{k_t} \quad (9)$$

Combining eqs. (6) and (7), an explicit dependence of $d\alpha/dt$ from the reaction time is obtained.

The SL5170 reaction is modeled as a parallel mechanism cationic photopolymerization. The commercial resin actually contains three different reactive groups: cycloaliphatic epoxides, glycidyl ethers, and vinyl ethers. According to FTIR analysis, the reaction of glycidyl ethers is much slower than those of disubstituted epoxy rings. FTIR analysis and literature data^{18,21} confirm the absence of copolymerization between cycloepoxy and vinyl ether resins. Accordingly, the first peak observed on DSC thermograms is attributed to the vinyl ether, whereas the second peak is attributed to the cycloepoxy groups reaction. Following a parallel mechanism hypothesis, at each time, the DSC signal can be obtained as the sum of the two distinct signals relative to vinyl ether and epoxy cycloaliphatic monomers. The same differential model, given by combining eqs. (6) and (7), was used to study both reaction mechanisms. The values of k_p , k_i^* and k_t , and k_t were determined for each reaction mechanism, at different values of temperature and light intensity. For each of the two reactions taking place during SL5170 photopolymerization, as $t \rightarrow \infty$, the maximum degree of reaction can be obtained from eq. (10):

$$k_2 = -\log(1 - \alpha_m) \quad (10)$$

It worth noting that k_2 is dependent from the value of α_m according to eq. (10). In turn, from experimental data it was observed that α_m is dependent from both temperature and light intensity, as reported in Tables I and II. This is not predicted by eq. (9), since k_2 is directly proportional to k_p and inversely proportional to k_t , which are usually considered dependent only from temperature^{5,7} and not from light intensity. In fact, in the classical approach proposed by Pappas, the

TABLE VI
Kinetic Constants of Eqs. (6) and (7) at Different Scan Temperatures for the Second Peak Reaction

| Temperature (K) | $[P_0] \times k_p$ (s^{-1}) | k_t (s^{-1}) | k_i^* (s^{-1}) | $\alpha_{m,ep}$ |
|-----------------|---------------------------------|--------------------|----------------------|-----------------|
| 303 | 0.0135 | 0.0107 | 0.00328 | 0.72 |
| 313 | 0.0186 | 0.0134 | 0.00331 | 0.75 |
| 323 | 0.0239 | 0.0168 | 0.00342 | 0.76 |
| 333 | 0.0298 | 0.0202 | 0.00347 | 0.77 |
| 343 | 0.0351 | 0.0223 | 0.00352 | 0.79 |

initiation rate is related to the incident light by the following expression:⁹

$$R_i = L_n \times F \times f$$

where L_n is the specific light intensity at a given depth, F is the fraction of initiating species, and f is an efficiency parameter. In cationic photopolymerization, the initiating species adsorbing light are the photosensitizers and hence the only parameter that should be affected by the light intensity is $k_i^* = k_i[I]$, while the other kinetic constants, k_t and k_p , should not depend on the light intensity. Consequently, k_2 and α_m , according to eqs. (9) and (10), also should be independent from light intensity. Nevertheless, eqs. (6) and (7) were obtained assuming equilibrium conditions. In actual laboratory and processing conditions, the light intensity is always so high that equilibrium conditions are no longer attained. In this case, as already stated previously, vitrification is delayed due to the different time scales of chemical reaction and free volume contraction.^{7,13} Consequently, the increase of k_2 with light intensity can be considered a direct consequence of nonequilibrium conditions,⁷ as was previously observed for α_m , and this is reflected in a dependence of the kinetic constants, k_t and k_p from light intensity.

The experimental curves such those reported in Figures 1 and 2 were used to calculate the parameter of the model according to the following procedure:

- At first, the second peak of each curve was fitted using eqs. (6) and (7), to determine the kinetic constants, k_t and k_p , and k_i^* of cycloepoxy resin reaction, by nonlinear regression. The value of k_2 was determined according to eq. (9), and consequently the value of $\alpha_{m,ve}$, the maximum degree of reaction of vinyl ether resin, was determined from the inverse form of eq. (10);
- The experimental data of the first peak, attributed to the reaction of the vinyl ether system, were then corrected subtracting the fitting curve, obtained in the former step, from the total experimental curve;
- The curve obtained in this way was then fitted using eqs. (6) and (7), to determine the kinetic constants, k_t and k_p , and k_i^* for vinyl ether resin reaction, by nonlinear regression. The value of $\alpha_{m,ep}$, the maximum degree of reaction of epoxy groups, was determined from the relation $\alpha_m = \alpha_{m,ve} + \alpha_{m,ep}$;
- The fitting of the overall DSC experimental data was obtained as the sum of the two contributions, according to eq. (12):

$$\frac{d\alpha}{dt} = \alpha_{m,ve} \left(\frac{d\alpha}{dt} \right)_{ve} + \alpha_{m,ep} \left(\frac{d\alpha}{dt} \right)_{ep} \quad (11)$$

where $(d\alpha/dt)_{ve}$ and $(d\alpha/dt)_{ep}$ are the contributions to the rate of reaction attributed to vinyl ether resin and epoxy bonds, respectively. The values of $\alpha_{m,ve}$ and $\alpha_{m,ep}$ are listed in Tables III through VI.

The values of the kinetic parameters calculated for the two peaks obtained at different light intensities are

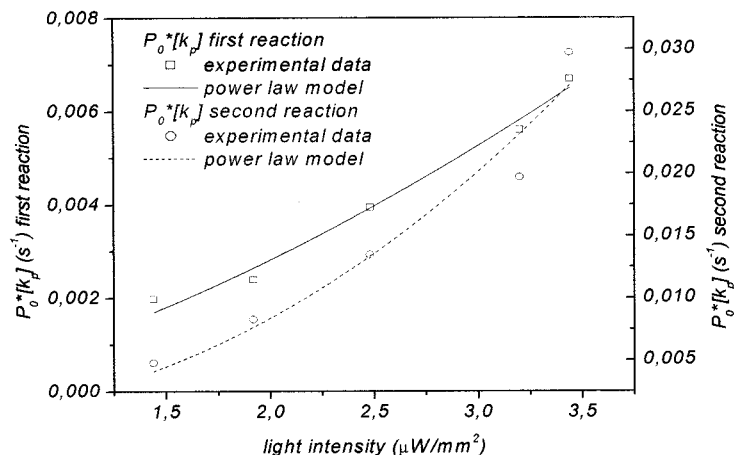


Figure 5 Experimental $[P_0]k_p$ values calculated from nonlinear regression of experimental data as a function of light intensity for the first peak (\square) and the second peak (\circ) and predicted values according to power law model: first peak (—) and second peak (⋯).

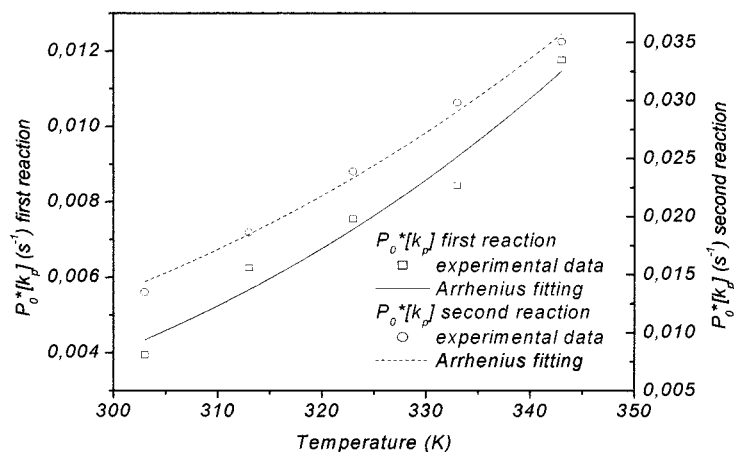


Figure 6 Experimental k_i^* values calculated from nonlinear regression of experimental data as a function of temperature for the first peak (\square) and the second peak (\circ) and predicted values according to Arrhenius model: first peak (—) and second peak (...).

reported in Tables III and IV, respectively. As can be observed, in both reactions, the kinetic constants increase with light intensity. In Tables III and IV, the result obtained at the highest light intensity is not reported, since, as previously observed in Figure 1, in this case the two peaks overlap and it is no longer possible to determine the parameters for the two different reactions.

Also, the dependence of kinetic constant on temperature was assessed keeping the light intensity constant at $2.48 \mu\text{W}/\text{mm}^2$. The results are reported in Table V for the vinyl ether reaction and in Table VI for the cycloepoxy reaction.

The dependence of kinetic constants on light intensity was modeled through a power law expression previously applied to radical photopolymerization.⁷ Therefore at each temperature the kinetic constants, k_t and k_p , and k_i^* are given by:

$$k = k_0 L^b \quad (12)$$

where L is the light intensity, and k_0 and b are two fitting parameters, which depend on temperature through an Arrhenius type expression. A good agreement between eq. (12) and experimental k_p values is shown Figure 5 for both reactions. The Arrhenius fitting for k_i^* as a function of temperature is reported in Figure 6.

Combining eqs. (6), (7), (10), (11), and (12) with Arrhenius fitting results, the full kinetic model was compared with experimental data. The results are reported in Figure 7 at constant temperature and for different light intensities and in Figure 8 at constant light intensity and for different temperatures. As it can be observed, in both cases the model compares well with experimental data. In particular, the model is able to predict the double peak observed at the lower

intensities. On the other hand, the model also predicts the disappearance of the first peak as light intensity increases.

CONCLUSION

In this paper the cationic photopolymerization of a commercial stereolithographic epoxy-based resin was studied by means of photo DSC and FTIR. Substantial information about the SL5170 chemical composition and curing mechanism was determined through FTIR analysis. In particular, the presence of a double reaction mechanism, involving, at first, vinyl ether monomers and, subsequently, cycloepoxy groups, was evidenced. This double mechanism reaction can explain the typical thermograms observed during DSC experiments characterized by two distinct reaction peaks. A mathematical model, derived from the one proposed by Nelson,⁵ including the dependence of k_t and k_p and

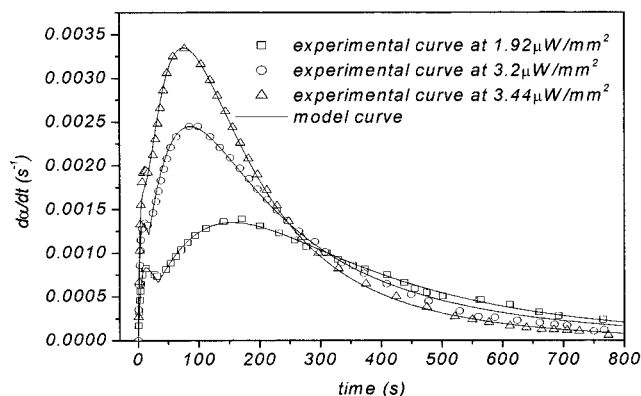


Figure 7 Experimental rate of reaction versus time at 1.92 (\square), 3.20 (\circ), and 3.44 (\triangle) $\mu\text{W}/\text{mm}^2$ and model prediction (—) according to eqs. (6) and (7).

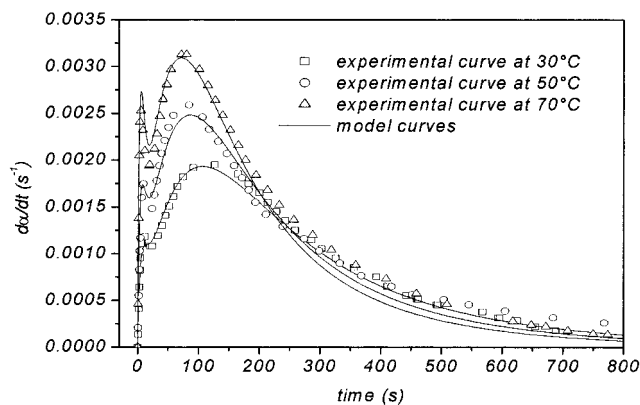


Figure 8 Experimental rate of reaction at 30 (□), 50 (○), and 70 (△) °C and model prediction (—) according to eqs. (6) and (7).

K_i^* from light intensity, was applied to study each reaction combined in parallel. A good agreement between experimental data and model predictions was obtained at different temperatures and light intensities.

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