Journal of Thermal Analysis and Calorimetry, Vol. 72 (2003) 687–693

PHOTOPOLYMERIZATION KINETICS OF AN EPOXY BASED RESIN FOR STEREOLITHOGRAPHY
Calorimetric analysis

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Abstract

Curing reactions of photoactivated epoxy resins are assuming an increasing relevance in many industrial processes, such as coatings, printing, adhesives. Besides these processes, stereolithography makes use of photoactivated resins in a laser induced polymerization for 3D building. The kinetic behaviour of photocuring is a key point for a full comprehension of the cure conditions occurring in the small zone irradiated by the laser beam. Furthermore, the kinetic analysis is very important in order to determine the cure time needed for part building in a stereolithographic equipment. The mechanisms involved in a cationic photopolymerization are complex when compared with radical photopolymerization. In this paper the photoinitiated polymerization of a commercially available epoxy based resin for stereolitography has been studied by means of differential scanning calorimetry (DSC). The polymerization rate and the amount of unreacted monomer are determined directly from the conversion *vs.* time curves during DSC isothermal scans. Kinetic characterization of epoxy photopolymerization has been carried out as a function of the temperature and experimental results have been compared with an original mathematical model.

Keywords: dark reaction, DSC, photopolymerization

Introduction

In recent years the growing interest in cationic photopolymerization is related to the development of very efficient photoinitiators and to the distinct advantages and applications of this method of radiation curing. As a result, UV-initiated cationic photopolymerization are finding application in a variety of areas, including coatings, inks, adhesives, and electronics. Besides these processes, stereolithography makes use of laser induced cationic polymerization for 3D building. Stereolithography (SL) 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 photo-curable liquid resin. The major steps of the process include the CAD design, interface with the equipment Software and the stereolithography build process [1]. The kinetic behaviour of the resins is a key point

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1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

for a full comprehension of the cure conditions occurring in the small zone irradiated by the laser beam and for the determination of the cure time needed for part building. The first photopolymer systems used for SL were based on acrylate monomers, which polymerizes through a free-radical mechanism [1]. 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. For this reason, cationic photopolymer monomers are nowadays used in SL. 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. 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, as those proposed for many thermoanalytical data [4], is not available for cationic polymerizations [5]. In this paper the photoinitiated polymerization of a commercially available stereolithographic epoxy based resin has been studied by means of modified differential scanning calorimetry. Kinetic characterization of epoxy photopolymerization has been carried out as a function of the temperature and exposure time, and experimental results have been compared with an original mathematical model derived from that proposed by Nelson *et al.* [6].

Experimental

The cure of the resin has been 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, is limited to a wavelength interval of 325±4 nm using a monochromator, in order to simulate the narrow irradiation band of a He-Cd laser beam of the SL apparatus. The beam is focused on the sample using a system of lenses and a mirror. Small size samples (0.8–1.3 mg) have been tested, in order to achieve isothermal conditions and a uniform degree of cure through sample thickness [7–9]. Isothermal scans have been run at different temperatures, 30, 40, 50, 60 and 70°C. A maximum temperature of 70°C has been chosen, corresponding to the glass transition temperature of a fully cured resin, as reported in the technical data sheet. At each temperature, the cure has been monitored until no exothermal signal was detected, and the reaction can be considered completed. Dark reaction experiments were performed at the same temperatures, irradiating the sample for 2, 4 and 7 s. After this time, the shutter was closed, and the cure was monitored until completion. The DSC measurements have been used for determination of the advancement of polymerization by assuming that the heat evolved at each time step is proportional to the overall extent of reaction given by the fraction of reactive groups consumed. Following this approach the degree of reaction, α, is defined as:

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

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

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

Results and discussion

Effect of temperature

DSC isothermal scans on SL5170 at different temperatures are shown in Fig. 1. After photopolymerization at 70°C, a sample has been heated in dark conditions up to 250°C at 10°C min^{-1}. During this test, the sample showed a residual reactivity of 43 J g^{-1}. This residual reactivity can be attributed to the activation of molecular mobility, once the temperature of the sample exceeds the glass transition temperature, (T_g), in presence of active centres entrapped in the polymer, and developed during isothermal curing. This is confirmed observating that the onset of residual reactivity has been calculated to be 75°C, just 5°C above the isothermal test temperature. The maximum heat of reaction $H_{\max}$ has been obtained by adding the heat evolved during the dynamic scan to the isothermal heat of reaction at 70°C. Dividing the isothermal heat of reaction for this reference value, the maximum degree of conversion, $\alpha_{\max}$ has been obtained (Table 1). As expected, the heat of reaction and $\alpha_{\max}$ increase 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 [10]. As isothermal temperature increases, vitrification is delayed, and a higher degree of reaction can be obtained. Further, in Table 1, the time needed to reach the maximum rate of reaction (corresponding to the peak of DSC signal) is reported as a function of temperature.

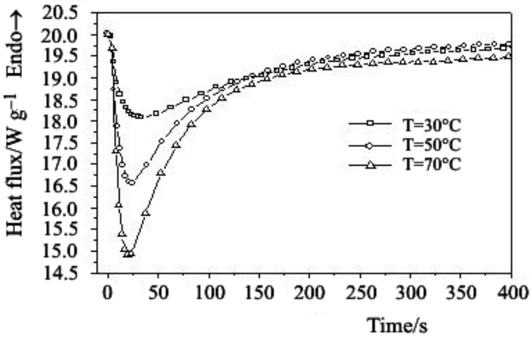

Fig. 1 Experimental heat flux *vs.* time at □ – 30, o – 50 and △ – 70°C

Table 1 Dependence of peak time, heat and maximum degree of reaction on temperature

Temperature/°C	Peak time/s	$\Delta H_{\text{reaction}}$/J g^{-1}	$\alpha_{\max}$
30	61.9	268	0.65
40	58.0	300	0.73
50	54.0	330	0.80
60	53.5	347	0.85
70	51.0	368	0.89

Dark reaction

In Fig. 2 dark reaction curves obtained at different irradiation times at 40°C are shown. Once the light source is removed the rate of reaction continues to increase, reaching a maximum after about 2 s and then decreases exponentially. Increasing exposure time the maximum rate of reaction increases, and the peak time is shifted to longer times. Also, as shown in Fig. 2, the maximum degree of reaction at a given temperature increases with increasing exposure time. On the other hand, at a given exposure time, it was found from experimental data that degree of reaction increases with temperature.

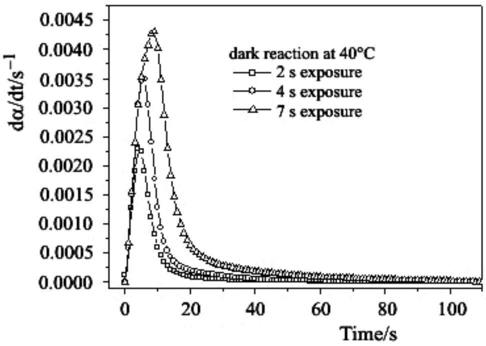

Fig. 2 Experimental rate of reaction at 40°C *vs*. time for different exposure times: □ – 2, o – 4 and △ – 7 s

Kinetic modelling

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 up to this wavelength. Photosensitizers are capable to initiate 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. SL5170 reaction kinetic is modeled modifying the equation proposed by Nelson *et al.* [6]:

$$R_\mathrm{p}=\frac{\mathrm{d}[M]}{\mathrm{d}t}=-k_\mathrm{p}[M][M^+] \tag{3}$$

In Eq. (3) $[M]$ and $[M^+]$ are the unreacted monomer and active centre 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]:

$$\frac{\mathrm{d}[M^+]}{\mathrm{d}t}=k_\mathrm{i}^*[P]_0\exp(-k_\mathrm{i}^*t)-k_\mathrm{t}[M^+] \tag{4}$$

In Eq. (4) k_t is the termination constant, $k_\mathrm{i}^*=k_\mathrm{i}[I]$, where k_i is the intiation constant and $[I]$ is the initiator concentration. $[P]_0$ is the initial photosensitizer concentration. Assuming that $[M]$ is related to the degree of cure α by $[M]=[M]_0(1-\alpha)$, being $[M]_0$ the initial monomer concentration, and determining $[M^+]$ by analytical integration of Eq. (4), the following expression can be obtained for the rate of conversion:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=[P]_0\frac{k_\mathrm{p}k_\mathrm{i}^*}{k_\mathrm{t}-k_\mathrm{i}^*}(\mathrm{e}^{-\mathrm{k}_\mathrm{t}^*\mathrm{t}})(1-\alpha) \tag{5}$$

With the initial condition $\alpha=0$ for $t=0$, Eq. (5) can be analytically integrated in isothermal conditions:

$$\log(1-\alpha)=-k_2-k_1\left(\frac{1}{k_\mathrm{t}}\mathrm{e}^{-\mathrm{K}_\mathrm{i}\,\mathrm{t}}-\frac{1}{k_\mathrm{i}^*}\mathrm{e}^{-\mathrm{K}_\mathrm{i}^*\mathrm{t}}\right) \tag{6}$$

where $k_1=\frac{[P]_0k_\mathrm{p}k_\mathrm{i}^*}{k_\mathrm{t}-k_\mathrm{i}^*}$ and $k_2=k_1\frac{k_\mathrm{t}-k_\mathrm{i}^*}{k_\mathrm{t}k_\mathrm{i}^*}=\frac{[P]_0k_\mathrm{p}}{k_\mathrm{t}}$. By imposing, in Eq. (6) the condition that at each temperature the degree of reaction is α_max for $t\to\infty$, a relation between $k_2(T)$ and $\alpha_\mathrm{max}(T)$ is obtained:

$$k_2(T)=-\log(1-\alpha_\mathrm{max}(T)) \tag{7}$$

Equation (6) has three unknown constants, namely k_2, k_t, and k_i^*. The values of k_2 at different temperatures are calculated directly from experimental degree of cure at the end of reaction, according to Eq. (7), and are reported in Table 2. During dark reaction, after the exposure time, t_c, the initiation constant is zero. In this case, the equation for $[M^+]$ is modified, and can be obtained from Eq. (4) by setting equal to zero. By integration of Eq. (3) with the new expression for $[M^+]$ and proper initial condition at time t_c for dark reaction, the following equation for α can be obtained:

$$\ln\frac{1-\alpha}{1-\alpha_\mathrm{tc}}=[M^+]_\mathrm{tc}\frac{K_\mathrm{p}}{K_\mathrm{t}}(\exp(-k_\mathrm{t}(t-t_\mathrm{c}))-1) \tag{8}$$

Table 2 Temperature dependence of kinetic constants

Temperature/°C	k_2/s^{-1}	k_t/s^{-1}	k_i^*/s^{-1}
30	1.06±0.02	0.146±0.015	0.00504±0.00004
40	1.31±0.03	0.157±0.037	0.00624±0.00005
50	1.62±0.01	0.183±0.030	0.00611±0.00004
60	1.87±0.04	0.200±0.045	0.00632±0.00004
70	2.26±0.01	0.220±0.024	0.00630±0.00003

Table 3 Arrhenius fitting parameters for the kinetic constants

	k_0/s^{-1}	E_0/R /K
k_i^*	exp(–3.60)	490
k_t	exp(1.72)	1109
k_2	exp(6.51)	1953

The value of α and $d\alpha/dt$ at time t_c can be determined from experimental data and the value of $k_p[M^+]_{tc}$ can be calculated from Eq. (3). Plotting $\ln(1-\alpha)/(1-\alpha_{tc})$ *vs.* $t-t_c$ the value of k_t can be determined by non-linear regression according to Eq. (8). The kinetic constants obtained at each temperature are reported in Table 2. Since at each temperature the value of k_t determined by dark reaction experiments should be the same, regardless of the exposure time, the average value of k_t is reported in Table 2. Finally k_i^* values are determined from non-linear regression according to Eq. (6) of experimenatal data reported in Fig. 1, and are reported in Table 2. The three constants have been fitted through an Arrhenius expression, and the values obtained for k_0 and E_0/R are reported in Table 3. The numerical integration of Eq. (6) using the parameters values reported in Table 3 led to the results shown in Fig. 3. Experimental curves and model prediction according to Eqs (6) and (8) for dark reactions at different exposure times at 30°C are compared in Fig. 4. Good agreeemnet between experimental

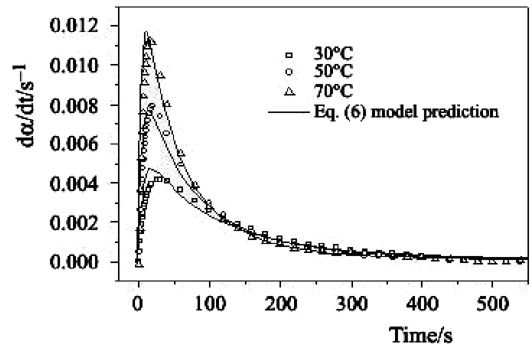

Fig. 3 Comparison between experimental data at □ – 30, o – 50 and △ – 70°C and model prediction according to Eq. (5) (—)

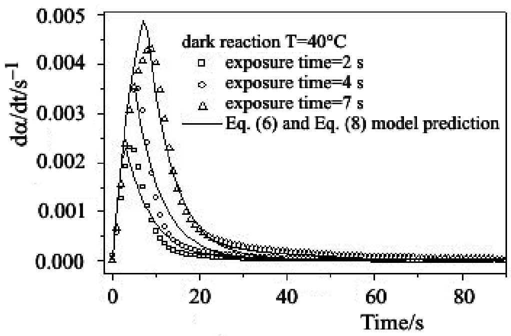

Fig. 4 Comparison between experimental data for dark reactions at 40°C and □ – 2, o – 4 and △ – 7 s exposure and model prediction according to Eq. (8) (—)

data and model prediction in Figs 3 and 4 indicate that the proposed models are well suitable to study the cure kinetics of epoxy based resin photopolymerization.

Conclusions

In this paper cationic photopolymerization of a commercial stereolithographic epoxy based resin has been studied by means of photo-differential scanning calorimetry (DSC). The isothermal rate and degree of reaction are determined directly from PhotoDSC experiments. PhotoDSC provides a rapid tool to study kinetic behavior of epoxy-based resin, introducing a simple correlation between the output of the instrument and the unreacted monomer fraction. The model proposed by Nelson has been modified and adapted to study the kinetic behaviour of SL commercial resin, both for complete curing and dark reaction. Good agreement between experimental data and model predictions is obtained, both in full cure test at different temperatures and in dark reaction experiments at different temperatures and exposure times.

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