Effect of irradiation intensity on the isothermal photopolymerization kinetics of acrylic resins for stereolithography

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Abstract

Three dimensional objects are built without the use of molds with a new technology called stereolithography. The objects are obtained in an additive way polymerizing under a laser beam a low viscosity liquid resin section by section. The kinetic behaviour of the resin represents a key point for a full comprehension of the cure condition occurring in the small zone exposed to laser irradiation. In this work, the isothermal kinetic behaviour of a commercial acrylic resin for stereolithography is analyzed by differential photocalorimetric analysis. A kinetic model, accounting for the effect of autoacceleration, vitrification and light intensity on the reaction kinetics is presented. In particular, the effect of irradiation intensity on the model parameters is studied correlating the kinetic constant and the final chemical conversion with the light intensity and with a characteristic time scale of the reaction. © 1998 Elsevier Science B.V.

1. Introduction

The conventional photolithographic technologies, based on UV polymerization of a thin resin film are widely used for the realization of two-dimensional patterns. Only recently three-dimensional objects are built without the use of molds with a similar technology called stereolithography. The objects are obtained polymerizing a low viscosity liquid resin section by section. The shape and the dimensions of the parts are directly transferred from a three-dimensional CAD system to the stereolithography equipment where a laser beam (usually He–Cd or Ar) polymerizes the different sections [1]. The objects, generated directly

from their drawing, are typically used as prototypes or for the construction of molds. The kinetic behaviour of the resin represents a key point for a full comprehension of the cure condition occurring in the small zone exposed to laser irradiation [2].

During curing of multifunctional acrylates typically used in stereolithography, strong structural changes, affecting the final properties of the materials, are observed. The polymerization of a thermoset polymer generally involves the transformation of a viscous liquid monomer into a rubber (gelation), and then into a solid glass (vitrification), as a result of the chemical reactions between multifunctional active groups present in the system which develop a progressively denser polymeric network. A significant shrinkage, associated with the degree of reaction and temperature gradients, may be responsible of the build up of

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residual stresses and distortion of the parts during cure.

Differential scanning calorimetry (DSC), already applied in the past to the study of photopolymerization [3–10] allows the direct determination of the rate of reaction assuming that the heat produced by the polymerization is proportional to the number of monomer units reacted.

In this study, the complex cure behaviour of a commercial acrylic based resin for stereolithography, activated by a He–Cd laser beam, is analyzed by differential photocalorimetric analysis. In order to simulate the photopolymerization process activated by a laser beam, the light emitted by Xenon lamp was filtered keeping only a narrow band around the He–Cd laser typical wavelength (325 nm). Very small samples are used in order to prevent the temperature increase due to the exothermal curing reaction and to limit the effects of light absorption through the sample thickness. The calorimetric measurements are used for the kinetic analysis in isothermal conditions highlighting the effects of the radiation intensity on the reaction kinetics. A model accounting for the diffusion effects as well as for different light intensities is proposed.

2. Experimental

The studied material is a commercial multifunctional acrylic resin, Cibatool XB5149 from Ciba Geigy, commonly used in stereolithography equipment working with a He–Cd laser characterized by

Table 1
Composition of the resin Cibatool XB5149

Component
Aliphatic urethane acrylate resin
Dimethacrylate ester
Diacrylate ester
Photoinitiator: not indicated

emission at 325 nm. The composition of the material is given in Table 1 according to information provided by the manufacturer.

The cure of the resin was carried out in isothermal conditions at 25°C and in non-isothermal conditions at different heating rates in a DSC Perkin–Elmer DSC−7 cell covered by a transparent quartz window. The DSC was modified for irradiation of the sample according to Fig. 1. The sample was photopolymerized in contact with a constant flow of 20 cm^3/min of N_2. The light reaching the sample, produced by a 300 W Xenon lamp Cermax LX 300, was limited to a wavelength interval of 325±4 nm using a monochromator, in order to simulate the irradiation band of a He–Cd laser beam. The beam was focused on the sample using a system of lenses and a mirror. The light intensity was modulated using a series of neutral filters and was measured at the beginning of each experiment using a power meter OPHIR PD2A. The heat generated by the light was negligible at the used UV wavelength.

Before starting irradiation, the sample was exposed to the nitrogen flow for 3 min. When the DSC signal was stable a shutter was opened allowing the
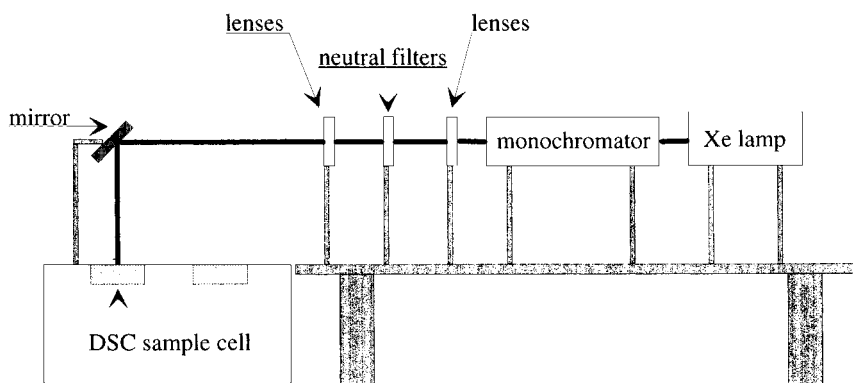

Fig. 1. Sketch of the DSC apparatus as modified for photocalorimetric measurements.

exposition of the sample to the UV light. Any heat effect associated with the light irradiating the sample was negligible at the selected wavelength. The samples were kept in dark conditions during preparation and during the elapsing time before activation by light exposure.

In order to maintain uniform sample thickness, the meniscus arising from the surface tension between the aluminum pan and the liquid resin was minimized modifying the standard aluminum pans according to the geometry proposed by Tryson and Shultz [5]. Therefore, the liquid resin was placed into a small cup, of 2 mm of diameter and 0.2 mm of depth, obtained with a small press into the standard pan. Experiments were performed on open pans containing 1 mg of resin corresponding to a thickness of about 0.1 mm.

The determination of residual reactivity was performed using a Thermo-mechanical analyzer (TMA),

Netzsch TMA 402, operating in air. TMA experiments were performed on the samples previously photo-polymerized in the DSC cell.

3. Results and discussion

3.1. Photopolymerization kinetics

Two typical DSC scans obtained on the studied resin at a constant temperature of 25°C and in non-isothermal conditions at 5°C min^{-1} are reported in Figs. 2 and 3, respectively. When the shutter was opened an exothermal heat flow was immediately detected. The measured signal goes through a maximum and then returns to the baseline value during continuous irradiation of the sample. DSC measurements are commonly used for determination of the advancement of the polymerization by assuming that
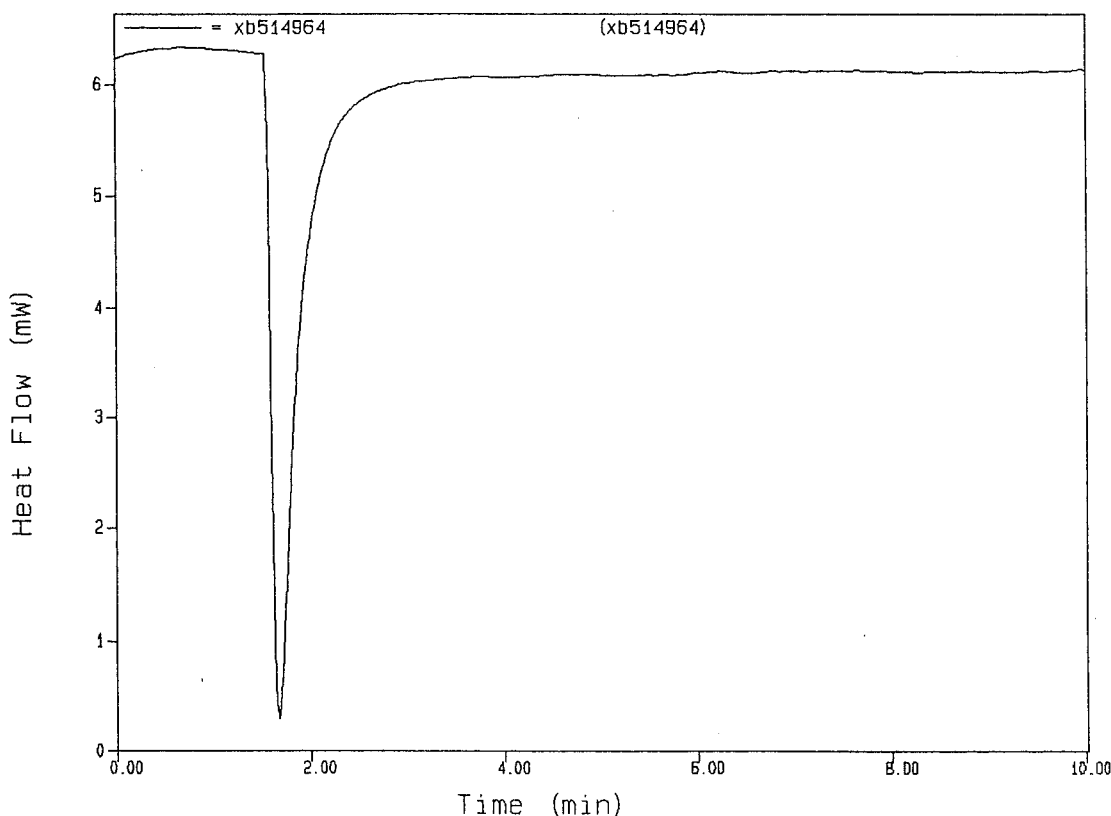

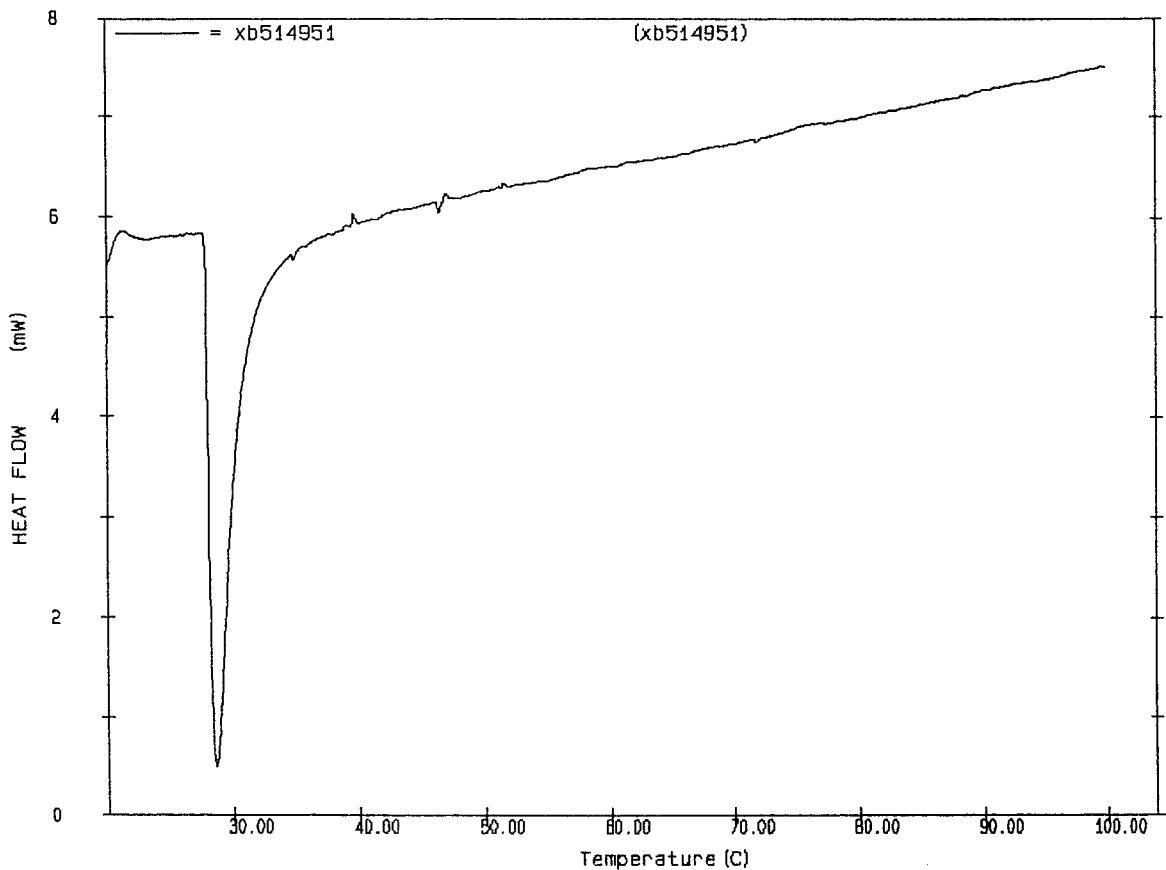Fig. 2. Isothermal DSC scan obtained during photopolymerization at 25°C using I_0=0.644 mW/cm^2.

Fig. 3. Non-isothermal DSC scan obtained 5°C/min using I_0=0.780 mW/cm^2.

the heat evolved during a polymerization reaction 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

$$\alpha = Q(t)/Q_{tot} \tag{1}$$

where $Q(t)$ is the partial heat of reaction developed during a DSC experiment and Q_{tot} represents the maximum heat of reaction measured in a non-isothermal experiment, taken as reference value. It must be noted that residual unreacted double bonds may still be present in a sample after heating at high temperature, as a consequence of caging of unreacted monomers in the densely crosslinked network. For this reason, Q_{tot} will not correspond to the complete reaction of all acrylic double bonds. However, from a processing point of view, Q_{tot} is the maximum reactivity that can be obtained from a given reactive

mixture and therefore, it represents the best choice as reference when a single resin is studied, as in this case. On the other hand, when two or more different mixtures of reactive monomers must be compared in terms of their reactivity, an evaluation of the degree of double bonds conversion should be assessed by other type of measurements. The reaction rate dα/dt, is thus obtained from the heat flow dQ/dt as

$$\frac{d\alpha}{dt} = \frac{1}{Q_{tot}}(dQ/dt) \tag{2}$$

A value of $Q_{tot} = 180$ J/g is assumed as an average of the heats of reaction measured in non-isothermal experiments.

The reaction kinetics during propagation is dominated by two effects of diffusion: the autoacceleration and the vitrification. The theoretical expression for steady state polymerization before autoacceleration

occurs is [11]

$$\frac{d\alpha}{dt} = k_p \left(\frac{2fk_d}{k_t}\right)^{0.5}(1-\alpha) \tag{3}$$

In Eq. (3) k_p, k_d and k_t represent the kinetic constants of propagation, initiation and termination reactions, respectively. According to Eq. (3), a first order kinetics should be observed before autoacceleration occurs [12]. However, in highly crosslinked acrylic resin the autoacceleration occurs before gelation and therefore, in correspondence with very low values of α [8,13]. Therefore, the assumption of steady state condition is no longer valid and Eq. (3) cannot be applied. The rate of reaction must be again expressed as a function of the radical concentration, $[R]$:

$$\frac{d\alpha}{dt} = k_p(1-\alpha)[R] \tag{4}$$

$[R]$ is a function of the ratio of the rates of initiation and termination reactions. The rate constant of termination decreases in correspondence of the onset of the autoacceleration of 3rd order of magnitude, as reported by Sack et al. [14]. On the other hand the rate of initiation, depending essentially on the concentration of initiator and on its efficiency, presents a much lower decrease, at least at the beginning of the reaction. Since the onset of autoacceleration occurs for very low values of α an apparent autocatalytic behaviour is detected at the beginning of the reaction, as clearly shown by the shape of the DSC reaction peak of Fig. 2. Then Eq. (4) may be modified introducing a dependence of the rate of reaction on α:

$$\frac{d\alpha}{dt} = k'(1-\alpha)\alpha^m \tag{5}$$

Although this expression has a functional shape similar to the DSC curves, it predicts a final degree of reaction equal to 1. This is not in agreement with the experimental data measured by DSC. In fact, the heat developed during isothermal DSC experiments (Q_{is}) is lower than Q_{tot}, indicating that residual reactivity can be still developed. Moreover this result can be explained taking into account the effect of diffusion occurring at high degrees of reaction [8,9,11,13,15]. The glass transition temperature, continuously increasing during cure, may approach the isothermal cure temperature strongly reducing the molecular mobility. At this stage of the reaction, the transition

to a glassy state (vitrification) strongly affects the polymerization kinetics reducing the mobility of monomers and radical whose efficiency goes to zero [14]. When the vitrification occurs, the reaction becomes diffusion controlled and the termination step of the polymerization is governed by this strong reduction in the molecular mobility. In these conditions, the kinetic constant of the propagation reaction, the radical efficiency and, consequently, the overall rate of reaction decrease to zero for a value of α lower than 1. This kinetic behaviour may be modelled using a simple pseudo-autocatalytic expression, obtained modifying a kinetic equation previously proposed for free radical polymerization of unsaturated polyester and acrylic dental composites [8,15]:

$$\frac{d\alpha}{dt} = K(I_a, T)\alpha^m(\alpha_m - \alpha)^n(1-\alpha) \tag{6}$$

where m and n are positive fitting parameters not dependent on temperature. In Eq. (6) α_m represents the maximum degree of reaction obtained in isothermal DSC cure experiments. α_m may be calculated from DSC as the ratio Q_{is}/Q_{tot}. In Eq. (6) K is a constant characterized by an Arrhenius type dependence on temperature, T, (7, 14) and on the absorbed light intensity (I_a). For a laser exposure at the wavelength $\lambda = \lambda^*$, I_a is given by

$$I_a = I_0(\lambda^*)(1 - 10^{-\epsilon(\lambda^*)[I]z}) \tag{7}$$

Where $\varepsilon(\lambda^*)$ is the molar absorbance of the photoinitiator, $[I]$ the initiator concentration and z the sample thickness.

3.2. Effect of light intensity on K

Following the classical approach [11] the overall rate of reaction should display a square root dependence on I_a and therefore, on I_0. In this case a single kinetic constant is used in Eq. (6) and for a constant sample thickness, the effect of the light intensity may be taken into account using a power-law dependence of the kinetic constant K on I_0:

$$K = K_0(T)I_0^b \tag{8}$$

where b is a fitting parameter and $K_0(T)$ is a temperature dependent kinetic constant. The kinetic constant K in Eq. (6) is determined by non-linear regression for each DSC. A comparison of the experimental data and
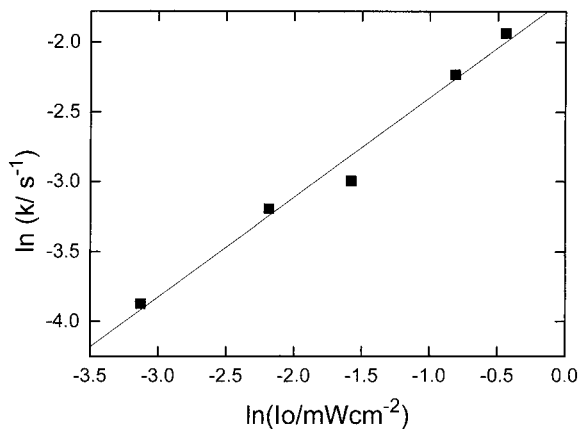
Fig. 4. Temperature dependence of the kinetic constant: experimental data and Eq. (8) predictions.
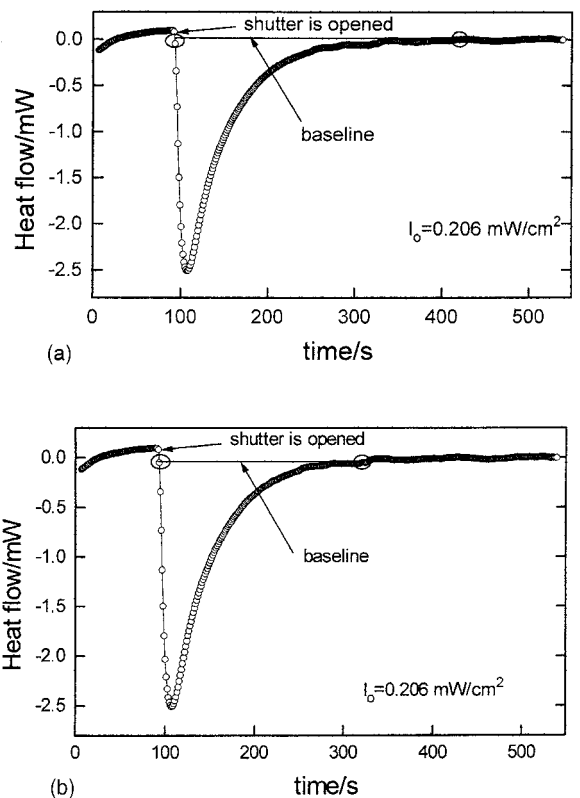

Fig. 5. Integration procedure of isothermal DSC data using equal doses, Fig. 5(a), are limiting the integration to a time corresponding to a signal value close to the apparent baseline (Fig. 5(b)).

Eq. (8) results is reported in Fig. 4. As observed by Tryson and Shultz [5] an exponent of I_0 between 0.5 and 1 may be observed if termination occurs following both, an unimolecular and a bimolecular pathway.

3.3. Effect of light intensity on α_m

As mentioned above the maximum degree of reaction, α_m, is calculated from the isothermal heat of reaction Q_{is}. If different values of I_0 are used, the integration of the exothermic peak of Fig. 2 may be performed following two criteria with respect to the dose, i.e. the product of I_0 by the exposure time:

1. The integration limits are imposed setting equal doses for different I_0. A very low DSC signal, probably corresponding to a reaction occurring under the control of diffusion in the glassy state, appears in the last part of the exothermic peaks (Fig. 5(a)).
2. Integration limits are imposed independently from the dose. Q_{is} and α_m values are calculated limiting the integration to a time corresponding to a signal value close to the apparent baseline (Fig. 5(b)). This procedure tends to limit the integration to the portion of the reaction occurring up to vitrification.

These integration procedures lead to different values of Q_{is} and consequently to different values of α_m. In particular, as shown in Fig. 6, α_m is an increasing function of I_0 when integration is performed according to the second procedure. On the

other hand α_m is about constant when the integration limits are set according to the first method (Fig. 6). The last result may be explained assuming that a very weak exothermic signal is still detected during light exposure, even after vitrification. Therefore, as also observed by Hoyle [10], a diffusion controlled photopolymerization reaction in the glassy polymer, is responsible for an increase of Q_{is}, and hence of α_m, up to a constant value.

The effect of I_0 on α_m resulting from the first integration method is also reported in Fig. 6. In this case higher values of α_m correspond to higher values of the glass transition temperature (T_g) of the cured polymer. The T_g of samples photopolymerized under different values of I_0 is measured heating the resin in a TMA up to 90°C in dark conditions. The TMA result obtained after two scan on the same sample are reported in Fig. 7. In the first scan, after an initial
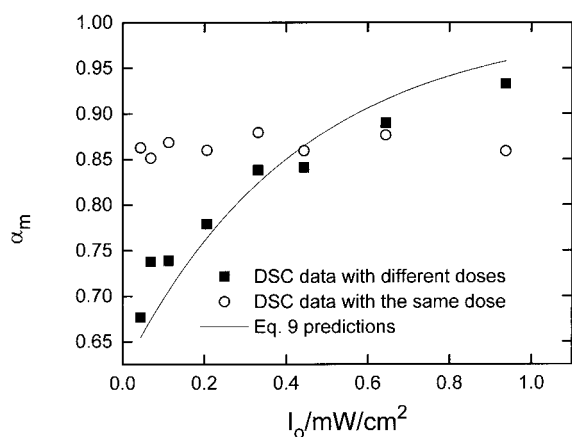
Fig. 6. α_m as a function of the light intensity calculated according to the procedures shown in (Fig. 5(a)) and (Fig. 5(b)).

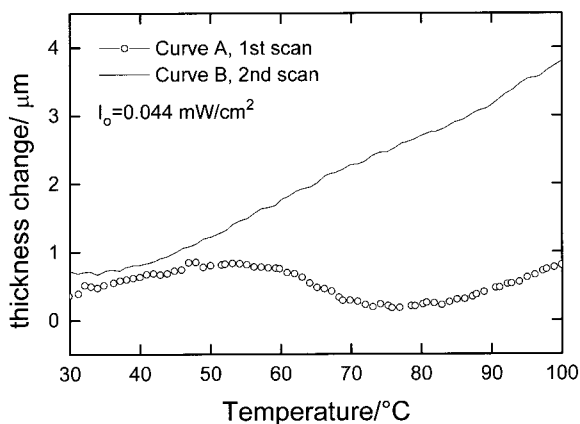Fig. 8. Comparison of TMA results obtained heating two samples cured under different light exposures.

Fig. 7. TMA results obtained heating a sample cured using I_0=0.044 mW/cm^2.

thermal expansion, a contraction, attributed to a residual reactivity, is detected (Fig. 7, curve A). As reported by Kloosterboer [4] free radicals, trapped in the glassy network, may be still present after isothermal photopolymerization of these systems. Therefore, as shown in Fig. 7 (curve A), the reaction may restart in conditions of enhanced molecular mobility by simply heating the sample at a temperature higher than the T_g developed during the isothermal cure. On the other hand a second scan leads to a continuous increase of the sample thickness (Fig. 7, curve B). The TMA data obtained on two samples photopolymerized at 25°C to vitrification using different light intensities are reported in Fig. 8. The onset
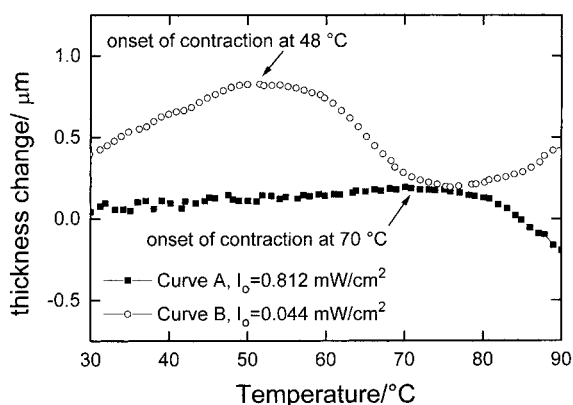
of the contraction is shifted to higher temperatures for the sample cured using a higher value of I_0 (Fig. 8, curve A), indicating that a higher T_g is developed before vitrification occurs and the reaction kinetics change to a diffusion controlled mechanism.

This effect may be explained taking into account a non-equilibrium effect occurring during the reaction. A delay between the DSC- and TMA-calculated degree of reaction was observed by Kloosterboer [4] and by the authors in a former paper [8] during photoactivated polymerization of acrylic resin. In fact, as reported in these studies, the volume shrinkage cannot keep up with chemical reaction, at least after gelation when the resin becomes a viscoelastic solid. The viscoelastic behaviour of the material leads to a delayed shrinkage with respect to the evolution of the chemical reaction as observed by DSC. Therefore, the rate of reaction acts as the driving force for the rate of volume change while the material response is governed by a retardation time, dependent on the cross-linking structure and hence on the degree of reaction.

In the first part of the cure, the rate of reaction is too high and the shrinkage of the material cannot keep up with the reaction. Although the retardation time increases with the degree of reaction, when $d\alpha/dt$ decreases in response to the vitrification, the contraction is slowly recovered and the volume moves toward the equilibrium value imposed by the value of α. The effect on the maximum degree of reaction and on T_g of the light intensity, clearly observed in Figs. 6–8, may therefore, be interpreted as the inability of the rate of volume shrinkage to follow the rate of chemical

conversion leading to an excess of free volume. In fact, as reported by Kloosterboer [4], the chemical reaction generates the free volume that is responsible for the diffusion of monomers and radicals. At the same time, the polymerization is the driving force for the volume shrinkage which follows with delay of the chemical conversion on the basis of the increasing bulk retardation times characterizing the resin during crosslinking. While in thermal, activated cure processes, an increase of the maximum degree of reaction is uniquely governed by temperature [8,13,15], in photoactivated processes an increases of α_m may be achieved also at constant temperature using higher values of I_0. Both variables, temperature and light intensity, act by increasing the molecular mobility and delaying the vitrification at a higher value of α. Therefore, the higher the value of I_0, the higher are the obtained values of α_m and T_g (up to their maximum value).

The inability of the rate of volume shrinkage to follow the rate of chemical conversion leads to non-equilibrium conditions, in which a degree of reaction calculated using volume shrinkage, α_v is always lower than the equilibrium value imposed by the actual degree of reaction measured by DSC [3,4,9]. A schematic comparison of isothermal behaviour of α_v, α calculated by DSC and the degree of reaction in equilibrium conditions α_e, is presented in Fig. 9. α_e represents the lowest possible value that would be obtained if the degree of reaction obtained by volume shrinkage, is capable of following the chemical con-

version as measured by DSC. These conditions may be obtained in a photopolymerization reaction with very low light intensities. However, as shown in Fig. 9, the most common reactive behaviour leads to a delay between α_v and α. The behaviour of α_v results in a volume creep recovery for a system characterized by a retardation time that is a function of the cure time [16]. In response to vitrification, the degree of reaction calculated from DSC is in equilibrium with a value of the specific volume lower than the actual volume of the sample. Further volume relaxation occurs in the glassy state toward the equilibrium as shown in Fig. 9. Moreover, it must be highlighted that at each temperature, vitrification occurs in respect of the same constant value of the specific volume, and hence of α_v. In summary, if the reaction is slow or the retardation time is short then $\alpha_v = \alpha = \alpha_e$. If the reaction is very fast or the retardation time is high then $\alpha > \alpha_v > \alpha_e$. The reactive behaviour is governed by the interaction between the photopolymerization process and a creep recovery process. At constant temperature, the higher the value of I_0, the lower is the time needed to reach the vitrification, t_v. t_v is the reaction time measured by integrating the DSC exothermal peak as shown in Fig. 5(b). The value of α_m, in isothermal conditions, is determined by the vitrification occurring when α_v reaches a given value, different for each cure temperature. Then, at each time step during the reaction, the volume, in non-equilibrium conditions with the crosslinked structure developed up to that time, moves
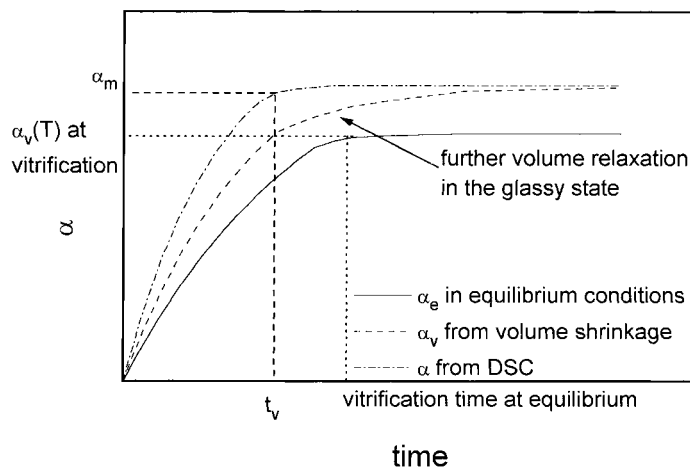

Fig. 9. Schematic comparison of isothermal cure behaviour obtained by DSC or by volume changes.
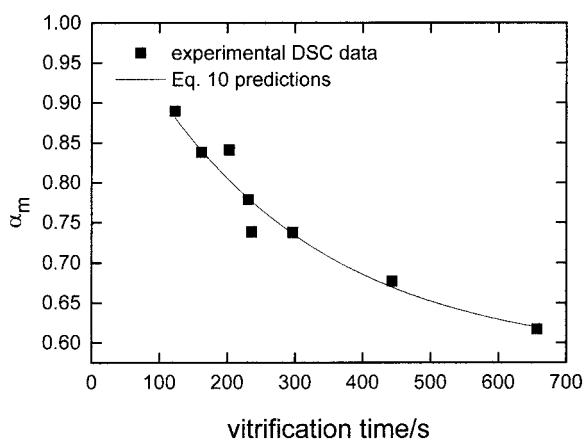
Fig. 10. α_m, calculated according to the procedure shown (Fig. 5(b)), as a function of the vitrification time, t_v; experimental data and Eq. (10) predictions.

towards the equilibrium conditions imposed by the instantaneous value of α, as in creep recovery experiments. The value of α_m, for different irradiation intensity, is the result of the complex evolution of the degree of reaction and of a characteristic retardation time that increases as the crosslinking density increases. This volume creep recovery occurs in a material characterized by different retardation times in a time interval measured by the vitrification time. Therefore, a dependence of α_m from t_v may be proposed as shown in Fig. 10. Although the dependence of α_m from t_v, is very complex, a dependence of α_m on the vitrification time still resembles a typical creep recovery behaviour (Fig. 10).

Therefore, the observed non-equilibrium behaviour can be described correlating either α_m with I_0 or with the measured reaction time, t_v. A good correlation of the dependence of α_m with I_0 is obtained using a simple exponential function:

$$\alpha_m(I_0, T) = \alpha_{mref}(T) + (1 - \alpha_m(T)) \times [1 - \exp(-qI_0)] \quad (9)$$

where q is a fitting parameter and $\alpha_{mref}(T)$ is a temperature dependent reference value. In particular $\alpha_m = \alpha_{mref}$ when I_0 goes to 0 indicating that α_{mref} may be considered the value achieved in equilibrium conditions for a very slow reaction, i.e. when the volume shrinkage is capable of keeping up with the chemical conversion. The other limit of $\alpha_m = 1$ is obtained when

I_0 goes to infinity. A comparison between Eq. (9) results and experimental data, is reported in Fig. 6 assuming that $\alpha_{mref} = 0.617$, the lowest value of α_m measured by DSC at $I_0 = 0.0188$ mW/cm^2 and calculating $q = 2.35$ mW/cm^2 from regression analysis. An extrapolation of the data of Fig. 6 according to Eq. (9) to $\alpha_{max} = 0.99$ leads to a value of 1.55 mW/cm^2. This value is very low compared to the typical light intensity, of the order of 10^4 mW/cm^2, delivered by a laser source in the stereolithographic process.

The vitrification time t_v, measured by DSC according to the procedure shown in Fig. 5(b) reported above, and α_m may be also correlated using a simple creep recovery function [16]:

$$\alpha_m(t_v, T) = \alpha'_{mref}(T) + (1 - \alpha'_{mref}(T)) \times [\exp(-(t_v - t^*)/p)] \quad (10)$$

This equation holds for $t \geq t^*$; for $t < t^*$ then $\alpha_m = 1$. In Eq. (10) p is a fitting parameter, $\alpha'_{mref}(T)$ is a temperature dependent reference value and t^* represents the limiting value of t_v leading to $\alpha_m = 1$. In Eq. (10) $\alpha_m = \alpha'_{mref}$ when t_v goes to infinity indicating that α'_{mref} may be considered, as its homologue α_{mref} in Eq. (9), the value achieved in equilibrium conditions for a very slow reaction, i.e. when the volume shrinkage is capable to keep up with the chemical conversion. A comparison between Eq. (10) results and the experimental data is reported in Fig. 10 assuming that $\alpha'_{mref} = 0.617$ the lowest value of α_m measured DSC at $I_0 = 0.0188$ mW/cm^2 and calculating $p = 265/s$ and $t^* = 35.4$ s. This value of t^* is significantly higher than the typical exposure time in laser activated polymerization indicating that the cure conditions in stereolithography lead to $\alpha_m = 1$.

3.4. Model verification

The degree of reaction is calculated in isothermal conditions by numerical integration of the full model given by Eqs. (6), (8) and (9). The details of the procedure are indicated elsewhere [17]. A comparison between the experimental degree of reaction obtained by DSC and the prediction of the full model, at 25°C for different values of I_0, is shown in Fig. 11. The values of the kinetic parameters of the general model, evaluated by regression analysis, are listed in Table 2. The good agreement observed in these figures
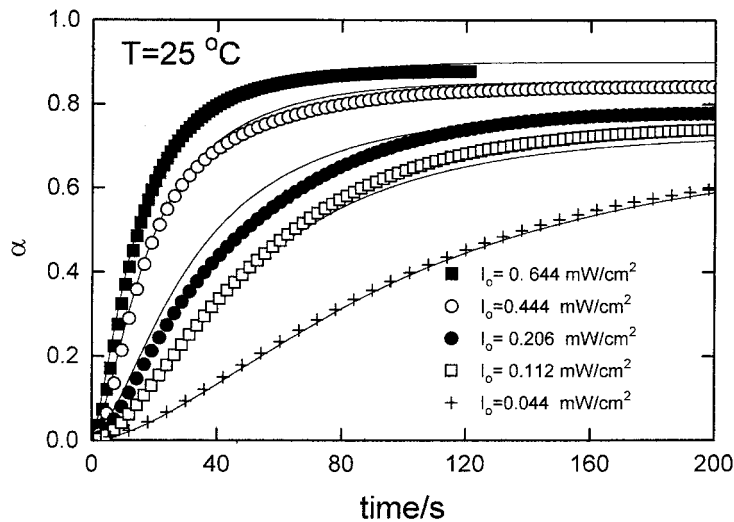
Fig. 11. Comparison between the degree of reaction measured by DSC and the results of the integration of the model given by Eqs. (6), (8) and (9).

Table 2
Parameters of Eqs. (6), (8), (9) and (10)

Parameter	Value
$\ln(K_0/\text{s}^{-1})$	−1.68
b	0.714
α_{mref}	0.617
$q/\ (\text{cm}^2\ \text{m/W}^{-1})$	2.35
α'_{mre}	0.617
$p/(\text{s})$	265
$t^*/(\text{s})$	35.4
n	0.745
m	0.429

indicates that the general cure behaviour above reported is correct and that a simple model can be used to represent a complex kinetic behaviour in which the light intensity affects both the kinetic constant and maximum degree of reaction.

4. Conclusions

In this study, the complex effects of different light intensities on the cure behaviour of a commercial acrylic resin for stereolithography has been presented. In particular, a dependence of the heat of reaction and of the glass transition temperature on the incident light intensity has been reported. This dependence has been clearly evidenced limiting the irradiation up to the vitrification of the sample. The higher values of the maximum degree of reaction and of T_g obtained using a higher light intensity have been interpreted as the inability of the rate of volume shrinkage to follow the rate of chemical conversion, leading to a reactive behaviour governed by the interaction between the photopolymerization process and a volume creep recovery process. Therefore, the observed non-equilibrium behaviour has been described correlating either α_m with I_0 or with the measured time for vitrification. It has been underlined that in photoactivated processes an increase of α_m may be achieved at constant temperature using higher values of I_0, while in thermal activated cure processes an increase of the maximum degree of reaction is uniquely governed by temperature.

Finally, a kinetic model, accounting for the effect of diffusion (autoacceleration and vitrification) and of the light intensity on the kinetic constant and the maximum degree of reaction, has been proposed. The model, integrated in isothermal conditions, has been successfully compared with the DSC experimental data obtained at different light intensities.

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