Simulation of Conversion Profiles and Temperature Distributions within Dimethacrylate thick Material during Photopolymerization

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SUMMARY : Photoinitiated polymerization of multifunctional monomers is an usual method to prepare highly crosslinked networks which have a wide variety of applications. This method leads to high reaction rates and the resulting exothermic effect of this reaction can be the cause of defects in the final material. The heterogeneities alter greatly the physical properties of ultimate products, particularly the optical ones, what causes problems in the design of thick and optically perfect materials. The knowledge of the conversion profile and the temperature distribution within the material during the photopolymerization is useful for the process optimization. Unfortunately, these parameters cannot be measured during the process. Thus, we decided to simulate them. Firstly, the necessary parameters (like conversion and reaction rate) were measured on thin material in isothermal conditions by photocalorimetry. Secondly, these kinetic data were used in a computational calculation to obtain the conversion profile and the temperature distribution within dimethacrylate thick material. The calculated temperature and conversion-time curves are in good agreement with the experimental curves determined under the same conditions.

1. Introduction

Photoinitiated polymerization of multifunctional monomers provides an easy method for producing highly crosslinked polymer networks. The rapid cure and the excellent physical properties of these networks have led to a growing demand and new applications for these materials. As compared to thermal polymerization, photoinitiated polymerization presents three mains advantages :

- the curing reaction at the room temperature ;

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- very high reaction rates ;
- the absence of a solvent.

For these reasons, photoinitiated polymerization has found applications in many fields such as film coatings [1)], packaging industries, optical and dental materials [2-4)] ... Unfortunately, in the case of thick optical glasses production, this process involves some problems such as heterogeneity within the material which induces, for example, colour density variation in the polymer. Reactions that produce such networks occur in the high-crosslinking regime where irregular behaviour is often observed. The extremely low mobility of the reactive species in the crosslinked network induces microstructural heterogeneity. Moreover, photoinitiated polymerization leads to high reaction rates and releases large heats of reaction which modify the photoinitiated polymerization kinetics.

The knowledge of the conversion profile and the temperature distribution within the material during the photoinitiated polymerization is useful for the process optimization ; however, the impossibility to measure these parameters (within a thick material) during the process leads us to simulating them. Firstly, the necessary parameters such as the conversion and the reaction rate were measured in a thin material in isothermal conditions by photocalorimetry. Then, we have checked that our experimental conditions correspond to isothermal ones. Indeed, kinetic constants are very sensitive to an increase of temperature. Secondly, the kinetic data so obtained were used in the calculation of the conversion profile and the temperature distribution within a thick dimethacrylate material.

2. Determination of the necessary parameters and constants for the simulation

2.1. Kinetic parameters

The photocalorimeter used is a differential scanning calorimeter (DSC 7 Perkin Elmer) topped by an irradiation unit with 2 quartz windows. Heat flow versus time was recorded in isothermal mode and under N_2 atmosphere during the photoinitiated polymerization reaction. Fig. 1 shows a typical thermogram.

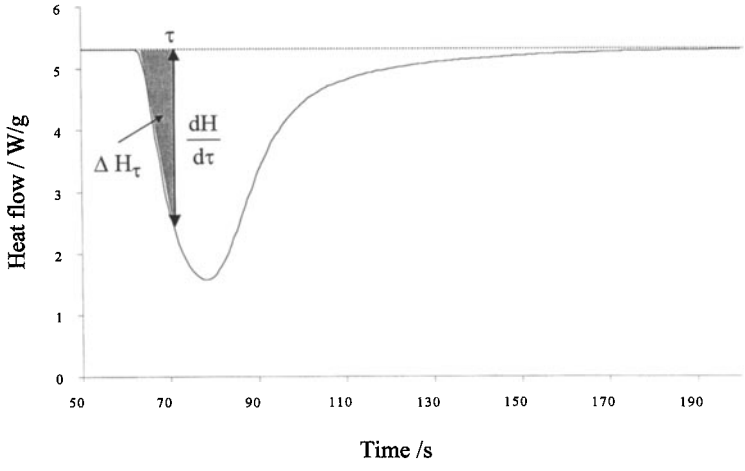


Fig. 1. Typical thermogram of a photoinitiated polymerization reaction.

Conversion was calculated from the overall heat at τ (ΔH_τ) corresponding to the dark area in Fig. 1 :

$$C = \frac{\Delta H_\tau}{\Delta H_0^{theor}} \cdot 100 \qquad (1)$$

where ΔH_0^{theor} is the theoretical heat evolved for complete conversion (-54.7 kJ/mol per methacrylate double bond, i.e. -190 J/g for our dimethacrylate oligomer [5]). Moreover, the polymerization rate was directly connected to the heat flow according to :

$$R_p = \frac{dC}{d\tau} = \frac{\frac{dH}{d\tau}}{\Delta H_0^{theor}} \qquad (2)$$

Conversion versus time and temperature was plotted in Fig. 2 for temperatures below 90°C. The light intensity of the UV radiation was 2.7 mW/cm^2 at 365 nm, and the photoinitiator concentration was 0.15 % (w/w) [6].

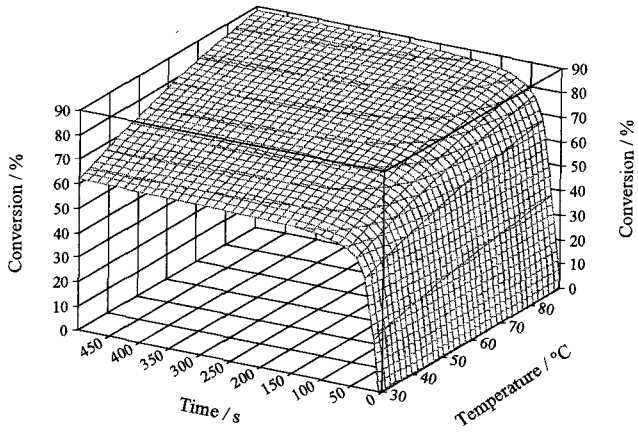


Fig. 2. Conversion versus time and temperature for $I_0 = 2.7$ mW/cm^2 and 0.15 % (w/w) of photoinitiator.

Decker and coworkers [7] have shown a significant increase of temperature within crosslinkable material when the photoinitiated polymerization is very fast. The kinetic constants are very sensitive to an increase of temperature. Thus, in order to strengthen our assumptions concerning the isothermal conditions for the reaction inside the photocalorimeter, it seems fundamental to us to estimate the exothermicity of the polymerization carried out in conditions similar to our experimental ones. A simulation of heat transfer showed that the temperature increase of the sample does not exceed 1°C for an half-time reaction (time to reach 50 % conversion) higher than 10 s for our polymer (Fig. 3). The numerical analysis was described in the previous paper [8].

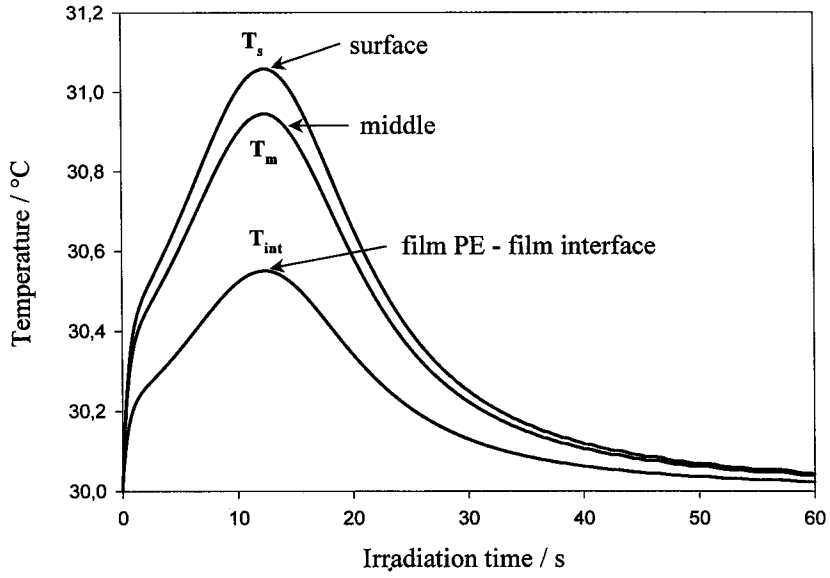


Fig. 3. Simulation of temperature of a dimethacrylate sample versus time for $\tau_{1/2}$ = 15 s. The sample is 0.2 mm thick on a PE film with 0.2 mm thickness.

2.2. Physical constants

Throughout this paper, the physical parameters are kept constant in order to simplify the analysis. The values obtained for these parameters are listed in Table 1. C_p is the heat capacity, a is the thermal diffusivity, λ is the thermal conductivity, H is the contact thermal resistance and ΔH_R is the ultimate experimental polymerization enthalpy. These values used for the calculation correspond either to average values or to measurements on the commercial dimethacrylate studied in our laboratory.

Table 1. Physical constants of the commercial dimethacrylate.

$a / (m^2 s^{-1})$	$C_p / (J kg^{-1} K^{-1})$	$\lambda / (W m^{-1} K^{-1})$	$\Delta H_R / (J g^{-1})$	$H / (W m^{-2} K^{-1})$
$1.616\ 10^{-7}$	1950	0.29	115	5

3. Theoretical considerations

3.1. Schematic shape of the experimental device

The simulation was performed on a semi-infinite slab with 15 mm thickness between 2 moulds. The slab is made of a homogeneous mixture of dimethacrylate resin and a photoinitiator. The UV radiation originates from a stationary light source and arrives at Face one (Fig. 4).

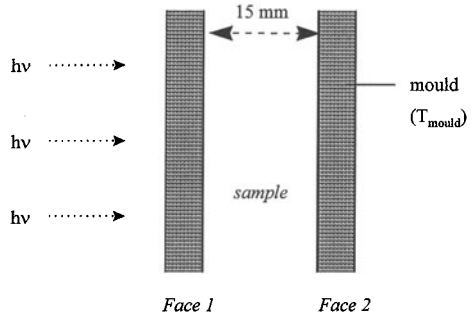


Fig. 4. Schematic shape of the experimental device.

3.2. Assumptions

Several assumptions were made concerning heat transfer process and kinetics of reaction in the thick sheet sample :

(i) Heat flow is unidirectional through the thinner dimension of the sample (the thickness of this sheet is shorter than all other dimensions) ;

(ii) There is no flow and no molecular diffusion, so that heat is transferred only by conduction ;

(iii) Thermal parameters such as thermal conductivity λ and thermal diffusivity a are constant during the reaction ;

(iv) Kinetic parameters are only function of reaction temperature and irradiation light intensity, as it was found with the photocalorimeter technique ;

(v) Initially, the temperature on polymer sample faces remains the same as that in the mould.

(vi) The slabs of the mould and sample are not in perfect contact ; there is a contact thermal resistance.

3.3. Mathematical treatment

The unidirectional heat flow through the thickness of the sample sheet is described by the classical equation of transient heat transfer where the contributions due to heat conduction and the internal heat generated by the photoinitiated polymerization and the light absorption are taken into account [9] :

$$\frac{\partial^2 T}{\partial x^2} - \frac{1}{a}\frac{\partial T}{\partial \tau} + \frac{S(x)}{\lambda} + \frac{\Delta H_R}{aC_p}\frac{dC(x)}{d\tau} = 0 \qquad (3)$$

T is the temperature, τ is the time, x is the thickness, S(x) is the first location-dependent heat source which corresponds to the radiative flux absorption. $\frac{\Delta H_R}{aC_p}\frac{dC(x)}{d\tau}$ is the second location-dependent heat source induced by the polymerization, where ΔH_R is the photopolymerization enthalpy, C_p is the specific heat capacity, C(x) is the conversion and $\frac{dC(x)}{d\tau}$ is the polymerization rate. At a given temperature T, the conversion C is a function of the radiative flux which is itself a function of the thickness x according to the relation $I(x) = I_0 \cdot e^{-\alpha x}$ where α is the absorption coefficient and I_0 is the incident light intensity.

Initial and boundary conditions

Initial conditions

Initially ($\tau = 0$), the temperature throughout the sample is assumed to have a uniform value T^0. Thus, at $\tau = 0$, if T_j^0 is the temperature at point j, $T_j^0 = T^0$ independently of j.

Boundary conditions

At τ, the flux across the surfaces is proportional to the difference between the surface temperature T_s^τ and the mould slabs temperature T_{mould} :

$$\frac{\partial T^\tau}{\partial x} = -\frac{H}{\lambda}\left(T_s^\tau - T_{mould}\right) \qquad (4)$$

where H is the contact thermal resistance.

3.4. Numerical analysis

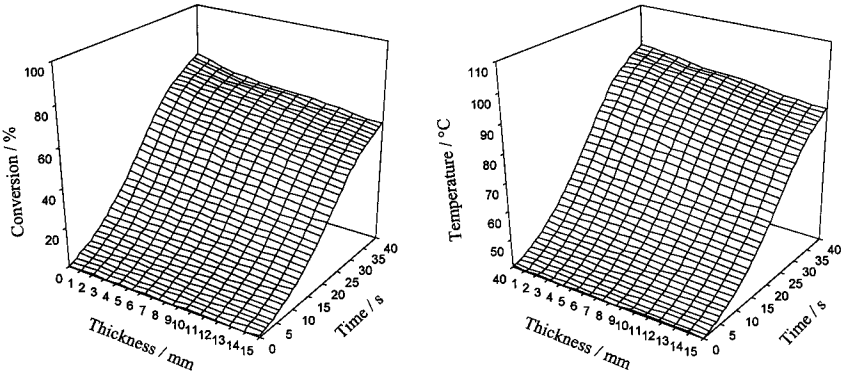
Because of the internal heat generated from the reaction which is a function of time and space, Eq. (3) cannot be integrated mathematically. The problem was solved by using an explicit numerical method with finite differences. In our method we respectively replace the space-derivative $\frac{\partial^2 T}{\partial x^2}$ and the time-derivative $\frac{\partial T}{\partial \tau}$ in (3) by the differences $\frac{T^k_{(J+1)\ell} - 2T^k_{J\ell} + T^k_{(J-1)\ell}}{\ell^2}$ and $\frac{T^{(n+1)k}_{\ell} - T^{nk}_{\ell}}{k}$. The physical significance of these differences corresponds to division of the solid into slabs of thickness ℓ and choosing for the calculation an interval of time k. For the convergence of the solutions and the stability of the calculation, we choose the values : $\ell = 10^{-3}$ m and $k = 10^{-1}$ s for the steps in space and in time. This also allowed a solution in a reasonable number of steps.

4. Results and discussion

Fig. 5A shows the conversion profile within a 15 mm thick sample during 40 s of irradiation. The low value of the absorbance induces a low decrease of the light intensity. Consequently, the conversion is relatively homogeneous (from 77 % to 60 % of conversion). The temperature increase inside the material results from the release of the heat generated by the photoinitiated polymerization. The low thermal conductivity of the polymer leads to a temperature profile very similar to that of the conversion (Fig. 5B). These results are in good agreement with experimental profile data.

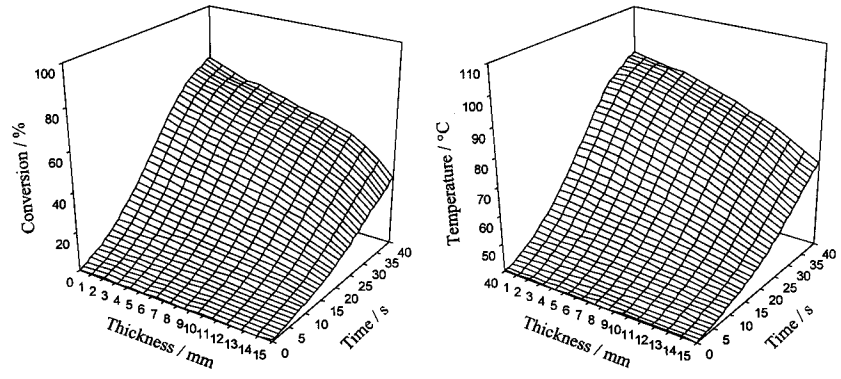
The results in Fig. 6 pertain to the same photoinitiator ; we only change the monomer absorption coefficient. We have a screen effect when the absorption coefficient increases : the light intensity within the material decreases quickly and the conversion is slower on the back of the sample. We observe in Fig. 6A and B the effects of this phenomenon on the temperature and conversion profiles. In this example, the absorption coefficient is larger by a factor of two as compared to the previous example. The difference in conversion between the front and the back of the sample is now 40 % (previously 17 %). These examples show clearly

the importance of the knowledge of the spectral sensibility of the photoinitiator and the monomer absorption coefficient.



A) B)

Fig. 5. A) Conversion profile versus time and thickness ($\alpha = 50\ m^{-1}$).
B) Temperature profile versus time and thickness ($\alpha = 50\ m^{-1}$).



A) B)

Fig. 6. A) Conversion profile versus time and thickness ($\alpha = 100\ m^{-1}$).
B) Temperature profile versus time and thickness ($\alpha = 100\ m^{-1}$).

5. Concluding remarks

The model described here, takes into account the kinetics of the photoinitiated polymerization (these kinetics have been determined by DSC using the material itself) and the thermal properties of the dimethacrylate. This method has allowed us to calculate the profiles of temperature and conversion developed through the dimethacrylate at different times. With the help of this simultaneously obtained information, we can get a good 'view' of the inside of the sample itself while the reaction is progressing.

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