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Polymer 47 (2006) 193–199

polymer

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Simulation of conversion profiles within dimethacrylate thick material during photopolymerization. Validation of the simulation by thermal analysis data. Application to the synthesis of a gradient structure material

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Received 30 June 2005; received in revised form 10 November 2005; accepted 10 November 2005
Available online 28 November 2005

Abstract

In a previous paper, a new synthesis method of gradient structure materials from a homogeneous system of monomers was described. These materials were made in two steps. The first one consisted in creating a photopolymerization gradient in methacrylic double bonds under UV exposure thanks to the decay of UV light intensity through the sample thickness. The second one consisted in setting the obtained gradient by a thermal crosslinking reaction. Here, we focussed our attention on the first step, i.e. the creation of the conversion gradient. The knowledge of this gradient is of fundamental importance to predict the final properties of the material. Unfortunately, the measurement of this parameter all over the thickness during the photopolymerization is impossible because no suitable technique is available. A numerical simulation based on the general heat equation transfer was developed on a dimethacrylate model system to calculate this conversion gradient. To describe the true conditions of kinetic experiments, some necessary parameters were measured, like conversion, reaction rate, spectral irradiance of the Hg vapour lamp, dimethacrylate spectral absorbance. The validation of the model by comparison between numerical simulation and experimental temperature results was checked. Finally, influence of physical and chemical parameters on the conversion gradient was discussed.

Keywords: Photocrosslinking; Thermal analysis; Numerical simulation

1. Introduction

Gradient polymers are multicomponent polymers whose structures or compositions are not macroscopically homogeneous, but vary as a function of position in the sample [1]. Recently, we developed a new method to create gradient materials without using a mixture containing at least one polymer, but involving a photopolymerization reaction from a homogeneous system, that is to say a system of monomers and oligomers [2]. The principle depends on two steps. In the first one, a polymerization gradient is photochemically created and obtained thanks to the variation of UV absorbance in the medium. The second step consists in setting the obtained gradient by a thermal crosslinking reaction. These first experiments showed the feasibility of gradient polymers using this new technique. Here, we focussed our attention on the first step of the synthesis, i.e. the creation of the conversion gradient. It should be stressed that a heterogeneous reaction can take place in the medium due to the decay of light intensity through the material thickness. Nevertheless, this characteristic of photopolymerization is the key to create a polymerization gradient. Indeed, thanks to the sample absorbance and the distribution of light intensity through the irradiated system predicted by Beer–Lambert's law, an intensity gradient, and consequently a polymerization gradient, can be created inside the sample when exposed to UV-radiation. The knowledge of this gradient is of fundamental importance for the prediction of the final properties of the material. However, the measurement of this parameter all over the thickness, during the process is impossible because no suitable technique is available to monitor their variations within a thick material. Moreover, it is well-known that polymerization continues after end of irradiation [3–7]. This postpolymerization reaction is very fast during the first seconds after the end of UV-radiation and continues at a lower speed later in time. Thus, even though it is

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doi:10.1016/j.polymer.2005.11.024

possible to cut a thick material in thin slices after the end of UV-radiation and to analyse them by FTIR spectroscopy, the obtained conversion values cannot be representative of the true ones at a time t and a place x in the initial thick material. We can therefore conclude that no valid experimental measurements can be performed until optimum conversion is reached in all the material. We have then developed a numerical simulation to calculate this conversion gradient. It is based on the general heat equation transfer with two location-dependant heat sources; the first one corresponds to the radiative flux absorption, the second one is induced by the polymerization enthalpy. This simulation links up the spectral irradiance and the UV light intensity of the mercury arc lamp with the material optical behaviour.

In order to simplify this study, a commercial dimethacrylate oligomer was chosen as photopolymerizable molecule model. The first step of this paper deals with the determination of some necessary parameters for numerical analysis. First of all, the conversion and reaction rate versus temperature and UV light intensity were measured by photocalorimetry for thin materials. Indeed, a previous study [8] has shown that the use of thin samples provides isothermal conditions, which are absolutely necessary for studying a reaction kinetic versus temperature. Moreover, thin samples allow us to have a uniform illumination of the whole material and therefore to study the influence of UV light intensity on conversion carefully. At the same time, the influence of the radiation wavelength on kinetics was studied. Subsequently, spectral irradiance of Hg vapour lamp and dimethacrylate spectral absorbance were performed. These measurements enable to describe the evolution of spectral radiation intensity in the sample thickness once the absorption coefficients are known.

In a second step, we deal with the validation of the model (especially the advisability to carry out the simulation from experimental kinetic data) by comparison between simulated and experimental temperature evolution inside the material. Effectively, during the photopolymerization process of a thick sample, the temperature and its increase induced by the reaction exothermicity inside the material are the only experimental parameter easily measurable. During the polymerization process, the sample temperature evolution is directly connected with the exothermicity of the polymerization reaction. Evolution of this temperature is therefore connected with the photopolymerization kinetics and, it seems to be reasonable to think that a good correlation between numerical and experimental temperature data lead to a good correlation between actual kinetics (impossible to measure) and numerical kinetics. Measurements of these temperature distributions during the actual process are performed with single use thermocouples drown in the polymer. To avoid difficulties in the determination of the boundary conditions, the mould geometry was chosen as simple as possible. This simulation was finally applied to the calculation of some conversion and temperature distribution profiles within a thick dimethacrylate sample to determine the influence of irradiation wavelength and photoinitiator concentration on the conversion gradient.

2. Experimental

2.1. Materials

The chemical formula of the dimethacrylate oligomer (Akzo, $M = 575\ \text{g mol}^{-1}$) used is the following one (Fig. 1):

The photoinitiator 2,2-dimethyl-2-hydroxyacetophenone (Darocur 1173: 0.15% (w/w) i.e. $10^{-2}\ \text{mol l}^{-1}$) was dissolved in the oligomer under stirring at room temperature for 3 h.

2.2. Photocalorimetry

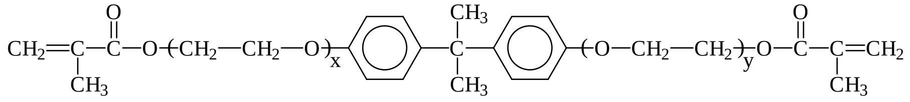
About 2 mg of mixture were placed on a polyethylene (PE) film (0.1 mm) covering the bottom of an aluminium DSC pan in order to get a maximum spreading out of the monomer as a thin and plane layer. Indeed, without PE film, a hemispherical drop is obtained and optical disturbance can affect experimental data.

Photopolymerization kinetics were monitored by a differential scanning calorimeter (DSC 7 Perkin-Elmer) topped by an irradiation unit with two quartz windows. Heat flow versus time was recorded in an isothermal mode under nitrogen atmosphere during the photoinitiated polymerization reaction [9].

The photoinitiated polymerization has a big thermal effect, and kinetic constants are very sensitive to any increase in temperature. A previous simulation of heat transfer within a monomer film during photocrosslinking shows that our experimental conditions (thin film of 0.2 mm, $t_{1/2}$ (time to reach 50% conversion) = 15 s) are suitable to work in isothermal mode [8]. Indeed, whatever the polymerization temperature (from 20 to 90 °C), the rise of temperature within the film, in the DSC oven, is always lower than 1 °C.

Conversion was calculated from the overall heat at t (ΔH_t) corresponding to the dark area in Fig. 2:

$$C = \frac{\Delta H_t}{\Delta H_0^{\text{theor}}} \times 100 \tag{1}$$



n = x + y = 4.8

Fig. 1. Chemical formula of the dimethacrylate oligomer.

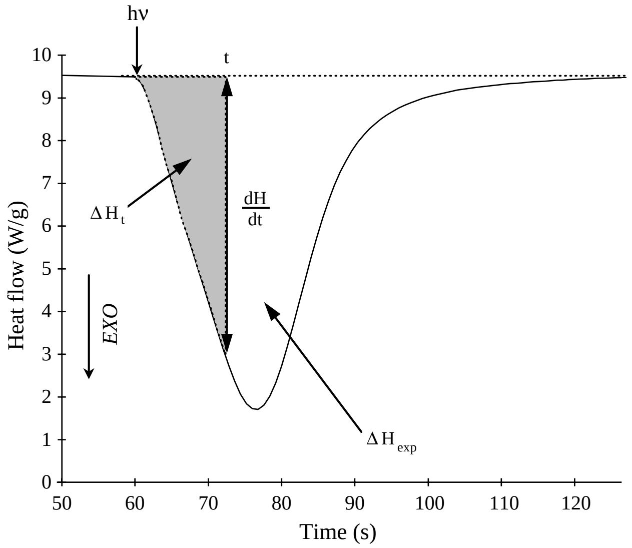


Fig. 2. Typical DSC thermogram of a photoinitiated polymerization reaction.

where $\Delta H_0^{\text{theor}}$ is the specific enthalpy polymerization (−54.7 kJ/mol per methacrylate double bond, i.e. −190 J/g for our dimethacrylate oligomer [10], Fig. 3).

2.3. Optical parameters

UV-irradiation was performed with an Osram HBO 100 W mercury arc lamp (medium pressure). Its spectral irradiance was measured at the sample level by using a spectroradiometer (Intraspec II Oriel). UV light intensity can be adjusted and, for experiments under monochromatic irradiation, the selection of a spectral band was obtained with interference filters.

2.4. Physical constants

Table 1
Physical constants of the commercial dimethacrylate

a (m^2 s^{-1})	C_p (J kg^{-1} K^{-1})	λ (W m^{-1} K^{-1})
1.616×10^{-7}	1950	0.29

Table 2
Absorption coefficient of the mixture and molar extinction coefficient of the photoinitiator

λ (nm)	313	335	365
α (m^{-1})	800	400	100
ε (l mol^{-1} m^{-1})	136	94	16

Throughout this paper, the values of material parameters such as diffusivity a, thermal conductivity λ and heat capacity C_p are assumed as constant in order to simplify numerical analysis, i.e. the expected increase in temperature and conversion evolution are supposed not to affect all these quantities. These values [11] are listed in Table 1.

The spectral absorbance of the oligomer–photoinitiator mixture was measured by using an UV–visible spectrophotometer (Perkin-Elmer Lambda 16). This mixture was previously dissolved in methanol with the same concentration of monomer and photoinitiator in the solution as in the irradiated film during bulk photopolymerization. Preliminary experiments have shown that no photopolymerization occurs at 405 nm and above. As dimethacrylate oligomer strongly absorbs below 300 nm, the photoinitiator is only efficient in the wavelength range from 300 to 380 nm. Absorption coefficient α of the mixture and molar extinction coefficient ε of the photoinitiator were determined for each main emission wavelength of the mercury arc lamp (Table 2).

2.5. Schematic shape of the experimental device

The experimental temperature data were obtained on an axis-symmetry sample with 10 mm diameter. Temperature inside the sample was measured using single use

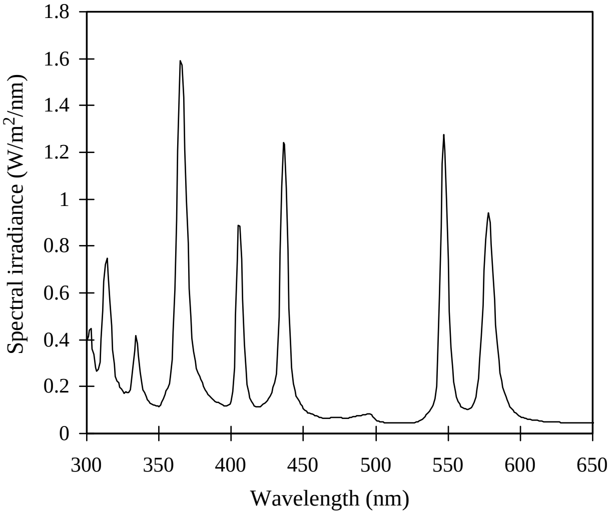


Fig. 3. Hundred watts mercury arc lamp spectral irradiance.

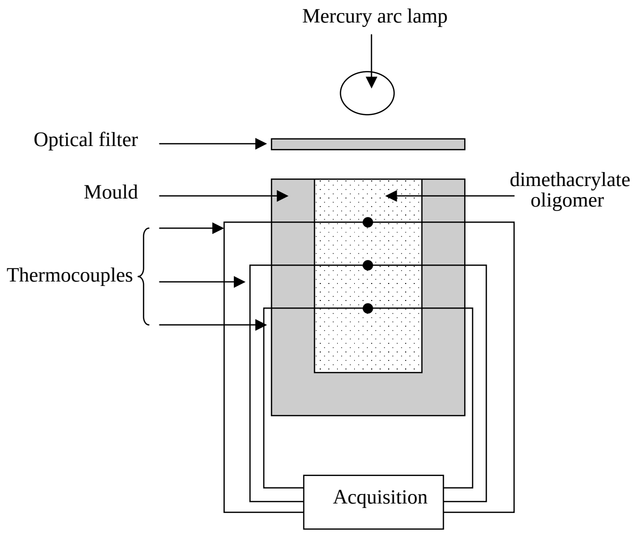


Fig. 4. Schematic shape of experimental device.

thermocouples drown in the polymer at different distances from the surface. The thermocouples were placed as well as possible on the middle of the sample. Their response time is 0.2 s for a temperature step of 80 °C. The UV-radiation coming from the mercury arc lamp arrives on the upper face (Fig. 4).

3. Theoretical considerations

Numerical calculations are based on the general heat equation with two location-dependent heat sources [12]:

$$\nabla^2 T - \frac{1}{a}\frac{\partial T}{\partial t} + \frac{S(r,\Phi,z)}{\lambda} + \frac{\Delta H_0^{\mathrm{theor}}}{aC_\mathrm{p}}\frac{\mathrm{d}C(r,\Phi,z,T)}{\mathrm{d}t} = 0 \tag{2}$$

T is the temperature, t is the time, r, Φ, z is the position, $S(r, \Phi, z, T)$ is the first location-dependent heat source which corresponds to the radiative flux absorption. In this case, the heat source is the divergence of the radiative flux $-\mathrm{d}\Phi/\mathrm{d}x$ and the radiative flux is: $\Phi = \Phi_0 \exp(-k_\lambda{}^* r)$ with k_λ the spectral absorption coefficient.

$$\frac{\Delta H_0^{\mathrm{theor}}}{aC_\mathrm{p}}\frac{\mathrm{d}C(r,\Phi,z,T)}{\mathrm{d}t} \tag{3}$$

is the second location-dependent heat source induced by polymerization, where $\Delta H_0^{\mathrm{theor}}$ is the theoretical photopolymerization enthalpy, C_p is the specific heat capacity, a is the thermal diffusivity, $C(r, \Phi, z, T)$ is the conversion and $\mathrm{d}C(r, \Phi, z, T)/\mathrm{d}t$, is the polymerization rate experimentally obtained in isothermal mode by photocalorimetry, λ is the thermal conductivity.

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

(i) There is no flow and molecular diffusion, so that heat is transferred only by conduction;
(ii) Kinetic parameters are only function of reaction temperature and irradiation light intensity, as it was found with the photocalorimeter technique;
(iii) Initially, the temperature on polymer sample remains the same as in the mould;
(iv) The slabs of the mould and sample are not in perfect contact; there is a contact thermal resistance H which is constant during the overall process.
(v) The brass mould slabs temperature is a constant during the process.
(vi) Because of the sample symmetry, the temperature is not a function of Φ and a two-dimension model can be used.

With these assumptions, the heat conduction equation (1) is simplified and given by:

$$\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2} - \frac{1}{a}\frac{\partial T}{\partial t} + \frac{\Delta H_0^{\mathrm{theor}}}{aC_\mathrm{p}}\frac{\mathrm{d}C(r,z,T)}{\mathrm{d}t} + \frac{S(r,\Phi)}{\lambda} = 0 \tag{4}$$

3.1. Initial conditions

Initially ($t = 0$), the temperature throughout the sample is assumed to have a uniform value T^0.

3.2. Boundary conditions

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

$$\frac{\partial T^\mathrm{t}}{\partial r} = -\frac{H}{\lambda}(T_\mathrm{s}^\mathrm{t} - T_{\mathrm{mould}}) \tag{5}$$

where H is the contact thermal resistance.

In this form, because of the internal heat generated by the reaction which is a function of time and space, Eq. (2) has no obvious analytical solution and cannot be integrated mathematically. The problem was solved by using an explicit numerical method with finite differences [13].

4. Results and discussion

4.1. Determination of the parameters for numerical analysis

4.1.1. Kinetic results for thin materials

In radical photopolymerization, the photo-process efficiency affects monomer conversion and the molecular weight of the polymer formed. Under condition of a steady-state in radical species, the following relationship can be applied for the polymerization rate R_p [9]:

$$R_\mathrm{p} = \frac{k_\mathrm{p}}{k_t^{1/2}}\sqrt{2.3\phi_\mathrm{i}\varepsilon I_0[A]_0}[M] \tag{6}$$

where k_p and k_t are the propagation and termination rate constants of the polymerization reaction, I_0 is the UV light intensity which is constant within a thin material, $[A]_0$ is the initial photoinitiator concentration, $[M]$ is the monomer concentration, ϕ_i is the initiation quantum yield and ε is the molar extinction coefficient of the photoinitiator. The factor ϕ_i takes into account the overall processes that lead to the first monomer radical $\mathrm{RM}^{\cdot}$. It is obvious that ϕ_i will be a function of several parameters. Generally, ϕ_i is described as a product of the yields of the elementary primary processes: the quantum yield of intersystem crossing ϕ_{ST}, the yield of cleavage ϕ_α, and the yield of $\mathrm{RM}^{\cdot}$ generation $\phi_{\mathrm{RM}^{\cdot}}$.

The kinetic results are obtained on thin samples (i.e. isothermal condition, uniform irradiation). Conversion versus time was performed for temperature sample between 20 and 90 °C under poly and monochromatic radiation for different intensity values (0.2–10 mW cm^{-2}). As an example, conversion versus time was plotted (Fig. 5) at 50 °C under poly and monochromatic radiation for the same intensity values (2.7 mW cm^{-2}). In case of polychromatic radiation, only the fraction of spectral flux intensity in the range 300–380 nm is considered.

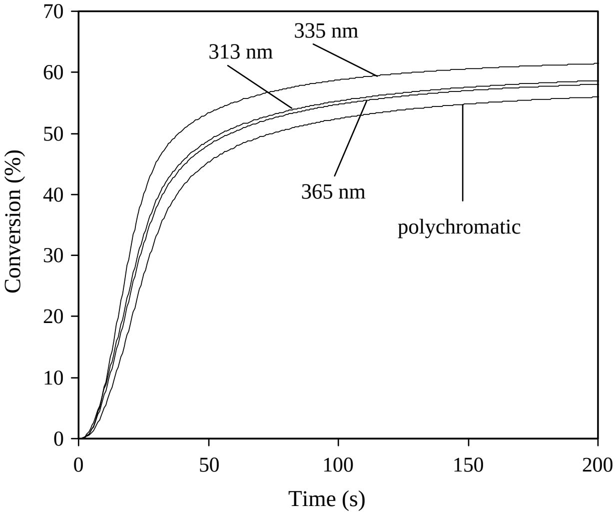


Fig. 5. Conversion versus time at 50 °C, $I_0 = 2.7$ mW cm^{-2}.

Reactions kinetics are very similar for all irradiation modes. Other experiments with different intensity values lead to the same experimental results. This clearly shows that, whatever the radiation (mono or polychromatic), the polymerization rate and the final degree of conversion are only function of radiation intensity and not of radiation wavelength

Identical reaction rates (Fig. 5) can only be justified in equation (4) if the product $\phi_i\varepsilon$ is nearly constant. As Table 2 shows, ε decreases as irradiation wavelength increases, which means that the quantum yield ϕ_i increases with wavelength. This result, which has not been explained up to now, was already mentioned in a recent work [14], where Lovell et al. come to identical results with a different photoinitiator but with the same bandwidth.

4.1.2. Transposition to thick materials

In case of thick materials, Eq. (4) is still valid for the description of reaction rates, but in such cases, UV light intensity can no longer be considered as constant. For monochromatic radiation, the evolution of light intensity is described by the Beer-Lambert law, as plotted in Fig. 6 for the three main efficient wavelengths.

For polychromatic radiation, the evolution of spectral radiation intensity within the material can be described by using both spectral data (Hg vapour lamp spectral irradiance and spectral absorbance of the sample) and Beer–Lambert law.

Previous results have shown (Fig. 5) that, whatever the UV-radiation wavelength, kinetic and final conversions are only function of radiation intensity and temperature. So, it is possible to add the spectral efficiency flux within the material to obtain the total spectral flux evolution (Fig. 6). This total spectral flux was given by:

$$I(x) = \int_{\lambda_1}^{\lambda_2} I_{0\lambda} \exp^{-\alpha_\lambda x} \mathrm{d}\lambda \tag{7}$$

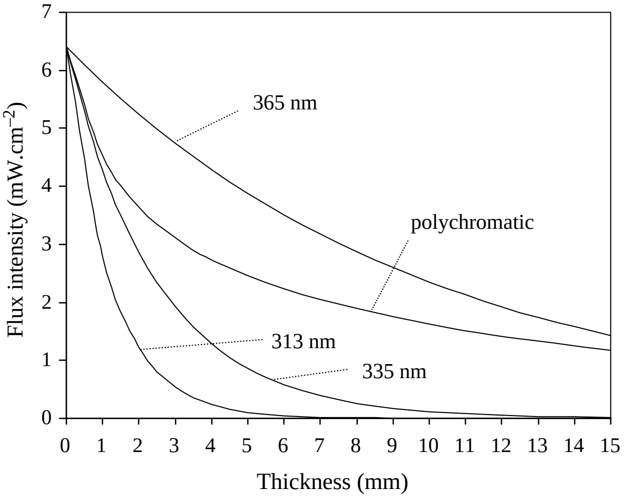


Fig. 6. Evolution of light intensity versus the thickness for different wavelengths: photoinitiator concentration 0.15% (w/w).

where $I_{0\lambda}$ is the spectral flux intensity at the sample surface ($x = 0$) and α_λ is the spectral absorption coefficient of the sample ($\alpha_\lambda = \varepsilon_\lambda[A]0$). λ_1 and λ_2 are the wavelengths delimiting the photoinitiator efficiency field.

4.2. Validation of the model, applications

All the samples of this study were brought to room temperature. The UV light intensity is always 10 mW cm^{-2} and the irradiation time is 600 s. The only varying parameters are radiation wavelength and photoinitiator concentration. To check the experimental results reproducibility, Fig. 7 presents the temperature evolution measured inside two samples irradiated by a polychromatic radiation and with a 0.15% (w/w) photoinitiator concentration. In spite of a precise positioning of the thermocouples, we can notice dispersion between the different measurements. The numerical

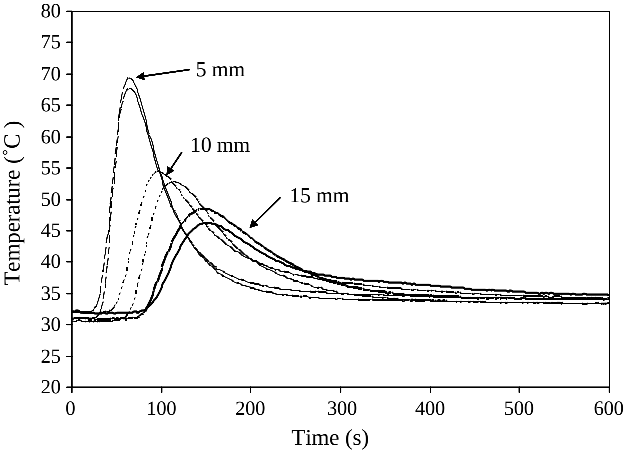


Fig. 7. Experimental temperature evolutions: photoinitiator concentration 0.15% (w/w).

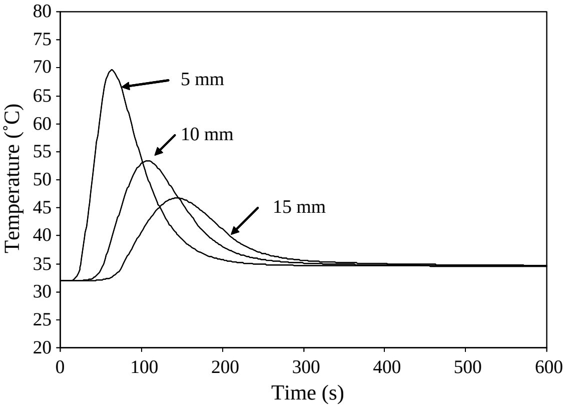


Fig. 8. Numerical temperature evolutions: photoinitiator concentration 0.15% (w/w).

temperature profiles obtained with these conditions are plotted in Fig. 8.

The absorption spectrum of the reactive mixture can easily be changed by modifying the photoinitiator concentration. An increase of photoinitiator concentration increases the absorbance of the mixture and the UV light intensity through the system rapidly decreases. Consequently, photopolymerization kinetics and temperature decrease versus the depth. On Figs. 9 and 10, we have plotted the experimental and numerical temperature evolution inside samples with respectively 0.35 and 1.5% (w/w) photoinitiator concentration. As expected, the more the photoinitiator concentration increases, the less the temperature increases.

We can notice a good correlation between experimental and numerical temperature results. These results validate the simulation and, therefore, the numerical photopolymerization kinetics which gave this good temperature correlation. Fig. 11 presents this numerical conversion versus time obtained with the conditions of Fig. 8.

As expected, photopolymerization kinetics and final conversion decrease with depth and this phenomenon is

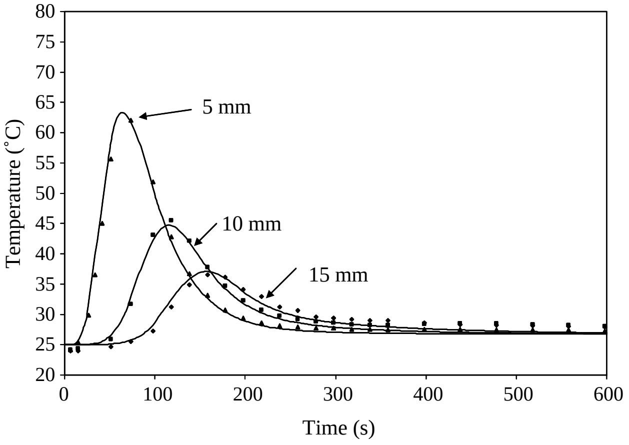


Fig. 9. Experimental (*) and numerical (—) temperature versus time: UV light intensity 10 mW cm^{-2}, photoinitiator concentration 0.35% (w/w).

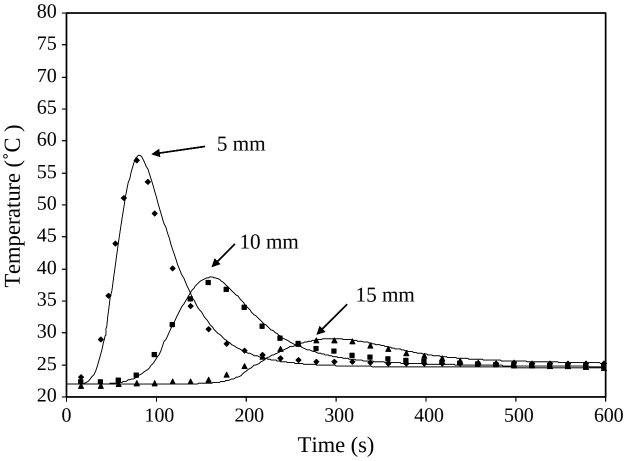


Fig. 10. Experimental (*) and numerical (—) temperature versus time: UV light intensity 10 mW cm^{-2}, photoinitiator concentration 1.5% (w/w).

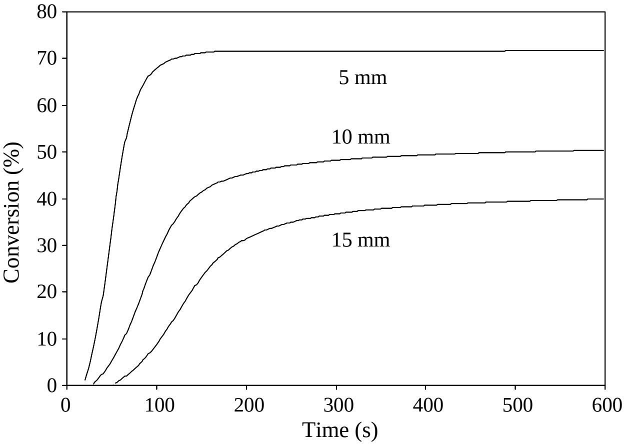


Fig. 11. Conversion computations versus time at different thickness. Polychromatic irradiation, photoinitiator concentration 0.15% (w/w).

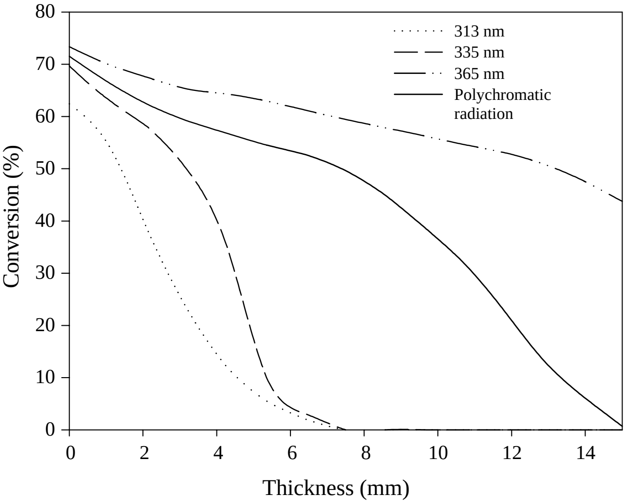


Fig. 12. Conversion computations profile at $t = 40$ s for mono and polychromatic irradiation. photoinitiator concentration 0.15% (w/w).

amplified when the photoinitiator concentration increases. The same behaviour is observed when we change the UV light wavelength. Effectively, thanks to the sample absorbance and the distribution of light intensity through the irradiated system (Fig. 6), an intensity gradient is created inside the sample when exposed to UV-radiation. The numerical gradients obtained with these different irradiation wavelengths are plotted in Fig. 12.

According to the evolution of spectral absorbance for these three wavelengths, a notable decrease in conversion versus depth is obtained. As expected, the more homogeneous the material, the smaller the absorption coefficient is. This is very clear at 313 and 335 nm, where a conversion wall is observed within the material at very small thickness.

On the other hand, by working with a 365 nm or with a polychromatic radiation, the decrease in the absorption coefficient profile is much lower and therefore the conversion gradient in the sample is reduced.

5. Conclusion

By means of numerical simulation and thanks to photopolymerization kinetics results obtained on thin dimethacrylate samples, the calculation of temperature and conversion profiles developed through thick dimethacrylate material was carried out for different irradiation modes and photoinitiator concentrations. Validation of the simulation was done by comparison between experimental and numerical temperature results. The influence of irradiation wavelength was investigated. The decrease in irradiation wavelength values induces a significant decrease of absorbed light intensity in the depth of the material and leads to a great conversion decrease. The low dimethacrylate thermal conductivity induces a low dissipation of the polymerization heat generated and, as a result, the greater the conversion, the higher the temperature is.

This study allows us to draw conclusions about the experimental conditions to produce a flat or a sharply conversion gradient. Thus, in our study, monochromatic radiation at 365 nm leads to the most homogeneous material and, at the opposite monochromatic radiation at 313 and 335 nm lead to a sharply conversion gradient. Unfortunately, high irradiation intensity in monochromatic mode cannot be applied to an industrial process since it causes losses in both yield and efficiency. The alternative solution in order to obtain a sharply gradient would be to increase the photoinitiator concentration and to use a lamp which develops a high intensity in the photoinitiator spectral efficiency field.

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