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Thermochimica Acta 410 (2004) 73–78
thermochimica acta
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Numerical simulation to correlate photopolymerization kinetics monitoring by RT-NIR spectroscopy and photocalorimetry

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Received 1 April 2003; received in revised form 11 July 2003; accepted 11 July 2003

Abstract

Photocalorimetry (DSC) and real time infrared (RTIR) spectroscopy are the two usual methods used to follow photopolymerization reactions. Kinetics obtained by DSC on thin samples and kinetics obtained by real time near-infrared (RT-NIR) spectroscopy on thick samples are not the same. The heat release during the photopolymerization induced a high temperature increase in thick samples because of the absence of temperature control. We think that this temperature offset is the main cause of this kinetic difference. In this paper, we want to verify this assumption. To reach this aim, conversion and temperature evolutions versus time were numerically simulated for a sample placed in the thermal conditions of NIR analysis by using experimental kinetic data obtained by photocalorimetry in isothermal mode. The boundary conditions were determined such as the simulated evolution of the sample temperature is the same as the experimental one. At last, conversion curves simulated to obtain these temperature profiles were compared to experimental results obtained by RT-NIR.

Keywords: RT-NIR spectroscopy; Photocalorimetry; Photopolymerization; Simulation

1. Introduction

Photoinitiated polymerization of multifunctional monomers is now very used in industrial processes for many applications: inks, varnishes, surface coatings [1–5] ... The advantages of this process are multiple: economical, ecological, high productivity, high quality of the final material. It constitutes an easy and rapid method for producing highly crosslinked polymer networks. However, the high speed and the exothermicity of the reaction play on the material homogeneity. To ensure the effective use of these materials and to tailor them for a particular application, good knowledge of conversion profiles within the material during photoinitiated polymerization is essential. In this aim, kinetic studies of the reaction are usually carried out.

Two methods are usually used to study photopolymerization kinetics: the photocalorimetry [6,7] and the real time infrared (RTIR) spectroscopy [8–11]. The choice of the first technique is justified by the exothermicity of such reactions. Its principle consists in measuring the heat flow evolved by the photoinitiated reaction as a function of time and at a given temperature. The main advantage of the photocalorimetry is a good temperature control for reactions having a $t_{1/2}$ (time to reach 50% conversion) higher than 15 s [13]. Nevertheless, this technique only provides a global heat flow but no information about the chemical reaction. Thus, when at least two monomers having different reactive groups take place in the network formation, the contribution of each one to the reaction cannot be distinguished. Moreover, because of the low thermal conductivity of the material, the increase in sample temperature due to the exothermicity of the photopolymerization reaction is high, preventing the study of very fast photopolymerization kinetics ($t_{1/2} < 15$ s). RTIR spectroscopy mitigates the disadvantages of the photocalorimetry. This technique consists in exposing a photopolymerizable sample to two radiations: an infrared radiation which allows the IR spectroscopic analysis, and an ultraviolet radiation which allows to initiate the photopolymerization reaction. It is then possible to follow in real time the decrease in the vibration bands absorption which are characteristic of each different reactive groups. The RTIR spectroscopy provides an immediate answer to all chemical changes. Therefore, very fast

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0040-6031/$ – see front matter © 2003 Published by Elsevier B.V.
doi:10.1016/S0040-6031(03)00394-0

reactions can be studied by this technique. RTIR analysis can be carried out by means of two techniques. The first one is a diamond ATR device (attenuated total reflection). In this method, the diamond and the metal plate in which it is mounted ensure a good thermal contact between the sample and ATR unit and enable an effective heat transfer. Moreover, the thickness of the layer could be less than 5 μm what reduces the total heat release due to the reaction enthalpy of the sample. In this case, RTIR results are comparable with DSC results. The second one is the laminate technique in which the polymer layer was thermally isolated between two thick polyethylene films surrounded by air and analyzed by transmission. When the mid-infrared region of the spectrum was used, the layer thickness is in the range of 10 μm and the heat release does not induced a high temperature increase in the sample. If this mid-infrared region of the spectrum is not exploitable, or if we have a thick material, the near-infrared spectroscopy could be used. In this case, the sample thickness is at least 1 mm. The exothermicity of the photopolymerization reactions leads to an increase in temperature and kinetic studies are not carried out under isothermal conditions.

Thus, study of photopolymerization kinetics by DSC and real time near-infrared (RT-NIR) techniques does not give exactly the same results. We think that the absence of temperature control during RT-NIR analysis is the main reason of this kinetic difference. To verify this assumption, one solution should consist in imposing to the DSC a temperature program corresponding to the temperature variation versus time which was observed during a RT-NIR analysis and then, in verifying if the kinetic obtained by DSC equals to the one obtained by RT-NIR spectroscopy. Unfortunately, this solution is technically impossible and we have decided to simulate the thermal heat transfer which occurs during this reaction. Using experimental kinetic data obtained by DSC in isothermal mode, we have simulated conversion and temperature evolutions versus time for a thick sample placed in the thermal conditions of NIR analysis. By playing on the boundary conditions, the simulated evolution of the sample temperature was adjusted to the experimental one. At last, conversion curves were simulated to obtain these temperature profiles and then compared to experimental results obtained by RT-NIR.

2. Experimental

2.1. Materials

The chemical formula of the dimethacrylate polyether of Bisphenol A (Akzo, $M = 575$ g/mol) used is shown in Fig. 1.

The photoinitiator 2,2-dimethyl-2-hydroxyacetophenone (Ciba Geigy-Darocur 1173: 0.35% (w/w), i.e. 2.3×10^{-2} mol/l) was dissolved in the oligomer under stirring at room temperature for 3 h.

2.2. Photocalorimetry

Photopolymerization kinetics were monitored by a differential scanning calorimeter (DSC 7 Perkin-Elmer) topped by an irradiation unit with two quartz windows. The optical part of the calorimeter includes a light source at a distance of 150 mm from the sample. The light source is a 350 W Oriel mercury vapor lamp. Heat flow versus time was recorded in isothermal mode under nitrogen atmosphere during the photoinitiated polymerization reaction. The optical part of the calorimeter, the sample preparation, the treatment of the thermogram and the computation of conversion and reaction rate were described elsewhere [7] ($\Delta H_0 = -54.7$ kJ/mol per methacrylate double bond [12]). The UV radiation intensity at 365 nm was measured at the sample level by using a radiometer (Intraspec II Oriel VLX/3W).

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, $t_{1/2} = 15$ s) are suitable to work in isothermal mode [13]. Indeed, whatever the polymerization temperature (from 30 to 90 °C), the rise of temperature within the film, in the DSC oven, is always lower than 1 °C.

2.3. Real time infrared spectroscopy

Photocrosslinking reactions were also followed by real time infrared spectroscopy (Perkin-Elmer FTIR 2000 spectrometer). UV radiation from a 350 W Oriel mercury vapor

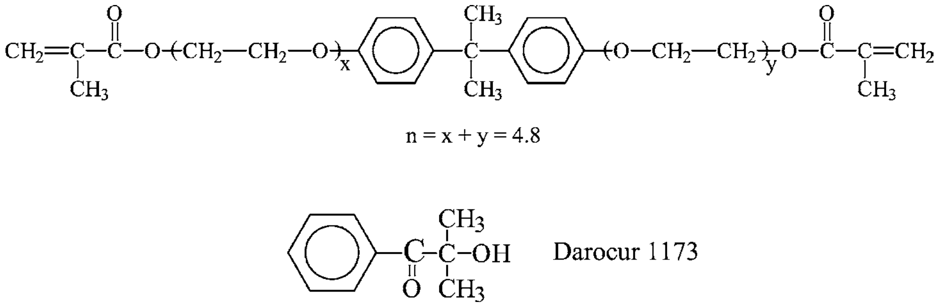

Fig. 1. Chemical formula of monomer and photoinitiator.

lamp was introduced into the FTIR spectrometer sample chamber by a light guide so that it did not interfere with the IR beam. The UV radiation intensity was also measured at the sample level at 365 nm with the same radiometer as previously. A set of neutral filters allows to modulate the UV light intensity. A homogeneous and constant sample thickness was ensured during the photopolymerization reaction by using a 1 mm thick metallic wedge between the two polyethylene films. Each of the IR spectra was obtained from the spectrophotometer with a resolution of 8 cm^{-1}. The time resolution of the method is 6 s. The 1st overtone of the C=C stretching vibrations of the methacrylate functional groups at 6165 cm^{-1} was monitored as a function of irradiation time. After baseline correction, conversion of the functional groups can be calculated by measuring the absorbance at each time of the reaction and determined as following:

$$\chi_{(t)} = \frac{A_0^{6165} - A_t^{6165}}{A_0^{6165}} \tag{1}$$

where $\chi_{(t)}$ is the conversion of the methacrylic double bonds at t time, A_0 the initial absorbance (before UV irradiation) and A_t is the absorbance of the double bonds at t time.

2.4. Temperature measurement

Temperature variation of the polyethylene films in contact with the reactional mixture was measured versus time (in the FTIR) by means of a IR pyrometer (Minolta/Land Cyclops 300AF). The pyrometer is connected to a computer via a RS 232 connection. The accuracy is better than 1 °C after calibration with the polyethylene emissivity.

3. Determination of the kinetic and physical parameters used for the simulation

3.1. Kinetic parameters

The simulation was carried out from kinetic data obtained by DSC. The necessary parameters such as conversion of the methacrylic double bonds versus time and reaction rate were measured in isothermal mode. For example, Fig. 2 collects results for temperatures below 80 °C and for a light intensity of 11 $\mathrm{mW/cm^2}$.

3.2. Physical parameters

Values of the physical parameters are listed in Table 1, where C_p is the heat capacity, a the thermal diffusivity, λ the thermal conductivity and ΔH_R is the ultimate experimental polymerization enthalpy. These values used for the calculation are kept constant throughout this paper in order to simplify the analysis, and correspond either to average values or to measurements on the studied commercial dimethacrylate monomer [14].

Table 1
Physical parameters of the dimethacrylate monomer

a ($\mathrm{m^2/s}$)	C_p (J/(kg K))	λ (W/(m K))	ΔH_R (J/g)
1.616×10^{-7}	1950	0.29	115

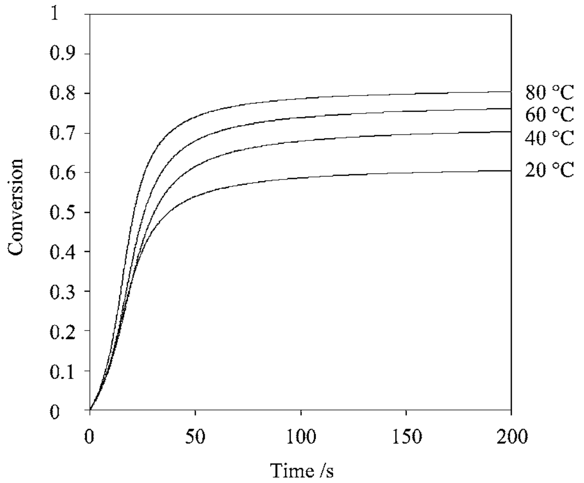

Fig. 2. Conversion vs. time and temperature for $I_0 = 11\,\mathrm{mW/cm^2}$ and 0.35% (w/w) of photoinitiator.

4. Theoretical considerations

4.1. Schematic shape of the experimental device

The simulation was performed on a semi-infinite slab with 1 mm thickness between two polyethylene films (0.1 mm thickness). The slab is made of a homogeneous mixture of dimethacrylate resin and photoinitiator. The UV radiation arrives on the upon face of the material (Fig. 3).

4.2. 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 [15]:

$$\frac{\partial^2 T}{\partial x^2} - \frac{1}{a}\frac{\partial T}{\partial \tau} + \frac{S(x)}{\lambda} + \frac{\Delta H_\mathrm{R}}{aC_\mathrm{p}}\frac{\mathrm{d}C(x)}{\mathrm{d}\tau} = 0 \tag{2}$$

where T is the temperature, τ the time, x the thickness, $S(x)$ is the first location-dependent heat source which corresponds to the radiative flux absorption. In addition, $(\Delta H_\mathrm{R}/aC_\mathrm{p})(\mathrm{d}C(x)/\mathrm{d}\tau)$ is the second location-dependent heat source induced by the polymerization, $C(x)$ and $\mathrm{d}C(x)/\mathrm{d}\tau$ are respectively conversion and polymerization rate at τ time, T temperature and x thickness. At a given temperature T, conversion $C(x)$ is also a function of the

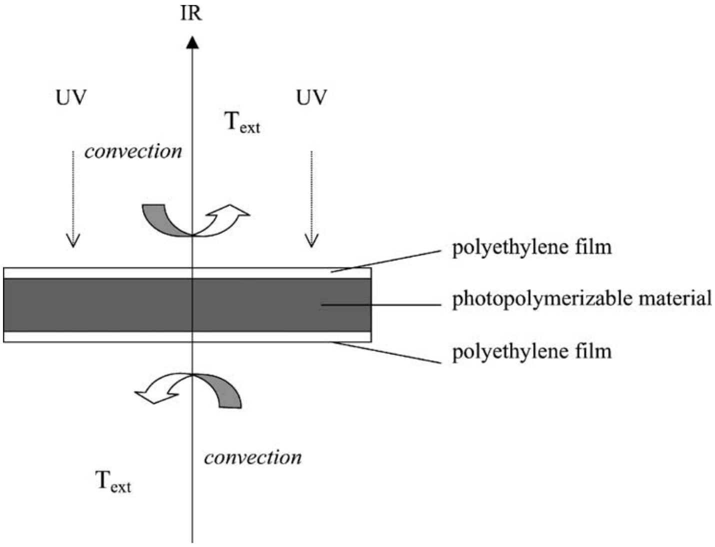

Fig. 3. Schematic shape of the experimental device.

radiative flux which is itself a function of the thickness x according to the relation $I(x) = I_0 e^{-\alpha x}$, where α is the absorption coefficient and I_0 is the incident light intensity.

4.3. Simplifications and 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 (λ, a) are constant during reaction.
(iv) Kinetic parameters are only function of reaction temperature and irradiation light intensity, as it was found with the photocalorimeter technique.
(v) Resin and polyethylene thermal parameters (λ, a) are equal.
(vi) There is no contact thermal resistance between resin sample and polyethylene film.
(vii) Thermal influence of the radiative flux (IR radiation) is neglected ($S(x) = 0$). This assumption is acceptable except for 50 mW/cm^2 irradiation which induces a temperature increase of 8 °C, as shown in Fig. 4 at the end of reaction.

4.4. Initial and boundary conditions

4.4.1. 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.

4.4.2. Boundary conditions

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

$$\frac{\partial T^\tau}{\partial x} = -\frac{h}{\lambda}(T_s^\tau - T_{ext}) \tag{3}$$

where h is the convection parameter.

4.5. Numerical analysis

Because of the internal heat generated from the reaction which is a function of time and space, Eq. (2) cannot be

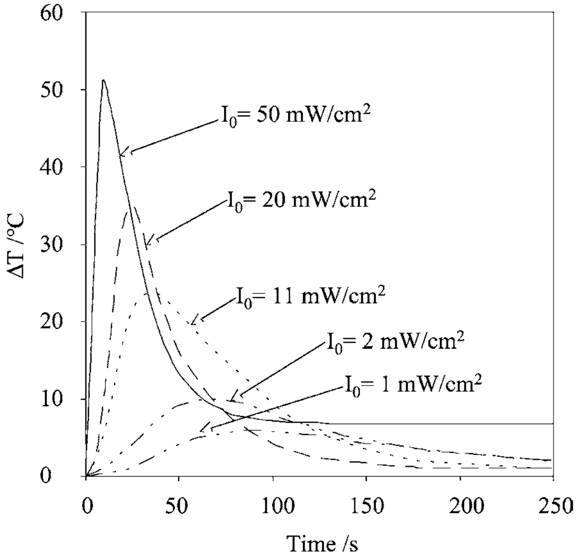

Fig. 4. Temperature variation vs. time measured by an IR pyrometer for a sample photocrosslinked at 25 °C under different UV light intensities.

integrated mathematically. The problem was solved by using an explicit numerical method with finite differences [16].

5. Results and discussion

Fig. 4 shows the sample temperature evolution measured by the IR pyrometer during the photopolymerization at different UV light intensities for a sample placed in the IR spectrophotometer at an initial temperature of 25 °C.

As expected, the higher the UV light intensity is, the faster the photopolymerization reaction is and the higher the temperature increase is. The maximum variation reaches 50 °C after about 10 s under 50 mW/cm^2 UV irradiation. It is obvious that, in this case, the reaction polymerization is no more carried out in isothermal conditions. Thus, kinetic monitored by RTIR spectroscopy is not representative of a kinetic at 25 °C. On the other hand, in a previous study [13], we have shown that a maximum increase of 1 °C is observed for a 50 mW/cm^2 UV irradiation for a sample placed in the photocalorimetry oven. In this case, the assumption of an isothermal reaction is certainly well founded.

Conversion curves versus reaction time carried out at an initial temperature of 25 °C (light intensity of 11 and 50 mW/cm^2) and followed by photocalorimetry and IR spectroscopy are collected in Fig. 5. One can see a difference between these curves which can be partially attributed to the temperature elevation measured in case of the IR monitoring (Fig. 4). Indeed, after consumption of the oxygen present in the IR sample, we can notice a slight variation of initial rates between the two techniques of analysis. At 60% of conversion, the progressive rate deceleration observed on the DSC curves, is caused by a decrease in the mobility and the diffusion of the reaction species induced by the gelation. The reaction completely stops when the glass transition temperature of the crosslinked material equals the analysis temperature. At the opposite, at 60% of conversion, because of the heat evolved by the reaction and not dissipated, the IR sample temperature is higher than the analysis temperature so that the glass transition temperature of the material is not reached and the reaction is still possible, allowing an increase in the final conversion. The conversion offset between DSC and IR analysis is 4% for the 11 mW/cm^2 experiment but it reaches 17% for the 50 mW/cm^2 one. This large offset at 50 mW/cm^2 is not only due to the heat transfer from the UV lamp. Effectively, this heat transfer induces a temperature increase of 8 °C and is not enough to explain a 17% offset. As expected, the higher the temperature variation is, the higher the conversion difference is.

Using conversion curves obtained by DSC in isothermal mode for temperature ranging from 25 to 90 °C and light intensities from 1 to 50 mW/cm^2, the numerical simulation has allowed us, in a first time, to simulate temperature evolution versus time for a sample placed in the thermal conditions of IR analysis. In this simulation, all the parameters were known except for the convection parameter h. Moreover, temperature evolution is the only parameter measurable (by pyrometer) and comparable with numerical values. Thus, a good fitting between experimental and numerical temperature evolutions allows to determine a correct value for the convection parameter. For example, Fig. 6 shows for a light intensity of 11 mW/cm^2 that a convection parameter value of 5 W/(m^2 K) gives a good result. This value was used for all simulations.

In a second time, the numerical conversion curves corresponding to these temperature profiles were compared to the experimental ones obtained by RT-NIR (Fig. 7).

With this temperature correction, we can notice that simulated curves well follow the experimental ones. In addition, because of the absence of the inhibiting time due to the dissolved oxygen at the beginning of the reaction in the DSC

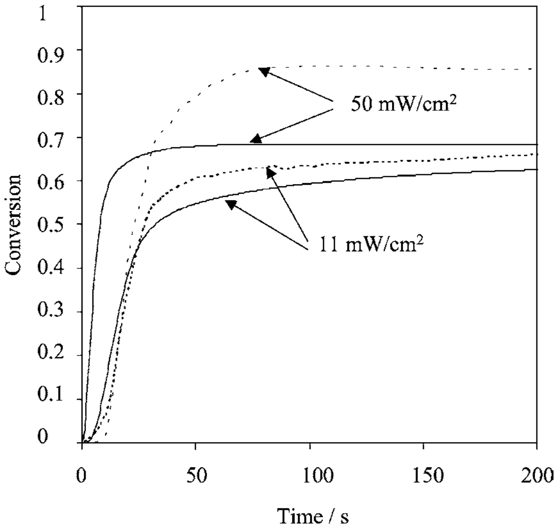

Fig. 5. Conversion curves vs. time at 25 °C for two irradiation intensities: (- - -) IR monitoring; (—) DSC monitoring.

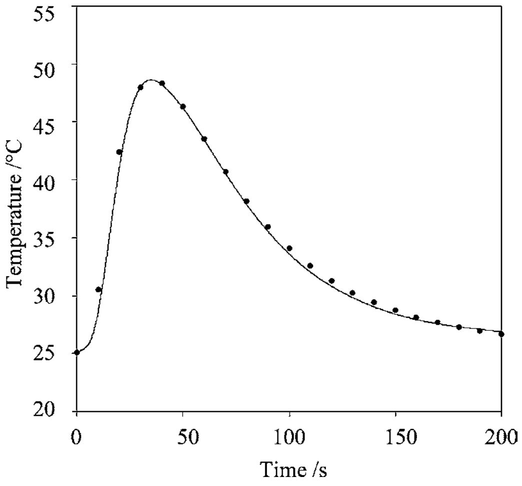

Fig. 6. Temperature evolution vs. time for a sample photocrosslinked in the IR analysis conditions at 25 °C and 11 mW/cm^2 irradiation intensity: (●) experimental curve; (—) simulated curve.

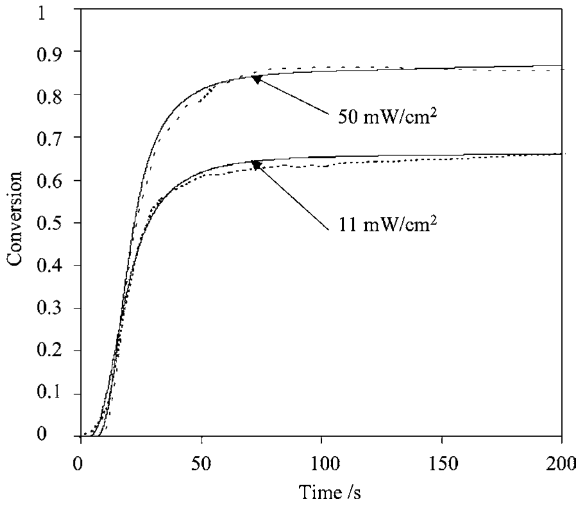

Fig. 7. Conversion curves vs. time at 25 °C for two irradiation intensities: (- - -) IR experimental curve; (—) simulated curve.

data, we have arbitrarily shifted the simulated curves to take into account this time and to be able to compare them to the experimental RTIR curves.

6. Conclusion

We have shown that kinetic difference obtained with the DSC and RT-NIR techniques mainly results from a sample temperature elevation during the NIR analysis. If the temperature offset induces a kinetic difference in the same order of experimental uncertainties for slow kinetics for which the temperature elevation does not exceed 20 °C, this difference becomes very important for fast kinetics. From kinetic data obtained with thin films in isothermal mode, a numerical simulation of temperature and conversion evolutions versus time for a sample placed in the thermal conditions of IR analysis was successfully realized since simulated curves well follow the experimental ones. Therefore, this simulation allows us to modify the DSC kinetics (obtained on thin films) in order to be compared with the RT-NIR ones (obtained on thick material).

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