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MATHEMATICAL MODEL FOR THERMAL PROCESSES IN PHOTOPOLYMERIZATION

Jarosław Siedlecki¹, Mariusz Ciesielski²

*¹Institute of Mathematics, ²Institute of Computer and Information Sciences
Czestochowa University of Technology, Poland
jaroslaw.siedlecki@im.pcz.pl, mariusz.ciesielski@icis.pcz.pl*

Abstract. In the paper the mathematical model for interaction of an intense light source on a photosensitive monomer/polymer mass with photoinitiator component is presented. Heat is released during the photopolymerization process. The thermal and photopolymerization processes occurring in the monomer/polymer mass which is located in the porcelain form are analysed. The equations of mathematical model in axially-symmetrical domain are solved numerically. In the work the effect of light dose on the processes is investigated. In the final part of this paper, the examples of computations are presented.

Introduction

In polymer chemistry, the process of polymerization [1] is related to linking small molecules (monomers) into a chain of larger molecules (polymers). The polymerization consists of three steps: initiation, propagation and termination. In photo-polymerization, this process is initiated by exposing photosensitive compounds (containing a photoinitiator) to an intense light source (i.e. light from a laser beam) whereby a photo-chemical process begins. A photoinitiator by reacting with an actinic photon decomposes into radicals which catalyse the polymerization process. Next, the reaction of the addition of the radical to a monomer molecule produces an initial activated monomer. In the second step (the propagation), the polymer chain is formed by reacting the activated monomer with other monomer. This step goes on (forming longer molecules) until a chain inhibition process terminates the polymerization reaction (the third step).

In the photo-polymerization, a temperature rise is observed which is caused by the exothermic reaction during the polymerization. Polymerization can be turned on and off by turning the light source off and on.

In this paper the mathematical models for the process of photo-polymerization are developed. In the models the changes in time of monomer and photoinitiator concentrations, the intensity of absorbed light by photoinitiator, the shape distribution of light source and the temperature profiles in the considered domain are taken into account.

1. Mathematical model

The domain considered in Figure 1 is presented. The cylindrical domain is limited by planes $z = 0$ and $z = Z$ and surface $r = R$. The domain consists of two sub-domains: the monomer/polymer mass (Ω_1) and the porcelain form (Ω_2). The monomer/polymer mass is placed inside the porcelain form shaped as a cylinder of radius R_1 and height Z_1 . On the upper surface limiting the domain, the stationary light spot on the photopolymerized material is exposed. The porcelain form play a role of an internal chill.

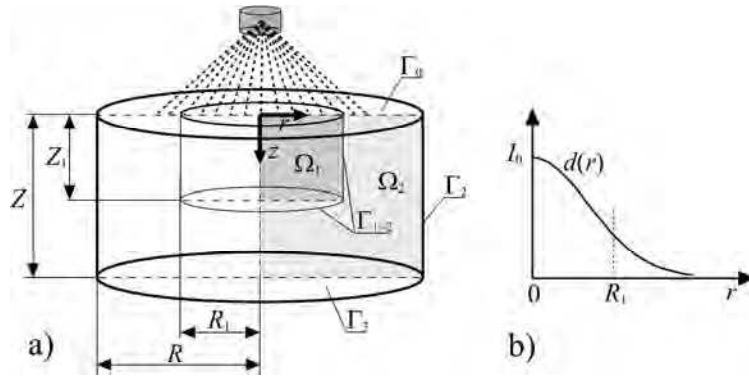


Fig. 1. The domain considered (a) and the light distribution on the top surface (b)

The temperature field in the system of the monomer/polymer and the form is described by the system of equations [2]

$$c_m \rho_m \frac{\partial T_m}{\partial t} = \lambda_m \nabla^2 T_m + q_m \quad (1)$$

where index $m = \{1, 2\}$ identifies the monomer/polymer and the form sub-domain, respectively, $T = T(r, z, t)$ [$^{\circ}\text{C}$] is the temperature, r, z [m], t [s] denote spatial coordinates and time, c [J/(kg $^{\circ}\text{C}$)], ρ [kg/m 3], λ [W/(m $^{\circ}\text{C}$)] are the specific heat, the density and the thermal conductivity of materials considered, respectively. The operator $\nabla^2 T$ in the cylindrical domain is of the form

$$\nabla^2 T_m = \frac{1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T_m}{\partial r} \right) + \frac{\partial^2 T_m}{\partial z^2} \quad (2)$$

The term $q_m = q_m(r, z, t)$ [W/m 3] is a heat source function, and this term for $m = 1$ can be written in the form [2]

$$q_1 = \Delta H_p R_p \quad (3)$$

where ΔH_p [J/mol] is the heat of polymerization and $R_p = R_p(r, z, t)$ [mol/(m³ s)] is the polymerization rate at the neighbourhood of the considered point $\{r, z\}$. Whereas, for $m = 2$ we assume $q_2 = 0$.

The Eq. (1) is supplemented by the following initial-boundary conditions. For $t = 0$ the initial condition is known

$$T_m|_{t=0} = T_{init}, \quad m = 1, 2 \quad (4)$$

On the contact surface between monomer/polymer and form, the IV type of boundary condition is assumed

$$\Gamma_{1-2}: \begin{cases} -\lambda_1 \frac{\partial T_1}{\partial n} = -\lambda_2 \frac{\partial T_2}{\partial n} \\ T_1 = T_2 \end{cases} \quad (5)$$

where $\partial/\partial n$ is a normal derivative. On the external surface of the both sub-domains (see Fig. 1) the II and III types of boundary conditions are given

$$\Gamma_0 \cup \Gamma_2: -\lambda_m \frac{\partial T_m}{\partial n} = -\alpha(T_{amb} - T_m) \quad (6)$$

$$\Gamma_3: \frac{\partial T_m}{\partial n} = 0 \quad (7)$$

$$\left. \frac{\partial T_m}{\partial r} \right|_{r=0} = 0 \quad (8)$$

where α [W/(m² °C)] is the heat transfer coefficient and T_{amb} [°C] is the ambient temperature.

On the boundary Γ_0 , the stationary light spot on the photopolymerized material is exposed. The intensity distribution of this light $I = I(r, z, t)$ is given in the form

$$I|_{z=0} = I_0 d(r) \Theta(t) \quad (9)$$

where I_0 [Einstein/(m² s)] is the intensity of the beam, $d(r)$ for $0 \leq r \leq R_1$ is a shape distribution function and $\Theta(t)$ determines variation light exposition in time (in this work the impulse light with duration time $[0, t_0]$ has been assumed: $\Theta(t) = H(t_0 - t)$, where H is the Heaviside function).

The light intensity decreases with depth into the monomer/polymer mass [1, 3]. This is due to the light absorption by the photoinitiator. The rate of change of the light intensity with depth is

$$\frac{\partial I}{\partial z} = -\varepsilon S I \quad (10)$$

where ε [m²/mol] is the molar absorptivity constant for photoinitiator and $S = S(r, z, t)$ [mol/m³] is the temporary concentration of photoinitiator at the considered point of the domain. The analytical solution of Eq. (10) with the boundary condition for $z = 0$ (9) is of the form

$$I = I_0 d(r) \Theta(t) \exp(-\varepsilon S z) \quad (11)$$

The intensity of the absorbed light $I_a = I_a(r, z, t)$ [mol/(m³ s)] is determined by the following relation

$$I_a = \varepsilon S I \quad (12)$$

In photopolymerization [1, 3], the rate of photochemical initiation $R_i = R_i(r, z, t)$ and the polymerization rate $R_p = R_p(r, z, t)$ play an important role. These rates are given as

$$R_i = \phi I_a \quad (13)$$

$$R_p = k_p M \sqrt{\frac{\phi I_a}{k_t}} \quad (14)$$

where ϕ [-] is the quantum yield for initiation, k_p [m³/(mol s)] and k_t [m³/(mol s)] are the propagation and termination rate constants, respectively; and $M = M(r, z, t)$ [mol/m³] is the temporary monomer concentration.

The changes in time of monomer and photoinitiator concentrations are determined by the following equations

$$\frac{\partial M}{\partial t} = -R_p \quad (15)$$

$$\frac{\partial S}{\partial t} = -R_i \quad (16)$$

with initial concentrations

$$M|_{t=0} = M_{init}, \quad S|_{t=0} = S_{init} \quad (17)$$

2. Examples of computations

Numerical simulations of a thermal and photopolymerization processes for the material (1,6 hexanediol diacrylate - HDDA) located in the porcelain form have been executed. The considered domain has the dimensions: $R_1 = 2$ mm, $R = 5$ mm, $Z_1 = 2$ mm, $Z = 5$ mm. At the stage of numerical computations, the control volume method [4-6] has been used.

The following thermophysical parameters of HDDA [7] have been assumed: $c_1 = 1700$ J/(kg °C), $\rho_1 = 1150$ kg/m³, $\lambda_1 = 0.2$ W/(m °C), $\Delta H_p = 166$ kJ/mol,

$k_p/(k_t)^{1/2} = 0.26 \text{ (m}^3/(\text{mol s}))^{1/2}$, $\varepsilon = 20 \text{ m}^2/\text{mol}$, $\phi = 0.1$, whereas thermophysical parameters of porcelain are the following: $c_2 = 2300 \text{ J}/(\text{kg } ^\circ\text{C})$, $\rho_2 = 840 \text{ kg}/\text{m}^3$, $\lambda_2 = 1.3 \text{ W}/(\text{m } ^\circ\text{C})$. The initial concentration of monomer and photoinitiator are $M_{mit} = 3 \text{ kmol}/\text{m}^3$, $S_{mit} = 0.15 \text{ kmol}/\text{m}^3$, the initial temperature is $T_{mit} = 20^\circ\text{C}$, the ambient temperature is $T_{amb} = 20^\circ\text{C}$ and the heat transfer coefficient is $\alpha = 10 \text{ W}/(\text{m}^2 \text{ } ^\circ\text{C})$.

In simulations, the function of the distribution of light source on the top surface of the considered domain of the Gaussian shape $d(r) = \exp(-r^2/R_1^2)$ has been used. Two tests depending on the intensity and the duration of the light source have been considered.

In the first test the following values $I_0 = 0.5 \text{ Einstein}/(\text{m}^2 \text{ s})$ and $t_0 = 0.25 \text{ s}$ have been taken into account. In Figure 2 the profile of monomer conversion and isotherms in the monomer/polymer sub-domain at time 0.25 s are shown. The kinetics of changes of monomer conversion and temperature at four selected points in the monomer/polymer sub-domain in Figure 3 is presented. One can observe that after turn off of the light source, the photopolymerization is terminated and temperature of sub-domains reaches to the equilibrium state.

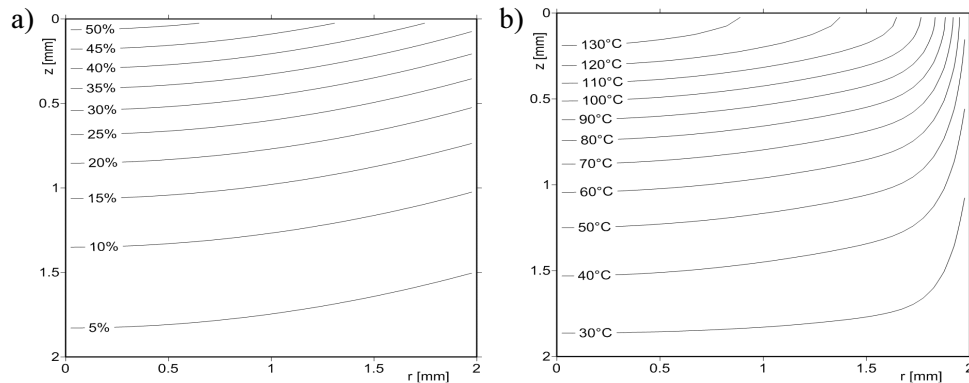


Fig. 2. Isolines for monomer conversion (a) and temperature (b) in the monomer/polymer sub-domain at time 0.25 s (parameters of the light: $t_0 = 0.25 \text{ s}$, $I_0 = 0.5 \text{ Einstein}/(\text{m}^2 \text{ s})$)

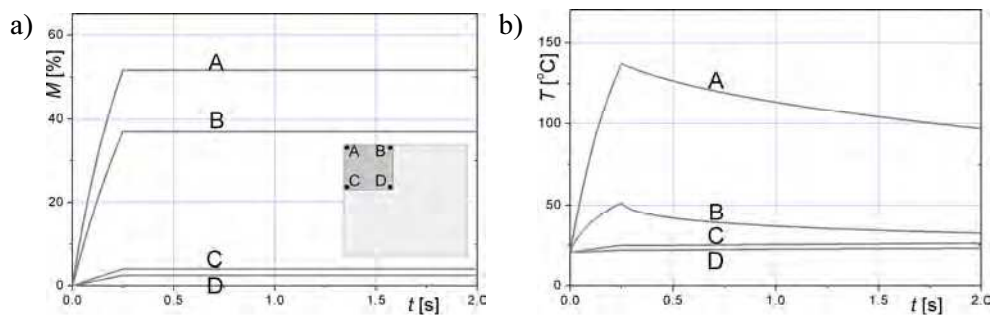


Fig. 3. The kinetics of changes of monomer conversion (a) and temperature (b) at selected points in the monomer/polymer sub-domain (parameters of the light: $t_0 = 0.25 \text{ s}$, $I_0 = 0.5 \text{ Einstein}/(\text{m}^2 \text{ s})$)

In the second test the values $I_0 = 0.25$ Einstein/(m² s) and $t_0 = 0.5$ s have been assumed. The results of calculations in Figures 4 and 5 are presented. In the both tests the same light source doses ($I_0 \cdot t_0$ Einstein/m²) have been used. Analyzing of obtained results one can note the monomer conversion and temperature rise in the second test.

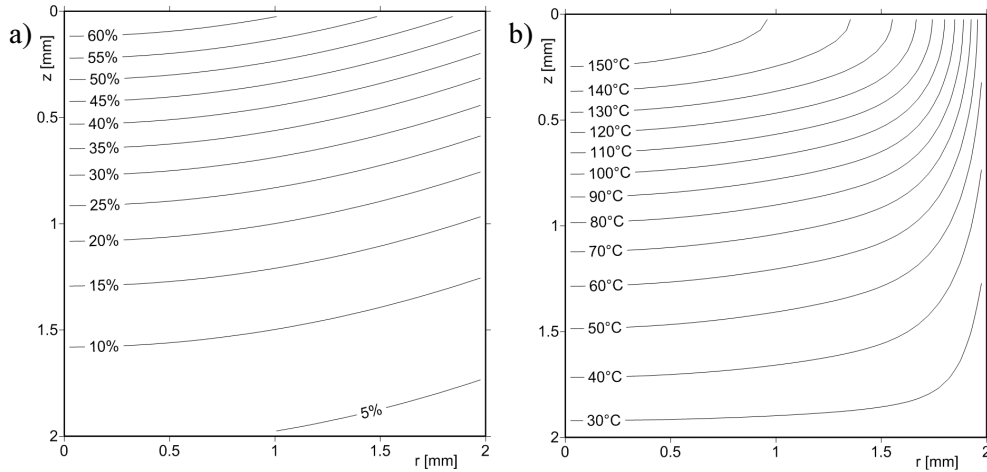


Fig. 4. Isolines for monomer conversion (a) and temperature (b) in the monomer/polymer sub-domain at time 0.5 s (parameters of the light: $t_0 = 0.5$ s, $I_0 = 0.25$ Einstein/(m² s))

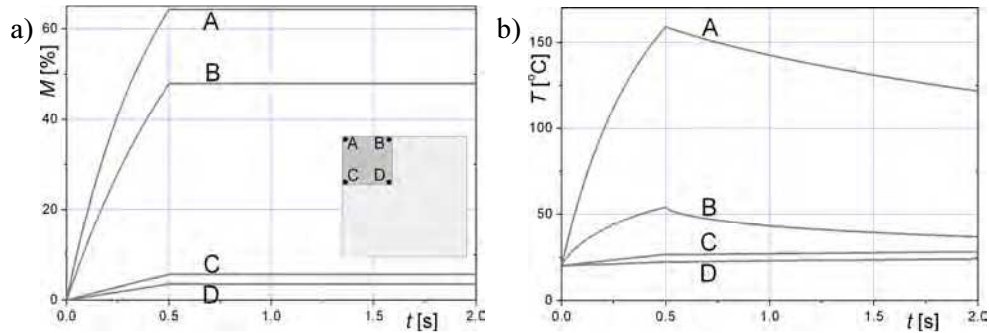


Fig. 5. The kinetics of changes of monomer conversion (a) and temperature (b) at selected points in the monomer/polymer sub-domain (parameters of the light: $t_0 = 0.5$ s, $I_0 = 0.25$ Einstein/(m² s))

Conclusions

In the present work, the mathematical model for photopolymerization in the cylindrical domain (2D task) was presented. The polymerization process proceeds in a short time. The effect of the same light source dose on the polymerization and thermal processes is very significant.

In the future we plan to use numerical simulations for polymerization of light-curable resin-based composites, which can be used as dental filling materials that are curable by light.

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