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Cure behaviour of visible light activated dental composites

Part II *Non-isothermal kinetics*

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In this paper, the non-isothermal cure behaviour of a dental composite, activated by visible light, is described using a heat transfer model that, coupled with a reaction kinetic expression, is able to predict the temperature and the degree of reaction in the composite. The temperature and the degree of reaction profiles inside the composite are calculated, as a function of the cure time, taking into account the system geometry, the thermal diffusivity of the composite, and the resin reaction rate. Material properties, boundary and initial conditions and the kinetic behaviour are the input data of the heat transfer model. Once the degree of reaction is known, the glass transition temperature profiles across the thickness of the composite are calculated. Experimentally measured glass transition temperatures are used for the evaluation of an extinction coefficient capable of accounting for the effects of the light absorption through the thickness on the polymerization kinetics. Finally, the effects of the non-isothermal cure conditions on the application of these materials in dental restorations are discussed.

1. Introduction

The theoretical aspects of light-activated photopolymerization has been studied by many researchers [1–4]. However, most traditional kinetic models consider only the isothermal behaviour, while light curing of dental composites is a fast and highly non-isothermal bulk polymerization. The analysis of the isothermal cure of a methacrylate-based commercial dental composite, activated by visible light, presented in the first part of this study [5], has lead to the determination of very low final glass transition temperatures (T_g) in the cured parts. This result appears in contrast with the good performances shown by these materials used for dental restorations. For isothermal cure conditions, the model presented in the first part of this study provides all the information needed to predict the behaviour of the material at a given temperature. However, the cure of a thermoset is always associated with significant development of heat. The temperature distribution inside the dental composite will depend on the competition between heat generation and heat diffusion through the thickness. While for very thin composite layers it can be assumed that the predominant heat diffusion will favour isothermal conditions, for thicker layers the conditions will clearly be non-isothermal. In this case, the reacting system must be viewed as a non-isothermal bulk reactor with volumetric heat generation and transfer.

Furthermore, the degree of reaction in light-cured composites varies within the bulk of the specimen because the rate of reaction is dependent upon light intensity available at different depths [6–10]. For applications in the restoration of an enamel cavity or a fractured tooth the composite material should cure at an adequate depth in order to minimize the need for application of successive layers. Reinforcements, fillers and pigments strongly reduce the intensity of the incident light, limiting the depth of cure. Most of the results reported in the literature are obtained measuring, by infrared spectroscopy, the degree of reaction on thick specimens (3–6 mm) [6–9], neglecting the effect of non-isothermal conditions occurring during photopolymerization. In fact, in these experimental conditions, a strong temperature increase is expected, leading to a local increase of the final degree of reaction. Therefore the measured depth of cure is the result of two competing variables:

(1) the light intensity that decreases through the thickness limiting the maximum degree of reaction;

(2) the temperature that increases into the composite enhancing the maximum degree of reaction and the final T_g [5].

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Most of the experimental determinations of depth of cure [6–9] are obtained without accurate control of the polymerization conditions. However, the experimental study of the depth of cure presented by Rueggeberg and Craig [10] on 0.5 mm thick samples, more closely approaches isothermal conditions. Moreover the shape of the experimental data presented by Rueggeberg and Craig [10] is closer to the theoretical prediction reported by Cook [9] for isothermal photopolymerization.

In this paper, the non-isothermal cure behaviour of a commercial dental composite activated by visible light is described using a heat transfer model that, coupled with a reaction kinetic expression, is able to predict the temperature and the degree of reaction in the composite. The temperature and the degree of reaction profiles inside the composite can be computed as a function of the cure time, taking into account the system geometry, the thermal diffusivity of the composite and the resin reaction rate. Material properties, boundary and initial conditions and the kinetic behaviour are the input data of the heat transfer model. Kinetic and heat transfer models are coupled and a numerical solution method is used. The glass transition temperature profiles across the thickness of the composite are calculated once the degree of reaction is known. Experimentally measured glass transition temperatures are used for the evaluation of an extinction coefficient capable of accounting for the effects of the light absorption through the thickness on the polymerization kinetics. Finally, the effects of non-isothermal cure conditions on the application of these materials in dental restorations are discussed.

2. Experimental procedure

The material studied is a commercial dental composite, Pekalux (universal shade), activated by visible light. The composition of the material and the light source are given in [5].

The determination of the T_g of cured samples is performed using a differential scanning calorimeter (DSC), Mettler DSC 30, operating with a constant air flow of 100 cm^3/min.

3. Non-isothermal cure behaviour

3.1. Energy balance

During cure, heat is generated in the material due to the exothermic nature of the curing reaction. For thick restorations, not all the heat can be dissipated quickly enough to maintain isothermal conditions. The processing conditions and the material characteristics will determine whether the highest temperature is in the core, at the skin or at some intermediate position. The temperature inside the composite can be calculated by solving the energy balance coupled with an appropriate expression for the cure kinetics [11, 12].

The simulation of the non-isothermal cure behaviour of the studied dental composite is performed introducing the following assumptions:

1. The thickness of the composite is small compared to the other two dimensions. Then, only conduction of heat in the transverse direction (x axis) is considered. The geometry of the system is shown in Fig. 1.
2. Average values of density $\rho = 1.5$ g/cm^3, specific heat $C_p = 1.26$ J/gK and thermal conductivity $k_x = 0.44$ W/mK are employed and no variation of these properties with temperature and/or degree of reaction is considered.
3. The radiative heat flow occurring during light exposure on the composite surface is neglected.

With these assumptions the law of conservation of energy takes the form

$$\rho C_p\, \partial T/\partial t = k_x \partial^2 T/\partial x^2 + \rho \mathrm{d}Q/\mathrm{d}t \qquad (1)$$

where dQ/dt is the rate of heat generated by the chemical reactions and is defined, as follows:

$$\mathrm{d}Q/\mathrm{d}t = Q_{\mathrm{tot}}\mathrm{d}\alpha/\mathrm{d}t \qquad (2)$$

where the heat of polymerization Q_{tot} is obtained from the isothermal kinetic analysis previously presented [5] and the rate of reaction dα/dt is given by

$$\mathrm{d}\alpha/\mathrm{d}t = K \exp(E_a/RT)\, \alpha^m(\alpha_m - \alpha)^n \qquad (3)$$

$$\alpha_m = c + dT \qquad \text{for } T < T_{\mathrm{gmax}} \qquad (4)$$

where K is a pre-exponential factor, R is the gas constant, E_a the activation energy, T the absolute temperature, and m and n are fitting parameters not dependent on temperature. In Equation 4, the temperature dependence of the maximum degree of reaction, α_m, is reported [5]. In order to analyse the photopolymerization kinetic of a thick specimen, the effect of light absorption must be taken into account, modifying Equation 4. According to the theoretical approach reported by Odian [1], the kinetic constant, K, may be correlated with the square root of the intensity of absorbed light. Assuming for the absorbed light, the exponential decrease given by the Lambert and Beer law, the following expression is obtained:

$$K = K_0[\exp(-bx)] \qquad \text{for } x > 0.2 \text{ mm} \qquad (5)$$

where K_0 is the pre-exponential factor obtained by calorimetric analysis and b is an empirical extinction factor. Since the kinetic analysis of the photopolymerization process is performed by DSC on 0.2 mm thick samples, Equation 5 may be applied only for $x > 0.2$ mm. The parameter b, not available from the DSC analysis previously performed [5], will be evaluated as a fitting parameter from T_g measurements on a cured specimen.

3.2. Dimensionless analysis

Dimensionless numbers may be introduced in order to better understand the relative weight of the different

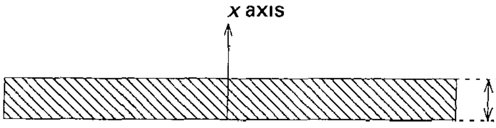

Figure 1 Sketch of the geometry used for the cure simulation.

terms of Equation 1 and to facilitate the numerical solution [11, 12]. A characteristic time of the material behaviour must be defined: the isothermal gel time, t_g, represents the time interval during which the material changes from the liquid to the rubbery state. The dimensionless variables of the model are defined as:

$$\text{Dimensionless temperature} \quad \theta = (T - T_o)/(T_a - T_o)$$
$$\text{Dimensionless time} \quad t^* = t/t_g \qquad (6)$$
$$\text{Dimensionless position} \quad X = x/h$$

where h is the composite thickness, T_o is the initial processing temperature, $T_a = T_o + Q_{tot}/C_p$ is the maximum temperature that can be reached in adiabatic conditions taken as reference temperature, and t_g is obtained by numerical integration, at $T = T_a$, of the kinetic model given by Equations 3–5 assuming a degree of reaction at gelation, $\alpha_g = 0.1$ [12]. The final equations then become

$$\partial\theta/\partial t = De\,\delta^2\theta/\partial X^2 + St\,d\alpha/dt^* \qquad (7)$$

$$d\alpha/dt^* = K^*[\exp(-bx)]\exp(E_a/RT)\,\alpha^m(\alpha_m - \alpha)^n \qquad (8)$$

In Equation 7 De is a dimensionless diffusion Deborah number [11, 12] given by

$$De = k_x t_g/\rho C_p h^2 \qquad (9)$$

The Deborah number represents the relationship between the heat transferred by conduction and the accumulation of heat in the material.

In Equation 7 the Stefan number, St, is introduced:

$$St = Q_{tot}/[(T_a - T_o)\,C_p] \qquad (10)$$

St may be considered as the relationship between the latent heat associated with the chemical reaction and the accumulation of heat in the material. In this case, with the given definition of $T_a = T_o + Q_{tot}/C_p$, $St = 1$. Isothermal cure conditions are verified if in the energy balance, the contribution of the thermal diffusivity (measured by the Deborah number) is much higher than the contribution of heat generation due to the polymerization reaction (measured by the Stefan number) and hence, if De is one order of magnitude higher than 1. On the other hand, adiabatic conditions are approached if De is one order of magnitude lower than 1. For a given reactive system, characterized by constant values of t_g, k_x, ρ and C_p, the value of De is determined by the thickness of the composite.

In Equation 7 K^* is a dimensionless kinetic constant given by

$$K^* = t_g K_o \qquad (11)$$

With these assumptions the dimensionless initial and boundary conditions are

Dimensionless initial conditions:

$$t^* = 0 \quad \alpha = 0 \quad \theta = 0 \qquad (12)$$

Dimensionless boundary conditions:

$$t^* > 0 \quad X = 0 \quad \partial\theta/\partial X = Bi\theta_o \qquad (13)$$

$$X = 1 \quad \theta = \theta_o \qquad (14)$$

where θ_o is given by Equations 6 calculated at the cure temperature, T_o, and Bi is the Biot number, a dimensionless number accounting for heat transfer by convection at the composite surface

$$Bi = hh_c/k_x \qquad (15)$$

where h_c represents the coefficient of heat transfer by convection. The Biot number represents the relationship between the heat transferred by convection at the composite interface and the heat transferred by conduction inside the material. In the oral cavity, a value of $h_c = 9$ W/m^2 K, corresponding to very weak heat dissipation, may be estimated [13]. In these conditions, Bi is on the order of 0.01, indicating that the composite–air interface behaves as a quasi-adiabatic surface.

A numerical solution of the mathematical model presented, Equations 7 and 8, is performed using implicit finite differences. Once the degree of reaction is known, the T_g of the material is calculated as a function of position and time using the linear expression previously introduced [5]

$$T_g = p + q\alpha \qquad (16)$$

3.3. Results

A thick sample (6 mm thick and 15 mm wide) was photopolymerized for 30 s at 20 °C. The cured sample was cut in thin layers and the measurement of the T_g across the thickness was performed by DSC. In Fig. 2 the T_g values are reported as a function of different depths. Following the results reported in the first part of this study [5], in isothermal conditions at 20 °C, a maximum degree of reaction of 0.47, corresponding to a $T_g = 30$ °C, would be developed, while as shown in Fig. 2, a final $T_g = 64$ °C is measured, indicating that non-isothermal cure conditions occur. It must be noted that the experimental T_g values shown in Fig. 2 follow the same path reported in the literature for the degree of reaction [6–9], confirming that all the specimens used for these works are photopolymerized in non-isothermal conditions.

The simulation of the experimental behaviour reported in Fig. 2 is obtained applying the proposed model (given by Equations 7 and 8) using the data given in Table I. The measured T_g values are used in a

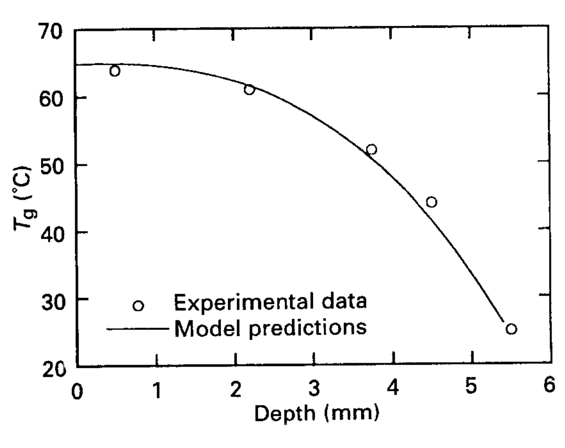

Figure 2 Glass transition temperatures as a function of the depth measured across a 6 mm thick sample photopolymerized at 20 °C (○ experiment; —— model predictions).

TABLE I Parameters of the full model

Kinetic parameters		Physical properties	
m	1.60	k_x (W/mK)	0.44
n	0.64	C_p (J/gK)	1.26
K_0 (s^{-1})	1.682	ρ (g/cm^3)	1.50
E_a (kJ/mol)	1.347	h_c (W/m^2 K)	9
c	− 1.564		
d (K^{-1})	0.006939		
p (K)	229.2		
q (K)	157.6		
α_g	0.1		
b (mm^{-1})	0.28		
Q_{tot} (J/g)	228.5		

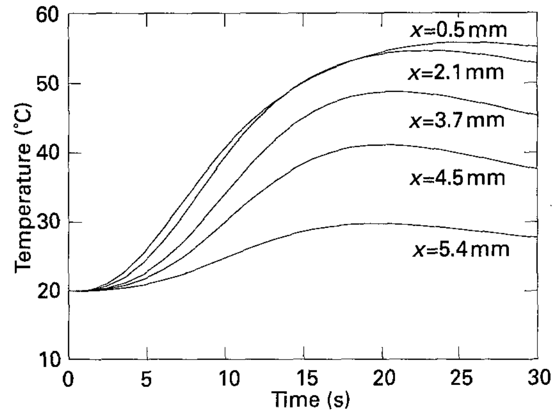

Figure 3 Results of the numerical simulation obtained on a 6 mm thick composite imposing as initial and boundary condition T_0 = 20 °C: temperature versus cure time at different positions across the material thickness.

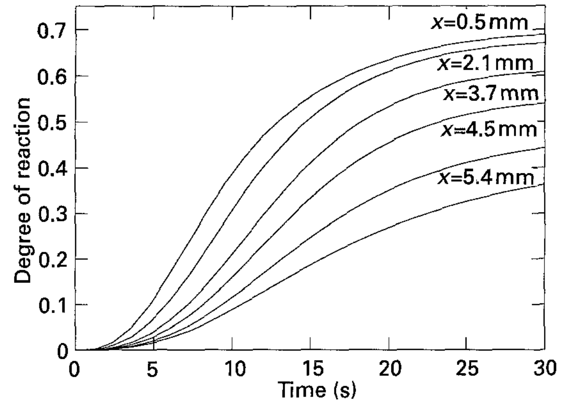

Figure 4 Results of the numerical simulation obtained on a 6 mm thick composite imposing as initial and boundary condition T_0 = 20 °C: degree of reaction versus cure time at different positions across the material thickness.

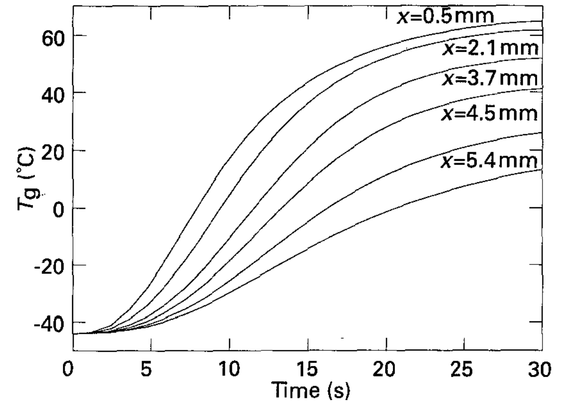

Figure 5 Results of the numerical simulation obtained on a 6 mm thick composite imposing as initial and boundary condition T_0 = 20 °C: glass transition temperature versus cure time at different positions across the material thickness.

fitting procedure for the evaluation of the extinction coefficient, b, of Equation 5. The full line shown in Fig. 2 is representative of the results of a simulation performed in the same processing conditions used for the experimental determination of these T_g values. The good agreement between experimental and predicted T_g values, shown in Fig. 2, is obtained by numerical integration of the model using a value of $b = 0.28\ mm^{-1}$.

A representative set of model results obtained using these processing conditions is displayed in Figs 3–5. Figure 3 shows the temperature evolution as a function of the cure time at the positions corresponding to the experimental T_g values reported in Fig. 2. In this case a value of $De = 0.026$ indicates that adiabatic cure conditions are approached. A very high rate of heat generation, coupled with low thermal diffusivity, determines a strong temperature increase in the first part of the process. When the balance between heat generation and thermal diffusivity is obtained, the temperature profile reaches a maximum. The results of the degree of reaction as a function of the cure time are shown in Fig. 4, in the same positions reported in the former figure. Moreover, for comparison purposes, the degree of reaction obtained integrating the kinetic model at 20 °C is also shown in Fig. 4. The effect of the different temperature developments across the thickness is clearly shown. Close to the external surface, the resin presents an accelerated kinetics due to the higher temperature, while the resin placed in contact with the mould (at 20 °C) follows a kinetic governed by the isothermal imposed temperature. The values of degree of cure have been used to compute the glass transition temperature as a function of cure time by means of Equation 16. The T_g values obtained in the same positions reported in the former figures are shown in Fig. 5. Also in this case, for comparison purposes, the T_g obtained during isothermal cure at 20 °C is reported in Fig. 5. The final T_g values obtained in isothermal conditions and in non-isothermal conditions show a dramatic difference as a consequence of the strong heating occurring in the composite.

As reported previously [5], the kinetic analysis is performed by DSC on samples of about 0.20 mm thickness. In order to verify that at least quasi-isothermal conditions are realized during DSC experiments, the model is applied to the simulation of the cure process for these sample geometries at different initial imposed temperatures T_0. In Table II the values of De and St numbers and of the maximum temperature increase, calculated as a function of the imposed initial temperatures, are listed. De numbers are significantly higher than St numbers at all temperatures, indicating

TABLE II Results of cure simulations obtained on a material thickness of 0.2 mm

Temperature (°C)	*De*	*St*	Maximum ΔT (°C)
25	20.5	1	0.3
30	18.1	1	0.3
35	16.4	1	0.4
40	14.7	1	0.5
50	12.3	1	0.6

that a quasi-isothermal cure, characterized by a very low maximum temperature increase, is expected.

The simulation of cure conditions occurring during an application of the studied dental composite to the restoration of an enamel cavity is presented in Figs 6–8. These figures report the temperature, the degree of reaction and the glass transition temperature profiles during cure, on the external surface (skin), at the centre (core) and in contact with the tooth where a constant temperature $T_0 = 37\,^\circ\mathrm{C}$ is imposed as a boundary condition. The irradiation time is set to 30 s and a thickness of 1.5 mm is considered. As a consequence of a low Deborah number ($De = 0.28$) a strong temperature peak is expected as shown in Fig. 6. The highest temperature is reached on the skin of the restoration as a consequence of the poor heat dissipation (low Biot number) at the interface with the air in the oral cavity (Fig. 6). The temperature increase enhances the reaction kinetic, α_m and the final T_g of the composite (Figs 7 and 8). Therefore the final degree of reaction and T_g are higher on the skin of the restoration than in contact with the tooth, where the photopolymerization follows an isothermal kinetic. In the last part of the cure, vitrification occurs and the reaction rate significantly decreases before light exposure is interrupted. The coexistence of regions with different temperatures and morphology histories may lead to the formation of inhomogeneous structures, affecting the mechanical performances and the durability of the restoration.

The low final T_g values predicted in isothermal cure conditions in the first part of this work are observed only for very thin composite layers corresponding to $De > 1$. On the other hand, as shown in Figs 7 and 8, typical cure conditions of thicker layers lead to a higher final degree of reaction and to T_g values on the order of 55 °C at the outer layer of the restoration skin, where higher mechanical wear and thermal resistances are required. However, the development of high T_g values depends on polymerization conditions that cannot be controlled during the application of these materials to dental restorations. In fact, the transition from isothermal to non-isothermal conditions, is observed when the Deborah number becomes significantly higher than 1. For a given reactive system, characterized by constant values of t_g, k_x, ρ and C_p, the value of De is proportional to $1/h^2$ (Equation 9) and therefore a very small decrease of the composite thickness (from $h \geqslant 1$ mm for non-isothermal cure to $h \leqslant 0.3$ mm for isothermal cure) induces this transition between these two different cure behaviours.

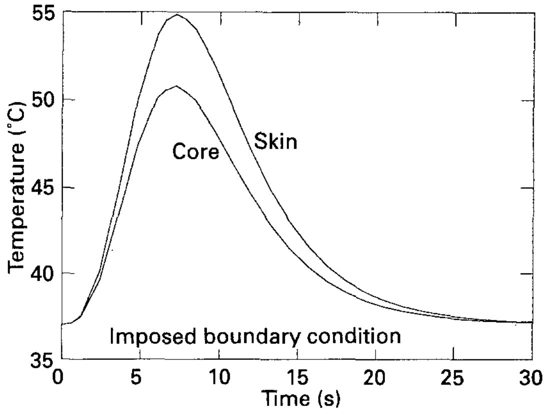

Figure 6 Results of the numerical simulation of the cure conditions occurring during an application of the studied dental composite to the restoration of an enamel cavity (thickness 1.5 mm, $T_0 = 37\,^\circ\mathrm{C}$) : temperature versus cure time on the external surface (skin) and at the centre (core) of the composite.

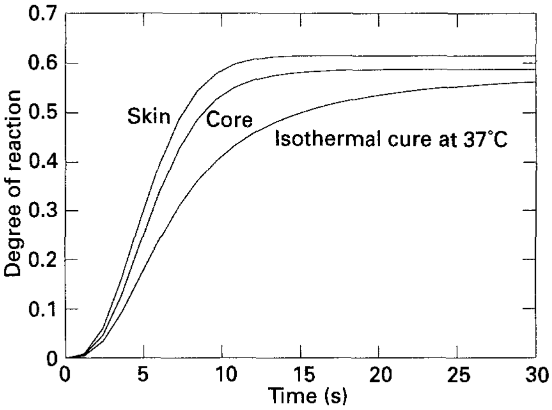

Figure 7 Results of the numerical simulation of the cure conditions occurring during an application of the studied dental composite to the restoration of an enamel cavity (thickness 1.5 mm, $T_0 = 37\,^\circ\mathrm{C}$) : degree of reaction versus cure time on the external surface (skin) and at the centre (core) of the composite.

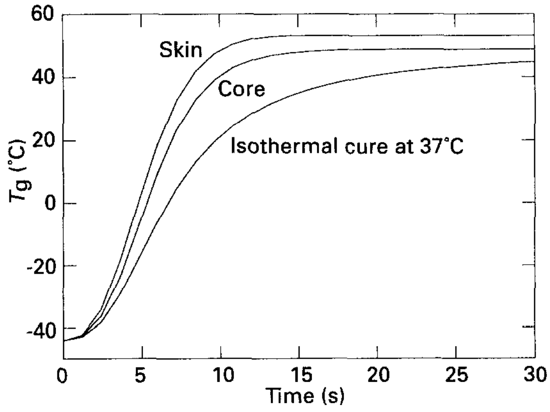

Figure 8 Results of the numerical simulation of the cure conditions occurring during an application of the studied dental composite to the restoration of an enamel cavity (thickness 1.5 mm, $T_0 = 37\,^\circ\mathrm{C}$) : glass transition temperature versus cure time on the external surface (skin) and at the centre (core) of the composite.

Moreover, it must be noted that the simulation accounts only for the heat exchanged across the thickness of the composite and hence can be applied only if the restoration thickness is small compared with the other two dimensions (Fig. 1). If this condition is not verified, the heat exchanged in the other two directions may not be neglected and lower α and T_g values are developed across the restoration thickness. If the restoration shape does not correspond to the flat laminate geometry reported in Fig. 1, the parameter that determines isothermal or non-isothermal cure conditions for a given reactive system is the aspect ratio, A_r, defined as the ratio between the volume, V, and the skin area, S, of the restoration

$$A_r = V/S \qquad (17)$$

Decreasing A_r the heat is more easily dissipated and isothermal conditions are approached.

The results obtained suggest that the development of a material characterized by adequate final values of T_g and α can be obtained photopolymerizing thick (or bulk) parts. Nevertheless, as mentioned above, a decrease in the rate of reaction occurs through the specimen thickness, as a consequence of the light absorption, mainly due to fillers and pigments. Optimal polymerization conditions can be obtained using an appropriate restoration thickness (or aspect ratio) as a result of two competing effects:

1. Increasing h (or A_r); the temperature grows in the material during cure, enhancing the rate of reaction and the final values of α and T_g.
2. On the other hand an increase of h (or A_r) corresponds to a decrease in the rate of reaction through the restoration thickness, possibly leading to uncured zones.

It can be stated that the achievement of a temperature increase in the material during photopolymerization is mainly responsible of the high final values of α and T_g. However, these cure conditions cannot be easily obtained and controlled during the application in a restoration of these light-activated dental composites, and strong differences in terms of mechanical properties and environmental resistance between restorations characterized by different shapes or positions in the oral cavity are expected.

4. Conclusions

In order to predict the temperature and the degree of reaction during photopolymerization of a dental composite, the non-isothermal cure behaviour was described using a heat transfer model coupled with a reaction kinetic expression. The temperature and the degree of reaction profiles inside the composite were computed as a function of the cure time, taking into account the system geometry, the thermal diffusivity of the composite, and the resin reaction rate. Experimentally measured glass transition temperatures were used for the evaluation of an extinction coefficient capable of accounting for the effects of the light absorption through the thickness on the polymerization kinetics. The application of the model to the simulation of the cure process during application of the material in a restoration was presented. The results indicated that a temperature increase in the restoration is responsible for final T_g and α values higher than in an isothermal cure. Adequate values of T_g and α were obtained only if non-isothermal conditions were achieved. The occurrence of non-isothermal polymerization conditions depends on processing parameters that cannot be controlled during normal photopolymerization operations in the oral cavity. For these reasons, restorations characterized by different shapes or positions in the oral cavity may present absolutely different mechanical properties and environmental resistance.

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