JOURNAL OF MATERIALS SCIENCE: MATERIALS IN MEDICINE 6 (1995) 155–160

Cure behaviour of visible light activated dental composites

Part I Isothermal kinetics

A. MAFFEZZOLI
Department of Materials Science, University of Lecce, Via per Arnesano, 73100, Lecce, Italy
R. TERZI
National Center for Research and Development of Materials, SS 7, Km 714, 72100, Brindisi, Italy
L. NICOLAIS
Department of Materials and Production Engineering, University of Naples Federico II, P. Tecchio, 80125, Napoli, Italy

During curing of multifunctional methacrylate-based composites for dental restorations, strong structural changes, significantly affecting the final properties of the materials, are observed. In fact, the polymerization of thermoset matrices involves the transformation of a viscous liquid in a glassy network. The final glass transition temperature of the composite matrix may be considered a relevant parameter for the durability of a restoration. In this study, the complex cure behaviour of a commercial dental composite, activated by visible-light, is analysed by differential scanning calorimetry (DSC). The maximum degree of reaction of the crosslinked resin and the characteristic glass transition temperature are quantitatively related to the cure temperature. Furthermore, a kinetic model, accounting also for the diffusion control effects associated with vitrification, is presented. Finally, the cure behaviour expected during practical application of these materials in the oral cavity for dental restorations, is discussed.

1. Introduction

The attention devoted to the photopolymerization of multifunctional methacrylates-based composites for dental restorations has markedly increased in the last 15 years as a consequence of their advantages such as the short application time and the aesthetic performances. However, many variables may affect the final properties of these materials. Incomplete polymerization occurring in normal operative conditions determines high levels of unreacted double bonds [1–6]. The adverse effect of unreacted methacrylate groups on the mechanical properties and on the environmental resistance of dental composites is widely recognized [5, 7]. Moreover the existence of reactive double bonds may affect the biocompatibility of the resin with the oral tissue [3]. It must be noted that incomplete polymerization of the composite matrix may lead to a final glass transition temperature lower than the temperatures typically reached in the oral cavity. In these conditions, a restoration, exposed to thermal cycles going through a thermal transition, undergoes strong volume changes and structural relaxation phenomena that may significantly affect the durability of the dental restorations.

Most of the available literature presents the correlation between the degree of reaction of the resin and the final properties of the composite, but only a little attention has been dedicated to a better understanding of the kinetic behaviour [8–12] and of the complex structural changes associated with processing of these thermoset-based composites. In fact, the formation of a three-dimensional glassy network from a viscous liquid, occurring during cure of multifunctional methacrylate-based dental composites, may strongly affect the final properties of the restoration.

Differential scanning calorimetry (DSC), already applied in the past to photopolymerization [10–14], has the advantage that the rate of the reaction can be measured directly, assuming that the heat produced by polymerization is proportional to the number of monomer units reacted. DSC has previously been applied to dental composites mainly for the determination of heat of polymerization [9, 15, 16]; its potential for the determination of the kinetic behaviour is not yet fully exploited.

In this study the general cure behaviour of a visible-light-activated dental composites is studied by DSC. This technique was used for the calculation of the degree of reaction of the composite matrix as a function of the cure time in isothermal conditions. The characteristic glass transition temperature (T_g) measured by DSC was correlated with the maximum degree of reaction obtained at different isothermal cure temperatures. Furthermore, DSC data were used for

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the quantitative determination of the rates of photopolymerization at different temperatures, and a phenomenological kinetic model was presented. Finally, the cure behaviour expected during the practical application of these materials in the oral cavity for dental restorations, is discussed.

2. General cure behaviour of thermosets

The mechanisms of reaction involved during chain polymerization, thermally or photochemically activated, are well known [8, 9, 17]. A series of complex independent reactions occur, involving free radicals, monomers and long-chain molecules. Furthermore, during the photopolymerization of dental composites dramatic rheological changes of the matrix, that may strongly influence the final properties and the quality of the composite, are observed. The polymerization of a thermoset polymer generally involves the transformation of a fluid resin into a rubber (gelation), and then into a solid glass (vitrification), as a result of the chemical reactions between multifunctional active groups present in the system which develop a progressively denser polymeric network [18–21]. The cure behaviour of thermoset matrices is strongly dependent on these physical property changes, characterizing the different stages of the curing process. Thermosetting reactions are not only associated with significant variations of the material viscosity but are also coupled with strong heat generation due to the exothermic nature of the polymerization reaction.

The growth and branching of the polymeric chains are due to intramolecular reactions that initially occur in the liquid state until a critical degree of branching is reached and an infinite insoluble network is formed. During gelification, occurring in chain polymerization at about 10–15% conversion, the abrupt increase of the viscosity does not affect reaction kinetics. On the other hand, the transition from a rubbery state to a glassy state may strongly affect the polymerization kinetic leading to a heat in the reaction. In fact, the glass transition temperature, continuously increasing during cure, may approach the isothermal cure temperature, greatly reducing the molecular mobility. In these conditions, the reaction becomes diffusion controlled, and the termination step of the polymerization is governed by this strong reduction in the molecular mobility determined by vitrification.

3. Experimental procedure

The material studied is a commercial dental composite, Pekalux (universal shade), activated by visible light. The composition of the material, as indicated by the supplier (Bayer), is given in Table I. The cure of the resin was carried out using a dental photopolymerization source (DEI Clever Lamp) consisting of a halogen lamp equipped with a system of optical filters and lenses that ensure emission only in the blue region, strongly reducing the radiative heat flow. The light source was provided with a light guide characterized by a diameter of 8 mm.

TABLE I Composition of the studied dental composite

Constituent	Vol %
Multifunctional methacrylic acid esthers	36.6
Spherical polymer filled with silica	35.3
Silica	23.6
Glass ceramics	3.9
Additives	0.6

The calorimetric analysis was carried out with a differential scanning calorimeter (DSC), Mettler DSC 30, operating with a constant air flow of 100 cm^3 min. In order to allow irradiation of the sample in the furnace, the light guide of the lamp was fitted into an appropriate hole on the furnace cover. The irradiation distance was 6 mm and the irradiation time was set to 30 s. In order to obtain true isothermal conditions, the experiments were performed at different temperatures on open pans containing 4–6 mg of composite corresponding to a thickness of 0.15–0.20 mm. Since the dental composite is activated by visible light, the preparation of the samples was made in dark conditions.

4. Results and discussion

4.1. Kinetic behaviour

A typical DSC thermogram obtained at 40 °C with five light exposures is reported in Fig. 1. The first peak, obtained on irradiation of the reactive resin, takes into account the exothermic effects due to both the cure reaction and the radiative heat generated by the lamp. Light exposures repeated on the same sample (Fig. 1) are associated with smaller heat outputs exclusively due to the contribution of the radiative heat flow of the lamp. The very similar four peak areas measured in this case indicate that no residual reactivity can be obtained after the first light exposure.

In accordance with the procedure suggested by Vaidyanathan [15, 16], the isothermal heat of cure of the resin (Q_{is}) is determined as the difference between the heat associated with the first peek (Q_1) and an average of the heats associated with the remaining peaks (Q_i)

$$Q_{\mathrm{is}} = Q_1 - (1/4) \sum_{i=2}^{5} Q_i \qquad (1)$$

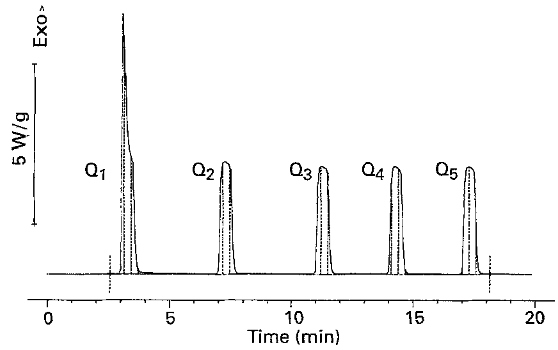

Figure 1 Isothermal DSC thermogram obtained during photopolymerization at 40 °C using five light exposures.

The heat flow due to the polymerization reaction in an isothermal experiment $(dQ/dt)_{is}$ can be evaluated from DSC signal $(dQ/dt)_i$ applying a similar subtraction procedure

$$(dQ/dt)_{is} = (dQ/dt)_1 - (1/4)\sum_{i=2}^{5} Q_i \qquad (2)$$

The thermogram of Fig. 2 (curve A) is obtained by heating a sample at 10 °C/min immediately after an isothermal cure at 40 °C. A typical residual reactivity peak, located at a temperature of 10–15 °C higher than the cure temperature, is observed, indicating that the material is not fully cured. As reported by Kloosterboer [10] free radicals, trapped in the glassy network, may still be present after isothermal photopolymerization of these systems. Therefore, as shown in Fig. 2 (curve A), the reaction may restart in conditions of enhanced molecular mobility by simply heating the sample to a temperature higher than the T_g developed during the isothermal cure. Since the rate of reaction is very high compared with the structural volume relaxation occurring during the glass transition, vitrification is not able to instantaneously arrest the reaction, as observed for other thermosets [19, 20], and the T_g may reach a temperature of 10–15 °C higher than the cure temperature.

A thermogram obtained by heating a sample at 10 °C/min photocured at 40 °C and stored in air at room temperature for one week in dark conditions is also shown in Fig. 2 (curve B). In this case, since radicals disappeared during the sample storage [11], the residual reactivity peak cannot be detected, while a T_g at a temperature of 10–15 °C higher than the cure temperature is clearly shown. It must be noted that the glass transition signal is observed at about the same temperature of the onset of the residual reactivity peak shown in curve A of Fig. 2, indicating that no dark reaction capable of an increase in the T_g of the matrix, occurs.

The DSC scan of Fig. 3 (curve A), performed at 10 °C/min on a photopolymerized sample postcured at 150 °C, shows a broad glass transition temperature in the range 96–119 °C. In this experiment, full development of the residual reactivity leads to a T_g that may be considered the maximum glass transition temperature, T_{gmax}, of the studied material. The glass transition temperature of the unreacted resin, $T_{go} = -51$ °C, is evaluated from the DSC thermogram reported in Fig. 3 (curve B).

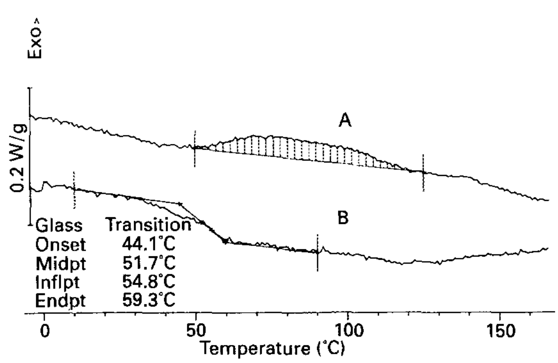

Figure 2 DSC thermograms obtained on samples cured at 40 °C (heating rate 10 °C/min). Curve A is obtained by heating a sample immediately after photopolymerization and curve B for a sample stored for one week after photopolymerization.

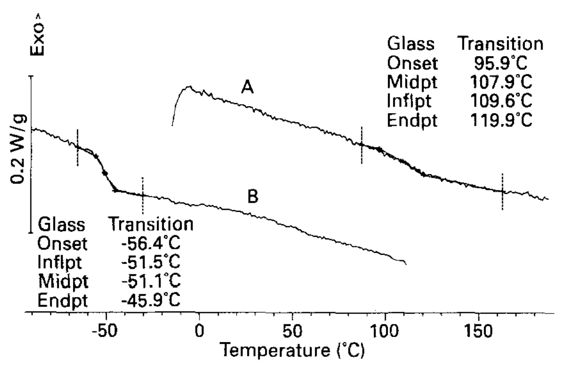

Figure 3 DSC thermograms showing the glass transition temperature of the fully cured resin (curve A) and of the unreacted resin (curve B).

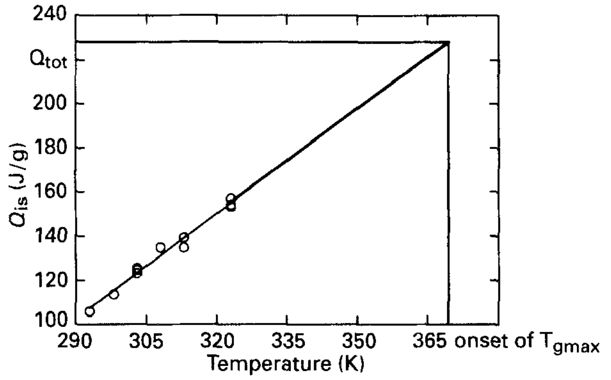

Figure 4 Temperature dependence of the isothermal heat of polymerization (experimental data and model predictions).

The isothermal heat of reaction (Q_{is}), measured using Equation 1, is a function of the cure temperature, as shown in Fig. 4. This result, also reported in the literature [15–21], is expected in accordance with the cure mechanism presented above. In this case a linear temperature dependence of Q_{is}, reported also for other thermosets [19, 20], is proposed

$$Q_{is} = a + bT \qquad (3)$$

A good agreement between Equation 3 predictions and experimental data is observed in Fig. 4, using the parameters listed in Table II. Moreover, the maximum heat of reaction (Q_{tot}) may be evaluated from Fig. 4. Q_{tot}, a relevant parameter for kinetic analysis, is measured, for thermally activated systems, in a DSC experiment imposing a constant heating rate up to the maximum glass transition temperature [18–20]. For a photochemically activated system this kind of procedure cannot easily be applied and the direct measurement of Q_{tot} in an isothermal experiment cannot be obtained as a consequence of the very high rates of reaction observed at high temperatures. Therefore an extrapolated value of $Q_{tot} = 228.5$ J/g may be calculated from Equation 3 at 96 °C, corresponding to the onset temperature of the glass transition of the fully cured material (Fig. 3, curve A). This extrapolated temperature, is chosen taking into account that the

TABLE II Parameters of the kinetic model

Parameter	Value
a (J g^{-1})	− 130.8
b (J g^{-1} K^{-1})	0.5804
m	1.60
n	0.64
K_o(s^{-1})	1.682
E_a(kJ mol^{-1})	1.347
c	− 1.564
d(K^{-1})	0.006939
p(K)	229.2
q (K)	157.6
T_{go}(K)	222
T_{gmax}(K)	381

glass transition temperature developed during isothermal cure is 10–15 °C higher than the cure temperature and that $T_{gmax} = 108$ °C (Fig. 3, curve A).

4.2. Kinetic model

Considerable attention has been devoted to the kinetic characterization of thermosetting polymers using differential scanning calorimetry (DSC) [12, 18–20, 22, 23]. DSC measurements may be used for determination of the advancement of the cure by assuming that the heat evolved during the polymerization reaction is proportional to the overall extent of the reaction given by the fraction of reactive groups consumed. Following this approach the degree of reaction, α, is defined as

$$\alpha = Q_{is}(t)/Q_{tot} \qquad (4)$$

where $Q_{is}(t)$ is the partial heat of reaction developed during a DSC experiment. The reaction rate, dα/dt, is thus given by

$$d\alpha/dt = (1/Q_{tot})(dQ/dt)_{is} \qquad (5)$$

where $Q_{is}(t)$ and $(dQ/dt)_{is}$ are measured following the subtraction procedure indicated in Equation 1.

The chain polymerization reactions of thermosetting matrices involves very complex reactions and several complex models have been reported for methacrylates polymerization [9, 24, 25]. However, a simple pseudo-autocatalytic expression, proposed for polyester resins in a previous paper [19], can be adopted to describe the general behaviour as an overall kinetic process

$$d\alpha/dt = K\alpha^m(\alpha_m - \alpha)^n \qquad (6)$$

where K is a temperature-dependent rate constant and m and n are fitting parameters not dependent on temperature. The temperature dependence is normally considered through the rate constant K given by an Arrhenius-type equation

$$K = K_0 \exp(E_a/RT) \qquad (7)$$

K_0 is the pre-exponential factor, R is the gas constant E_a the activation energy and T the absolute temperature.

In Equation 6 α_m represents the maximum degree of reaction obtained in isothermal DSC cure experiments

$$\alpha_m = Q_{is}/Q_{tot} \qquad (8)$$

The temperature dependence of α_m is shown in Fig. 5. This behaviour is similar to the correlation between the glass transition temperature and the degree of reaction in thermoset polymerization [26]. In this case, however, a linear temperature dependence, reported also for other thermosets [19, 20], is proposed:

$$\alpha_m = C + dT \qquad \text{for } T < T_{gmax} \qquad (9)$$

When T approaches the T_g of the fully cured system (T_{gmax}), α_m becomes close to 1. The fitting parameters c and d, reported in Table II, are related to a and b of Equation 3 by the maximum heat of reaction Q_{tot}. The very low values of α_m between 30 °C and 40 °C are consistent with the results obtained by infrared spectroscopy reported in the literature for visible-light-cured materials [1–6, 15].

The full model given by Equations 6, 7 and 9 clearly predicts the expected kinetic behaviour: the rate of reaction during an isothermal process goes to zero when the degree of reaction equals α_m.

The values of the kinetic parameters of the general model, evaluated by regression analysis, are listed in Table II. The ability of the model to represent the overall kinetic behaviour has been tested by comparing the theoretical predictions given by Equations 6, 7 and 9, with the experimental data in Figs 6–8. The good agreement observed in these figures indicates that the general cure behaviour reported above is correct and that a simple model can be used to represent a complex kinetic behaviour.

Finally, a correlation between the glass transition temperature, as measured in Fig. 2, and the maximum degree of reaction can be stated. In fact, both T_g and α_m depend on the isothermal cure temperature. In Fig. 9 a linear relationship between T_g and α_m is clearly depicted

$$T_g = p + q\alpha_m \qquad (10)$$

where p and q are two fitting parameters (Table II). The dashed line in Fig. 8 is obtained from the following expression:

$$T_g = T_{go} + (T_{gmax} - T_{go})\alpha_m \qquad (11)$$

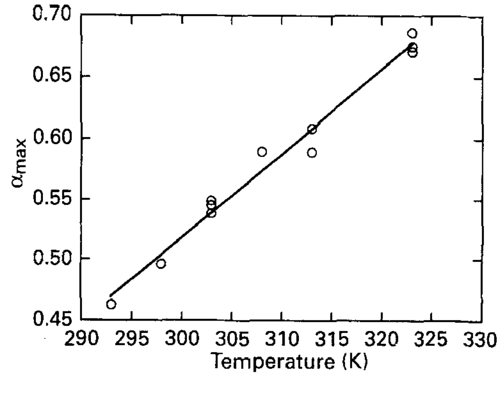

Figure 5 Maximum degree of reaction obtained from isothermal DSC photopolymerization experiments (experimental data (○) and model predictions (—)).

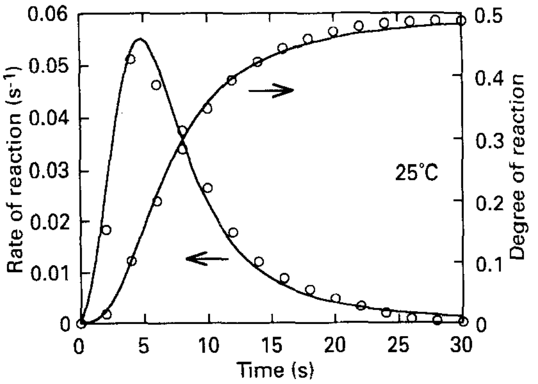

Figure 6 Comparison between kinetic model predictions and experimental DSC data at 25 °C.

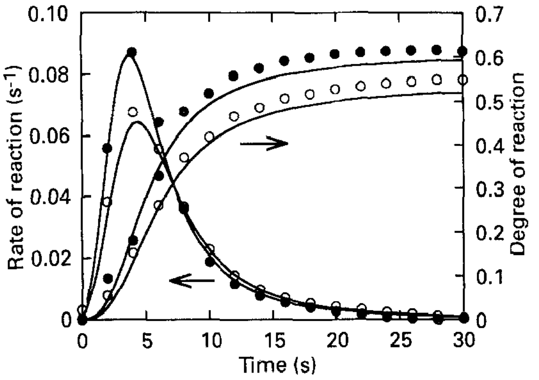

Figure 7 Comparison between kinetic model predictions and experimental DSC data at 30 °C (○) and 40 °C (●).

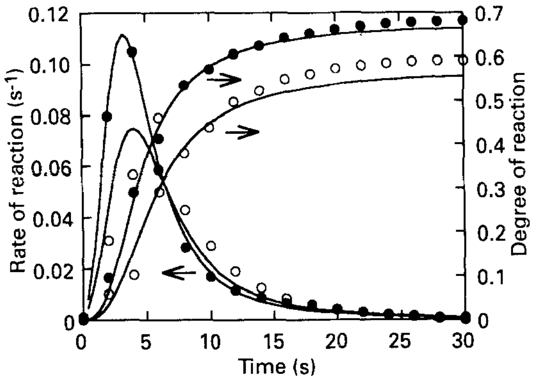

Figure 8 Comparison between kinetic model predictions and experimental DSC data at 35 °C (○) and 50 °C (●).

As shown in Fig. 9, the predictions of Equations 10 and 11 are very close. However, the parameters of Equation 11, given by T_{go} and T_{gmax}, can be easily evaluated by simply performing two DSC scans, one on the unreacted resin and one on a fully cured sample.

From a practical point view these results indicate that a fully cured material cannot be obtained during application of these materials in dental cavities in isothermal conditions. In fact, during cure at about 35 °C, a maximum degree of reaction of 0.55 is obtained (Fig. 5) and a corresponding glass transition temperature of about 48 °C is developed (Fig. 9).

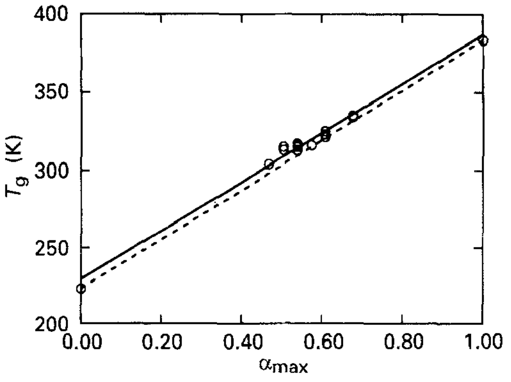

Figure 9 Glass transition temperature as a function of the degree of reaction (experimental data (○) and model predictions: —— Equation 10; ---- Equation 11).

Therefore the isothermal cure of the studied material leads to low values of T_g for the resin that may adversely affect the physical and mechanical properties and the environmental resistance of the dental composite. Moreover, the glass transition temperature of the restorative material must be higher than the maximum temperature that can be reached in the oral cavity, in order to prevent failures of the restorations due to thermal fatigue. These considerations apparently are in contrast with the good practical results displayed by the studied composite, and in general by all photopolymerizable dental composites. This can be explained taking into account that non-isothermal cure conditions may occur during the application of these restorative materials. In fact, during this analysis, in order to obtain true isothermal conditions, the experiments were performed on samples of thickness about 0.2 mm; during practical applications of these composites in dental restorations, material layers of 1–2 mm are usually applied. For these thicknesses, due to the strong exothermic nature of the polymerization reaction and to the very high reaction rates, adiabatic conditions may be approached and a sensible temperature increase may determine a higher final degree of reaction and T_g. These non-isothermal cure conditions, eventually occurring, are analysed in the second part of this work. In fact, the kinetic model predicting the amount of heat given off during the reaction can be integrated in an energy balance in order to calculate the temperature and the degree of reaction distributions inside a dental composite during photopolymerization in all process conditions of practical significance.

5. Conclusions

In this paper the general cure behaviour of a commercial dental composite activated by visible light was analysed using differential scanning calorimetry. This technique was applied to the determination of the degree of reaction and of the characteristic glass transition temperature of the composite matrix as a function of the time at different isothermal cure temperatures. Furthermore, the proposed phenomenological kinetic model, accounting also for the diffusion control effects associated with vitrification, compared well with experimental data. The relatively low T_g values observed for isothermally photocured samples suggested that non-isothermal conditions must also be considered. The results obtained for the commercial composite studied may be considered representative of the general kinetic behaviour of multifunctional methacrylates-based composite resins.

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Received 15 November 1993
and accepted 7 February 1994