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## Thermal analysis of visible-light-activated dental composites<sup>☆</sup>

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### Abstract

In this study the complex cure behaviour of a commercial dental composite, activated by visible light, is analysed by differential scanning calorimetry (DSC) and thermo-mechanical analysis (TMA). Flat plane samples must be used in both techniques in order to prevent the temperature increase due to the exothermic nature of the curing reaction and to avoid the effect of light absorption through the thickness. The isothermal cure of the studied material leads to low values of the final degree of reaction and glass transition temperature that may adversely affect the physical and mechanical properties and the environmental resistance of the composite. The linear shrinkage measured by TMA is a function of the aspect ratio of the sample as a consequence of the adhesion between the sample and the glass plates. True linear shrinkage can be measured only if a low-friction coupling agent between the sample and plates is employed. Isothermal TMA and DSC data, collected at the same temperatures, are processed in order to obtain the degree and the rate of reaction. The comparison of the kinetic behaviour resulting from DSC and TMA indicates that volume relaxation effects due to the viscoelastic nature of the composite matrix may be responsible for the delayed response in TMA. The dark reaction detected by TMA after interruption of light exposure suggests a higher sensitivity of this technique at low rates of reaction compared with DSC.

**Keywords:** Dental composite; DSC; TA; TMA; Visible-light activation

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## 1. Introduction

During curing of multifunctional methacrylate-based composites for dental restorations, strong structural changes, significantly affecting the final properties of the materials, are observed. The polymerisation 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. Incomplete polymerisation occurring in normal operative conditions determines high levels of unreacted double bonds [1–6] that may adversely affect the mechanical properties and the environmental resistance of dental composites [5, 7]. Moreover an incomplete polymerisation of the matrix determines a low final glass transition temperature [8, 9]. A significant polymerisation shrinkage, associated with degree of reaction and temperature gradients through a restoration thickness, is responsible for the build up of residual stresses during cure [10–12], significantly limiting the durability of the restoration.

Differential scanning calorimetry (DSC), already applied in the past to the study of photopolymerisation [13–21], allows the direct determination of the rate of reaction assuming that the heat produced by the polymerisation is proportional to the number of monomer units reacted. Therefore, DSC can be applied to the development of kinetic models; this represents a fundamental step for the optimisation of conditions during application of these materials in the oral cavity [8, 9].

Different types of dilatometers have been applied to the measurements of the polymerisation shrinkage, mainly for comparison of different commercial composites [10–12]. However, the potential of thermo-mechanical analysis (TMA) for the cure monitoring has not been fully exploited. In particular, dental composites, presenting an initial high viscosity and good dimensional stability, are suitable systems for polymerisation shrinkage measurements. Furthermore the shrinkage kinetic, coupled with the measurements of the mechanical properties during cure, represents an input for theoretical calculations of the residual stresses in a restoration.

In this study, the complex cure behaviour of a commercial dental composite, activated by visible light, is analysed by calorimetric and thermo-mechanical analysis. Flat plane samples are used in both techniques in order to prevent the temperature increase due to the exothermic nature of the curing reaction and to limit the effects of light absorption through the sample thickness. DSC and TMA measurements are applied to the prediction of an incomplete polymerisation and the results obtained by these techniques are compared. Isothermal TMA and DSC data, collected at the same temperatures, are processed in order to obtain the degree and the rate of reaction. Finally, a comparison of the isothermal kinetic behaviour resulting from DSC and TMA is presented.

## 2. Experimental

The material studied is a commercial dental composite, Pekalux (universal shade), activated by visible light. The composition of the material is given in Table 1 according to the supplier (Bayer), although the nature of the composite matrix is not explicitly

Table 1  
Composition of the dental composite studied (Pekalux)

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

indicated. However, as reported in the literature [1, 5], most of the dental composite matrices contain an aromatic methacrylate, bisphenol A-diglycidyl-methacrylate (Bis-GMA), and low-viscosity aliphatic methacrylates such as Triethylen-glycol-dimethacrylate (TEGDMA) and ethylen-glycol-dimethacrylate (EGDMA).

The cure of the resin was carried out using a dental photopolymerisation source (DEI Clever Lamp) consisting of halogen lamp equipped with a system of optical filters and lenses that emit only in the blue region, strongly reducing the radiative heat flow. The light source was provided with a light guide characterised by a diameter of 8 mm. 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 0.2–0.3 mm.

The calorimetric analysis was carried out with a differential scanning calorimeter (DSC), the Mettler DSC 30, operating in air. In order to allow the irradiation of the sample in the furnace, the light guide of the lamp was fitted into a hole on the furnace cover situated over the test sample, as shown in Fig. 1.

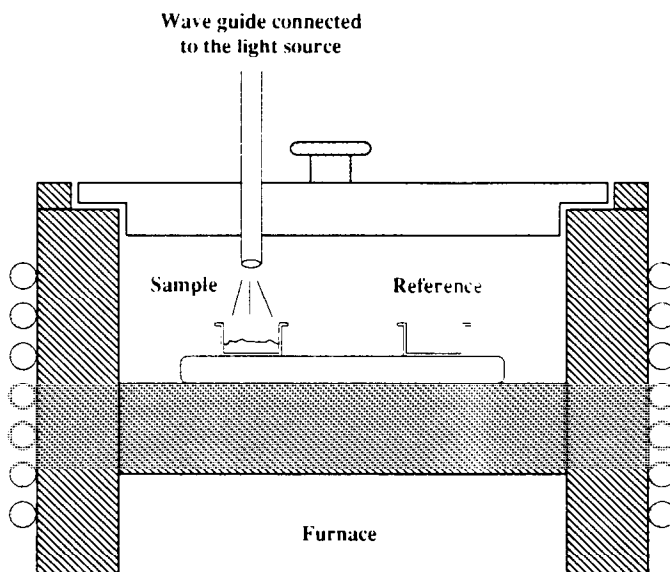


Fig. 1. Sketch of the DSC apparatus as modified for photocalorimetric measurements.

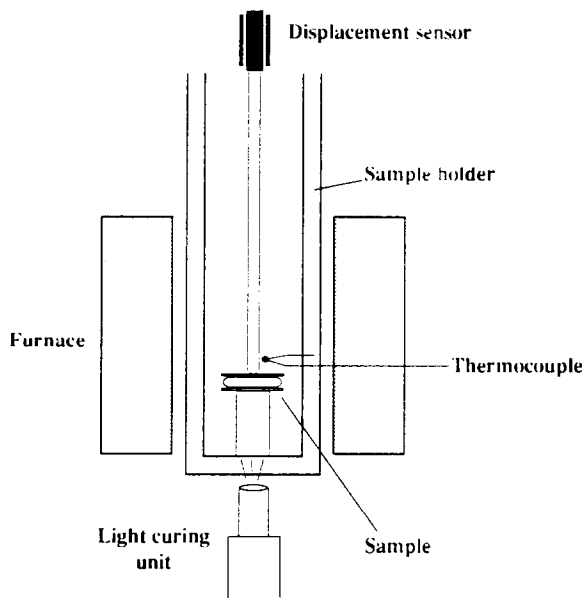


Fig. 2. Sketch of the TMA apparatus as modified for photodilatometric measurements.

The thermo-mechanical analysis was carried out with a Netzsch TMA 402 operating in air. In order to irradiate the sample the standard furnace was removed and a heating device, connected with a thermostatic bath, was fitted around the probe and the sample, as shown in Fig. 2. TMA experiments were performed using samples as thin as those used for the DSC tests. The composite film was contained between two glass covers and the probe, loaded with 5 g, was placed in contact with the upper glass plate while the irradiation was performed on the opposite side (Fig. 2). As reported by de Gee et al. [12], adhesion between the sample and the glass covers must be prevented since it may lead to overestimated values of shrinkage. For this reason, a Teflon lubricating spray was applied to both glass plates in contact with the composite sample.

For both techniques, the measured signal (heat flow or linear contraction) was stable before an irradiation set of 30 s. Because the dental composite is activated by visible light, the samples were kept in dark conditions during preparation and during the time before activation light exposure.

### 3. Results and discussion

#### 3.1. Calorimetric analysis

A typical DSC thermogram obtained at 40°C with five light exposures is reported in Fig. 3. The first peak, obtained on irradiating the uncured material, is given by the sum

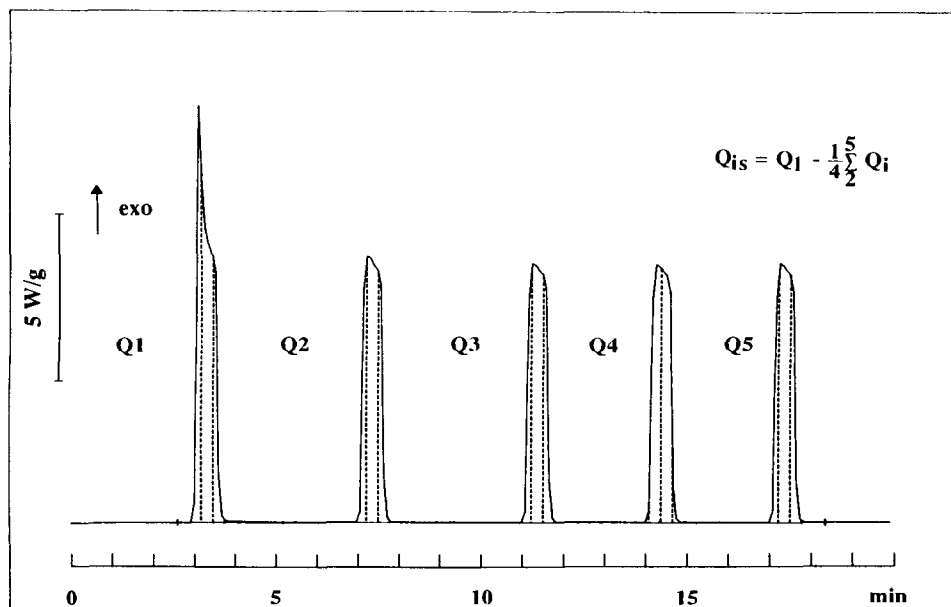


Fig. 3. Isothermal DSC thermogram obtained during photopolymerisation at 40°C using five light exposures.

of two contributions: the exothermic effects due to the cure reaction and the radiative heat flow from the lamp. Repetition of the light exposure another four times on the same sample produces very similar peak areas, indicating that no further reaction occurred; residual reactivity would result in different areas, at least between the second and the last three peaks. Therefore, the heat measured as an average of the last four peak areas is attributed to the radiative heat output of the lamp and is used for the analysis of the DSC data. According to the procedure suggested by Vaidyanathan and Vaidyanathan [21], the isothermal heat of cure of the resin  $Q_{is}$  is calculated as the difference between the heat associated with the first peak  $Q_1$  and an average of the heats associated with the last four peaks  $Q_i$

$$Q_{is} = Q_1 - \frac{1}{4} \sum_{i=2}^5 Q_i \quad (1)$$

The heat flow due to the polymerisation reaction in an isothermal experiment,  $(dQ/dt)_{is}$ , can be evaluated from the DSC signal,  $(dQ/dt)_i$ , of Fig. 3, applying a similar subtraction procedure

$$(dQ/dt)_{is} = (dQ/dt)_1 - \frac{1}{4} \sum_{i=2}^5 \left( \frac{dQ}{dt} \right)_i \quad (2)$$

The heat flow data reported in Fig. 4, normalised by the sample weight, are obtained by processing the experimental DSC data using Eq. (2). From this figure it is evident

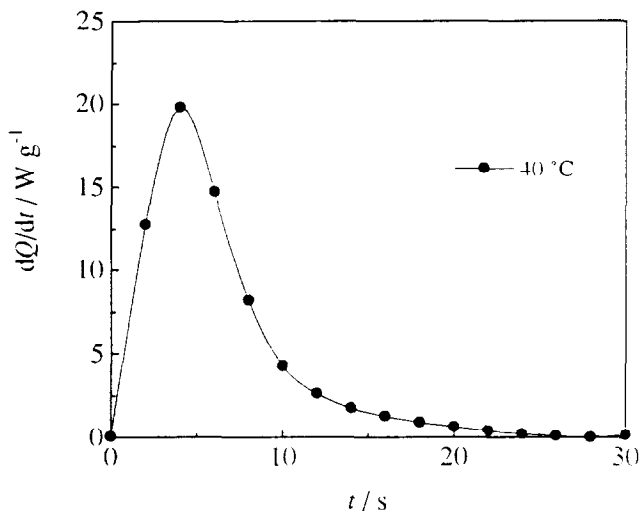


Fig. 4. DSC curve obtained at 40°C from the subtraction procedure of Eq. (2).

that, before interrupting the light exposure after 30 s, the heat flow corresponds to the baseline value at all temperatures.

If the same sample is heated at  $10^{\circ}\text{C min}^{-1}$  immediately after the isothermal cure in the DSC at 40°C (Fig. 3), a typical residual reactivity peak, located at a temperature 10–15°C higher than the cure temperature, is observed, indicating that the material is not fully cured. As reported by Kloosterboer et al. [16], free radicals, trapped in the glassy network, may still be present after isothermal photopolymerisation of these systems. Therefore, as shown in Fig. 5 (curve A), the reaction may restart in conditions of enhanced molecular mobility by simply heating the sample at a temperature higher than the  $T_g$  developed during the isothermal cure. However, vitrification is not able to arrest instantaneously the reaction, as observed for other thermosets [22, 23], and the  $T_g$  may reach a temperature 10–15°C higher than the cure temperature.

A thermogram obtained by heating at  $10^{\circ}\text{C min}^{-1}$  a sample photocured at 40°C and stored in air at room temperature for one week in dark conditions is also shown in Fig. 5 (curve B). In this case, because radicals disappeared during the sample storage [16], the residual reactivity peak cannot be detected, while a  $T_g$  10–20°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. 5, indicating that no dark reaction capable of an increase in the  $T_g$  of the matrix, is detectable by DSC. The measured  $T_g$  values are reported in Table 2 as a function of the cure temperature.

A DSC scan, performed at  $10^{\circ}\text{C min}^{-1}$  on a sample post-cured at 150°C, (Fig. 6, curve A) shows a broad glass transition temperature in the range 96–119°C. In this experiment, the full development of the residual reactivity leads to a  $T_g$  that may be considered the maximum glass transition temperature,  $T_{g\text{max}}$ , of the studied material.

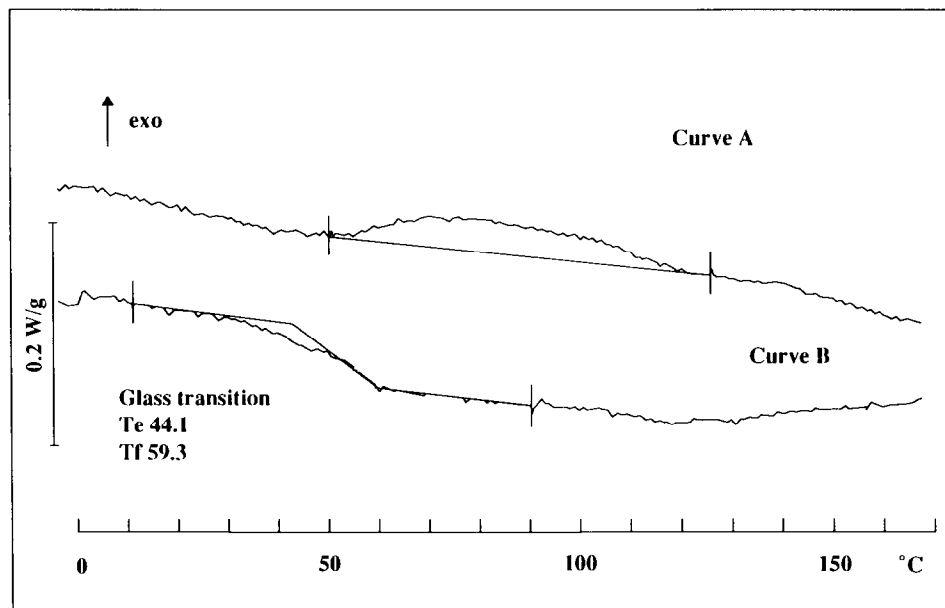


Fig. 5. DSC thermograms obtained on samples cured at 40°C (heating rate, 10°C min<sup>-1</sup>). Curve A is obtained by heating a sample immediately after photopolymerisation and curve B by heating a sample stored for one week after photopolymerisation.

Table 2  
Glass transition temperature and linear shrinkage as a function of the cure temperature

Temperature/°C	$T_g/°C$	$\Delta l_{n30}$	$\Delta l_{n20}$
20	31	0.0203	0.0256
25	40	0.0221	0.0264
30	42	0.0245	0.0303
35	43	0.0284	0.0324
40	52	0.0290	0.0332
50	61	0.0311	0.0369

The glass transition temperature of the unreacted resin,  $T_{g0} = -51^\circ\text{C}$ , is evaluated from the DSC thermogram reported in Fig. 6, curve B.

The isothermal heat of reaction ( $Q_{is}$ ), measured using Eq. (1), is a function of the cure temperature, as shown in Fig. 7. This result, also reported in the literature [21–23], is expected according to the cure mechanism presented above. In this case a linear temperature dependence of  $Q_{is}$ , also reported for other thermosets [22, 23], is proposed

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

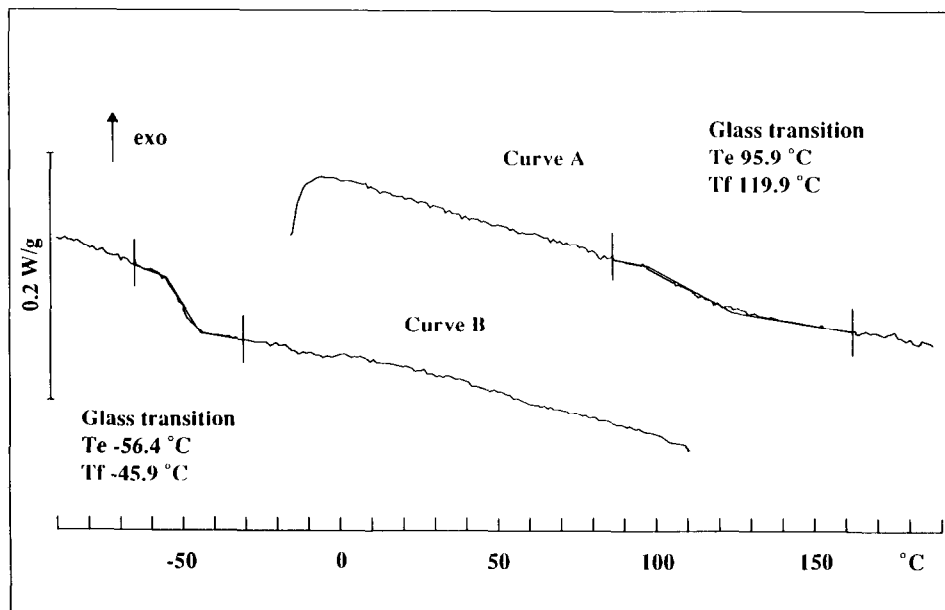


Fig. 6. DSC thermograms showing the glass transition temperature of the fully cured resin (curve A) and of the unreacted resin (curve B).

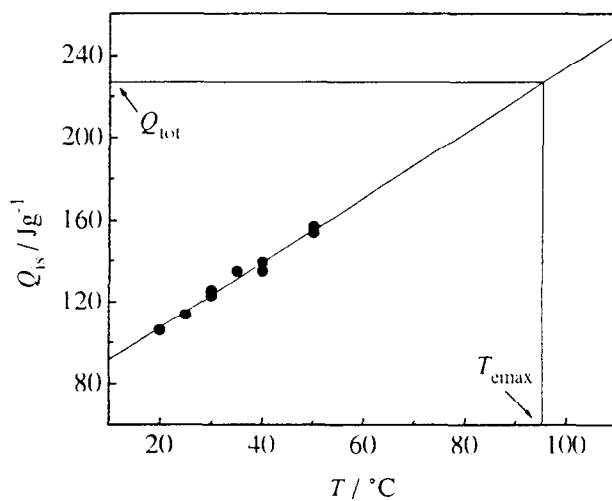


Fig. 7. Temperature dependence of the isothermal heat of polymerisation.



Table 3  
Parameters of Eqs. (3) and (8)

Parameter	Value
$a/\text{J g}^{-1}$ , DSC data	28.45
$b/\text{J g}^{-1} \text{ } ^\circ\text{C}^{-1}$ DSC data	0.5804
$a$ , TMA data ( $\Delta l_{n30}$ )	0.0142
$b/^\circ\text{C}^{-1}$ , TMA data ( $\Delta l_{n30}$ )	0.000356
$a$ , TMA data ( $\Delta l_{n\infty}$ )	0.0172
$b/^\circ\text{C}^{-1}$ , TMA data ( $\Delta l_{n\infty}$ )	0.000407
$c$ , DSC data	0.33
$d/^\circ\text{C}^{-1}$ , DSC data	0.00693
$c$ , TMA data ( $\Delta l_{n30}$ )	0.294
$d/^\circ\text{C}^{-1}$ , TMA data ( $\Delta l_{n30}$ )	0.00736

A good agreement between Eq. (3) predictions, obtained with the parameters listed in Table 3, and the experimental measured heats of cure is observed in Fig. 6. Moreover, the maximum heat of reaction ( $Q_{\text{tot}}$ ) may be evaluated from Fig. 4.  $Q_{\text{tot}}$ , a relevant parameter for kinetic analysis, is normally measured, for commercial thermally activated systems, in a DSC experiment imposing a constant heating rate up to the maximum glass transition temperature [22–24]. For photochemically activated system, this kind of procedure cannot easily be applied and the direct measurement of  $Q_{\text{tot}}$  in an isothermal experiment, at a temperature close to the  $T_{\text{gmax}}$  of the resin, cannot be obtained because of the very high rates of reaction observed at high temperatures. Therefore, an extrapolated value of  $Q_{\text{tot}} = 228.5 \text{ J g}^{-1}$  may be calculated from Eq. (3) at  $96^\circ\text{C}$ , corresponding to the onset temperature of the glass transition of the fully cured material (Fig. 6, curve A). This extrapolated temperature is chosen, taking into account the fact that the glass transition temperature developed during the isothermal cure is  $10\text{--}15^\circ\text{C}$  higher than the cure temperature and that  $T_{\text{gmax}}$  is  $108^\circ\text{C}$  (Fig. 5, curve A).

$Q_{\text{tot}}$  could be calculated theoretically by accounting for the complete reaction of all double bonds in the material. However, it must be noted that unreacted double bonds always remain trapped in the polymeric network formed by thermosetting resins and do not show any residual reactivity peak when heated in the DSC [16, 19]. For this reason it is more reasonable to assume  $Q_{\text{tot}}$  equal to the maximum heat of reaction appropriately measured by DSC [22–24], rather than a theoretical value. The theoretical value of  $Q_{\text{tot}}$  cannot be calculated for commercial resins whose chemical composition and molecular weight are not known.

### 3.2. Thermo-mechanical analysis

The results of a typical TMA experiment at  $40^\circ\text{C}$  are shown in Fig. 8. After a few minutes for stabilisation of the probe displacement, the sample is irradiated and a sudden contraction is observed. While the heat flow measured by DSC reaches the baseline value after 30 s, as shown in Fig. 4, the TMA can detect sample shrinkage even

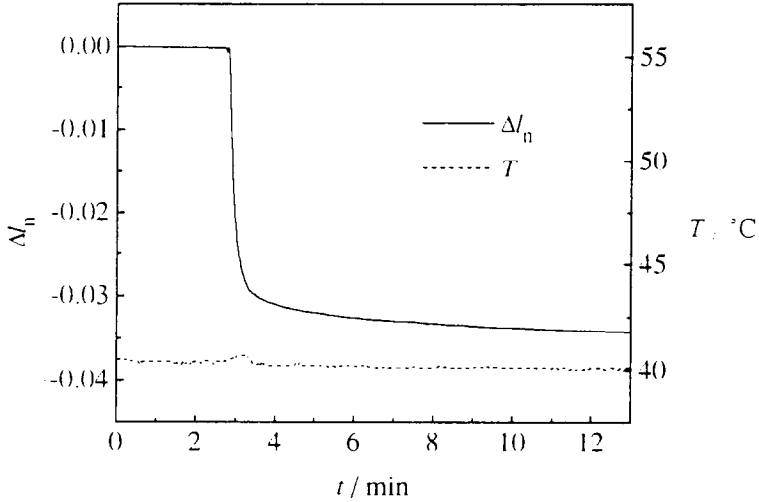


Fig. 8. Results of a TMA experiment obtained during photopolymerisation at 40°C using a single light exposure.

after the interruption of light exposure ( $t > 30$  s). A subsequent light exposure, repeated after the stabilisation of the signal, did not lead to any further shrinkage. These results clearly indicate that TMA presents a higher sensitivity at low rates of reaction than DSC and that no further reaction can be measured after vitrification of the sample.

A normalised sample shrinkage,  $\Delta l_n$ , is calculated as

$$\Delta l_n = \Delta l / L \quad (4)$$

where  $\Delta l$  represents the thickness change and  $L$  the initial thickness of a sample. The values of  $\Delta l_n$  measured after 30 s of irradiation,  $\Delta l_{n30}$ , and the maximum values measured when the signal is completely stable at long times,  $\Delta l_{n\infty}$ , are reported in Table 2. Comparing the data listed in Table 2, it is clear that a significant portion (about 20%) of the reaction occurs in dark conditions ("dark reaction"). Therefore the reaction is not instantaneously arrested by vitrification before the interruption of light exposure, as suggested by DSC data. The lack of any discontinuity corresponding to the interruption of the irradiation can be attributed to a damping effect due to the viscoelastic nature of the composite matrix. Therefore, this viscoelastic response of the material may lead to a smoothed TMA curve corresponding to the light interruption. However, the heat flow measured by DSC is not limited by any mechanical constraint and can be directly related to the rate of reaction. The effect of the thermal conductivity of the sample in DSC experiments may be neglected as reported elsewhere [9]. Moreover, this dark reaction may be responsible for the significant increase in  $T_g$  above the cure temperature, as reported in Table 2.

A plot of  $\Delta l_{n30}$  and  $\Delta l_{n\infty}$  as a function of the cure temperature is reported in Fig. 9. For both quantities, a linear temperature dependence, already observed for  $Q_{is}$ ,

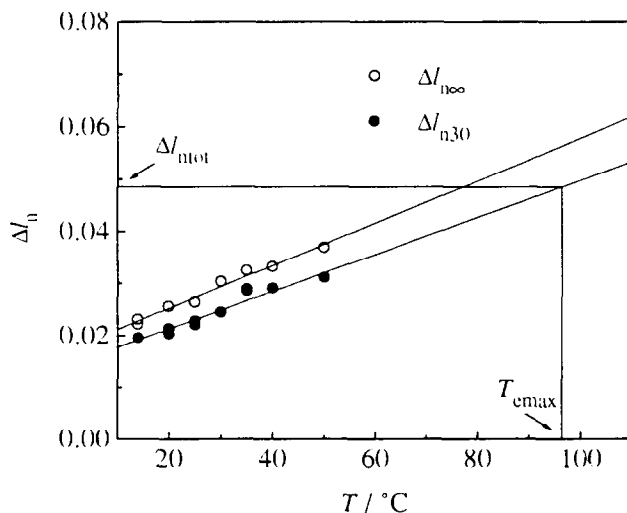


Fig. 9. Temperature dependence of the normalised shrinkage measured after 30 s,  $\Delta l_{n30}$ , and of the maximum observed normalised shrinkage,  $\Delta l_{n\infty}$ .

is clearly shown. The parameters of Eq. (3) rewritten for  $\Delta l_{n30}$  and  $\Delta l_{n\infty}$  are reported in Table 3.

### 3.3. Kinetic behaviour

In order to compare the kinetic behaviour observed using the two different techniques, DSC and TMA data must be used for the quantitative determination of the advancement of the cure. Moreover, since the heat flow measured by DSC is limited to the irradiation time (30 s),  $\Delta l_{n30}$  is taken as a measure of the advancement of the cure obtained from TMA.

DSC measurements may be used for determination of the advancement of the cure by assuming that the heat evolved during the polymerisation reaction is proportional to the overall extent of reaction given by the fraction of reactive groups consumed [22–24]. Following this approach, the degree of reaction  $\alpha$  is defined as

$$\alpha = \frac{1}{Q_{\text{tot}}} \int_0^t \frac{dQ}{dt} dt \quad (5)$$

where  $dQ/dt$  is the heat flow measured during a DSC experiment according to Eq. (2). The reaction rate,  $d\alpha/dt$ , is thus given by

$$\frac{d\alpha}{dt} = \frac{1}{Q_{\text{tot}}} \left( \frac{dQ}{dt} \right) \quad (6)$$

Taking  $Q_{\text{tot}}$  as a reference, it is possible to determine the maximum degree of reaction  $\alpha_{\text{max}}$  reached in an isothermal DSC test

$$\alpha_{\text{max}} = \frac{Q_{\text{is}}}{Q_{\text{tot}}} \quad (7)$$

The temperature dependence of  $\alpha_{\text{max}}$  is shown in Fig. 10. This behaviour recalls the correlation between the glass transition temperature and the degree of reaction in thermoset polymerisation [25]. In this case, however, a linear temperature dependence, reported also for other thermosets [23, 24], is proposed

$$\alpha_{\text{max}} = c + dT \quad \text{for } T < T_{\text{gmax}}; \quad \alpha_{\text{max}} = 1 \quad \text{for } T > T_{\text{gmax}} \quad (8)$$

when  $T$  approaches the  $T_{\text{g}}$  of the fully cured system ( $T_{\text{gmax}}$ ),  $\alpha_{\text{max}} = 1$ . The fitting parameters  $c$  and  $d$ , reported in Table 3, are related to  $a$  and  $b$  of Eq. (3) by the maximum heat of reaction  $Q_{\text{tot}}$ . The very low values of  $\alpha_{\text{max}}$  between 30 and 40°C are consistent with the results obtained by infrared spectroscopy reported in the literature for visible-light-cured materials [1–6].

Following the same approach used for the determination of  $Q_{\text{tot}}$  by isothermal DSC experiments, an extrapolation procedure is also applied to the evaluation of the maximum shrinkage  $\Delta l_{\text{n30tot}}$ . As shown in Fig. 9, a value of  $\Delta l_{\text{n30tot}} = 0.0475$  is calculated from linear extrapolation at the same temperature (96°C) as used for the determination of  $Q_{\text{tot}}$ .

TMA measurements may be applied to the determination of the advancement of the cure by assuming that the normalised linear shrinkage (Eq. (4)) is proportional to the

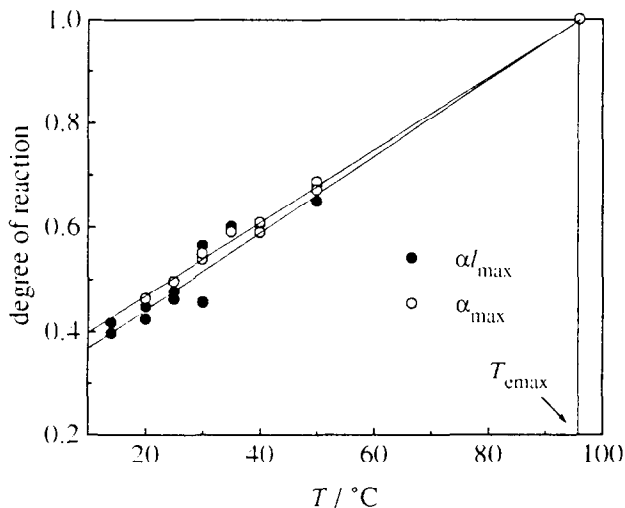


Fig. 10. Comparison of the maximum degree of reaction obtained from isothermal DSC and TMA photopolymerisation experiments.

overall extent of reaction given by the fraction of reactive groups consumed. Following this approach, the degree of reaction obtained from TMA,  $\alpha_1$ , is defined as

$$\alpha_1 = \frac{\Delta l_n(t)}{\Delta l_{n\max}} \quad (9)$$

The reaction rate obtained by TMA,  $d\alpha_1/dt$ , is thus given by

$$\frac{d\alpha_1}{dt} = \frac{1}{\Delta l_{n\max}} \frac{d[\Delta l_n(t)]}{dt} \quad (10)$$

Taking  $\Delta l_{n30\text{tot}}$  as a reference, it is possible to determine the maximum degree of reaction,  $\alpha_{1\max}$ , reached in an isothermal TMA test

$$\alpha_{1\max} = \Delta l_{n30} / \Delta l_{n30\text{tot}} \quad (11)$$

The linear temperature dependence of  $\alpha_{\max}$  is shown in Fig. 10 and the parameters of Eq. (8), rewritten for  $\alpha_{1\max}$  data, are reported in Table 3. Although a further increase in the shrinkage is observed by TMA after 30 s, the use of  $\Delta l_{n30\text{tot}}$  for a comparison of DSC and TMA results can be justified, bearing in mind that only the portion of the reaction occurring during light exposure is detected by DSC. Then, since the same extrapolation procedure is used for both techniques, any eventual error should not affect the comparison of DSC and TMA measurements in terms of rate and degree of reaction.

The values of  $\alpha_{\max}$  and  $\alpha_{1\max}$ , representative of the advancement of the reaction during light exposure, are very close, as shown by the plot of Fig. 10 and by the parameters of Eq. (8) listed in Table 3. At this point, a full comparison of the kinetic behaviour

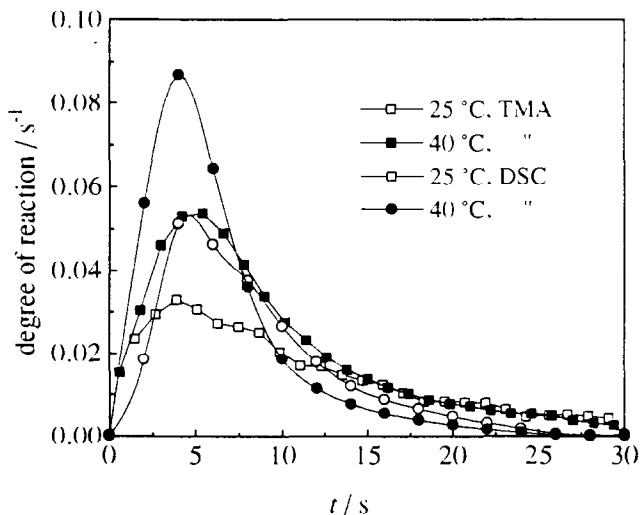


Fig. 11. Comparison between the rate of reaction measured by DSC and TMA at two different temperatures.

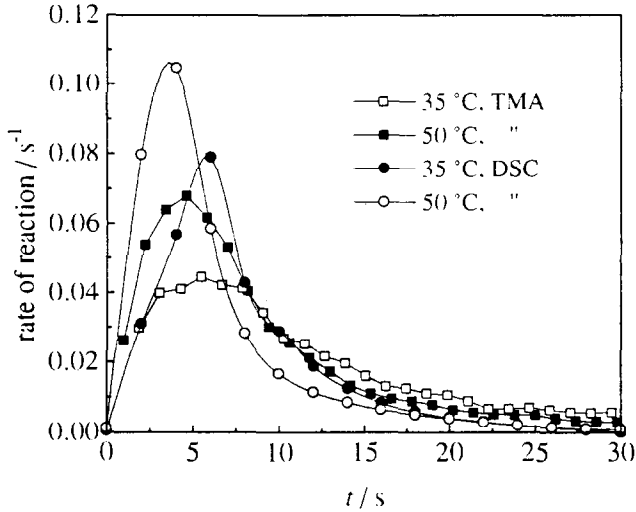


Fig. 12. Comparison between the rate of reaction measured by DSC and TMA at two different temperatures.

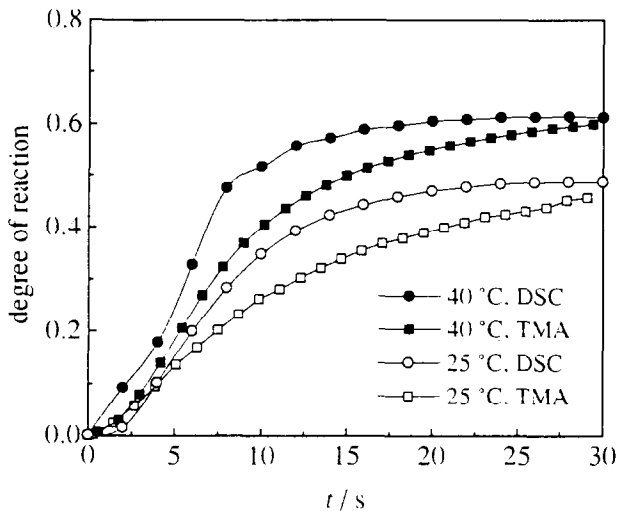


Fig. 13. Comparison between the degree of reaction measured by DSC and TMA at two different temperatures.

observed by DSC and TMA can be achieved. The rate and the degree of reaction data are compared respectively in Figs. 11 and 12, and in Figs. 13 and 14 for four different temperatures. The TMA data present a slower kinetics in the first part of the reaction (Figs. 11 and 12), while, following the interruption of the light exposure (after 30 s), the values of the degree of reaction obtained from these two techniques are very close at all

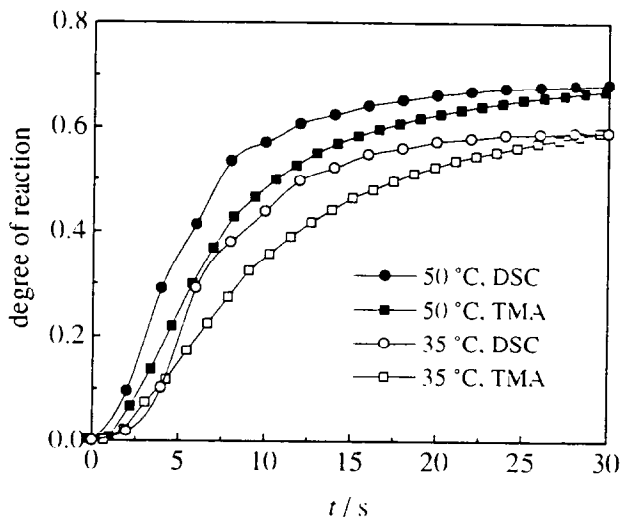


Fig. 14. Comparison between the degree of reaction measured by DSC and TMA at two different temperatures.

temperatures (Figs. 13 and 14). These results are not in agreement with those reported by Kloosterboer et al. [16]. However, it must be noted that Kloosterboer et al. [16] calculated the rate of reaction only from DSC, while the TMA data are presented in the same plot in terms of the rate of change of the sample thickness,  $l$  ( $-dl/dt$ ). This representation may be a source of error in the analysis of the data.

During gelation, occurring in chain polymerisation in the range 0.03–0.1 conversion [23], the abrupt increase of the viscosity does not affect the reaction kinetics measured by DSC [22–24]. However, the transformation of the fluid resin into a rubber (gelation) may be responsible for the lower rates of reaction measured by TMA for  $\alpha > 0.03$ –0.05 (Figs. 11 and 12). This results in a delay of the degree of reaction measured by TMA (Figs. 13 and 14). In fact, as also reported by Kloosterboer et al. [16], the linear (and the volume) shrinkage cannot keep up with chemical reaction, at least after gelation when the rubbery matrix becomes a viscoelastic solid. The viscoelastic behaviour of the material leads to a delayed shrinkage with respect to the evolution of the chemical reaction as observed by DSC. Therefore, the rate of reaction acts as the driving force for the rate of volume change, while the material response is governed by a relaxation time, dependent on the crosslinking structure and hence on the degree of reaction. In the first part of the cure, the rate of reaction is too high and the shrinkage of the material cannot keep up with the reaction. Although the relaxation time increases with the degree of reaction, when  $d\alpha/dt$  decreases the contraction is recovered and the  $d\alpha_v/dt$  becomes higher than  $d\alpha/dt$  as shown in Figs. 11 and 12. In this second part of the reaction, the composite matrix goes through vitrification, inducing a dramatic reduction in the rate of reaction measured by DSC. Moreover, the results obtained by DSC indicate that  $d\alpha/dt = 0$  just before the interruption of the light exposure; however, a value of

$d\alpha_1/dt \neq 0$  more than one order of magnitude lower than the maximum of  $d\alpha/dt$ , is measured by TMA at the same time. These low rates may be attributed to a dark reaction and can be measured only by TMA. The higher sensitivity of TMA is the result of this technique measuring an integral quantity  $\alpha_1$  that presents only small changes during the photopolymerisation reaction. DSC measures directly the rate of reaction,  $d\alpha/dt$ , presenting a change of more than one order of magnitude which overcomes the sensitivity of the instrument as set for the photocalorimetric measurements.

#### 4. Conclusions

In this study, the complex cure behaviour of a commercial dental composite activated by visible light was analysed by DSC and TMA appropriately adapted for light exposure of the sample during measurements. Isothermal TMA and DSC data, collected at the same temperatures, were processed in order to obtain the degree and rate of reaction. DSC and TMA measurements were applied to the prediction of an incomplete polymerisation and the results obtained by these techniques were compared. Finally, the comparison of the isothermal kinetic behaviour resulting from these techniques suggests that a lower rate of reaction is measured by TMA as a consequence of the viscoelastic nature of the material after gelation. However, TMA can detect a dark reaction after interruption of the irradiation which is not observed by DSC.

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