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A vitrification and curing study by simultaneous TMDSC-photocalorimetry

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Abstract The development of photopolymers was helped by the development of photocalorimetry, which is now a basic technique for the study of these materials. This work shows how to obtain vitrification times in single isothermal curing experiments by monitoring the reversing heat capacity along time in modulated temperature DSC–photocuring systems, overcoming the time-consuming problem of standard DSC. The effects of the light intensity and the isothermal curing temperature on the vitrification time of a photocurable system were evaluated. The results obtained at a given curing temperature with different light intensities indicate that the UV-light affects the molecular mobility hindering the vitrification process. The effects of the curing temperature on the vitrification time, the conversion at the vitrification time and the maximum conversion were also evaluated.

Keywords Photocalorimetry · TMDSC · Photocuring · Vitrification time

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Introduction

It is well known that thermosetting materials are widely used in industrial and scientific applications. At present, they approximately represent two-thirds of the organic matrix materials used for composites [1, 2]. Differential scanning calorimetry (DSC) and modulated temperature DSC (TMDSC) are extensively used to monitor the curing reaction of these materials [3]. Most of the curing reactions are thermally induced, but there are important applications, i.e. dental composites, where the curing reaction is induced by UV or visible light [4, 5]. Photocalorimetry is a powerful technique for characterization of UV-light-induced curing reactions. Photopolymerization is frequently based in one of these two mechanisms: (a) Free radical propagation in acrylates or methacrylates [6, 7] and (b) opening of an epoxy ring and addition of vinyl-esters through the double bond [8–11]. Photoinitiated polymerization of acrylates and methacrylates was investigated by photocalorimetry [12, 13]. A possible replacement of industrial furnaces by UV lamps would imply not only an important cost reduction but also an improvement from the environmental point of view [14]. TMDSC can provide very useful information in order to characterise curing reactions. In TMDSC, a sinusoidal modulation (oscillation) is over-imposed on a conventional linear heating or cooling ramp so that the average sample temperature continuously changes with time in a no linear way that, mathematically, can be expressed as

$$T = T_0 + \beta t + A_{\mathrm{T}} \sin(wt) \tag{1}$$

where T_0 is the initial temperature of the experiment, β is the heating rate, A_{T} the amplitude of the temperature sinusoidal wave and w is the oscillation frequency. The heat flow resulting from the application of a modulated temperature ramp is also sinusoidal in shape, with an amplitude A_{HF}.

The reversing heat capacity, $Cp_{\mathrm{rev},}$ can be then defined as

$$Cp_{\mathrm{rev}} = K_{Cp}\frac{A_{\mathrm{HF}}}{A_{\mathrm{T}}w} \tag{2}$$

where K_{Cp} is a calibration constant, A_{T} is the temperature amplitude and w the frequency. $A_{\mathrm{T}}w$ represents the heating rate amplitude. Thus, the Cp_{rev} is calculated by dividing the amplitude of the heat flow by the amplitude of the heating rate, and the reversing heat flow, $\mathrm{HF}_{\mathrm{rev}}$, is equal to the Cp_{rev} multiplied by the underlying heating rate. In quasi-isothermal experiments, the underlying heating rate is zero, so the $\mathrm{HF}_{\mathrm{rev}}$ is also zero and the total heat flow, HF, is equal to the non-reversing heat flow, $\mathrm{HF}_{\mathrm{nonrev}}$. It deserves mention that, depending on the experimental conditions and other factors, reversible physical processes may be reflected on the $\mathrm{HF}_{\mathrm{rev}}$ or $\mathrm{HF}_{\mathrm{nonrev}}$ or both signals. The same happens with the non-reversible physical processes. In this context, the terms reversing and non-reversing are used to identify the processes reflected in the $\mathrm{HF}_{\mathrm{rev}}$ and $\mathrm{HF}_{\mathrm{nonrev}}$ signals, respectively.

Curing reaction studies performed by DSC are based on total heat flow measurements, which allows for calculation of the conversion degree, α. However, vitrification is associated to the Cp_{rev} progress and, thus, vitrification studies should be based on that magnitude [15]. The experimental determination of the vitrification time, t_{vit}, by conventional DSC is very time-consuming, requiring a series of separate isothermal cure experiments for increasing cure times. Each isothermal experiment is followed by a second heating DSC scan, from which the glass transition temperature of the partially cured system is evaluated [16]. Since Gobrecht et al. [17] proposed to use temperature modulation to measure the heat capacity change and the heat flow due to the reaction, TMDSC has been successfully employed to characterise the vitrification process of reacting thermosetting systems [18–25]. In addition to the total heat flow given by conventional DSC, TMDSC also allows the determination, continuously throughout the reaction, of the reversing heat capacity from a single TMDSC quasi-isothermal experiment. Although it falls out of the scope of the present work, the frequency-dependent diffusion control contribution on the reaction kinetics and the frequency dependence of vitrification time were conveniently studied [26–28]. Nevertheless, as far as we know, there is no any report about the simultaneous use of UV-photocuring and TMDSC. The aim of this work is to illustrate how a combined photocuring–TMDSC system can be used to track the reversing heat capacity along time in photocuring experiments, allowing for determination of the t_{vit} in single quasi-isothermal curing experiments, overcoming the standard DSC time-consuming problem. Additionally, it will be shown that the Tzero (tm) technology allows for direct measurement of the incident light energy in both reference and sample thermocouples and no external radiometer is needed.

Experimental

Materials

A commercial all-in-one Reactmer paste (Shofu Inc., Kyoto, Japan) was used. It is a pre-reacted glass-ionomer product in which the fluoridated glass filler had been fully reacted with acid to form an extensive glass-ionomer hydrogel layer before blending with a resin. Composition of this material includes a full-reaction type pre-reacted glass ionomer filler, fluoroaluminosilicate glass, 4-acryloxyethyltrimellitic acid, 4-acryloxyethyltrimellitate anhydride, aliphatic urethane dimethacrylate, 2-hydroxyethyl methacrylate (HEMA) and a photoinitiator [29, 30].

Instrumental setup

Photocalorimetry involves the application of an UV–visible light to a sample while it is subjected to a calorimetric test. It allows for measuring the heat evolved from the reaction, which was induced by the photons in the appropriate wavelength range. Light intensity is usually measured by an external radiometer. In this work, a high pressure mercury lamp (200 W cm^{-2}) was used in connection with a Q2000-TA Instruments TMDSC. The light was guided to and focused on the reference and sample thermocouples by two quartz optical guides. The length of the optical guides is 1 m and they are connected to a window on the top of the DSC cell, at about 1 cm above the sample and reference crucibles. The light produced by the lamp is in the 250–650 nm range. This range was constrained to 350–500 nm by insertion of an optical filter in the light path. The light intensity can be adjusted between 1 and 2000 mW cm^{-2}. Since the TMDSC instrument used in this work is furnished with the Tzero (tm) technology, it is possible to perform a direct measurement of the incident energy in the reference and sample thermocouples, and no external radiometer is needed. So, the light intensity was measured by the instrument previously to the placement of the crucibles.

Indium and sapphire standards were used for temperature, heat flow and heat capacity calibrations. Amplitude of 0.5 K and 40 s period were chosen for the modulated quasi-isothermal curing tests. In all the cases, the sample mass was in the 10–14 mg range. A 50 mL min^{-1} purge of N_2 was used.

In order to quantify the effect of the temperature and the light intensity on the curing and on the vitrification time, three temperatures and eight intensity levels at each temperature were chosen for the quasi-isothermal experiments. The temperatures were 25, 35 and 45 °C, and the light intensities were 6.8, 5.9, 5.1, 4.0, 3.1, 2.3, 1.9, and 1.5 mW cm^{-2}.

Open aluminium crucibles were used for sample and reference. The UV–visible light was trigged after a 10 min period, which was allowed for stabilization of the isothermal conditions. The light was simultaneously applied on both sample and reference crucibles and it was kept for enough time to reach the steady state. Then, the light was switched off but the isothermal conditions were kept for enough time to reach the steady state again.

Results and discussion

Figure 1 shows a typical plot obtained from a photo-curing TMDSC experiment. Enough time was allowed for the heat flow trace becoming stable before applying the light. As soon as the light source was switched on, an exothermic peak started, indicating the progress of the photo-initiated reaction. Upon reaching the maximum, the heat flow decreases until maximum conversion at that temperature is achieved. From that point, the baseline becomes stable. Then, a shift of the baseline is observed as a consequence of the light switching off. The area percent is also plotted. It was obtained by integration of the heat flow curve, using an horizontal baseline at the asymptotic heat flow value. It represents the conversion with respect to the maximum degree of curing that can be obtained at that temperature.

As aforementioned, TMDSC allows for obtaining the *Cp* progress along time. *Cp* is directly related to the vitrification time and the *Cp* inflection point is an important parameter that can be used as an indication of the change from chemical to diffusive control [19]. Before making use of the Cp_{rev} and total heat flow signals, it was checked that the modulated temperature profile produced by the instrument was actually sinusoidal and that the sample was able to follow the modulated profile. Figure 2 plots the modulated temperature and the modulated heat flow. It can be observed that both signals are sinusoidal in shape and that the heat flow corresponds to the temperature on a cycle by cycle basis. Lissajous figure can be used to check if some deviation from the linearity exists in each cycle. Figure 3 plots the Lissajous figure corresponding to the modulated temperature versus the modulated heat flow. The plot is composed of ellipses with no trace of non-linearity. Each ellipse corresponds to a modulated cycle. It can be observed a shifting of the average heat flow with time, which is due to the progress of the curing reaction.

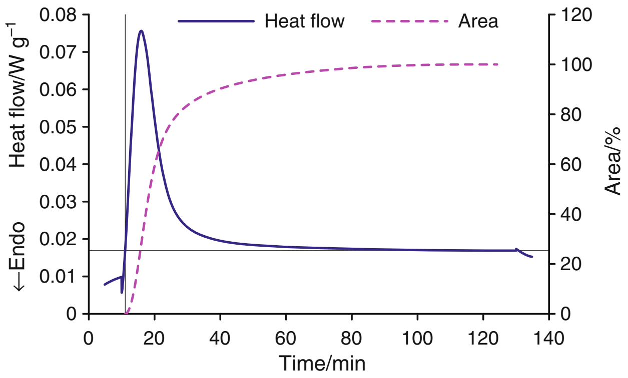

Fig. 1 Heat flow and conversion obtained in a quasi-isothermal TMDSC–photocuring experiment

Figure 4 plots the reversing heat capacity along time. The vitrification time, t_{vit}, was taken from the minimum of the first derivative of Cp_{rev} vs. time, which corresponds to the inflection point of the Cp_{rev} curve. The heat of curing of

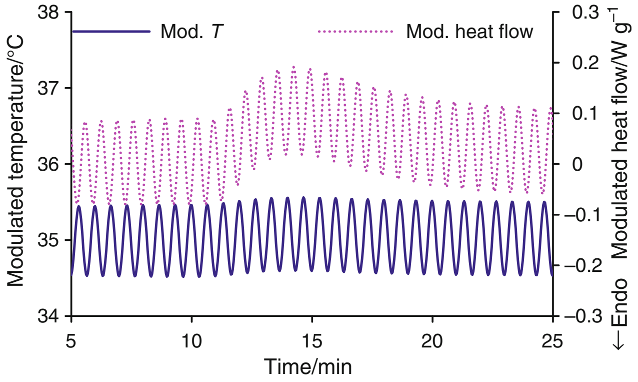

Fig. 2 Modulated heat flow and modulated temperature curves obtained from a 35 °C quasi-isothermal photo-curing test

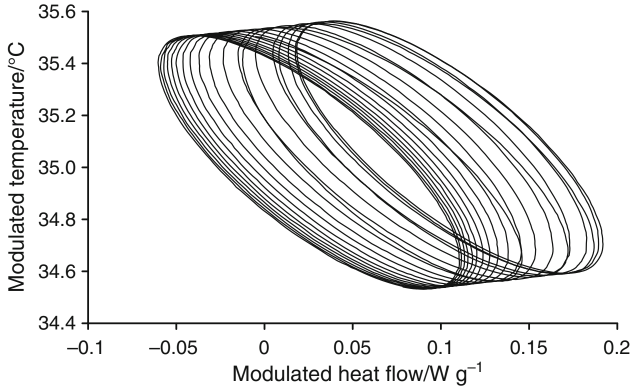

Fig. 3 Plot of modulated temperature versus modulated heat flow, obtained from a 35 °C quasi-isothermal photo-curing test

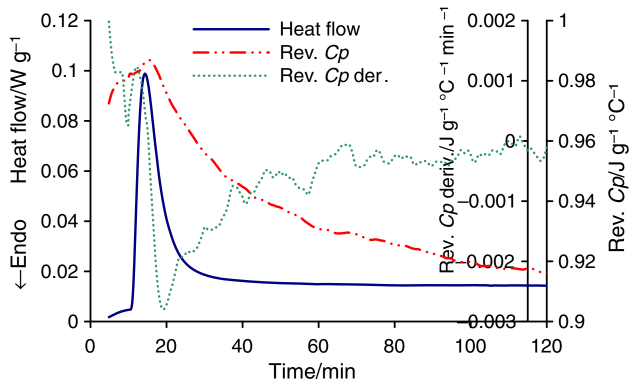

Fig. 4 Heat flow, Cp_{rev} and Cp_{rev} derivative versus time

each experiment was determined by integration of the heat flow curve. The relative conversions at the t_{vit} were obtained, in each experiment, by partial integration and comparison with the total heat of curing obtained in the same experiment. Figure 5 plots the vitrification times obtained with different light intensities at 25 °C, the corresponding conversions at t_{vit} and the heat of curing. The conversions were normalised with respect to the maximum heat flow obtained in all the experiments presented in Figs. 5 and 6. In all three cases a strong dependence on the light intensity is observed. The measured values of t_{vit}, heat of curing and normalised conversion obtained with a light intensity of 1.5 mW cm^{-2} were 46 min, 23.37 J g^{-1} and 34%, respectively. The corresponding values obtained with a 6.8 mW cm^{-2} light intensity were 3.2 min, 41.8 J g^{-1} and 61%. It means that the light intensity affects not only the kinetics of the pre-vitrification stage but also the vitrification process itself, so that the higher the light intensity the higher the conversion at which the vitrification takes place at a given temperature. This fact, not earlier reported, indicates that the UV-light seriously affects the molecular mobility hindering the vitrification process.

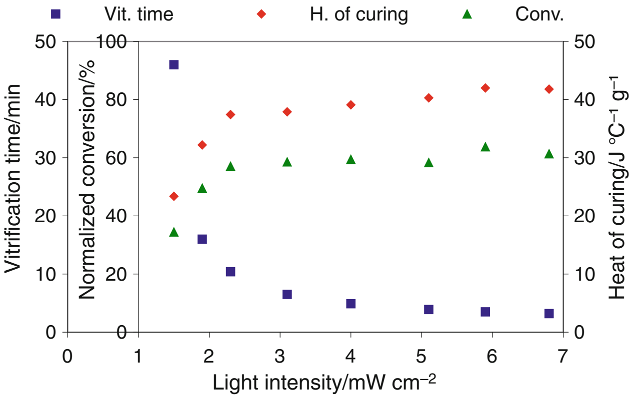

Fig. 5 Vitrification times, the corresponding conversions at t_{vit} and the heat of curing obtained with different light intensities at 25 °C

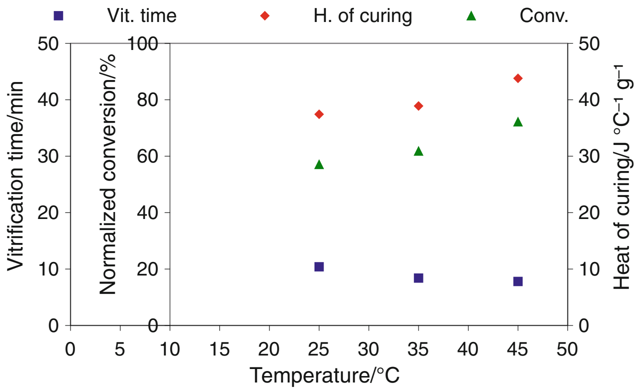

Fig. 6 Vitrification time, normalised conversions and heats of curing obtained with a 2.3 mW cm^{-2} light intensity at different temperatures

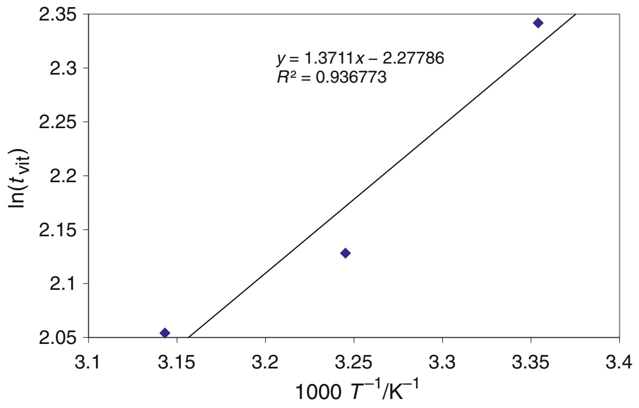

Fig. 7 Plot of $\ln(t_{\mathrm{vit}})$ vs. T^{-1}, obtained with a 2.3 mW cm^{-2} light intensity

The temperature effect on the curing reaction rate can be used to obtain the activation energy, E_{a}, through the Arrhenius law:

$$k = Ae^{-\frac{E_{\mathrm{a}}}{RT}} \tag{3}$$

where k is the rate constant, A is the pre-exponential factor and R is the gas constant. A similar approach was used to relate t_{vit} with E_{a} in TMDSC [31].

$$t_{\mathrm{vit}} = t_{\mathrm{v0}}e^{\frac{E_{\mathrm{a}}}{RT}} \tag{4}$$

where t_{v0} is a pre-exponential factor and E_{a} the apparent activation energy. Thus, Fig. 7 shows the plot of $\ln(t_{\mathrm{vit}})$ vs. T^{-1}, obtained with a 2.3 mW cm^{-2} light intensity. The E_{a} value resulting from the slope was 11.39 kJ mol^{-1}. Table 1 shows the E_{a} values and the regression coefficient of determination, R^2, obtained with different light intensities. These low values of E_{a} are in line with other reports of photoinitiated polymerization of acrylates and methacrylates [13, 32].

Figure 6 plots the t_{vit} values, the corresponding normalised conversions and the total heats of curing obtained

Table 1 E_a and R^2 values obtained with different light intensities

Light intensity/mW cm^{-2}	E_a/kJ mol^{-1}	R^2
1.5	12.11	0.9422
1.9	10.98	0.9289
2.3	11.39	0.9368
3.1	11.90	0.9411
4	12.30	0.9298

Table 2 Vitrification times obtained with different light intensities at 25 °C

Light intensity/mW cm^{-2}	Vitrification time, t_{vit}/min
1.5	46
1.9	16
2.3	10.4
3.1	6.5
4	4.9
5.1	3.9
5.9	3.5
6.8	3.2

with a 2.3 mW cm^{-2} light intensity at different temperatures. An increase of the curing temperature from 25 to 45 °C produced a shortening of t_{vit} from 10.4 to 7.8 min, an increase of the heat of curing from 37.43 to 43.8 J g^{-1} and an increase of the conversion at the vitrification time from 57 to 72%. This increase of the heat of curing is normal when curing at temperatures below the glass transition temperature of a fully cured polymer, $T_{g\infty}$. When increasing the curing temperature, the t_{vit} shortens and the conversion reached at t_{vit} increases. It indicates a clear effect of the temperature on the reaction rate at the pre-vitrification stage. These effects were expected since it is well known that at temperatures below $T_{g\infty}$, the vitrification process starts when the actual glass transition of the reacting polymer reaches the curing temperature. So, the higher the curing temperature the higher the converted-fraction at the t_{vit} and the higher the maximum degree of curing in each experiment.

In spite of the suitability of the instrument to perform this kind of tests, it should be taken into account that, in general, 4 or 5 modulation cycles per transition are needed to perform a reliable separation of the reversing and non-reversing TMDSC signals. A relatively fast reaction would distort the Lissajous figure preventing an optimal calculation of Cp_{rev}. In this case, it applies to the experiments with vitrification times lower than 5 min. Those results were underlined in Table 2.

Conclusions

Vitrification times at different temperatures with different light intensities were evaluated in single quasi-isothermal curing experiments. It was accomplished by using a combined TMDSC–photocuring system, where the light intensity was measured by the TMDSC instrument.

The apparent activation energy calculated from the vitrification times was in line with other reported values for photoinitiated polymerization of acrylates.

A strong dependence of the vitrification time with respect to the light intensity was observed. A slight dependence with respect to the temperature was also observed in the range of temperature considered.

As expected, it was observed that the conversion at the vitrification time and the maximum conversion in isothermal experiments depend on the curing temperature.

Unexpectedly, it was observed that the conversion at the vitrification time and the maximum conversion in isothermal experiments also depend on the light intensity. It indicates that the vitrification process is influenced by the light intensity. This finding brings the challenge to investigate possible light intensity–temperature interactions.

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