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Dedicated to Prof. Antonius Kettrup on the occasion of his 60th birthday

DSC INVESTIGATIONS ON A COMMERCIAL PHOTOCURING SHEET MATERIAL

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Abstract

The photopolymerization of a commercial sheet material as used in the dental laboratory was investigated by using the photocalorimeter DSC7/DPA7 (Perkin-Elmer). Using normal reaction conditions (light wavelength ≤ 400 nm, light intensity ≥1 mW cm^{-2} and sample thickness ≤2.5 mm), the curing was completed within few min. The reaction rate was nearly independent on the light wavelength in the range between λ=300 and 380 nm, but decreased distinctively at longer wavelenghts. After desmearing the DSC curves, the dependence of the reaction rate on light intensity and sample thickness could be described in very good approximation by an equation derived by Tryson [1]. Comparable with pure acrylates or methacrylates, a pronounced dark reaction was found after interruption of the illumination.

Keywords: DSC, impression materials, photopolymerization

Introduction

The combination DPA7/DSC7 permits the effective and comfortable investigation of light curing materials. In this paper we have examined the polymerization of a photocuring sheet material as used in the dental laboratory. The reactive substance of the impression material is methylmethacrylate, the desired plasticity is reached by thickening with about 77% solid filler. The radical photoinitiator is unknown. The producer gives illumination times of 6 min for the complete curing, using blue light lamps (400–500 nm). We have investigated the influence of the light wavelength, sample thickness and light intensity on the curing reaction. Moreover, we have made some experiments with interrupted illumination at different conversion degrees.

Experimental

The essential points of view are fully discussed in the book of Höhne [2]. The photocuring was made in the isothermal mode at room temperature, using a

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200 W Hg/Xe lamp as light source. The undesired infrared portion of the spectrum was quantitatively absorbed by a quartz cell filled with water. The desired wavelength (from 300 to 460 nm every 20 nm) was chosen using the monochromator optics version, the half width of the radiation was about 10 nm. To measure the incoming light intensity, a graphite disk with a diameter of 6 mm was substituted for the sample. The disk absorbed 90–95% of the incident light and transferred it to the calorimeter in the form of a heat flow. The desired light intensity was adjusted by means of metal sieves with different mesh width. In addition, the sieves were rotatable to the direction of the beam crossways.

Reproducible results were only then obtained, if the sample preparation guaranteed uniform and known sample thicknesses. To realize this, we prepared the samples as follows. A piece of the soft impression material with the desired mass (thickness) was placed into a standard sample pan. Then, the sample was covered with a thin quartz disk of the same diameter as the sample pan. An even layer thickness was reached by gentle pressing down on the disk using a cylindrical plunger. With a pan of 6.4 mm diameter and an approximate specific sample mass of 1.84 g cm^{-3} follows the simple relation between sample thickness and mass: d (in mm) = 0.0169 m (in mg). Each DSC experiment included a short dark period (typically 6 s) and the subsequent illumination period. After the first run an additional run was started using the same experimental conditions. The subtraction of both runs removed the effect that there are different baselines for the dark and the illumination period during the runs. To facilitate the desmearing [2, 3] of the very fast photopolymerizations, the response of the sample to a light flash (50 ms) was recorded after the completed reaction.

Results and discussion

The average reaction enthalpy for the complete curing reaction was found to be 43±1 J g^{-1}. This value is independent on the light intensity, light wavelength and sample thickness using normal reaction conditions. Figure 1 shows a typical

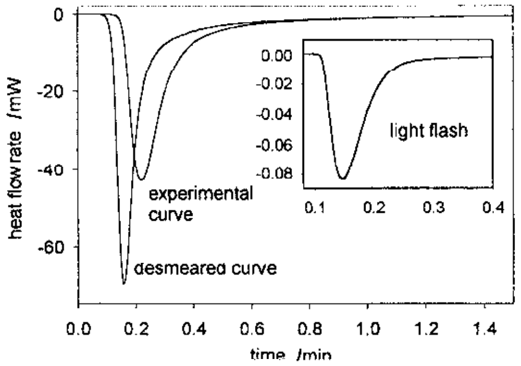

Fig. 1 Measured and desmeared DSC curve, using a light flash as apparatus function; I_0=4 mW cm^{-2}, λ=380 nm

DSC curve for such conditions. The light intensity was 4.4 mW cm^{-2} at 380 nm, the sample thickness was 0.17 mm. The small picture in Fig. 1 shows the response of the DSC to a light flash after the completed reaction. Shape and maximum heat flow of the recorded curve clearly differ from the true (desmeared) curve. These differences increase with increasing light intensity and sample thickness. Therefore, nearly all evaluations are senseless without previous desmearing! In contrast to pure methylmethacrylate, an initial first order behaviour of the sample is not found. Due to the high filler content, the viscosity of the matrix is so high that the so-called gel or Trommsdorff-Norrish effect dominates from the start.

Influence of the light wavelength

The reaction rate has a maximum value between 340 and 380 nm. If a shorter wavelength (320 or 300 nm) is used, the rate is hardly decreased. Otherwise, using a longer wavelength a very pronounced deceleration was found as shown in Fig. 2, for the first two min of the curing. Of course, this has a strong effect on the reaction times for a complete curing. Even in using a very thin (0.17 mm) sample, the conversion degree was only 0.97 after 15 min at 440 nm. However, the usual thickness of the impression material is about 2.5 mm. To reach a complete curing of such samples within practicable times, the wavelength should not be longer than 400 nm. Like many usual radical photoinitiators, the used photoinitiator has obviously an absorption maximum in the near UV range. Therefore, all following investigations were made at 380 nm.

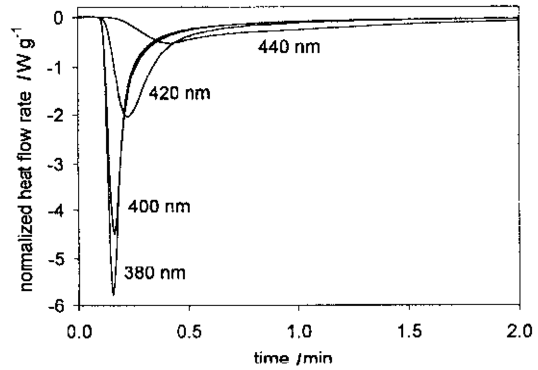

Fig. 2 Influence of the light wavelength on the reaction behaviour at constant light intensity (I_0=4.4 mW cm^{-2}) and sample thickness (d=0.17 mm)

Influence of sample thickness and light intensity

The investigated samples had finite thickness and it follows from the Lambert-Beer law that there is a varying light absorption and hence a gradient of the reaction rate within the sample. However, the calorimeter always recorded an overall heat flow rate. Tryson [1] derives the following expression between the square root of the (observed) average reaction rate on the one hand and sample thickness and light intensity on the other hand:

$$\sqrt{R_{\text{average}}} = \sqrt{\frac{4I_0}{\varepsilon c d^2}}\left[1-\exp\left(-\frac{\varepsilon c d}{2}\right)\right]$$

where I_0 is the incident light intensity, c is the concentration of the reactive component, ε is the molar absorption coefficient of the photoinitiator and d is the total thickness of the sample. Investigating the polymerization of multifunctional acrylates, Tryson found only qualitative agreement i.e. higher average reaction rates for thinner samples, between observed and calculated reaction rates. The workers think that the discrepancy could be caused for the most part by the fact that his measurements were not desmeared. Because ε and c are not known for our samples, the above equation was used in the following form:

$$\sqrt{R_{\text{average}}} = \sqrt{\frac{2I_0}{\text{const. } d^2}}(1-\exp(-\text{const. } d))$$

where const.=$\varepsilon c/2$ was introduced as fitting parameter. The evaluation was restricted to the maximum reaction rates of the desmeared curves where the conversion degree was between 0.2 and 0.25 at this time. The results of the nonlinear regression for sample thicknesses between 0.17 and 1.89 mm are shown in Fig. 3. Clearly, there is a well defined correlation between average reaction rate and sample thickness if the above equation is used. The same equation should also describe the linear correlation between average reaction rate and incident light intensity. This was tested for thin (0.15–0.19 mm) and thick (1.89 mm) samples at light intensities between 0.13 and 15.16 mW cm^{-2}. Again, the fit of the experimental data is excellent (Fig. 4). Disregarding the results at the two highest intensities of the thin sample, all experiments are described by the same

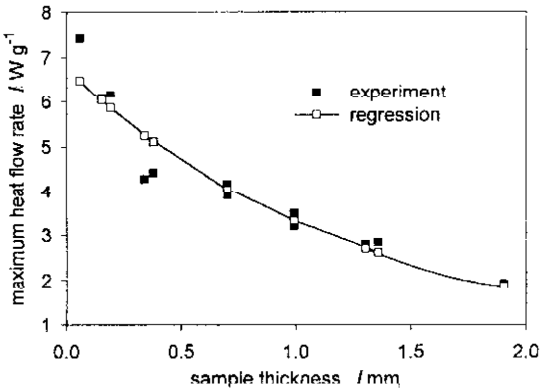

Fig. 3 Correlation between average reaction rate of the peak maximum and sample thickness (I_0=4.4 mW cm^{-2}, λ =380 nm)

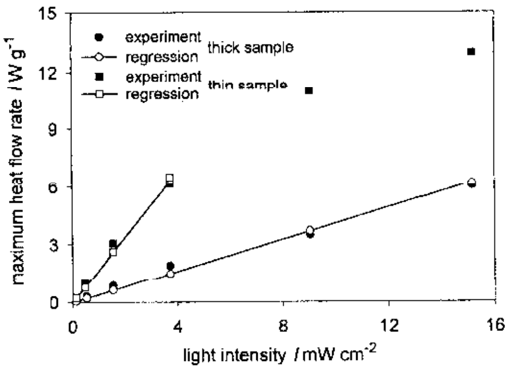

Fig. 4 Correlation between average reaction rate of the peak maximum and light intensity for thin (d=0.15–0.19 mm) and thick (d=1.89 mm) samples (λ=380 nm)

fitting parameter const. = 0.88 ±0.1 cm^{-1}. The differences at very high light intensities are probably caused by two factors:

1. The reaction rate is so fast that the linear signal range of the calorimeter is exceeded.
2. The pseudo-stationary radical density is not yet reached at the peak maximum.

Investigations at interrupted illumination

If a number of ideal conditions can be assumed, the polymerization rate is given by [1]:

$$-\frac{\mathrm{d}c_\mathrm{M}}{\mathrm{d}t}=k_\mathrm{p}\sqrt{\frac{\Gamma I_\mathrm{abs}}{k_\mathrm{t}}}c_\mathrm{M}$$

where ΓI_abs is the product of the quantum yield of the photoinitiator and the photon absorption rate, c_M is the concentration of the monomer and k_p and k_t are the rate constants of the chain propagation and termination. During the gel effect this ratio is formally dependent on the degree of reaction reached. The rate constant k_t decreases with increasing viscosity of the matrix much faster than k_p. The result is a pronounced dark reaction after switching off the light during the photopolymerization, because the chain termination reactions of the growing macroradicals are increasingly hindered in the more and more viscous matrix. Table 1 summarizes some results of such experiments. The mentioned effect becomes particularly clear, if the total increase of the conversion degree during the dark period (column 3 in Table 1) is related to the amount of the remaining monomer at the start of the dark reaction (the last column of Table 1).

Assuming a strict bimolecular chain termination, there should be a linear correlation between $-c_\mathrm{M}/(\mathrm{d}c_\mathrm{M}/\mathrm{d}t)$ and t [1, 4]. Figure 5 shows the corresponding

Table 1 The dependence of the increasing conversion degree during the dark reaction on the conversion reached at the light interruption

α_1 at the start of the dark reaction	α_2 at the end of the dark reaction	$\Delta\alpha$	$\Delta\alpha/(1-\alpha_1)$
*0.016	0.072	0.056	0.057
*0.083	0.249	0.166	0.181
0.141	0.463	0.322	0.375
*0.300	0.634	0.324	0.463
0.495	0.787	0.292	0.578
0.657	0.868	0.211	0.615

* The light was interrupted after 1.2 s illumination

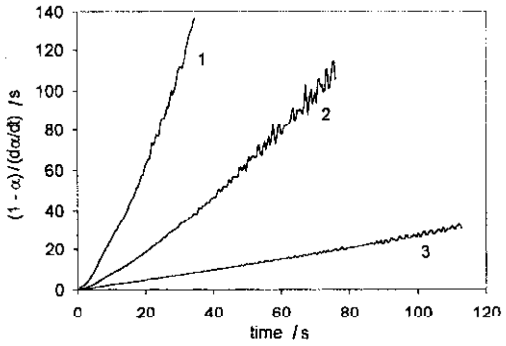

Fig. 5 Dark reaction after interrupting the light at different reaction degrees: 1: α=0.016, 2: α =0.083, 3: α=0.300; The slope of the curves is given by the ratio k_t/k_p

evaluation for a sample at which the light was three times interrupted after 1.2 s illumination respectively (the asterisks in Table 1). Because the actual monomer concentration was not known, the quantity $(1-\alpha)/(\mathrm{d}\alpha/\mathrm{d}t)$ was plotted *vs.* t. As expected, the higher the conversion degrees at the moment of the light interruption the less steep is the slope of these curves. The small discrepancies from the linearity could be caused by uncertainties of the desmearing procedure and by a more complicated radical termination mechanism. Because the monomer concentration and the quantum yield were not known the calculation of k_p and k_t according [1, 4] was not made.

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