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Determination of curing heat and curing time of light-cured composite resins by differential scanning calorimetry

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Palabras clave: resinas compuestas fotocuradas, tiempo de curado, calor de curado, calorimetría diferencial de barrido.
Key words: light-cured composite resins, time of curing, curing heat, differential scanning calorimetry.

RESUMEN. El comportamiento del calor de fraguado en las resinas compuestas fotocuradas, con bis-GMA y 3G incorporados, fue investigado por calorimetría diferencial de barrido (CDB). La polimerización activada por luz visible de estos sistemas monoméricos fue estudiada usando canforquinona (CQ) y metacrilato de dimetilaminoetilo (DMAEMA) como agente retardador. En particular, la CDB es fácilmente usada para medir el calor de polimerización por la facilidad en preparación de la muestra. Cuatro muestras de resinas compuestas fotocuradas (dos de ellas sin relleno y dos con relleno) fueron estudiadas a dos tiempos de exposición a la luz. Los materiales utilizados para su preparación fueron bis-GMA, 2,2-bis[*p*- γ -metacriloxi- β -hidroxipropoxi]fenilpropano; 3G, dimetacrilato de trietilenglicol; CQ, canforquinona y DMAEMA, metacrilato de dimetilaminoetilo. Los dos composites rellenos se prepararon con dióxido del silicio (77 % en peso, 30 μ m tamaño de partícula promedio). El sistema de análisis termal Mettler TA-3000, DSC-30 fue usado para realizar las determinaciones, en un segmento isoterma a 37 °C durante 5 min bajo programa de calentamiento controlado. Los especímenes eran polimerizadas iluminándolas en el aparato de CDB con radiación de una fuente de luz visible (Heliolux II) a 0,3 y 0,67 min y el calor era determinado. De esta manera, parece que el pico exotérmico de la curva de CDB para las resinas fotocuradas depende del calor de polimerización de cada monómero contenido en cada resina.

ABSTRACT. The behavior of curing heat of in light-cured restorative composite resins, containing bis-GMA and 3G, was investigated by differential scanning calorimetry (DSC). Visible light-activated polymerization of these monomer systems was studied using camphorquinone (CQ) and dimethylaminoethyl methacrylate (DMAEMA) as reducing agent. In particular, DSC can be easily used to measure the heat of polymerization because of the easy features in the sample preparation. Four samples of a visible light-cured restorative composite resin (two of them unfilled and two filled) were studied at two different light exposition times. The used materials in this study were bis-GMA, 2,2-bis[*p*- γ -methacryloxy- β -hydroxypropoxy]phenylpropane; 3G, triethylene glycol dimethacrylate; CQ, camphorquinone and DMAEMA, dimethylaminoethyl methacrylate. The two filled composites were prepared with silicon dioxide (77 wt %, 30 μ m particle size average). A system of thermal analysis Mettler TA-3000, DSC-30 was used to carry out measurements, in an isothermal segment at 37 °C during 5 min under a controlled thermal program. The specimens were polymerized by illuminating them in a DSC apparatus with radiation from a visible light source (Heliolux II) for 0.33 and 0.67 min and the heat output was determined. It seems that the exothermic peak of the DSC curve for light-cured resins depend on the heat of polymerization of each monomer itself contained in the resins.

INTRODUCTION

Visible light-cured dental composite resins have been extensively applied in modern cosmetic dentistry for applications in anterior and posterior teeth. These composites are mostly based on dimethacrylate monomer systems. Most of visible light-cured resins contain a photosensitizer like camphorquinone, and a reducing agent like tertiary amine¹⁻⁴ which cause the initiation of polymerization processes by visible light irradiation. It is important to study the polymerization of these resins, because various properties (hardness, wear resistance, mechanical strength and colour stability) of the set resins are doubtlessly affected by the degree of polymerization.^{5,6} The polymerization reaction of dental composite resins has been investigated by various methods including Fourier transform infrared spectroscopy (FTIR), Laser Raman spectroscopy (LSR) and differential scanning calorimetry (DSC).⁷⁻⁹

In particular, DSC can be easily used to measure the heat of polymerization for the difficulties in sample preparation and strong interference among monomers found in other techniques.¹⁰ Moreover, the properties of dimethacrylate monomers can be measured by the isothermal¹¹⁻¹² or dynamic method,¹³ and the polymerization heat of light-cured composite resins by irradiation can be measured by isothermal DSC measurement.¹⁴⁻¹⁸

The purpose of this investigation was to study the curing heat and curing time of a light-cured composite resin filled and unfilled; containing 2,2-bis[*p*- γ -methacryloxy- β -hydroxypropoxy]phenyl]propane (bis-GMA) and triethylene glycol dimethacrylate (3G) as monomer systems, a combination of camphorquinone (CQ) and dimethylaminoethylmethacrylate (DMAEMA) as reducing agents. Here, we employ DSC without light irradiation the so-called isothermal DSC measurement and discuss the curing heat and time behavior of experimental system of light-cured composite resins.

MATERIALS AND METHOD

Four samples of a visible light-cured restorative composite resin (two of them unfilled R1, irradiation time 0.33 min and R2, irradiation time 0.67 min and two filled RR1, irradiation time 0.33 min y RR2, irradiation time 0.67 min) were used. The used materials in this study were bis-GMA, 2,2-bis[*p*- γ -methacryloxy- β -hydroxypropoxy]phenyl]propane; 3G, triethylene glycol dimethacrylate; CQ, camphorquinone and DMAEMA, dimethylaminoethylmethacrylate. The two filled composites were prepared with silicium dioxide (77 wt %, 30 μ m particle size average); the pastes were processed by rolling to eliminate air traps and to disperse the filler uniformly. The composition of investigated materials are given in Table 1.

A system of thermal analysis Mettler TA-3000, DSC-30 was used to perform measurements, in an isothermal segment at 37 °C during 5 min under a controlled thermal program. Twenty to twenty-five milligram samples were placed on the aluminum sample pan and the temperature stabilized at 37 °C. The specimens were polymerized by illuminating them in a DSC apparatus with radiation from a visible light source (Heliolux II) for 0.33 and 0.67 min and the heat output was determined. Both the sample and the reference pans were simultaneously exposed to the light.

RESULTS AND DISCUSSION

In the polymerization reaction of visible light-cured resins, an exothermic nature peak was found¹⁹ and a thermoanalytical method has previously been reported for commercial dental composites.²⁰⁻²³ Figure 1 shows typical DSC curves for bis-

Table 2. Result of DSC study. Isothermal temperature 37 °C.

Sample	Irradiation time [min]	Peak time [min]	Peak end [min]	Heat of curing [Jg ⁻¹]
R1	0.3	0.42 $\pm$ 0.2	1.6 $\pm$ 0.2	197.4 $\pm$ 6.2
R2	0.6	0.42 $\pm$ 0.2	1.6 $\pm$ 0.2	247.8 $\pm$ 8.4
RR1	0.3	0.42 $\pm$ 0.2	1.6 $\pm$ 0.2	37.78 $\pm$ 3.8
RR2	0.6	0.41 $\pm$ 0.2	1.7 $\pm$ 0.2	92.1 $\pm$ 5.1

GMA resins after 0.33 and 0.67 min irradiation. Table 2 indicates peak time and curing heats peaks for all visible light-cured resins. The setting time could be considered as a time evolved from the beginning of experiment to the maximum of the peak generate by the polymerization. The heat for curing is defined as the area under of the DSC curve. It was obtained a heat of curing per gram of sample, from the DSC curve.

As observed in the Table 2, a significant increase of the heat of curing produced when increasing the time of illumination. However, significant details can be pointed out.

All the samples, without filler (R1 and R2) and with filler (RR1 and RR2) have the same peak time. A similar behavior was observed to the end of the pick (polymerization reaction). In conclusion, the filler quantity and the illumination time

don't influence over the setting time (peak time) and the end of the polymerization process (end of the peak).

In the resins without filler the curing heat is much bigger than for the composites with filler; since the amount of monomers per gram of sample is greater. This in turn increases considerably for both cases when being duplicated the time of illumination; because at more time of illumination there is a bigger formation of polymerization centers and therefore a bigger advance of the polymerization reaction.

The second peak overlap in DSC curve is probably due to secondary cure and consequent shrinkage in the resin. Support for the possibility of shrinkage due to secondary cure is also evident from the exotherms observed in the posture DSC thermal curve in figure 1. This process remarks the fact of heat absorption by the filler discussed for the first peak.

It seems that the exothermic peaks of the DSC curve for light-cured resins depend on the heat of polymerization of each monomer itself contained in the resins.

CONCLUSION

The heat curing behavior of light-cured restorative composite resins, containing bis-GMA monomers and 3G by isothermal programs with dif-

Table 1. Compositions of materials used in this study.

Compound	wt [parts in wt]
Bis-GMA	60
3G	40
CQ	0.5
DMAEMA	0.5

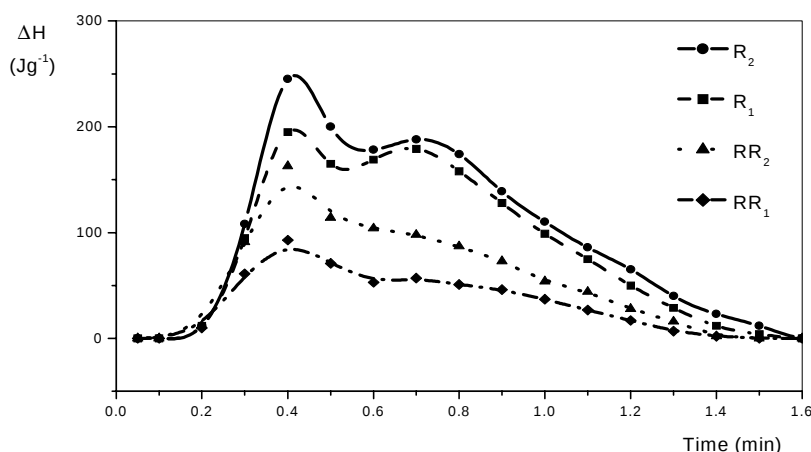


Fig. 1. Typical DSC curves for resins. Isothermal temperature 37 °C and twenty to twenty five of sample.

ferential scanning calorimetry has revealed important information on the cure. The light-cured composite showed a sharp exothermic peak over 0.41 min. The shoulder in the peaks reveal secondary cure.

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