POLYMERIZATION OF PHOTOCURABLE COMMERCIAL DENTAL METHACRYLATE-BASED COMPOSITES
Photocalorimetry study

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Due to their excellent aesthetics, photopolymers have been extensively used in several dentistry applications. However, several problems are reported, e.g. low mechanical and abrasion resistance, shrinkage during polymerization, etc. Properties of the final restorations are intrinsically related to the polymerization stage, which can be conveniently studied by photocalorimetry. In the present work the polymerization reaction and the filler content of different photocurable commercial dental methacrylate-based composites were studied by means of photocalorimetry and thermogravimetry, respectively. The results show that the values of curing rate, the heat of polymerization and the filler content vary significantly from one composite to another.

Keywords: composite resin, dental polymers, photocalorimetry, polymerization kinetics

Introduction

Due to their excellent aesthetics and improvements in the chemical and mechanical resistance, dental composite materials are extensively used in several dentistry applications nowadays. These materials are composed basically by two phases: a resinous matrix, comprising dimethacrylate monomers and/or oligomers, photoinitiator and an inorganic phase, known as filler, generally composed by particulate glass and pyrogenic silica.

The main monomers/oligomers used in the resinous phase are bisphenylglycidyl dimethacrylate (BisGMA), triethylene glycol dimethacrylate (TEGDMA) and urethane dimethacrylate (UDMA). The photoinitiator system is commonly camphorquinone associated with a tertiary amine. Silicate-based glasses, zirconia, alumina, quartz, pyrogenic silica and barium aluminum silicate are used as fillers, normally surface modified by a coupling agent aiming to improve the mechanical properties.

According to their particle size, the available commercial composites are classified to three main categories: traditional (1–50 µm), hybrid (0.04–20 µm) and microfilled (0.04 µm) [1].

Despite of all advantages in the application of composite materials in dentistry, there are several problems reported including low abrasion resistance, shrinkage during polymerization that causes micro-infiltration and consequently secondary caries and low color stability [1–8].

The properties of the final restorations, mainly the shrinkage stress are intrinsically related to the polymerization's kinetics [9–13]. Among the several available experimental techniques to study the photopolymerization process, infrared spectroscopy (FTIR) is one of the most frequently used (however, shrinkage and microhardness measurements are also used). These techniques allow only evaluating the composite before and after curing (except the real time FTIR). On the other hand, photocalorimetry allows following the reaction in real time through the released heat during polymerization, making it one of the most reliable technique to study the kinetic of polymerization.

Thus, the purpose of this study was to evaluate the photopolymerization and the amount of filler of different commercial dental composites by photocalorimetry and thermogravimetry to relate these parameters to the final properties of the composites in future works.

Experimental

Commercial dental composite resins used in this study were the following brands at color A_2: Vit-l-escence (Ultradent Products, Inc. USA), Filtek Z-250 (3M/ESPE, Dental Products St. Paul, MN), Z-100 (3M/ESPE, Dental Products St. Paul, MN), Prisma APH (Dentsply, Indústria e Comércio Ltda. Petrópolis/RJ, Brazil), Tetric Ceram

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(Ivoclar/Vivadent, Liechtenstein), Point 4 (Kerr Corporation, USA), XRV Herculite (Kerr Corporation, USA), Solitaire (Heraeus-Kulzer, Germany).

The photocalorimetric measurements were performed with a DSC Q100 (Differential Scanning Calorimeter, TA Instruments) coupled to a PCA (Photocalorimeter Accessory – Q Series, TA Instruments) equipped with a high-pressure mercury lamp. The wavelength was adjusted between 390 to 500 nm using cut-off filters, the light intensity on the samples was about 240 mW cm^{-2}, the irradiation time was 3 min and the purge gas was nitrogen (75 mL min^{-1}). 15.0 mg of each resin were weighed in an open aluminum pan and the DSC-PCA cell was thermostated at 25°C. The calibration of the device was performed under the same experimental conditions, according to procedure available on TA Instruments online help. The heat flow signal used was T4 (mW). The resistance and the heat capacity were calibrated by heating the empty cell and using two sapphire disks with equal masses. The cell constant and temperature calibration was performed using a high purity sample of indium through its melting peak.

TG plots of uncured composites were recorder using a SDT Q600 (TA Instruments). The experimental conditions were: 25°C as initial temperature; 700°C for the final temperature with oxygen (flow rate: 100 mL min^{-1}) alumina pan; heating rate: 10°C min^{-1} and sample mass ~55 mg; Calibration of the device was performed according to standard procedure available on TA Instruments online help. The TG mass and baseline calibration was conducted with and without α-alumina standards positioned on the sensors. The temperature calibration was performed using a high purity zinc sample.

Results and discussion

Figure 1 shows the results obtained during the photopolymerization of the different commercial dental composites to the end of the polymerization.

All samples showed the same 3 stages pattern described by Decker [14] with important differences in the contribution of each one for the different brands. In the first stage autoacceleration occurs at the very beginning of the irradiation because of the rapid increase in viscosity when the reaction reaches its maximum value $(Rp)_{max}$. It is followed by a period where polymerization occurs at a constant rate, the time after which autodeceleration takes place when propagation becomes diffusion controlled. Vitrification leads to a complete stop of the curing process. After 0.6 min the heat flow becomes constant indicating that the polymerization process finished, although post-curing process occurs after long periods, with lower values com-
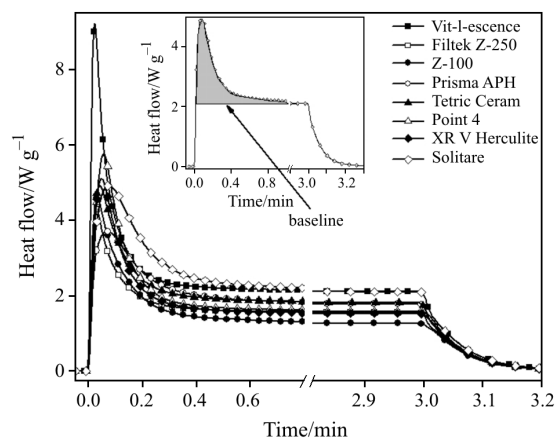
Fig. 1 Heat evolution *vs.* time for the photopolymerization of different composites at 25°C.
Light intensity=240 mW cm^{-2}; *m*=15.0 mg; purge gas: nitrogen (75 mL min^{-1})

pared to the initial stages of the polymerization. The increase in the baseline at about 2 W g^{-1} from the beginning of the polymerization to the end occurs through light absorption by the samples and dissipation in the form of the heat. When the light is turned off, the baseline returns near to zero.

The different heat flow values and time at the maximum of the polymerization reaction indicate different cure kinetics. Shorter time and highest heat flow at the maximum is an evidence of a faster polymerization. Total heat released is obtained by integrating the curves shown in Fig. 1 using Origin 7.0 software (Fig. 2).
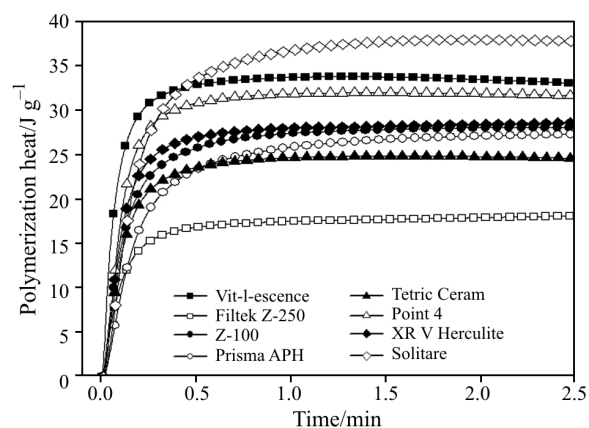
Fig. 2 Heat of polymerization *vs.* time

The baseline used in these calculations is shown in the same figure and was adopted because the heat flow after the deceleration process is occasioned by light absorption and not by the polymerization process.

The total heat released and the time that the heat becomes constant during polymerization reaction varies from one composite to another. It is proportional

Table 1 Values obtained from photocalorimetric and thermogravimetric measurements

Commercial composites	Heat flow at the peak/W g^{-1}	Time at the peak/s	Filler content/%	Polymerization acceleration/J g^{-1} s^{-2}	Total polymerization heat/J g^{-1}
Vit-l-escence	9.2	1.27	73.4	9.9	33.9
Filtek Z-250	4.3	1.75	78.1	3.7	18.0
Z-100	4.6	1.89	79.5	3.3	27.7
Prisma APH	3.7	4.22	75.3	2.0	25.6
Tetric Ceram	4.9	2.39	77.4	3.8	25.1
Point 4	5.8	3.27	71.1	2.6	33.4
XRV Herculite	5.1	2.77	75.9	3.0	28.3
Solitaire	4.9	4.49	73.2	2.5	37.4

to the number of vinyl groups converted and therefore the different results obtained can be related to a higher C=C density or to a highest degree of conversion due to a most efficient photoinitiator system.

The results suggest that e.g. for the Z-100 product should have a higher vinyl density compared to Filtek Z-250. As the filler content influences the vinyl density and consequently the heat released during polymerization, the thermogravimetric measurements of the composites was performed and the results are shown in Fig. 3.
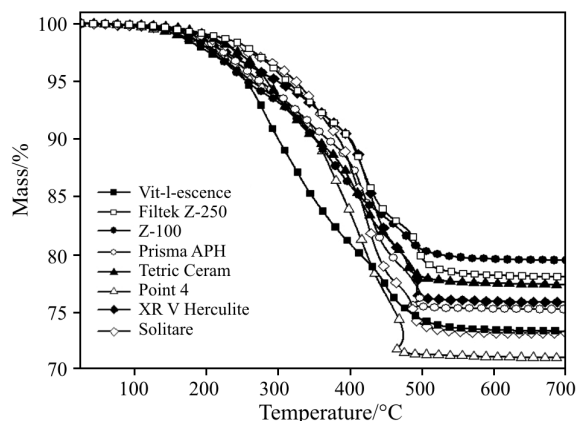
Fig. 3 TG curves of the uncured commercial dental composites

Although Z-100 releases more heat during polymerization compared to Z-250, it has higher filler content. This fact indicates that in the Z-250 formulation there are monomers/oligomers with large molecular masses or pre-polymerized resin particles causing a decrease in the C=C density. The profiles of the plots obtained during the thermogravimetric measurements suggest that all composites except the Vit-l-escence have very similar compositions. The unusual behavior presented by Point 4 during the TG run at around 450–500°C, where was a temperature decrease as the reaction preceded can be explained by a strong exothermic event exceeding the established heat rate. Furthermore, the filler content varied significantly for the different composites and this is related directly to the total heat released during polymerization. In general, for resins with higher filler contents a lower heat release was observed.

Finally, by fitting a straight line to the experimental data points referring to the region of the auto-acceleration stage of Fig. 1, accelerating values of the reaction can be obtained. Table 1 gathers all results.

The Solitaire product presented the highest number of vinyl groups converted while the Filtek Z-250 presented the lowest one. This can be related to the factors already cited. Vit-l-escence presented the most accelerated reaction while Prisma APH presented the least one.

It should be stressed out that the different values obtained in this study are not an indicative of the quality of the composites, which is related also to other characteristics like color stability, chemical and mechanical resistance, shrinkage during polymerization, adhesion to the teeth, etc.

Conclusions

Photocalorimetry is an important tool to obtain kinetic parameters as a function of the number and nature of photopolymerizable groups. Moreover, organic and inorganic counterpart ratio may be readily evaluated. A preliminary analysis with known commercial products was performed showing important variations in the photopolymerization process.

Acknowledgements

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