

Thermal analysis of light-curing composites

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Abstract The aim of this study has been to evaluate light-curing composites polymerization quality (monomer/polymer) with an halogen and diode lamp through the thermal analysis (TG-DTA). Samples have been polymerized at 20, 40 and 50 s through a constant and a soft start polymerization and, subsequently, analyzed by TG-DTA. The TG/DTA analysis shows that different light-curing times affect the degree of conversion of the composite, since by increasing the curing time the quantity of the monomer that has not reacted (residual) decreases. The halogen lamp, compared to the diode lamp, produces a lower mass loss at 20 s, while for 40 and 50 s the results are overlapping. The soft start polymerization (20 s) initially produces a higher mass loss, if compared to the constant intensity, but, by performing a polymerization for at least 40 s, the results can be overlapped.

Keywords Thermal analysis · TG-DTA · Polymerization · Composite

Introduction

Dental composite materials are extensively used in dental field; these materials are composed basically by two phases: a resinous matrix (organic phase), comprising dimethacrylate monomers and/or oligomers, photoinitiator, and an inorganic phase, known as filler, generally composed by particulate glass [1]. When the composite resins

are irradiated, the radicals generated attack the double bonds of the monomers, creating cross-linked three-dimensional network polymers [2]. The main monomers/oligomers used in the resinous matrix 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 and barium aluminium silicate are used as fillers which normally are surface modified by a coupling agent aiming to improve mechanical properties [3, 4]. Nevertheless, several problems concerning the lack of mechanical resistance mainly associated with restoration in posterior teeth and heterogeneity in the polymerization frequently are mentioned as drawbacks for the use of polymer restoration dental composites as repairing materials. Both problems are related to the polymerization process responsible for the formation of the crosslinking network that provides mechanical resistance and hardness to the final composite [5, 6].

The knowledge of polymerization mechanisms offers the possibility to check the properties of the material set in cavity. The degree of conversion (DC) of conventional dental composites depends on several factors: power and intensity of the bright source, time and distance of irradiation, dimensions of the particles of the filler, etc. [7–10]. Therefore, a lower DC value is expected to cause a premature failure of the restoration because of increasing wear, precocious staining and marginal microleakage [11–15].

Besides, in a wet environment, as the oral cavity, the residual unpolymerized monomer pours out from the polymerized material [16–18] and it is well known that this can cause several problems, such as toxic effects in the pulpal cells [19–23].

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Many experimental techniques have been used to study the DC or the number of ethylene double carbon which are converted into single bonds [24–26].

It has been demonstrated that the validity of the thermal analysis to evaluate light-curing composites conversion degree, differential thermal analysis (DTA) and thermogravimetry analysis (TG) are thermal analysis techniques. DTA is used to gather information on transitions, heats and kinetic of reaction, and others. TG have been used to quantify the inorganic part of dental composites and the rate of mass change, respectively [27, 28].

The aim of this study is to evaluate light-curing composites polymerization quality with an halogen and diode lamp through the thermal analysis (TG-DTA).

Materials and methods

The materials used were Gradia Direct (GC, USA), X Duo Ceram (Dentsply, UK), Enamel Plus HFO (Micerium, Italy); resins composite composition has been showed in Table 1. Samples have been prepared with 2-mm thickness and a 4-mm diameter by a stainless steel matrix to obtain an equivalent mass of about 50 mg. Before proceeding with the TG/DTA analysis, a double weighing with a Gibertini electronic (mod. E42, Milano, Italy) and a TG/DTA scale is made, through which the following thermogravimetric analyses have been carried out. Eight

samples of each material (number of materials = 3) for each group (number of groups = 9) have been cured (216 samples total analysis) according to the Table 2.

Moreover, five samples of each material (controls) underwent TG-DTA cycles without light-curing procedures (15 controls total analysis).

The light intensity was 1200 mW/cm² (Mini Led Sat-elec, Acteon Group, Merignac, France) and 450 mW/cm² (Spectrum 800 Dentsply Caulk, Milford, USA).

Simultaneous thermal analyzer was used to measure the mass change and heat effects (TG-DTA) of dental composites performed by TG/DTA 6300 (Model TG/DTA 6300, Seiko Instruments Inc. Torrance, CA, USA). The samples were heated at a constant rate of 10 °C min⁻¹, from 25 to 600 °C under nitrogen atmosphere (100 mL/min).

In our figures, values are represented up to 500 °C to remark peaks, as we did not observed other significant differences between all materials while reaching 600 °C.

In the figures, we also used the curves of a single composite because all samples showed a similar behaviour.

Statistical analysis

Fisher's PLSD, Scheffe and Bonferroni/Dunn were used to evaluate the presence of statistically significant differences. We did not insert the standard deviation because curves are often overlapped.

Table 1 The resin composite composition

Materials	Manufactures	Inorganic filler/wt%
Gradia Direct	GC	Methacrylate monomers 27%, silica 38%, pre-polymerised filler 35%, pigments, catalysts Inorganic filler: n.d.
Enamel Plus HFO	Micerium	Glassfiller silanized, siliciumoxide silanized, Bis-Gma, urethandimethacrylate, butandioldimethacrylate and pigments Inorganic filler: 75 wt%
X Duo Ceram	Dentsply	Methacrylate modified polysiloxane, dimethacrylate resin, fluorescence pigment, UV stabilizer, stabilizer, Camphorquinone, ethyl-4(dimethylamino)benzoate, barium-aluminium-borosilicate glass, methacrylate functionalised silicon dioxide nano filler, iron oxide pigments and titanium oxide pigments and aluminium sulfo silicate pigments according to shade. Inorganic filler: n.d.

Results and discussion

Table 3 gather properties of the composites taken from the TG curves: temperature of 5% mass loss (thermal stability) [28]; residues at 600 °C (filler content after burning the polymeric matrix). The percentage differences regarding the mass loss resulted by the differences of materials compositions, organic/inorganic compositions ratio.

It is well known that during the preparation of the light-curing composite resins, the laboratories work first the inorganic part by making it react with the silane (silanization process), and second, in the clinical phase, through the photopolymerization, the reaction of the organic and inorganic part is fulfilled [2, 18]. The final product of these chemical interactions between silane and filler is affected by the silanization that brings to the creation of reactive molecules on the filler-silane interface; the subsequent photopolymerization of the matrix with the silane-filler reactive molecules gives a more stable final product that improves the composite physical capacities. The TG/DTA analysis allows to highlight the points where the resinous parts (silane and matrix) deabsorb [9, 29, 30].

Table 2 The light-curing modes

Lamp	Polymerization time		
	20 s	40 s	50 s
Spectrum 800	Constant intensity (Group A)	Constant intensity (Group B)	Constant intensity (Group C)
Mini LED	Soft start polymerization (Group D)	20 s Incremental + 20 s constant intensity (Group E)	20 s Incremental + 30 s constant intensity (Group F)
	Constant intensity (Group G)	Constant intensity (Group H)	Constant intensity (Group I)

Table 3 Thermogravimetric (TG) results (%)

Materials	Temperature of 5% mass loss/±2 °C					Mass loss at 600 °C/%
	Mini LED			Spectrum 800		
	20 s Soft start polymerization	20 s Constant intensity	50 s 20 s Incremental + 30 s constant intensity	20 s Constant intensity	50 s Constant intensity	
Gradia Direct	304	322	328 330 ^a	325	329	49.62 ± 0.57%
Enamel Plus HFO	337	339	343 344 ^a	340	345	24.98 ± 0.21%
X Duo Ceram Dentsply	375	387	393 394 ^a	388	394	19.45 ± 0.23%

^a Samples cured 50 s with constant intensity

Figure 1 shows the representatives TG-DTA curves obtained with the composite resins, uncured and cured. The DTA curves exhibited exothermic peaks below ~200 °C which are due to the curing of the sample. The endothermic DTA peaks between ~250 and ~500 °C are due to the mass losses. Thermal stability and degradation of the dental composite resins were monitored by measuring their TG curves. These results have to be attributed to the visible light-cure that creates the cross-linked network polymers and due to the interaction between the polymer chains and inorganic particles. Cross-linked network consequently prevents the dental composite resins from thermal decomposition by the enhancement of their thermal stability.

Figure 2 compares the uncured and cured (40 s) TG curves samples: non-cured composite (a) has shown a mass loss of 5.7% at 270 °C and 14.9% at 350 °C, on the other hand cured composite (b) has shown a mass loss of 0.4% at 270 °C and 7.4% at 350 °C. At about 270 °C, mass loss is most probably caused by the weak bonds (hydrogen or Van der Waals strengths) break-up between monomer and silane, and by the loss of the same molecules that have not reacted [31, 32]. On the other hand at about 350 °C, we observe a mass loss due to the break-up of the strong (covalent) silane–silane, silane–filler and silane–resin bonds.

Figure 3 shows TG analysis curves expressing composites thermal behaviour, cured, respectively, in 20 and

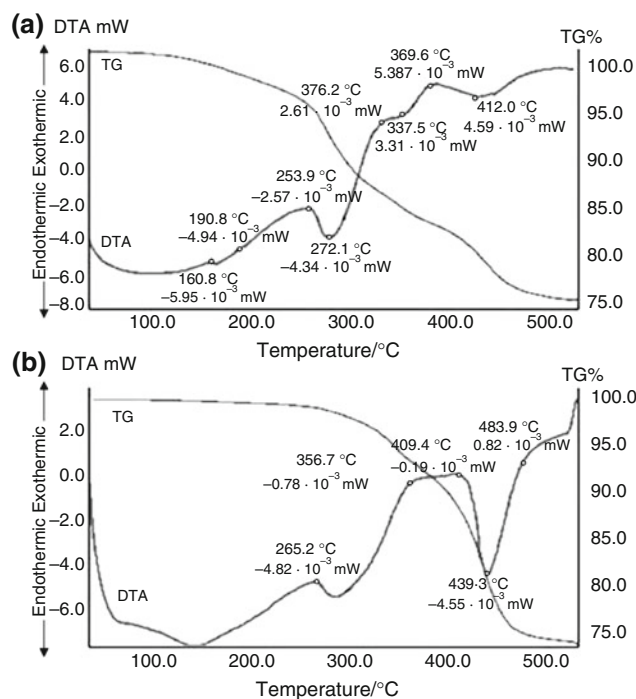


Fig. 1 TG-DTA curves for uncured (a) and cured (b) composite resins

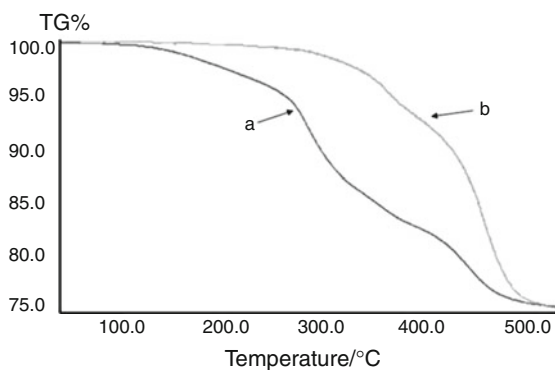


Fig. 2 Comparative TG curves for Enamel Plus HFO: (a) uncured (five samples), (b) cured in 40 s (eight samples). There are statistically significant differences at $p < 0.001$ level: curve a vs. curve b

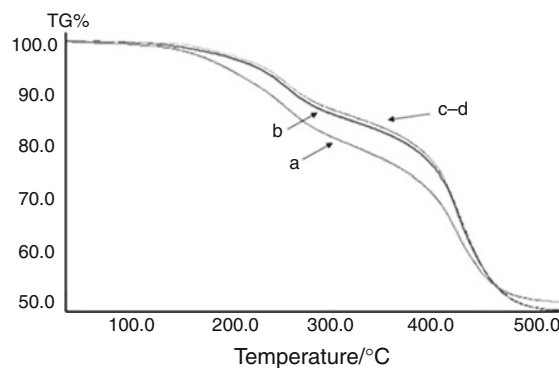


Fig. 4 Comparative TG curves of dental composite cured with a diode lamp: (a) 20 s (soft start polymerization), (b) 20 s (constant intensity), (c) 50 s (20 s soft start polymerization + 30 s constant intensity), and (d) 50 s (constant intensity). There are statistically significant differences at $p < 0.001$ level: curve a vs. curve b, curve a vs. curve c-d, and curve b vs. curve c-d

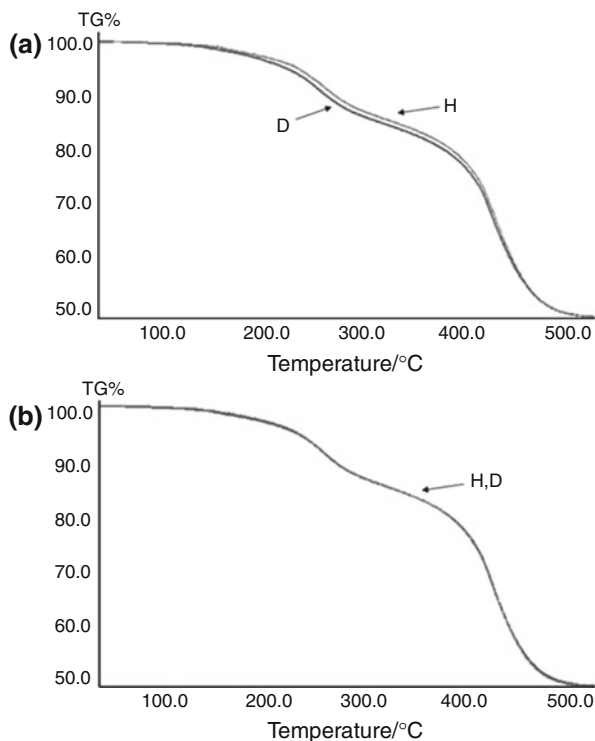


Fig. 3 Comparative TG curves for Gradia Direct GC cured in 20 s (a) and 40 s (b) (constant intensity): D diodes lamp, H halogen lamp

40 s by halogen and diodes lamps. It is possible to observe a higher thermal stability of samples cured by halogen lamp at 20 s, but this does not mean that is clinically better because many factors can interfere with the efficient functioning of halogen units including: fluctuations in the line voltage; the condition of the bulb and filter; contamination of the light guide; damage to the fibre-optic bundle, and heat buildup within the unit [33]. Moreover, at 40 and 50 s the curves overlap.

On the other hand, it is always necessary to consider the polymerization contraction problems; for this reason, lamps allowing a polymerization at ramped curing have been produced. Figure 4 shows diode lamp cured samples; it has been carried out a differentiation between the light-curing techniques (soft start and constant intensity). The 20-s soft start polymerization show a higher mass loss than samples cured constant intensity 20 s technique, whereas curing time increases, the curves tend to overlap.

Therefore, it is evident that the importance of a correct polymerization in the clinical procedure, to avoid the release of the monomer, improves the physical-chemical characteristics of the material and, so, make the restoration more lasting.

It is important to emphasize that in this study a quality comparison between the materials has not been made.

Conclusions

The thermal behaviour of all samples was investigated using simultaneous TG/DTA methods. The TG/DTA analysis shows different thermal behaviours between samples. The halogen lamp, compared to the diode lamp, produces a lower mass loss at 20 s, instead at 40 and 50 s the results overlapped. Diode lamp soft start polymerization (20 s) initially produces higher mass loss compared to the constant intensity, instead at 40 s the results overlapped.

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