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Characterization of dental composites by thermal analysis, infrared spectroscopy and scanning electron microscopy

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Abstract Commercial light-cured dental composites were used in this study. Two laboratorial composites, Resilab (Wilcos/Brazil), Epricord (Kuraray/Japan) were compared under cured and uncured conditions. Thermal analysis, infrared spectroscopy and scanning electron microscopy were used to evaluate the dental composites. The mass change and heat flow signals (TG–DSC) were recorded simultaneously by using STA 409 PC Luxx (NETZSCH), in the 25–800 °C temperature range at a heating rate of 10 °C/min under nitrogen atmosphere (70 mL/min). Employing thermo-microbalance TG 209 C F1 Iris (NETZSCH) coupled to the BRUKER Optics FTIR TENSOR, the samples were analyzed by combined thermogravimetric and spectroscopic methods (TG–FTIR). The initial sample mass was about ~12 mg, the data collection have been done in the 35–800 °C temperature range at a heating rate of 20 K/min in nitrogen atmosphere (flow rate: 40 mL/min). Finally, superficial topographic was analyzed by scanning electron microscopy (SEM). Dental composite evaluation suggests a high thermal stability and inorganic content in RES D sample. Degrees of conversion (DC) values were almost the same and there was no direct relationship between DC and amount of particles and size. Similar compositions were found in all samples.

Keywords Dental composites · Thermal analysis · FTIR

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 polymeric matrix, comprising dimethacrylate monomers and/or oligomers and an inorganic phase. The main monomers/oligomers used in the resinous phase are bisphenylglycidyl dimethacrylate (BisGMA), triethylene glycol dimethacrylate (TEGDMA) and urethane dimethacrylate (UDMA). Silicate based glasses, zirconia, alumina, quartz; pyrogenic silica and barium aluminum silicate are used as fillers, normally surface modified by a coupling agent. This interphase is typically derived from organosilanes and is designed to chemically bind to the matrix and filler phases with aiming to improve the mechanical properties [1–3].

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 [4–6]. The degree of conversion (DC) of conventional dental composites depends on several factors, such as the organic and inorganic components, specimen geometry, amount and type of the photoinitiator and light intensity [7, 8]. Therefore, a lower DC value is expected to cause a premature failure of the restoration because of increasing wear, precocious staining, and marginal microleakage [9]. According to their particle size, the available commercial composites are classified to three

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main categories: microfilled (~0.04 µm), hybrid (>1 µm) and microhybrid (<1.0 µm) [10, 11].

Among the several available experimental techniques to study the degree of conversion (DC) or the number of ethylene double carbon which are converted into single bonds, infrared spectroscopy (FTIR) is the most frequently used one. This technique allows evaluating the composite before and after curing. On the other hand, differential scanning calorimetry allows quantify the heat liberated or absorbed in cure reaction. Since polymerization is an exothermic reaction, DSC analysis permitted the degree of conversion of composites to be monitored [12, 13].

Differential scanning calorimetry (DSC), thermogravimetry (TG) and its derivate (DTG) are thermal analysis techniques. DSC is used to gather information on transitions, heats and kinetic of reaction, and others. TG and DTG have been used to quantify the inorganic part of dental composites and the rate of mass change, respectively [12, 14].

In this study, the simultaneous TG–DSC and TG–FTIR techniques were used to analysis dental composites. Topographic superficial was analyzed by Scanning Electron Microscopy (SEM).

Thus, the purpose of this study was to evaluate the degree of conversion and the amount of filler of two different commercial dental composites by DSC and TG; the principal chemical groups presents in the samples by FTIR; to identify its superficial topography by SEM and to relate these parameters to the final properties of the composites.

Materials and methods

Specimen preparation

Commercial dental restoration composites named Resilab (shade A2-dentine) manufactured by Wilcos (Brazil) and Epricord (shade A2-dentine) manufactured by Kuraray (Japan), cured (C) and uncured (NC), were evaluated. Before cure the sample was pressed by two glass plates into 2 mm thick and placed in a light curing unit and exposed from the top for 3 min. (Table 1). After that, the samples were left in dry place without light.

Characterization of composites

Simultaneous thermal analyzer was used to measure the mass change and heat effects (TG–DSC) of dental composites performed by STA 409 PC Luxx (NETZSCH).

About ~15 mg of each sample was measured between 25 and 800 °C, at a heating rate of 10 °C/min under nitrogen atmosphere (70 mL/min). Data acquisition and evaluation, as well as instrument control was carried out using a MS-Windows software package. The software allows the computation of the rate of mass change, mass change steps, onset and peak temperatures, inflection points, peak area integration etc.

Employing thermo-microbalance TG 209 C F1 Iris (Netzsch) coupled to the Bruker Optics FTIR Tensor, the samples were analyzed by thermogravimetric and spectroscopic methods (TG–FTIR). With initial mass of ~12 mg, the analysis was conducted from 35 to 800 °C at a heating rate of 20 K/min in nitrogen (flow rate: 40 mL/min). For control of the measurements as well as for data acquisition, digital electronics Netzsch Proteus 32-bit Software were employed. Data exchange between Netzsch Proteus software and Bruker Opus software was done online during the measurement.

The conversion rate of dental composite after curing light irradiation was determined by measuring the residual heat of reaction. The following equation shows the way of calculation: Conversion = (Residual heat of reaction obtained from the sample after irradiation)/(Heat of reaction obtained from sample without irradiation) × 100%.

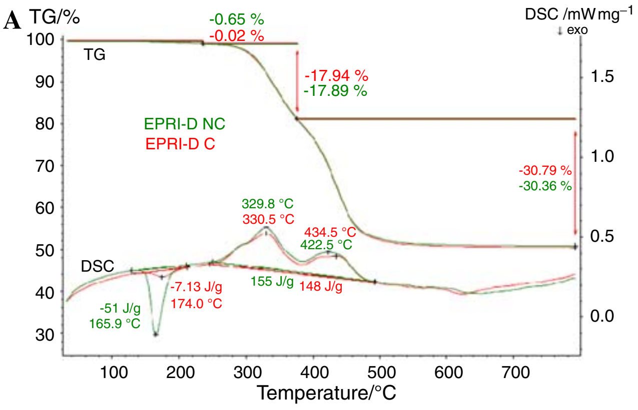
SEM micrographs were obtained from the fractured samples by Scanning Electron Microscopy, JEOL, model JSM 5610LV.

Results and discussion

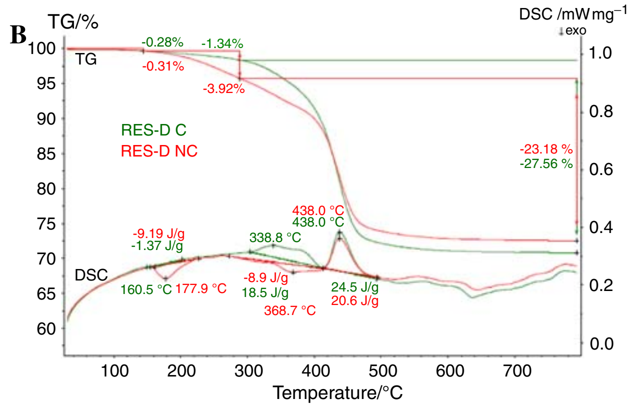
Figure 1 depicts the mass changes (TG) and heat flow curves (DSC) of non-cured and cured, EPRI-D NC and

Table 1 Commercial composites and selected details according the suppler

Brand	Designation	Monomer	Filler	Classification	Spectral irradiance/nm	Time cure/min	Light	Cure Equipment
Epricord	EPR D	Methacrylate multi-functional	Microfilled	Hybrid	320–400	3.0	Ultraviolet	Kota Lux, Brazil
Resilab	RES D	BisGMA BisEMA UDMA TEGDMA	88% SiO_2, quartz, Ba–Al silicate (~0.05 mm)	Hybrid	320–400	3.0	Ultraviolet	Power Lux, EDG, Brazil



Samples EPRI D



Samples RES D

Fig. 1 TG–DSC curves of dental composites

EPRI-D C samples, respectively. The two samples showed almost identical TG curves. The mass loss steps of 0.6, 17.9 and ~30.6% are most probably due to the evaporation of humidity and solvents and the decomposition of the polymer content.

The DSC curves exhibited exothermic peaks below ~200 °C which are due to the curing of the sample. The non-cured sample showed a significantly larger curing peak (−51 J/g) than the cured one (−7 J/g) which was obviously not fully cured before the experiment. The endothermic DSC peaks between ~250 °C and ~500 °C are due to the mass losses. The RES-D NC and RES-D C samples showed a significantly different decomposition behavior. The curing peaks were significantly smaller compared to the samples discussed above.

Figure 2 compares the TG curves for all samples. The results are comparable to the results of STA measurements. EPRI D NC and EPRI D C samples do not differ that much but in case of samples RES D, the thermal behavior is significantly different depending on the cured and non-cured state. The final mass represents the content of pyrolytic residues.

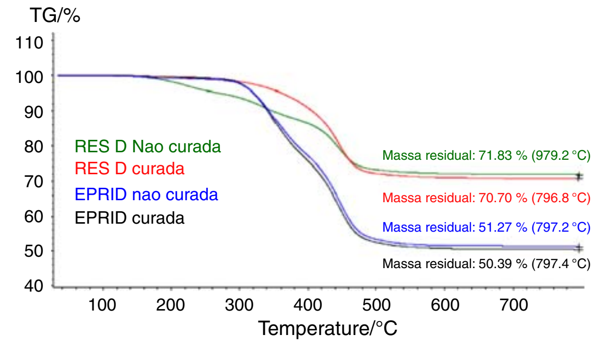


Fig. 2 Comparative TG curves for all samples

Table 2 Thermogravimetric (TG) results

Samples	Temperature of 5% mass loss/°C	Residues at 800 °C/%	Degree of conversion/%
EPR D	320	50,39	86,02
RES D	350	70,70	85,09

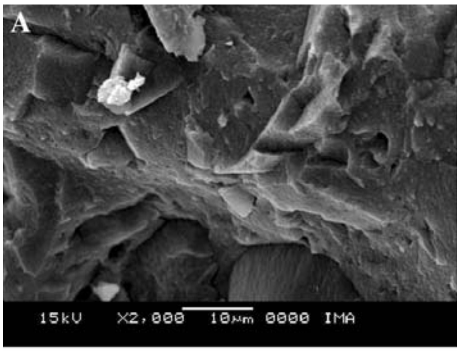
Table 2 gather the properties of the composites taken from the TG curves: temperature of 5% mass loss [13] (thermal stability); residues at 800 °C (filler content after burning the polymeric matrix) and degree of conversion (the number of ethylene double carbon with are converted into single bonds).

Thermal stability in RES D was higher than EPR D (350 vs. 300 °C). This result from the presence of inorganic filler, which greatly reduces chemical bond movement of the organic component in thermal decomposition and RES D showed higher filler content. Additionally, interfacial interactions particle–matrix increase thermal stability [3, 4]. SEM micrographs in Fig. 3 showed RES D with particles size know as microhybrid composite. These materials incorporate a high volume-fraction of filler particles, with a mean size below 1 µm, and narrow particle size distribution [9]. On the other hand, EPR D micrographs showed larger particle size distribution (5–50 µm) and particle shapes suggests absence of interfacial layer (silane). This can affect interfacial interactions and thermal stability [3].

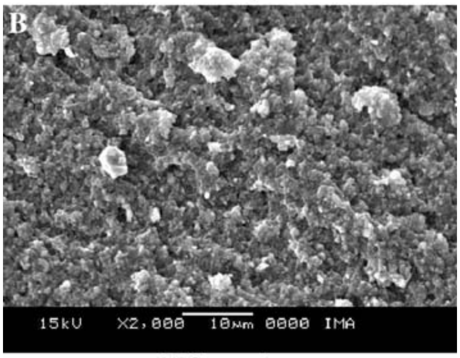
Samples RES D and EPR D showed almost the same degree of conversion (85% vs. 86%). The diversity of values found in the available literature on degree of conversion is essentially related to the composition.

The chemical and structural nature of the monomers and fillers, as well as their relative content directly influences the DC value.

With respect to filler, factors like the type, amount, particle size and distribution influences DC. Light can be scattered between matrix and particle interfaces and be absorbed by both; this results in a continuous decrease in the light intensity during the cure reaction in dental composites.



EPR sample



RES sample

Fig. 3 SEM micrographs (N = 2000)

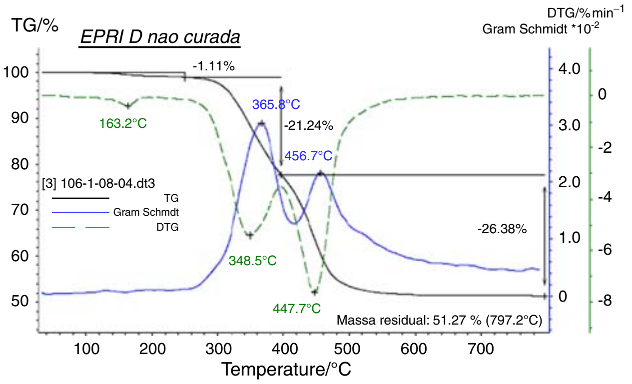


Fig. 4 TG, DTG and Gram-Schmidt curves of EPRI D non-cured sample

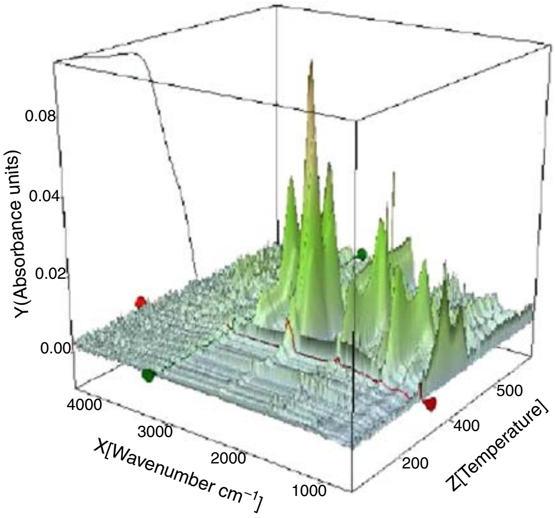


Fig. 5 TG curve and 3D view of all detected IR-spectra *vs.* temperature of EPRI D sample

Scattering of light in dental composites is straightforwardly proportional to refractive index and inversely proportional to the particle diameter. If the particle size is around 1 µm and the wavelength of the incident light is around 0.32–0.40 µm (UV; Table 1), large light scattering is expected [15].

Larger filler size and lower filler concentration (~50%) in EPR D caused the same curing rate than RES D with smaller filler size and higher filler concentration. Thus, the DC was not affected by filler in this study. Recent studies have reported to similar results [5, 16].

Figure 4 shows the TG and DTG curves (black solid and green dashed lines, respectively) for uncured EPRI D. The DTG line represents the rate of mass change. Corresponding to this, the Gram–Schmidt trace (blue line) indicates that the evolved compounds are IR-active. A collection of all detected IR-spectra is shown in Fig. 5.

The 3D-cube is temperature scaled and additionally the TG-signal is depicted at the side face. The Gram–Schmidt trace is more or less the mirrored view of the DTG curve (dashed green line), it shows that the gases—as soon as they are released and transferred to the gas cell—are interacting with the infrared beam.

From the 3D-cube, single spectra are extracted at 374 °C (blue) and 442 °C (red; Fig. 6). The measured data is compared with library data in order to identify the released gases. A good correlation of the measured data to the spectrum of formic acid butylester (green) and carbon dioxide (black) indicates the formation of compounds containing carboxylic functional groups (1,750 cm^{-1}) and alkyl groups (2,950 cm^{-1}), suggesting the dimethacrylate presence in the samples.

Additionally, CO_2 is formed as indicated by the library data (black) from de decomposition of the polymeric content. The absorbance intensities are very similar for all the four samples. This indicates that basically similar compounds as discussed above are evolved for all samples.

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

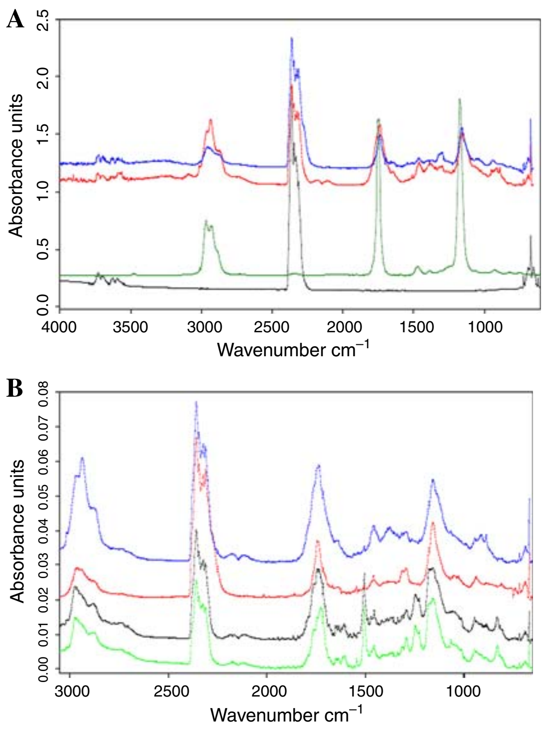


Fig. 6 Single spectra of sample and comparison with library data (**a**), single spectra of all samples (**b**). **a**—EPRI D non-cured at 374 °C (*blue*), 442 °C (*red*), formic acid, butyl ester (*green*) CO_2 (*black*). **b**—EPRI D non-cured (*blue*), EPRI D C (*red*), RES D C (*black*) and RES (Color figure online)

Conclusions

The thermal behavior of all samples was investigated using TG–FTIR and simultaneous TG–DSC methods. The decomposition behavior with identification of the evolved compounds is useful information for the characterization of the thermal properties of the samples. In addition, dental composite evaluation suggest a high thermal stability and inorganic contend in RES D sample. With respect to the degree of conversion the DC values for RES D and EPR D were almost the same and there was not a direct relationship between DC and the amount of particle and size. FTIR analysis of all cured and non-cured samples indicate the formation of compounds containing carboxylic functional groups, alkyl groups and CO_2 indicating similar compounds in the samples.

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