

Thermal behavior of direct resin composites: glass transition temperature and initial degradation analyses

Comportamento térmico de resinas compostas de uso direto: temperatura de transição vítrea e temperatura de degradação inicial

Abstract

Purpose: The association of direct resin composites with simple thermal treatments may improve the mechanical properties of these materials. However, the ideal temperature for heat application depends on the thermal behavior of each material, such as glass transition (T_g) and initial degradation temperatures. To propose a heat treatment methodology, this study evaluated the thermal behavior of five commercial direct resin composites using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA).

Methods: Photo-irradiation was achieved in cylindrical specimens (3×2 mm) using a photo-activator source (600 mW/cm² for 40 s). Thermal analyses were performed by DSC and TGA using a temperature range from 25 °C to 900 °C.

Results: T_g values obtained by DSC were 130.6 °C for FillMagic, 129 °C for Glacier, 143.5 °C for Te-Econom, 147.5 °C for Prisma APH and 143.7 °C for Natural Look. A moderate weight loss began at around 270 °C for all materials, which represented the initial degradation temperature.

Conclusion: Regarding the heat treatment itself, it was concluded that the effective temperature for heat treatment is material dependent.

Key words: Dental composite; thermal treatment; DSC; TGA

Resumo

Objetivo: A associação de resinas compostas de uso direto com tratamentos térmicos pode melhorar as propriedades mecânicas destes materiais. No entanto, a temperatura ideal de aplicação está na dependência do comportamento térmico individual, como a temperatura de transição vítrea (T_g) e a temperatura inicial de degradação. Com o objetivo de propor uma metodologia de aplicação do tratamento térmico, o objetivo deste trabalho foi caracterizar cinco resinas compostas de uso direto usando calorimetria exploratória diferencial (DSC) e termogravimetria (TGA).

Metodologia: Corpos-de-prova cilíndricos (3×2 mm) foram fotoirradiados utilizando um aparelho de fotopolimerização (600 mW/cm² – 40s). As análises térmicas foram realizadas nas temperaturas de 25 °C a 900 °C.

Resultados: Os valores de T_g após análise de DSC foram: 130,6 °C para FillMagic, 129 °C para Glacier, 143,5 °C para Te-Econom, 147,5 °C para Prisma APH e 143,7 °C para Natural Look. Para todos os materiais estudados a degradação iniciou-se por volta de 270 °C.

Conclusão: Considerando a aplicação do tratamento térmico em resinas compostas de uso direto, é possível sugerir que a temperatura efetiva é dependente do material em uso.

Palavras-chave: Resina composta; tratamento térmico; DSC; TGA

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Introduction

Since direct resin composites were developed as an aesthetic and more conservative alternative to silver amalgams, many efforts have been made to increase the longevity of dental restorations. Although several improvements have been made, mechanical properties such as wear, fracture resistance and hardness are challenged by chewing forces and microleakage caused by polymerization contraction stress (1).

One possible way to minimize the problems related to microleakage and polymerization stress is to use aesthetic indirect composite bonded restorations instead of direct composites (2). In the indirect technique, specific resin systems are applied to the damaged tooth area to form a cast restoration that is then heat-treated using special ovens under controlled laboratory conditions (3,4). The heat treatment improves mechanical properties and contributes to the relief of stresses that originate during the resin polymerization and finishing procedures (4-6). However, the disadvantage of this technique is the high cost, because special equipment are required for the laboratory process (3,7,8), and the increase in the number of required appointments.

Direct resins and resin systems for indirect use display similar compositions (9,10). Therefore, many authors have proposed that the association of direct composites with simple thermal treatments may produce similar results when compared to the indirect technique, such as the improvement in material cure, thus enhancing clinical and mechanical properties (9-14). An advantage would be the lower cost because the special ovens could be replaced by other heat sources, such as cast furnaces or auto-claves (13), which are commonly available in a prosthetic laboratory and dental offices.

However, the ideal temperature for heat treatment application depends on the thermal behavior of each

composite, such as glass transition temperature analysis (T_g) and initial degradation temperature (14). The T_g can successfully be used as a reference to sign the ideal heat treatment for photo-irradiated resin composites. Above T_g , the secondary molecular interactions are weakened and, as a consequence, material properties are optimized once trapped radicals are given the opportunity to react (7,15). In addition, the maximum temperature for heating without damaging, *i.e.*, initial degradation temperature, needs to be determined to avoid weight loss (13,14).

Thermal analysis techniques using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) are suitable for examining the characteristics of polymers (6,13,14,16-18). DSC techniques assess the energy (enthalpy) absorbed or released by a specimen during a temperature increase, decrease or even at isothermal conditions. With this method, it is possible to identify the critical temperature, such as T_g , for the analyzed material. TGA is a precise quantitative method for determining combustion, volatilization and decomposition by analyzing weight alterations (gain or loss) of a specimen as a function of temperature and/or time (13).

The objective of our research group has been to study the clinical performance of different heat-treated direct resin composites. However, the determination of specific critical temperatures for each composite studied was still not a focus. To propose a heat treatment methodology, this work examined the thermal behavior of various commercial direct resin composites using DSC and TGA analysis.

Methods

Five commercial direct resin composites were evaluated. Technical specifications of the materials are listed in Table 1.

Table 1. Technical specifications of direct resin composites according to the suppliers.

Composite	Manufacturer	Characteristic	Composition		Batch n.
			Organic Matrix*	Filler	
<i>FillMagic</i>	Vigodent S.A. Ind. Com. Bonsucesso, RJ, Brazil	Micro-hybrid composite	bis-GMA, bis-EMA, TEGDMA and UDMA	Barium and aluminum silicate glass and pyrogenic silicon (0.5 μm). 80% wt.	129/08
<i>Glacier</i>	SDI Limited Bayswater, Victoria, Australia	Condensable micro-hybrid composite	Multifunctional methacrylic ester	Strontium glass and amorphous silica (0.4-1.0 μm). 81% wt.	07/0507
<i>TE-Econom</i>	Ivoclar Vivadent, Schaan, Liechtenstein	Hybrid composite	bis-GMA, TEGDMA and UDMA	Barium glass, aluminum and barium fluorosilicate glass, high/dispersed silicon dioxide and mutual spheroid oxides (1.0 μm). 72% wt.	16366
<i>Natural Look</i>	DFL Ind. Com, RJ, Brazil	Micro-hybrid composite	bis-GMA bis-EMA TEGDMA	Barium crystal glass and amorphous silica (0.5 μm). 77% wt	08050692
<i>Prisma APH</i>	Dentsply Ind. Com. Petrópolis, RJ, Brazil	Hybrid composite	Modified urethane	Barium and aluminum silicate, silanized barium, pyrogenic silicon (1.0 μm).	091391B

* bis-GMA = bisphenol A-glycidyl dimethacrylate; bis-EMA = bisphenol diethylmethacrylate; TEGDMA = triethylene glycol dimethacrylate; UDMA = urethane dimethacrylate.

Specimen preparation

Specimens were prepared in a cylindrical mould with a 3 mm diameter and a 2 mm height; there were thirty specimens in each one. The mould was positioned over a polyester film (Mylar, Labordental Ltda., São Paulo, SP, Brazil) lying over a glass slab. A single bulk of each resin composite was inserted into the mould and then covered with another piece of Mylar film. To standardize composite thickness, a glass slide was pressed over the film allow excess material extrusion from the mould. After excess removal, the upper surface was irradiated for 40 s using a 600 mW/cm² photo-activator source (Ultraled, Dabi Atlante, Ribeirão Preto, SP, Brazil) with a 12 mm diameter tip that was in contact with the Mylar film. The device irradiance was measured by a radiometer (serial #111231, Demetron Research Danbury, CT, USA). The irradiated face of each specimen was then identified using a permanent marker. After being removed from the mould, specimens were submitted to finishing with a number 15 scalpel (Lamedid Comercial e Serviços Ltda., Barueri, SP, Brazil). Immediately after the specimen preparation, specimens were stored in dark boxes at 37°C for 24 h.

DSC and TGA analyses

Thermal analyses were simultaneously performed by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) using a single device (STA Jupiter 449, Netzch, Brazil). Temperatures ranged from 25°C to 900°C under high purity argon atmosphere (20 mL/min) and were at a heating rate of 10°C min⁻¹ using ceramic crucibles. The equipment was calibrated with barium carbonate (BaCO₃), cesium chloride (CsCl), potassium chromate IV (K₂CrO₄) rubidium nitrate (RbNO₃) and benzoic acid (C₆H₅COOH) as standards. For both tests, curves were obtained with empty crucibles in the same experimental conditions of the tests (baseline). Those baselines were used to correct the thermo analytical curves of the samples. Descriptive statistics were calculated using the BIOESTAT 5.0 program.

Results

In Figures 1 through 5, representative derivative curves were calculated to assist the identification of the thermal events of each direct resin composite. Mean values and standard deviations for T_g and degradation temperatures are represented in Table 2. The T_g values obtained by DSC analyses were 130.6°C for FillMagic, 129 °C for Glacier, 143.5°C for Te-Econom, 147.5°C for Prisma APH and 143.7°C for Natural Look. TGA revealed that the weight loss and consequent initial degradation for all resin specimens occur in steps. For temperatures above 270°C, there was a significant weight loss, which may have been due to the unreacted monomer volatilization or other degradation processes.

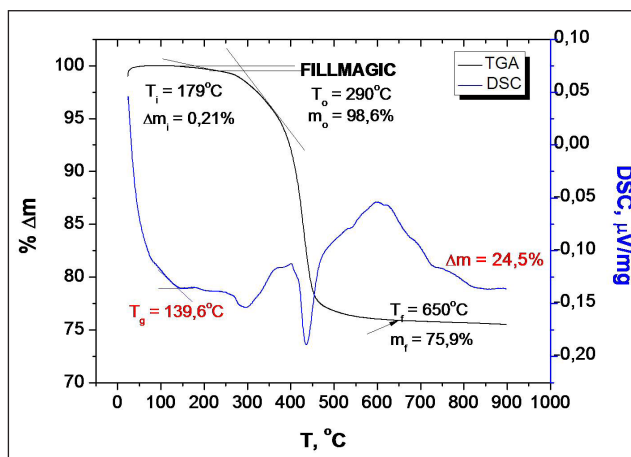


Fig. 1. Representative thermogravimetric and derivate curves for FillMagic.

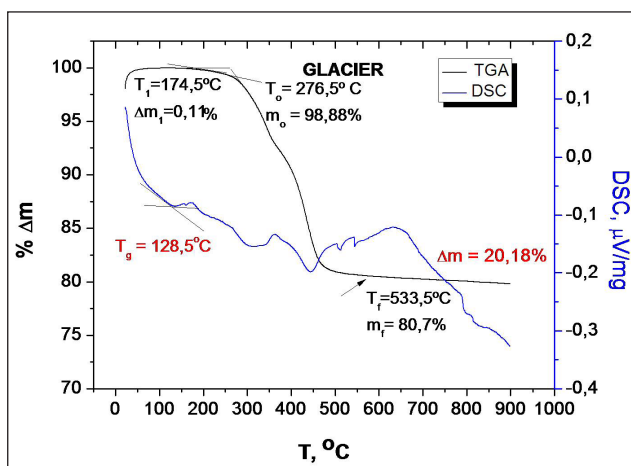


Fig. 2. Representative thermogravimetric and derivate curves for Glacier.

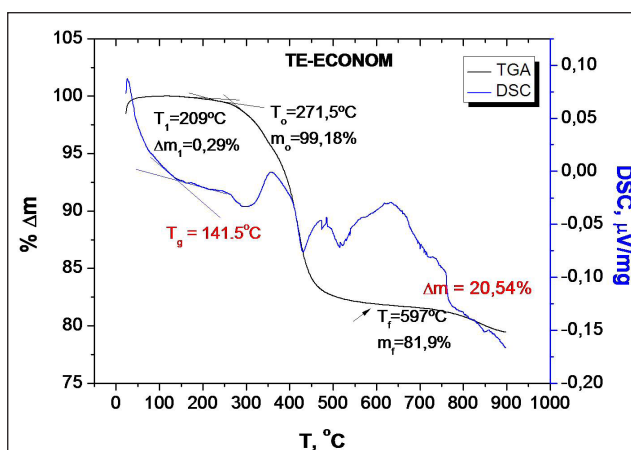


Fig. 3. Representative thermogravimetric and derivate curves for Te-Econom.

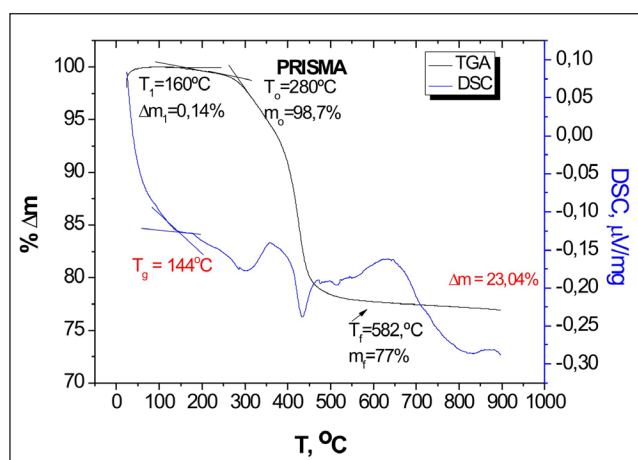


Fig. 4. Representative thermogravimetric and derivate curves for Prisma APH.

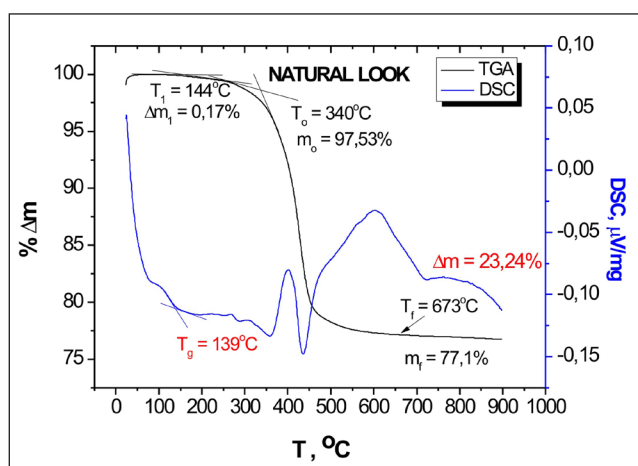


Fig. 5. Representative thermogravimetric and derivate curves for Natural Look.

Table 2. Mean and standard deviations of glass transition temperature (T_g) and degradation temperature.

Composite	Glass transition temperature (T_g)	Degradation temperature
FillMagic	130.6°C±11.1	293.8°C±12.9
Glacier	129.0°C±5.5	277.3°C±6.3
Te-Econom	143.5°C±5.0	275.8°C±8.3
Prisma APH	147.5°C±11.4	282.5°C±9.7
Natural Look	143.7°C±12.9	344.7°C±8.0

Discussion

DSC is a technique that, by energy variation, measures the temperature difference between the sample and a reference at a temperature controlled program. With this method, it is

possible to identify the critical temperatures for the analyzed material, which allows for the observation of thermal events in ceramics, glass or polymers (e.g., crystallization, melt, T_g). T_g refers to the temperature of each material in which there is an increase in the coefficient of linear thermal expansion (CLTE) and a reduction in viscosity and the elastic modulus (13,14). This temperature can be used as a reference point to design the ideal heat treatment. Above T_g , the degree of conversion can increase once the monomers are given further opportunity to react (7,15). However, the T_g of direct composites varies, among other aspects, as a function of composition (monomer blend, filler type and concentration) and crosslink density (which depends on the degree of conversion/polymerization, etc.) (19).

All results for DSC obtained in this study were higher than the values obtained by previous studies for other direct resin composites, which report values ranging from 35 to 120°C (6,9,10,15,20,21). This large difference derives from many reasons, such as different materials (experimental composites with or without filler, commercial composites, matrix resin), techniques (DSC, thermo-mechanical analysis), atmosphere conditions (air, nitrogen, vacuum), heating rate, resin mass, etc. (15,19,20). In fact, the T_g values found in this study are a function of the methodology employed (photoactivation mode, specimen thickness, etc.).

With TGA it is possible to determine, by mass alteration, the thermal degradation of a material (6). In this study, this test sought to determine the maximum secure temperature in which it is possible to submit direct resin composites without the occurrence of marked degradation of the components. TGA revealed that the weight loss and consequent degradation for all resin composites studied began around 270°C and this process occur in steps, similar to the results of other studies (16-18).

In addition, some authors use TGA to compare the filler loading in dental composites as stated by the manufacturer with the experimental results obtained (16,22,23).

The results for FillMagic suggested that an initial weight loss up to 1.4% began around 293.8°C. Above 650°C, the mass tended to stabilize, corresponding to the inorganic fraction of the resin (Fig. 1). In this study, FillMagic was 75.5% wt, which is not in agreement with the values stated by the manufacturer (80% wt).

Initial degradation of Glacier was observed around 277.3°C, which presented a weight loss up to 1.12%. Above 533.5°C, an inert residue of 79.82% was left, which corresponded to the inorganic fraction (Fig. 2). The high content of inorganic filler confirmed that its value is very close to the figure given by the supplier (81% wt).

A moderate weight loss began around 275.8°C for Te-Econom. Between 275.8 and 500°C, weight loss reached 16.58% and became 20.54% at 900°C. After mass stabilization, we observed an inorganic content of 74.96%, which is not in agreement with the values given by the manufacturer (72% wt) (Fig. 3).

A moderate weight loss began around 282.5°C for Prisma APH. Between 282.5 and 580°C we detected the highest

mass degradation. After mass stabilization, we observed an inorganic content of 76.96% (Fig. 5). This data could not be compared because they were not reported by the manufacturer.

For Natural Look, initial degradation was observed around 344.7°C, which presented a weight loss up to 2.47%. Above 500°C, an inert residue of 76.76% was left that corresponded to the inorganic fraction (Fig. 4). This content of inorganic filler was very close to the figure given by the manufacturer (77% wt).

Several factors, such as differences in the organic matrix composition (5), type and content of the inorganic filler (9,10) may be the basis to explain the results for each material. Differences in organic matrix, such as the type of monomers and the photoinitiators present, might play a role in the observed results. Variations among monomers from different resins result in distinct hydrophilic properties, different degrees of conversion and different capacities to form crossed chains during polymerization (18). Little variation in the organic matrix composition among the assessed resins can be observed, with the exception of Glacier. This resin has ester-methacrylic acid, a low-molecular-weight monomer, which probably negatively

affects T_g values because, as a general rule, it is accepted that the lower the mean molecular weight of the monomer, the lower the boiling temperature and the greater the percentage of shrinkage (13). Furthermore, differences in the amount of filler loading among the resins studied have been directly related to the T_g . The greater the percentage of filler loading, the higher the polymer structure homogeneity and, therefore, the higher the T_g (13,14).

Conclusions

The association of direct resin composites with simple heat treatments could be an alternative to the expensive current indirect composite systems. Regarding the heat treatment itself, it was assumed that the effective temperature for heat treatment is material dependent. In addition, this study has clinical relevance considering that we revealed the maximum secure temperature in which it is possible to submit five commercial direct resin composites without the occurrence of marked degradation of the components. Despite these results, more studies are needed to assess the thermal behavior of other resins due to the wide variety of aesthetic materials on the market.

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