Heat treatment of a direct composite resin: influence on flexural strength

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Abstract: The purpose of this study was to evaluate the flexural strength of a direct composite, for indirect application, that received heat treatment, with or without investment. One indirect composite was used for comparison. For determination of the heat treatment temperature, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed, considering the initial weight loss temperature and glass transition temperature (T_g). Then, after photoactivation (600 mW/cm² - 40 s), the specimens (10 × 2 × 2 mm) were heat-treated following these conditions: 170°C for 5, 10 or 15 min, embedded or not embedded in investment. Flexural strength was assessed as a means to evaluate the influence of different heat treatment periods and investment embedding on mechanical properties. The data were analyzed by ANOVA and Tukey's test ($\alpha = 0.05$). TGA showed an initial weight loss temperature of 180°C and DSC showed a T_g value of 157°C. Heat treatment was conducted in an oven (Flli Manfredi, Italy), after 37°C storage for 48 h. Flexural strength was evaluated after 120 h at 37°C storage. The results showed that different periods and investment embedding presented similar statistical values. Nevertheless, the direct composite resin with treatments presented higher values (178.7 MPa) compared to the indirect composite resin (146.0 MPa) and the same direct composite submitted to photoactivation only (151.7 MPa). Within the limitations of this study, it could be concluded that the heat treatment increased the flexural strength of the direct composite studied, leading to higher mechanical strength compared to the indirect composite.

Descriptors: Composite resins; Thermic treatment; Tensile strength.

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Introduction

Direct and indirect composites present equivalent composition, but different processing methods. After photoactivation, polymerization can be completed by an additional treatment with light and/or heat, which can be done under controlled environmental conditions. Those additional treatments lead to an increase in the degree of conversion, improved mechanical properties, color stability and a reduction of wear.[1,2]

One disadvantage of indirect commercial composites is their cost, mainly because special equipment is needed to process them. These devices include ovens and stoves, which associate stroboscope or continuous light, nitrogen or argon pressure and vacuum.[1,2]

As an alternative for indirect commercial systems, many authors have proposed the use of direct composites associated to heat treatments in a conventional sterilization oven, autoclave or porcelain furnace.[3-5] After photoactivation, heat treatment can be conducted in conventional devices projected for other applications (sterilization in dry or humid conditions, porcelain sinterization, etc.), which are readily available in the dental office. These can be used as an option to improve the mechanical properties of direct composite resins.[3,6,7] An advantage would be the low cost. Besides that, this treatment can provide an increase in the degree of conversion, also named as secondary cure or post cure.[8]

There is no consensus in the literature about the ideal time and/or temperature for direct composite heat treatment after photoactivation. To assess the ideal time × temperature, some aspects must be observed: the glass transition temperature (T_g), by differential scanning calorimetry (DSC), and the initial degradation temperature, by thermogravimetric analysis (TGA).[9]

The glass transition temperature (T_g) is a designation adapted from the characteristic temperature of glassy materials. It refers to a temperature characteristic of each material, in which there is an increase in the coefficient of linear thermal expansion (CLTE) and a reduction in the viscosity and elastic modulus. This temperature can be used as a reference to design the ideal heat treatment. Above T_g, the secondary molecular interactions are weakened, which allows for molecular relaxation through lateral groups bending / rotation. As a consequence, the degree of conversion has an opportunity to increase, once the trapped radicals are given further opportunity to react.[8,10-12] 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.).[13] The composites T_g can be observed by an endothermic event in DSC.[14] By TGA, it is possible to determine, by mass alteration, the thermal stability / degradation of the material.[15]

In order to propose a heat treatment methodology for dental composite resins, a thermal characterization was previously conducted by TGA and DSC. After that, a safe and efficient temperature (without polymer degradation and above T_g, respectively) was indicated. Different periods for the heat treatment were also investigated, with or without investment coating. The direct composite studied has low cost and the parameter used to verify the influence of treatments was flexural strength. For comparison, an indirect commercial composite was used.

Material and Methods

The composite resins used in this study are described in Table 1.

TGA and DSC were used for thermal characterization of the direct composite. Cylindrical speci-

Table 1 - Description of the composite resins studied.

Material	Manufacturer	Composition	Lot
FillMagic	Vigodent S.A. Ind. Com. Bonsucesso, RJ, Brazil	Barium glass (0.5 μm) 80% wt. Organic matrix: bis-GMA, TEGDMA, bis-EMA and UDMA.	123/04
BelleGlass	Belle de St. Claire, Orange, CA, USA	Barium-borosilicate glass (0.6 μm) 74% wt and 63% vol. Organic matrix: UDMA.	406066

mens (approximately 15 mg) were accommodated in a thermobalance model TGA-50 (Shimadzu, Tokyo, Japan), in the temperature range of 25 to 900°C, under dynamic nitrogen atmosphere (50 ml/min), heating rate of 10°C/min, using platinum crucibles. For the device calibration, a monohydrate calcium oxalate sample was used, following the standard ASTM 1582 (1993).[16]

For DSC, cylindrical samples of 3 × 2 mm (height × diameter) (approximately 30 mg) were prepared. DSC curves were obtained in a DSC-50 cell (Shimadzu, Tokyo, Japan), in the temperature range from 25 to 550°C, under dynamic nitrogen atmosphere (100 ml/min), heating rate of 10°C/min, using aluminum crucibles. DSC cell was previously calibrated with an indium standard (T_{melt} = 156.6°C) and zinc (T_{melt} = 419.5°C) samples, with 99.99% purity. For the heat amount, the ΔH_{melt} of metallic indium (28.7 J/g) was used.

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 thermoanalytical curves of the samples.

Flexural strength

Specimen preparation

The specimens (n = 7) were prepared in a stainless steel split mould[17] (10 × 2 × 2 mm). All procedures were carried out by a single operator at controlled temperature (23°C) and relative humidity (50%). The mould was positioned on a mylar strip (Labordental Ltda., São Paulo, SP, Brazil), over a glass slab. The composite was inserted into the mould, which was then covered with another mylar strip. A glass slide was gently pressed for excess material to extrude from the mold. Photoactivation for 40 s, in the upper surface, was accomplished with Optilux 501 (Demetron, Danbury, CT, USA), with a 12 mm diameter tip, in contact with the mylar strip. The device irradiance (600 mW/cm²) was measured by a radiometer (serial #111231, Demetron Research, Danbury, CT, USA). Immediately after specimen preparation, they were stored in lightproof boxes at 37°C (Ética Equip. Cient. S.A., São Paulo, SP, Brazil).

Heat treatment

Direct composite specimens (Fill Magic) were submitted to the experimental heat treatment. For this purpose, after 48 h storage at 37°C, the specimens received a heat treatment at 170°C. After the heat treatment, the specimens were stored at 37°C for 120 h. The non treated specimens were stored for 120 h at 37°C.

The experimental heat treatment, for the direct composite, was conducted in a digital oven (Mod. 10060, Flli MANFREDI, Scientific Apparatus Electronic Devices, SAED, San Secondo di Pinerolo, TO, Italy), in dry condition at 170°C, for three periods of time (5, 10 and 15 min). Moreover, the investment coating effect on the treated specimens was tested using a stone bonded investment (Cristobalite, Dentsply, Petrópolis, RJ, Brazil), in relation to the non-coated specimens.

For coating, before the heat treatment, empty match boxes were half-filled with the investment. Specimens were placed on top of the set investment and then covered with another portion of the same material. Specimen separation was facilitated by guiding incisions fabricated in the investment material.

The indirect composites specimens (BelleGlass, n = 7) were heat-treated according to the manufacturer's instructions: after photoactivated, they were treated in a HP unit (SDS Kerr, CA, USA), with a 20 min cycle at 140°C, under nitrogen pressure (5.5 bar).

Flexural strength test

The specimens' dimensions were measured by a digital caliper (Mitutoyo, Tokyo, Japan). A three point bending test was carried out in a universal testing machine (Kratos Din. Ltda., Cotia, SP, Brazil), at a cross-head speed of 0.5 mm/min. An aluminum guide was used for correct alignment of the specimen, providing equidistant load for the spans. The distance between supports (cylindrical, 2 mm diameter) was set to 8 mm, and the irradiated surface was positioned under load incidence. Flexural strength was calculated according to the following equation:

$$\sigma = \frac{3 \cdot P \cdot l}{2 \cdot w \cdot t^2}$$

Where σ is the flexural strength (MPa), P is the fracture load, l is the distance between supports (8 mm), w and t are the width and thickness (mm) of the specimen, respectively.

Statistical analysis

The data were analyzed by two-way ANOVA (heating exposure time and investment coating). Tukey's test was applied for contrast ($\alpha = 0.05$).

Results

TGA/DSC

A moderate weight loss started around 180°C, for the direct composite. This may have represented an initial degradation. Between 200 and 400°C, weight loss reached 10.6%, becoming 26.3% at 600°C. Above this temperature, the mass tended to stabilize, corresponding to the inorganic fraction of 73.74% wt (Graph 1).

For the direct composite, the glass transition was observed at 157°C. Thereafter, 170°C was determined as the heat treatment temperature, as it is above the observed T_g and under the initial degradation temperature.

Flexural strength

Through statistical analysis, the results showed that neither one of the heat treatments proposed (regardless of embedding or not embedding in investment), nor the different periods of time led to significantly different flexural strength values (Table 2).

Discussion

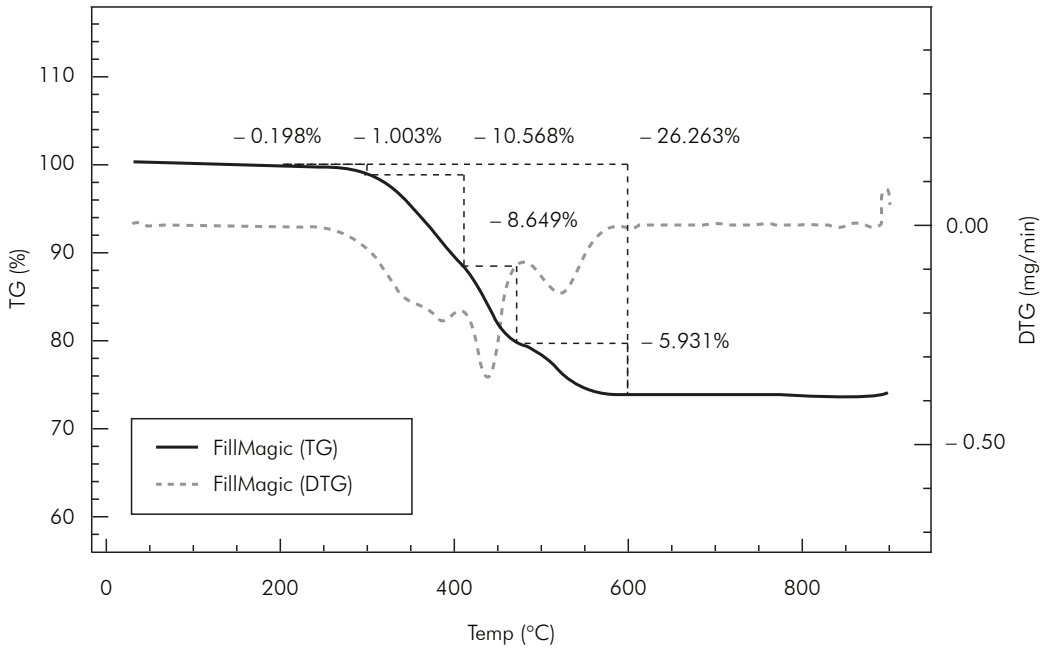
Previously to heat treatment, the maximum temperature for heating without damaging the material needs to be determined to avoid weight loss. Thus, TGA was applied, since this test evaluates weight alterations (gain or loss) as a function of temperature and/or time, when a sample is submitted to a program with controlled temperature.[15] The results suggested that, in temperatures above 200°C, the composite resin presented a weight loss up to 0.2%. Other authors compared the filler loading in dental composites informed by the manufacturer with the

Table 2 - Flexural strength of the studied composites.

Conditions	Means (MPa)
FillMagic photoactivated	151.7 ± 30.7 b
FillMagic with treatments	178.7 ± 20.8 a
BelleGlass	146.0 ± 16.3 b

Same letters represent similar values ($p < 0.05$).

Graph 1 - TG/DTG curves for the direct composite FillMagic.



experimental results obtained by TGA.[18,19] In this study, total filler percentage for the direct composite Fill Magic was 73.74% wt, which is not in agreement with the values presented by the manufacturer (80% wt).

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 test, a T_g of 157°C for direct composite Fill Magic was observed, which was higher than the values obtained by most of the previous studies in the literature for other direct composites, which show values ranging from 35 to 186°C.[8,11,13,20-23] This great 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, composite resin mass, etc.[8,11,13,20-23] T_g can be measured by a vast range of techniques and depends on the degree of conversion. When a bulk density of crosslinking is present, there is a smaller mobility of the polymeric chain section. This fact increases the T_g values.[11,22] So, the T_g value found in this research is also a function of the methodology employed (photoactivation mode, specimen thickness, etc). Thus, based on the TGA and DSC results, the temperature of 170°C was stipulated for the heat treatment of the composite resins.

To minimize ambient atmosphere effects inside the heat treatment furnace, investment coating was used for some groups. By doing this, it was possible to evaluate eventual differences in heat flow during the heat treatment, when the composite resin was involved by a material with lower conductivity. It was also possible to analyze the effect of the controlled atmosphere during the procedure (oxygen reduction), as well as a simulation of the conditions applied for indirect composite resins. However, the results indicated that flexural strength values did not differ between the materials embedded or not embedded in investment. This showed that this procedure is not necessary for this parameter.

Notwithstanding, the heat treatment factor was highly significant, regardless of the period used. Even with the shorter period without investment coating (173.5 MPa), an increase in flexural strength was achieved in relation to the composite only photoactivated (151.7 MPa). Many studies compared direct composites just photoactivated in relation to direct composites that received heat treatment, by parameters as flexural strength and diametral tensile strength.[21,23,24] Although results obtained by different tests may not be compared, they all followed the same marked trend: the heat treatment improved the evaluated mechanical properties, regardless of the parameter considered.

According to Loza-Herrero *et al.*[6] (1998), heat application, aiming at an increase in the degree of conversion, must be used, ideally, immediately after photoactivation. Higher monomer conversion took place up to 6 h after photoactivation. They also affirm that there is a reduction in the amount of residual monomers after 6 h, and that, after that period, the heat treatment did not lead to an increase in flexural strength. In the present study, the heat treatment was applied only after 48 h of photoactivation, so as to isolate the heat treatment effect from the effect that occurs earlier. However, the temperature for the heat treatment, which was different from that of the former study, was higher than T_g. The objective was to improve properties, not only necessarily by an increase in the degree of conversion, but also probably by an increase in stress relaxation (induced during photoactivation).[11,25]

Bagis, Rueggeberg[26] (2000), in another study, submitted specimens to immediate post-cure heating, for 7 min, at the following temperatures: 50, 75, 100 and 123°C. They were compared to specimens only photoactivated. High pressure liquid chromatography was used to measure residual monomer leached from the specimens. Post-cure heating at 75°C and above resulted in the lowest amount of residual monomers, without significant decrease with an increase in post-cure temperature.[26] Post-cure treatment at 100°C leads to a decrease in residual monomers remaining in the polymer (measured by FTIR), but the mechanical properties are not always improved for all composites.[3]

In the present study, no statistical difference was found in flexural strength values, according to period of heating. This is indicative that the shortest

period of time (5 min) was capable of promoting thermal balance and producing the desired effects of strength increase.

Even without measuring the degree of conversion, it can be speculated that the different levels of conversion attained by the different groups might have accounted for differences in flexural strength. Since the heat treatment was conducted above T_g, this would allow for increased radical mobility, enhancing conversion.[9,12] However, stress relaxation brought about by the thermal treatment might also explain why there was an increase in flexural strength. It is important to emphasize that stress relaxation is time-dependent. Since it depends upon atom or molecule movements, it varies in an exponential function with temperature.[9]

The three-point bending test develops complex stresses (compressive, tensile and shear), similarly to *in vivo* conditions. Other parameters need to be studied to evaluate the phenomenon, as residual monomers quantification, leaching, color alteration, toughness, microhardness, degree of conversion, etc.

Conclusion

The experimental heat treatment employed in this study increased the flexural strength of the direct composite Fill Magic, enabling its indirect use with high mechanical strength. Within the limitations of this study, the results led to the conclusion that the association of common composites with a simple post-cure heat treatment may be an alternative for current indirect composite systems, although more studies are needed to assess other properties of the composites for this application.

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