

Effect of Experimental Heat Treatment on Mechanical Properties of Resin Composites

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The aim of this study was to verify the influence of an experimental heat treatment (170°C/10 min) using a casting furnace on the mechanical properties (hardness and flexural strength) of 2 commercial direct resin composites (TPH Spectrum and Filtek P60) compared to a commercial indirect resin system (BelleGlass). Heat treatment temperature was determined after thermal characterization by thermogravimetry (TG) and differential scanning calorimetry (DSC). Data was analyzed by ANOVA and Tukey's test at 5% significance level. There was statistical significance for the main factor heat treatment ($p=0.03$) and composite ($p=0.02$), for flexural strength. For Knoop hardness, only the main factor composite was statistically significant ($p=0.00$). P60 presented higher hardness than TPH. No statistically significant correlation between mechanical properties tested was detected. Based on these results, it was possible to conclude that heat treatment influenced flexural strength of direct composites, while it was not observed for hardness. The association of direct composites with a simple post-cure heat treatment may be an alternative for current indirect composite systems, although more studies are needed to verify other properties of the composites for this application.

Key Words: composite resins, heat treatment, flexural strength, hardness.

INTRODUCTION

Since the introduction of resin composites in 1960, many efforts have been made in a way to increase the longevity of resin restorations. Although some progress has been made, mechanical properties in this class of materials are yet to be improved. Wear and fracture, due to chewing forces and microleakage caused by polymerization contraction stress, are the main concerns (1). These are some of the drawbacks that may compromise direct composites performance as substitutes for amalgam in posterior teeth, mainly when large restorations are necessary (2). Thus, the constant demand for esthetic restorations led to the development of new materials and techniques.

One possible way to minimize the problems re-

lated to microleakage and polymerization stress is to use esthetic indirect composite bonded restorations instead of direct composites. In the indirect technique, the lost tooth structure is rebuilt in a cast and the material is polymerized under controlled conditions in the laboratory, which allows the use of higher irradiances during photoactivation and extend exposure to internal surfaces. This has been shown to improve mechanical properties, such as hardness and flexural strength, due to an increase in degree of conversion (3). Moreover, this procedure allows better proximal and occlusal shaping, which facilitates the subsequent cementation into the cavity (4).

Specific resin systems have been developed for indirect use. Some examples are BelleGlass (Belle de St. Claire, Orange, CA, USA), Sculpture (Jeneric/Pentron Inc., Wallingford, CT, USA). Manufacturers

recommend an initial polymerization of the restoration followed by a special treatment that may include extra doses of light and/or heat, carried out under specific environment conditions in ovens, developed by the manufacturer for this purpose. There is a consensus in literature that, in general, the heat supplies results with an increase in mechanical properties of cured composites due to improved conversion and a consequent reduction of unreacted monomers (1,3,5,6). The heat treatment may also contribute for the relief of stresses originated during resin polymerization and finishing procedures (7).

The temperature usually used in indirect systems ranges from 120 to 140°C. Ideally, the temperature applied in this treatment must be above composite's glass transition temperature (T_g) (8). This allows a significant increase in polymer chain mobility, favoring additional cross-linking and stress relief (7,9). Nevertheless, it is noteworthy that overheating may cause degradation of the composite (10). However, there may be alternatives for these more sophisticated systems.

For instance, there is evidence that the association of direct light-cured composites with simple thermal treatments may produce results similar to the conventional heat treatments, with increase in the material's properties (11). In addition, the special ovens could be replaced by other heat sources, as cast furnaces or autoclaves, commonly employed in the prosthetic laboratories, which are able to reach relatively high temperatures.

The purposes of this study were to evaluate the

thermal characteristics, such as degradation temperature of the composites by thermogravimetry and T_g by differential scanning calorimetry, and to verify the influence of an experimental heat treatment using a casting furnace on the mechanical properties (hardness and flexural strength) of 2 commercial direct resin composites compared to a commercial indirect resin system.

MATERIAL AND METHODS

Two commercial direct resin composites - TPH Spectrum and Filtek P60 - and one indirect resin system as a control - BelleGlass - were used in this study. Manufacturers' information is presented in Table 1.

TG and DSC Analyses

Solid specimens used for thermal characterization were activated for 40 s with Optilux 501 light-curing unit (Demetron; Kerr Corp., Danbury, CT, USA; 11-mm-diameter tip, 600 mW/cm² light intensity). TG/DTG curves were obtained with a thermobalance (model TGA-50; Shimadzu Corporation, Kyoto, Japan) at a temperature range of 25-900°C, using platinum pans containing approximately 15 mg specimens, under dynamic air atmosphere (50 mL min⁻¹) and heating rate of 10°C min⁻¹.

An isothermal TG at the experimental heat treatment temperature was recorded to observe the weight loss of the studied composites at a constant temperature as a function of time.

DSC curves were obtained in a DSC-50 cell (Shimadzu Corporation), using standard aluminum pans, under dynamic nitrogen atmosphere (50 mL min⁻¹) and heating rate of 10°C min⁻¹ at a temperature range from 25 to 550°C. The DSC cell was calibrated with indium (*m.p.* 156.6°C; ΔH_{melt} =28.54 Jg⁻¹) and zinc (*m.p.* 419.6°C) as standards.

Flexural Strength and Knoop Hardness

Specimens with rectangular cross-sectional area (10

Table 1. Composites descriptions (manufacturers, lot numbers and compositions).

Material	Manufacturer	Matrix	Filler (type and vol. %)	Mean particle size (μm)	Batch number
Filtek P60	3M/ESPE, St. Paul MN, USA	Bis-GMA, UDMA, Bis-EMA	Zirconia, silica, 61%	0.19-3.3	4MM
TPH Spectrum	Dentsply De Trey, Konstanz, Germany	Bis-GMA, Bis-EMA, TEGDMA	Barium boro fluoroaluminosilicate glass, silica, 57%	0.8	72562
BelleGlass	Belle de St. Claire, Orange, CA, USA	UDMA	Barium silicate glass, 65%	0.5-1.0	406066

mm length x 2 mm width x 2 mm height) were built using a stainless steel split mould. The composite was inserted in bulk, filling the mould completely. After adjusting the composite thickness, the upper surface was irradiated for 40 s, using the same light source previously described. All specimens were dry stored in lightproof containers at 37°C for 48 h. After that, they were randomly assigned to 5 groups (n=7): direct composites (Filtek P60 or TPH Spectrum) with or without heat treatment, and indirect composite (Belleglass). The heat-treated groups of the direct composites were dry heated (170°C, previously determined) in a digitally controlled furnace (OVMAT 7, Manfredi S.p.A., Torino, Italy) for 10 min. After heat treatment, the specimens were stored again in lightproof containers at 37°C for 72 h.

After the storage period, the specimens were placed in a 3-point bending flexural device, with the aid of a guide to standardize their position, and were subjected to mechanical test in a universal testing machine (Kratos Dinamômetros, São Paulo, SP, Brazil) at a crosshead speed of 0.5 mm/min, and with a span distance of 8 mm. Flexural strength was then calculated using the following equation:

$$\tau = \frac{3fl}{2hw^2}$$

where f is the fracture load, l is the span distance, w is the specimen's width and h the specimen's thickness.

The fractured specimens were embedded in slow-setting epoxy resin in PVC cylinders, in such a way to expose their lateral surface, parallel to the longitudinal axis. Knoop hardness was evaluated using a microhardness tester (model HMV-2/2 T, Shimadzu Corporation) with 100 g load and a dwell time of 15 s. Three indentations were made at 1.0 mm depth of the irradiated surface. For each specimen, the mean value of Knoop hardness (KHN) was obtained by 3 readings.

The indirect composite specimens were built and irradiated similarly. The heat treatment was done according to the manufacturer's instructions, regarding temperature, pressure and time (140°C, 80 psi nitrogen, 20 min).

Statistical Analysis

Flexural strength and KHN data were subjected to 2-way ANOVA to assess the possible effect of the heat treatment on the direct composites (P60 and TPH) properties (main factors: *composite* and *heat treatment*).

One-way ANOVA was used to compare heat-treated direct and indirect composites. Tukey's test ($\alpha=0.05$) was performed for multiple comparisons. The occurrence of significant linear correlation between flexural strength and KHN was examined by means of Pearson's correlation test.

RESULTS

TG and DSC

The T_g values obtained by DSC analysis were: 162°C for P60 and 159°C for TPH (Fig. 1). TG revealed that the weight loss and consequent degradation for both composite specimens occur in steps. For temperatures above 180°C, there was a significant weight loss, which may have been due to the unreacted monomer volatilization or other degradation processes.

Based on this information, it was assumed that an effective and more safe temperature for the heat treatment for both composites would be 170°C. The isothermal TG showed that the weight loss at 170°C was negligible for short periods (Fig. 2), confirming this temperature to be safe in terms of composite degradation.

Flexural Strength and Hardness

Comparing the direct composites, only the main factor *heat treatment* was statistically significant for flexural strength ($p=0.031$). Mean values for flexural strength of the groups with and without heat treatment were, respectively, 180.8 ± 30 and 159.9 ± 17.6 MPa.

For Knoop hardness analysis, only the main factor

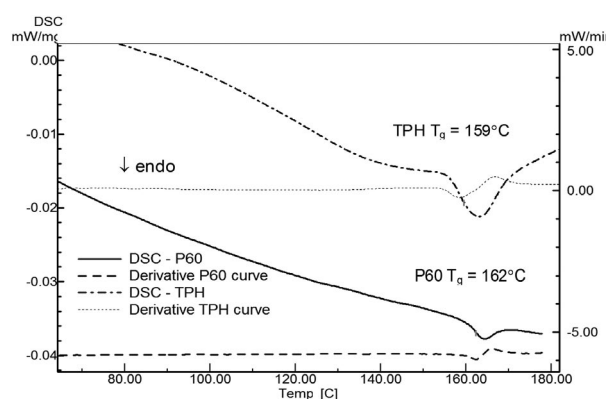


Figure 1. DSC curves of TPH and P60 composites.

composite was statistically significant ($p=0.000$). P60 presented higher KHN than TPH (99.8 ± 5.3 and 73.8 ± 5.6 , respectively).

Comparing only the heat-treated composites, the main factor *composite* was significant for flexural strength and Knoop hardness analysis ($p=0.02$, for both). Means and standard deviations for these parameters are presented in Figure 3.

No statistically significant correlation between hardness and flexural strength was detected in either 2-way or 1-way ANOVA (Pearson's p -value= 0.43 and p -value= 0.46 , respectively).

DISCUSSION

The DSC technique assesses the energy (enthalpy) absorbed or released by a specimen during temperature rise, reduction or even at isothermal conditions, compared to a reference specimen. With this method, it is possible to identify the critical temperatures for the analyzed material, which allows the observation of thermal events in ceramics, glass or polymers (e.g. crystallization, melt, T_g). In Figure 1, derivative curves were calculated to assist the identification of the thermal events.

TG provides the change in weight of a specimen as a function of temperature. It is a precise quantitative method of determining combustion, volatilization and decomposition by analyzing weight changes. In this study, this test assisted to determine the maximum secure temperature in which it is possible to submit the resin composite without the occurrence of marked

degradation of the components (10).

In-lab composite techniques were introduced as an attempt to develop materials with improved properties compared to direct composites. Post-cure heating leads to an increase in the degree of conversion, which improves physical and mechanical properties (12), mainly tensile strength (4), flexural strength (4,5,13), wear (14), hardness (15), and color stability (6).

It is important to observe that, after photoactivation, the polymerization reaction still proceeds in the

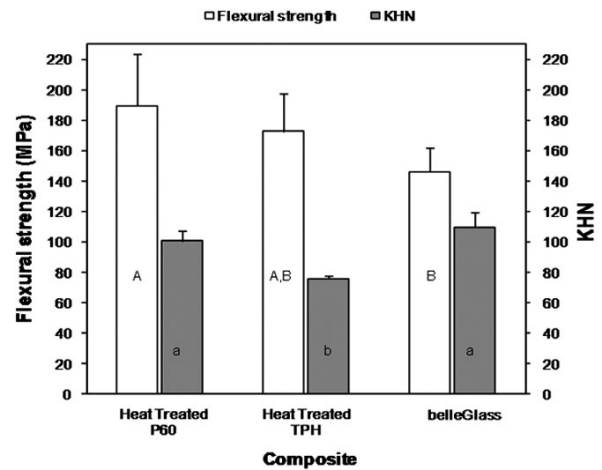


Figure 3. Flexural strength (MPa) and Knoop hardness number (KHN) of the heat-treated composites. Same uppercase letters indicate no statistically significant difference in flexural strength and same lowercase letters indicate no statistically significant difference in Knoop hardness. Values are expressed as mean and standard deviation.

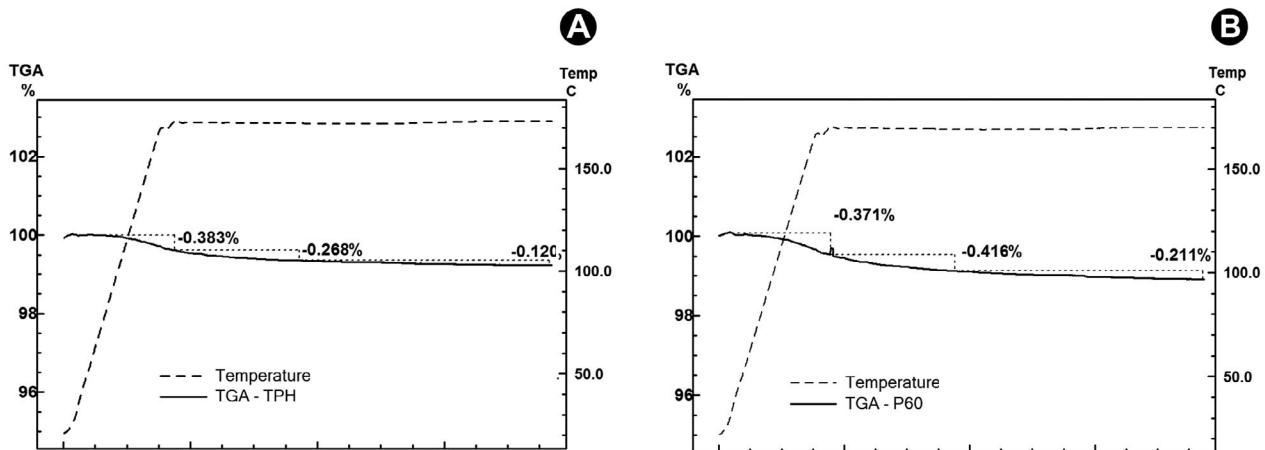


Figure 2. TG isothermal curves of TPH (A) and P60 (B) composites.

dark at room temperature, and this residual reaction has been related to increased degree of polymerization (5). In this study, the specimens storage (between the photoactivation and the experimental heat treatment) for a long period (48 h) may have overshadowed the possible differences in conversion rates in the early stages of polymerization and this could have washed out the real effect of the heat treatment on the mechanical properties of the materials (13). Indeed, a previous study demonstrated that even post-cure temperatures as low as 50°C were capable of greatly reducing the levels of all types of residual monomers in the tested material (16).

Regarding the treatment itself, post-cure heating of resin composite materials decreases the levels of unreacted monomer after the initial light-curing stage (16). Basically, 2 mechanisms can be involved in this phenomenon. First, the residual monomer would be covalently bonded to the polymer network, as a result of the heat treatment, leading to increase in conversion itself. Second, unreacted monomers would be volatilized during the heating process. It is still possible that both mechanisms act simultaneously, but their relative contribution is still not totally elucidated (16).

Most conventional post-curing heat treatments employ temperatures below 130°C. However, in this study, an important concern was the determination of the specific critical temperatures (glass transition and initial loss of weight temperatures) which present a range for each material. Both parameters of the tested composites were established initially, which assured that the heat treatment was carried out using an effective and safe temperature. As observed, T_g values obtained for both composites were around 160°C. When higher temperatures, just above composite T_g , are applied to composites, mechanical properties have been shown to be optimized (4,8), by effectively increasing the mobility of polymer networks. This leads to further monomer conversion, increasing the crosslink density (17) and also allows for some stress relief, induced during the polymerization process (9).

In this study, there was no statistical significance in the interaction composite x heat treatment since post-cure treatment affected the flexural strength of both composites in the same way.

The heat-induced improvement in flexural strength could be explained by the post-cure process and by stress relief, which is common in annealing processes (16). Polymerization shrinkage stresses, initially

concentrated mainly around the filler particles, became more homogeneously distributed by the heat treatment, reducing filler/matrix interfacial stresses (18). Hybrid composites may have benefited from these mechanisms in a more pronounced way, since their higher filler content accounts for a larger filler/matrix interface area, which explains the heat-treated composites results in flexural strength.

P60 and BelleGlass presented similar hardness results while TPH had lower hardness. This is probably due to the difference in matrix composition (19) and filler content (Table 1). P60, in addition to presenting higher filler content (61%), also includes zirconia, which is a very stiff filler, which may have accounted for the higher values of hardness compared to TPH. The microhardness test, however, is only capable to perform localized assessments, since it includes very diminutive areas of the specimen in a very superficial region. Therefore, the values obtained with this test are a function of type and content of inorganic filler present in the composite, rather than matrix characteristics (20).

On the other hand, flexural strength test involves the bulk of the specimen and as a result provides a better assessment of the influence of post-cure heat treatment on the resin matrix (4). Therefore, the lack of correlation between flexural strength and hardness is justified because each test takes in consideration different areas of the specimen. The increase in flexural strength of the heat-treated composites may be explained by both an increase in degree of conversion and stress relief, as previously mentioned, caused by temperature increase above composite's T_g , suggesting that this can be a relevant mechanism to improve material's mechanical properties.

Any composite with similar or superior values of hardness and flexural strength as those presented by composites specifically indicated for indirect uses may be used for in-lab procedures. The association of direct composites with simple heat treatments would be an alternative to the expensive composite/post-cure unit systems. However, other studies are needed to elucidate the behavior of the different categories and brands of direct composites after post-cure heat treatment, such as the influence of different treatment protocols regarding temperature and atmosphere conditions during the treatment, in order to facilitate the choice among so many commercially available materials. In addition, it is very important to reach a consensus on the ideal temperatures

for the best treatment of each material.

Based on these results, it may be concluded that heat treatment influenced flexural strength of direct composites while it was not observed for hardness. The association of direct composites with a simple post-cure heat treatment may be an alternative for current indirect composite systems, although further studies are needed to verify other properties of composites for this application.

RESUMO

O objetivo deste estudo foi avaliar a influência de um tratamento térmico experimental (170°C/10 min), em um forno de fundição, sobre as propriedades mecânicas (dureza e resistência à flexão) de 2 resinas compostas comerciais de uso direto (TPH Spectrum e Filtek P60), em relação a uma resina comercial indireta (Belle-Glass). A temperatura de tratamento térmico foi determinada após caracterização térmica por termogravimetria (TG) e calorimetria exploratória diferencial (DSC). Os dados foram analisados por análise de variância, que mostrou, para a resistência à flexão, diferença estatística para os fatores principais tratamento térmico ($p=0,03$) e material ($p=0,02$). Para a dureza Knoop, somente o fator principal material foi estatisticamente significativo ($p=0,00$). A P60 apresentou maiores valores de dureza em relação à TPH Spectrum. Não foi detectada nenhuma correlação estatisticamente significativa entre as propriedades mecânicas avaliadas. Baseado nos resultados foi possível concluir que o tratamento térmico influenciou na resistência à flexão das resinas compostas de uso direto, enquanto, para a dureza, o mesmo não foi observado. A associação de resinas compostas a um simples tratamento térmico de pós-cura pode ser uma alternativa para os sistemas indiretos atuais. Entretanto, mais estudos são necessários para verificar outras propriedades das resinas compostas para esta aplicação.

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