J Therm Anal Calorim (2010) 102:361–367
DOI 10.1007/s10973-010-0739-3

Thermal characterization of dental composites by TG/DTG and DSC

Caroline Lumi Miyazaki ·
Igor Studart Medeiros · Jivaldo do Rosário Matos ·
Leonardo Eloy Rodrigues Filho

Received: 19 October 2009 / Accepted: 25 February 2010 / Published online: 20 March 2010

Abstract Dental composites can be improved by heat treatment, as a possible way to increase mechanical properties due to additional cure (post-cure). Direct dental composites are essentially similar to the indirect ones, supposing they have the same indication. Therefore, to establish a heat treatment protocol for direct composites, using as indirect (photoactivated by continuous and pulse-delay techniques), a characterization (TG/DTG and DSC) is necessary to determine parameters, such as mass loss by thermal decomposition, heat of reaction and glass transition temperature (T_g). By the results of this study, a heat treatment could be carried out above 160 °C (above T_g, and even higher than the *endset* exothermic event) and under 180 °C (temperature of significant initial mass loss).

Keywords Composite resins · Dental materials · Glass transition temperature · Photoactivation · Polymerization · Post-cure

Introduction

Indirect dental composites were developed in order to overcome some of the drawbacks of direct composites, such as polymerization shrinkage, the difficulty to obtain the proximal contact and the correct anatomy of the restoration, and the impossibility to improve degree of polymerization by means of a secondary treatment [1–4]. However, one should consider that the indirect composites have the disadvantage of needing special equipments like furnaces and chambers with controlled atmosphere, which increases the cost of the final restoration [5].

Since direct and indirect dental composites have in essence the same organic composition (mostly bisphenol A glycidyl methacrylate—bis-GMA and triethyleneglycol-dimethacrylate—TEGDMA, in some cases mixed with urethane dimethacrylate—UDMA and ethoxylated bisphenol A dimethacrylate—bis-EMA), several researchers have suggested that direct composites should be used in the indirect technique, especially in the case of large restoration like *onlays*, *overlays* and crowns. The most commonly used method used as a secondary treatment in this case is heating in a furnace [6–8] as a means to improve the degree of conversion (DC: ratio of double bonds into single bonds) of these materials [9] due to the post-cure polymerization caused by heat energy [10–14].

There is no consensus in the literature regarding the ideal temperature for the heat treatment. There are many indications for the use of ovens and stoves, with temperatures ranging from 60 to 170 °C, with heating time varying from 7 min to 1 h [7–9, 11, 12, 15–18]. Therefore, a thermal characterization of direct composites is necessary to determine a safe temperature, capable of inducing additional polymerization (secondary cure) without causing any degradation of the polymer formed. Heating over the glass transition temperature (T_g) of the composite results in an increase in the kinetic energy of monomers and free radicals, leading to a higher degree of polymerization and also contraction stress relaxation. The most adequate

---

C. L. Miyazaki (✉) · I. S. Medeiros · L. E. Rodrigues Filho
Department of Dental Materials, School of Dentistry, University of São Paulo, Av. Prof. Lineu Prestes, 2227, Cidade Universitária, 05508-000 São Paulo, SP, Brazil
e-mail: clm@usp.br

J. d. R. Matos
Thermal Analysis Laboratory, Department of Fundamental Chemistry, Institute of Chemistry, University of São Paulo, Av. Prof. Lineu Prestes, 748, Cidade Universitária, 05508-000 São Paulo, SP, Brazil

temperature for a secondary cure may be determined by thermogravimetry (TG) [19] and differential scanning calorimetry (DSC) [20].

Clinicians usually apply continuous (C) photoactivation technique to polymerize direct dental composites, i.e., a same dose irradiation during 20 or 40 s for each 2 mm-thick composite layer, which leads to a high polymerization stress. In order to reduce this stress, other polymerization techniques were developed, such as pulse-delay (PD) [21–23]. PD method is characterized by a low initial power density followed by a short period in the dark and by a higher final power density. The lower initial power density and the dark period allow the material to flow during the pre-gel phase, causing a release of part of the stress created due to polymerization shrinkage [13, 24–27]. Also, better mechanical properties and marginal adaptation have been reported when this technique is used for direct composites [28–32].

The objective of this study was to evaluate, by means of thermal analysis, the thermal behavior of direct composites photoactivated by two methods (C and PD). Additionally, mass loss was determined by thermogravimetric analysis (TG) and both heat of reaction and T_g were assessed by means of DSC analysis. The final objective was to determine an optimal heating protocol to be used during secondary heat treatment of resin composites.

Materials and methods

Materials

The direct dental composites studied are listed in Table 1.

Specimen preparation

For TG/DTG, a polyacetal matrix was used (0.49 mm thickness × 4 mm diameter) and the specimens were photoactivated with Optilux 501 device (Kerr, Danbury, CT, USA), using the turbo tip (8 mm in diameter). Before photoactivation, light characterization was performed in a spectroradiometer (Ocean Optics 1000, Dunedin, FL, USA) and the power density was measured by a powermeter (Ophir 10A-V2-SH, Ophir Optronics, Har-Hotzvim, Jerusalem, Israel) connected to a microprocessor NOVA (Ophir Optronics, Har-Hotzvim, Jerusalem, Israel).

For C method, photoactivation was performed at 996 mW cm^{-2} for 20 s (19.9 J cm^{-2}). For the PD method, a black polyacetal spacer (22 mm length, 8 mm internal diameter, and 10 mm external diameter) was adapted in the photoactivator tip, always in the same position, providing 90 mW cm^{-2}, which was applied for 5 s. Then, the specimen was maintained in the dark for 3 min, followed by the final photoactivation, without the spacer, for 20 s at

Table 1 Studied materials, manufacturers, and composition (according to manufacturers' description)

Material	Manufacturer	Composition
Z100	3M ESPE (St. Paul, MN, USA)	Filler: zirconia/silica particles (71 vol.%, 85 wt%), mean size of 4.5 μm. Matrix: bis-GMA and TEGDMA. Shade A3
Filtek Z250	3M ESPE (St. Paul, MN, USA)	Filler: zirconia/silica particles (60 vol.%, not silanized, 82 wt%), mean size between 0.19 and 3.3 μm. Matrix: bis-GMA, UDMA and bis-EMA. Shade A3
Filtek Z350	3M ESPE (St. Paul, MN, USA)	Filler: zircon/silica particles (5–20 nm) (59.5 vol.%, 78.5 wt%), mean size between 0.6 and 1.4 μm. Matrix: bis-GMA, UDMA, TEGDMA and bis-EMA. Shade A3
Filtek Supreme XT	3M ESPE (St. Paul, MN, USA)	Filler: zircon/silica particles (5–20 nm) (57.7 vol.%, 78.5 wt%), mean size between 0.6 and 1.4 μm. Matrix: bis-GMA, UDMA, TEGDMA and bis-EMA. Shade A3
Esthet-X	Dentsply (Milford, DE, USA)	Filler: aluminum fluoride borosilicate glass and silanized barium (mean size under 1 μm), colloidal silica (0.4 μm) and nanometric silica (60 vol.%, 77 wt%). Matrix: bis-GMA and TEGDMA. Shade A3
TPH Spectrum	Dentsply (Milford, DE, USA)	Filler: aluminum borosilicate and barium silanized particles (mean size < 1.5 μm), silanized pyrolitic silica (0.04 μm) (57 vol.%, 77 wt%). Matrix: bis-GMA uretane modificated. Shade A3
Herculite XRV	SDS Kerr (Orange, CA, USA)	Filler: mean size particles of 0.6 μm (59 vol.%, 79 wt%). Matrix: bis-GMA and TEGDMA. Shade A3
Charisma	Heraeus Kulzer (Hanau, Germany)	Filler: aluminum fluoride borosilicate glass and silanized barium (0.002–0.2 μm) and high dispersive silica (0.02–0.7 μm), mean size of 0.7 μm (61 vol.%, 78 wt%). Matrix: bis-GMA and TEGDMA. Shade A3
Tetric Ceram	Ivoclar Vivadent (Schaan, Liechtenstein)	Filler: barium glass and ytterbiumtrifluoride particles, alluminum and barium fluorsilicate glass, high dispersive silica and oxides (average size of 0.7 μm) (60 vol.%, 78 wt%). Matrix: bis-GMA, UDMA and TEGDMA. Shade A3
Point 4	Kerr (Orange, CA, USA)	Filler: barium aluminum silicate particles and zinc oxide, mean size of 0.4 μm (57 vol.%, 76 wt%). Matrix: bis-GMA and TEGDMA. Shade A2

996 mW cm^{-2}, with a final total dose of 20.3 J cm^{-2}. The specimens were produced under controlled temperature (25 °C) and humidity (50%).

For DSC test, the specimens (disks: 1 mm thickness × 4 mm diameter) were prepared as described above, the only difference being the matrix dimensions. Samples were weighted using an analytical scale (Shimadzu, Japan) and inserted separately in aluminum pans (C201-52943, Japan, imported by Sinc do Brasil Instrumentação Científica Ltda.).

Thermogravimetry (TG) and derivative thermogravimetry (DTG)

TG/DTG curves were obtained in a temperature range 25–900 °C, utilizing the software TA60WS (Shimadzu, Japan) and the thermobalance model TGA-50 (Shimadzu, Japan), under dynamic air atmosphere (50 mL min^{-1}), heating rate of 10 °C min^{-1}, platinum pan containing a mass around 15 mg. Before the test, a verification of the calibration was held employing a monohydrated calcium oxalate, following ASTM (1582-93). Data were analyzed by TA60WS software, after the subtraction of blank curve for baseline correction.

Differential scanning calorimetry (DSC)

DSC curves were obtained in the temperature range 25–200 °C, utilizing the software TA60WS (Shimadzu, Japan) and the DSC cell model DSC-50 (Shimadzu, Japan), under nitrogen dynamic atmosphere (100 mL min^{-1}), heating rates of 10 °C min^{-1} (first run) and 20 °C min^{-1} (second run), with aluminum pan containing sample mass around 25–30 mg. Aluminum pan with lids were used as reference. The DSC cell was previously calibrated with indium (mp = 156.6 °C, $\Delta H_{\text{fus}} = 28.54$ J g^{-1}) and zinc (mp = 419.6 °C). Also for DSC, data were analyzed by TA60WS software after subtraction of blank curve for baseline correction.

Statistical analysis

Data were submitted to analysis of variance and Tukey's test with level of significance of 5% ($p < 0.05$). Level of significance (p) is correlated to the probability of similarity between mean values. Thus, p-values lower than 5% will be considered statistically significant differences.

Results and discussion

Several authors indicate direct composites for indirect use, applying heat treatment after photoactivation, with mechanical properties improvement, such as flexural strength, hardness, degree of conversion, etc. Nevertheless, there is not a literature consensus about the ideal temperature for the heat treatment, in other words, a temperature range in which no degradation of the polymer will occur and some mechanical properties could be enhanced. The results of this study allowed for determination of a safe temperature range.

TG/DTG

Figure 1, obtained from composite Z100, is a representative TG curve of the studied composites. The continuous line represents the TG curve, whereas the dashed one represents the derivative (DTG). Based on the TG/DTG curves, it is possible to observe the material thermal stability and obtain the organic and inorganic percentage (Table 2). Initial mass loss started, significantly, above 180 °C (Table 2), what can be observed as a light curvature in the dashed line. This curvature is more easily noted in the continuous line (Fig. 1). It was in the order of 0.64% around 200 °C (0.78% in Fig. 1), and above that limit there was a significant decrease. These observations may be explained by the volatilization of components due to heating (example: solvents [33], or lower molecular mass components, such as plasticizers or monomers). The inflexion in DTG curve ($T_{\text{peak}} = 423$ °C) (Fig. 1) exhibits the point with higher mass loss [20], i.e., 1.839 mg, corresponding to 12.97% of the total initial (14.18 mg).

Table 2 shows mass loss (%) between 25 and 600 °C (23.21%). Samples were heated up to 900 °C to guarantee the burning of all organic fraction, with heating rate of 10 °C min^{-1}, according to other references [34, 35], under dynamic air atmosphere. But at 600 °C there was another plateau continuous until 900 °C, indicating that organic fraction was burnt [14, 35, 36]. Therefore the temperature of 600 °C was used as the major value for x axis (Fig. 1), and at this temperature the final mass represented the

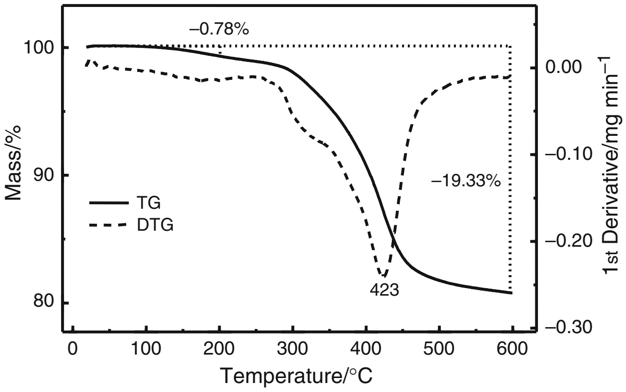

Fig. 1 TG/DTG representative curves of the composite Z100

Table 2 Mass loss according to heat range of the studied composites

Composite	Mass loss/%			
	25–170 °C	25–180 °C	25–200 °C	25–600 °C
Z100	0.47	0.57	0.77	19.32
Z250	0.34	0.39	0.49	19.32
Z350	0.53	0.60	0.76	22.91
Supreme	0.55	0.65	0.80	22.35
Esthet-X	0.28	0.34	0.44	23.73
TPH Spectrum	0.34	0.39	0.47	23.90
Herculite XRV	0.11	0.26	1.05	23.53
Charisma	0.42	0.48	0.56	27.26
Tetric Ceram	0.08	0.11	0.16	21.89
Point 4	0.66	0.76	0.91	27.87
Mean and standard deviation	0.38 ± 0.19	0.45 ± 0.20	0.64 ± 0.27	23.21 ± 2.82

content of pyrolytic residues [33]. Based on the values on this table, the organic percentage values, which correspond to mass loss, could be calculated. Considering the last column in Table 2, the difference to 100 corresponds to the inorganic compounds percentage (filler content) or residue. The inorganic compounds percentage found were similar to those reported by some manufacturers, and some of them were close to the amount found by other researchers [19]. Mass loss variation between 25 and 170 or 180 °C was calculated to determine which temperature was higher and safer.

DSC (exothermic event)

DSC measurements were carried out in two cycles (Fig. 2) in order to remove the thermal history of the material, and also to make possible the evaluation of the material behavior during heating. Figure 2 (Filtek Supreme) shows the representative curve of DSC, and Fig. 3 (Z350) displays the amplification (zoom) of the exothermic event region.

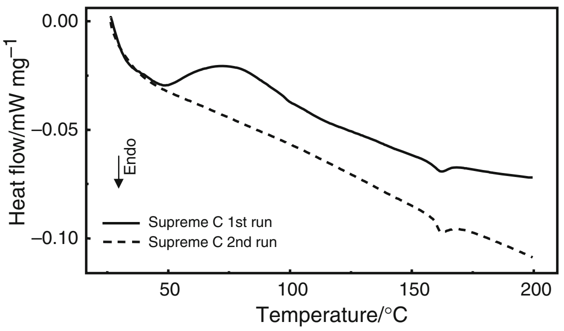

Fig. 2 DSC representative curve of the composite Filtek Supreme: 1st run (*full line*) and 2nd run (*dashed line*)

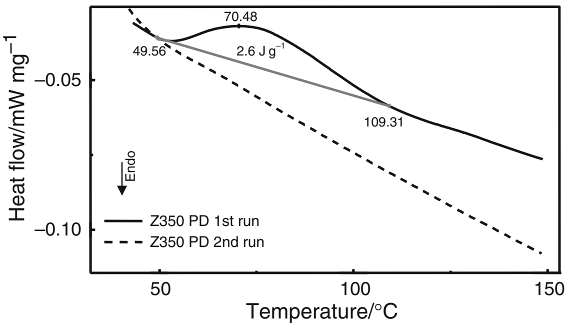

Fig. 3 Exothermic event—representative curve of the composite Z350 photoactivated by PD method, for heat determination (J g^{-1}), related to post-cure

Samples were heated up to 200 °C. In the first run—first heating cycle (continuous line in Fig. 2), it was possible to note the exothermic event, represented by a curve inflexion. The exothermic event peak temperature was determined by averaging six readings ($n = 3$) (ten materials and two photoactivation techniques), because differently from exothermic events, peak temperatures (regardless of the photoactivation method) did not show significant differences (photoactivation mode: $p = 0.07$ and interaction between factors: $p = 0.09$). Mean peak values were between 70 and 80 °C.

The mean values for photoactivation methods, in °C, for *onset* and *endset* temperatures were: 55.0 ± 2.9 and 94.6 ± 5.8 for C, and 51.7 ± 2.6 and 102.2 ± 4.2 °C for PD. The area under the exothermic event, delimited by the *onset* and *endset* temperatures, allows the software TA60WS to calculate the amount of heat release (J g^{-1}) (Table 3) [14], for the composites photoactivated by C and

Table 3 Heat data (mean and standard deviation) (J g^{-1}) of the studied composites photoactivated by C and PD methods

Composite	Mean/J g^{-1} and stardard deviation		
	C	PD	Material
Z100	1.3 ± 0.3	1.4 ± 0.3	1.4 c
Z250	2.2 ± 0.1	2.8 ± 0.4	2.5 b,c
Z350	2.7 ± 0.2	3.4 ± 0.5	3.1 a,b
Supreme	2.7 ± 0.4	3.8 ± 0.8	3.3 a,b
Esthet-X	3.8 ± 0.3	4.4 ± 1.0	4.1 a
TPH Spectrum	3.5 ± 0.5	4.7 ± 0.6	4.1 a
Herculite XRV	1.8 ± 0.2	2.8 ± 0.5	2.3 b,c
Charisma	4.6 ± 0.9	4.7 ± 0.5	4.7 a
Tetric Ceram	2.3 ± 0.2	3.1 ± 0.4	2.7 b
Point 4	1.1 ± 0.2	1.8 ± 0.1	1.4 c
Activation	2.6	3.3	

Different letters represent values statistically different. Same letters represent values statistically similar

PD methods. This heat release can be indicative of the transformation of unsaturated into saturated bonds, what leads to the desired DC increase in “post cure” [9–11]. This is an irreversible phenomenon, which appears only in the first heating cycle, and represents the material’s thermal history [20] (not seen in the second run). It can be indirectly measured by the heat determined by the exothermic events [14, 33, 37]. DC can increase even after photoactivation, when heat is applied. Thus it was interesting to determine the exothermic temperature peak, since it would be possible to achieve an increase in DC and in the mechanical properties by applying a heat treatment above this temperature [8, 26, 28].

It can be noticed that heat release (J g^{-1}) of PD samples was higher than for C samples (Table 3). Although the energy doses for C and PD methods had the same magnitude (20 J cm^{-2}) (20.4 for PD and 19.9 J cm^{-2} for C), specimens photoactivated by C method presented a lower heat release and a shorter release interval (between *onset* and *endset*). The literature does not report differences between DC using different methods [29]. Despite showing DC values similar to those achieved by C method, there is another problem related to PD method, which is the lower degree of conversion obtained at the nonirradiated side (on the opposite side from the light cure device) [23]. Perhaps this problem could be solved by the heat treatment, what explains the higher heat release.

Still regarding the exothermic event, it was possible to observe (Table 3) that the factor material also determined the observed differences: the composites Charisma (4.7 J g^{-1}), Esthet-X (4.1 J g^{-1}) and TPH Spectrum (4.1 J g^{-1}) showed the highest values. Differences in heat release, considering the factor material ($p = 0.00$), could be explained by the different compositions of the studied materials, as type, amount, size and distribution of filler content, monomer type in the matrix, inhibitor and initiator content, the monomer’s blend, among other factors [29, 36, 38–40]. For example, monomers as bis-GMA are very reactive; however, their high viscosity results from the aromatic rings, which reduce the conversion. On the other hand, TEGDMA is less reactive and more viscous and, therefore, has a higher conversion. UDMA is also more reactive than bis-GMA, and both can be mixed together for viscosity reduction [38, 41].

Filler content also indirectly interferes with exothermic events since the smaller it is, the higher is heat release [20]. This can explain the higher heat release for the composites Charisma, Esthet-X and TPH Spectrum. However, although Point 4 has matrix content similar to Charisma, this composite showed a lower exothermic event. Therefore, other fonts of variation must be considered, such as light scattering, amount and quality of initiators, and others already cited before.

To verify if this heat release difference correlates to other factors, further studies are needed, such as analysis of DC by spectroscopy (FTIR, Raman, FT-Raman) [13, 36, 39, 40, 42] and mechanical tests (flexural strength, hardness, among others) [9, 11, 17, 18, 31, 36, 43], preferably using experimental composites with systematic variation in the microstructure and chemical composition.

DSC (T_g)

Figure 4 shows the amplification (zoom) of the composite Filtek Supreme curve, representative of DSC second run (20 °C min^{-1}). The entire curve can be seen in Fig. 2. The difference between first and second run recorded during DSC measurements is a result of the curing reaction. After analysis in TA60WS software, an endothermic peak (157.5 °C) was observed in the second run (Fig. 4). In the derivative curve (DDSC), it was possible to determine a more accurate temperature for this measurement (159.9 °C). This temperature determined was defined as glass transition temperature (T_g), which represents a second-order transition, with the transformation from a glass state (more ordered) into a rubber state (more flexible and less ordered). It was first stipulated for glasses, but latter transposed to polymers [44]. T_g can lead to the relaxation of the stresses generated during the polymerization process, achieved by the increase in radical mobility [14, 45]. So, mean values for T_g were determined for each material (Table 4), because a heat treatment over T_g could lead to an improvement in the mechanical properties.

Although the literature shows different values of T_g, ranging from 35 to 186 °C [38, 45–47], some factors could be used as explanation, such as composition (different monomers and comonomers, blends, initiators, experimental or commercial composites, amount and type of filler, etc.) and color of the composite, dose and photoactivation technique, measurement technique (DSC [38, 45] and TMA tests [47]), among others. The T_g results obtained in this study

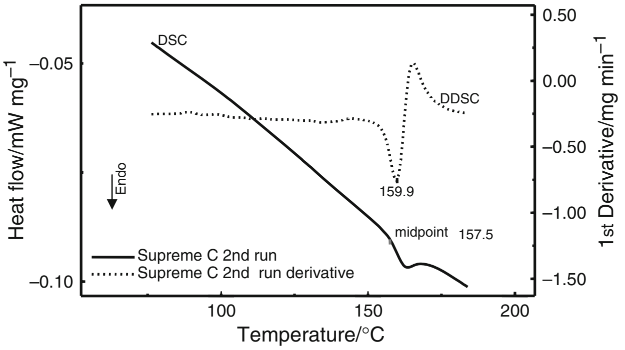

Fig. 4 DSC/DDSC representative curve of the composites Filtek Supreme for T_g analysis (2nd run)

Table 4 T_g: mean values of the studied composites

Composites	Mean/°C		
	C	PD	Materials
Z100	158.4	158.5	158.5
Z250	159.0	159.7	159.3
Z350	158.9	160.0	159.4
Supreme	156.6	157.5	157.1
Esthet-X	155.9	158.9	157.4
TPH Spectrum	157.5	160.6	159.1
Herculite XRV	158.6	160.4	159.5
Charisma	159.3	157.9	158.6
Tetric Ceram	156.6	157.8	157.2
Point 4	156.7	159.3	158.0
Activation	157.8	159.1	

were relatively high; however, they were comparable to those obtained by Rojas et al. [48]. The difference may be due to the application of different energy doses, which was higher in this study, and to the different light sources (halogen in this study versus blue emitting diodes in the other).

In this study, the analysis of variance showed that both the material ($p = 0.04$) and photoactivation method ($p = 0.02$) had a significant effect on the results, but this difference presented a short range (mean values between 157.1 and 159.5 °C) as p value was close to 5%. The numerically similar results could be due to the fact that current commercial composites would be less susceptible to activation sources/modes, with optimization of the initiators and comonomers balance. Interaction between material and photoactivation method was not significant, as shown by the analysis of variance ($p = 0.34$).

Heat treatment

It is reasonable that, considering the results obtained by TG/DTG, a temperature below 180 °C should be chosen for the heat treatment, as such temperature is safe enough to avoid mass loss. Moreover, this temperature range is above either the exothermic peak or a temperature above T_g. In this way, the increase in radical mobility within the already polymerized material could increase DC and consequently improve the mechanical properties of the polymer [14, 38]. In addition, the heat treatment above T_g causes relaxation of stresses generated due to polymerization shrinkage. Thus, the alterations that occur due to heating above the T_g could have resulted in an increase in mechanical properties. To verify the efficacy of a heat treatment above the T_g and under a temperature that causes mass loss, other studies are necessary (flexural strength, hardness, fatigue, hydrolytic degradation, for example).

Conclusions

Based on the results of this study it is possible to conclude that both thermal analyses performed (TG/DTG) and (DSC/DDSC) were effective in determining the thermal properties of the resin composites studied. The results support the fact that there is an optimal heat treatment that is able to improve the mechanical properties without causing any perceivable degradation of the polymer network. Such treatment involves an ideal temperature that is above the T_g (159.5 °C) and below the temperature in which the polymer degradation initiates (180 °C), as this range of temperature is also above the *endset* of the exothermic event ($\sim$100 °C).

Acknowledgements The authors would like to acknowledge the Brazilian agencies CAPES, CNPq, and FAPESP for the financial support, the PhD Student Maurício Neves Gomes and the PhD Professor Paulo Francisco Cesar for the cooperation with this research.

References

1. Leinfelder KF. Posterior composite resins: the materials and their clinical performance. J. Am. Dent. Assoc. 1995;126(5):663–76.
2. Rueggeberg FA, Craig RG. Correlation of parameters used to estimate monomer conversion in a light cured composite. J. Dent. Res. 1988;67(6):932–7.
3. Ruyter IE. Types of resin-based inlay materials and their properties. Int. Dent. J. 1992;42(3):139–44.
4. Terry DA, Touati B. Clinical considerations for aesthetic laboratory/fabricated inlay/onlay restorations: a review. Pract. Proced. Aesthet. Dent. 2001;13(1):51–8.
5. Cesar PF, Miranda WG Jr, Braga RR. Influence of shade and storage time on the flexural strength, flexural modulus, and hardness of composites used for indirect restorations. J. Prosthet. Dent. 2001;86:289–96.
6. Tanoue N, Matsumura H, Atsuta M. Comparative evaluation of secondary heat treatment and high intensity source for the improvement of properties of prosthetic composites. J. Oral Rehabil. 2000;27:288–93.
7. Wendt SLJ, Leinfelder KF. The clinical evaluation of heat-treated composite resin inlay. J. Am. Dent. Assoc. 1990;120(2):177–81.
8. Santana IL, Lodovici E, Mator JR, Medeiros IS, Miyazaki CL, Rodrigues Filho LE. Effect of experimental heat treatment on mechanical properties of resin composites. Braz. Dent. J. 2009;20(3):205–10.
9. Peutzfeldt A, Asmussen E. The effect of postcuring on quantity of remaining double bonds, mechanical properties, and in vitro wear of two resin composites. J. Dent. 2000;28:447–52.
10. Loza-Herrero MA, Rueggeberg FA, Caughman WF, Schuster GS, Lefebvre CA, Gardner FM. Effect of heating delay on conversion and strength of a post-cured resin composite. J. Dent. Res. 1998;77(2):426–31.
11. Peutzfeldt A, Asmussen E. Effect of temperature and duration of post-cure on selected mechanical properties of resin composites containing carboxylic anhydrides. Scand. J. Dent. Res. 1992;100(5):296–8.
12. Tezvergil A, Lassila LVJ, Vallettu PK. The effect of fiber orientation on the thermal expansion coefficients of fiber-reinforced composites. Dent. Mater. 2003;19:471–7.

13. Trujillo M, Newman SM, Stansburry JW. Use of near-IR to monitor the influence of external heating on dental composite photopolymerization. Dent. Mater. 2004;20:766–77.
14. Vaidynathan J, Vaidynathan TK, Wang Y, Viswanadhan T. Thermoanalytical characterization of visible light cure dental composites. J. Oral Rehabil. 1992;19:49–64.
15. Bausch JR, de Lange C, Davidson CL. The influence of temperature on some properties of composite resins. J. Oral Rehabil. 1981;8(4):309–17.
16. Ferracane JL, Condon JR. Post-cured heat treatments for composites: properties and fractography. Dent. Mater. 1992;8(5):290–5.
17. Mante F, Saleh N, Mante M. Softening patterns of post-cured heat-treated dental composites. Dent. Mater. 1993;9(5):325–31.
18. Miyazaki CL, Medeiros IS, Santana IL, Matos JR, Rodrigues Filho LE. Heat treatment of a direct composite resin: influence on flexural strength. Braz. Oral Res. 2009;23(3):241–7.
19. Sabbagh J, Ryelandt L, Bachérius L, Biebuyck J-J, Vreven J, Lambrechts P, et al. Characterization of the inorganic fraction of resin composites. J. Oral Rehabil. 2004;31:1090–101.
20. Canevarolo, Jr. S.V.: Técnicas de caracterização de polímeros, 1st edn, pp. 19–39, 209–259. Artliber, São Paulo (2004).
21. Imazato S, Mc Cabe JF, Tarumi H, Ehara A, Ebisu S. Degree of conversion of composites measured by DTA and FTIR. Dent. Mater. 2001;17:178–83.
22. Pianelli C, Devaux J, Bebelman S, Leloup G. The micro-Raman spectroscopy, a useful tool to determine the degree of conversion of a light-activated composite resin. J. Biomed. Mater. Res.: Appl. Biomater. 1999;48:675–81.
23. Yap AU, Soh MS, Siow KS. Effectiveness of composite cure with pulse activation and soft-start polymerization. Oper. Dent. 2002;27(1):44–9.
24. Davidson CL, de Gee AJ. Relaxation of polymerization contraction stress by flow in dental composites. J. Dent. Res. 1984;63(2):146–8.
25. Lim BS, Ferracane JL, Sakaguchi RL, Condon JR. Reduction of polymerization contraction stress for dental composites by two-step light activation. Dent. Mater. 2002;18:436–44.
26. Sideridou I, Tserki V, Papanastasiou G. Effect of chemical structure on degree of conversion in light-cured dimethacrylate-based dental resins. Biomaterials. 2002;23:1819–29.
27. Truffier-Boutry D, Demoustier-Champagne S, Devaux J, Biebuyck JJ, Mestdagh M, Larbanois P, et al. A physic-chemical explanation of the post-polymerization shrinkage in dental resins. Dent. Mater. 2006;22(5):405–12.
28. Asmussen E, Peutzfeldt A. Flexural strength and modulus of a step-cured resin composite. Acta Odontol. Scand. 2004;62:87–90.
29. Bayindir YZ, Yildiz M, Bayindir F. The effect of "soft-start polymerization" on surface hardness of two-packable composites. Dent. Mater. J. 2003;22(4):610–6.
30. Hofmann N, Markert T, Hugo B, Klaiber B. Effect of high intensity vs soft-start halogen irradiation on light-cured resin-based composites. Part I: temperature rise and polymerization shrinkage. Am. J. Dent. 2003;16(6):421–30.
31. Hofmann N, Markert T, Hugo B, Klaiber B. Effect of high intensity vs soft-start halogen irradiation on light-cured resin-based composites. Part II: hardness and solubility. Am. J. Dent. 2004;17(1):38–42.
32. Small BW. A review of devices used for photocuring resin-based composites. Gen. Dent. 2001;49(5):457–60.
33. Almeida CC, Mothé CG. Characterization of dental composites by thermal analysis, infrared spectroscopy and scanning electron microscopy. J. Therm. Anal. Cal. 2009;97:585–9.
34. Acharya A, Greener EH. Thermogravimetric analysis of composite restorative resins. J. Dent. Res. 1972;51(5):1363–8.
35. Kim KH, Ong JL, Okuno O. The effect of filler loading and morphology on the mechanical properties of contemporary composites. J. Prosthet. Dent. 2002;87(6):642–9.
36. Neves AD, Discacciati JAC, Oréfice RL, Jansen WC. Correlation between degree of conversion, microhardness and inorganic filler in composites. Braz. Oral. Res. 2002;16(4):349–54.
37. Lloyd CH, Brown EA. The heat of reaction and temperature rises associated with the setting of bonding resins. J. Oral Rehabil. 1984;11:319–24.
38. Jancar J, Wang W, Dibenedetto AT. On the heterogeneous structure of thermally cured Bis-GMA/TEG-DMA resins. J. Mater. Sci. Mater. Med. 2000;11:675–82.
39. Park SH. Comparison of degree of conversion for light-cured and additionally heat-cured composites. J. Prosthet. Dent. 1996;76:613–8.
40. Yoon TH, Lee YK, Lim BS, Kim CW. Degree of polymerization of resin composites by different light sources. J. Oral Rehabil. 2002;29:1165–73.
41. Floyd CJE, Dickens SH. Network structure of Bis-GMA and UDMA-based resins systems. Dent. Mater. 2006;22:1143–9.
42. Tanoue N, Koishi Y, Matsumura H, Atsuta M. Curing depth of different shades of a photo-activated prosthetic composite material. J. Oral Rehabil. 2001;28:618–23.
43. Peutzfeldt A, Asmussen E. Mechanical properties of heat treated restorative resins for use in the inlay-onlay technique. Scand J Dent Res. 1990;98:564–7.
44. Phillips RW. Skinner's science of dental materials. 9th ed. Philadelphia: Saunders; 1991.
45. Viljanen EK, Skrifvars M, Vallitu PK. Dendritic copolymers and particulate filler for dental applications: degree of conversion and thermal properties. Dent. Mater. 2007;23(11):1420–7.
46. Broer DJ, Mol GN. Temperature effects on the kinetics of photoinitiated polymerization of dimethacrylates. Polymer. 1991;32(4):690–5.
47. Sideridou I, Achilias DS, Kyrikou E. Thermal expansion characteristics of light-cured dental resins and resin-composites. Biomaterials. 2004;25(15):3087–97.
48. Rojas SS, Frigo GJM, Bernardi MIB, Rastelli ANS, Hernandes AC, Bagnato VS. Thermal and structural properties of commercial dental resins light-cured with blue emitting diodes (LEDs). J. Therm. Anal. Cal. 2010;99:263–8.