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Understanding the Effect of Thermal Treatment on the Physico-Mechanical Properties of Light-Cured Composites for use in Indirect Restorations

Keywords

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ABSTRACT

Objectives: To study the potential benefits of a post-cure thermal treatment on key physico-mechanical properties of light-cured resin-based composites for use in indirect restorations, a CAD/CAM composite block being used as control. Material and methods: Six commercial composites were light-cured before being thermally treated in a furnace at 90°C during 15 minutes (CAD/CAM composite used as a control). The properties measured with or without thermal treatment were: degree of conversion, flexural strength, elastic modulus, Vickers microHardness, organic mass content and eluted and absorbed mass before and after storage in ethanol. The data were analysed using one-way ANOVA, and Weibull distributions. Results: A general increase in the properties measured was observed for all materials after thermal treatment, except a general decrease in mass elution and absorption (most statistically significant: $p<0.05$). Weibull analysis showed a tendency ($p>0.05$) of increased reliability of the flexural strength after thermal treatment for all materials. Conclusion: The present data revealed clear physico-mechanical improvements after thermal treatment of light-cured composites. Such method could hence be beneficially used to produce indirect restorations as compared to stratifying and light-curing the same composites in situ. However, most properties of the control CAD/CAM composite were higher, but CAD/CAM technologies aren't available everywhere.

INTRODUCTION

There are numerous advantages to use resin-based composites (RBCs) to restore damaged teeth: good aesthetics, fast and on-demand setting thanks to light-curing, mechanical properties described as relatively well adapted to the tooth structures,[1] adhesion to dental tissues thanks to bonding agents,[2] simplicity of clinical use (notably ease of polishability, reparability, long working time and short setting time) and good longevity,[3,4] compared with other restorative materials. These advantages place the RBCs as choice materials to restore damaged teeth nowadays.

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Despite those advantages, RBCs are associated with some major drawbacks. Their limited depth of cure (depending on the material considered, the light irradiance, and the curing characteristics)[5-7] require clinicians to build up large restorations in multiple layers in the patient mouth. This is both time consuming, and a potential source of defects, which may lead to a reduction of restoration longevity. Indeed, clinical and meta-analysis data indicate that fracture both of the tooth and of the restoration remain a major cause for failure of direct composite restorations.[8,9] The other drawbacks of the direct use of RBCs are the technical challenges associated with large direct restorations, such as the restoration of an optimal contact point, the management of the occlusal anatomy and of the resulting contacts with antagonist teeth. These drawbacks can be partly overcome by using these materials in an indirect fashion, which requires making a dental impression, the manufacturing of the restoration in a dental lab or with a computer-assisted design and machining (CAD/CAM) system, and the adhesive placement of the restoration at a second appointment.[10]

Until recently, RBC indirect restorations were manufactured by a dental technician on a replica by shaping and light-curing successive layers. Then appeared the machining of pre-cured blocks in CAD/CAM systems (cured under high temperature and high pressure (HT/HP)), with broad indications in fixed prosthodontics, including crowns, inlays, onlays, overlays or endocrowns.[11] The advantages of such blocks over stratified light-cured materials include a higher degree of conversion (DC),[10] a decrease of un-reacted monomer elution, less porosities which translates into higher mechanical properties,[12] higher wear resistance,[13] higher static mechanical properties and resistance to fatigue compared with RBCs light-cured at room temperature[14-16] and reduction of the flaws linked to the layering and light-curing of light-curable RBCs, which is in fact a rather complex process[17] often underestimated by clinicians.[18-20] In several aspects, RBCs may be viewed favourably when compared to ceramics: they can be manipulated easily, are manufactured more quickly and can be easily repaired while also being cheaper to manufacture.[11,21] This makes composite an interesting material for use in indirect restorations in the new era of CAD/CAM technology.

However, despite its high annual growth rate, the use of CAD/CAM technology is still not widespread in all prosthetic laboratories worldwide, most of the workload being still handled by use of conventional methods.[22] This has for example led companies to develop kits for in-office impression and the manufacture of RBC inlay-onlays, allowing one-appointment procedures.[23] Hence, the need to optimize the properties of modern light-curable RBCs for use in indirect restorations remains very relevant. Therefore, although some of the mechanical properties of direct RBCs are still lower than those of the dental structures,[24] thermal treatment looks promising to increase the range of applications for RBCs and their use in indirect strategies.

To our knowledge, only one clinical study[25] compared in a randomized fashion a direct to an indirect composite restoration strategy with regards to restoration longevity. The authors reported no statistical difference between both approaches after 5 years. One of the major causes of failure of RBC restorations (both direct and indirect) was cohesive failure,[25] which suggests that mechanical properties of RBCs must still be optimized to increase restoration longevity. Such optimization relies both on intrinsic and extrinsic factors.[17]

Regarding intrinsic aspects, a very large diversity of commercial products are available on the market, with very different resulting properties, making it difficult for practitioners to select the “best” material;[26] a classification based on the inorganic filler content has been suggested as a simple and unambiguous, yet imperfect, way to somehow guide dentists in their RBC selection. In terms of extrinsic factors, temperature increase after photopolymerization has been described as a simple and low-cost way to improve the properties of RBCs used for indirect restoration.[27] The positive influence of temperature increase both during and after photopolymerization has been known for a long time. For dental polymers, a temperature rise during polymerization was shown to increase DC more than two decades ago.[28-30] Such an effect is explained by an increase in monomer mobility, which enables additional polymer chain growth before vitrification.[31] More specifically, the influence is positive so long as the temperature is increased above the glass transition temperature, thereby enabling free monomers or unreacted functional groups to react with the remaining radicals trapped in the polymer network.[32,33] Even the difference between intra-oral and extra-oral temperatures is sufficient to significantly ($p<0.05$) improve DC and hardness.[28]

In such a context, the objective of the present work was to study the potential benefits of a post-cure thermal treatment on key physico-mechanical properties of light-cured composites for use in indirect restorations. Specifically, the aim was to measure the evolution of flexural strength (FS), elastic modulus (Emod), degree of conversion (DC), Vickers microhardness (VNH) and mass variation before and after thermal treatment for a range of six commercially available RBCs, and a CAD/CAM RBC.

MATERIALS AND METHODS

Six commercially available RBCs for direct restorations were tested in shade A3: Clearfil™ Majesty Posterior (CMP), Clearfil™ AP-X (APX), Grandio® (Gr), Z100™ (Z100), Essentia® (Ess) and Filtek™ Supreme XTE (XTE). We added a CAD/CAM composite material: Grandio® Disc (Gr-D).

Rectangular specimens were light-cured in white Teflon moulds: 25 mm in length, cross-section of 2x2 mm^2 (as specified by ISO 4049 standard and by manufacturers). These specimens were used to determine the flexural strength (FS) and flexural modulus (Emod), the degree of conversion (DC) and

Vickers microhardness (VHN). Prior to light-curing, specimens were covered on each side with Mylar film, the overall setup resting on a glass slide. A Bluephase G2 was used as curing light, applied for 40 seconds in "high power mode" (providing 1100mW/cm^2) in three successive and non-overlapping spots along a bar, starting in the middle of the sample. The light fiber diameter was 10 millimeters and was placed in direct contact with the Mylar film. The spectral output was within the range [385nm-515nm]. Forty specimens of each materials were prepared, half of which was submitted to a thermal treatment after being light-cured. All specimens were tested to determine FS and Emod, but only half was tested to determine DC and VHN given the smaller standard deviations associated with these techniques.

To determine the absorbed and eluted masses with or without thermal treatment, composite discs were prepared in white Teflon molds (8 mm diameter, 0.5 mm thickness), light cured as described above, this time with a single 40s irradiation (n=6, half thermal-treated).

A similar number of sample of Gr-D specimens (bars and disks) was prepared for each property using a Zirkonzahn M1 Milling Unit.

All specimens were polished using silicon carbide paper (grit 1000 and 2000), before being stored in demineralized water at 37°C (temperature-controlled oven, Memmert®) during one week.

Half of the specimens were submitted to a thermal treatment 15 minutes after light curing by placing them in an oven Heraeus™ T12, at 90°C for 15 minutes. These conditions were determined based on preliminary tests at two temperatures (90 – 120°C) for either 15 or 120 minutes. No statistical difference was observed between these conditions ($p<0.05$) in terms of DC (Appendix 1). It was also verified that 120 °C was lower than the temperature above which RBCs degrade (Appendix 2).

The flexural modulus and flexural strength were determined by three-point bending (n=20). The tests were performed using a universal testing machine, with a distance of 20 mm between the supports and a 0.75 mm/min crosshead speed. Emod and FS were calculated according to the following equations:

Equation 1: $$\boldsymbol{Emod} = \frac{l^3F}{4wt^3d}$$

Equation 2: $$\boldsymbol{FS} = \frac{3F_{max}l}{2wt^2}$$

were F is the load (in Newton), l is the distance between supports (in millimeters), w and t are the width and thickness of a specimen (in millimeters) and d is the deflection due to the load F (in millimeters).

After light curing and mechanical testing, the bar-shaped samples were stored 'dry' in a container, in the dark during one week at room temperature before being analyzed in three different spots located on the upper surface by Raman spectroscopy to determine the DC (in %, n = 10).[34] A frequency stabilized diode laser (785 nm) excited the upper side of the samples through a microscope objective (50x). The following parameters were used: 50 µm slit, 400 lines/mm grating, 60s acquisition time, accumulation of five spectra for each measurement in order to reduce the signal-to-background noise. A computer collected and processed the data corresponding to spectra in the range 1000-2000 cm^{-1}. To calculate DC, the intensity of the peak height corresponding to the C=C bond of methacrylate groups at 1640 cm^{-1} was compared with that of an non polymerized (NP) specimen. The intensity of the peak height corresponding to C=C bonds in aromatic groups at 1610 cm^{-1} was used as the internal standard.[35]

For Gr-D, since VOCO could not provide uncured material, it was assumed that the composition was close to the one of Grandio; hence, DC was calculated using the data from uncured Gr as standard.

Equation 3: $$\boldsymbol{DC}(\%) = \mathbf{100x}\left(\mathbf{1} - \frac{\frac{A^{1640cm-1}}{A^{1610cm-1}}}{\boldsymbol{NP}}\right)$$

were A is the Absorbance, at the peak 1640 or 1610 respectively, and NP is the value of the ratio of the peak heights corresponding to the methacrylate C=C group at 1640 cm^{-1} and 1610 cm^{-1} for the non polymerized RBC. The value of NP is different for each RBC tested.

The VHN (n=10) was determined using a microhardness tester equipped with a 200 g load (F=0.2kgf). The upper surface of the specimens was indented in three different spots using an indentation duration of 30 seconds.

Indentations appear as squares (Vickers indenter) under a microscope and the mean of the length of the three diagonals (d, in mm) is determined and used to calculate the VHN (kgf/mm^2) as shown in equation 4.

Equation 4: $$\mathbf{VHN} = \frac{1.854F}{d^2}$$

To determine mass variations (absorbed (m_a) and eluted (m_e) masses when stored in solvent), composite discs (n=3) were first stored in the dark under vacuum for seven days. The disks were then weighed using a precision scale XP2U (accuracy 0.1 µg) to determine an "initial mass" (m_1), and then immersed in a 100 % ethanol solution (ethanol absolute, >= 99.8 %, Sigma Aldrich) at 37°C for seven days. Following incubation the specimens were removed and blotted dry, before being weighed again (30 seconds after removal from the ethanol solution), to determine an "intermediate mass" (m_2). The discs were again stored under vacuum for seven days and then weighed to obtain a "final mass" (m_3). Then, the m_e and the m_a were calculated using the equations below.

Equation 5: $$\boldsymbol{me}(\%) = \mathbf{100}\,\frac{m1-m3}{m1}$$

Equation 6: $$\boldsymbol{ma}(\%) = \mathbf{100}\,\frac{m2-m3}{m1}$$

Where m_a=absorbed mass; m_e= eluted mass; m_1= initial mass; m_2=intermediate mass; m_3= final mass.

The inorganic filler content (n=3) was determined using thermogravimetric analysis (TGA). The heating cycle parameters were: heating ramp from 30 °C to 900°C at a rate of 10 °C/min. The inorganic filler content (%) was calculated as the ratio between the initial and final specimen mass after the cycle. Note that some RBCs may contain pre-polymerized fillers, which are burned during TGA and are hence not taken into account in filler fraction calculation.

Statistical analysis was performed using the statistical software JMP Pro 14. For the variables which exhibited a normal distribution, an analysis of variance (one-way ANOVA test) could be performed followed by a post-hoc test (Student's t test, alpha = 0.05) to investigate the effect of the thermal treatment. A Tukey-Kramer test was used for multiple comparisons. The flexural strength data associated with APX did not exhibit a normal distribution. Therefore, to compare the means between materials the non-parametric Kruskall-Wallis test was performed. The aims were translated into statistical hypotheses with a significance level set at 0.05. The null hypotheses tested were that there is no effect in terms of FS (1), Emod (2), DC (3), VNH (4) and mass variation (5) for these RBC before and after thermal treatment.

The flexural strength data (n=20) were analyzed to determine a Weibull modulus (m) and characteristic strength (σ0) for each material, after having verified with a Cramer von Mises's test the fit quality. For the Ess material, the test indicated a poor fit with the Weibull model and the corresponding data was not fitted. The modulus estimates the reliability of the material and the characteristic strength corresponds to the strength noted for the failure probability of 63.2 %.[36,37] A high Weibull modulus is associated with a narrow strength distribution, meaning a more predictable and reliable material. Differences between σ0 were considered significant ($p<0.05$) when the 95% confidence intervals did not overlap.

RESULTS

Regarding flexural properties, the thermal treatment was associated with an increase of Emod and FS for all RBCs tested *(Figure 1a & 1b*). The increase was significant ($p<0.05$) and so the null hypotheses (1) and (2) were rejected in all but three conditions (Gr for Emod and FS, Z100 for FS). The values measured for the flexural properties varied greatly between the RBC materials included, Emod, ranging from 7 GPa (Ess) to 19 GPa (CMP) and FS from 81 MPa (Ess) to 210 MPa (Gr-D). There was no statistical difference in Emod between Gr and Gr-D; on the contrary, FS of Gr-D was largely and significantly ($p<0.05$) higher than that of all the other RBCs, with an almost 80% increase compared to its light-curable counterpart.

Regarding polymer conversion, the thermal treatment was associated with an increase in DC *(Figure 1c*). The difference between non-treated and thermal-treated specimens was statistically significant ($p<0.05$) and so the null hypothesis (3) for all RBCs except XTE was also rejected. The percentage of increase in DC was the highest for Z100, Gr and Ess, i.e. above 10 %.

Similarly to what was observed for DC, VHN results showed a significant increase ($p<0.05$) for all thermal-treated RBCs compared with non-treated groups *(Figure 1d*), meaning that the null hypothesis (4) was rejected as well. The percentage of increase was the highest for Ess and Gr (36%). The VHN was the highest for Z100 and Gr-D (around 150 kgf mm^{-2}) and the lowest for Ess (around 50 kgf mm^{-2}).

Thermal treatment was associated with a decrease in m_a and m_e for all materials considered *(Figure 1e & 1f*, respectively), and the decrease was statistically significant ($p<0.05$) meaning that the null hypothesis (5) was rejected for all but one material (Z100 for m_e). The thermal treatment reduced the levels of m_a of all RBCs (except Ess) to levels lower than 0.5%, comparable to those of the Gr-D *(Figure 1e*); similarly, the m_e of all RBCs reached levels lower than 0.5%, i.e. in the same range as Gr-D. The percentage of m_a and m_e was the highest for Ess (3 % and 1.5 %, respectively) and the lowest for Z100 (0.5 % and 0.3 % respectively) and APX (0.45 % and 0.35 % respectively). The percentage of reduction of m_e observed for Ess following thermal treatment (91.1%) was much higher than that of the other RBCs (from 6.2 to 46.8%).

The organic mass content varied from 12 % for CMP and 37 % for Ess *(Figure 2*). APX, Gr and Gr-D exhibited similar organic mass contents ($p>0.05$) with an average of 16 %.

The mechanical strength data were further analysed by fitting it with a two parameter Weibull distribution *(Table 1, Figure 3*). The highest σ0 was noted for the Gr-D (223 MPa), followed by APX and CMP (174 MPa), the last two being statistically similar. The highest Weibull modulus was found for Gr-D (14.3), and the lowest for Z100 (7.2). The thermal treatment led to a general increase in both Weibull modulus and σ0, although the differences were not statistically different for σ0 except for APX and XTE. Gr-D presented a higher σ0 and Weibull modulus as compared to its conventional counterpart (Gr) after thermal treatment, although not in a significant manner for Weibull modulus ($p>0.05$).

DISCUSSION

This study confirms that applying a thermal post-cure treatment had a significant impact on the physico-mechanical properties of the RBCs tested. It is important to note that the thermal procedure was not detrimental to any of the materials tested, but rather influenced the properties in a favourable manner. Indeed, DC, VHN, FS and Emod are all increased, and both the absorbed and eluted mass decreased. This confirms the potential of such a procedure to improve the properties of conventional RBCS for use as indirect restorations.

The results of this study corroborated previous studies, especially by Phan *et al.*,[12] which described significant improvements when conventional RBCs were prepared under HP/HT conditions. The authors reported the advantages of CAD/CAM resin-based materials over "artisanal" materials, the former being certainly the material manufacturing method of choice

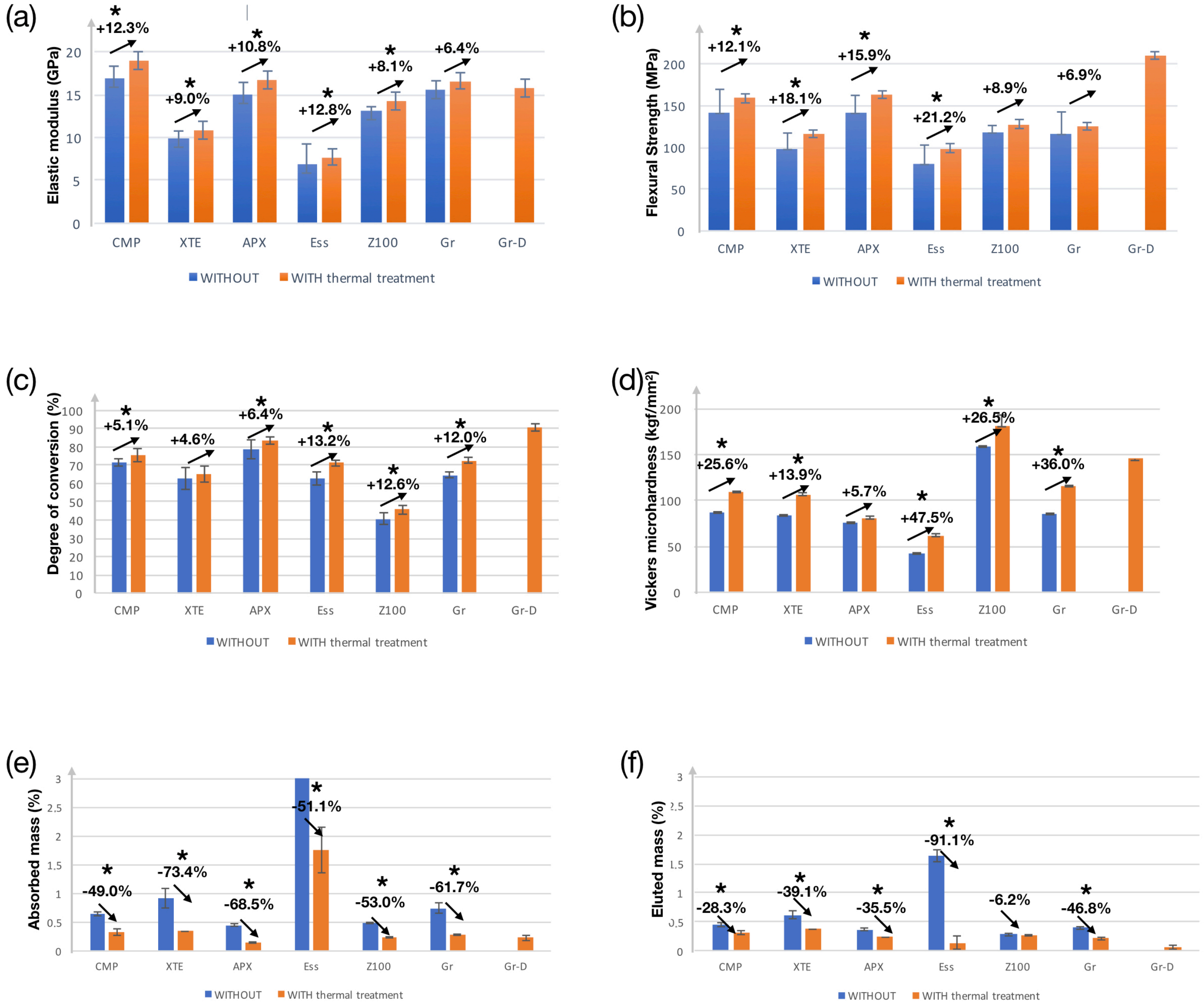


Figure 1: Evolutions of various physico-mecanical properties (means and standard deviations) for each RBCs without and with thermal treatment. The relative differences following thermal treatment are indicated as percentages over arrows. * indicates a significant difference ($p < 0.05$) between conditions without and with thermal treatment for each material.

in the RBC category. However, as mentioned earlier, the access to such technologies still represents the minority of the indirect restorations produced worldwide.[22] Composite post-processing with temperature increase after light cure seems to be a simpler, more accessible and affordable method than the increase in pressure during RBCs polymerization. The present work underlines to which extent this method would be beneficial when producing RBC-based indirect restorations with several modern light-curable commercial materials, especially in areas with no access to CAD/CAM technologies. Nevertheless, a CAD/CAM bloc (Gr-D) was used in order to compare the thermal post-processing of the present work to the properties of industrial HP/HT RBC. In the absence of knowledge regarding the precise composition (not available in safety data sheets), we made the assumption that Gr-D was based roughly on the same components as Gr but manufactured by the company under HP/HT. This assumption was based on the very close values of Emod and filler load. Assuming that, one could expect an increase in mechanical properties from Gr to Gr-D, which was confirmed in our results for all properties but the Emod. The latter was shown to be mostly influenced by the amount of inorganic fillers,[26] which in this case did not change from Gr to Gr-D *(Figure 2)*.

Some of the RBCs considered responded more favourably to thermal treatment than others. Interestingly, the RBC with the highest resin content (Ess) *(Figure 2)* was systematically associated with the largest relative (%) change in properties following thermal treatment *(Figure 1)*. As will be discussed further, this can be expected, since most of the changes due to thermal treatment are expected to occur in the resin matrix. However, the impact of the organic mass fraction on the relative change in properties is much more difficult to highlight for the other materials. The absence of clear trend can first be due to the

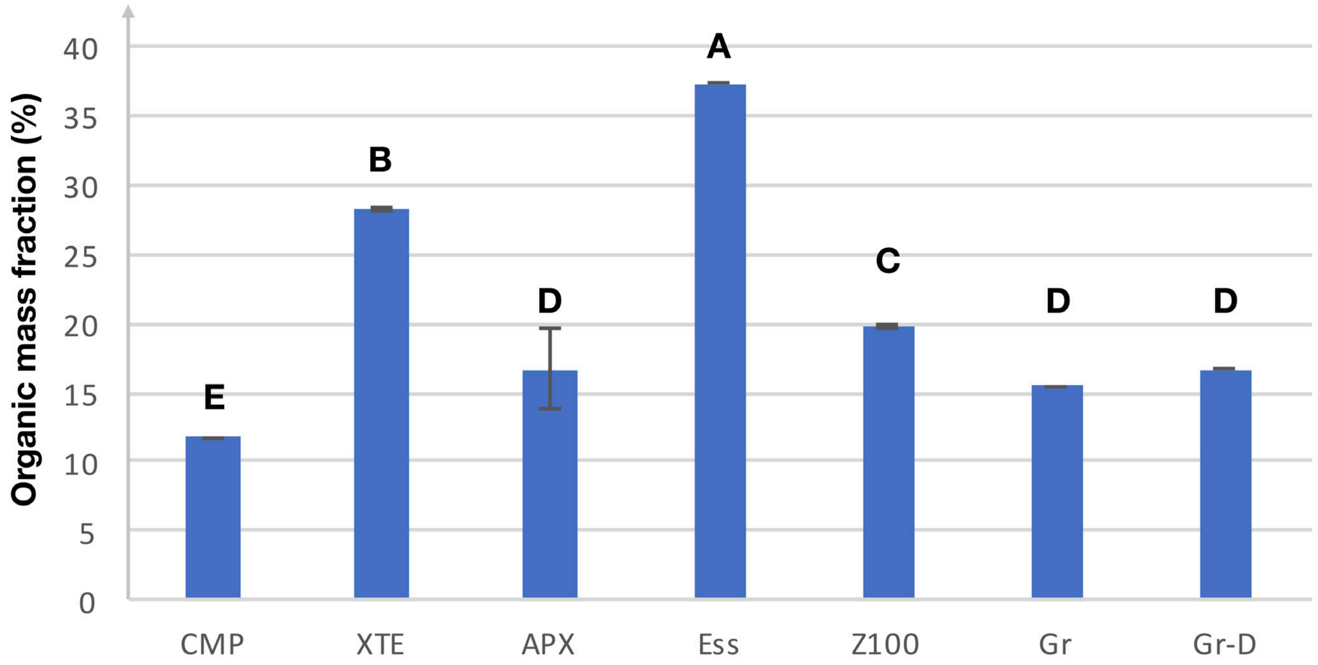


Figure 2: Organic mass fraction (means and standard deviations) for each RBC; identical letters indicate no statistically significant difference (p>0.05).

Table 1. Weibull parameters and 95 % confidence intervals. Similar letters in each row indicate no statistical difference (p> 0.05)

RBC	Weibull characteristic strength (σ0, MPa)		IC95 W characteristic strength		Weibull modulus (m)		IC95 W modulus	
	Without	With	Without	With	Without	With	Without	With
CMP	154	173	142-164	163-182	6.7	8.7	4.6-9.3	5.9-12.2
	a	a			A	A		
XTE	105	122	98-114	116-128	6.4	9.6	4.4-9.0	6.7-13.0
	a	b			A	A		
APX	147	174	138-157	165-184	7.5	8.9	5.2-10.3	6.2-12.2
	a	b			A	A		
Z100	127	136	115-141	127-146	4.7	7.2	3.3-6.2	5.0-9.6
	a	a			A	A		
Gr	125	133	116-135	126-141	6.6	8.7	4.5-9.1	6.1-11.7
	a	a			A	A		
Gr-D	/	223	/	216-231	/	14.3	/	9.7-20.0

lower organic mass fractions, and second to other compositional differences such as the monomer type and ratio or the photo initiator type and concentration. In materials with lower resin fraction, the impact of such differences can be higher, and influence differently the properties considered. As stated in a previous work, it is always very challenging (albeit very clinically relevant) to analyse the impact of a given variable (e.g. here the organic fraction) in commercial materials, both because full constituents are rarely disclosed and because several components are modified at the same time.[24]

Note that the thermal treatment applied following light cure was already suggested two decades ago and was shown to lead to higher DC, flexural modulus, fracture toughness and Knoop hardness of two commercial materials.[38] In this study,

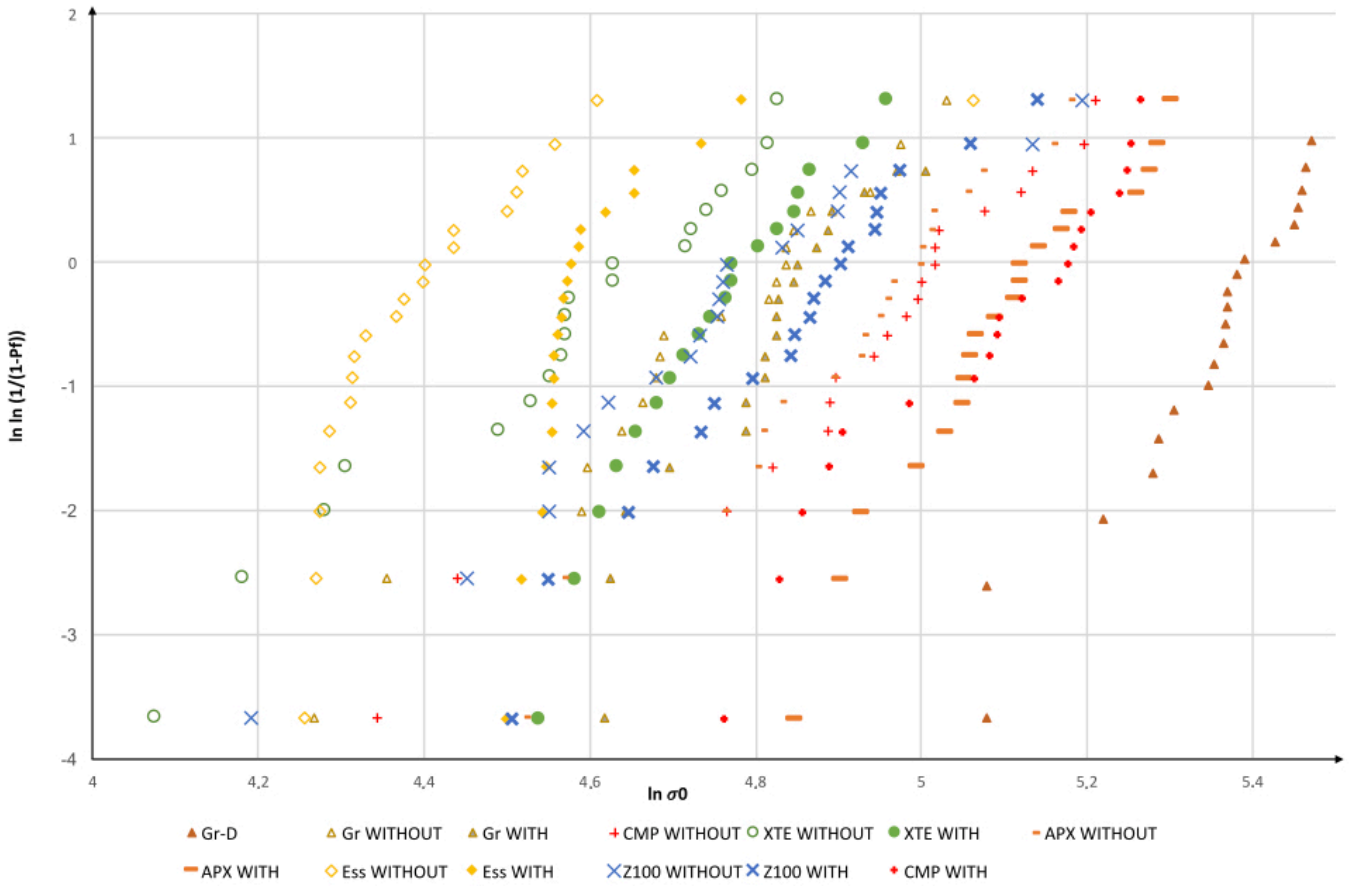


Figure 3: Weibull plots of the RBCs tested comparing the strength distribution for specimens tested in three-point bend test. In bold, the results after thermal treatment.

the increase in DC varied from 2 to 18% (by thermal treatment at 120°C) compared with 4 to 13% (by thermal treatment at 90°C) in our work. It is also worth mentioning that the authors recommended a longer storage period before measurement than the one applied (one day). Our work was conducted with a one week storage duration.

Despite the clear conclusions of that older study, it was stated in two recent comprehensive reviews on dental dimethacrylate polymers that understanding their polymerization and predicting the resulting physico-mecanical behaviour is quite difficult.[17,39] It is notably material specific, hence the need to verify the trend in a range of modern composites, which was done in the present work. In the context of temperature treatment applied following light-curing, it is important to consider the effect of such treatment on the physico-mechanical properties of such complex material as RBCs. As was written by Barszczewska-Rybarek, precise understanding of polymer network is a difficult task, because the specific properties are the result of the complex interaction of the chemical structure of monomer, the molecular structure of polymer network and the morphology.[39]

In the original work by Ferracane and Condon, the improvement in properties was attributed to either a toughening of the organic matrix and an improved filler/matrix interface specifically in composites containing pre-polymerized fillers.[38]

To our knowledge, only Ess contained pre-polymerized fillers among the presently investigated materials. As mentioned above, Ess happens to be the material with the largest relative change in properties, which could confirm partly the improved adhesion between the polymer matrix and the resin of the pre-polymerized fillers, due to a temperature increase above T_g. This increase would increase the molecular mobility both within the resin-containing fillers and in the freshly polymerized matrix, enabling additional molecular connections and macromolecular entanglements between the polymer chains of both matrices.[38] Nevertheless, a definite conclusion is hindered by a confounding factor, i.e. the fact that Ess also presents the largest amount of resin matrix, where most of the changes in the polymer matrix are expected to happen upon temperature rise above T_g. At such temperatures, an increase in monomer mobility enabling additional polymerization and a relaxation of internal stresses were described.[17,33,40] Since the improvement in physico-chemical properties following thermal treatment was observed for all materials regardless of the presence of pre-polymerized fillers, this improvement is most likely due in majority to both a relaxation of the internal stresses not dissipated during the light curing, and the additional polymerization of the freshly polymerized organic matrix. Again, these processes would be facilitated by the additional mobility of monomers and of pendant methacrylate groups and possibly free radicals. Put differently, increasing the temperature above T_g would enable further radical recombination and additional propagation, by re-enabling the diffusion of un-reacted monomers in the polymer network.[33] This mechanism would occur in all incompletely polymerized resin-based materials, which is the case of all light-cured dimethacrylate resin-based dental composites. In the case of dimethacrylate-based resins used in dental composites, T_g of cured systems ranges between 50°C and 90°C.[41-44] By using a temperature of 90 °C, the thermal treatment used in our work was therefore adequate to target unreacted monomers and trapped radicals, as shown by the increased DC.

With this in mind, the investigation of several properties was carried out in the present work to help discriminate between changes in crosslink density and/or DC. This is a difficult task since both characteristics are intimately linked in such highly cross-linked systems.[17] Positive linear correlations have been reported for a given resin-based material between DC, VHN and Emod.[44-48] Similarly, a negative linear correlation was described between DC and monomer elution.[49] In the present work, the general increase in DC after thermal treatment was also associated with an increase in Emod, in VHN and with a reduction of absorbed and eluted mass, in line with previous reports in the literature.[50] However, the relative change in the last three properties is much higher than for DC. We suggest that it underlines that the additional polymerization upon thermal treatment was not only linear addition, but also an increase in the degree of cross-linking within polymer matrices. Specifically, longer polymer chains between crosslinks (low crosslink density) should theoretically result in higher water sorption,[39] which in the present work was observed when the RBCs are thermal treated. The decrease in sorption was higher than 50% although the increase in DC remained between 5 and 13%. It should be noted that the measurement of the conversion of Z100 was more difficult. The reading of the peak of interest was disturbed by the presence of un additional band, which could lead to a certain degree of imprecision. The absolute values should therefore be considered with caution. However, the goal here was not to compare the properties between the different materials, but for a same RBC, after thermal treatment or not. Hence, despite the limitations regarding the possible lower precision, the intra-material comparison remains valid.

The correlation between DC and flexural strength for a given composite material is generally weak[48] since FS depends not only on material composition and polymerization, but also to a large extent on aspects related to the quality of sample preparation such as surface flaws or internal porosities.[51] Nevertheless, it is interesting to note that FS increase significantly after thermal treatment, despite the fact that the "handmade" samples are as likely to present surface flaws before and after thermal treatment. Hence, the FS improvement is likely due to either the above-mentioned strengthening of the polymer matrix, or to an improvement of the filler-matrix interface related to the improved conversion and cross-link density. Such an explanation would remain valid to explain some of the improvement of FS measured for CAD/CAM samples. However, these materials also benefit from a surface presenting less irregularities, which is in line a recent state of the art on indirect composites.[10] The present FS results are in accordance with the data presented in other studies from the same research group.[12,52] For example, FS results of Paradigm™ and VITA Enamic© materials are close to the values measured presently for Z100 and Gr, and the results reported for Lava Ultimate are in the same range as the present values for thermally treated CMP and APX.

Finally, considering the works of Lohbauer's group,[15,53] a Weibull analysis was also performed in our work. This was implemented to provide information on the mechanical reliability of the materials before and after thermal treatment. The Weibull modulus (m, *Table 1*) shows the dispersion of the strength data. Higher m should mean fewer and smaller flaws/defects within a RBC. The present Weibull results are in the same range as comparable materials tested in the aforementioned works. Although not significant statistically, the improvement in the reliability following thermal treatment is again in favour of such procedure.

The results presented in our work highlight the benefit of thermally treating modern light-cured RBCs to improve their physico-mechanical properties and reduce their potential flaws in clinical use. Long term prospective clinical evaluations of extensive posterior restorations showed that fracture of the restorative material is one of the two main failure causes, along with caries.[8,9] Therefore, an improvement of the physico-mechanical properties of the restorative material can be expected to lead to a higher resistance to fracture in clinical use. This potential advantage is combined to the fact that the use of RBC in indirect way offers clinical advantages (contacts points and occlusions are more predictable). Since the access to CAD/CAM technology is still not possible to every dental lab and practice worldwide, the thermal treatment of those RBC could be beneficially used to restore severely damaged posterior teeth. There is unfortunately a lack of clinical studies comparing in randomized fashion the performance of the various materials available for indirect restorations to direct ones. The evaluation of the impact of thermal treatment would fit well as an additional group.

CONCLUSION

The present data revealed clear physico-mechanical improvements after thermal treatment of light-cured RBCs. Such method could hence be beneficially used to produce indirect restorations as compared to stratifying and light-curing the same RBCs in situ. This is especially interesting in areas with no access to CAD/CAM technologies. However, most properties of the CAD/CAM RBC material were higher than its light-curable counterpart material and is therefore likely to be the material manufacturing method of choice in the RBC category.

MANUFACTURER'S DETAILS

- Clearfil™ Majesty Posterior and Clearfil™ AP-X: from Kuraray-Noritake, Japan
- Grandio®: from VOCO, Germany
- Z100™: from 3M ESPE, USA
- Essentia®: from GC, Europe
- Filtek™ Supreme XTE: from 3M ESPE, USA
- Grandio® Disc: VOCO, Germany
- Bluephase G2: from Ivoclar-Vivadent, Liechtenstein
- Zirkonzahn M1 Milling Unit: from Zirkonzahn, Italy
- Silicon carbide paper: from Struers® Silicon Carbide, grit 1000 and 2000
- Temperature-controlled oven: from Memmert®, Germany
- Oven Heraeus™ T12 used for thermal treatment: from Heraeus, Germany
- Universal testing machine: from Lloyd LRX Plus, Lloyd Instruments Ametek, USA
- Raman spectroscopy: DXR Raman Microscope from Thermo Scientific, USA
- Microhardness tester from Durimet, Leitz, Germany
- Precision scale XP2U: from Mettler Toledo®, USA
- Thermogravimetric analysis: TGA/SDTA851e, Mettler Toledo, Switzerland

REFERENCES

1. Ferracane JL. Resin composite-state of the art. *Dent Mater.* 2011;**27**:29-38.
2. Van Meerbeek B, Yoshihara K, Yoshida Y, Mine A, De Munck J, Van Landuyt KL. State of the art of self-etch adhesives. *Dent Mater*. 2011;**27**:17-28.
3. Hickel R, Brushaver K, Ilie N. Repair of restorations-criteria for decision making and clinical recommendations. *Dent Mater*. 2013;**29**:28-50.
4. Wierichs RJ, Kramer EJ, Wolf TG, Naumann M, Meyer-Lueckel H. Longevity of composite build-ups without posts-10-year results of a practice-based study. *Clin Oral Investig*. 2019;**23**:1435-42.
5. Cook WD. Factors affecting the depth of cure of UV-polymerized composites. *J Dent Res*. 1980;**59**:800-8.
6. Erickson RL, Barkmeier WW, Halvorson RH. Curing characteristics of a composite - part 1: cure depth relationship to conversion, hardness and radiant exposure. *Dent Mater*. 2014;**30**:e125-33.
7. Erickson RL, Barkmeier WW. Curing characteristics of a composite. part 2: the effect of curing configuration on depth and distribution of cure. *Dent Mater*. 2014;**30**:e134-45.
8. Van Nieuwenhuysen JP, D'Hoore W, Carvalho J, Qvist V. Long-term evaluation of extensive restorations in permanent teeth. *J Dent*. 2003;**31**:395-405.
9. Opdam NJ, van de Sande FH, Bronkhorst E, Cenci MS, Bottenberg P, Pallesen U, *et al*. Longevity of posterior composite restorations: a systematic review and meta-analysis. *J Dent Res*. 2014;**93**:943-9.
10. Mainjot AK, Dupont NM, Oudkerk JC, Dewael TY, Sadoun MJ. From Artisanal to CAD-CAM Blocks: State of the Art of Indirect Composites. *J Dent Res*. 2016;**95**:487-95.
11. Miyazaki T, Hotta Y, Kunii J, Kuriyama S, Tamaki Y. A review of dental CAD/CAM: current status and future perspectives from 20 years of experience. *Dent Mater J*. 2009;**28**:44-56.
12. Phan AC, Tang ML, Nguyen JF, Ruse ND, Sadoun M. High-temperature high-pressure polymerized urethane dimethacrylate-mechanical properties and monomer release. *Dent Mater*. 2014;**30**:350-6.
13. Ferracane JL, Mitchem JC, Condon JR, Todd R. Wear and marginal breakdown of composites with various degrees of cure. *J Dent Res*. 1997;**76**:1508-16.
14. Belli R, Wendler M, de Ligny D, Cicconi MR, Petschelt A, Peterlik H, *et al*. Chairside CAD/CAM materials. Part 1: Measurement of elastic constants and microstructural characterization. *Dent Mater*. 2017;**33**:84-98.
15. Wendler M, Belli R, Petschelt A, Mevec D, Harrer W, Lube T, *et al*. Chairside CAD/CAM materials. Part 2: Flexural strength testing. *Dent Mater*. 2017;**33**:99-109.
16. Wendler M, Belli R, Valladares D, Petschelt A, Lohbauer U. Chairside CAD/CAM materials. Part 3: Cyclic fatigue parameters and lifetime predictions. *Dent Mater*. 2018;**34**:910-21.
17. Leprince JG, Palin WM, Hadis MA, Devaux J, Leloup G. Progress in dimethacrylate-based dental composite technology and curing efficiency. *Dent Mater*. 2013;**29**:139-56.
18. Kopperud SE, Rukke HV, Kopperud HM, Bruzell EM. Light curing procedures - performance, knowledge level and safety awareness among dentists. *J Dent*. 2017;**58**:67-73.
19. Watts DC. Let there be light! *Dent Mater*. 2013;**29**:603-4.
20. Watts DC. Let there be More Light! *Dent Mater*. 2015;**31**:315-6.
21. Giordano R. Materials for chairside CAD/CAM-produced restorations. *J Am Dent Assoc*. 2006;**137**:14S-21S.
22. Research PM. Global Market Study on Dental CAD/CAM & Dental Prosthesis: 3D Dental Prosthesis Segment to Register Fastest Growth Through 2026 2018 [Available from: https://www.persistencemarketresearch.com/market-research/dental-cad-cam-dental-prosthesis-market.asp.
23. Dental V. GrandioSO Inlay System 2020 [Available from: https://www.voco.dental/fr/produits/restaurations-indirectes/inlays-en-composite/grandioso-inlay-system.aspx.
24. Leprince J, Palin WM, Mullier T, Devaux J, Vreven J, Leloup G. Investigating filler morphology and mechanical properties of new low-shrinkage resin composite types. *J Oral Rehabil*. 2010;**37**:364-76.
25. Fennis WM, Kuijs RH, Roeters FJ, Creugers NH, Kreulen CM. Randomized control trial of composite cuspal restorations: five-year results. *J Dent Res*. 2014;**93**:36-41.
26. Randolph LD, Palin WM, Leloup G, Leprince JG. Filler characteristics of modern dental resin composites and their influence on physico-mechanical properties. *Dent Mater* 2016;**32**:1586-99.
27. Grazioli G, Francia A, Cuevas-Suarez CE, Zanchi CH, Moraes RR. Simple and Low-Cost Thermal Treatments on Direct Resin Composites for Indirect Use. *Braz Dent J*. 2019;**30**:279-84.
28. Price RB, Whalen JM, Price TB, Felix CM, Fahey J. The effect of specimen temperature on the polymerization of a resin-composite. *Dent Mater* 2011;**27**:983-9.
29. Daronch M, Rueggeberg FA, De Goes MF. Monomer conversion of pre-heated composite. *J Dent Res*. 2005;**84**:663-7.
30. Cook WD. Fracture and structure of highly crosslinked polymer composites. *J. Appl. Polym. Sci*. 1991;**42**:1259–69.

31. Daronch M, Rueggeberg FA, De Goes MF, Giudici R. Polymerization kinetics of pre-heated composite. *J Dent Res.* 2006;**85**:38-43.
32. Leprince JG, Lamblin G, Devaux J, Dewaele M, Mestdagh M, Palin WM, *et al*. Irradiation modes' impact on radical entrapment in photoactive resins. *J Dent Res.* 2010;**89**:1494-8.
33. Leprince J, Lamblin G, Truffier-Boutry D, Demoustier-Champagne S, Devaux J, Mestdagh M, *et al*. Kinetic study of free radicals trapped in dental resins stored in different environments. *Acta Biomater*. 2009;**5**:2518-24.
34. Pianelli C, Devaux J, Bebelman S, Leloup G. The micro-Raman spectroscopy, a useful tool to determine the degree of conversion of light-activated composite resins. *J Biomed Mater Res.* 1999;**48**:675-81.
35. Leprince JG, Palin WM, Vanacker J, Sabbagh J, Devaux J, Leloup G. Physico-mechanical characteristics of commercially available bulk-fill composites. *J Dent.* 2014;**42**:993-1000.
36. Quinn JB, Quinn GD. Material properties and fractography of an indirect dental resin composite. *Dent Mater.* 2010;**26**:589-99.
37. Quinn JB, Quinn GD. A practical and systematic review of Weibull statistics for reporting strengths of dental materials. *Dent Mater.* 2010;**26**:135-47.
38. Ferracane JL, Condon JR. Post-cure heat treatments for composites: properties and fractography. *Dent Mater*. 1992;**8**:290-5.
39. Barszczewska-Rybarek IM. A Guide through the Dental Dimethacrylate Polymer Network Structural Characterization and Interpretation of Physico-Mechanical Properties. *Materials (Basel).* 2019;**12**(24).
40. Shah MB, Ferracane JL, Kruzic JJ. R-curve behavior and micromechanisms of fracture in resin based dental restorative composites. *J Mech Behav Biomed Mater.* 2009;**2**:502-11.
41. Truffier-Boutry D, Demoustier-Champagne S, Devaux J, Biebuyck JJ, Mestdagh M, Larbanois P, *et al.* A physico-chemical explanation of the post-polymerization shrinkage in dental resins. *Dent Mater.* 2006;**22**:405-12.
42. Dewaele M, Asmussen E, Peutzfeldt A, Munksgaard EC, Benetti AR, Finne G, *et al.* Influence of curing protocol on selected properties of light-curing polymers: degree of conversion, volume contraction, elastic modulus, and glass transition temperature. *Dent Mater.* 2009;**25**:1576-84.
43. Sideridou ID, Vouvoudi EC, Adamidou EA. Dynamic mechanical thermal properties of the dental light-cured nanohybrid composite Kalore, GC: effect of various food/oral simulating liquids. *Dent Mater.* 2015;**31**:154-61.
44. Leprince JG, Leveque P, Nysten B, Gallez B, Devaux J, Leloup G. New insight into the "depth of cure" of dimethacrylate-based dental composites. *Dent Mater*. 2012;**28**:512-20.
45. Bouschlicher MR, Rueggeberg FA, Wilson BM. Correlation of bottom-to-top surface microhardness and conversion ratios for a variety of resin composite compositions. *Oper Dent.* 2004;**29**:698-704.
46. Ferracane JL. Correlation between hardness and degree of conversion during the setting reaction of unfilled dental restorative resins. *Dent Mater*. 1985;**1**:11-4.
47. Li J, Li H, Fok AS, Watts DC. Multiple correlations of material parameters of light-cured dental composites. *Dent Mater*. 2009;**25**:829-36.
48. Peutzfeldt A, Asmussen E. Resin composite properties and energy density of light cure. *J Dent Res*. 2005;**84**:659-62.
49. Ferracane JL. Elution of leachable components from composites. *J Oral Rehabil*. 1994;**21**:441-52.
50. Bagis YH, Rueggeberg FA. The effect of post-cure heating on residual, unreacted monomer in a commercial resin composite. *Dent Mater.* 2000;**16**:244-7.
51. Ilie N, Hilton TJ, Heintze SD, Hickel R, Watts DC, Silikas N, *et al.* Academy of Dental Materials guidance-Resin composites: Part I-Mechanical properties. *Dent Mater*. 2017;**33**:880-94.
52. Ruse ND, Sadoun MJ. Resin-composite blocks for dental CAD/CAM applications. *J Dent Res.* 2014;**93**:1232-4.
53. Belli R, Geinzer E, Muschweck A, Petschelt A, Lohbauer U. Mechanical fatigue degradation of ceramics versus resin composites for dental restorations. *Dent Mater.* 2014;**30**:424-32.

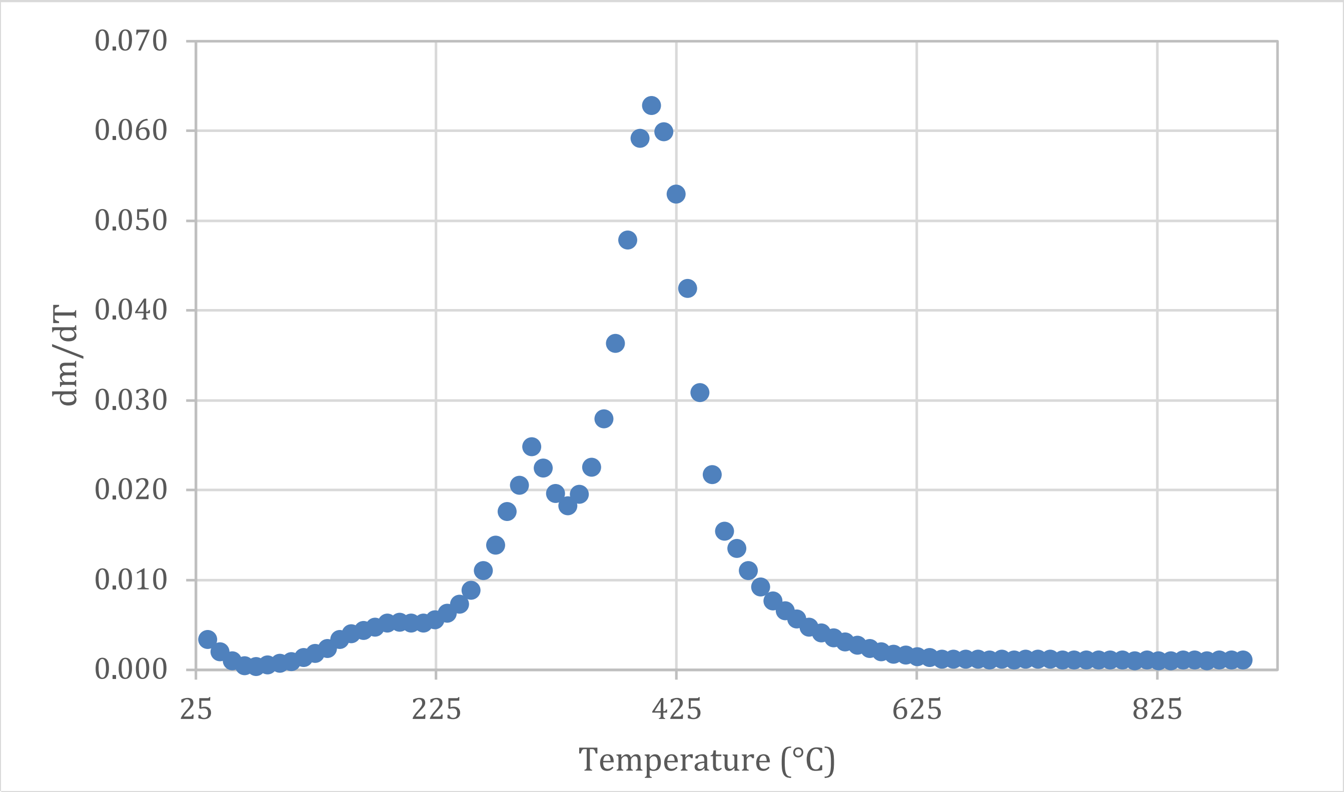
APPENDICES

APPENDIX 1

Grandio	DC (%)
Control : without thermal treatment	67 +-1 b
15 minutes 90°C	74 +-1 a
15 minutes 120°C	74 +-1 a
120 minutes 90°C	71 +-1 a
120 minutes 120°C	73 +-0.5 a

Preliminary tests. Grandio specimens cured during 20s with BPG2 (high mode), before being thermal-treated at different temperatures and durations and then analyzed with Raman Spectrometry to measure the DC. Student-t-test showed no significant differences ($p > 0.05$) between the thermal-treated specimens, but significant differences ($p < 0.05$) when compared with samples without thermal treatment.

Appendix 2



Example of thermogravimetric analysis (TGA) performed on the Filtek Supreme XTE to determine the temperature of degradation of the RBC's tested in this work, showing the initiation of degradation of the RBC above 200°C.