UNIVERSIDADE DE SÃO PAULO
FACULDADE DE ODONTOLOGIA DE BAURU

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In vitro evaluation of intra pulp chamber heating and degree of conversion of a cementation system added with TiO_2 nanotubes

Avaliação *in vitro* do aumento de temperatura intra câmara pulpar e grau de conversão de um sistema de cimentação aditivado com nanotubos de TiO_2

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Orientador: Prof. Dr. Rafael Francisco Lia Mondelli

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Dedico essa conquista a Deus e a todos da minha família.

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ABSTRACT

The achievement of aesthetic and long lasting ceramic adhesive restorations in teeth has always been a major objective of studies in the context of materials and techniques development. The use of resin cements could provide better outcomes, however, studies have shown that factors such as: restoration thickness color, dental structure thickness, curing light, polymerization time and energy density could influence the amount of light that reaches the resin cement layer, which may interfere in the heating of the intra pulp chamber, and in the polymerization reaction. So it is important to assess these properties, responsible for their biological results and clinical behavior. The purpose of the present study was to evaluate the temperature variations inside the pulp chamber, color stability and degree of conversion of resin cement through different curing protocols. For intra pulp chamber temperature measures, Teflon molds were milled with different depths to settle disks of bovine dentin and ceramic disks (0.5, 1.0 and 1.5 mm both), standardize of the cementation line in 100 micrometers, positioning the tip of the light curing unit (LCU) and the tip thermocouple sensor. Study design determined groups according to thickness of bovine dentin (B 0.5; B 1.0 and B1.5 mm), ceramic disk (C 0.5, C 1.0 and C 1.5 mm), and to additivation of 0.3wt% dioxide titanium nanotubes - ntTiO_2 (NT) to the Relyx Ultimate (3M ESPE) (U). The temperature in the pulp chamber was measured every 10 s during 40 s of light activation with Valo (Ultradent) pre-programmed with 1000mW/cm^2 irradiance. All data was evaluated regarding their homogeneity using Shapiro-Wilk test. A Variance Analysis (ANOVA) with repeated measures was conduced, followed by Sidak test ($p \leq 5\%$). For intra pulp chamber measures (ºC), higher temperature means were observed in the group NT light cured through C 0.5+ B 0.5 mm (5.66±0.16). Lower temperature means were shown in the group U light cured through 1.5mm C 0.5 + B 0.5 mm (0.88±0.18). All groups showed intra pulp chamber temperature increasing during light activation with significant differences. Regardless materials thickness, the resin cement reinforced with ntTiO_2 provided higher heating means than the group commercially available. For color stability (ΔE), groups were determined according to the ntTiO_2 additive in the resin cement (U and NT), kind of curing process (40 s of light activation or 6 min of chemical curing), ceramic thickness (C 0.5, C 1.0 and C 1.5 mm), and time of storage (24h and 8 days)

(n=10). Data were obtained by Vita Easyshade (VITA) after the curing process, 24h and 8 days after dry dark storage and were submitted to a 3-way ANOVA, followed by Tukey's ($p \leq 5\%$). NT groups light cured through C 0.5 mm storage for 8 days, presented lower ΔE mean values (1.47±0.88) when compared to your respective group U light cured through C 0.5mm storage for 8 days (3.07±1.07). Higher ΔE mean values were observed in the group U chemically cured, after 24 hours of storage (11.11±2.4), followed by group U light cured though C 1.5mm (6.24±1.89). For degree of conversion, a Differential Scanning Calorimetriy (DSC) was conduced to obtain the enthalpy graphs. The enthalpies were evaluated according to the ntTiO_2 additive in the resin cement (U and NT), kind of curing process (40 s of light activation or 6 min of chemical curing) and ceramic thickness (C 0.5, C 1.0 and C 1.5 mm) in triplicate method. Enthalpies (J/mg) were collected during the curing process. Data were submitted to a 2-way ANOVA for DSC, followed by Tukey's ($p \leq 5\%$). Higher enthalpies mean values were observed in the group U light cured trough C 0.5 mm (123.67±13) followed U light cured though C 1.0 mm (119.17±6.0). For NT groups, those light cured trough C 0.5 mm (89.76±10.1) remained close to the group U light cured trough C 1.5 mm (82.23±15.2). In conclusion, the LCU irradiation time, ceramic/dentin thickness and ntTiO_2 interfered in the temperature variation inside the pulp chamber. Besides that, 0.3wt% ntTiO_2 additive into resin cement increased color stability, and interfered negatively in enthalpy values related to degree of conversion.

Keywords: Light curing units, Resin Cements, Temperature, Degree of conversion, Nanotubes.

RESUMO

A obtenção de restaurações adesivas cerâmicas estéticas e duradouras nos dentes sempre foi um dos principais objetivos dos estudos no contexto do desenvolvimento de materiais e técnicas. O uso de cimentos resinosos pode proporcionar melhores resultados, entretanto, estudos demonstraram que fatores fonte de luz, tempo de polimerização e densidade de energia podem influenciar a quantidade de luz que chega à linha de cimentação interferindo no aquecimento intra câmara pulpar e na reação de polimerização. Por isso, é importante avaliar tais propriedades, no quesito de seus resultados biológicos e comportamento clínico. O objetivo do presente estudo foi avaliar as variações de temperatura no interior da câmara pulpar, grau de conversão (por meio da aferição da estabilidade de cor e entalpia) de um cimento resinoso por meio de diferentes protocolos de polimerização. Para as medidas de temperatura intra-câmara pulpar, foram desenvolvidos moldes de Teflon com para adaptar discos de cerâmica e dentina bovina com diferentes espessuras (0,5; 1,0 e 1,5 mm), ademais as matrizes foram utilizadas para padronização da linha de cimentação em 100 micrômetros, posicionamento do fotopolimerizador (LCU) e o sensor de termopar. O desenho do estudo determinou os grupos de acordo com a espessura da dentina bovina (B 0,5, B 1,0 e B1,5 mm), disco cerâmico (C 0,5, C 1,0 e C 1,5 mm) e aditivação de nanotubos de dióxido de titânio 0,3wt% - ntTiO_2 (NT) ao cimento Relyx Ultimate (3M ESPE) (U). A temperatura na câmara pulpar foi aferida a cada 10 segundos, durante 40 segundos de ativação da luz com Valo (Ultradent) pré-programado com irradiância de 1000 mW/cm^2. Todos os dados foram avaliados quanto à sua homogeneidade pelo teste de Shapiro-Wilk. Foi realizada uma análise de variância (ANOVA) com medidas repetidas, seguida do teste de Sidak ($p \leq 5\%$). Para as medidas de temperatura intra câmara pulpar, maiores médias de temperatura (ºC) foram observadas no grupo NT fotoativado através de C 0,5+B 0,5 mm (5,66 ± 0,16). As menores médias de temperatura foram apresentadas no grupo U fotoativado através de C 1,5 mm+B 1,5 mm (0,88 ± 0,18). Todos os grupos apresentaram aumento da temperatura da câmara pulpar durante a ativação da luz, com diferenças significativas. Independentemente da espessura dos materiais, o cimento

resinoso reforçado com $ntTiO_2$ proporcionou maior aquecimento do que o grupo comercialmente disponível. Para determinação do grau de conversão, a os grupos foram avaliados por meio da estabilidade de cor (ΔE) e entalpias (J/mg). Os grupos utilizados para avaliação do ΔE, foram determinados de acordo com o aditivo $ntTiO_2$ no cimento resinoso (U e NT), tipo de polimerização (40 s de fotoativação e 6 min de cura química), espessura cerâmica (C 0,5; C 1,0 e C 1,5 mm) e tempo de armazenamento (24h e 8 dias) (n = 10). Os dados foram obtidos pelo Easyshade (VITA) após o processo de cura, 24h e 8 dias após o armazenamento à seco e sem luz, e foram submetidos a ANOVA de três fatores, seguida de teste de Tukey ($p \leq 5\%$). Grupos NT fotoativados por C 0,5 mm e armazenados por 8 dias, apresentaram menores valores médios de ΔE (1,47± 0,88) quando comparados ao seu respectivo grupo U fotopolimerizado por C 0,5 mm e armazenamento por 8 dias (3,07±1,07). Maiores valores médios de ΔE foram observados no grupo U quimicamente polimerizado após 24 horas de armazenamento (11,11±2,4), seguido pelo grupo U fotoativado através de C 1,5 mm (6,24±1,89). Para Calorimetria de Varredura Diferencial (DSC), as entalpias foram avaliadas quanto ao aditivo $ntTiO_2$ no cimento resinoso (U e NT), tipo de polimerização (40 s de fotoativação ou 6 min de cura química) e espessura cerâmica (C 0,5, C 1,0 e C 1,5 mm), em triplicata. As entalpias (J/mg) foram coletadas durante o processo de polimerização. Os dados foram submetidos a ANOVA a dois fatores para DSC seguidos pelo teste de Tukey ($p \leq 5\%$). Maiores valores médios das entalpias foram observados no grupo U fotoativado através de C 0,5 mm (123,67±13) seguido do grupo U fotoativado através C 1,0 mm (119,17±6,0). O grupo fotoativado através de C 0,5 mm (89,76±10,1) permaneceu próximo ao grupo U fotoativado através de C 1,5 mm (82,23 ± 15,2). Desta forma foi possível concluir que o tempo de irradiação da LCU, a espessura da cerâmica/dentina e $ntTiO_2$ interferiram na variação de temperatura no interior da câmara pulpar. Além disso, o aditivo de 0,3wt% $ntTiO_2$ em cimento resinoso aumentou a estabilidade de cor e interferiu negativamente nos valores de entalpia relacionados ao grau de conversão.

Palavras-Chave: Fontes de luz, Cimento resinoso, Temperatura, Grau de conversão, Nanotubos.

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1 INTRODUCTION

1 INTRODUCTION

Dental ceramics are extensively used by their esthetic potential and mechanical, optical and biological properties. For bonding ceramic materials, resin-based cements are currently applied as an essential part of the success and quality of esthetic treatments, ensuring high bond strength and improving esthetics and clinical survival rates (Aguiar, Di Francescantonio et al. 2010). Amid so many options availabe nowdays, self-adhesive and dual-polymerization resin cements are preferred due to their simplifyied cementation procedures, decreasing clinical time (Anusavice 1997, Anusavice 1998).

The intention to be dual curing, is for chemical polymerization to occur at its best in areas where light energy deprivation exists. Regardelss of polymerizarion protocol, it is desired that monomers gave high conversion degree and the resin cement posses same physico-chemical, mechanical and biological properties over time (Pegoraro 2010, Morgan, Teixeira et al. 2015).

But is already known that light activation of dual curing resin cements could provide better properties (Pegoraro 2010). As degree of conversion can be considered one of the most important property for esthetic success and longevity of indirect restorations (Caughman, Chan et al. 2001), authors tightly recommend complementary light supplying aiming to increase the energy delivery to the resin cement layer (Arikawa, Kanie et al. 2008, Aranha, Giro et al. 2010, Giannini 2013, Pretel 2016), and potencialize degree of conversion.

For induce the physical polymerization, the most traditional devices in the market are based on light emitting diodes (LED) and can be commercially found with increased irradiances. The development of these high power devices, aimed to increase light transmitance (Arikawa, Takahashi et al. 2009), and the depth of polymerization (Arikawa, Kanie et al. 2008, Baseggio 2011, Randolph, Palin et al. 2014).

Nevertheless, the increase in irradiation time can be responsible for a warming in the pulp chamber (Asmussen 1982, Barghi, Berry et al. 1994, Andreatta 2015) and can become a concern about pulp chamber vitality (Zach and Cohen 1965, Choi, Roulet et al. 2014).

In order to improve some catalistic properties of the resinous materials, nanostructures started to be used. The addition of titanium dioxide ($ntTiO_2$) nanotubes has demonstrated positive results in the composites behavior due to its reactivity and photocatalysis potential (Asmussen 1982, Asmussen and Peutzfeldt 2001, Asmussen and Peutzfeldt 2003, Arruda 2015). The reactivity and photo catalysis potential of titanium dioxide nanotubes ($ntTiO_2$) may be interesting to decrease the light irradiation time and potentialize the polymerization process where light energy doesn't arrives still allowing a high degree of conversion and avoiding harmful warming in the pulp chamber complex. Since there are still a few evidences in the literature until the addition of TiO_2 in dentistry, it may be interesting to evaluate the polymerization behavior of resin cement reinforced with $ntTio_2$ trough different kinds of curing process to provide new approaches for the development or improvement of a materials with better properties. Based on these considerations, the present study aimed to evaluate effect of additive $ntTiO_2$ in warming of intra pulp chamber, color stability and degree of conversion of dual curing resin cement.

2 ARTICLES

2 ARTICLES

2.1 ARTICLE 1

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In vitro evaluation of intra pulp chamber heating during light activation of a cementation system added with TiO_2 nanotubes.

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ABSTRACT

The aim of the present study was to evaluate "in vitro" the temperature variation inside the pulp chamber during 40 seconds (s) of light activation of a resin cement system (RelyX™) additive with titanium dioxide nanotubes ($ntTiO_2$) trough bovine and ceramic disks (0.5, 1.0 and 1.5 mm both). Teflon molds we milled to settle the specimens, standardize of the cementation line in 100 micrometers, positioning thermocouple sensor and the light curing unit. Study design determined groups according to thickness of bovin dentin, ceramic disk, and additivation of 0,3% by weight of titanium oxide nanotubes ($ntTiO_2$) to the resin cement (n=10).The temperature in the pulp chamber was measured every 10 s during 40 s of light activation with Valo (Ultradent) pre-programmed with 1000 mW/cm^2 irradiance. All ANOVA tests were followed by Sidak test and was adopted as significance level ($p \leq 0.001$). Higher intra pulp chamber temperature means (ºC) were observed in the group NT cured through 0.5 mm ceramic and bovine disks (5.66±0.16). Lower temperature means were shown in the group RelyX™ cured through 1.5 mm ceramic and bovine disks (0.88±0.18). All groups showed intra pulp chamber temperature increasing during light activation with significant differences. Regardless materials thickness, the resin cement additive with $ntTiO_2$ provided higher heating means than the group RelyX™ commercialy availabe. It may be concluded that the light source, irradiation time, ceramic/dentin thickness and $ntTiO_2$ additivation interfered in the heating inside the pulp chamber. Temperature increase during light activation of resin composites is still a concern fator. High power curing units, with extended time of irradiation combined with $ntTiO_2$ can increase the temperature above critical parameters.

Keywords: Light curing units, Resin Cement, Temperature, Pulp Chamber, Nanotubes, Polymerization.

INTRODUCTION

Ceramic restorations have been considered superior to composites due to their aesthetic quality, excellent clinical performance, biocompatibility with gingival tissues and high survival rate (1-3). They are also chemically stable and present coefficient of linear thermal expansion similar to tooth enamel and, therefore, ceramics have been occupying a prominent place within dental-materials field (1). However, the clinical success of indirect restorations is based on proper quality of the interfacial bond with dental substrate (4), which is acquired by the choice of luting agent and adequate execution of the cementation technique to generate a strong bond between the tooth and the restoration (5).

Amid so many options of available resin cements in clinical practice (6), dual curing self-adhesive resin cements are the material of choice by clinicians due to their simplified cementation procedures extempet treatment substrate as required and, therefore, a shortening clinical treatment time and decreasing technique sensitivity is expected (7).

Dual-cure resin cements were also developed in attempt to combine the favorable characteristics of self and light-activated cements to polymerize properly even when the light is severely attenuated such as in deep cavities and root canals procedures. In these systems, the catalyst paste containing a chemical activator, is mixed with a base to increase free radical concentration even under insufficient light. However, dual-cure resin cements are dependent on light activation and lower mechanical properties are expected when exposed to low irradiance.

Regardless of the polymerization protocol it is desired that monomers have a high degree of conversion and that the resin cement maintain the physicochemical and biological properties over time (8). For induce the physical polymerization, the most traditional devices in the market are based on light emitting diodes (LED) and can be commercially found with different irradiances varying from 200mW/cm^2 to 3200mW/cm^2 (9). The increased irradiance of these devices aimed to increase light transmitance (10), depth of polymerization and decrease the irradiation time (9, 11, 12).

However, even with high power Leds generally used nowadays, authors still reccomend complementary light supplying to resin cements (9, 13-15). Nevertheless, the increase in irradiation time can be responsible for a warming in the pulp chamber (16-18) and can become a concern about pulp chamber vitality (19, 20).

In order to improve some catalistic properties of the resinous materials, nanostructures started to be used. The addition of titanium dioxide ($ntTiO_2$) nanotubes has demonstrated positive results in the composites behavior due to its reactivity and photocatalystic potential (18, 21-23).

This way, the use of nanotubes may be interesting to decrease the light curing irradiation of the resin-based cements, still allowing a high degree of conversion avoiding harmful warming in the pulp chamber complex. Thus, the aim of this “in vitro” study is to evaluate intra pulp chamber heating during light activation of a resind-based cement system added with $ntTiO_2$.

The null hypotheses tested in the present study were: The polymerization time of the resin cement, the $ntTiO_2$ additive and the thickness of ceramic and dentin disks does not interfere in intra pulp chamber warming.

MATERIAL AND METHODS

The experimental design was composed of 3 factors: resin cement, bovine dentine thickness, ceramic thickness and curing time protocol. The fators were divided into 2, 3, 3 and 4 levels respectively, which determined the groups (n = 10).

Nanotubes were synthesized by the alkaline method in the Advanced Materials Laboratory, Department of Physics, Faculty of Sciences, Bauru, São Paulo (21) and added manually to the resin cement. The amount of nanotubes corresponded to the percentage (0.3%) of the weight of the cement. Therefore, for each dose cement of the Mettler PB 303 scale (Toledo, Barueri, SP, BR), the corresponding percentage of $ntTiO_2$ was also be weighed and calculated. After the proportioning, the $ntTiO_2$ were added to the cement base paste. The manipulation was standardized and performed in a spatula block using a 24F spatula (SS White, Duflex, Rio de Janeiro, Brazil) following the manufacturer’s instructions.

Polytetrafluoroethylene (Teflon) bipartite matrices were milled (Figure 2) for the accommodation of bovine (B) and ceramic disks (C), standardize the cementation line in 100 µm and positioning of the tip of the LCU. These matrices were designed in Inventor 2016 software (Autodesk, Inc. San Rafael, CA, USA) and milled at the Discovery 560 Machining Center (ROMI S.A., Santa Bárbara d'Oeste, SP, Brazil). For conducting the experiment, the lower half of these matrices were partially inserted in a thermal tank with water at 37±1ºC (BIO PDI, São Carlos, SP, BR). The dentin specimens were accommodated in the nests (9.7x 9.7 cm) located at the lower half of the matrices and then the thermal paste (Implastec Eletrochemistry, Votorantim, SP, BR) and the thermocouple sensor (Contemp, São Caetano do Sul, SP, BR) were placed on the outside of these matrices, in contact with the water and the dentin disks (Figure. 1).

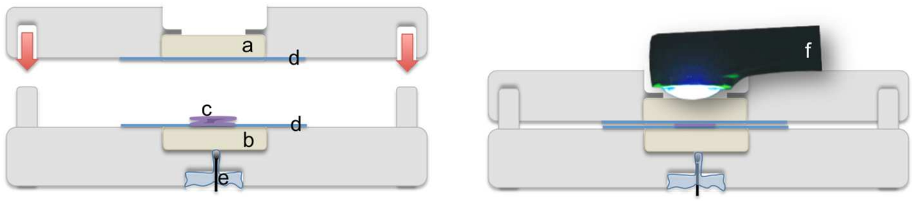

Fig. 1: Schematic drawing of the positioning the (a) ceramic disk, (b) bovine dentin disk, (c) resin cement, (d) polyester matrix, (e) thermal paste and thermocouple sensor, (f) light curing unit VALO™.

Ceramic disks (IPS e-max Press system) were made in A1 color with high translucency (HT) using the lost wax technique. The furnace (FDG3P-S; EDG Equipamentos, São Carlos, SP, Brazil) was used for volatilize the wax and then to the combined furnace EP 3000 (Ivoclar Vivadent, Barueri, SP, Brazil) for ceramic injection. The specimens had 9.7 × 9.7 cm dimensions and 0.5, 1.0 and 1.5 mm thicknesses.

Healthy bovine incisors (Ethics Committee in Animal Education and research 003/2017) were sectioned in the root portion were demarcated on the vestibular face (9.7 × 9.7 mm). In the demarcated area, the disks are obtained. These were planned in metallographic polish with sandpaper disks (3M, Sumaré, SP, BR) until a dentine thickness of 0.5; 1.0 and 1.5mm. The thickness were measured with a digital caliper (Mitutoyo Absolute 6, Suzano, SP, BR).

The spectral irradiance of the light source (VALO) was obteined by 2936-R Power Meter (New Port, Irvine, CA, USA) and Avantes spectrometer (Broomfield, CO, USA) (Figure 2).

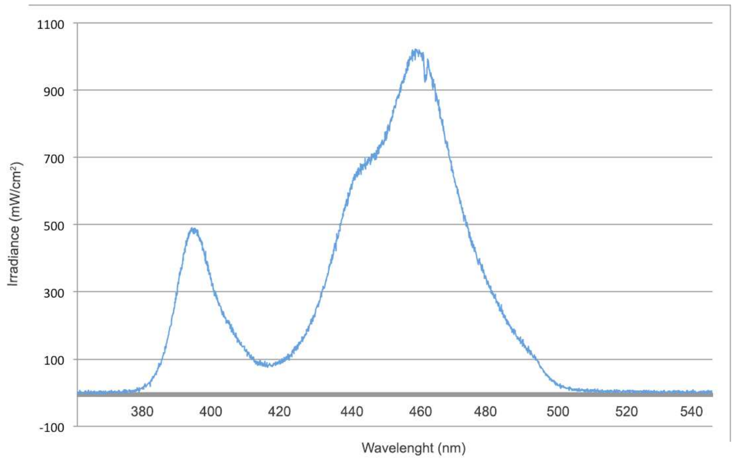

Fig. 2: VALO™ spectral irradiance graph (Department of Physics, UNESP Campus Bauru).

For cementation protocol and pulp chamber temperature evaluation, the resin cement was spatulated following the manufacturer's instructions and the upper half of the matrix was placed on the lower half and adapted with digital pressure until the two are tilted, thus standardizing the cementation line at 100 μm. For the groups with ntTiO_2 additivation, amount was added manually base paste and after catalyst paste (24).

On the hole located in the external upper half of the matrix, the VALO™ lens were adapted, allowing it be stabilized and still on the ceramic specimen. The light curing protocol consisted of applying light for 40 seconds with the equipment in the pre-programmed irradiance of 1000mW/cm^2. Temperature values were acessed every 0, 10, 20, 30 and 40 s during light activation.

A Variance Analysis (ANOVA) with repeated measures was conduced followed by Sidak test and was adopted as significance level ($p \leq 5\%$).

RESULTS

The heating mean values (ºC) after 40 s of light activation suggested that pulp chamber temperature was higher for the group NT light cured through B 0.5+C 0.5 mm (5.66±0.16), followed by B 1.0 mm bovine + C 1.5 mm (4.64ºC±0.19). Lower mean heating was shown in the group U light cured through B 1.5+C 1.5 mm (0.88ºC ±0.18). Mean heating values with standart deviation are shown in the Table 1.

Table 1. Mean heating values (ºC) with standart deviation (±) during 40 s of light uring through bovin dentin disks (B) and ceramic disks (C).

Set	U	NT
B 0.5+C 0.5	3.94(±0.20)aA	5.66(±0.16)bA
B 0.5+C 1	3.58(±0.24)aA	3.83(±0.16)bB
B 0.5+C 1.5	2.21(±0.22)aB	3.08(±0.28)bC
B 1+C 0.5	3.74(±0.25)bA	4.40(±0.27)cB
B 1+C 1	2.39(+0.41)bB	3.99(±0.15)cB
B 1+C 1.5	1.41(±0.24)bC	4.64(±0.19)cB
B 1.5+C 1	1.30(±0.10)cC	2.34(±0.39)dC
B 1.5+C 0.5	1.37(±0.39)cC	2.31(±0.33)dC
B 1.5+C 1.5	0.88 (±0.18)cD	1.18(±0.17)dD

Different lower case letters represent statistically significant difference between the columns; Different capital letters represent statistically significant difference between the lines as evaluated by Anova with repeated measures ($p \leq 5\%$).

For intra pulp chamber heating, higher warming values was observed in the end of 40 s light activation in group NT light activated through C 0.5 mm + B 0.5 mm.

Regardless the groups evaluated, VALO™ provided intra pulp chamber heating. All groups showed temperature increase during the 40 s of light activation regardless the disks thickness. The heating decreased according to increasing thickness of the specimens. In all groups, NT presented higher warming than groups U with statistical differences.

The heating caused by the LCU was statistically different for all the groups (disks' thickness, time of light curing and ntTiO_2 additive) ($p \leq 5\%$).

Mean values and standard deviations of intra pulp chamber heating are shown in Figure 3. Profiles about the groups' behavior in different ways according to the combination Ceramic-Base during the 40 s are shown in Figure 4.

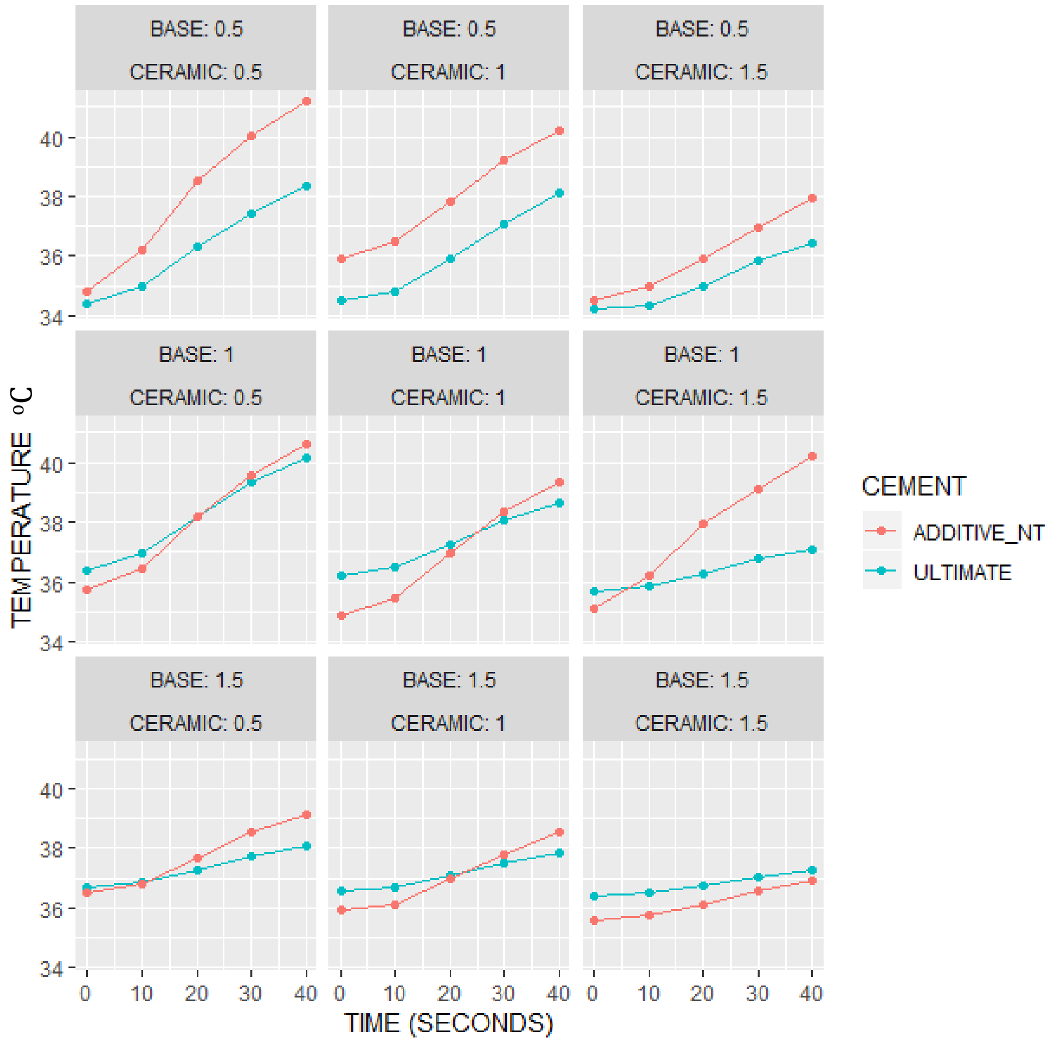

Fig. 3: Difference in temperature (mean values ºC) of intra pulp chamber heating during 40s of light activation in function of ceramic and bovine (base) disks. Base refers to bovine dentin disks thickness and ceramic refers to ceramic disks thickness.

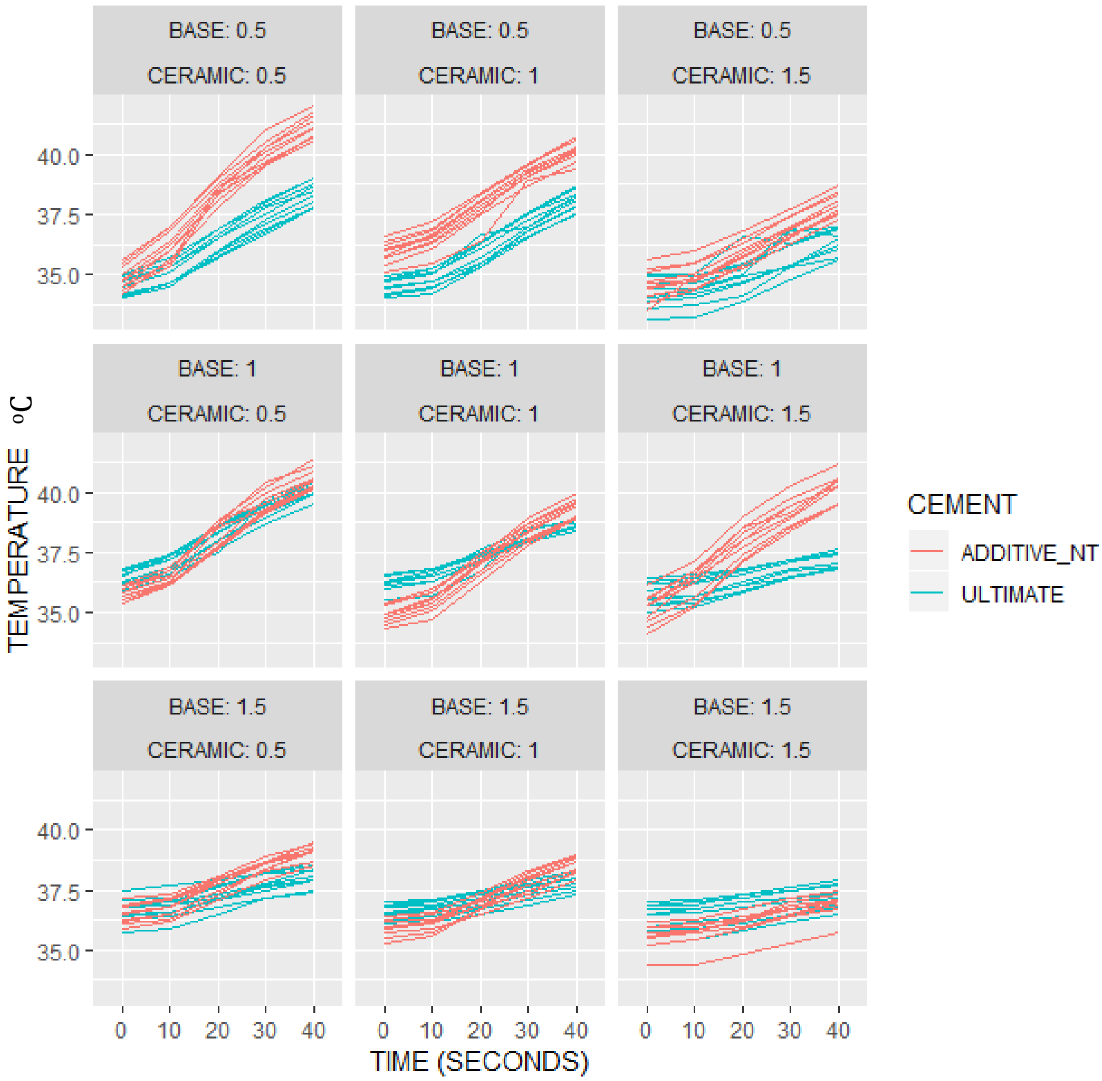

Fig. 4: Profiles about the groups temperature (ºC) according to the sets ceramic and bovine disks.

DISCUSSION

LEDs are becoming the most used equipment in clinical practice. The broadband spectrum and the increased irradiances of the newest light sources aims to reduce the irradiation time and increase the depth of curing (25). Still more, the companies announce the evolution of the LCUs as if the increase in irradiation were an absolute advantage about depth of polymerization and decrease the irradiation time (9, 12). For this reason, this device VALO™ in pre programed irradiance 1000 mW/cm^2 was chosen. For the sake of better defining the irradiance ranges of LCU, in the present study, spectral irradiance distributions was evaluated with a power-meter (New Port, Irvine, CA, USA) and a spectrometer Avantes (Broomfield, CO, USA), respectively. This was conducted to ensure a more precise characterization of the device (16, 25).

Curing resin-based materials can increase the temperature and cause concerns regarding the heating pulp chamber. This warming was observed in the present study, in agreement with other authors, it can be related to the used light source, the characteristics of the tooth substrate (dentin) and the resin composite (resin cement) (16-18).

Even with high irradiances LEDs commercially found, authors still recommend complementary light supplying to resin cements (9, 10, 13-15), to avoid compromising the polymerization degree of the resin cement and the quality of the restoration (8, 14). But the extended time could be harmful to the pulp chamber complex (19, 20), and in the present study heating values close or more than to 5.5ºC were observed.

Teflon matrices have been developed to be used in investigations since 2006 (26). This pattern aimed to standardize the cementation line in 100 µm, stabilize the disks, the tip of the LCU and the thermocouple sensor (16, 17) just in contact with reminiscent inner dentin. In current International Organization for Standardization standards requires a film thickness thinner than 50µm for resin-based cements (27) but in a clinical situation that the crowns are cemented by digital pressure, the cement line could be worse than the acceptable (28). Moreover when simulated a clinical situation, there was a limitation on milling process which shows a restriction of the study, but makes it reproduceble.

Higher intra pulp chamber temperature values were observed in the NT light activated through C 0.5 + B 0.5 mm, maybe due to the thickness specimens and catalytic potential of $ntTiO_2$, in agreement to other findings (16). Previous studies used dentin disks to simulate remaining dentin (26, 29) and ceramic disks to simulate indirect restorations (30). As light intensity can increase or decrease exponentially in function of the restoration thickness, more light penetration and pulp chamber warming was expected when thinner restorations are used in resin cements beneath such restorations as observed elsewhere (16).

However, these findings must be interpreted with a certain amount of caution. The pulp circulation could be able to dissipate some of the applied heat. The current *in vitro* model tried to simulate heat transfer to pulpal tissues using the thermal paste thanks to de difficulty to conduce this tests *in vivo*. Some higher temperature values observed in some groups, could be a potential hazard to 15% of odontoblasts capacity to recover itself (20).

The TiO_2 structures have also been used as an additive in dental materials, due to it multifunctional characteristic. The photo catalytic behavior of nanostructures ntTiO_2 (18, 21-23) could be an intrinsic parameter (21) responsible for a grater warming in the set. But in spite of the heating, the use of nanostructures can potentiate the reaction rate of the resin cement in less time of photo activation, avoiding even the additional photoactivations.

More than improve resin-based cement reactivity, the strong ionic bonds could provide better performace and chemical stability even with a possibility of antibacterial properties (31).

Temperature increases during light activation of resin composites, is still a concern factor. High power curing units, with extended time of irradiation combined with ntTiO_2, can increase the temperature above critical parameters. The null hypotheses tested in the present study were rejected since the polymerization time of the resin interfered in intra pulp chamber warming.

Since there are still a few evidences in the literature until the addition of nanostructures in resin-based cements (24, 32) and it started to be used for promising results in the composites behavior, the use of nanotubes may be interesting to decrease the photo activation time of the resin cements, still allowing a high conversion degree in the resin cements for regions with difficult or absent light passing allowing the expected behavior in the two modes of polymerization(24).

CONCLUSION

Considering the limitations of the present study, it is possible to conclude that light curing resin-based cements warm the pulp chamber complex. The cement system added with ntTiO_2 and light cured with high power LED provided largest temperature increases regardless of specimens disks.

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2.2 ARTICLE 2

This article was written to <u>Brazilian Dental Journal</u>

Degree of conversion of a resin cement system added with TiO_2 nanotubes. A Differential Scanning Calorimetry and Spectrophotometry analysis.

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ABSTRACT

The aim of this present study was to evaluate the influence of 0.3%wt of dioxide titanium nanotubes ($ntTiO_2$) added to a resin cement RelyX^{TM} (3M ESPE) on degree of conversion and color stability. Spectrophotometry was conduced to determine color stability (ΔE), groups were sort according to the $ntTiO_2$ additive in the resin cement (U and NT), kind of polymerization process (40 s of light activation or 6 min of chemical curing), ceramic thickness (C 0.5; C 1.0 and C 1.5 mm), and time of storage (24 h and 8 days) (n=10). Data were obtained by Easyshade (VITA) after the curing process, 24h and 8 days after storage. For Differential Scanning Calorimetry (DSC), data were evaluated according to the $ntTiO_2$ additive in the resin cement and kind polymerization process (n=3). Enthalpies (J/mg) were collected during the curing process of the resin cement. Data were submitted to a 3-way ANOVA for ΔE and a 2-way ANOVA for DSC, followed by Tukey's ($p \leq 5\%$). NT groups light cured through C 0.5 mm and storage for 8 days, presented lower ΔE mean values (1.47±0.88) when compared to your respective U with C 0.5 mm storage for 8 days (3.07±1.07). Higher ΔE mean values were observed in group U chemically cured after 24 hours of storage (11.11±2.4) followed by Control group LC though 1.5 mm ceramic (6.24+1.89). Higher total enthalpies (J/mg) values were observed in the group U light cured trough C 0.5 mm (123.67±13) followed by group U light cured trough C 1.0 mm (119.17±6.0). For NT groups, the enthalpies values of those light cured trough C 0.5 mm (89.76±10.1), remained close to the group U light cured trough C 1.5 mm (82.23±15.2). In conclusion, 0.3wt% $ntTiO_2$ additive, into resin cement increased color stability, and decreased degree of conversion.

Keywords: Light curing, Resin Cement, Degree of conversion, Color Stability, Nanotubes.

INTRODUCTION

Dental ceramics are extensively used by their esthetic potential and mechanical, optical and biological properties. For bonding ceramic materials, resin-based cements are currently applied as an essential part of the success and quality of esthetic treatments, ensuring high bond strength and improving esthetics and clinical survival rates (1). Amid so many options available nowadays, self-adhesive and dual-curing resin cements are preferred due to their simplified cementation procedures, decreasing clinical time (2,3).

The intention to be dual curing is for chemical polymerization to occur at its best in areas where light energy deprivation exists. Regardless of polymerization protocol (dual or chemical induced), it is shown that self-curing mode is less effective when compared to the dual-cured mode(4). So, light curing those resin cements can provide higher degree of conversion and better properties over time (5-9).

For the success of this procedure, an adequate degree of conversion is a crucial factor and it could be related to intrinsic characteristic of ceramic restoration and resin cement system. The thickness of the ceramic may influence the light transmittance (10), but complementary light supplying is still tightly recommended to dual cure resin cements (11).

It has been proposed to increase the irradiation time to delivery more energy for the resin cement layer, however a warming in the pulp chamber can become a concern about pulp the complex vitality (12,13).

In order to improve some properties of the resinous materials, nanostructures started to be used. The reactivity and photo catalysis potential of titanium dioxide nanotubes ($ntTiO_2$) has demonstrated positive results in the composites behavior (14). This characteristic may be interesting to decrease the light irradiation time and potentialize the polymerization process where light energy doesn't arrives still allowing a high degree of conversion and avoiding harmful warming in the pulp chamber complex.

Based on these considerations, the present study aimed to evaluate effect of additive $ntTiO_2$ in degree of conversion of dual curing resin cement by ΔE and enthalpy values. The null hypotheses tested were: the light activation, $ntTiO_2$ additive and thickness of ceramic disks does not interfere in degree of conversion and color stability of a self etching dual curing resin cement.

MATERIALS AND METHODS

A dual curing resin cement (RelyX Ultimate; 3M ESPE, St. Paul, MN, USA), shade A1, was evaluated by curing process below ceramic disks with different thickness. Ceramic disks IPS e-max Press system (Ivoclar Vivadent, Liechtenstein) were made in A1 color and with high translucency (HT) using the lost wax technique. The specimens had 9.7×9.7mm dimensions and 0.5; 1.0 and 1. 5 mm thickness.

Nanotubes of TiO_2 were synthesized by the alkaline method (14) and added manually to the base paste of resin cement and mixed following the manufacturer's instructions(15). The amount of nanotubes corresponded to 0,3% weight of the resin cement, both scaled on Mettler PB 303 scale (Toledo, Barueri, SP, BR).

The light curing unit (LCU) (VALO – Ultradent South Jordan, UT, USA) was applied in pre programed irradiance of 1000mW/cm^2, but had its irradiance confirmed before using. The power (J) was measured by placing the tip of the light source in close contact with a digital flat-response power-meter (New Port – model 2936-R; Irvine, CA, USA) and the spectral distributions was assessed by a spectrometer (Avantes, Apeldoorn, The Netherlands) connected to a computer running the Software Ava Soft 8.2.1. The diameter of the LCU tip was checked with a digital caliper (Mitutoyo Absolute Digimatic, Kawasaki, Japan). The irradiances (mW/cm^2) were obtained dividing the power (mW) by the area of the curing tip (cm) (Fig.1).

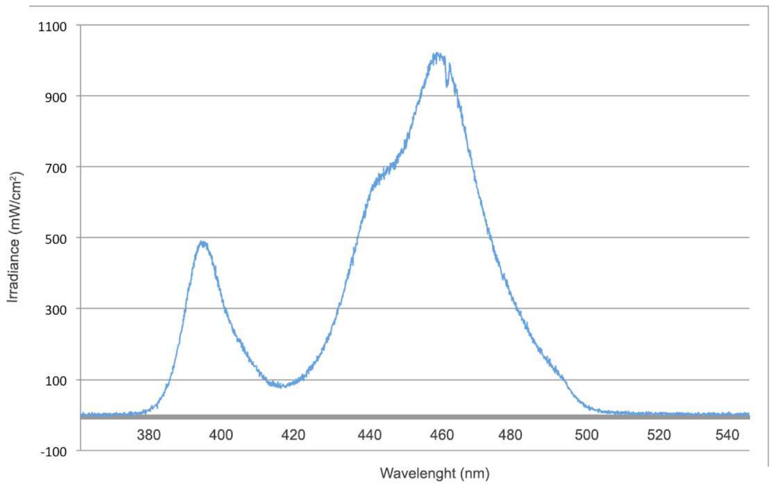

Fig. 1: VALO™ spectral irradiance graph (Department of Physics, UNESP Campus Bauru).

For Spectrophotometry analysis (ΔE), resin cement groups (n=10) were determined according to $ntTiO_2$ (U and NT) kind of polymerization (dual or chemical) and time of storage (24h and 8 days at 37˚C-dry-dark-storage). After the proportioning, the $ntTiO_2$ were added to the cement base paste. The manipulation was standardized and performed in a spatula block following the manufacturer's instructions. Immediately, the resin cement was inserted into a bipartide teflon matrice measuring 6x2mm (Fig. 2 a).

For dual curing groups, a light activation was performed for 40 s with VALO Cordless (1000 mW/cm^2) in contact with ceramic disks (Figure 2 c), and for chemical curing, specimens stayed in dark environment for 6 minutes after mixing.

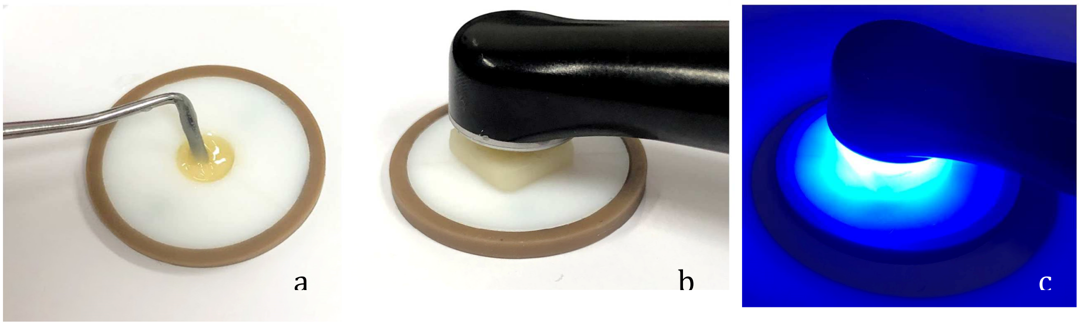

Fig. 2: (a) Resin cement insertion into the Teflon matrix, (b) position of the LCU right in contact with the ceramic disk and, (c) light activation of the resin cement through ceramic disk.

Immediately after curing, the specimens were removed from the matrix and the color as recorded on the upper face with a spectrophotometer (Easyshade Advance Vita; Vita Zahnfabrik, Bad Sackingen, Germany), using the CIE-*Lab color parameters. Before readings, the spectrophotometer was calibrated with the standard ceramic block provided by the manufacturer. Color change (ΔE) was calculated based on the following equation: $\Delta E^*=[(\Delta L^*)2 + (\Delta a^*)2 + (\Delta b^*)2]^{1/2}$
Where L*, a*, and b* correspond to the color differences between the baseline and after different storage periods, considering the resin cement (U an NT), type of curing (dual and chemical), and ceramic disk (C 0.5; 1.0; 1.5 mm). The ΔE at different times (ΔE_{24h} and $\Delta E\ 8_{days}$) was defined as a repeated variable.

After the baseline color measurement (ΔE_o), the specimens were dry-stored at 37°C for 24 hours in dark canisters, fully protected from light. After this period, the color parameters were measured (ΔE_{24}), and the specimens were stored in the same canisters for more 7 days. After the storage time, the color parameters were measured again (ΔE_{8days}). The color measurements taken immediately after the curing process were baseline for ΔE_{24}, and ΔE_{24} was considered the baseline for ΔE_{8days} ($p \leq 5\%$).

For DSC analysis, groups were determined according to the $ntTiO_2$ additive in the resin cement and kind of polymerization (40 s of light activation and chemical curing) (n=3). After proportioning, the $ntTiO_2$ were added manually to the cement base paste. The manipulation was standardized and performed in a spatula block following the manufacturer's instructions. Immediately, after the manipulation, aluminum panels containing 20mg of the resin cement was inserted into Q2000 (TA Instruments, Woodland, CA). For dual curing groups, a light activation was performed for 40 s with VALO Cordless (at 1000mW/cm^2) in contact with ceramic disks (Figure 2 c), and for chemical curing, specimens stayed in dark environment for 6 minutes after mixing (Figure 3).

The degree of conversion was measured by the enthalpy values of polymerization taken under isothermal conditions at 37°C. The isothermal measurements were therefore always started exactly 20s after the initial placement of aluminum pan. Enthalpy was calculated from the area under the peak of the isothermal curve, based on the extrapolated baseline at the end of the reaction. The released heat (enthalpy) was considered proportional to the percentage of reacted monomers(16), and thus, the degree of conversion.

Fig. 3: Equipment Q2000 with panels filled with resin cement during light activation through ceramic disk.

Data were submitted to statistical analysis and a 3-way Variance Analysis (ANOVA) was performed for ΔE and 2-way ANOVA for degree of conversion. All ANOVA tests were followed by Tukey's test with a significance level ($p \leq 5\%$).

RESULTS

The ΔE_{24h} and ΔE_{8d} mean values and standard deviations are shown in Table 1. Both types of curing process, ntTiO_2 additive, and time of specimens' storage determined significant interactions (Table 1).

Most of the groups additive with ntTiO_2 remained with ΔE beneath the clinically perceptible amount, with emphasis on NT groups light cured through C 0.5 mm storage for 8 days, that presented lower ΔE mean values (1.47 ± 0.88) when compared to your respective control group U light cured through C 0.5 mm storage for 8 days (3.07 ± 1.07). Higher ΔE mean values were observed in the group U chemically cured and after 24 hours of storage (11.11±2.4), followed by group U cured though C 1.5 mm (6.24±1.89) (Figure 4).

According to the data recorded in DSC analysis, total enthalpy mean values with standard deviations are shown in Table 2. Higher enthalpies mean values were observed in the group U light cured trough C 0.5 mm (123.67±13) followed by U light cured though C 1.0 mm (119.17±6.0), (Table 2).

Therefore, the groups additive with ntTiO_2 presented lower enthalpy values (Figure 4).

Table 1: Mean values and standard deviations of ΔE due to ntTiO_2 additive, curing protocols and time of storage.

Group	Curing Protocol	Ceramic Disk	ΔE 24	ΔE 8d
U	Dual	0.5mm	5.31 ± 2.00^{bcA}	3.07 ± 1.07^{abcB}
		1.0mm	3.40 ± 1.66^{abcA}	4.08 ± 1.10^{abcA}
		1.5mm	6.29 ± 1.89^{cA}	3.74 ± 2.16^{abcB}
	Chemical		11.11 ± 2.40^{dA}	3.60 ± 2.64^{abcB}
NT	Dual	0.5mm	1.68 ± 0.58^{aA}	1.47 ± 0.88^{aA}
		1.0mm	2.04 ± 0.44^{abA}	2.34 ± 0.74^{abA}
		1.5mm	3.07 ± 0.69^{abcA}	1.49 ± 1.22^{aB}
	Chemical		2.01 ± 0.23^{abA}	2.75 ± 1.80^{abA}

Different lower case letters represent statistically significant difference between the columns; Different capital letters represent statistically significant difference between the lines as evaluated by Anova with repeated measures (p ≤ 5%).

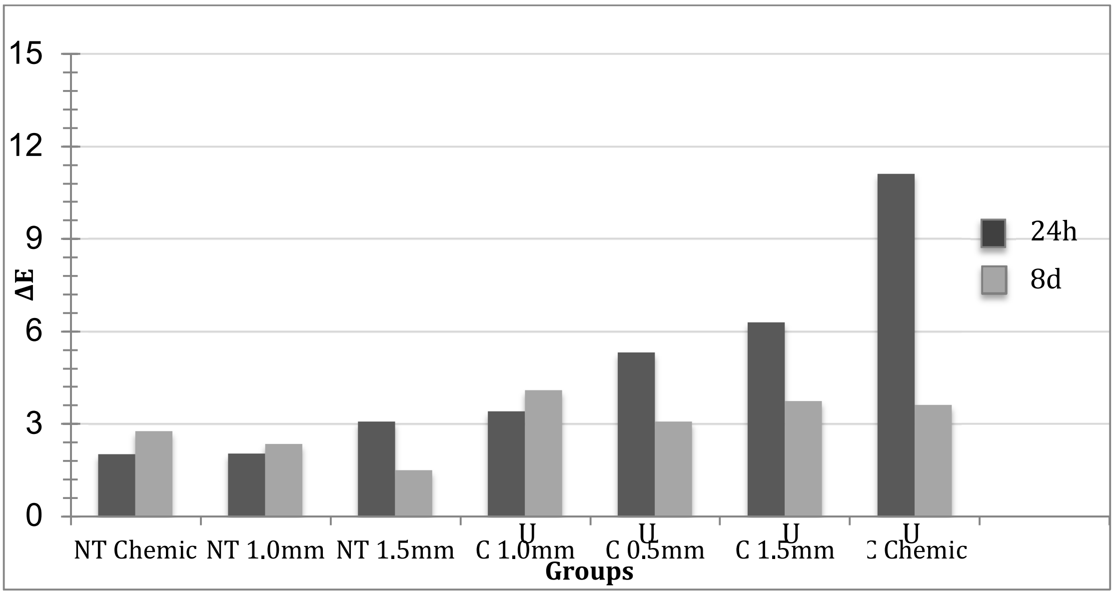

Fig.4: Color change after different times of storage in function of the groups studied.

Table 2: Mean values and standard deviations of total Enthalpy (J/mg) due to $ntTiO_2$ additive and curing protocols.

Material	Curing Protocol	Ceramic	Total Enthalpy (J/mg)
U	Dual	0.5mm	123.67±13.3[a]
		1.0mm	119.17±6.0[a]
		1.5mm	82.23±15.2[b]
	Chemical		12.90±3.7[c]
NT	Dual	0.5mm	89.76±10.1[b]
		1.0mm	69.39±5.7[d]
		1.5mm	37.75±7.5[d]
	Chemical		8.86±5.6[f]

Different lower case letters represent statistically significant difference between the rows (p ≤ 5%)

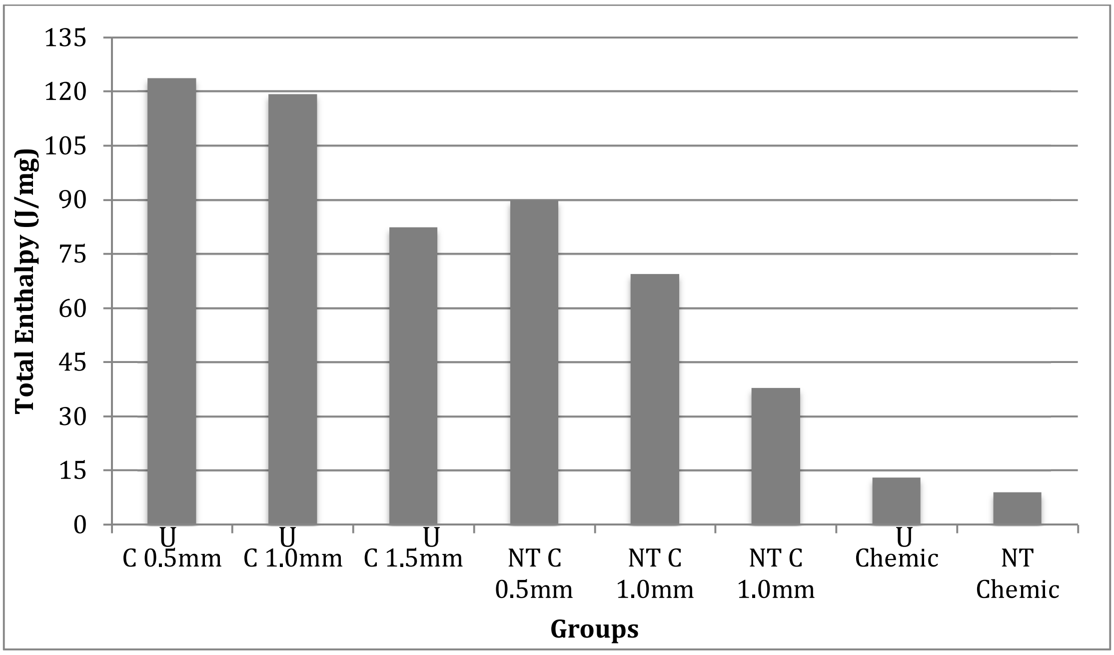

Fig. 5: Total enthalpy mean values (J/mg) due to ntTiO$_2$ additive and curing protocols.

DISCUSSION

Mechanical-physical properties and clinical performance of dental resins has been underlined by many studies. As degree of conversion can be considered one of the most important parameters for esthetic success and longevity of indirect restorations (17), it was evaluated in two ways: by the measures of color stability (ΔE) (17) and enthalpy values by the direct measurement in the calorimetric analysis (18).

The polymerization process and color stability of a dual curing resin cement was performed in the present study as found in literature (18-20), even with the same resin cement Relyx Ultimate (21). The outcomes enable to reject null hypothesis tested, since the light activation, ntTiO$_2$ additive, and thickness of ceramic disks interfered in degree of conversion and color stability.

The ceramic disks with different thickness intended to simulate a clinical situation and were used to mimic different clinical conditions of indirect aesthetic restorations. For light activation, VALO™ with 1000mW/cm^2 was chosen due to its high irradiance and broad spectra high availability in the market (Figure 1). Irradiance ranges and characterization of the device was performed as it is in the literature (22,23).

Data have shown in previously studies the light attenuation by interposing different ceramic specimens during irradiation of resin cement specimens (24). In the present study, the supposed light attenuation interfered in ΔE and enthalpy results, once higher ΔE mean values and lower enthalpy outcomes were observed in the groups cured by thicker ceramic disks, these finds corroborate to other investigations (17,19).

The incorporation of TiO_2 nanostructures has shown promising results physical-chemical, mechanical and biological behavior of dental materials. The addition of 0.3wt% of ntTiO_2 in the dual curing resin cements were shown the positive influence on flexural strength, elastic modulus, micro hardness and indirect fibroblast cell viability (25), without compromise viscosity and agglomeration of nanotubes. There are still a few evidences in the literature until the addition of nanostructures in resin cements and, therefore, the characterization of properties presents a new approach for the development or improvement of a material with better properties.

For indirect measurement of degree of conversion, the ΔE analysis with Easyshade spectrophotometer conduced measuring spectral coordinate, within the CIE-L*a*b* color space. Higher ΔE mean values were observed in the groups chemically cured without nTiO_2 additive. Better values of ΔE with clinical acceptance(26) were obtained in the light activated groups additive with nTiO_2 and storage for 8 days. Because the cements after storage were not exposed to light, the color change over time may be due to the polymerization process or post-irradiation conversion(17). These findings confirm the nTiO_2 potential to act as to increase strong crosslinking points in the formed polymer network (27).

For direct measurement of degree of conversion, the DSC analysis was performed because it is a reliable direct method for analyzing the resin composite behavior and its kinetics of the curing reaction(18). DSC determines the DC based on the assumption that the heat produced during the reaction (enthalpy) is proportional to the percentage of monomers that have reacted(28). In the present study the materials were tested under isothermal conditions (37ºC) to simulate pulp chamber temperature (12) and the DSC equipment isolated the LCU heating intervention to separate the results of the exothermic reaction from the warming caused by LCU.

The behavior of DSC results follows the ΔE_{24h} groups where the chemical polymerization provided worse values of enthalpy and ΔE24h as supported by other findings (29). For worse outcomes of enthalpy and ΔE_{24h}, it could be speculated that the $ntTiO_2$ would be entrapped the polymeric noteworthy groups due its increased energy between the valence band and the conduction band (30), absorbing part of light energy. However, further studies with late enthalpy evaluation are needed to confirm these hypotheses.

Clinically, the results of the present study would be carefully considered, because only one dual-cured resin cement was evaluated due to $ntTiO_2$ additive, and degree of conversion changes may be dependent to the light activation, material and time. Another limitation of the present study is related to the cement and nanotube manual manipulation: the lack of equality in the results could be improved by the functionalization of nanotubes, once the nano-scale structures tend to agglomerate (31). Other limitation as the understanding the real chemical interaction of $ntTiO_2$ with resin monomers and dental tissue, that implies an important hole neutralizing reaction of acid monomers of self-adhesive resin cement(32).

Although it is difficult to predict whether different clinical performances are likely to occur for restorations light cured under similar conditions to those tested here. The degree of conversion of resin cements with $ntTiO_2$ the could be promising when cementing thick ceramic restorations, even more to prevent complementary light irradiation, that could be harmful to the pulp complex and potentialize degree of conversion in late times, providing better either chemical properties.

Furthermore, it should be considered that the clinical success of resin cement agents depends not only on their mechanical properties, but also on their handling properties, bond strength to the tooth and restoration, film thickness, and color stability.

CONCLUSION

In conclusion, degree of conversion of the resin cement agent was dependent on the $ntTiO_2$ additive, ceramic thickness and time of light curing. Reinforce resin cements with 0.3wt% $ntTiO_2$ provide better color stability over the time, but could interfere negatively into imadiate degree of conversion.

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3 DISCUSSION

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Temperature tests are important to predict the damage potential of light curing units once it can be related to involvement of dentin enamel complex (Zach and Cohen 1965, Choi, Roulet et al. 2014). LEDs are becoming the most used equipment in clinical practice and it increased irradiances are announced as (Atai and Motevasselian 2009) as an absolute advantage about depth of polymerization and decrease the irradiation time.

But curing resin-based materials can cause concerns once light intensity can increase or decrease exponentially in function of the restoration thickness, more light penetration and pulp chamber warming was expected (Andreatta, Furuse et al. 2016). When thinner disks were used, the set presented greater warming.

Highest warming was observed in the groups reinforced with ntTiO_2 with thinner disks of bovine dentin and ceramic disks (NT C 0.5+B 0.5 mm), probably due to its photo catalytic behavior (Asmussen 1982, Asmussen and Peutzfeldt 2001, Asmussen and Peutzfeldt 2003, Arruda 2015) that could be an intrinsic parameter (Arruda 2015) responsible for a grater warming in the set and low absorption potential of bovine dentin and ceramic disks due theis thicknesses.

Previous studies used dentin disks to simulate remaining dentin (Loney and Price 2001, Uhl, Volpel et al. 2006) and ceramic disks to simulate indirect restorations (Atmadja and Bryant 1990). This warming in intra pulp chamber was observed in the present study, in agreement with other studies (Andreatta, Furuse et al. 2016), However, these findings must be interpreted with a certain amount of caution. The pulp circulation could be able to dissipate some of the applied heat. The current *in vitro* model tried to simulate heat transfer to pulpal tissues using the thermal paste thanks to de difficulty to conduce and make reproducible these tests *in vivo*.

But in spite of the greater heating provided by the groups reinforced with nanostructures, the behavior of resin composites in function of degree of conversion and color stability was heterogeneous.

The addition of 0.3wt% of $ntTiO_2$ in the dual curing resin cements has shown the positive influence on flexural strength, elastic modulus, micro hardness and indirect fibroblast cell viability (Ramos-Tonello, Lisboa-Filho et al. 2017). Since there are still a few evidences in the literature until the addition of TiO_2 in dentistry, it may be interesting to evaluate the polymerization behavior of resin cement reinforced with $ntTio_2$ trough different kinds of curing process to provide new approaches for the development or improvement of a materials with better properties.

The polymerization process and color stability of a dual curing resin cement was performed in the present study as found in literature (Cotti, Scungio et al. 2011, Runnacles, Correr et al. 2014, Dotta 2018) even with the same resin cement Relyx Ultimate (Sulaiman, Abdulmajeed et al. 2015). The outcomes enable to reject null hypothesis tested, since the light activation, $ntTiO_2$ additive, and thickness of ceramic disks interfered in degree of conversion and color stability.

Data have shown in previously studies the light attenuation by interposing different ceramic specimens during irradiation of resin cement specimens (Pick, Gonzaga et al. 2010). In the present study, the supposed light attenuation interfered in ΔE and degree of conversion, once higher ΔE mean values and lower enthalpy outcomes were observed in the groups cured by thicker ceramic disks, these finds corroborate to other investigations (Runnacles, Correr et al. 2014, Furuse, Santana et al. 2018).

Higher ΔE mean values were observed in the groups chemically cured without $nTiO_2$ additive. Better values of ΔE with clinical acceptance (Ruyter, Nilner et al. 1987) were obtained in the light activated groups additive with $nTiO_2$ and storage for 8 days. Because the cements after storage were not exposed to light, the color change over time may be due to the polymerization process or post-irradiation conversion(Furuse, Santana et al. 2018). These findings confirm the $nTiO_2$ potential to act as to increase strong crosslinking points in the formed polymer network (Sun, Forster et al. 2011).

For direct measurement of degree of conversion, the DSC analysis was performed because it is a reliable direct method for analyzing the resin composite behavior and its kinetics of the curing reaction(Cotti, Scungio et al. 2011). DSC determines the DC based on the assumption that the heat produced during the reaction (enthalpy) is proportional to the percentage of monomers that have reacted(Emami and Soderholm 2005). In the present study the materials were tested under isothermal conditions (37ºC) to simulate pulp chamber temperature (Andreatta, Furuse et al. 2016) and the DSC equipment isolated the LCU heating intervention o separate the results of the exothermic reaction from the warming caused by LCU.

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Although it is difficult to predict whether different clinical performances are likely to occur for restorations light cured under similar conditions to those tested here, degree of conversion of resin cements with $ntTiO_2$ the could be promising when cementing thick ceramic restorations, even more to prevent complementary light irradiation, that could be harmful to the pulp complex and potentialize degree of conversion in late times, providing better either chemical properties.

Furthermore, it should be considered that the clinical success of resin cement agents depends not only on their mechanical properties, but also on their handling properties, bond strength to the tooth and restoration, film thickness, and color stability.

4 Final Considerations

4 FINAL CONSIDERATIONS

Resin composites reinforced with $ntTiO_2$ still present very heterogeneous behavior due to temperature increase, color stability and degree of conversion. The 0.3wt% $ntTiO_2$ additive into resin cement, increased intra pulp chamber temperature, late color stability, but decreased enthalpy values.

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