UNIVERSIDADE DE SÃO PAULO
FACULDADE DE ODONTOLOGIA DE BAURU

LEANDRO EDGAR PACHECO

Titanium dioxide nanotubes as reinforcement of a self-adhesive resin cement in self-curing mode

Nanotubos de dióxido de titânio como reforço de um cimento resinoso autoadesivo na fase de polimerização química

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Dissertação apresentada a Faculdade de Odontologia de Bauru da Universidade de São Paulo para obtenção do título de Mestre em Ciências no Programa de Ciências Odontológicas Aplicadas, na área de concentração Dentística.

Orientador: Prof. Dr. Paulo Afonso Silveira Francisconi

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"Quanto mais me elevo, menor pareço aos olhos de quem não sabe voar. "

Friedrich Nietzsche

ABSTRACT

Titanium dioxide nanotubes as reinforcement of a self-adhesive resin cement in self-curing mode

Objective: This study has analyzed bond strength to root dentine and to fiberglass posts, and the radiopacity of self-adhesive dual resin cement in addition of titanium dioxide nanotubes (nt-TiO2) in self-curing polymerization.

Material and Methods: The self-adhesive resin cement **(**RelyX U200^{TM}, 3M ESPE) was enhanced with different concentrations (0.3, 0.6, and 0.9% by weight) of nt-TiO_2 and evaluated at only self-curing mode. To test the bond strength to root dentine and fiberglass posts was applied the push out bond strength test (PO). To analyze the radiopacity was follow the ISO standard (9917-2/2010). Data were statistically analyzed by one-way ANOVA test, followed by post hoc multiple comparisons Fisher's test for PO and Tukey's test for RO ($p<0.05$).

Results: Reinforced self-adhesive resin cement influenced the increase in values of PO, especially in the S06 group (0.6 wt%), which demonstrated a higher value of bond strength, mainly in the apical third. However, this analysis not demonstrated statistical difference between the groups with nt-TiO_2 addition (S03, S06 and S09) and the control group (SCT). For radiopacity, the addition of nt-TiO_2 may provide an increase in value, especially to the S09 group, which showed a higher value with statistical difference in comparison with SCT group.

Conclusion: The addition of nt- TiO_2 showed influence at behavior of the self-cure mode of the self-adhesive resin cement, and its use in other concentrations may be considered for future studies, since reinforced cement may prove better results in indirect restorative procedures.

Key words: Resin Cements. Dental Cements. Nanotubes. Titanium.

RESUMO

Nanotubos de dióxido de titânio como reforço de um cimento resinoso autoadesivo na fase de polimerização química

Objetivo: Este estudo analisou a resistência de união à dentina radicular e aos pinos de fibra de vidro, e a radiopacidade de um cimento resinoso dual autoadesivo com a adição de nanotubos de dióxido de titânio (nt-TiO_2) na sua fase de polimerização química.

Material e métodos: O cimento resinoso auto-adesivo **(**RelyX U200^{TM}, 3M ESPE) foi reforçado com diferentes concentrações de nt-TiO_2 (0,3, 0,6, and 0,9% em peso) e avaliado somente em seu modo de polimerização química. Para avaliar a resistência de união à dentina radicular e aos pinos de fibra de vidro foi aplicado o teste push out (PO). Para a análise da radiopacidade (RO) foi seguido o padrão ISO (9917-2/2010). Os dados foram submetidos à análise estatística por ANOVA seguido de comparações múltiplas de Fisher para PO e Tukey para RO ($p<0,05$).

Resultados: O cimento resinoso autoadesivo reforçado influenciou no aumento dos valores de PO, em especial no grupo S06 (0,6% em peso), o qual demonstrou um maior valor de resistência de união, principalmente no terço apical. Entretanto essa análise não apresentou diferença estatística entre os grupos com a adição de nt-TiO_2 (S03, S06 e S09) e o grupo controle (SCT). Para radiopacidade, a adição de nt-TiO_2 promoveu um aumento em valores, especialmente para S09, que mostrou um maior valor com diferença estatística em comparação com SCT.

Conclusão: A adição de nt-TiO_2 mostrou influência no comportamento do modo de polimerização química do cimento resinoso autoadesivo, e seu uso em outras concentrações pode ser considerado para futuros estudos, já que o cimento reforçado pode revelar resultados superiores em procedimentos restauradores indiretos.

Palavras-chave: Cimentos Resinosos. Cimentos Dentários. Nanotubos. Titânio.

LIST OF ILLUSTRATIONS

LIST OF TABLES

LIST DE ABBREVIATIONS AND ACRONYMS

TiO_2-nt	Titanium dioxide nanotubes
wt%	Per cent by weight
SCT	Control group
S03	0.3 wt% TiO_2-nt group
S06	0.6 wt% TiO_2-nt group
S09	0.9 wt% TiO_2-nt group
BS	Bond strength
PO	Push out bond strength
SBS	Shear bond strength
RO	Radiopacity
ct	Cervical third
mt	Medium third
at	Apical third
A-C/D	Adhesive failure between the cement and the dentin
A-C/P	Adhesive failure between the cement and the post
CP	Cohesive failure in the post
CC	Cohesive failure in the cement
M	Mixed failure
RDM	Material radiographic density
SEM	Scanning electron microscopy
ISO	International Organization for Standardization

TABLE OF CONTENTS

1 INTRODUCTION

1 INTRODUCTION

Endodontically treated teeth with insufficient coronal structure generally require root posts to assist in restoring to function[1]. In these situation, fiberglass posts are considered a better alternative when compared to metal posts[2]. Fiberglass posts cementation can be performed with various resin cements that can be classified by the polymerization mode (light cure, self cure and dual cure). The best option for glassfiber posts cementation is a dual-cure cement because it having the advantages of command light-cure cements and also contain chemical initiators for deep areas where light access is difficult to achieve[3,4].

However, even though are considered dual-polymerization and indicated for all luting procedure, neither all cements have the same rate monomers conversion under the different cure conditions. The photopolymerization in dual self-adhesive resin cements come out higher monomers conversion[5], resulting in excellent mechanical properties[6] and better biological properties[7]. But, when indicated for fiblerglass posts cementation, where the light acess is inefficient or absent, is expected that the self-cure provides the same physicochemical, mechanical and biological properties over time. In evaluations on the mode activation of self-adhesive resin cements, a reduction of 30 to 54% was observed when only chemical polymerization was used, compared with photopolymerization[8].

Self-adhesive resin cements are designed to adhere to tooth structure without the need for a separate adhesive or etchant step. They were introduced in the dental market within the past decade, but have gained popularity fast, with more than a dozen commercial brands now available[9]. The functional acidic monomers, dual cure setting mechanism, and fillers capable of neutralizing the initial low pH of the cement are clinically relevant characteristics of these cements[10]. Their low pH and high hydrophilicity at early stages after mixing yields good wetting of tooth structure and promote surface demineralization, similar to the adhesion mechanism in self-etching adhesives[9,10]. As the reaction advances, the acidity of the cement is gradually neutralized, due to the reaction with the apatite from dental substrates[10-12] and with the metal oxides present in the basic, acid-soluble inorganic fillers[9,10,13,14]. This is important, as the polymerization of self-adhesive resin cements can be significantly delayed by low pH, via the deactivation of free radicals, ultimately compromising the curing reaction[10].

There is scarce literature on the evaluation of the self-adhesive resin cements when used in the absence of light-curing (i.e., relying only in their self-cure mode). This is important because decreased mechanical properties have been demonstrated in the areas in the cement line where light penetration is not sufficient. Therefore, the redox polymerization must be enough to ensure cure in areas under thick sections of ceramic restorations or on the apical thirds of posts, for example[9,15]. In addition, in situations where the light penetration still results in a low intensity being delivered to the material, studies have shown that the redox portion of the polymerization may be jeopardized by a partially gelled/vitrified structure, leading to lower values of hardness (for example) as compared to the material that undergoes redox alone[15]. Both situations result in an insufficient polymerization, which can affect the cement's adhesion to dentin and fiberglass posts in indirect procedures in restorative dentistry.

To overcome that and improve mechanical and adhesive properties, there are several reports in the literature on different nanostructures that have been added to dental composites, such as titanium dioxide nanotubes (TiO_2-nt)[16-19]. Nanotubes, like nanofibers, have a high aspect ratio and a high surface area to volume ratio, which may lead to significantly enhanced physical and mechanical properties[18,20]. The hollow structure of the nanotube provides additional interlocking with the matrix through both the interior and exterior surfaces of the tubes[18]. Ramos-Tonello et al., 2017[19], found positive results for a self-adhesive resin cement with TiO_2-nt reinforcement, such as improvement in selected physical-chemical, mechanical and biological properties. These findings, especially in the self-cure mode, are important for the longevity and clinical performance of this cement. Therefore, the aim of this investigation was to determine the bond strength through push out bond strength to bovine dentin, shear bond strength to Y-TZP and radiopacity of a self-adhesive resin cement (RelyXU200™ - 3M ESPE, St. Paul, MN, United States) modified by TiO_2-nt at three concentrations: 0.3%, 0.6%, and 0.9% (wt/wt), only in self-cured mode. The hypothesis of this study was that the TiO_2-nt modified groups would increase bond strength values (push out bond strength) and of the radiopacity.

2 Article

2 ARTICLE

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Titanium dioxide nanotubes as reinforcement of a self-adhesive resin cement in self-curing mode

Leandro Edgar Pacheco[a] (e-mail: le.edpacheco@gmail.com)
Ana Paula Rodrigues de Magalhães[b] (e-mail: anapaulardm@gmail.com)
Carla Müller Ramos-Tonello[c] (e-mail: carla_muller@yahoo.com.br)
Orisson Ponce Gomes[d] (e-mail: orissongomes@gmail.com)
Adilson Yoshio Furuse[e] (e-mail: furuse@usp.br)
Paulo Noronha Lisboa-Filho[f] (e-mail: plisoba@fc.unesp.br)
Carmem Silvia Costa Pfeifer[g] (e-mail: pfeiferc@ohsu.edu)
Ana Flávia Sanches Borges[h] * (e-mail: afborges@fob.usp.br)
Paulo Afonso Silveira Francisconi[h] (e-mail: pasf@fob.usp.br)

a Master Student, Department of Operative Dentistry, Endodontics and Dental Materials, Bauru School of Dentistry, University of São Paulo, Bauru, SP, Brazil
b Full Professor, Department of Operative Dentistry, School of Dentistry, Paulista University, GO, Brazil
c Assistant Professor Department of Operative Dentistry, School of Dentistry, United Metropolitan Colleges, SP, Brazil.
d Master Student, Department of Physics, Faculty of Science, State University of São Paulo, Bauru, SP, Brazil
e Assistant Professor, Department of Operative Dentistry, Endodontics and Dental Materials, Bauru School of Dentistry, University of São Paulo, Bauru, SP, Brazil
f Associate Professor, Department of Physics, Faculty of Science, State University of São Paulo, Bauru, SP, Brazil
g Associate Professor, Biomaterials and Biomechanics, School of Dentistry, Oregon Health & Science University, Portland, OR, USA

h Associate Professor, Department of Operative Dentistry, Endodontics and Dental Materials, Bauru School of Dentistry, University of São Paulo, Bauru, SP, Brazil

Corresponding author:

Ana Flávia Sanches Borges

Correspondence: Alameda Dr. Octávio Pinheiro Brisolla, 9-75 – Vila Universitária, 17012-901, Bauru, São Paulo, Brazil.

Telephone: +55 (14) 3235-8323

E-mail: afborges@fob.usp.br

Abstract

Objectives. This study has analyzed bond strength to root dentine and fiberglass posts, and the radiopacity of a self-adhesive dual resin cement modified by the addition of titanium dioxide nanotubes (TiO2-nt) in self-curing polymerization.

Methods. The self-adhesive resin cement (RelyX U200™, 3M ESPE) was modified with different concentrations (0.3, 0.6, and 0.9% by weight) of TiO_2-nt and evaluated in self-curing mode. The bond strength to root dentine and fiberglass posts was assessed with the push out bond strength test (PO). To analyze the radiopacity was follow the ISO standard (9917-2/2010).

Results. Reinforced self-adhesive resin cement showed no difference compared to the control group for PO; S06 group (0.6 wt%) showed higher values, mainly at the apical third, compared to S03 (0.3 wt%) and S09 (0.9 wt%) groups ($p<0.05$). Radiopacity showed higher value for the 0.9 wt% TiO_2-nt addition (S09) in comparison with control group (SCT) ($p<0.05$).

Conclusion. The addition of TiO_2–nt did not show difference between modified groups and control group for push out bond strength. The addition of TiO_2–nt had influence on a higher radiopacity of the cement when adding 0.6 wt% to 0.9 wt%.

Statement of Significance. TiO_2-nt showed influence at behavior of the self-cure mode of the self-adhesive resin cement, and its use in other concentrations may be considered, since reinforced cement may prove better results in restorative procedures.

Keywords: dental cements, nanotubes, resin cements, titanium.

TiO_2-nt (Titanium Dioxide Nanotubes); S03 (TiO_2-nt 0.3 wt%); S06 (TiO_2-nt 0.6 wt%); S09 (TiO_2-nt wt%); PO (Push Out Bond Strength); SBS (Shear Bond Strength); RO (Radiopacity).

1. Introduction

Self-adhesive resin cements are designed to adhere to tooth structure without the need for a separate adhesive or etchant step. They were introduced in the dental market within the past decade, but have gained popularity fast, with more than a dozen commercial brands now available [1]. The functional acidic monomers, dual cure setting mechanism, and fillers capable of neutralizing the initial low pH of the cement are clinically relevant characteristics of these cements [2]. Their low pH and high hydrophilicity at early stages after mixing yields good wetting of tooth structure and promote surface demineralization, similar to the adhesion mechanism in self-etching adhesives [1,2]. As the reaction advances, the acidity of the cement is gradually neutralized, due to the reaction with the apatite from dental substrates [2-4] and with the metal oxides present in the basic, acid-soluble inorganic fillers [1,2,5,6]. This is important, as the polymerization of self-adhesive resin cements can be significantly delayed by low pH, via the deactivation of free radicals, ultimately compromising the curing reaction [2].

There is scarce literature on the evaluation of the self-adhesive resin cements when used in the absence of light-curing (i.e., relying only in their self-cure mode). This is important because decreased mechanical properties have been demonstrated in the areas in the cement line where light penetration is not sufficient. Therefore, the redox polymerization must be enough to ensure cure in areas under thick sections of ceramic restorations or on the apical thirds of posts, for example [1,7]. In addition, in situations where the light penetration still results in a low intensity being delivered to the material, studies have shown that the redox portion of the polymerization may be jeopardized by a partially gelled/vitrified structure, leading to lower values of hardness (for example) as compared to the material that undergoes redox alone [7]. Both situations result in an insufficient polymerization, which can affect the cement's adhesion to dentin, ceramic and fiberglass posts in indirect procedures in operative dentistry.

To overcome that and improve mechanical and adhesive properties, there are several reports in the literature on different nanostructures that have been added to dental composites, such as titanium dioxide nanotubes (TiO_2-nt) [8-11]. Nanotubes, like nanofibers, have a high aspect ratio and a high surface area to volume ratio, which may lead to significantly enhanced physical and mechanical properties [10,12]. The hollow structure of the nanotube provides additional interlocking with the matrix through both the interior and exterior surfaces of the tubes [10]. Ramos-Tonello et al., 2017 [11], found positive results for a self-adhesive resin cement with TiO_2-nt reinforcement, such as improvement in selected physical-chemical, mechanical and biological properties. These findings, especially in the self-cure mode, are important for the longevity and clinical performance of this cement. Therefore, the aim of this investigation was to determine the bond strength through push out bond strength to bovine dentin and radiopacity of a self-adhesive resin cement (RelyXU200™ - 3M ESPE, St. Paul, MN, United States) modified by TiO_2-nt at three concentrations: 0.3%, 0.6%, and 0.9% (wt/wt), only in self-cured mode. The hypothesis of this study was that the TiO_2-nt modified groups would increase bond strength values (push out bond strength) and of the radiopacity.

2. Materials and methods

2.1. Experimental design

In this in-vitro study, different concentrations of TiO_2-nt (0.3, 0.6 and, 0.9% wt/wt) were added to a self-adhesive resin cement RelyX U200™ (3M ESPE). The cement was evaluated in self-cured mode only, and specimens were tested for bond strength (BS) through the push out bond strength test (PO), and radiopacity (RO). In accordance by Ramos-Tonello et al., 2017 [11], the specimens were randomly divided in four groups: **SCT**= self-adhesive resin cement, without TiO_2-nt (control group); **S03** = self-adhesive resin cement with 0.3 % of TiO_2-nt; **S06** = self-adhesive resin cement with 0.6 % of TiO_2-nt; **S09** = self-adhesive resin cement with 0.9 % of TiO_2-nt.

2.2. Resin cement preparation

The TiO_2-nt were manufactured and characterized according to the method described by Arruda et al., 2015 [13]. Equal lengths of base and catalyst pastes were dispensed with the clicker on a paper pad and weighed. The TiO_2-nt nanotubes were weighed to achieve the pre-set percentages for each individual sample using a scale with precision of 0.0001 g (Denver Instrument, São Paulo, Brazil). Nanotubes were manually added to the base paste and mixed for 10 s. Subsequently, the base paste with TiO_2-nt was mixed with the catalyst paste for another 10s, in a room with low light, and controlled temperature (23ºC) and humidity (50%).

2.3. Bond strength (BS)

2.3.1 Push-out bond strength (PO)

Twenty bovine anterior teeth, with internal root canal diameter less than 3.0 mm, without curves, and a minimum length of 30.0 mm were selected according to the Animals Use Ethics Committee of the Bauru Dental School from the University of São Paulo, Brazil (CEUA/FOB/UP register number: 003/2019). The teeth were measured, cleaned and stored under refrigeration in a 0.1 % Thymol solution. The roots were separate of the crows, below cement-enamel junction, to create a standard access to the root canal and to obtain 17.0mm length. The glide path was made using a stainless-steel K-file #15 with 21 mm (Dentsply Maillefer, Ballaigues, VD, Switzerland) to remove pulp tissue and debride the foramen. Next, the root canal shaping and cleaning was performed with the working length established at 16 mm (1 mm from the root apex), with nickel-titanium rotary instruments (ProTaper® Universal, Dentsply Maillefer, Ballaigues, VD, Switzerland) in the following order: SX, S1, S2, F1, F2, F3, F4, F5. After each instrument, NaOCl 2.5% solution (Rioquímica, São José do Rio Preto, SP, Brazil) irrigation was carried out. After that, the root canals were rinsed with 5 mL of distilled water to neutralize the irrigation agents and the roots were stored under refrigeration in a 0.1 % Thymol solution. Subsequently, 5 mL of EDTA (Biodinâmica, Ibiporã, PR, Brazil) was applied into the root, for 5 min, then irrigated with 10 ml of distilled water and dried with paper points (Tanari, Manaus, AM, Brazil). The root canals were filled by lateral condensation technique with gutta-percha cones (Tanari, Manaus, AM, Brazil) and epoxy calcium hydroxide based sealer (Sealer 26, Dentsply, Petrópolis, RJ Brazil). Roots were coronally sealed with glass ionomer cement (Maxxion R, FGM, Joinville, SC, Brazil) and stored at 37 ± 1 ºC in 100% humidity.

After 24 h, the glass ionomer cement was removed and the root canals was unsealed up to 13 mm length, using Gates-Glidden drills (#2,3,4) and Largo® Peeso Reamer (#3,4,5) (Dentsply Maillefer, Ballaigues, VD, Switzerland). A low-speed drill, provided by the manufacturer of the posts-system (Whitepost DC #2, FGM, Joinville, SC, Brazil), was used to prepare the posts-space into the root canals, to obtain the dimensions of 1.8 mm diameter in the coronal third and 1.05 mm diameter in the apical third, and 13 mm length, resulting in 3 mm of apical gutta-percha sealing. The root canals were then washed with distilled water, dried with absorbent paper cones, and distributed randomly into four groups (n=5), according to the luting protocol used (SCT, S03, S06 and S09).

Before the luting procedure, glass fiber posts (Whitepost DC #2, FGM, Joinville, SC, Brazil) were tested in the root canals to check the position and fitting, according to the manufacturer. After that, the posts were cleaned with 70% ethanol, dried, silanized (Silane, Angelus, Londrina, PR, Brazil) for 1 min and dried again. For the luting procedure, one click of the clicker packing of the cement RelyX U200™ (3M ESPE) was used for each post. The cement used was distributed according to the groups shown in item *2.1*: SCT, S03, S06 and S09 (n=10). The fiber glass posts were covered with the resin cement modified or not with TiO_2-nt, and were introduced into the root canals. This stage was carried out in a room with low light, and controlled temperature (23ºC) and humidity (50%) to ensure the self-cure mode, and after 30 min, the specimens were stored in an oven at 37 ± 1 ºC in 100% humidity (distilled water).

After 24 h, the roots were fixed on a low-speed cutting-machine (Isomet, Buehler, Lake Bluff, IL, United States) and sliced with a diamond disc, under water-cooling, perpendicularly to the long axis. Nine specimens were obtained out of each root: three cervical, three medial, and three apical. Each slice (1.0 ± 0.2 mm thick) was measured with a digital caliper (Absolute Digimatic, Mitutoyo, Tokyo, Japan), marked on their apical side and stored in 3 mL of artificial saliva solution at 37 ± 1 ºC in a container with coded identifier, not disclosed to the operator (blind trial).

After 7 days, the push-out bond strength test was performed in a universal testing machine Instron 3342 (Instron Co., Canton, MA, United States) with a 500 Kg (50 N) load-cell at a cross-head speed of 0.5 mm/min in the apical-coronal direction. Each slice was placed on the test base with its coronal side directed to the device, and aligned with the corresponding perforation. A plunger compatible with the posts diameter (0.9 – 1.1 mm) pushed the post portion, making no contact with the dentin (Figures 1-2).

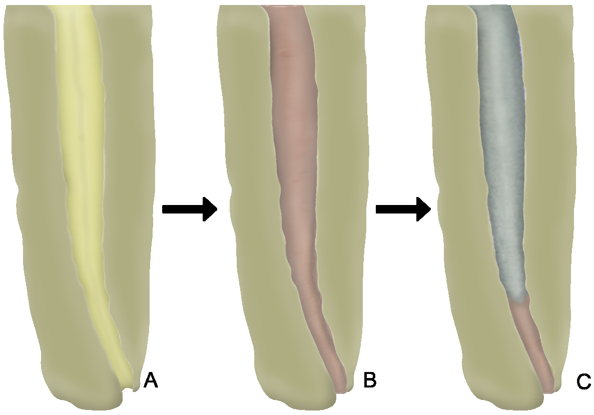


Figure 1. Methods for PO 1: ***A***. root canal shaped; ***B.*** root canal filled with gutta-percha cones and epoxy calcium hydroxide based sealer; ***C.*** root canal unsealed until 13 mm length; fiberglass post luted into the root canal.

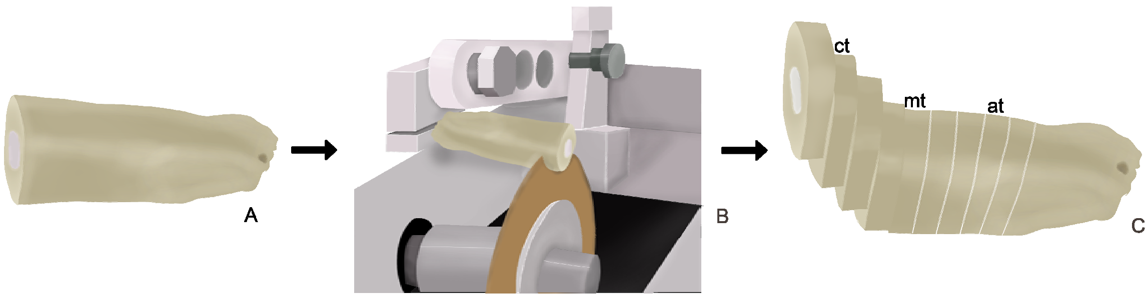


Figure 2. Methods for PO 2: ***A.*** root with fiberglass post luted; ***B.*** root at the cutting machine; ***C.*** slices of the root (specimens): tree of each third (*ct* – cervical third; *mt* – medium third; *at* – apical third).

The value of the strength on fiberglass posts displacement was recorded in kgf and converted to MPa. For this calculation, the following formula was used:

$$\alpha = F/A$$

where, F (MPa) is the strenght to move the post, and A is the area (mm^2) of the specimen.

Since the specimens had a conic shape, the luting diameters (coronal and apical) and thickness was measured with a digital caliper (Absolute Digimatic, Mitutoyo, Tokyo, Japan), and the total area (mm^2) was calculated using the formula:

$$A = \pi\ (R2+R1)\ [h^2 + (R2-R1)^2]^{0,5}$$

where π = 3.14; R2 = fragment coronal radius; R1 = fragment apical radius; h = slice thickness.

After testing, the failure modes were analyzed with a 200 x magnification optical microscope (Dino - Lite Plus Digital Microscope, AnMo Eletronics Co., Taipei, Taiwan) and categorized as: 1) A - C/D (adhesive between the cement and the dentin); 2) A - C/P (adhesive between the cement and the post); 3) CP (cohesive in the post); 4) CC (cohesive in the cement); 5) Mixed (adhesive and cohesive simultaneously). The two more representative failures of each group were processed for analysis in Scanning Electron Microscopy (SEM) by variable pressure, APEX Express (APEX Corporation, Delmont, PA, United States) with 400 and 1000 x magnification.

2.4. Radiopacity (RO)

Forty resin cement specimens were manufactured (ISO 9917-2/2010) [16] by the same operator and divided in the groups determined in item 2.1: SCT, S03, S06 and S09 (n=10). A split polytetrafluoroethylene mold (15.0 mm ø x 1.0 mm) (Figure 3. A) was used. To guarantee the surface smoothness of the specimens, a transparent polyester strip of 50 ± 30 µm thickness was placed over a glass plate (10.0 mm thickness). Three clicks of the clicker packing resin cement RelyX U200™ (3M ESPE) were used and the TiO_2–nt were added according to the group being prepared.

The resin cement was handled in a room with ambient light and inserted in a single portion in the mold to slightly overfill it, then covered with a second film/plate system. After30 min, the polymerization on the self-cure mode of the resin cement allowed for the specimen to be removed from the mold. The thickness of the specimens was checked with a digital caliper (Absolute Digimatic, Mitutoyo) to guarantee 1.0 ± 0.1 mm of final thickness (*T*s), to calculate radiopacity [16]. Then, specimens were stored in grade 3 water (ISO 3696), during 7 days.

To avoid specimens' dehydration, the determination of RO was carried out up to 30 min after removing the specimens from deionized water. An aluminum step wedge (purity 98%; 50.0 mm long/ 20.0 mm wide; with a thickness range 1.0 - 10.0 mm in equally spaced steps of 1.00 ± 0,01 mm) was used to convert the RO in equivalent mm of aluminum. An occlusal film size X-ray sensor (Intraoral image plate #4, VistaScan, Dürr Dental, Bietigheim-Bissingen, Germany), calibrated for use with single-phase dental X-ray unit with appropriate software (VistaScan Perio Plus, Dürr Dental, Bietigheim-Bissingen, Germany), was used to obtain the images. The aluminum step wedge was placed near the center and, right above it, one specimen of each of the four groups: SCT, S03, S06 and S09 (Figure 3. B).

Radiographic images were obtained with a conventional dental X-ray equipment (Yoshida Kaycor, X-707, Japan), at 70 kVp and 7 Ma, with a total filtration equivalent of 1.5 mm of aluminum. The exposure time was previously determined in a pilot study at 30 s, at a distance of 400 mm (Figure 3. C). Three images were obtained of each set X-rayed, which was filed in 1070 dpi resolution, in JPG format (Figure 3. D). Digital images were evaluated for optical density by grey scale analysis software Adobe® Photoshop® CC 2017 (Adobe Systems Incorporated, CA, United States), by the same operator. The grey scale values for the aluminum step wedge steps (3 points in each step) and for all specimens (5 points in each specimen) were measured and the correspondent means were calculated. The RO value was determined in line with the radiographic density; and converted in aluminum millimeters (mm Al), in accordance with Duarte et al., 2009 [17], by the formula:

$$A \times 1/B + mm/AL \text{ immediately below } RDm$$

where: ***A*** = material radiographic density (RDm) – aluminum step immediately below radiographic density (RDm); ***B*** = aluminum step immediately above radiographic density (RDm) – aluminum step immediately below radiographic density (RDm); ***1*** = 1 mm increment between each aluminum step.

In addition to this, data were also evaluated with the [16] formula as follows:

$$T_a/T_s$$

where: T_a = thickness of the equivalent aluminum step; T_s = thickness of the specimen. If this value is ≥ 1, the material is deemed to have complied with ISO requirements.

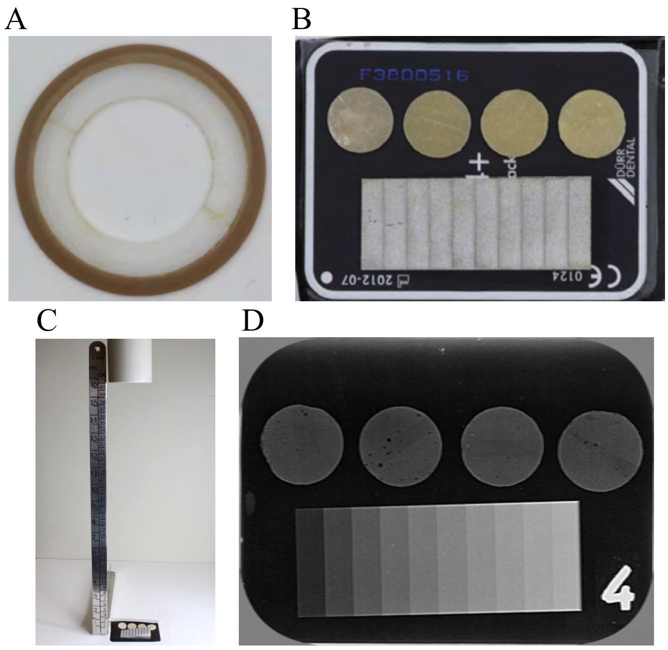


Figure 3. Methods for RO: A. Split polytetrafluoroethylene mold (15.0 mm ø x 1.0 mm); B. X-ray sensor, specimens and aluminum step wedge; C. X-ray sensor, specimens and aluminum step wedge positioned at 400mm from the X-Ray device; D. Digital image in JPG format.

2.5. Statistical analysis

Statistical analysis was carried out with the software Stat Soft (Statistica v10.0 Entrerprise, TBICO Software Inc., CA, United States). PO and RO values were subjected to the Kolmogorov-Smirnov and Shapiro-Wilk normality tests. PO and RO data were normally distributed, so data were analyzed by one-way ANOVA test at the $\alpha = 0.05$ significance level, followed by post hoc multiple comparisons Fisher's test for PO and Tukey's test for RO.

For comparisons of the roots thirds' PO and to compare RO methods, ANOVA with repeated measures was performed at the $\alpha = 0.05$ significance level, followed by post hoc multiple comparisons Fisher's test for PO, and Tukey's test for RO.

3. Results

3.1. Push-out bond strength (PO)

The results for PO per root are presented in Table 1 and Figure 4. The modified groups (S03, S06 and S09) did not showed difference in values for the SCT. Statistical difference was observed between groups S03 and S06 ($p<0.05$). The highest value for PO was found for S06 group, while the lowest result for PO was observed for the group with less TiO_2-nt, S03. These were similar to SCT and S09, which showed intermediate results ($p<0.05$).

Table 1. Means and standard deviations for PO (per root). Lowercase letters show significant statistical differences among groups ($p<0.05$).

	Groups	**PO (MPa)**
RelyX U200	SCT	0.54 (0.15)^{a,b}
	S03	0.42 (0.10)^{b}
	S06	0.68 (0.27)^{a}
	S09	0.63 (0.18)^{a,b}

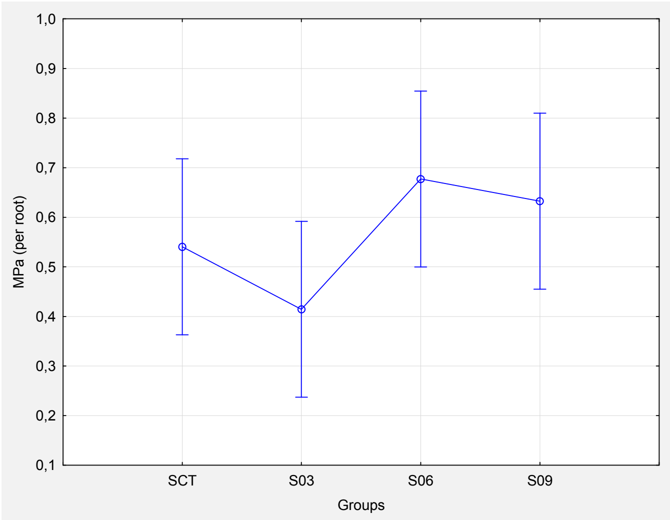


Figure 4. PO values of all groups tested (per root).

The results for PO per thirds are presented in Table 2 and Figure 5. In general, the cervical third for all tested groups showed the highest values for PO in MPa; except for group S06, for which the highest value was obtained for the apical third. The only group in which significant difference among thirds was observed was S09 group (the cervical third's PO was higher than the medium third's ($p<0.05$)). PO values of other groups presented no difference among thirds (Figure 5). Overall S03 group showed the lowest results per third, but the medium third of S09 was the lowest value of all thirds and all groups.

Table 2. Means and standard deviations for PO (per thirds). Lowercase letters show significant statistical differences among groups ($p<0.05$).

Groups	**PO (1/3 C) (MPa)**	**PO (1/3 M) (MPa)**	**PO (1/3 A) (MPa)**
SCT	0.69 (0.33)[a,b]	0.46 (0.21)[a,b]	0.47 (0.22)[a,b]
S03	0.43 (0.14)[a,b]	0.41 (0.21)[a,b]	0.40 (0.15)[a,b]
S06	0.60 (0.39)[a,b]	0.67 (0.36)[a,b]	0.70 (0.48)[a]
S09	0.76 (0.58)[a]	0.35 (0.14)[b]	0.67 (0.35)[a,b]

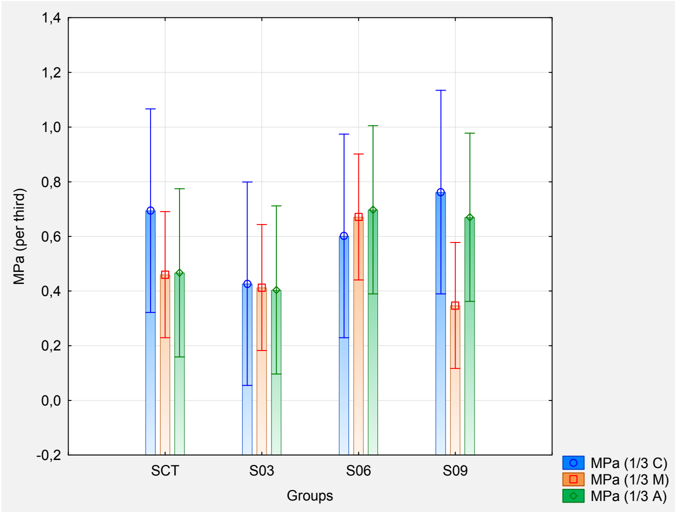


Fig 5. PO values of all groups tested (per thirds).

Figure 6 shows the failure distribution (in %) for PO for each group. The PO failure analysis - SEM images obtained for each failure type in representative samples from the evaluated groups are presented in Figure 7 (A–E). The failure analysis showed predominance of adhesive failure in all the studied groups; the cervical thirds of S03 and S06, and the medium third of SCT presented only adhesive failures. The predominant adhesive failure was type 1 (A – C/D) (SCT, S03, S06), except for S09, which showed more prevalence for type 2 (A – C/P). All groups presented cohesive failures of the resin cement. S03 and S06 did not show cohesive failures of the posts, but SCT and S09 presented this failure in the cervical and apical thirds, respectively. S06 showed the following failures: adhesive, cohesive in the cement and mixed; however, this group presented higher values for adhesive failures in all thirds, especially in the apical third, in comparison to the other groups.

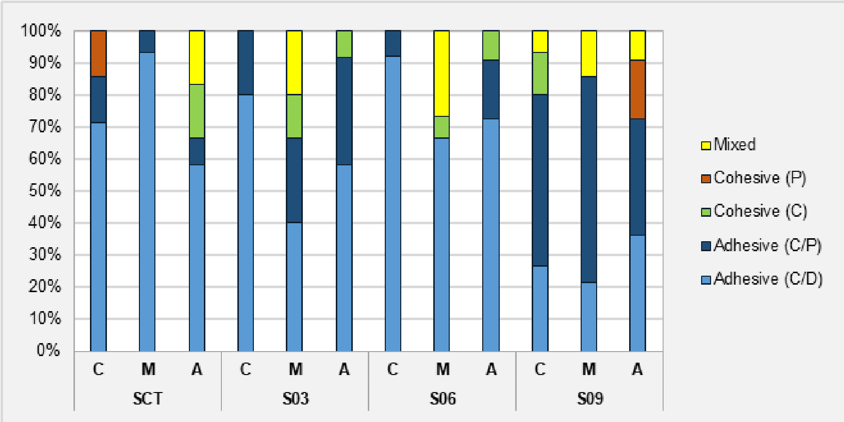
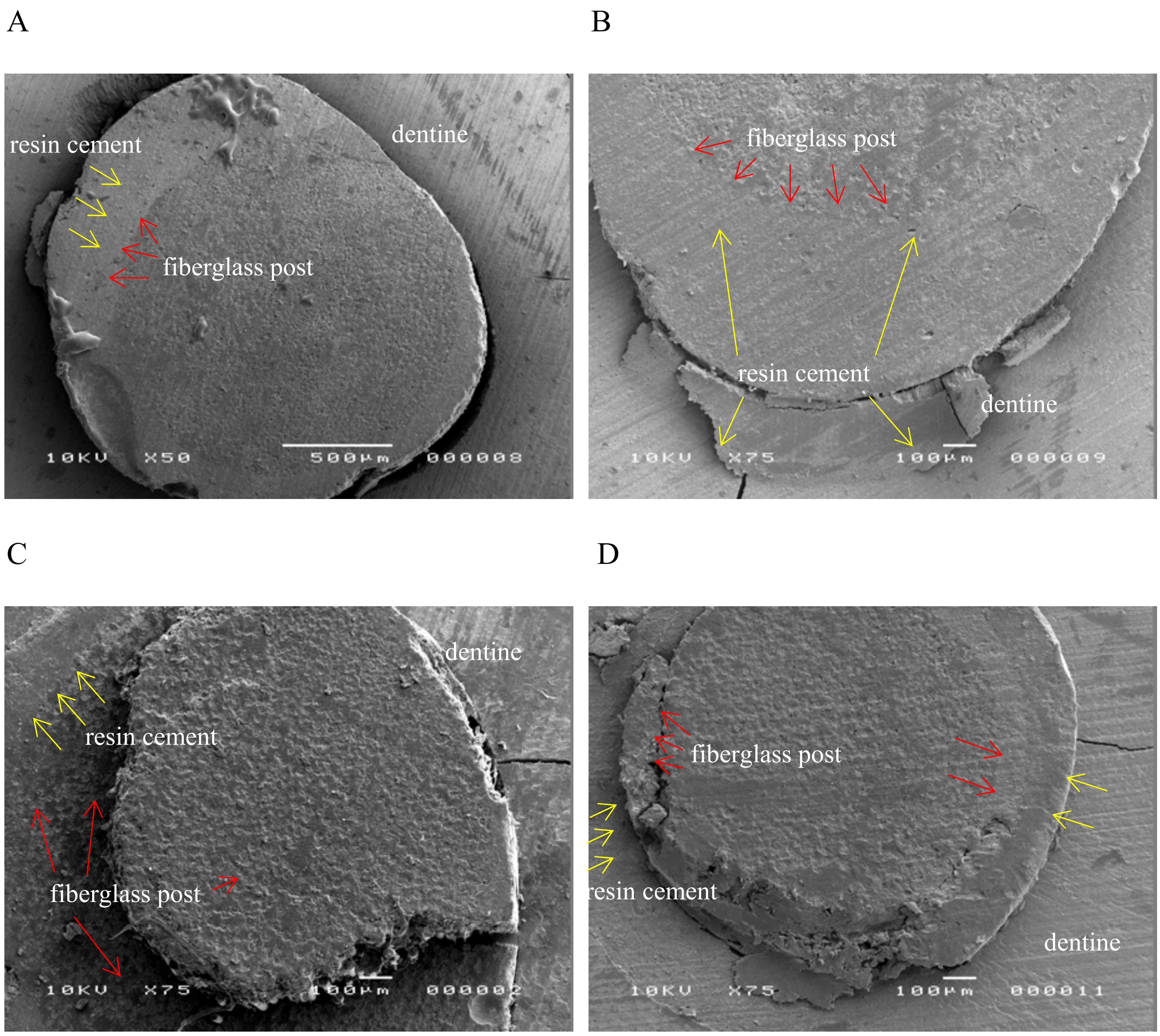


Figure 6. Values (%) failure analysis of each group tested for PO.



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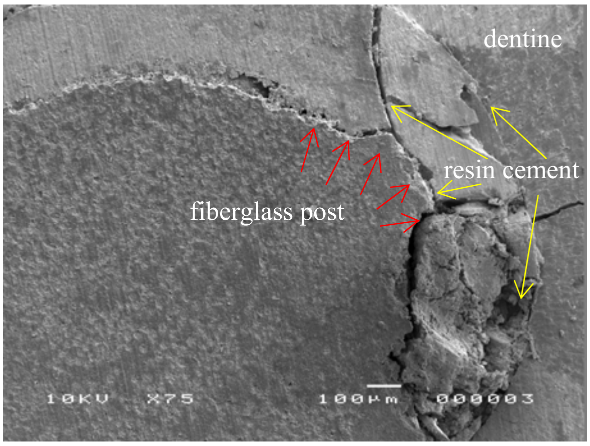

Figure 7. PO failure analysis - SEM image of each group showing failure type: failure 1 (A-C/D) of a slice #3 of the cervical third of S03 group; (8A); failure 2 (A-C/P) of a slice #2 of the cervical third of S03 group; (8B); failure 3 (CP) of a slice #2 of the cervical third of S09 group (8C); failure 4 (CC) of the slice #1 of the apical third of S03 group (8D); failure 5 (M) of a slice #2 of the cervical third of S09 group (8E).

3.2. Radiopacity (RO)

The results for RO are presented in Table 3 and Figure 8. The variance of the RO values analysis showed correlation with the addition of TiO_2-nt (Table 3).

Table 3. Means and standard deviations for RO (Duarte et al., 2009) [17] are presented. Lowercase letters show significant statistical differences.

	Groups	**RO (mm Al)**
RelyX U200	SCT	2.00 (0.16)^{c}
	S03	1.96 (0.15)^{b}
	S06	2.19 (0.20)^{a,b}
	S09	2.27 (0.11)^{a}

Figure 8 shows the confidence interval of RO (Duarte et al., 2009) [17] values for the groups evaluated. The S06 and S09 groups presented significantly higher RO when compared to the SCT group. The S03 group showed the lowest RO ($p<0.05$) but presented no statistical difference from SCT and S06 ($p>0.05$).

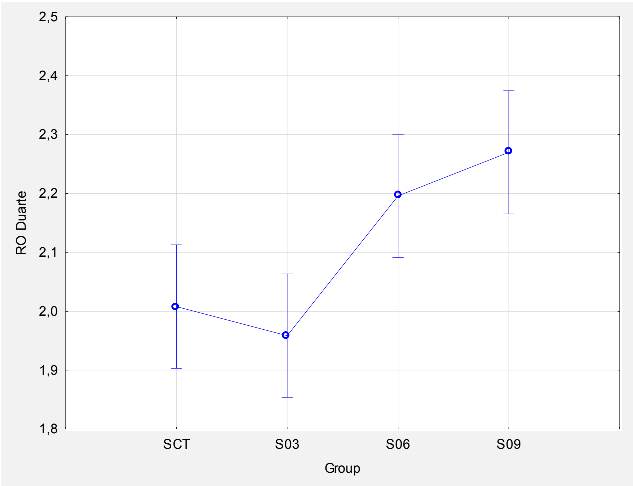

Figure 8. RO [17] values of all groups tested.

ISO analysis [16], the means and standard deviations of each group studied, and comparisons among the groups are displayed on Table 4 and Figure 9. Modification with TiO_2-nt led to a monotonic increase of RO in all groups when compared with SCT, however, only group S09 showed statistical difference from all other groups ($p<0.05$). All groups complied with the minimal value established by ISO standard.

Table 4. Means and standard deviations for RO ISO [16] are presented. Lowercase letters show significant statistical differences.

	Groups	RO (mm Al)
RelyX U200	SCT	1.85 (0.07)[a]
	S03	1.90 (0.12)[a]
	S06	2.00 (0.40)[a]
	S09	2.37 (0.43)[b]

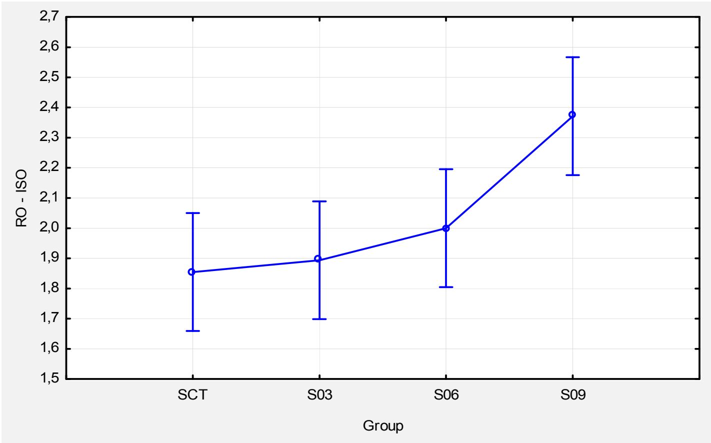

Figure 9. RO [16] values of all groups tested.

When both Duarte [17]; ISO [16] were evaluated, no significant statistical difference between the analysis in each group SCT, S03, S06 and S09 were found. All data are detailed on Table 5 and Figure10.

Table 5. Means and standard deviations for radiopaticity ISO [16]; Duarte [17] are presented as follows. Lowercase letters show significant statistical differences between columns.

Groups	RO (ISO)	RO (Duarte)
SCT	1.85 (0.07)[a]	2.00 (0.16)[a]
S03	1.90 (0.12)[a]	1.96 (0.15)[a]
S06	2.00 (0.40)[a]	2.19 (0.20)[a]
S09	2.37 (0.43)[a]	2.27 (0.11)[a]

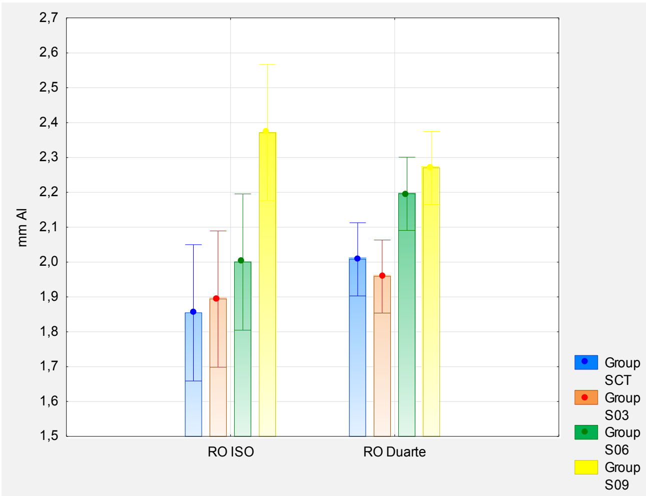

Figure 10. Values of RO in mm Al ISO [16]; Duarte [17] of all groups tested.

4. Discussion

The push-out test chosen for this study, according to literature, allows for a more accurate analysis of the overall bonding mechanism, as it evaluates the structural variability of the dentinal substrate inside the root canal, and it is considered to better simulate the clinical scenario [18,19]. RelyX U200 is indicated for luting of fiberglass posts, and in fact, self-adhesive resin cements have shown higher push-out strength values when compared to total-etch resin cements, in all thirds of the root canal dentin [19]. However, dual-cure resin cements depend on photoactivation to achieve the highest values of conversion. It was suggested that lower degrees of conversion results in lower bond strength, especially at root canal depth levels at which photoactivation is ineffective [20].

In this study, the results for PO showed a slight increase in values at TiO_2-nt adition groups (S03, S06, S09) in comparison with SCT, but without statistical difference. This result can be speculated to have been due to increased conversion, as previous reports have found that the addition of TiO2-nt at 0.3% to 0.9% increases the degree of conversion of self-adhesive resin cement [11]. The addition of these percentages likely played a role in initial viscosity, which in turn influences mobility of polymerizing species [21]. The increase in viscosity was likely enough to decrease the rate of termination, allowing for propagation to proceed to a greater extent in conversion, but not as dramatic to also decrease the rate of propagation – the net result is likely an increase in conversion [21]. Even though polymerization kinetics was not evaluated here, the increase in push out bond strength in tandem with previously reported results [11] adds evidence to the utility of using TiO2-nt-modified materials in clinical situations that rely more predominantly on the self-cure mode, such as the cementation of fiberglass posts in root canals. When the thirds were evaluated, S06 group showed an increase of the push-out strength values in the apical third in comparison with the cervical and medium thirds; However, SCT, S03 and S09 groups showed lower results in the medium and apical thirds in comparison with the cervical third. Moreover, S09 group showed statistically higher push-out strength value in the cervical third than in the medium third. The decrease in bond strength in deeper portions of the root canal is a concern that remains in the literature. Several studies have demonstrated the lower push-out strength in the apical third compared with the middle and cervical thirds, and this has been attributed to the difficulty in instrument access to narrow and deep areas, the incomplete removal of the smear layer before cementation, and the poor cement penetration into the dentin in the root canal [19,20,22]. In addition, these regions are further from curing light access, likely impacting the degree of conversion of the resin cement. Dual polymerized materials have better conversion values when light activation is used during polymerization [18,22,23]. In accordance with literature [20,24,25], the failure analysis exhibited predominance of adhesive failures in all thirds and all groups, and these results shown that the interface cement/dentin was more prevalent in the SCT, S03 and S06, but in the S09 group the cement/post interface was the most observed.

The International Organization for Standardization (ISO) standard for resin-modified cements requires them to have radiopacity equal to, or greater than that of the same thickness of aluminum (ISO 9917-2:2010) [17]. Radiopacity is a prerequisite for luting cements, as these materials need to be sufficiently radiopaque for detection of marginal overhangs, open gingival margins, recurrent caries, or excess luting material [26-29]. The radiopacity values of enamel and dentin ranged between 1.8 - 2.0 and 0.9 - 1.0 mm Al, respectively [30]. Overall, groups (SCT, S03, S06, S09) complied with the ISO standard for material radiopacity and exceeded the radiopacity of enamel and dentin, with values ranging between 1.90 - 2.37 mm Al. Furthermore, all the groups with TiO2-nt addition exhibited higher values in comparison with the control group in the ISO analysis and the values of S09 group demonstrated significant statistical difference in the both analysis. These results confirm the literature, which reports that TiO_2-nt is potentially a suitable radiologic contrast agent [31].

It is important to understand the self-cured reaction of the dual self-adhesive resin cements to better predict the cement behavior in this condition. This cure mode should be considered especially in areas with restricted access to light, such as in most indirect thick and opaque restorations and fiberglass posts cementation [32]. Since the use of the TiO_2-nt in the concentrations of 0.3 wt% to 0.9 wt% in self-adhesive resin cements led to an increase of the conversion in the self-cured mode [11], this study further analyzed this possible combination that may lead to better clinical performance in terms of bond strength. In fact, this study demonstrated increased values of bond strength for materials modified with 0.3 wt% of TiO_2 for ceramic bonding and 0.6 wt% of TiO_2 for fiberglass posts luting. In addition, radiopacity increased with the addition of 0.9 wt% of TiO_2. Both characteristics evaluated benefit the clinical situations mentioned above, and better adhesion of fiberglass posts to dentin in regions with lower light access, may increase longevity of the indirect restorative procedures. In the same fashion, better radiopacity may help the diagnosis of the proper sealing of the resin cement.

5. Conclusions

The addition of TiO_2–nt to self-adhesive resin cement in self-cured mode did not show difference between modified groups and control group for bond strength (PO). However, the addition of TiO_2–nt had influence on a higher radiopacity of the cement when adding 0.6 wt% to 0.9 wt%.

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3 Discussion

3 DISCUSSION

Self-adhesive cements when polymerized by self-cure alone, can present a more complete reaction than when the same cement is light-cured with insufficient light[10]. Acidic functional monomers are believed to deactivate free radicals of methacrylate and produce an acid-base setting reaction, inducing a low rate of co-polymerization and more delayed polymerization[9,16]. Therefore, unconsumed residual acidic monomers can have an impact on the polymerization reaction, especially by inhibiting the action of the amine accelerator[10,17]. According to Yang et al., 2017[16], self-adhesive dual-cure resin cements with an insufficient light exposure (20 seconds of light-curing time) through thick ceramic restoration (4 mm thick) resulted in a conversion degree even lower than that of self-curing alone. Such clinical situation is evident in push out bond strength, because in the canal roots the light for the resin cement cure is insufficient, promoting a predominantly self-cure reaction.

The introduction of nanoscale materials offers new promise for augmenting the mechanical properties of dental composites due to their high surface area to volume ratio which enhances their interfacial interaction with the resin[18,19]. The selection by TiO2-nt for this study is justified by their large surface area, that can give rise to strong external, and also internal, interactions, chemical stability and a high refractive index[20]. According to the results of Ramos-Tonello et al., 2017[21], the addition of 0.3% to 0.9% of TiO2-nt to a self-adhesive resin cement in the self-cured mode, increased the conversion degree to values close to the ones obtained by the dual-cured condition, since TiO2-nt were capable of improving the afore mentioned properties, this study evaluated bond strength and radiopacity, to further analyze this enhanced material.

The push-out test chosen for this study, according to literature, allows for a more accurate analysis of the overall bonding mechanism, as it evaluates the structural variability of the dentinal substrate inside the root canal, and it is considered to better simulate the clinical scenario[4,22]. RelyX U200 is indicated for luting of fiberglass posts, and in fact, self-adhesive resin cements have shown higher push-out strength values when compared to total-etch resin cements, in all thirds of the root canal dentin[4]. However, dual-cure resin cements depend on photoactivation to achieve the highest values of conversion. It was suggested that lower degrees of conversion results in lower bond strength, especially at root canal depth levels at which photoactivation is ineffective[23].

In this study, the results for PO showed a slight increase in values at TiO_2-nt adition groups (S03, S06, S09) in comparison with SCT, but without statistical difference. This result can be speculated to have been due to increased conversion, as previous reports have found that the addition of TiO2-nt at 0.3% to 0.9% increases the degree of conversion of self-adhesive resin cement[21]. The addition of these percentages likely played a role in initial viscosity, which in turn influences mobility of polymerizing species[24]. The increase in viscosity was likely enough to decrease the rate of termination, allowing for propagation to proceed to a greater extent in conversion, but not as dramatic to also decrease the rate of propagation – the net result is likely an increase in conversion[24]. Even though polymerization kinetics was not evaluated here, the increase in push out bond strength in tandem with previously reported results[21] adds evidence to the utility of using TiO2-nt-modified materials in clinical situations that rely more predominantly on the self-cure mode, such as the cementation of fiberglass posts in root canals. When the thirds were evaluated, S06 group showed an increase of the push-out strength values in the apical third in comparison with the cervical and medium thirds; However, SCT, S03 and S09 groups showed lower results in the medium and apical thirds in comparison with the cervical third. Moreover, S09 group showed statistically higher push-out strength value in the cervical third than in the medium third. The decrease in bond strength in deeper portions of the root canal is a concern that remains in the literature. Several studies have demonstrated the lower push-out strength in the apical third compared with the middle and cervical thirds, and this has been attributed to the difficulty in instrument access to narrow and deep areas, the incomplete removal of the smear layer before cementation, and the poor cement penetration into the dentin in the root canal[4,23,25]. In addition, these regions are further from curing light access, likely impacting the degree of conversion of the resin cement. Dual polymerized materials have better conversion values when light activation is used during polymerization[22,25,26]. In accordance with literature[23,27,28], the failure analysis exhibited predominance of adhesive failures in all thirds and all groups, and these results shown that the interface cement/dentin was more prevalent in the SCT, S03 and S06, but in the S09 group the cement/post interface was the most observed.

The International Organization for Standardization (ISO) standard for resin-modified cements requires them to have radiopacity equal to, or greater than that of the same thickness of aluminum (ISO 9917-2:2010)[29]. Radiopacity is a prerequisite for luting cements, as these materials need to be sufficiently radiopaque for detection of marginal overhangs, open gingival margins, recurrent caries, or excess luting material[30-33]. The radiopacity values of enamel and dentin ranged between 1.8 - 2.0 and 0.9 - 1.0 mm Al, respectively[34]. Overall, groups (SCT, S03, S06, S09) complied with the ISO standard for material radiopacity and exceeded the radiopacity of enamel and dentin, with values ranging between 1.90 - 2.37 mm Al. Furthermore, all the groups with TiO2-nt addition exhibited higher values in comparison with the control group in the ISO analysis and the values of S09 group demonstrated significant statistical difference in the both analysis. These results confirm the literature, which reports that TiO_2-nt is potentially a suitable radiologic contrast agent[35].

It is important to understand the self-cured reaction of the dual self-adhesive resin cements to better predict the cement behavior in this condition. This cure mode should be considered especially in areas with restricted access to light, such as in most indirect thick and opaque restorations and fiberglass posts cementation[9]. Since the use of the TiO_2-nt in the concentrations of 0.3 wt% to 0.9 wt% in self-adhesive resin cements led to an increase of the conversion in the self-cured mode[29], this study further analyzed this possible combination that may lead to better clinical performance in terms of bond strength. In fact, this study demonstrated increased values of bond strength for materials modified with 0.3 wt% of TiO_2 for ceramic bonding and 0.6 wt% of TiO_2 for fiberglass posts luting. In addition, radiopacity increased with the addition of 0.9 wt% of TiO_2. Both characteristics evaluated benefit the clinical situations mentioned above, and better adhesion of opaque ceramic crowns and overlays, as well as of fiberglass posts to dentin in regions with lower light access, may increase longevity of the indirect restorative procedures. In the same fashion, better radiopacity may help the diagnosis of the proper sealing of the resin cement.

4 Final Considerations

4 FINAL CONSIDERATIONS

Even though literature may be scarce considering the self-cured reaction of dual self-adhesive cements, it is of utmost importance to understand the cement behavior in this condition. The self-cured mode should be considered especially in areas with restricted access to light, like the apical third into root canals. As the use of the TiO_2-nt in self-adhesive resin cements showed an increase of the monomers' conversion degree in the self-cured mode, this study further analyzed this possible combination that may lead to better clinical performance in adhesion and in radiopacity. Both characteristics evaluated benefit the clinical situations mentioned above, as the better adhesion of the fiberglass posts to dentin may increase longevity of the indirect procedures; as well as a better radiopacity may help the diagnosis of the proper sealing of the resin cement. More researches should be carried out on the self-adhesive resin cements enhanced, not only by other concentrations of TiO_2-nt, but also with other materials that may increase degree of conversion and other properties.

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APPENDIXES

APPENDIXES

APÊNCIDE A - DECLARAÇÃO DE USO EXCLUSIVO DE ARTIGO EM DISSERTAÇÃO/TESE

DECLARATION OF EXCLUSIVE USE OF THE ARTICLE IN DISSERTATION/THESIS

We hereby declare that we are aware of the article (Titanium dioxide nanotubes as reinforcement of a self-adhesive resin cement in self-curing mode) will be included in (Dissertation/Thesis) of the student (Leandro Edgar Pacheco) and may not be used in other works of Graduate Programs at the Bauru School of Dentistry, University of São Paulo.

Bauru, march 01th, 2019.

Leandro Edgar Pacheco
Author

Signature

Paulo Afonso Silveira Francisconi
Author

Signature