UNIVERSIDADE FEDERAL DO RIO GRANDE DO SUL
FACULDADE DE ODONTOLOGIA
PROGRAMA DE PÓS-GRADUAÇÃO
DOUTORADO EM ODONTOLOGIA
ÁREA DE CONCENTRAÇÃO CLÍNICA ODONTOLÓGICA –
MATERIAIS DENTÁRIOS

Síntese de blendas co-monoméricas radiopacas de aplicação odontológica

Fabrício Mezzomo Collares

Porto Alegre, 2010.

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Fabrício Mezzomo Collares

Tese apresentada como requisito obrigatório para obtenção de título de **Doutor em Odontologia** na área de concentração em Clínica Odontológica/Materiais Dentários.

Susana Maria Werner Samuel
Orientadora

Porto Alegre, 2010.

“*There are no such things as applied sciences, only applications of science***”**

Louis Pasteur (1822-1895)

Dedicatória

Ao meu filho **Bruno** pela imensa alegria proporcionada a cada sorriso, gesto, brincadeira e cada ato de alegria oferecido por ele. E, pelos momentos revigorantes que passamos juntos durante este período.

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RESUMO

A radiopacidade dos materiais restauradores deve permitir distinguí-los da estrutura dental. Os adesivos dentinários normalmente, não possuem radiopacidade satisfatória a qual pode ser buscada com o acréscimo de substâncias que apresentem essa característica. Entretanto, esses materiais não devem interferir negativamente nas propriedades do polímero formado. O objetivo deste estudo foi avaliar a influência da adição de substâncias radiopacificantes em uma resina adesiva experimental nas propriedades do polímero. Uma resina adesiva experimental foi formulada com 50 % de Bis-GMA, 25 % TEGDMA, e 25 % HEMA, em peso, acrescido de Canforoquinona e EDAB (1% /mol). Para formar os grupos experimentais seis substâncias foram adicionadas à resina base: dióxido de titânio, óxido de bismuto, sulfato de bário, quartzo, dióxido de zircônio e trifluoreto de itérbio, em diferentes concentrações. A radiopacidade foi avaliada utilizando um sistema digital com placas de fósforo VistaScan (Dürr Dental GmbH & CO. KG, Bietigheim-Bissingen, Alemanha) sendo analisadas através do software DBSWIN 4.5, quanto a densidade radiográfica. As demais propriedades avaliadas foram: grau de conversão através de FTIR; resistência à flexão, baseada na normatização da ISO 4049/2010. Radiopacidade de resinas adesivas experimentais com ao menos 30% sulfato de bário ou óxido de bismuto ou 40% de zircônia apresentaram radiopacidade semelhante a 2mm de alumínio. Resinas adesivas com ao menos 20% de fluoreto de itérbio apresentaram radiopacidade satisfatória (2mm de Al) sem influenciar outras propriedades.

Palavras-chave: Adesivo Dentinário; Radiopacidade; FTIR; Resistência à flexão.

ABSTRACT

The radiopacity of restorative materials should be sufficient to allow the clinician to distinguish the material from normal and demineralized tissues. It is recognized that unfilled resin adhesives are radiolucent which could be reached with radiopaquing agents' addition. The aim of this study is to evaluate, in an experimental adhesive resin, the influence of radiopaquing agents at polymer properties. A model adhesive resin was formulated with 50% of Bis-GMA, 25% of TEGDMA, 25% of HEMA in weight, and camphorquinone and EDAB (1%mol). The experimental groups were formed with addition of six radiopaquing agents: titanium dioxide, bismuth oxide, barium sulfate, quartz, zirconium, and ytterbium trifluoride at different concentration. The radiopacity was evaluated using an aluminum step-wedge and VistaScan (Dürr Dental GmbH & CO. KG, Bietigheim-Bissingen, Alemanha) phosphorous plates radiographs digital system and DBSWIN 4.5 software. The other properties evaluated were degree of conversion with FTIR and flexural strength, based at ISO 4049/2010. Radiopacity of model adhesive resins with at least 30% of barium sulfate or bismuth oxide or 40% of zircon showed no significant differences to 2mm of aluminum. Adhesive resin with at least 20% addition of ytterbium trifluoride presented satisfactory radiopacity (Al 2mm) without influencing other properties.

Keywords: Dentinal adhesive; Radiopacity; FTIR; Flexural strength.

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INTRODUÇÃO

A radiopacidade dos materiais restauradores deve ser suficiente para permitir ao clínico distinguir o material restaurador da estrutura dental normal, ou descalcificada ou amolecida. Essa necessidade se intensifica quando falamos de cárie recorrente, assim como excessos e degraus proximais de restaurações uma vez que os adesivos dentinários não possuem radiopacidade semelhante à do material restaurador (Krejci et al., 1991; Schulz et al, 2008). Esta situação pode gerar uma confusão na identificação entre o adesivo dentinário e uma lesão de cárie, dificultando o diagnóstico principalmente em restaurações de cavidades proximais, onde a determinação de cárie recorrente é mais complexa (Murchison et al., 1999).

A acurácia de diagnóstico de lesões de cárie recorrentes, variando a radiopacidade de materiais restauradores, foi objeto de análise de pesquisa, concluindo que quanto maior a radiopacidade do material mais eficiente é o diagnóstico (Sewerin et al, 1980). Resultados dos estudos indicam que a radiopacidade do material restaurador é uma característica valiosa na detecção de cárie secundária e lesões recorrentes de cárie. Além disso, um grande número de diagnósticos falso positivos pode ser explicado pela existência de materiais de baixa radiopacidade sob as restaurações (Sewerin et al, 1980). A adição de agentes radiopacificantes a materiais odontológicos deve permitir a correta distinção entre o tecido dental comprometido e o material restaurador sem alterar as demais propriedades do material. A efetividade da adesão formada é diretamente relacionada à qualidade do polímero formado e a correlação entre as propriedades mecânicas e o grau de conversão dos polímeros durante a polimerização tem sido demonstradas. Sugere-se que o

grau de conversão se apresenta como o principal fator a influenciar na efetividade da adesão de um adesivo ao esmalte, baseados na correlação encontrada entre o grau de conversão e a resistência ao cisalhamento (Peutzfeldt, 1997).

Verifica-se que, quanto menor o número de ligações duplas alifáticas entre carbonos restantes depois de polimerizados, melhores são as propriedades mecânicas do polímero formado (Peutzfeldt, 1997; Ferracane, 2006). Diferentes composições dos sistemas adesivos podem interferir no grau de conversão final do polímero aumentando o número de ligações duplas não convertidas e, conseqüentemente, podem alterar a longevidade da adesão de materiais resinosos à estrutura dentária.

OBJETIVO

Avaliar a influência da adição de substâncias radiopacificantes a uma resina experimental na radiopacidade, grau de conversão, resistência à flexão.

Artigo 1*:

Influence of the composition of an experimental adhesive on conversion kinetics, flexural strength and radiodensity.

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*Publicado nesta tese com a autorização do periódico (ANEXO I)

Influence of the composition of an experimental adhesive on conversion kinetics, flexural strength and radiodensity

Influência da composição de um adesivo experimental na cinética de conversão, resistência à flexão e radiodensidade

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Abstract

Purpose: To evaluate the effect of the addition of three radiopaque agents to an experimental adhesive on conversion kinetics, flexural strength and radiodensity.

Methods: The model adhesive was formulated by mixing 50 wt% Bis-GMA, 25 wt% TEGDMA and 25 wt% HEMA. Barium sulfate, Titanium dioxide and Zirconium in 0.1, 0.2, 0.4, 0.8 and 1.6 wt% were added separately resulting in 15 experimental groups and 1 control group. The conversion kinetics of the model adhesive was evaluated using real time Fourier Transform Infrared Spectroscopy. The flexural tests were performed on 5 specimens ($12 \times 2 \times 2$ mm) for each group (total n = 80) in a universal testing machine. The radiodensity was evaluated by using an aluminum step-wedge and VistaScan phosphorous plates radiographs digital system with 0.6 s exposure and focal distance of 40 cm.

Results: No statistical difference ($P > 0.05$) was found in flexural strength among all groups. The values of degree of conversion ranged from 45.51% e 62.46%. All groups showed higher values than 0.54 mm of aluminum for the evaluation of radiopacity.

Conclusion: The addition of radiopaquing agents increased the adhesive radiodensity and did not affect its degree of conversion and flexural strength.

Key words: Dental adhesive; radiopaque; degree of conversion; flexural strength

Resumo

Objetivo: Avaliar a influência da adição de três substâncias radiopacificadoras na cinética de conversão, resistência à flexão e radiodensidade de um adesivo experimental.

Metodologia: O adesivo foi formulado com 50% de Bis-GMA, 25% TEGDMA e 25% HEMA, em peso. Foram adicionados 0,1%; 0,2%; 0,4%; 0,8%; 1,6%, em peso, de Sulfato de Bário, Óxido de Titânio e Dióxido de Zircônia, totalizando 15 grupos experimentais e um grupo controle. A cinética de polimerização foi avaliada por FTIR em tempo real. O ensaio de miniflexão foi realizado com 5 espécimes ($12 \times 2 \times 2$ mm) para cada grupo (n total = 80) em uma máquina de ensaios universal. A radiodensidade foi obtida utilizando um sistema digital com placas de fósforo VistaScan, 0,6 s de exposição e distância focal de 40 cm e os valores foram comparados a uma escala de alumínio.

Resultados: Não houve diferença estatisticamente significativa no ensaio de miniflexão entre os grupos ($P > 0,05$). Os valores de grau de conversão ficaram entre 45,51% e 62,46%, enquanto a radiodensidade foi superior a 0,54 mm de alumínio, sem diferença entre os grupos.

Conclusão: O acréscimo das substâncias radiopacificadoras aumentou a radiopacidade do adesivo e não alterou o grau de conversão e a resistência à flexão.

Palavras-chave: Adesivo dentinário; radiopacidade; grau de conversão; resistência à flexão

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Introduction

The radiopacity of restorative materials should be sufficient to allow the clinician to distinguish the material from normal and demineralized tissues. This requirement is even more important for an accurate diagnosis of recurrent or secondary caries, as well as proximal restoration overhangs. It is widely recognized that unfilled resin adhesives are radiolucent and can present a diagnostic challenge (1,2), especially in class II restorations, where the clear assessment of recurrent caries can be compromised (3).

The effectiveness of adhesion is directly related to the quality of the formed polymer. A strong correlation between mechanical properties and conversion degree during polymerization has been shown elsewhere (4,5). The assessment of the conversion degree of a dentin adhesive is essential and suggests that it is an important factor in the effectiveness of the bond strength of an adhesive to enamel (6). A high percentage of non-reacted aliphatic carbon double bonds indicate that the material presents a more open structure and, therefore, is more susceptible to deterioration of the mechanical properties (4,7). Different compositions of adhesive systems may interfere at the final conversion degree and the flexural strength of the polymer, therefore increasing the unreacted double bonds as well as reducing the flexural strength and, consequently, can influence on the longevity of the adhesion of resin materials to tooth structure. The addition of inorganic particles into polymer may be responsible for changes in the mechanical properties and the conversion degree, considering that the refractive index of substances may change the availability of light energy within the polymer (8).

Since the diagnosis of caries under restorations or at the tooth/restoration interface is performed by radiography exam in clinical practice, the synthesis of radiopaque adhesive is extremely important for Dentistry. However this should be achieved without a negative effect on their properties. Therefore, the purpose of this study is to evaluate, in an experimental adhesive, the influence of radiopaquing agents on its conversion kinetics, radiodensity and flexural strength.

Methodology

Experimental base resins with five concentrations (0.1, 0.2, 0.4, 0.8 and 1.6% wt) of three inorganic substances (Barium Sulfate, Titanium Dioxide and Zirconium Dioxide) were formulated, resulting in 15 experimental groups. One control group, without inorganic filler, was used for the flexural strength test. Table 1 shows the tested groups. Experimental adhesive resins were evaluated by conversion kinetics, flexural strength and radiodensity.

Reagents

The monomers used in this study were bisphenol A glycol dimethacrylate (BisGMA), triethylene glycol dimethacrylate (TEGDMA) and 2-hydroxyethyl methacrylate (HEMA), camphorquinone (CQ) and Ethyl 4-dimethylaminobenzoate (EDAB), from Aldrich Chemical Co (Milwaukee, USA). These materials were used without further processing. Titanium dioxide, Barium sulfate (Vetec Química Fina, Brazil) and Zirconium dioxide (Sigma-Aldrich) were used as radiopaque agents. To perform monomer photo-activation, a halogen light-activation unit (XL 3000, 3M ESPE, USA) was used. An irradiation value of 700 mW/cm^2 was confirmed with a digital power meter (Ophir Optronics, Danvers, MA, USA).

Table 1. Composition and concentrations, in wt%, of all groups.

Group	Composition in wt%					
	Bis-GMA	TEGDMA	HEMA	$BaSO_4$	TiO_2	Zirconium
G_0	50	25	25	–	–	–
$SB_{0.1}$	50	25	25	0.1	–	–
$SB_{0.2}$	50	25	25	0.2	–	–
$SB_{0.4}$	50	25	25	0.4	–	–
$SB_{0.8}$	50	25	25	0.8	–	–
$SB_{1.6}$	50	25	25	1.6	–	–
$OT_{0.1}$	50	25	25	–	0.1	–
$OT_{0.2}$	50	25	25	–	0.2	–
$OT_{0.4}$	50	25	25	–	0.4	–
$OT_{0.8}$	50	25	25	–	0.8	–
$OT_{1.6}$	50	25	25	–	1.6	–
$ZE_{0.1}$	50	25	25	–	–	0.1
$ZE_{0.2}$	50	25	25	–	–	0.2
$ZE_{0.4}$	50	25	25	–	–	0.4
$ZE_{0.8}$	50	25	25	–	–	0.8
$ZE_{1.6}$	50	25	25	–	–	1.6

Formulations

The model adhesive was formulated by mixing 50 wt% Bis-GMA, 25 wt% TEGDMA, and 25 wt% HEMA. CQ and EDAB were added at 1 mol% for all groups, according to the monomer moles. The tree radiopaque agents were investigated at various concentrations to fabricate the experimental groups: 0.1 ($SB_{0.1}$), 0.2 ($SB_{0.2}$), 0.4 ($SB_{0.4}$), 0.8 ($SB_{0.8}$), 1.6 ($SB_{1.6}$) wt% of Barium Sulfate ($BaSO_4$); 0.1 ($OT_{0.1}$), 0.2 ($OT_{0.2}$), 0.4 ($OT_{0.4}$), 0.8 ($OT_{0.8}$), 1.6 wt% ($OT_{1.6}$) of Titanium Dioxide (TiO_2); and, 0.1 ($ZE_{0.1}$), 0.2 ($ZE_{0.2}$), 0.4 ($ZE_{0.4}$), 0.8 ($ZE_{0.8}$), 1.6 wt% ($ZE_{1.6}$) of Zirconium dioxide. Specimens were produced without inorganic fillers (G_0) for flexural strength test. No radical scavenger was added. All formulations were weighed with an analytical balance (AG 200, Gehaka, Brazil), mixed and ultrasonicated (CBU 100/1LDG, Plana, Brazil) for 1 hour.

Conversion degree

The conversion degree of the experimental adhesives was evaluated using real-time Fourier Transform Infrared Spectroscopy (RT-FTIR) with a Shimadzu Prestige 21 (Shimadzu Prestige 21, Japan) spectrometer equipped with an attenuated total reflectance device. This device was composed by a horizontal ZnSe crystal with a mirror angle of 45º (PIKE Technologies, USA). A support was coupled to the spectrometer to fix the light-curing unit and standardize the distance between the fiber tip and the specimen in 5 mm. Analysis was performed at a controlled room temperature of 23º ± 2C and 60 ± 5% relative humidity. The temperature of the attenuated total reflectance crystal surface was approximately 25°C. One specimen (3 µL) for group (9) was directly dispensed onto the ZnSe crystal and light-activated for 60 s (n = 3). The conversion degree was calculated as described in a previous study (10), considering the intensity of carbon-carbon double bond stretching vibration (peak height) at 1635 cm^{-1}, and using the symmetric ring stretching at 1610 cm^{-1} from the polymerized and unpolymerized samples as an internal standard. To compute the resulting conversion degree the following formula was used (1):

$$GC = 1 - \left[\frac{\text{absorbance (1640 cm}^{-1}\text{) / absorbance (1610 cm}^{-1}\text{) polímero}}{\text{absorbance (1640 cm}^{-1}\text{) / absorbance (1610 cm}^{-1}\text{) monômero}} \right] \times 100 \quad (1)$$

Radiodensity

The radiopacity was evaluated with five specimens per group. Specimens (n = 75) were 4.0 mm (±0.5 mm) in diameter and 1.0 mm (±0.2 mm) thick. X-ray images were obtained with the phosphorous plates Digital System (VistaScan, Dürr Dental GmbH & CO. KG, Bietigheim-Bissingen, Germany) at 70 kV and 8 mA, with 0.6 seconds of exposure time and a focus-film distance of 400 mm. In each film, one specimen from each group with the same concentration was positioned, for a total of five films per concentration. An aluminum step-wedge was exposed simultaneously with the specimens in all images. The aluminum step-wedge thickness ranged from 0.5 mm to 5.0 mm in increments of 0.5 mm. The images were saved in TIFF format for less compressed files. Digital images were handled with the Photoshop software (Adobe Systems Incorporated, CA, USA). The means and standard deviations of the gray levels (pixel density) of the aluminum step-wedge and the specimens were obtained in a standardized area of 2 mm^2.

Flexural Strength

The adhesive specimens were fabricated using customized stainless steel molds according to ISO 4049/2000 specifications, except for the dimensions (12 mm in length, 2 mm in width and 2 mm in height) (10). The model adhesives were placed into the mold, which was positioned on the top of an acetate strip. The top and bottom surfaces of the specimens were light-polymerized with two irradiations of 20 s on each side. After polymerization, specimens were removed from the mold and stored in distilled water at 37 ± 1°C for 24 h. Five specimens were produced for each group (total n = 75 specimens). The flexural strength tests were performed using a universal testing machine (EMIC, São José dos Pinhais, PR, Brazil) at a crosshead speed of 1.0 mm/min. The flexural strength (σ) of each specimen was calculated in megapascal (MPa) according to the formula (2):

$$\sigma = 3LF/2BH^2 \quad (2)$$

where F is the maximum load in Newtons, L is the distance in millimeters between the supports, B is the width in millimeters of the specimen measured immediately prior to testing, and H is the height in millimeters.

Statistical Analysis

Data were analyzed by one-way ANOVA and Tukey's post-hoc test at the 0.05 level of significance.

Results

No statistical difference in radiodensity was found among the tested groups ($P > 0.05$), but all groups showed more than 0.54 mm of Aluminum of radiodensity (Table 2).

Conversion degree values are depicted in Figure 1. Conversion degree of all groups was higher than 45% in 70 s of photoactivation and most of which showed values higher than 50%. Barium sulfate 0.4% showed the highest conversion degree (63.5%). Conversion kinetics is shown in Figure 2.

The flexural strength values showed no statistical difference ($P > 0.05$) between control e tests groups (Table 3).

Table 2. Mean (±SD) of the radiodensity of the experimental adhesives, in Aluminum mm.

	0.1%	0.2%	0.4%	0.8%	1.,6%
Barium Sulfate	0.55 (±0.09)[a]	0.60 (±0.04)[a]	0.66 (±0.11)[a]	0.57 (±0.09)[a]	0.62 (±0.04)[a]
Titanium Dioxide	0.54 (±0.06)[a]	0.58 (±0.07)[a]	0.66 (±0.16)[a]	0.56 (±0.06)[a]	0.58 (±0.06)[a]
Zirconia Dioxide	0.55 (±0.06)[a]	0.58 (±0.06)[a]	0.63 (±0.18)[a]	0.56 (±0.05)[a]	0.59 (±0.07)[a]

* Same letters represents no statistically significant difference between means ($P<0.05$).

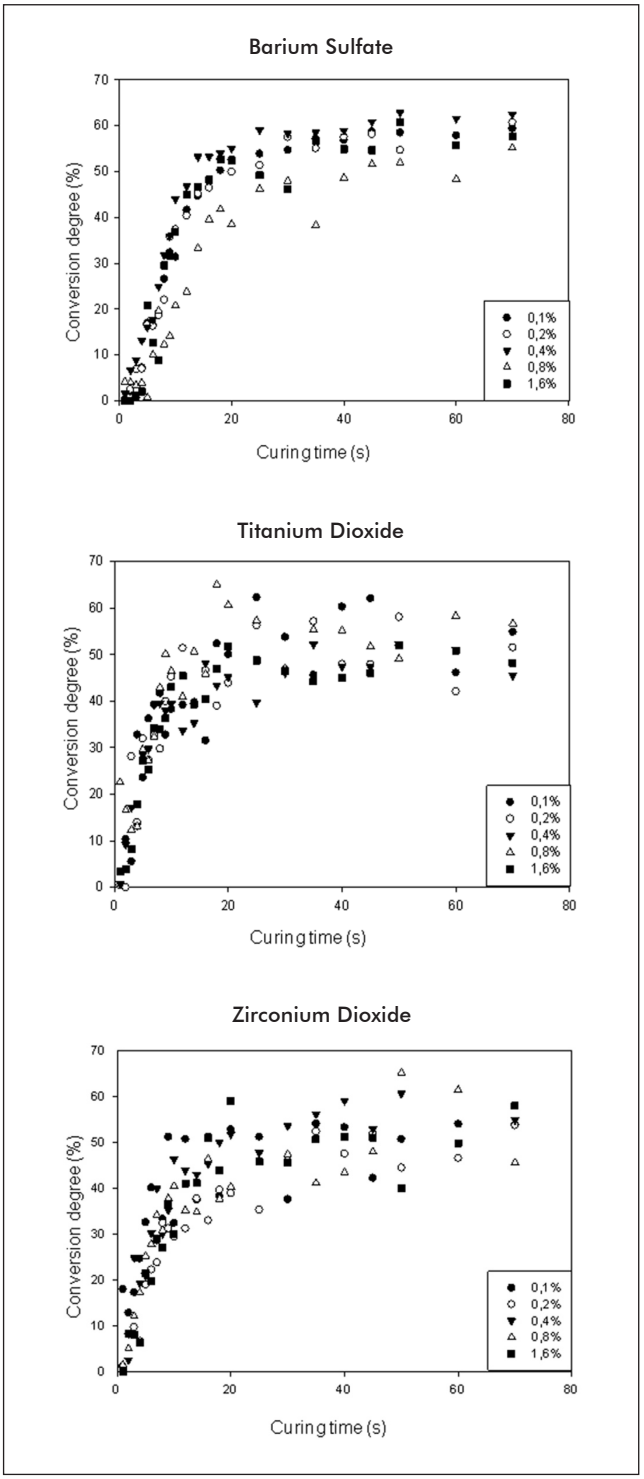

Fig. 1. Conversion degree of adhesives with the three radiopaquing agents and their different concentrations.

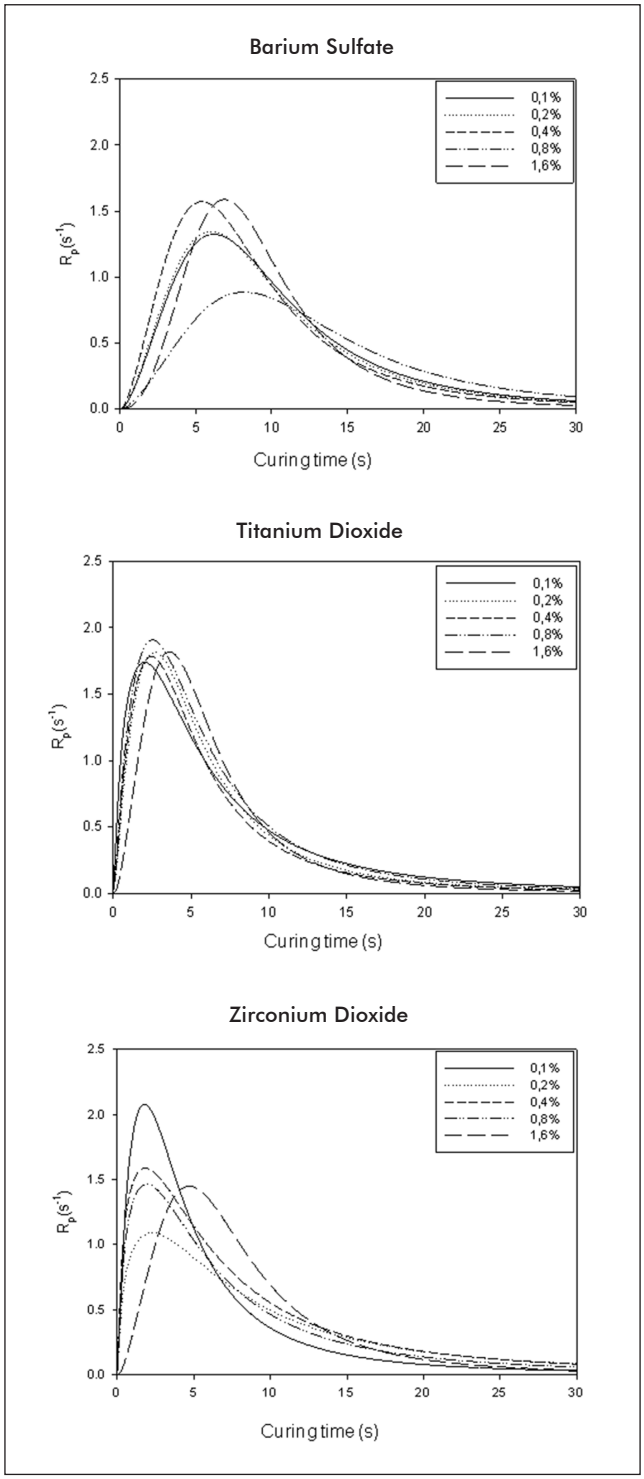

Fig. 2. Polymerization rate (R_p) as function of curing time.

Table 3. Flexural strength of experimental adhesives, in MPa: mean (±SD)*.

	0%	0.1%	0.2%	0.4%	0.8%	1.6%
Barium Sulfate	–	89.53 (±31.00) [a]	96.92 (±31.28) [a]	112.11 (±32.66) [a]	111.24 (±29.61) [a]	100.05 (±23.55) [a]
Titanium Dioxide	–	135.71 (±29.39) [a]	133.81 (±5.86) [a]	112.62 (±35.99) [a]	130.58 (±44.37) [a]	100.05 (±47.45) [a]
Zirconia Dioxide	–	121.71(±21.99) [a]	116.29 (±11.05) [a]	96.06 (±37.07) [a]	120.97 (±26.95) [a]	139.83 (±15.16) [a]
Control	106.32 (±46.23) [a]	–	–	–	–	–

* Same letters represents no statistically significant difference between means ($P < 0.05$).

Discussion

Restorative dental materials should be radiopaque ideally. In this study, a radiopaque dentin adhesive was produced with inorganic filler particles. Despite no statistical difference between groups was found, the experimental adhesive resins showed radiodensity that ranged from 0.54 (±0.06) mm of Aluminum to 0.66 (±0.16) mm of Aluminum. Since most commercially available dentin adhesive are not radiopaque, this experimental adhesive represents an increase in radiopacity.

The increase in radiopacity of a restorative material improves the diagnosis accuracy of recurrent caries at restoration margins (3,11). Moreover, a large number of false positive diagnosis can be explained by low radiopacity materials under restorations (1) leading to unnecessary re-intervention. On the other hand, a material with high radiopacity may difficult the diagnosis of incipient carious lesions by masking the image of the lesion, superimposing the image of the restorative material (11), since the radiographic images of common use in dental practice are in two dimensions. To reach a correct diagnosis, a material with an ideal radiopacity is necessary.

The radiopacity of a substance is related to the element's atomic number, density and size (12-14). Elements with high atomic numbers can absorb or reflect more X-rays (*e.g.*, photoelectric and Compton effects), leading to an opaque radiographic image. Barium (Z=56), Zirconium (Z=40) and Titanium (Z=22) show higher atomic numbers than Aluminum (Z=13); a higher radiopacity could be reached with increased concentrations of these substances. Dental materials that require radiopacity for different applications can be developed, such as adhesive resins, endodontic fillers and resin cements (15).

The addition of inorganic particles to the polymer could change its properties, such as the conversion degree, considering that the refractive index of substances may decrease the availability of light energy within the polymer (8). However, in this study, the substances added to provide radiopacity of the adhesive resin showed no influence on the conversion degree of the resulting polymer, similarly to the values reported in literature (16). The conversion degree is an important parameter for evaluating the quality and longevity of the resulting polymer, since a low conversion degree leads to increased water sorption, reducing the frictional forces and leading to a separation of polymer chains (17). An increase in water sorption could increase the plasticization of the formed polymer, decreasing their mechanical properties (5,18). High polymerization rates are related to high values of conversion degree and crosslink density of dentin adhesives (19,20), resulting in a higher mechanical strength of the polymer (21).

In the present study, the substances added to the polymer did not decrease flexural strength in comparison with the control group. Since the amount of adhesive used in a restoration is small, the flexural strength test was carried out with reduced dimension specimens in a so called miniflexural strength test. Another advantage of this test is the reduction of approximately 300% in laboratoy time to fabricate the test specimens (10).

In summary, substances added to a material to promote radiopacity should not negatively alter their mechanical properties. Thus, substances added to the polymer that do not alter the mechanical properties and increase radiopacity show potential for wide application in Dentistry.

Conclusion

The addition of radiopaquing agents increased the adhesive radiodensity and did not affect its degree of conversion and flexural strength.

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Artigo 2:

Influence of radiopaquing agents on the physico-mechanical properties of a model adhesive resin

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Influence of radiopaquing agents on the physico-mechanical properties of a model adhesive resin

Abstract

The aim of this study was to evaluate the radiopacity, degree of conversion (DC) and flexural strength of a model adhesive resin with different radiopaque substances. Titanium dioxide, quartz, zirconia, bismuth oxide, barium sulfate and ytterbium trifluoride were added to a model blend with five different concentrations. Radiopacity was evaluated with phosphorous plates system and radiodensity of specimens were compared with an aluminum step-wegde. DC was evaluated with FT-infrared spectroscopy with 20 seconds of photo-activation. Specimens with 12 x 2 x 2 mm were used for flexural strength test. Data were analyzed with two-way ANOVA and Tukey's post hoc test at 5% level of significance. Radiopacity of model adhesive resins with at least 30% of barium sulfate or bismuth oxide or 40% of zircon showed no significant differences to 2mm of aluminum. Adhesive resin with at least 20% addition of ytterbium trifluoride presented satisfactory radiopacity (Al 2mm) without influencing other properties.

Keywords: ytterbium trifluoride, radiopacity, adhesive resin

Introduction

Radiopaque intraoral dental materials are of extreme importance to clearly detect the interface between materials and surrounding anatomic structures, to enable the detection of obturation longitudinal gaps, marginal defects, interfacial gaps, obturation longitudinal gaps and cement overhangs (1-3). Evaluation of some clinical procedures (i.e., restorative procedures, endodontic treatment and post cementation) depends on radiographic examination to verify technical quality of treatment (4, 5). Materials with low radiopacity are a concern for misinterpretation of marginal gap leading to retreatment with enhanced cost, chair time and patient discomfort. To overcome this diagnosis problem, radiopaque agents are added to materials compositions(6).

The X-ray beam interacts with matter through absorption and scattering effects at atomic level allowing the production of radiographic images for diagnosis (7). The degree of radiopacity of a molecule is dependent of the atomic number, density and size of the elements that constitutes the radiopaque agent (8, 9). Adhesive systems have in its composition inorganic particles with elements like zirconium, silica and quartz as filler particles.

The diagnosis of caries under restorations or at the tooth/restoration interface is performed by radiography exam in clinical practice. However, the radiopacity of adhesive systems are low compared to other restorative materials and there are few studies evaluating radiopacity of adhesive systems. Inorganic fillers addition (i.e., radiopaquing agents) could modify material properties leading to different application and efficacy. Therefore, the aim of this study is

evaluate the radiopacity, degree of conversion and flexural strength of model adhesive resins with different radiopaque substances.

Materials and Methods

The monomers used in this study were bisphenol A glycol dimethacrylate (BisGMA), triethylene glycol dimethacrylate (TEGDMA) and 2-hydroxyethyl methacrylate (HEMA), camphorquinone (CQ) and Ethyl 4-dimethylaminobenzoate (EDAB), provided by Esstech Inc, USA; and used without further processing. Titanium dioxide, bismuth oxide, barium sulfate (Vetec Química Fina, Brazil), quartz (MG Minérios Gerais, Brazil), zirconium dioxide (Sigma-Aldrich) and ytterbium trifluoride (Nanostructured &Amorphos Materials, USA) were used as radiopaque agents. To perform the monomer photo-activation, a halogen light-activation unit (XL 3000, 3M ESPE, St. Paul, MN, USA) was used and the irradiation value (700 mW/cm^2) was confirmed with a digital power meter (Ophir Optronics, Danvers, MA, USA).

The model adhesive resins were formulated through the mixing of 50 wt.% Bis-GMA, 25 wt. % TEGDMA, and 25 wt. % HEMA. CQ and EDAB were added at 1 mol % for all groups, according to the monomer moles. Six radiopaque agents were investigated at various concentrations: titanium dioxide, quartz, zirconia, bismuth oxide, barium sulfate and ytterbium trifluoride at 5 %, 10%, 20%, 30% and 40% in weight. No radical scavenger was added. All formulations were weighted with an analytical balance (AG 200, Gehaka, Brazil), mixed and ultrassonicated (CBU 100/ 1LDG, Plana, Brazil) into a becker, for 1 hour.

The radiopacity of model adhesive resins was evaluated with five specimens per group with 4.0 mm (± 0.5 mm) of diameter and 1.0 mm (± 0.2 mm) of thickness, totalizing 150 specimens. X-ray images were obtained with phosphorous plates Digital System (VistaScan, Dürr Dental GmbH & CO. KG, Bietigheim-Bissingen, Germany), at 70kV, 8mA, 0.2 seconds of exposure time and a focus-film distance of 400mm. In each film, 1 specimen of each group with the same concentration was positioned, totalizing 5 films per concentration. The position of the specimen varied at each image to permit allocation concealment. An aluminum step-wedge was exposed together the specimens in all images. The aluminum step-wedge thickness ranged from 0.5mm to 5.0mm in steps of 0.5mm. The images were saved in TIFF format for less compressed files. Digital images were handled in software Photoshop (Adobe Systems Incorporated, San Jose, CA, USA). The means and standard deviations of the gray levels (pixel density) of the aluminum step-wedge and the specimens were obtained in a standardized area.

The degree of conversion of the model adhesive resins was evaluated using real time Fourier Transform Infrared Spectroscopy (RT-FTIR) with a Shimadzu Prestige21 (Shimadzu, Japan) spectrometer equipped with an attenuated total reflectance device composed of a horizontal ZnSe crystal, with a mirror angle of 45º (PIKE Technologies, USA). A support was coupled to the spectrometer to fix the light curing unit and standardize the distance between the fiber tip and sample at 5mm. Analysis was performed at a controlled room temperature of 23º±2C and 60±5% of relative humidity. The temperature of the attenuated total reflectance crystal surface was around 25°C. The sample (3μL) was directly dispensed onto the ZnSe crystal and light activated for 20s (n=3).

The degree of conversion was calculated as described in a previous study, considering the intensity of carbon-carbon double bond stretching vibration (peak height) at 1635cm^{-1}, and using the symmetric ring stretching at 1610cm^{-1} from the polymerized and unpolymerized samples, as internal standard (10).

The flexural tests specimens of the model adhesive resins were fabricated according to ISO 4049 specifications, except for the dimensions (12mm length, 2mm width, 2mm height), in customized stainless steel moulds. The model adhesive resins were placed into the mould, which was positioned on top of an acetate strip. The top and bottom surfaces of the specimens were then light polymerized in two irradiations of 20 seconds in each side. After polymerization, specimens were removed from the mould and stored in distilled water at 37±1°C for 24h. Five specimens were produced for each group, totalizing 150 specimens for flexural strength test. The flexural strength test was carried with a universal testing machine at a crosshead speed of 1.0 mm/min. Flexural strength (σ) of each specimen was calculated, in megapascal (MPa), according to the equation:

$$\sigma = 3LF/2BH^2$$

where: F is the maximum load, in newtons; L the distance, in millimeters, between the supports; B the width, in millimeters, of the specimen measured immediately prior to testing; H is the height, in millimeters.

Statistical analysis was performed using two-way ANOVA and Tukey's post hoc test at the 0.05 level of significance. Additionally, nonlinear regression

analyses were carried out in order to investigate the relationship between the gradual additions of radiopaque agents at radiopacity of model adhesive resins.

Results

The radiodensity values of the evaluated model adhesive resins are presented in Figure 1. Radiodensity of all groups strongly increased as the radiopaque agent concentration increased (r^2 > 0.81), except for Titanium dioxide group (r^2 = 0.37). Titanium dioxide and quartz groups showed radiodensity values below 100 pixels, significantly lower than aluminum ($p<0.05$). At 20% concentration, only ytterbium trifluoride group showed no significant difference from 2mm aluminum stepwedge. At 30% concentration, ytterbium trifluoride, barium sulfate and bismuth oxide presented no significant difference from 2mm aluminum stepwedge. Ytterbium trifluoride at 30% showed no significant difference from 3mm of aluminum. At 40%, Ytterbium trifluoride, barium sulfate and bismuth oxide showed similar radiopacity from 3mm of aluminum.

Degree of conversion of dental model adhesive resins showed no significant differences from the control group (0%), except for 30% and 40% titanium dioxide concentrations. At titanium dioxide group, increased concentration of the radiopaque agent promoted decreased degree of conversion as shown in Figure 2.

The flexural strength of evaluated model adhesive resins is presented in Table 1. Increased concentration of radiopaque agents showed no significant differences of flexural strength values for quartz, zirconia, bismuth oxide and

barium sulfate groups ($p>0.05$). Ytterbium trifluoride addition showed decreased flexural strength of 10%, 20%, 30% and 40% compared to 5% addition ($p<0.05$). However, at 20%, 30% and 40% ytterbium trifluoride presented no significant differences from barium sulfate and bismuth oxide at the same concentrations. The specimens formed at 30% and 40% concentration of titanium dioxide were shown to be not strong enough to undergo the flexural test.

Discussion

Radiopaque agent addition to adhesive systems should ideally be enough to enable visualization and assessment on the radiograph without compromising material properties. Therefore, concentration and type of radiopaque agent addition should be evaluated. In this study, higher concentration of radiopaque substances increased radiopacity of model adhesive resins. The ISO 4049:2010 require a minimal radiopacity equivalent to 2 mm of aluminum to restorative materials (11). In this study, ytterbium trifluoride, barium sulfate and bismuth oxide, and zircon presented sufficient radiopacity without significantly compromise material mechanical and chemical properties.

Radiopacity of a substance is related to its elements atomic number, density and size (8, 9, 12). Elements with high atomic numbers could absorb or reflect more X-rays, photoelectric and Compton effects, leading to an opaque radiographic image (12). Ytterbium (Z=70), Barium (Z=56) and Bismuth (Z=83) has the highest elements atomic number of this study, which could explain its radiopacity. At 30% of ytterbium trifluoride the radiopacity shows no significant differences to 3mm of aluminum; the same equivalence was observed at 40% concentrations of ytterbium trifluoride, barium sulfate and bismuth oxide ($p>0.05$). Ytterbium trifluoride has been used as radiopaque agent and filler particle for development of microfill and hybrid composite resin (13) and glass ionomer cement (14).

Radiopacity in polymeric dental materials is generally achieved with addition of ground glasses (i.e., barium, strontium) (15). Despite that the

addition of these glasses tend to hydrolyze in the oral environment (16), inorganic fillers are known to improve mechanical properties of polymeric materials. In this study, flexural strength values of ytterbium trifluoride at 20%, 30% and 40% showed no significant differences of barium sulfate and bismuth oxide at same concentrations. Furthermore, leachability of ytterbium trifluoride filler particle has been investigated (17) and a low solubility at dental resins was shown. The authors (data not shown) are investigating the longitudinal stability of these particles at adhesive resin matrix. Titanium dioxide group above 20% concentration presented decreased flexural strength restricting its clinical indications; 30% and 40% addition lead to a flexible polymer avoiding the specimens' fixation in the flexural test device. Decreased mechanical properties with metal oxide addition have been described elsewhere (6, 18). A low degree of conversion may explain the decreased mechanical properties of adhesive resins with titanium dioxide.

The degree of conversion of photo-activated resinous materials increases with higher levels of irradiant energy. Initial free radical generation of dimethacrylate monomers is directly related to the irradiance absorbed by the material (i.e, adhesive resin). The rate of polymerization of resin composites is proportional to the square root of absorbed light intensity and photo-initiator concentration, as showed elsewhere (19). Titanium dioxide has a high refractive index (2.7) which could decrease absorption of the emitted light by the reflection of photons at the surface of flexural specimens. In this study, high concentrations of titanium dioxide significantly decreased degree of conversion. However, the addition of others radiopaque agents presented no influence at degree of conversion of model adhesive resins.

Considering that adhesive resin should present sufficient radiopacity without negatively influence other properties, adhesive resins with at least 20% addition of ytterbium trifluoride presented satisfactory results. Therefore, in addition to the advantage of ytterbium trifluoride on the radiopacity, potentially reducing the radiopaque agent concentration, the low water solubility of ytterbium trifluoride(17) could avoid a long term degradation of the adhesive resin. This is of particular importance in maintaining the integrity of tooth/material interface and the tooth structure for the treatment success.

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Table1. Mean (±sd) flexural strength, in MPa, of model adhesive resins

Radiopaquing agent	Concentration (%)				
	5	**10**	**20**	**30**	**40**
Ytterbium Fluoride	147.9 (±25.8)^{Aab}	135.5 (±24.5)^{Babc}	130.0 (±23.5)^{Ba}	98.2 (±15.5)^{Bb}	97.5 (±9.9)^{Ba}
Barium Sulfate	102.5 (±46.3)^{Ab}	127.8 (±43.9)^{Aabc}	102.2 (±30.8)^{Aab}	101.5 (±12.8)^{Aab}	111.5 (±33.9)^{Aa}
Bismuth Oxide	136.3 (±34.6)^{Aab}	102.0 (±14.6)^{Ac}	100.6 (±17.3)^{Aab}	97.6 (±18.6)^{Ab}	95.7 (±12.7)^{Aa}
Zircon	151.6 (±51.0)^{Aab}	170.4 (±43.2)^{Aa}	123.3 (±14.0)^{Aa}	115.4 (±17.2)^{Aab}	94.0 (±28.1)^{Aa}
Quartz	131.6 (±37.7)^{Aab}	153.0 (±24.1)^{Aab}	132.5 (±31.6)^{Aa}	151.6 (±20.9)^{Aa}	123.9 (±19.9)^{Aa}
Titanium Oxide	89.0 (±25.0)^{ABc}	116.0 (±16.9)^{Abc}	60.8 (±31.3)^{Bb}	-*	-*

Means values followed by different capital letters in the same line shows statistically significant differences. Mean values followed by different small letters in the same column show statistically significant differences ($p<0.05$). * Not strong enough to undergo the flexural test.

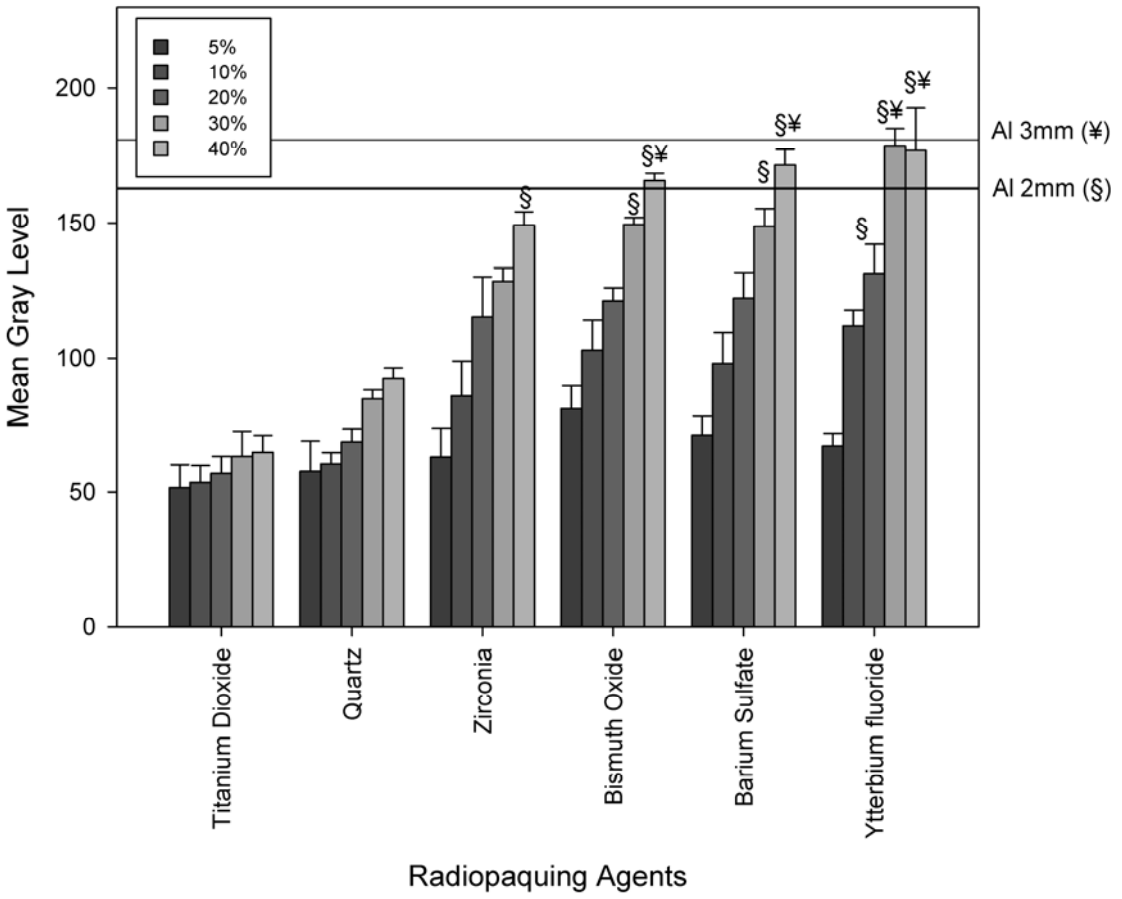

Figure 1. Means and standard deviations of radiopacity values for model adhesive resin specimens, 1 mm thick. Columns marked with § represent groups and concentrations with no significant differences with respect to a 2-mm aluminum step wedge. Columns marked with ¥ represent groups and concentrations with no significant differences with respect to a 3-mm aluminum step wedge ($p>0.05$).

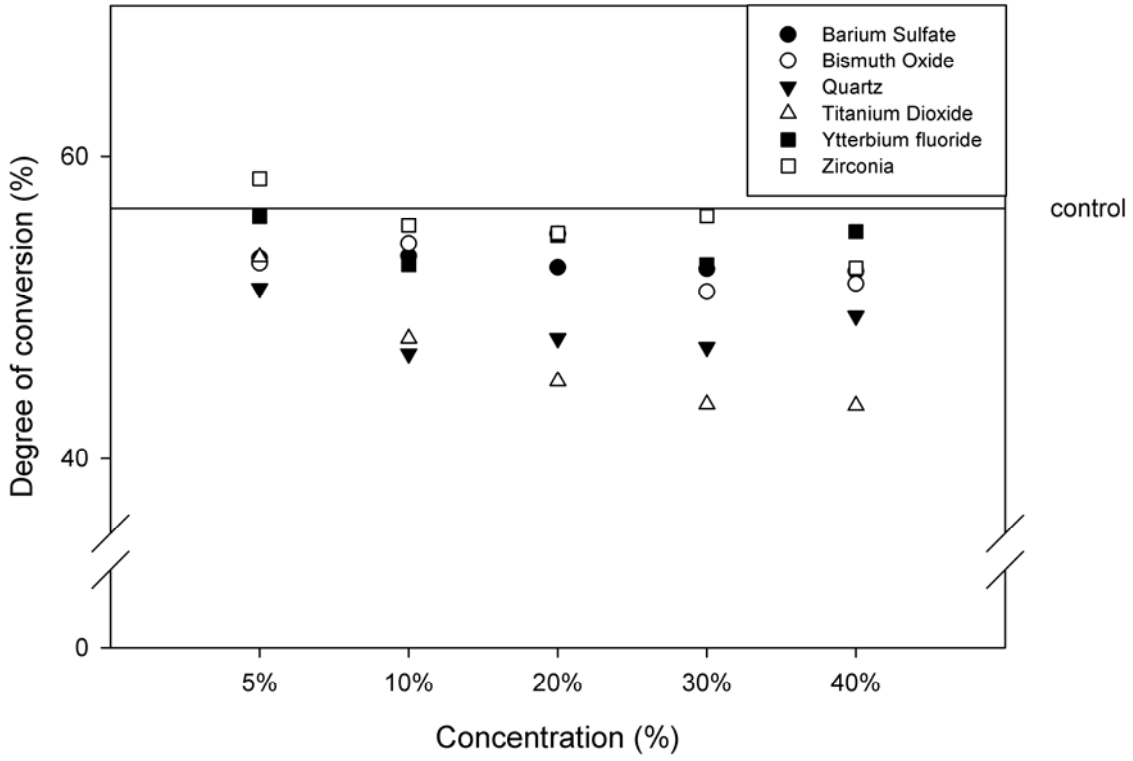

Figure 2. Mean degree of conversion with a 20-second photoactivation time in model adhesive resin. The reference line represents the degree of conversion of adhesive resin without a radiopaquing agent (control).

Considerações Finais

Os achados deste estudo sugerem que a adição de pelo menos 30% de trifluoreto de itérbio ou sulfato de bário ou óxido de bismuto ou 40 % de zircônia conferem radiopacidade adequada à resina adesiva sem alterar as propriedades analisadas. Os grupos com quartzo e dióxido de titânio não apresentaram radiopacidade adequada mesmo em concentrações elevadas. Além disso, a adição de concentrações elevadas de dióxido de titânio alterou significativamente as propriedades mecânicas e grau de conversão da resina adesiva formada. O dióxido de titânio tem o aspecto de um pó branco e opaco. Seu índice de refração é de 2,7 e o da resina adesiva de aproximadamente 1,5. Provavelmente, a diferença nesta propriedade ótica foi a responsável pela alteração do grau de conversão destas resinas adesivas. Para o desencadeamento do processo de polimerização de monômeros metacrilatos de uso odontológico há a necessidade de excitação da canforoquinona através da luz azul (470nm). Um material que possua um índice de refração muito elevado pode alterar a capacidade de penetração desta luz diminuindo a taxa de polimerização do material e conseqüentemente seu grau de conversão. O grau de conversão diminuído de um polímero esta relacionado a uma diminuição das propriedades mecânicas do material devido à diminuição das ligações cruzadas formadas. Os grupos com o quartzo não apresentaram alterações nas propriedades mecânicas nem no grau de conversão. Mas, a radiopacidade não foi considerada satisfatória para nenhuma das concentrações. Para um material ser radiopaco ele precisa apresentar em sua composição elementos com número atômico elevado e/ou configuração

molecular adequada. O quartzo é composto por tetraedros de dióxido de silício (SiO_2). Apesar de sua estrutura ser romboédrica, o silício possui um número atômico baixo (z=14) o que não lhe confere a propriedade de ser opaco a radiação. O trifluoreto de itérbio é uma terra rara e se apresenta como um pó branco levemente translúcido e quando incorporado na resina adesiva mantém a translucidez da resina. O número atômico do itérbio é relativamente alto (z=70) o que lhe confere a propriedade de ser radiopaco. O trifluoreto de itérbio possui um índice de refração de aproximadamente 1,5, semelhante ao da resina adesiva utilizada o que não altera a capacidade da luz de penetrar em seu interior. O agente radiopacificante trifluoreto de itérbio foi o que apresentou radiopacidade satisfatória em menores concentrações (20%) sem alterar as demais propriedades analisadas.

Perspectivas

As resinas adesivas deste estudo serão submetidas a análises de sorção e solubilidade e biocompatibilidade dos agentes radiopacificantes. A adição de cargas a uma resina adesiva pode alterar as propriedades deste material, como a sorção de água e a solubilidade das resinas adesivas, de acordo com a ISO 4049:2009, e das próprias cargas inorgânicas (agentes radiopacificantes). A solubilização destes agentes pode causar algum dano às células pulpares através da difusão pelos túbulos dentinários. Além destas análises, as resinas adesivas que tiveram propriedades radiopacas deverão ser transformadas em dois sistemas adesivos: um autocondicionante de dois passos clínicos e um convencional de três passos clínicos. No sistema autocondicionante um primer experimental com monômeros acídicos será formulado e, no sistema convencional, um primer com monômeros hidrófilos e solventes orgânicos será produzido para aplicação no substrato dentinário. Os sistemas adesivos formados serão aplicados ao substrato dentário para análise da resistência da união imediata e longitudinal da interface adesiva.

Os agentes radiopacificantes também poderão ser usados em materiais com outras aplicações como resinas compostas, cimentos de obturação endodôntica, cimentos para prótese e pinos de fibra.

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ANEXO I

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Um abraço,
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