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 ($P<0.05$).

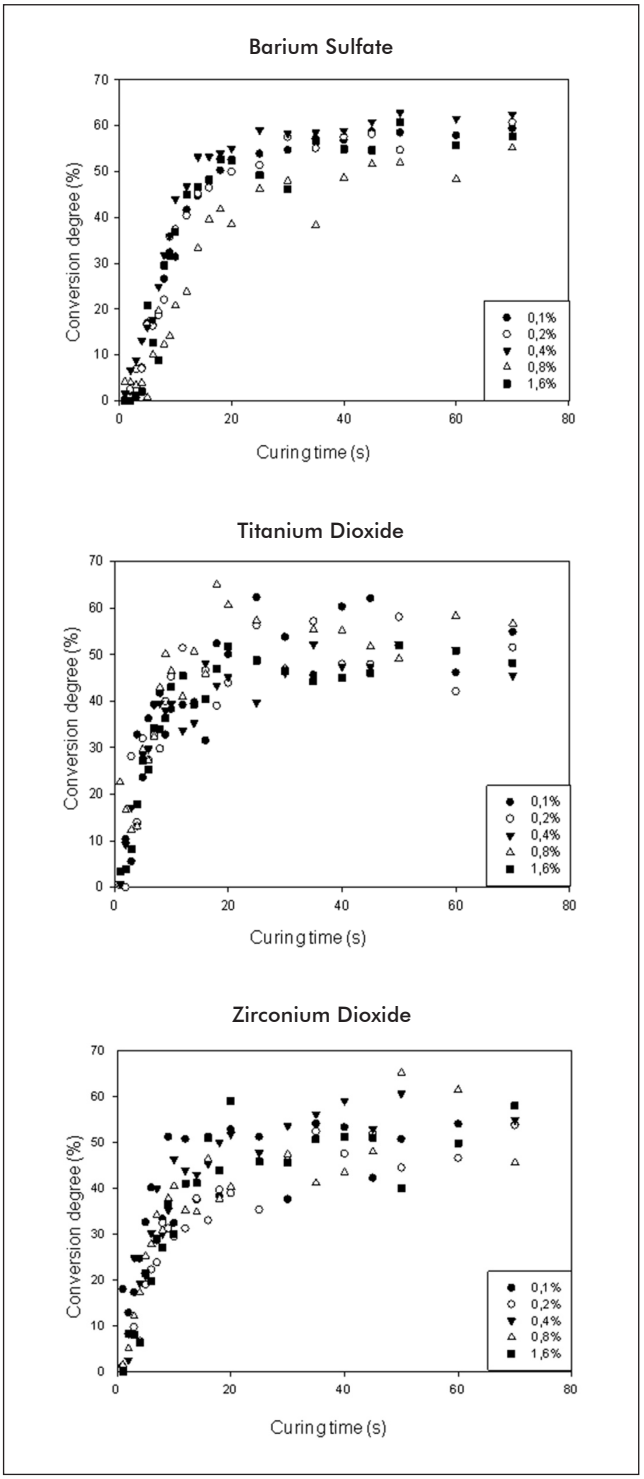

Fig. 1. Conversion degree of adhesives with the three radiopaquing agents and their different concentrations.

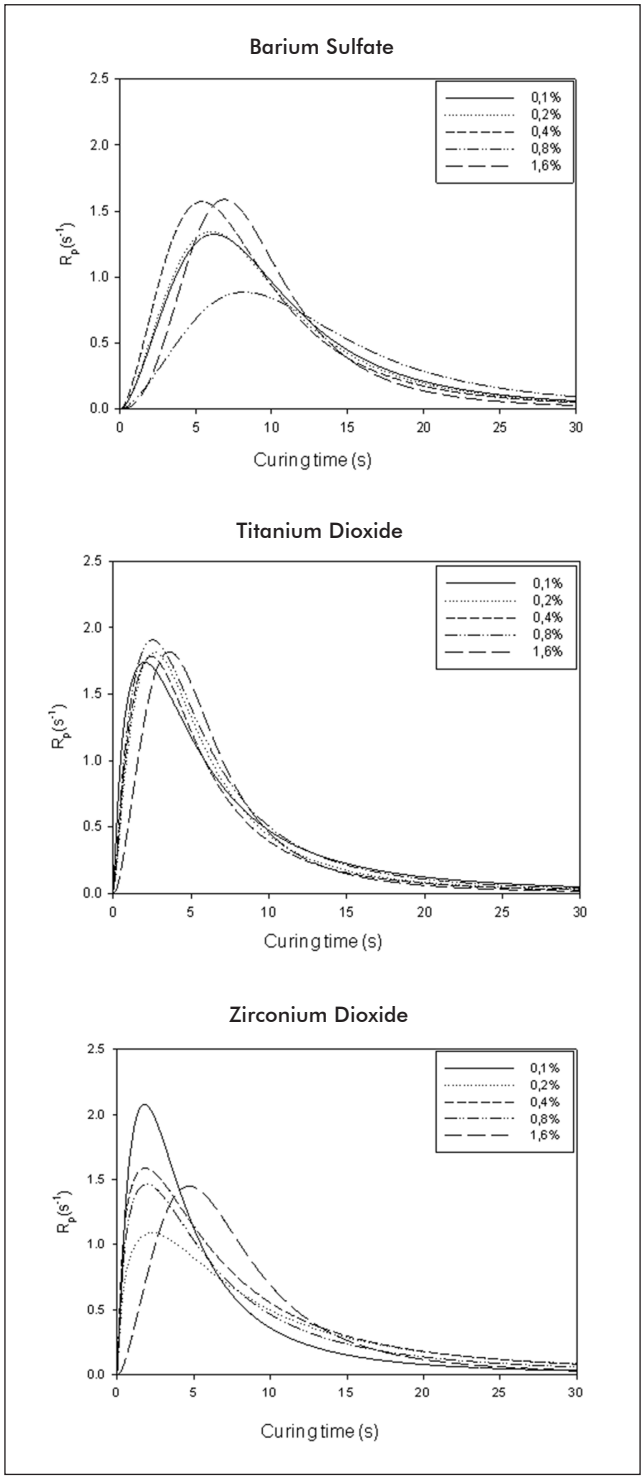

Fig. 2. Polymerization rate (R_p) as function of curing time.

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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