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GISLAINE CRISTINE MARTINS

EFEITO DA INCLUSÃO DE PARTÍCULAS DE CARGA NA RADIOPACIDADE E EM PROPRIEDADES DE SISTEMAS ADESIVOS EXPERIMENTAIS

Tese apresentada como pré-requisito para obtenção do título de Doutor em Odontologia na Universidade Estadual de Ponta Grossa, no Curso de Doutorado em Odontologia – Área de concentração em Dentística Restauradora. Linha de Pesquisa em Propriedades Físico-Químicas e Biológicas dos Materiais.

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Ponta Grossa, 13 de novembro de 2012.

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"Você nunca sabe que resultados virão da sua ação.
Mas se você não fizer nada, não existirão resultados"
MAHATMA GANDHI

RESUMO

Martins, GC. **Efeito da inclusão de partículas de carga na radiopacidade e em propriedades de sistemas adesivos experimentais** [tese]. Ponta Grossa: Universidade Estadual de Ponta Grossa; 2012.

Objetivo: Este estudo objetivou avaliar a radiopacidade, resistência máxima à tração, (RMT), microdureza (KHN), grau de conversão (GC), sorção de água (SA), solubilidade (SO), resistência de união (µTBS) de sistemas adesivos experimentais pela adição de nanopartículas de zircônia ou micropartículas de vidro de bário-borosilicato. **Material e métodos:** Dez sistemas adesivos experimentais com diferentes concentrações de nanopartículas de zircônia [0(EX0), 15(EX15), 25(EX25), 35(EX35) e 50%(EX50) ou com micropartículas de óxido de bário-borosilicato [0(R0), 30(R30), 40(R40), 50(R50) e 60%(R60)] foram formulados tendo como base o sistema adesivo Ambar (FGM). O sistema adesivo Adper Single Bond^{TM} 2 (SB, 3M ESPE) foi utilizado como referência comercial. Foram confeccionados espécimes de adesivo para os testes de radiopacidade (n=5), KHN (n=5), SA (n=10) e SO (n=10) utilizando matriz metálica com 5,0 mm de diâmetro e 1,0 mm de profundidade e, para a RMT (n=5) uma matriz metálica com 10 mm de comprimento, 2 mm de largura, 1 mm de profundidade e, área de sessão transversal de 0,8 mm^2. Os espectros FTIR foram obtidos de espécimes não polimerizados e polimerizados dos adesivos para determinar o GC dos materiais. Para µTBS, aplicou-se os adesivos na superfície de dentina de dentes molares humanos (n=7). Os dentes foram reconstruídos com resina composta e cortados para obtenção de espécimes em forma de palitos que foram testados imediatamente (IM) ou após 6 meses de armazenamento em água (6M). Os dados foram submetidos a ANOVA e pós-teste de Tukey´s (α=0,05). **Resultados:** Todos os sistemas adesivos experimentais mostraram radiopacidade semelhante a do esmalte dental. Apenas o R60 mostrou valores de RMT mais elevado que os outros materiais. Os sistemas adesivos experimentais apresentaram valores mais altos de dureza Knoop quando comparado ao SB. Em geral, o GC dos adesivos experimentais não foi afetado pela adição de partículas e, significantemente superior ao SB. A maioria dos adesivos experimentais mostraram menor SA e SO que o SB. **Conclusões:** Tanto a adição de nanopartículas quanto de micropartículas foi capaz de conferir radiopacidade aos adesivos experimentais e, a adição de carga influenciou nas propriedades testadas. De modo geral, pode-se dizer que o melhor desempenho foi para a adição de micropartículas na concentração de 30%.

Palavras-chave: Adesivos Dentinários. Resistência à Tração. Resinas Compostas.

ABSTRACT

Martins, GC. **Effects of of filler addition to experimental adhesives on radiopacity and properties** [tese]. Ponta Grossa: Universidade Estadual de Ponta Grossa; 2012.

Purpose: The aim of this study was to evaluate the radiopacity, ultimate tensile strength (UTS), microhardness (KHN), degree of conversion (DC), water sorption (WS), solubility (SO), microtensile bond strength (µTBS) and of experimental dental adhesives with increased addition of barium-borosilicate zirconia nanoparticles or glass microparticles. **Methods:** Ten experimental adhesive systems with different concentrations of zirconia nanoparticles [0(EX0), 15(EX15), 25(EX25), 35(EX35) and 50%(EX50) and barium-borosilicate oxide microparticles [0(R0), 30(R30), 40(R40), 50(R50) e 60%(R60)] were formulated based on the adhesive system Ambar (FGM). The adhesive Adper Single Bond^{TM} 2 (SB, 3M ESPE) was used as commercial reference. For the radiopacity (n=5), KHN (n=5), WS (n=10) and SO (n=10) tests, adhesive specimens were constructed using a stainless steel mold (5.0 mm in diameter and 1.0 mm in deep), while for UTS (n=5), a hourglass shape metallic matrix (10 mm long, 2 mm wide, and 1 mm deep with cross-sectional area of 0.8 mm^2) was employed. The FTIR spectra of uncured and cured specimens of adhesives were used to determine the DC of the materials. For µTBS, adhesives were applied to flat dentin surfaces of third molars (n=7). Resin composite buildups were constructed and sectioned to obtain resin-dentin bonded sticks to tested immediately (IM) or after 6 months (6M) of water storage. Data were submitted to a one-way ANOVA and Tukey´s test ($\alpha=0.05$). **Results:** All experimental bonding adhesives showed radiopacity similar to enamel. Only R60 showed higher UTS than the other materials. The experimental adhesives showed higher KHN values when compared to the commercial SB. In general, the DC of the experimental solutions was not affected by filler addition and was statistically higher than SB. Although filler addition did not affect WS, it generally reduced the SO. Most of the experimental adhesives showed lower WS and SO than SB. **Conclusions:** Both the addition of nanoparticles as microparticles were able to confer radiopacity to adhesives experimental, and adding load influence on the properties tested. In general, it can be said that the best performance was for the addition of microparticles in a concentration of 30%.

Keywords: Dentin-Bonding Agents. Tensile Strength. Composite Resins.

LISTA DE ILUSTRAÇÕES

LISTA DE ABREVIATURAS E SIGLAS

4-EDAMB - Etil-4-dimetilaminobenzoato
Bis-GMA - Bisfenol A glicil metacrilato (Bisphenol A glycidyllmetacrylate)
FTIR - Espectroscopia de infravermelho transformada por Fourier (Fourier Transform Infrared Spectrometry)
g-MPTS - gama-metacriloxipropiltrimetoxisilano
h - Hora
H_3PO_4 - Ácido fosfórico
HEMA - 2-hidroxietil metacrilato (2-hydroxyethyl methacrylate)
MPS - 3-metacriloxipropiltrimetoxisilano
NaOCl - Hipoclorito de sódio
s - Segundos
UDMA - Dimetacrilato de uretano (Urethane dimethacrylate)

LISTA DE SÍMBOLOS

α - Alfa (nível de decisão)
γ - Gama
° - Grau
° C - Grau Célsius
= - Igual
± - Mais ou menos
< - Menor
µm - Micrômetro
% - Porcentagem
® - Registrado
cm - Centímetro
cm^{-1} - Centímetro elevado a menos um
Kgf - Kilograma Força
kVp - Kilovoltagem de pico
mA - Miliampère
min - Minuto
mL - Mililitro
mm - Milímetro
mm/min - Milímetro/minute
mm^{2} - Milímetro quadrado
mm^{3} - Milímetro cúbico
mW/cm^{2} - Miliwatts por centímetro quadrado
nm - Nanômetro
P - Significância
wt% - Porcentagem em peso

SUMÁRIO

1 INTRODUÇÃO

A integridade da união dentina-adesivo tem implicações importantes no sucesso das restaurações de resina composta (De Munck et al.[1] 2003, Amaral et al.[2] 2007, Abdalla, Feilzer[3] 2008), assim como, adaptação marginal dos materiais dentários com a estrutura dental. Apesar da evolução dos materiais dentários, a cárie secundária ainda é o principal fator relacionado à falha das restaurações (Mjor et al.[4] 2002). Para acompanhamento e avaliação adequada da qualidade da restauração o exame radiográfico é de grande valia, porém, para tal os materiais dentários devem ser suficientemente radiopacos a fim de serem detectados e permitir correta avaliação da presença de cárie secundária, defeitos marginais, contorno da restauração, contato com os dentes adjacentes, excesso de cimento e, presença de gaps ou fendas marginais (Tveit, Espelid[5] 1986, Espelid et al.[6] 1991 e Bouschlicher, Boyer[7] 1999).

A radiopacidade do material odontológico é uma propriedade importante que permite o contraste, em radiografias, do material com a estrutura dental (Shah et al.[8] 1997). Desta forma, o sistema adesivo deve ser suficientemente radiopaco para ser facilmente distinguido da estrutura dental em uma radiografia. Estudos mostraram que radiopacidade não é um problema para resinas compostas de baixa viscosidade (Alonso et al.[9] 2004 e Ergücu et al.[10] 2010), cimentos resinosos (Goshima, Goshima[11] 1991, Shah et al.[8] 1997, Tanomaru-Filho et al.[12] 2008, Ergücu et al.[10] 2010), resinas compostas (Amirouche-Korichi, Mouzali, Watts[13] 2009), entre outros.

Porém, a radiopacidade ainda é um problema para os sistemas adesivos (Bouschlicher, Boyer[7] 1999; Hotta, Yamamoto[14] 2009). Alguns sistemas adesivos testados recentemente não mostraram radiopacidade semelhante ao esmalte (Hotta, Yamamoto[14] 2009). Desta forma, é importante o desenvolvimento de um sistema adesivo radiopaco frente aos exames radiológicos, uma vez que, a radiolucidez pode induzir o cirurgião-dentista a confundir o excesso do material nas paredes cavitárias com lesão de cárie remanescente e consequentemente substituir desnecessariamente a restauração (Espelid et al.[6] 1991, Akerboom et al.[15] 1993, Alonso et al.[9] 2004, Pamir et al.[16] 2010).

Para que um sistema adesivo apresente radiopacidade é necessário adicionar em sua composição partículas de carga (Hotta, Yamamoto[14] 2009, Pamir et al.[16] 2010). Os estudos têm sido realizados com objetivo de mostrar o impacto da adição de carga nas propriedades mecânicas (Debnath et al.[17] 2004, Kim et al.[18] 2005, Van Landuyt et al.[19] 2007), como a resistência de união (Miyazaki et al.[20] 1995, Kim et al.[18] 2005, Giannini et al.[21] 2011) e microinfiltração (Kim et al.[18] 2005, Lee et al.[22] 2006, Can Say et al.[23] 2006, Conde et al.[24] 2008, Schulz et al.[25] 2008), porém, não encontraram melhorias significativas em tais propriedades o que desmotivou estudos relacionados a esse assunto.

Embora, sistemas adesivos convencionais simplificados disponíveis no mercado contêm partículas de carga em sua composição, tais como, Adper Single Bond^{TM} 2 (3M ESPE), Prime & Bond NT (Dentsply), Optibond Solo Plus (Kerr), Excite (Ivoclar Vivadent), One Step Plus (Bisco Inc.); a sua concentração e composição química impedem que estes materiais apresentem radiopacidade similar ao esmalte. De acordo com Hotta, Yamamoto[14] (2009) o conteúdo de partículas da maioria dos sistemas adesivos varia de 0,6 a 29% do peso. Tal porcentagem pode representar um problema quando se quer diferenciar uma camada espessa do adesivo de fendas marginais com potencial para cáries secundárias.

A radiopacidade pode ser um benefício adquirido pela adição de carga no sistema adesivo. Entretanto, a adição de partículas de carga para obtenção de radiopacidade a um sistema adesivo não deve influenciar negativamente nas propriedades mecânicas e numa boa interação com o substrato dentinário. Por isso, o objetivo deste estudo foi avaliar o efeito da inclusão de nanopartículas (zircônia, 20-30 nm) ou de micropartículas (vidro de bário-borosilicato, 1µm), de diferentes tamanhos e concentrações num sistema adesivo experimental, na radiopacidade, resistência máxima à tração, grau de conversão, microdureza, sorção e solubilidade, resistência de união e, micromorfologia da interface de união.

2 PROPOSIÇÃO

2.1 PROPOSIÇÃO GERAL

Avaliar propriedades de um sistema adesivo experimental onde será incluído em sua composição cargas de nanopartículas (zircônia, 20-30 nm) ou micropartículas (vidro de bário-borosilicato, 1µm) dispersas na matriz orgânica variando a concentração destas partículas.

A hipótese nula a ser testada nos grupos experimentais é:

- H0 = a inclusão de nano ou micropartículas não afeta as propriedades do(s) sistema adesivo(s) experimental(is);

2.2 PROPOSIÇÃO ESPECÍFICA

1. Avaliar a radiopacidade de adesivos experimentais à base de HEMA contendo nanopartículas e micropartículas de diferentes concentrações.
2. Avaliar a resistência máxima à tração de adesivos experimentais à base de HEMA contendo nanopartículas e micropartículas de diferentes concentrações.
3. Avaliar o grau de conversão e microdureza de adesivos experimentais à base de HEMA contendo nanopartículas e micropartículas de diferentes concentrações.
4. Avaliar a sorção/solubilidade de adesivo experimentais à base de HEMA contendo nanopartículas e micropartículas de diferentes concentrações.
5. Avaliar a resistência de união à dentina imediata e após 6 meses de armazenamento em água de adesivos experimentais à base de HEMA contendo nanopartículas e micropartículas de diferentes concentrações.
6. Avaliar a micromorfologia da interface de união resina-dentina após adesão com adesivos experimentais à base de HEMA contendo micropartículas de diferentes concentrações.

3 MATERIAL E MÉTODOS

3.1 FORMULAÇÃO DOS ADESIVOS EXPERIMENTAIS

Os sistemas adesivos experimentais do presente estudo foram formulados pela empresa FGM. Tendo como base uma versão do sistema adesivo Ambar (FGM Dental Products, Joinville, SC, Brasil) adicionou-se nano ou micropartículas. A composição detalhada desse sistema adesivo comercial pode ser visualizada no quadro 1. Um sistema adesivo convencional simplificado (Adper Single Bond^{TM} 2, 3M ESPE, St. Paul, MN, EUA) foi utilizado como referencial comercial.

Quadro 1 – Composição e modo de aplicação dos sistemas adesivos

Sistema Adesivo	Composição	Modo de aplicação	Lote
Adper Single Bond™ 2 (3M ESPE, St. Paul, MN, USA)	1. Adesivo: Bis-GMA; co-polímero de ácido polialcenóico; dimetacrilato; HEMA; fotoiniciadores; etanol; água; nanopartículas	1. Condicionamento ácido por 15 s e lavar por 30 segundos; 2. Aplicar uma camada generosa de adesivo e esfregar ativamente por 15 s; 3. Aplicação de uma segunda camada de adesivo; 4. Remoção do excesso de solvente com leves jatos de ar por 15 s a 15 cm de distância; 5. Fotoativação por 10 s	8RF 2011-05
Adesivos experimentais *(FGM Produtos Dentais, Joinville, SC, Brasil)	1. UDMA (5-40), HEMA (5-40), monômero de metacrilato (1–20), monômero de metacrilato hidrofílico (5-40), dióxido de silício silanizado(<1), canforoquinona (<1), 4-EDAMB (<1), etanol (<20)		EX0: 0606231 EX15: 080410 EX25: 080410 EX35: 080410 EX50: 080410 R0: 0606231 R30: 080410 R40: 080410 R50: 080410 R60: 080410

(*) Para os adesivos experimentais variou-se na composição do adesivo Ambar a concentração de nano ou micropartículas adicionada conforme descrito no material e métodos

3.2 RADIOPACIDADE

Com o auxílio de uma matriz de aço inoxidável com um orifício de 5 mm de diâmetro e 1 mm de altura foram confeccionados 5 corpos-de-prova (cp´s) por condição experimental do estudo. Foi gotejado na matriz de aço duas gotas de sistema adesivo, o solvente foi evaporado por 40 s com leve jato de ar e, o material foi fotoativado por 80 s com intensidade de luz de 450 mW/cm^2 (VIP, Bisco Inc, Schaumburg, EUA). Antes da tomada radiográfica, obteve-se uma fatia de dente molar humano (Isomet 1000, Buehler®, Lake Bluff, IL, EUA), com espessura de 1 mm, utilizada como parâmetro para mensuração da radiopacidade. Na sequência, os discos de adesivo foram posicionados junto com uma fatia de dente molar humano para tomada radiográfica com o Heliodent Vario (Sirona, Bensheim, Alemanha), operando a 7 mA e 70 kVp. Padronizou-se o tempo de exposição de 0,2 s, à distância foco/filme em 30 cm e a distância cone de 13 cm. A radiopacidade digital (% de branco) foi mensurada pela contagem de *pixels* com o *software* Image Tool® 3.0 (UTHSCSA) e, pela média do nível de cinza do histograma (Adobe Photoshop CS5 Extended, Adobe System Inc, San Jose, CA, EUA) (Figura 1).

	Black Count	White Count	Black %	White %
Mean	507,20	1255,80	28,77	71,23
Std. Dev.	130,97	130,97	7,43	7,43
1	322	1441	18,26	81,74
2	505	1258	28,64	71,36
3	627	1136	35,56	64,44
4	447	1316	25,35	74,65
5	635	1128	36,02	63,98
6				

Figura 1 – Delineamento experimental para a radiopacidade. **A –** Matriz metálica para confecção do CP; **B –** Gotejamento de duas gotas de sistema adesivo; **C –** Fotopolimerização; **D –** Radiografia com fatia de dente molar e 5 corpos-de-prova; **E –** *Software* Image Tool; **F –** Análise dos pixels (% branco)

3.3 RESISTÊNCIA MÁXIMA À TRAÇÃO

Para a confecção dos cp´s de adesivo foi empregado uma matriz metálica com 10 mm de comprimento, 2 mm de largura, e 1 mm de profundidade que permite a confecção de cp´s no formato de ampulheta. Uma matriz de poliéster foi colocada entre a base da matriz e a “máscara” previamente vaselinada. O adesivo comercial Adper Single Bond^{TM} 2 (3M ESPE, St. Paul, MN, EUA) e os adesivos experimentais foram gotejados dentro da matriz até o completo preenchimento da mesma e, em seguida o solvente evaporado com leve jato de ar por 40 s. Após, foi polimerizado por 80 s com intensidade de luz de 450 mW/cm^2 (VIP, Bisco Inc, Schaumburg, EUA). Ao término da confecção cada cp foi submetido ao ensaio de tração, realizado na máquina universal de ensaios (Kratos Dinamômetros, São Paulo, SP, Brasil) a uma velocidade de 0,5 mm/min. Os cp´s em forma de ampulheta foram fixados a uma garra com o auxílio de cola à base de cianoacrilato gel (Super Bonder, Loctite, São Paulo, Brasil) e esta adaptada na máquina universal de ensaios. A resistência máxima à tração (MPa) foi determinada pela razão entre a carga registrada no momento da ruptura (Kgf) e a área de secção transversal do cp (mm^2) (Figura 2).

Figura 2 – Delineamento experimental para a resistência máxima à tração. **A –** Matriz metálica para confecção do CP; **B –** Gotejamento de duas gotas de sistema adesivo; **C –** Fotopolimerização; **D –** CP em forma de ampulheta; **E –** Tração; **F –** CP fraturado após o teste

3.4 GRAU DE CONVERSÃO

Duas gotas de cada solução adesiva experimental e do adesivo comercial foram gotejadas sobre um filme de acetato para obter uma película de 8 mm de diâmetro. Aplicou-se um leve jato de ar por 20 s para evaporação do solvente e, em seguida, um novo filme de acetato foi posicionado sobre a solução adesiva. O espectro FTIR do material não polimerizado foi mensurado e então os espécimes foram fotoativados por 10 s com intensidade de luz de 450 mW/cm^2 (VIP, Bisco Inc, Schaumburg, EUA). Cada cp foi cuidadosamente removido com o auxílio de uma lâmina de bisturi e armazenado por 24 h no escuro e em ambiente seco até o momento da realização da análise do grau de conversão pela espectrofotometria FTIR (Spectrum 100, Perkin Elmer, Massachusetts, EUA). O espectro foi obtido com 32 varreduras com uma resolução de 4 cm^{-1} no método de transmissão. A razão entre as bandas de absorção referentes às duplas ligações de carbono alifáticas (1640 cm-^{1}) e aromáticas (1610 cm^{-1}) do adesivo não polimerizado foi utilizada para cálculo do grau de conversão. O grau de conversão foi determinado subtraindo a % C = C de 100%. Cinco espécimes foram testados para cada grupo experimental (Figura 3).

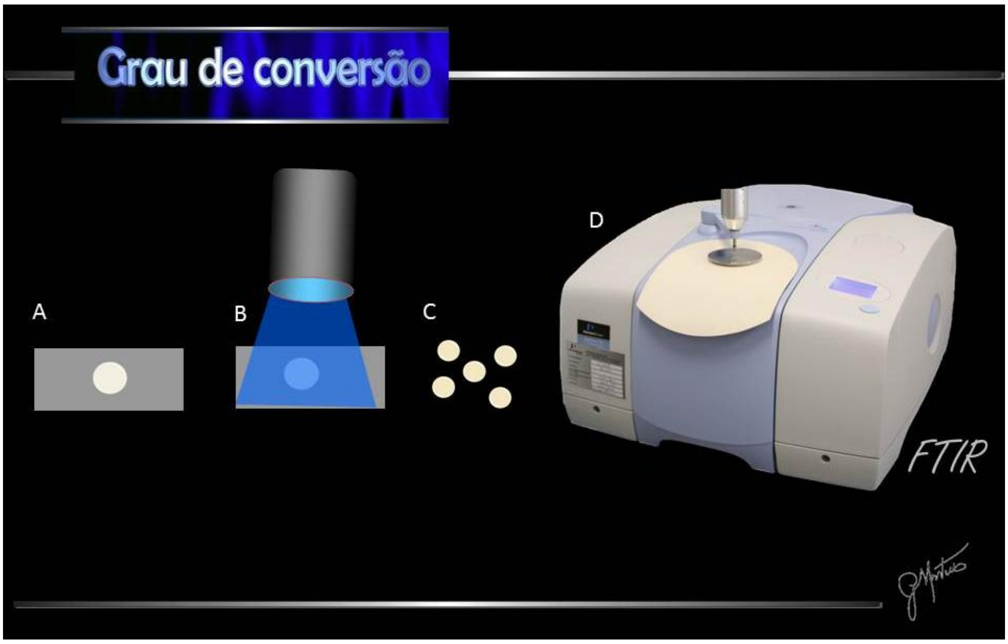

Figura 3 – Delineamento experimental para o Grau de conversão (FTIR). **A –** Gotejamento de duas gotas de sistema adesivo numa tira de acetato; **B –** Fotopolimerização; **C –** Corpos-de-prova; **D –** FTIR

3.5 MICRODUREZA KNOOP

Da mesma forma que foi descrito para o teste de radiopacidade foram confeccionados 5 cp´s para cada condição experimental e do adesivo comercial Adper Single Bond^{TM} 2 (3M ESPE, St. Paul, MN, EUA). Após o gotejamento do adesivo dentro da matriz realizou-se aplicação de jatos de ar para evaporação do solvente por 40 s. Ao término do preenchimento, o material foi fotoativado por 80 s com intensidade de luz de 450 mW/cm^2 (VIP, Bisco Inc, Schaumburg, EUA). Os cp´s foram armazenados em recipientes escuros e fechados por 24 h e, após esse período os cp´s foram levados a um microdurômetro (HMV-2, Shimadzu, Tóquio, Japão) e o diamante Knoop pressionado com carga de 15 g por 15 s sobre a superfície plana de cada cp. Realizou-se 3 medidas (3 pontos ao acaso) em cada cp e a média deles foi utilizada para análise estatística (Figura 4).

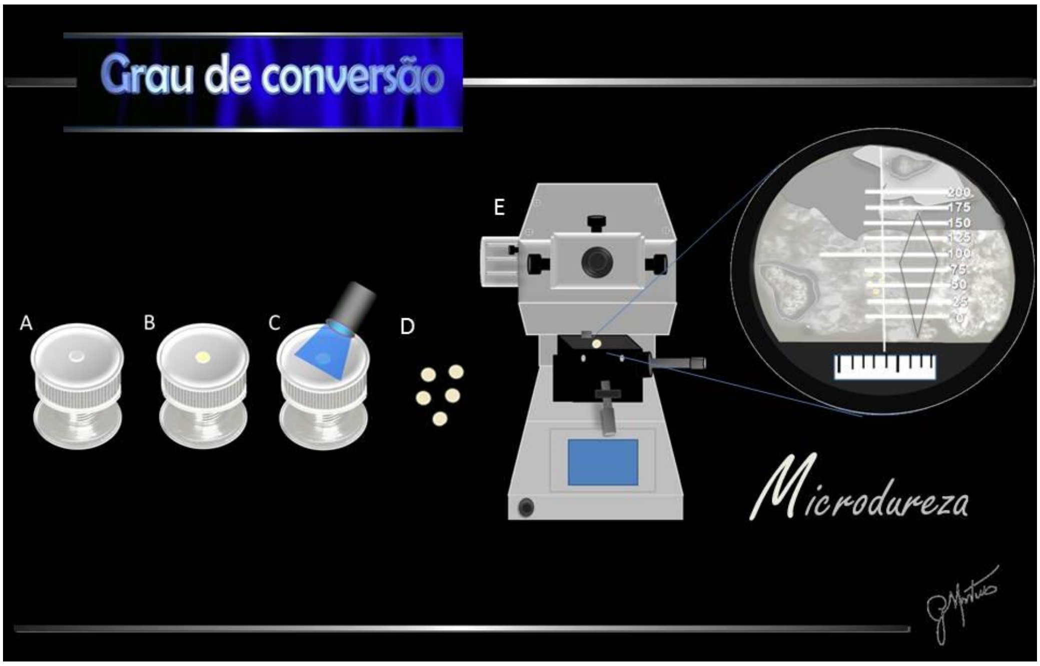

Figura 4 – Delineamento experimental para o Grau de conversão (Microdureza). **A –** Matriz metálica para confecção do CP; **B –** Gotejamento de duas gotas de sistema adesivo; **C –** Fotopolimerização; **D –** Corpos-de-prova; **E –** Microdurômetro e zoom /desenho esquemático da microdureza Knoop

3.6 SORÇÃO E SOLUBILIDADE

Confeccionaram-se dez espécimes para testes de sorção e solubilidade da mesma forma descrita para a radiopacidade. Imediatamente após a polimerização, os cp´s foram colocados em um dessecador e mantidos a 37°C. Após 24 h os cp´s foram periodicamente pesados em uma balança analítica (AG200, Gehaka, São Paulo, SP, Brasil) até obtenção de uma massa constante (*m1*). A espessura e diâmetro dos cp´s foram mensurados por meio de um paquímetro digital com duas casas decimais de precisão, com o objetivo de calcular o volume em mm^3. A seguir os cp´s foram colocados em recipientes individuais hermeticamente selados contendo 10 mL de água destilada a 37°C em estufa. Após intervalos de tempo de 1, 2, 3, 4, 5, 6, 7, 14, 28 dias de armazenamento, os recipientes foram removidos da estufa e mantidos em temperatura ambiente por 30 min. Após, os cp´s foram lavados em água corrente, secos com papel absorvente, pesados na balança analítica (*m2*) e colocados novamente na água destilada. Após os 28 dias de armazenamento, os cp´s foram colocados no dessecador contendo sílica gel e foram pesados diariamente até obtenção de uma massa constante (*m3*) (Figura 5).

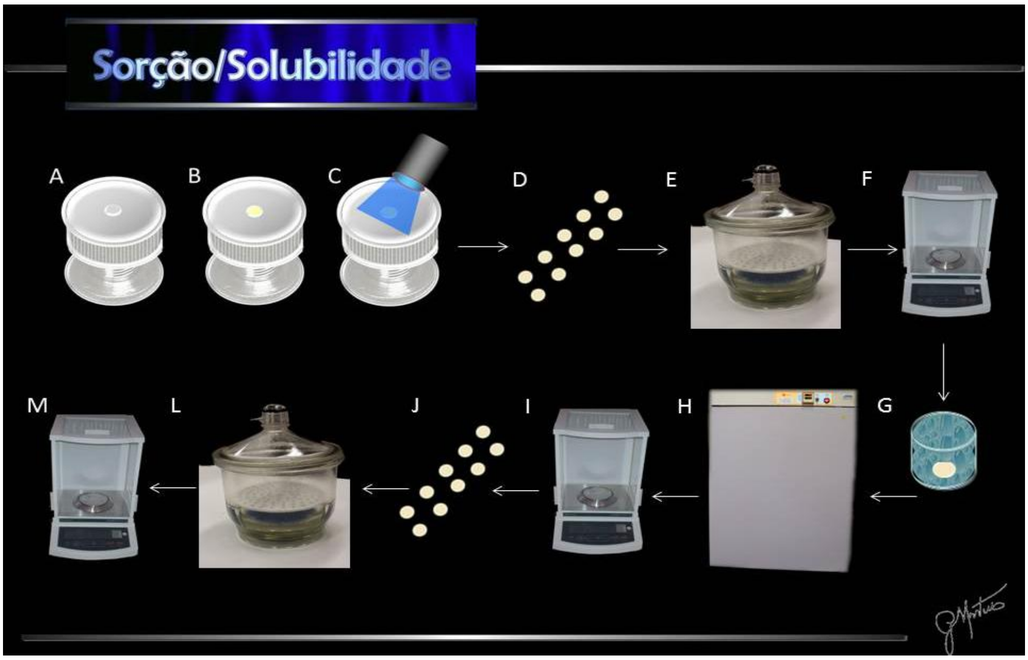

Figura 5 – Delineamento experimental para sorção e solubilidade. **A –** Matriz metálica para confecção do CP; **B –** Gotejamento de duas gotas de sistema adesivo; **C –** Fotopolimerização; **D –** Corpos-de-prova; **E –** Dessecador a 37° C; **F –** Pesagem (m1); **G –** CP em água destilada; **H -** Estufa a 37° C; **I -** Pesagem diferentes períodos de tempo (m2); **J -** CP; **L** – CP em dessecador a 37° C; **M** – Pesagem até obtenção de m3

Os valores de sorção de água (SA) foram calculados em microgramas por milímetro cúbico, para cada um dos dez espécimes usando a seguinte equação: **$SA = (m2 – m3)/V$**

Onde:

$m2$ é a massa do cp, em microgramas, após imersão em água em cada um dos respectivos intervalo de tempo (1, 2, 3, 4, 5, 6, 7, 14, 28 dias)
$m3$ é a massa do cp recondicionado, em microgramas
V é o volume do cp, em milímetros cúbicos

Os valores de solubilidade (SO) foram calculados em microgramas por milímetro cúbico, para cada um dos dez cp usando a seguinte equação: **$SO = (m1 – m3)/V$**

Onde:

$m1$ é a massa do cp, em miligramas, antes da imersão em água;
$m3$ e ***V*** são descritas acima.

3.7 RESISTÊNCIA DE UNIÃO

Utilizou-se 80 dentes molares humanos doados pelo Banco de Dentes da Universidade Estadual de Ponta Grossa com devida aprovação da Comissão de Ética em Pesquisa da Universidade Estadual de Ponta Grossa (COEP-UEPG), pelo parecer de n° 28/2010 e Protocolo n° 16242/09, cujo documento está em Anexo.

O esmalte da superfície oclusal dos dentes foi removido por um desgaste progressivo com lixas de carbeto de silício de granulação 180 sob irrigação constante com água, até se obter uma superfície dentinária totalmente livre de esmalte. As bordas periféricas restantes em esmalte foram também removidas com o auxílio de pontas diamantadas 2135 (KG Sorensen, Barueri, São Paulo, Brasil) em alta rotação com irrigação constante, para que apenas tecido dentinário ficasse exposto. Posteriormente, realizou-se a padronização da *smear layer* utilizando a Politriz com lixa de carbeto de silício com granulação 600 por 60 s. A dentina oclusal foi condicionada (15 s) com ácido fosfórico 35%, sendo a seguir lavada (30 s) e seca. As soluções adesivas experimentais e do adesivo comercial Adper Single Bond^{TM} 2 (3M ESPE, St. Paul, MN, EUA) foram aplicados nas superfícies dentinárias de acordo com as instruções do Quadro 1.

Após aplicação de cada camada de adesivo, um jato de ar por 15 s à 15 cm de distância foi aplicado, seguido de fotoativação por 10 s (LED light curing unit, Radii-cal, SDI - Austrália) com intensidade de luz de 1000 mW/cm^2. Coroas de resina composta foram confeccionadas (Opallis, A2, FGM, Joinville, SC, Brasil) com aproximadamente 4,0 mm de altura, em três incrementos. Cada incremento de resina foi fotoativado por 40 s (LED light curing unit, Radii-cal, SDI – Austrália, 1000 mW/cm^2). Um total de 7 dentes foram empregados para cada condição. Cada unidade experimental foi fixada com cera pegajosa no dispositivo da máquina de corte (ISOMET 1000 – Buehler, Illinois, EUA) com a interface de união perpendicular ao disco de corte. Realizaram-se duas sequências de cortes longitudinais e perpendiculares entre si para obtenção de cp´s com formato de palitos e com área de seção transversal de aproximadamente 0,8 mm^2. Os cp´s de cada dente foram divididos de forma aleatória em 2 grupos, ou seja, para serem testados imediatamente e, após 6 meses de seu armazenamento em água. Cada cp, em seu respectivo período de análise, foi fixado com cola de cianoacrilato gel (Super Bonder, Loctite, São Paulo, Brasil) numa garra acoplada na máquina de ensaios universal (Kratos Dinamômetros, São Paulo, SP, Brasil) a uma velocidade de 0,5 mm/min. Para calcular a tensão de ruptura de cada cp em MPa, a área da seção transversal dos espécimes foi mensurada com o auxílio do paquímetro digital (Absolute Digimatic, Mitutoyo, Tóquio, Japão) para cálculo do valor de resistência de união (Figura 6).

Figura 6 – Delineamento experimental para resistência de união. **A –** Terceiro molar hígido; **B –** Corte da coroa dental; **C –** Padronização da *smear layer;* **D –** Procedimento adesivo; **E –** Reconstrução da coroa em resina composta; **F –** Corte para obtenção de palitos composta; **G –** Palitos para teste imediato; **H -** Palitos armazenados para teste após 6 meses de armazenamento; **I -** Teste de microtração; **J -** Palito fraturado após o teste

3.8 MICROMORFOLOGIA DA INTERFACE

De forma semelhante como foram descritos para o teste de microtração, coroas de resina composta (n=2) foram confeccionadas após o procedimento adesivo com as diferentes soluções experimentais e com o adesivo comercial Adper Single Bond^{TM} 2 (3M ESPE, St. Paul, MN, EUA). As interfaces foram submetidas ao polimento com a utilização de lixas de granulação 1000, 1200, 1500, 2000 e 2500 e pastas diamantadas Arotec (São Paulo, SP, Brasil) com granulação decrescente (1 μm, ¼ μm e 0,05 μm). O polimento foi realizado sempre no mesmo sentido durante 60 s para cada lixa e cada pasta. Intercalando cada agente de polimento as amostras receberam banhos com água destilada por 5 min em cuba ultra-sônica Dabi Atlante - 3L (Ribeirão Preto, SP, Brasil) para a remoção de possíveis resíduos resultantes do polimento.

As interfaces polidas foram desmineralizadas com solução ácida de H_3PO_4 50% por 20 s. Após, os espécimes ficaram imersos em etanol 100% por 15 min e desproteinizado em NaOCl 1% por 10 min. Os espécimes foram montados em *stubs* e permaneceram em estufa por 24 h a temperatura de 37 °C antes de serem metalizados com camada de 10-nm de ouro. Os espécimes foram analisados pela MEV (LEO 435 VP, LEO Electron Microscopy Ltd, Cambridge, Reino Unido) usando modo secundário de elétrons com 12 KV de voltagem. A análise micromorfológica foi somente qualitativa (Figura 7).

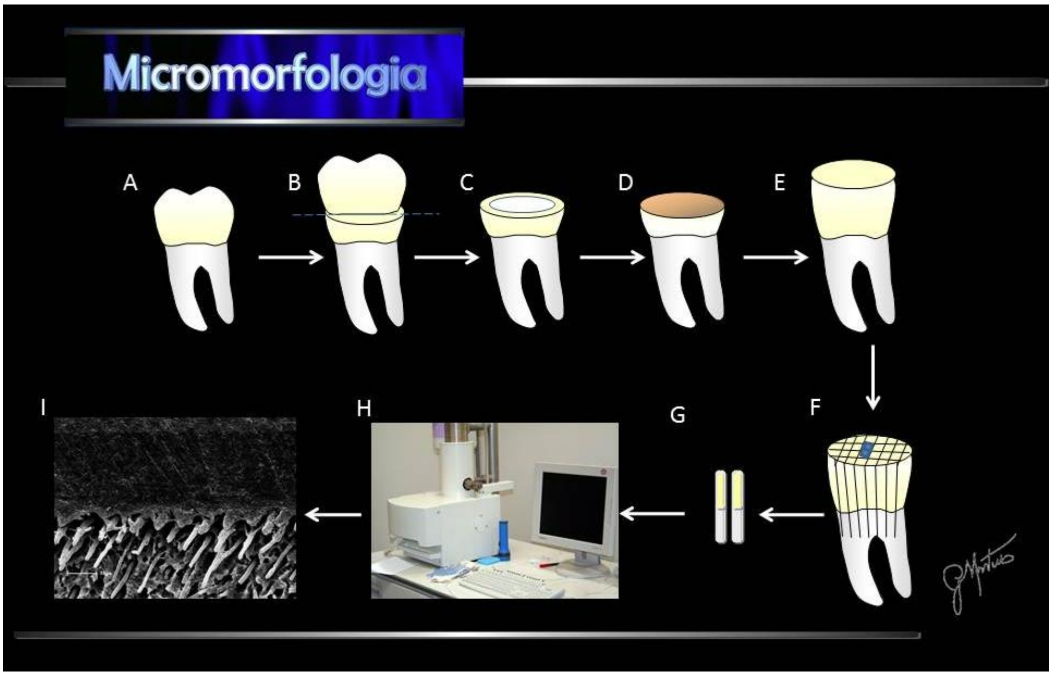

Figura 7 – Delineamento experimental para micromorfologia. **A –** Terceiro molar hígido; **B –** Corte da coroa dental; **C –** Padronização da *smear layer;* **D –** Procedimento adesivo; **E –** Reconstrução da coroa em resina composta; **F –** Corte para obtenção de palitos composta; **G –** Palitos; **H -** MEV; **I -** Imagem obtida na MEV

4 CAPÍTULOS

4.1 ARTIGO 1

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Effects of barium-borosilicate glass addition to a simplified etch-and-rinse adhesive on radiopacity and selected properties

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Effects of barium-borosilicate glass addition to a simplified etch-and-rinse adhesive on radiopacity and selected properties

Abstract

Purposes: To evaluate the radiopacity, ultimate tensile strength (UTS), microhardness (KHN), degree of conversion (DC), water sorption (WS) and solubility (SL) of experimental adhesives.

Methods: Five experimental adhesive with different concentrations of barium-borosilicate oxide microfillers [0(R0), 30(R30), 40(R40), 50(R50) e 60%(R60)] were formulated based on the adhesive system Ambar (FGM). The adhesive Adper Single Bond^{TM} 2 (SB, 3M ESPE) was used as commercial reference. For the radiopacity (n=5), KHN (n=5), WS (n=10) and SL (n=10) tests, adhesive specimens were constructed using a stainless steel mold (5.0 mm in diameter and 1.0 mm in thickness), while for UTS (n=5), a hourglass shape metallic matrix (10 mm long, 2 mm wide, and 1 mm deep with cross-sectional area of 0.8 mm^2) was employed. The FTIR spectra of uncured and cured specimens of adhesives were used to determine the DC. Data were submitted to a one-way ANOVA and Tukey´s test (α=0.05).

Results: All experimental adhesives showed radiopacity similar to enamel, except from R0 and SB. Only R60 showed higher UTS than the other materials. The experimental adhesives showed higher KHN values when compared to the SB. In general, the DC of the experimental solutions was not affected. Although filler addition did not affect WS, it generally reduced the SL. Most of the experimental adhesives showed lower WS and SL than SB.

Conclusions: The addition of barium-borosilicate glass up to 50% did not jeopardize the mechanical properties of the adhesive layer and seems to reduce its solubility.

Keywords: Radiopacity, Filler particles, Degree of conversion, Microhardness, Strength, Water sorption and solubility.

Clinical relevance: The addition of 30% of barium-borosilicate oxide microfillers is already enough to yield radiopacity to a simplified adhesive without jeopardizing its mechanical properties.

Effects of barium-borosilicate glass addition to a simplified etch-and-rinse adhesive on radiopacity and selected properties

Introduction

The clinical success of direct and indirect restorations depends on the integrity of the bonding and marginal adaptation of the dental materials to the tooth structure. Although dental materials have developed significantly, secondary caries is still the main factor related to restoration failure[36]. For adequate assessment of the restoration quality both at baseline and in recall examinations, radiographic evaluation are very useful and for such, dental materials should be sufficiently radiopaque to be detected against a background of sound and caries-affected enamel and dentin substrate and thus allow correct evaluation of the presence of secondary caries, marginal defects, contour of restoration, and contact with adjacent teeth, cement overhangs and interfacial gaps[4,16,48].

However not only restorative materials but also bonding agents used in the restorations should be sufficiently radiopaque to be easily distinguished from the tooth structure on a radiograph. Several studies showed that radiopacity is not a problem for flowable composites[2,15], resin cements[15,22.43.47] or composite resins[3], etc. however this is still a problem for bonding agents[4]. Fifteen current adhesive systems tested in a recent investigation[24] were shown to not have radiopacity similar to the enamel.

Although adhesive layers as thin as 16 µm, which would be not distinguishable in radiograph, were already reported[8], the bonding layer thickness can vary significantly according to the viscosity of the material, the number of steps and layers applied as well as the surface geometry. For instance, on smooth and convex surfaces, the adhesive layer can be 60-80 µm, while in concave regions, such as marginal chamfer, the thickness of the adhesive layer might be higher than 200-300 µm [12,14,30,44,51].

Bonding agents to be radiopaque need to have in their formulation high filler content with the presence of heavier atoms of elements, as filler content and chemical composition are the most important factors that influence the material's radiopacity. The study of the impact of filler addition on the adhesive systems properties is not new in the literature as has been focus of several earlier studies[5,9,20,21,27,29,35,46]. However the primary aim of such studies was to investigate the effects of filler addition on the mechanical properties of adhesives[20,21,27,39] and bonding features, such resin-dentin bond strength and microleakage[5,9,27,29,39,42]. So far, just one has investigated the impact of filler addition on the material´s radiopacity[42]. In general, these studies did not find significant improvements in such properties when compared to the unfilled versions which discouraged further studies on this field.

Although several simplified etch-and-rinse adhesive systems available in the market contain filler particles in their composition such as Adper Single Bond™ 2 (3M ESPE), Prime&Bond NT (Dentsply), Optibond Solo Plus (Kerr), Excite (Ivoclar Vivadent), One Step Plus (Bisco Inc.), etc., their concentration and chemical composition prevent these materials from having the enamel´s radiopacity. According to Hotta, Yamamoto[24], the inorganic content of most adhesives is within the range of 0.6 to 29 wt%. This could be problematic when trying to differentiate between marginal gaps, with potential for secondary caries, from a thick layer of adhesive resin that has been applied too liberally.

It is likely that increased amounts of filler loading than the ones usually employed by the manufacturer´s should be added to the adhesive´s formulation to make it radiopaque. However, such addition cannot impair the mechanical properties of such materials. Therefore, the aim of the present investigation was to evaluate the effect of adding barium-borosilicate glass filler in varied concentrations to experimental bonding agents on the adhesive´s radiopacity, ultimate tensile strength, microhardness, degree of conversion and water sorption and solubility.

Material and Methods

Formulation of the experimental adhesives

The experimental adhesive from the present study were formulated by using the simplified unfilled version of the adhesive system Ambar (FGM Dental Products, Joinville, SC, Brazil) as base. The adhesive was formulated specifically for this study and used as base for filler addition. This product is different from the commercial one as it does not contain the nanofillers reported by the manufacturer in the commercial version. The detailed composition of this adhesive system, as provided by the manufacturer, can be seen in Table 1. The simplified etch-and-rinse adhesive system (Adper Single Bond^{TM} 2, 3 M ESPE, St. Paul, MN, USA) was used as commercial reference (Table 1).

Barium-borosilicate glass microfillers (1 µm average particle size) were silanized by gamma-methacryloxypropyltrimethoxysilane (g-MPTS, Aldrich Chemical Co., Milwalkee, WI, USA). The microfiller were added in an ethanol (Labsynth Ltda., Diadema, SP, Brazil) solution containing g-MPTS (5 wt% of filler) and a slurry was formed. The mixture was stored for 24 h at 50 °C to assure the complete solvent removal. After storage, the fillers were sieved through a 150 mm sieve to remove excess of bubbles.

Five experimental adhesive systems were formulated according to the filler weight percentage (wt%): 0 (R0), 30 (R30), 40 (R40), 50 (R50) and 60% (R60). The filler was added to the resin and mechanically mixed by a motorized mixer (stirring). In order to assure the adequate dispersion of the filler, the experimental resins were ultrasonicated during 1 h.

Radiopacity

Using a stainless steel mold, five specimens measuring 5.0 mm in diameter and 1.0 mm in thickness were prepared for each experimental and commercial adhesive system. The adhesive was directly dispensed to completely fill the mold. All visible air bubbles trapped in the adhesives were carefully removed. Solvent was evaporated by gentle air blowing from a dental syringe for 40 s. A glass cover slip was placed on top of the adhesive. Each specimen was polymerized for 80 s with a visible-light curing unit (VIP, Bisco Inc, Schaumburg, USA) with a light intensity of 450 mW/cm^2. Enamel and dentin specimens were obtained from 1.0-mm thick longitudinal sections of human molar that had been recently extracted and donated by the human teeth bank. Slices were prepared using an Isomet low-speed saw (Buehler; Lake Bluff, IL, USA) with a diamond blade operating in water.

A total of five radiographs were made. Each radiograph was taken with all experimental and commercial adhesive specimens as well as the enamel-dentin positioned on the digital sensor. An intra-oral X-Ray digital radiography (70 kVp and 7 mA) were then taken with an exposure time of 0.2 s and the radiographic position was standardized (the x-ray central beam focusing in a 90° angle with the surface of the image receptor, and at a 30 cm focus-object distance and parallelism between the sensor and the specimen with the Sirone machine (Asahi Roentgen IND; Kyoto, Japan). The digital radiopacity (% white) was measured by pixels counting using the UTHSCSA ImageTool 3.0 software (Department of Dental Diagnostic Science, University of Texas Health Science Center, San Antonio, Texas, USA).

Ultimate tensile strength (UTS)

A metallic matrix 10 mm long, 2 mm wide, and 1 mm deep with an hourglass shape and cross-sectional area of 0.8 mm^2 was employed for the construction of the experimental and commercial adhesive system specimens. After isolating the matrix, the adhesive was dropped into the mold and then they were gently air-dried oil and water-free compressed air (40 s) to allow for solvent evaporation. Then, a plastic matrix strip was placed on the adhesive and the surface was light-cured for 80 s at 450 W/cm^2 using the same light curing unit previously described. Five specimens were performed for each bonding resin and the specimens were stressed to failure using a universal testing machine (Kratos Dinamômetros, São Paulo, SP, Brazil) at a cross-head speed of 0.5 mm/min.

KNOOP microhardness

Five resin disks of each material were produced in the same way as described for the radiopacity test. After preparation, specimens were stored in a dark vial for 24 h before microhardness measurement. Specimens were then taken to a HMV-2 microhardness tester (Shimadzu, Tokyo, Japan) equipped with a Knoop indenter. The measurements were performed on the exposed surface at three randomized with 10 g of load for 15 s. The values obtained in the same specimen were averaged for statistical purposes.

Degree of conversion (DC)

Drops of the bonding resin solutions were placed between acetate strips to achieve a thin film with 8 mm in diameter. Before covering the adhesive with the upper acetate strip, they were gently air-dried with oil and water-free compressed air (20 s) to allow for solvent evaporation followed by light-curing for 10 s using VIP light curing unit. Each specimen was carefully removed with a narrow surgical knife and stored for 24 h in a dark, dry environment until the Fourier Transformed Infrared analysis of the DC (Spectrum 100, Perkin Elmer, Massachusetts, USA).

The spectrum of the cured and uncured bonding resin was obtained with 32 scans at 4 cm^{-1} resolution in transmission method. The percentage of unreacted carbon–carbon double bonds (% C=C) was determined from the ratio of absorbance intensities of aliphatic C=C (peak height at 1640 cm^{-1}) against internal standard before and after curing of the specimen. The aromatic carbon–carbon bond (peak height at 1610 cm^{-1}) absorbance was used as an internal standard. The DC was determined by subtracting the % C=C from 100%. Five specimens were tested for each group.

Water sorption and solubility

Water sorption (WS) and solubility (SL) were determined according to the ISO specification 4049, except for specimens' dimensions and period of water immersion that was extended up to 28 days [32]. Ten resin disks of each material were produced as described for the radiopacity test. With the adopted energy density specimens allowed removal from the brass mold without undergoing permanent deformation. Immediately after polymerization, the specimens were placed in a desiccator and transferred to a pre-conditioning oven at 37°C and left undisturbed for 10 days. After this period, specimens were repeatedly weighed after 24 h intervals until a constant mass (m1) was obtained (i.e., variation was less than 0.2 mg in any 24 h period).

Thickness and diameter of the specimens were measured using a digital caliper, rounded to the nearest 0.01 mm, and these measurements were used to calculate the volume (V) of each specimen (in mm^3). They were then individually placed in sealed vials containing 10 mL of distilled water (pH 7.2) at 37 °C. After fixed time intervals of 1, 2, 3, 4, 5, 6, 7, 14 and 28 days of storage, the vials (15 mL, Eppendorf of Brazil, São Paulo, SP, Brazil) were removed from the oven and left at room temperature for 30 min. The specimens were washed in running water, gently wiped with a soft absorbent paper, weighed in an analytical balance (m2) and returned to the vials containing 10 mL of fresh distilled water.

Following the 28 days of storage, the specimens were dried in a desiccator containing fresh silica gel in an oven at 37 °C and left undisturbed for 10 days. They were weighed daily until a constant mass (m3) was obtained (as previously described). The initial mass determined after the first desiccation process (m1) was used to calculate the change in mass after each fixed time interval, during the 28 days of storage in water. Changes in mass were plotted against the storage time in order to obtain the kinetics of water absorption during the entire period of water storage.

WS and SL over the 28 days of water storage were calculated using the following formulae: $WS = (m2 - m3)/V$ and $SL = (m1 - m3)/V$.

Statistical analysis

Data from radiopacity, UTS, microhardness and DC was submitted to a one-way ANOVA. The mean water sorption of all materials throughout the 28-day period was plotted against time for each adhesive system. Data from WS and SL after 28 days were analyzed by two individual one-way

ANOVA (one for each property). Post-hoc multiple comparisons were performed using Tukey's test for analysis of all properties. Statistical significance was pre-set at alfa = 0.05.

Results

Radiopacity

One-way ANOVA detected statistically significant difference among groups (Table 2; P < 0.0001). All experimental bonding adhesives showed radiopacity similar to enamel, except from R0 and SB. These two adhesives showed radiopacity similar to the dentin substrate.

Ultimate tensile strength, microhardness and degree of conversion

One-way ANOVA detected significant differences between groups for UTS microhardness and DC (Table 3; p = 0.029, p < 0.0001, p = 0.0003, respectively). Only the addition of 60% of microparticules was shown to increase significantly the UTS values of the adhesives. In regard to microhardness, the experimental adhesives showed higher values when compared to the commercial SB, although variations could be seen among experimental formulations. The hardness of the formulation R30 e R50 did not differ from R0.The highest hardness were observed for the groups R40 and R60.

In general, the DC of the experimental solutions was not affected by filler addition, since the mean of R0 was statistically similar to R40, R50 and R60. Only the experimental solution R30 showed lower DC than the other experimental adhesives. The commercial adhesive SB showed the lowest DC, although not statistically different than R30 and R50.

Water sorption and solubility

All adhesives tested showed the same pattern of WS and most of the WS occurred within the first day of water storage (Figure 1). The magnitude of WS and SL, however, varied only depending on the adhesive formulation (Table 4; p < 0.0001). The addition of filler to the experimental solutions did not seem to affect the WS since the mean water sorption observed for R0 was statistically similar to R30, R40, R50 and R60. However, all experimental adhesives showed lower WS than the commercial SB. On the other hand, the addition of filler seemed to reduce the SL of some experimental adhesive solutions (R30, R50 and R60), since these materials showed statistically lower SL than the unfilled experimental R0 adhesive. The commercial adhesive SB again showed the highest SL, being statistically similar only to the unfilled R0 adhesive.

Discussion

To the extent of the author´s knowledge no study only one earlier study has studied the impact of filler addition on the adhesive radiopacity[42] and this is therefore a novel study that attempts to investigate this issue. The results of the present study showed that the addition of increased concentrations of barium-borosilicate glass microparticles yielded enamel radiopacity to the experimental adhesives evaluated.

The radiopacity of esthetic restorative materials has been established as an important requirement, improving the radiographic diagnosis[16,34,48]. Radiolucent areas around restorations may result from either a halo effect or radiographic density of the adhesives. Therefore, the use of an adhesive with radiopaque fillers can avoid inappropriate replacements[2,37] due to misinterpretations on the diagnosis of secondary caries[1,2,16] and detection of gaps near the restoration[1].

In regard to the DC, the addition of filler in the experimental adhesive did not affect this property, which is in agreement with Kim et al.[27] and Conde et al.[9] studies, who did not find significant differences in adhesives when 0.5-3% of silica and 0-10% of hydrophilic nanofillers were added to the adhesive formulations, respectively. This similar DC among filled and unfilled adhesives may be due to the adequate dispersion of the fillers within the matrix, avoiding the formation of clusters that could interfere in the light penetration. Although in general the filled adhesive showed similar DC one another, their means were generally inferior to the unfilled adhesive. This may be due to the differences in the refraction index between the radiopaque glass and the polymer, which makes the bonding material more opaque and less prone to light penetration. This issue however, may not be a clinical concern, since very thin layers of adhesive are usually employed during bonding procedures.

The commercial adhesive SB showed lower DC when compared to the unfilled version of the experimental adhesives, which may be due to differences in the monomer blends. SB contains Bis-GMA while the experimental adhesives do not. Because the aromatic hydroxylated monomer Bis-

GMA is more viscous, it presents limited mobility and consequently, the DC of Bis-GMA-matrix has been found to be lower than UDMA-based matrix[19,38].

Although the microhardness test is usually employed as an indirect measurement of the DC of polymeric materials[13], the increased microhardness values observed when filler was added to the experimental adhesives cannot be explained by increases in the DC, since this property was somewhat not affected by filler loading. However as it was already demonstrated that there is a positive correlation between the volume fraction of filler and the Knoop hardness of composites[7] since filler particles are harder than the organic phase of the material.

The incorporation of inorganic particles is well-established as a reinforcing mechanism of polymer-based materials [28] and as such, one might also expect increases in UTS of the filled adhesives. However this was only reached for the formulation with the highest filler loading (i.e. 60 wt%). In a recent study, Giannini et al.[20] evaluated the effects of filler addition on biaxial flexural strength and flexural modulus of six commercial adhesives and reported no differences between filled vs. unfilled materials. We speculate that the absolute amount of the fillers put into the adhesive in that study was still small to improve this selected mechanical property.

The degradation of the resin-dentin bonds has been matter of concern in several studies[10,11,23,33,40]. Theoretically, as the addition of filler particles to bonding resins reduces the organic matrix fraction of the material, which is the one that suffers hydrolytic degradation[18] over time, one could expect reduced WS and SL for the filled adhesives compared to the unfilled version. However, this was not observed in the present investigation. All adhesives evaluated absorbed significant amount of water, mainly within the first day of water storage, as well as shown in earlier studies[17,25,31,32,41,45]. This WS behavior was shown to be unaffected by increased filler loading, suggesting that formulation compromises are made when hydrophilic monomers are employed in polymeric materials. The presence of hydroxyl, carboxyl and phosphate groups in the most commonly used monomers in dental adhesive systems[49] and their resultant polymers make them more hydrophilic and, supposedly, more prone to water sorption[25,32].

Besides that, if on one hand, filled adhesives contain reduced organic content, it has increased interfacial area between the filler particles and the coupling silane agent (3-methacryloxypropyltrimethoxysilane [MPS]). The hydrolytic stability of MPS is of continuous concern since the oxane bond (Si–O–Si) that forms between the silane agent and the filler can be especially vulnerable to hydrolysis, because this covalent bond has significant polar character[6,26]. Thus, it is likely that the benefits of reduced organic matrix are over-weighted by the increase in the interfacial filler area with MPS.

The results of WS observed for SB in the present investigation are very similar to what was already reported by earlier studies[17,32]. Significant differences in the amount of WS were only observed between the commercial SB adhesive and the other experimental versions. This may be in fact explained by the different monomer compositions. Recently, Yiu et al.[50] demonstrated a significant correlation between Hoy's solubility parameters and the relative hydrophilicity of a series of experimental dental adhesives. Although it was not possible to calculate the solubility parameters of the commercial SB adhesive employed in this study, as it would be necessary to know the exact amount of each component in the materials, the highest values of WS and SL of the SB is suggestive that this adhesive presents a more hydrophilic behavior than the unfilled and filled experimental adhesives.

Water softens the polymer by swelling the network and reducing the frictional forces between the polymer chains[18]. After the relaxation process, unreacted monomers or unbounded oligomers trapped in the polymer network are released to the surroundings through nanovoids in the material. It is fair to speculate that the lower the organic fraction of the matrix, the lower the absolute fraction of unreacted monomers and oligomers that can be released to the surroundings.

This may be the reason of why lower SL was seen for the filled experimental adhesives when compared to the unfilled version.

The addition of increased concentrations of barium-borosilicate glass to adhesive formulations produced a material with adequate radiopacity without jeopardizing other important properties of the adhesive systems. In general, the overall mechanical properties and WS and SL of the experimental filled adhesives were either improved or remained unchanged when compared to the unfilled experimental adhesive. However, further studies should be conducted in order to evaluate the bonding effectiveness of such formulation to the dentin substrate.

Conclusions

The addition of barium-borosilicate glass up to 50% did not jeopardize the mechanical properties of the adhesive layer and seems to reduce its solubility.

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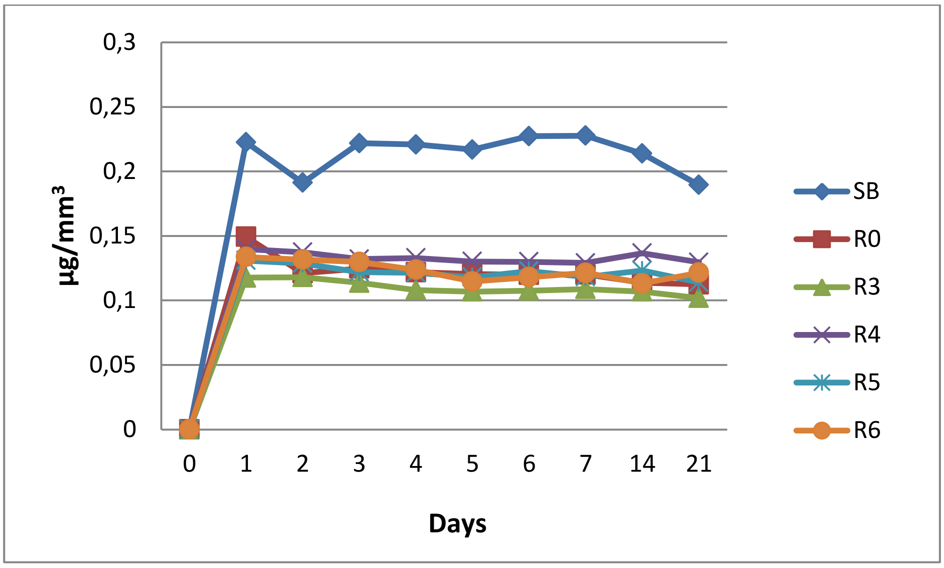


Figure 1 - Changes in mass of a commercial (SB) and experimental adhesives over 28-days of water storage. Symbols represent mean values (*n* = 10).

Table 1 – Composition of adhesive systems and application mode

Adhesive systems	Composition	Application mode	Batch number
Adper Single Bond™ 2 (3M ESPE, St. Paul, MN, USA)	2. Scotchbond acid: 35% phosphoric acid. 3. Bond: Bis-GMA; polyalkenoic acid co-polymer; dimethacrylates; HEMA; photoinitiators; ethanol; water; nanofiller particles	*1. Acid etching for 15 s* *2. Apply generous amounts of adhesive. Actively scrub for 15 s;* *3. Application of a second coat of adhesive, as above;* *4. Removal of excess solvent by gently drying with an air-stream for 15 s at 15 cm away from the surface, gradually bringing it to within 10 mm of distance;* *5. Light cure for 10 s*	*8RF* *2011-05*
Ambar *(FGM Dental Products, Joinville, SC, Brazil)	2. Condac 37: 37% phosphoric acid 3. UDMA (5-40), HEMA (5-40), methacrylate acidic monomers (1–20), methacrylate hydrophilic monomers (5-40), silanized silicon dioxide (<1), camphorquinone (<1), 4-EDAMB (<1), ethanol (<20)		*R0: 0606231* *R30: 080410* *R40: 080410* *R50: 080410* *R60:080410*

Bis-GMA - bisphenol-glycydil methacrylate; HEMA: 2-Hydroxyethyl methacrylate; UDMA - urethane dimethacrylate; (*) To the original composition of the adhesive Ambar, varied concentrations of barium-borosilicate glass particles were added to produce the R0, R30, R40, R50 and R50 and R60 formulations, described in the materials and methods section.

Table 2 – Means and standard deviations of the radiopacity of enamel, dentin and adhesive systems by pixel intensity

Groups	Pixel intensity
Enamel	68.8 ± 15.3 A
Dentin	33.0 ± 8.1 B
SB	26.9 ± 1.3 B
R0	27.1 ± 1.1 B
R30	64.1 ± 6.8 A
R40	72.4 ± 15.4 A
R50	75.9 ± 11.9 A
R60	66.0 ± 11.7 A

Averages identified with the same letters indicate means statistically similar ($p > 0.05$).

Table 3 – Means and standard deviations of the ultimate tensile strength (MPa), microhardness (KNH) and degree of conversion (%) as well as the statistical significance for each method.

Groups	Ultimate tensile strength	Microhardness	Degree of conversion
SB	20.3 ± 6.9 A	3.3 ± 1.2 D	45.1 ± 2.4 C
R0	24.9 ± 5.9 A,B	5.8 ± 0.7 C	56.4 ± 3.0 A
R30	23.0 ± 3.2 A,B	7.6 ± 0.2 B,C	47.2 ± 3.9 B,C
R40	32.1 ± 8.3 A,B	10.3 ± 1.6 A,B	52.5 ± 2.3 A,B
R50	28.3 ± 4.5 A,B	8.0 ± 0.8 C	50.2 ± 3.9 A,B,C
R60	33.0 ± 4.9 B	10.1 ± 2.8 A	51.8 ± 4.3 A,B

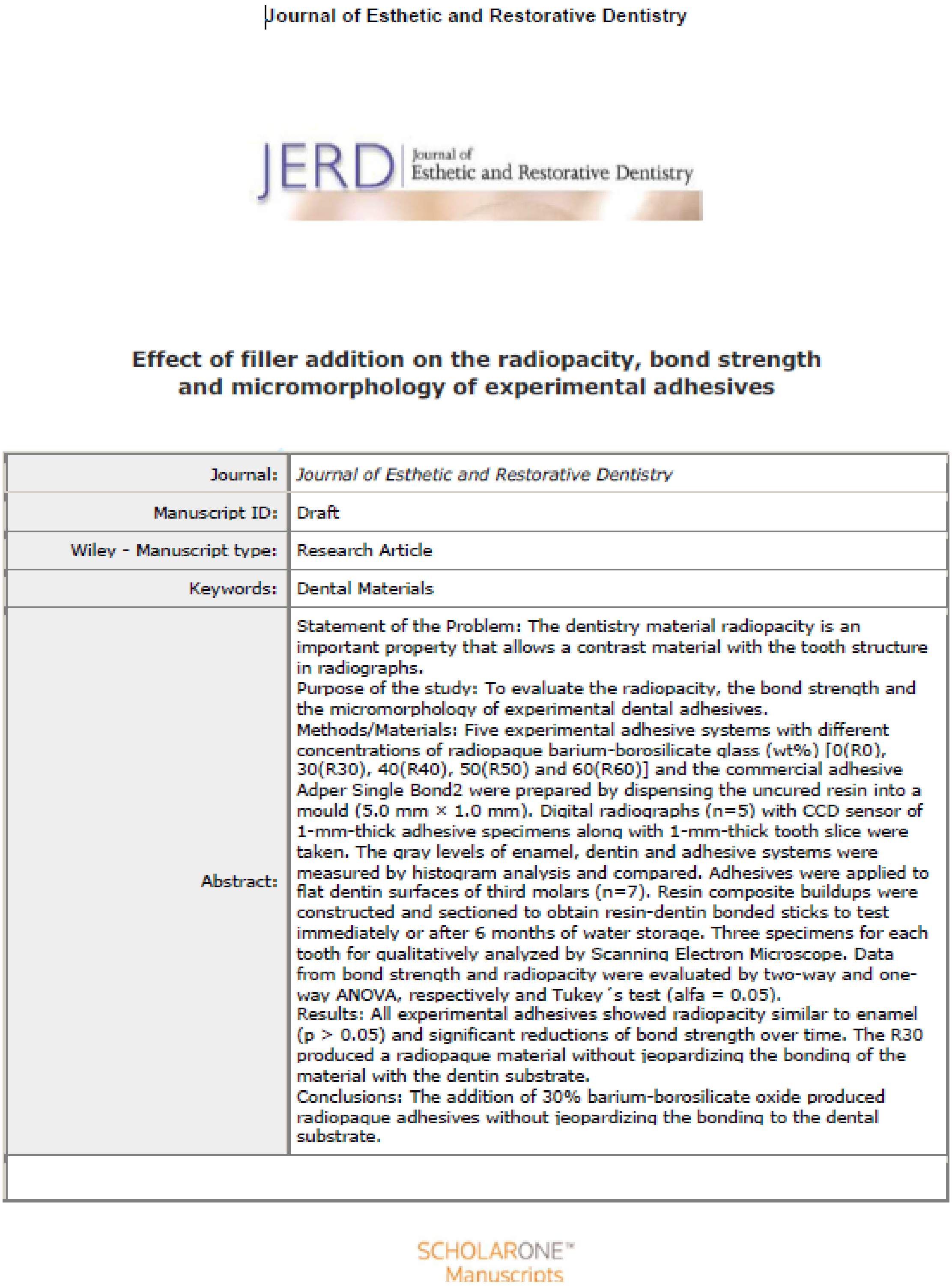
Comparisons are only valid within columns. Averages identified with the same letters indicate means statistically similar ($p > 0.05$).

Table 4 - Water sorption (μg/mm^3) and solubility (μg/mm^3) of the adhesives after 28 days of water storage.

Adhesive systems	Water sorption	Solubility
SB	189.5 ± 65.6 B	65.8 ± 11.6 C
R0	112.4 ± 35.8 A	63.2 ± 3.5 B,C
R30	101.9 ± 10.3 A	48.9 ± 11.8 A
R40	129.5 ± 19.4 A	53.0 ± 3.6 A,B
R50	113.9 ± 11.6 A	44.2 ± 5.1 A
R60	121.5 ± 9.8 A	50.2 ± 9.7 A

Comparisons are only valid within columns. Averages identified with the same letters indicate means statistically similar ($p > 0.05$).

4.2 ARTIGO 2



Journal of Esthetic and Restorative Dentistry

Effect of filler addition on the radiopacity, bond strength and micromorphology of experimental adhesives

Journal:	*Journal of Esthetic and Restorative Dentistry*
Manuscript ID:	Draft
Wiley - Manuscript type:	Research Article
Keywords:	Dental Materials
Abstract:	Statement of the Problem: The dentistry material radiopacity is an important property that allows a contrast material with the tooth structure in radiographs. Purpose of the study: To evaluate the radiopacity, the bond strength and the micromorphology of experimental dental adhesives. Methods/Materials: Five experimental adhesive systems with different concentrations of radiopaque barium-borosilicate glass (wt%) [0(R0), 30(R30), 40(R40), 50(R50) and 60(R60)] and the commercial adhesive Adper Single Bond2 were prepared by dispensing the uncured resin into a mould (5.0 mm × 1.0 mm). Digital radiographs (n=5) with CCD sensor of 1-mm-thick adhesive specimens along with 1-mm-thick tooth slice were taken. The gray levels of enamel, dentin and adhesive systems were measured by histogram analysis and compared. Adhesives were applied to flat dentin surfaces of third molars (n=7). Resin composite buildups were constructed and sectioned to obtain resin-dentin bonded sticks to test immediately or after 6 months of water storage. Three specimens for each tooth for qualitatively analyzed by Scanning Electron Microscope. Data from bond strength and radiopacity were evaluated by two-way and one-way ANOVA, respectively and Tukey´s test (alfa = 0.05). Results: All experimental adhesives showed radiopacity similar to enamel ($p > 0.05$) and significant reductions of bond strength over time. The R30 produced a radiopaque material without jeopardizing the bonding of the material with the dentin substrate. Conclusions: The addition of 30% barium-borosilicate oxide produced radiopaque adhesives without jeopardizing the bonding to the dental substrate.

Effect of filler addition on the radiopacity, bond strength and micromorphology of experimental adhesives

Introduction

The immediate bonding effectiveness of contemporary adhesives is quite favorable, regardless of the bonding approach used.[1-3] However, gradual reductions of resin-dentin bond strength is reported over time, regardless the moisture pattern used for the bonding procedure,[4] which has led several authors to investigate the durability of the bonding between resin and tooth structure, since this seems to be of significant importance for the longevity of adhesive restorations.[5-9]

Among the different aging phenomena occurring at the resin-dentin interfaces, some are considered pivotal in degrading the hybrid layer.[3] Since bonding is created by the impregnation of the dentin substrate by blends of resin monomers, the stability of the bonded interface relies on the creation of a compact and homogenous hybrid layer in a way to avoid hydrolysis of the organic component and degradation of the collagen fibrils not encapsulated by resin monomers by host-derived metalloproteinase.[10]

Following this rationale, the addition of filler particles could be an alternative to reduce the degradation of the resin-dentin bonded interfaces, as this procedure would reduce the organic content of the material making it less prone to water storage and hydrolysis over time. Early studies has so far demonstrated that filler addition can increase the thickness of the adhesive layer improving stress distribution and increase the immediate resin-dentin bond strength.[11-13] Besides that, filled adhesives was shown to have lower resin shrinkage which could be a reason for improved resin-dentin bond.[14]

However the benefits of filler addition is yet controversial in the literature, since other studies did not detect any improvement in the resin-dentin bond strength [15] or the elastic modulus of the hybrid layer [16] when filled *vs.* unfilled adhesives were compared. These negative findings should not discourage further studies on this topic, since other important features can be obtained with the addition of filler such as material radiopacity.

In dentistry, the material radiopacity is an important property that allows a contrast material with the tooth structure in radiographs.[17] This property does not seem to be a problem for root-end filling materials,[18] flowable composites, [14, 19] resin cements,[17-20] or composite resins.[12, 21] However this is still a problem for adhesive systems,[22] since the great majority of the commercial adhesives available in the market are radiolucent.[22] The use of an adhesive with radiopaque fillers can avoid inappropriate replacements [14, 23] due to misinterpretations on the diagnosis of secondary caries [14, 24, 25] and detection of gaps near the restoration.[25]

However the addition of filler cannot impair the bonding properties of the material to the dental substrates. Therefore, the present study was conducted to evaluate the effect of adding barium-borosilicate glass microparticle in varied concentrations to experimental bonding agents on the adhesive´s radiopacity, immediate and 6-month resin-dentin bond strength and on the hybrid layer micromorphology.

Materials and Methods

This research project was approved by the Institutional Review Board of the local Dental School under protocol # 28/2010.

Formulation of the experimental adhesives

The experimental adhesive resins from the present study were formulated by using the simplified adhesive system Ambar (FGM Dental Products, Joinville, SC, Brazil) as base. The detailed composition of this adhesive system, as provided by the manufacturer, can be seen in Table 1. The simplified etch-and-rinse adhesive system (Adper Single Bond 2, SB, 3M ESPE, St. Paul, MN, USA) was used as commercial reference (Table 1).

Barium-borosilicate glass microfillers (1 µm average particle size) were silanized by gamma-methacryloxypropyltrimethoxysilane (g-MPTS, Aldrich Chemical Co., Milwalkee, WI, USA). The microfiller were added in an ethanol (Labsynth Ltda., Diadema, SP, Brazil) solution containing g-MPTS (5% of the filler wt) and a slurry was formed. The mixture was stored for 24 h at 50 °C to assure the complete solvent removal. After storage, the fillers were sieved through a 150 mm sieve to remove excess of bubbles.

Five experimental adhesive systems were formulated according to the filler weight percentage (wt%): 0 (R0), 30 (R30), 40 (R40), 50 (R50) and 60 (R60). The filler was added to the resin and mechanically mixed by a motorized mixer (stirring). In order to assure the adequate dispersion of the filler, the experimental resins were ultrasonicated during 10 min to remove excess of bobbles.

Radiopacity

Using a stainless steel mold, specimens measuring 5.0 mm in diameter and 1.0 mm in thickness were prepared for each adhesive system. The solvent was evaporated by gentle air blowing from a dental syringe for 40 s. Five samples were prepared for each bonding agent and polymerized for 80 s with a visible-light curing unit (VIP, Bisco Inc, Schaumburg, USA) with a power density 450 mW/cm^2. Enamel and dentin specimens were obtained from 1.0-mm thick longitudinal sections of human molar that had been recently extracted and donated by the human teeth bank.

A total of five radiographs were made. Each radiograph was taken with all bonding resin specimens as well as the enamel-dentin positioned on the digital sensor. An intra-oral X-Ray digital radiography was then taken with an exposure time of 0.2 s and the radiographic position was standardized (the X-ray central beam focusing in a 90° angle with the surface of the image receptor, and at a 30 cm focus-object distance and parallelism between the sensor and the specimen with the Heliodent Vario (Sirona, Bensheim, Germany), operating at 7 mA e 70 kVp. The digital radiopacity (gray levels) of enamel, dentin and adhesive systems was measured by histogram analysis.

The mean gray values (MGV) for each test specimen was measured by using the histogram function of computer graphics software (Adobe Photoshop CS5 Extended, Adobe System Inc, San Jose, CA, USA). The histogram analysis was performed in Adobe Photoshop CS5 Extended to check different specimens tone. Digital radiography determines gray levels ranging from 0 to 255, with nuances, where the extremes "0" is black and "255" is the white color In this procedure, the MGV of each pixel was represented within a scale ranging between 0 (black) to 255 (white).

Microtensile bond strength (µTBS)

Forty two extracted human third molars were stored in water and used within 6 months after extraction. A flat dentin occlusal surface was exposed by means of a diamond wheel (Isomet 1000, Buehler; Lake Bluff, IL, USA). The exposed mid-coronal dentin surfaces were further polished on wet # 600-grit silicon-carbide paper for 60 s to standardize the smear layer.

All adhesive systems were applied according to manufacturer´s instructions (Table 1) and polymerized for 10 s using a LED light curing unit (Radii-cal, SDI - Australian). Light intensity was monitored throughout the experiment to ensure that a consistent intensity was maintained (1000 mW/cm^2). After bonding procedures (n = 7 teeth), a 6 mm-thick layer of resin composite (Opallis, FGM, Joinville, SC, Brazil) was added to the dentin surface in 4 increments of ± 1.5 mm. Each increment was light-cured for 40 s with the same light curing unit used in the bonding procedures.

The teeth were then bucco-lingually and mesio-distally sectioned through the restoration using with a diamond saw under water cooling/lubrication (Isomet 1000, Buehler; Lake Bluff, IL, USA) to obtain resin-dentin bonded sticks with a cross-sectional area of about 0.8 mm^2. Specimens originated from the same teeth were randomly divided to be tested immediately (IM) or after 6 months (6M) of water storage. The storage solution was not changed over time; however water was added in order to keep the water volume constant in case water evaporation occurred over time.

The resin-dentin sticks from each adhesive group was attached to the Geraldeli's device (Odeme Biotechnology, Joaçaba, SC, Brazil) with cyanoacrylate resin (Super Bonder Gel, Loctite, São Paulo, SP, Brazil) and subjected to tensile strength until to failure using a universal testing machine (Kratos Dinamômetros, São Paulo, SP, Brazil) at a crosshead speed of 0.5 mm/min. The failure modes were evaluated at 40x magnification using a stereomicroscope (Microscopy, Nikon Eclipse E200, Melville, NY, USA) and were classified as cohesive (failure exclusively within dentin or resin composite) or adhesive/mixed (failure at resin-dentin interface or mixed with cohesive failure of the neighboring substrates). The data from the fracture pattern was evaluated by a chi-square test ($\alpha = 0.05$).

The bond strength values of specimens from the same tooth in each storage period were averaged for statistical purposes. Specimens with cohesive and premature failures were excluded from the data analysis. The µTBS data from sticks were submitted to a two-way repeated measure ANOVA with the Adhesive and Storage period as the main factors. Tukey's post-hoc test was used for pair-wise comparisons at a pre-set alpha of 0.05.

Interface micromorphology

For each storage period, a total of two resin-dentin bonded sticks were not tested in the microtensile test and left for interface micromorphology analysis. The adhesive interfaces were polished with descending grits of SiC papers (1000; 1200; 1500; 2000 and 2500) and 1 and 0.25 µm diamond paste (Buehler, Lake Bluff, IL, USA) using a polishing cloth. After each polishing, the specimens were rinsed with running water and ultrasonically cleaned for 5 min. Specimens were then demineralized with a 50% H_3PO_4 acid solution for 20 s. After that, the specimens were ultrasonicated in 100% ethanol for 15 min and deproteinized in 1% NaOCl for 10 min.

Specimens were then mounted on stubs and left in a desiccator for 24 h in an oven at 37 °C before being sputter-coated with a 10-nm gold layer. Specimens were then analyzed by SEM (LEO 435 VP, LEO Electron Microscopy Ltd, Cambridge, UK) using the secondary electrons mode with 12 KV of voltage. The micromorphology analysis was only qualitatively evaluated.

Results

Radiopacity

One-way ANOVA detected significant differences between groups ($p < 0.05$). The mean values and standard deviations of the adhesives radiopacity as well as those of enamel and dentin are shown in Table 2. All filled experimental bonding resins showed radiopacity similar to enamel and higher than dentin. The commercial adhesive SB and the unfilled experimental adhesive (R0) showed radiolucency similar to dentin ($p > 0.05$) and lower than enamel. A representative X-Ray radiography can be seen in Figure 1.

Microtensile bond strength (µTBS)

The mean cross-sectional area ranged from 0.73 to 1.0 mm, and no difference was detected among the groups ($p > 0.05$). The percentage of specimens with premature failures (PF) and the frequency of each fracture pattern mode are shown in Table 3. No cohesive failure was observed in the present investigation. Groups R50 and R60 showed a very high percentage of PF being statistically different from the other groups ($p < 0.05$). For the other experimental and commercial adhesives, most of the fracture modes were adhesive or adhesive/mixed (Table 3).

The overall µTBS values for SB and the experimental adhesives are shown in Table 4. From a total of 7 teeth, just one bonded with R60 survived the specimen preparation. Therefore the data of this adhesive was excluded from the statistical analysis. The two-way ANOVA detected that the cross-product interaction Adhesive vs. Storage period was not statistically significant ($p = 0.60$), but the main factors Adhesive ($p = 0.0006$) as well as Storage period ($p = 0.0001$) were. Lower µTBS values were observed for R60 at both storage periods. After six months significant reductions of µTBS values were observed regardless the adhesive composition.

Interface micromorphology

The Interface micromorphology analysis of adhesive interfaces produced with the experimental adhesives can be seen in Figure 2. One can observe that for the commercial adhesive SB and the experimental solutions R0 and R30, resin infiltration occurred within the interfibrillar spaces and dentinal tubules producing a dense and hybrid layer. On the other hand, for the R40 and R50 formulation, an empty space can be seen in the area that should be occupied by the hybrid layer, suggesting a poor resin infiltration within the interfibrillar spaces. The specimens produced with R60 did not survive the polishing procedures required for SEM evaluation and therefore could not be qualitatively evaluated.

Discussion

The investigation of filler addition on adhesives is not a new issue. However, filled adhesives have been proposed to increase the thickness of the adhesive layer, to improve the immediate µTBS and to reduce marginal leakage.[13, 15] Although beneficial effects were observed in favor of filled adhesive version [14] this finding is not consensual in the literature [15, 26] as previously mentioned in the introduction section.

To the extent of the author´s knowledge no study has so far studied the impact of filler addition on the adhesive radiopacity and this is the first one that attempts to investigate this issue. The radiopacity of esthetic restorative materials has been established as an important requirement, improving the radiographic diagnosis. [24, 27] The results of the present study demonstrated that even the smallest percentage of barium oxide particle evaluated in this study (30%) was able to confer radiopacity to the experimental adhesive system similar to that of the enamel substrate.

The addition of 30% or 40% of barium-borosilicate oxide microparticles to the adhesive composition did not jeopardize the bonding of this material to the dentin substrate, meaning that the bond strength of the unfilled vs. these filled versions was statistically similar. Although this was not seen as positive in earlier studies [15, 26] this indicates that the presence of such particles did not prevent the resin monomers from infiltrating the interfibrillar spaces and the dentinal tubules. This was somehow seen in the SEM images of the adhesive interfaces produced with these experimental adhesives. The micromorphological features of the adhesive interfaces produced by the unfilled and R30 were quite similar and very different from the one produced by the R40 and R50 formulation. In the latter, incomplete resin infiltration was observed within the demineralized interfibrilar spaces. The excessive filler loading of the R40, R50 and R60 formulations likely prevented resin infiltration within the interfibrilar spaces, probably due to the formation of filler clusters which may have increased significantly the particle sizes, as previously reported by Kim et al. [11], 2005. These authors reported that even adhesives containing small percentage of fillers (3.0 wt%) could aggregate into large filler clusters when applied to a wet dentin surface. This filler aggregation likely obstructed resin monomer penetration within the interfibrilar spaces [28] and could be the reason for the lower bond strength values and poor resin infiltration observed for R50 and R60 formulations.

Another aspect investigated in this study was the degradation of the bonded interfaces over time. Water tree propagation may be a symptom of degradation in the resin bonding layer of resin–dentin bonds[9] .This degradation was reported by several studies in the literature.[4, 5, 8, 9, 29-31] Theoretically, as the addition of filler particles to bonding resins reduces the organic matrix fraction of the material, which is the one that suffers hydrolytic degradation,[32] reduced degradation were expected to occur for the filled experimental adhesives. However this hypothesis was not confirmed in the present study. Regardless of the adhesive composition, significant reductions of percentage of the resin-dentin bonds (12-32%) occurred after 6 months of water storage for all filled and unfilled adhesives evaluated.

In the present study, filler particles were previously treated with 3-methacryloxypropyltrimethoxysilane (MPS). Silane provides a crucial link between the matrix, protects the filler against fracture,[33] improves stress distribution and transition from the flexible organic matrix to the stiffer and stronger inorganic filler particles [34] and finally improves the resistance of composite to hydrolytic degradation.[35]

However in spite of these advantages, the hydrolytic stability of MPS is of continuous concern. The oxane bond (Si–O–Si) that forms between the silane agent and the silica can be especially vulnerable to hydrolysis, because this covalent bond has significant ionic character. [36, 37] Although this is a slow process in composite resins, where monomers with hydrophobic features are used in their formulation, this is not the case when it comes to adhesive systems composed mainly of hydrophilic monomers.[12] Thus, it is likely that the benefits of reduced organic matrix could have been over-weighted by the increase in the interfacial filler area with MPS.

The analysis of bond strength values and the number of premature failures during specimen preparation allows us to conclude that barium oxide concentrations higher than 40% should not be used. Although reductions of bond strength values was not very high as compared to the unfilled and R30 formulation, a very higher number of premature failures was observed, mainly for concentrations higher than 40% and this has been associated lower quality of adhesion.[38] Besides that, inadequate resin infiltration was shown under the SEM images for R40 and R50 formulations. Other types of filler particles and coupling agents should be studied in order to stimulate the production of high quality bonding resins with radiopacity similar to enamel.

Conclusion

Within the limitations of this study it was possible to conclude that the addition of 30% barium-borosilicate oxide microparticles produced radiopaque adhesives without jeopardizing the bonding to the dental substrate.

Effect of filler addition on the radiopacity, bond strength and micromorphology of experimental adhesives

Abstract

Statement of the Problem: The dentistry material radiopacity is an important property that allows a contrast material with the tooth structure in radiographs.

Purpose of the study: To evaluate the radiopacity, the bond strength and the micromorphology of experimental dental adhesives.

Methods/Materials: Five experimental adhesive systems with different concentrations of radiopaque barium-borosilicate glass (wt%) [0(R0), 30(R30), 40(R40), 50(R50) and 60(R60)] and the commercial adhesive Adper Single Bond2 were prepared by dispensing the uncured resin into a mould (5.0 mm × 1.0 mm). Digital radiographs (n=5) with CCD sensor of 1-mm-thick adhesive specimens along with 1-mm-thick tooth slice were taken. The gray levels of enamel, dentin and adhesive systems were measured by histogram analysis and compared. Adhesives were applied to flat dentin surfaces of third molars (n=7). Resin composite buildups were constructed and sectioned to obtain resin-dentin bonded sticks to test immediately or after 6 months of water storage. Three specimens for each tooth for qualitatively analyzed by Scanning Electron Microscope. Data from bond strength and radiopacity were evaluated by two-way and one-way ANOVA, respectively and Tukey´s test (alfa = 0.05).

Results: All experimental adhesives showed radiopacity similar to enamel ($p > 0.05$) and significant reductions of bond strength over time. The R30 produced a radiopaque material without jeopardizing the bonding of the material with the dentin substrate.

Conclusions: The addition of 30% barium-borosilicate oxide produced radiopaque adhesives without jeopardizing the bonding to the dental substrate.

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Table 1 – Adhesive systems, composition, application mode and batch number.

Adhesive systems	Composition	Application mode	Batch number
Adper Single Bond™ 2 (3M ESPE, St. Paul, MN, USA)	1. Scotchbond acid: 35% phosphoric acid. 2. Bond: Bis-GMA; polyalkenoic acid co-polymer; dimethacrylates; HEMA; photoinitiators; ethanol; water; nanofiller particles	*1. Acid etching for 15 s* *2. Apply generous amounts of adhesive. Actively scrub for 15 s;* *3. Application of a second coat of adhesive, as above;* *4. Removal of excess solvent by gently drying with an air-stream for 15 s at 15 cm away from the surface, gradually bringing it to within 10 mm of distance;* *5. Light curing for 10 s*	*8RF*
Ambar *(FGM Dental Products, Joinville, SC, Brazil)	1. Condac 37: 37% phosphoric acid 2. UDMA (5-40), HEMA (5-40), methacrylate acidic monomers (1–20), methacrylate hydrophilic monomers (5-40), camphorquinone (<1), 4-EDAMB (<1), ethanol (<20)		*R0: 0606231* *R30: 080410* *R40: 080410* *R50: 080410* *R60: 080410*

Bis-GMA - bisphenol-glycydil methacrylate; HEMA: 2-Hydroxyethyl methacrylate; UDMA - urethane dimethacrylate; (*) To the original composition of the adhesive Ambar, varied concentrations of barium-borosilicate glass particles were added to produce the R0, R30, R40, R50 and R50 and R60 formulations, described in the materials and methods section.

Table 2 – Means and standard deviations of the radiopacity of enamel, dentin and adhesive systems by histogram analysis of gray levels.

Adhesive systems	Gray level
Enamel	134.0 ± 25.0 AB
Dentin	87.6 ± 4.0 CD
SB	77.1 ± 2.7 D
R0	79.7 ± 6.9 D
R30	123.0 ± 19.5 BC
R40	153.0 ± 22.3 AB
R50	167.0 ± 20.8 A
R60	150.0 ± 35.1 AB

Averages identified with the same letters indicate means statistically similar ($p > 0.05$).

Table 3 – Percentage of specimens (%) according to the fracture pattern* and percentage of premature failures for each experimental condition during specimen preparation.

Adhesive systems	Fracture			
	A/M	R	S	PF
SB	90.3	0	0	9.7
R0	98.7	0	0	1.3
R30	75.0	0	0	25.0
R40	69.9	0	0	30.1
R50	36.9	0	0	63.1
R60	18.2	0	0	81.8

** A/M = adhesive or mixed failure; R = cohesive failure in resin; S = cohesive failure in dental substrate; PF = premature failures.*

Table 4 – Means, standard deviation (MPa) and statistical significance of resin-dentin bond strength values for each experimental condition.

Adhesive systems	immediate	6 months	Main factor Adhesive
SB	51.7 ± 4.6	42.0 ± 2.3	46.8 ± 5.9 AB
R0	59.8 ± 2.1	43.2 ± 11.1	49.4 ± 11.3 A
R30	44.0 ± 5.9	31.1 ± 2.5	39.2 ± 7.6 ABC
R40	38.5 ± 11.7	34.2 ± 5.9	36.5 ± 9.1 BC
R50	40.6 ± 16.1	27.9 ± 7.7	35.0 ± 13.2 C
R60	--	--	--
Main factor Storage Period	45.2 ± 11.6 a	36.4 ± 8.5 b	

Groups identified with the same upper or lowercase letter are not significantly different (p > 0.05)

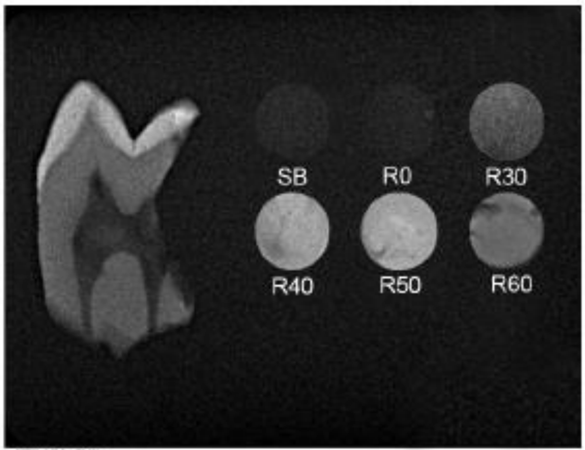

Figure 1 – X-ray radiograph showing the commercial and experimental adhesives along with the 1-mm thick tooth slice. It can be seen that except from the unfilled adhesive R0 and commercial adhesive SB, all experimental filled adhesives show radiopacity similar to the enamel.

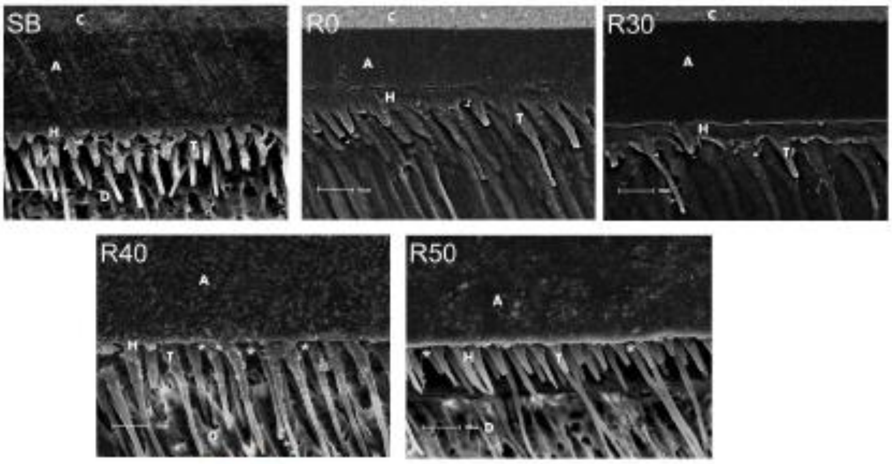

Figure 2 – Scanning electron micrographs showing the adhesive interfaces produced by the commercial and experimental adhesives investigated. The funnel-shaped aspect of the resin tags close to the adhesive layer of the SB, R0 and R30 adhesives indicates that a good resin infiltration occurred within the interfibrilar collagen spaces, producing a more compact hybrid layer. This cannot be seen in the hybrid layers produced by R40 and R50 formulations, where gaps (asterisks) can be seem in this area, suggesting incomplete resin infiltration within interfibrilar collagen spaces. *C: composite; A: adhesive layer; H: hybrid layer; D: dentin.*

4.3 ARTIGO 3

Journal of Materials Science

Effects of zirconia nanoparticles addition to experimental adhesives on radiopacity, mechanical and bonding properties

--Manuscript Draft--

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Abstract:	To evaluate the radiopacity, microhardness (KHN), degree of conversion (DC), ultimate tensile strength (UTS), water sorption (WS), solubility (SL), and microtensile bond strength (µTBS) of experimental dental adhesives (EX). Five EX with different concentrations of zirconia nanoparticles [0(EX0), 15(EX15), 25(EX25), 30(EX30) e 50%(EX50)] were incorporated in a UDMA/HEMA adhesive (control). Adper Single BondTM 2 (SB, 3M ESPE) was used as a commercial reference. For the radiopacity (n=5), KHN (n=5), WS (n=10) and SL (n=10) tests, adhesive specimens were constructed using a stainless steel mold. For UTS (n=5), a hourglass shape metallic matrix was employed. The FT-IR spectra of uncured and cured specimens of adhesives were used to determine the DC of the materials. The µTBS resin-dentin bonded sticks were tested immediately or after 6 months of water storage. Data were submitted to a one-way ANOVA and Tukey´s test (α=0.05). Results: The filler addition on the EX showed radiopacity similar to enamel and higher than SB. The EX25, EX35 and EX50 showed higher KHN values when compared to the commercial SB. In general, the UTS and DC of the EX was not affected by filler addition. All EX showed lower WS and SL than SB. For all EX adhesives, lower µTBS values were observed at both storage periods than the commercial SB and the EX0. Conclusions: The addition of filler loading in moderate concentration (EX25 and EX35) produced radiopaque materials with mechanical properties that were either improved or remained unchanged compared to the unfilled version.

Effects of zirconia nanoparticles addition to experimental adhesives on radiopacity, mechanical and bonding properties

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Effects of zirconia nanoparticles addition to experimental adhesives on radiopacity, mechanical and bonding properties

Abstract

Purpose: To evaluate the radiopacity, microhardness (KHN), degree of conversion (DC), ultimate tensile strength (UTS), water sorption (WS), solubility (SL), and microtensile bond strength (µTBS) of experimental dental adhesives (EX) incorporated with different percentage of zirconia nanoparticles. Materials and Methods: Five EX with different concentrations of zirconia nanoparticles [0(EX0), 15(EX15), 25(EX25), 30(EX30) e 50%(EX50)] were incorporated in a UDMA/HEMA two-step etch-and-rinse adhesive (control). Adper Single Bond^{TM} 2 (SB, 3M ESPE) was used as a commercial reference. For the radiopacity (n=5), KHN (n=5), WS (n=10) and SL (n=10) tests, adhesive specimens were constructed using a stainless steel mold (5.0 mm in diameter and 1.0 mm thick). For UTS (n=5), a hourglass shape metallic matrix (10 mm long, 2 mm wide, and 1 mm deep with cross-sectional area of 0.8 mm^2) was employed. The FT-IR spectra of uncured and cured specimens of adhesives were used to determine the DC of the materials. The µTBS resin-dentin bonded sticks (0.8 mm^2) were tested immediately (IM) or after 6 months (6M) of water storage. Data were submitted to a one-way ANOVA and Tukey´s test (α=0.05). Results: The filler addition on the EX showed radiopacity similar to enamel and higher than SB. The EX25, EX35 and EX50 showed higher KHN values when compared to the commercial SB. In general, the UTS and DC of the EX was not affected by filler addition. All EX showed lower WS and SL than SB. For all EX adhesives, lower µTBS values were observed at both storage periods than the commercial SB and the EX0. Conclusions: The addition of filler loading in moderate concentration (EX25 and EX35) produced radiopaque materials with mechanical properties that were either improved or remained unchanged compared to the unfilled version.

Keywords: Radiopacity, Filler particles, Degree of conversion, Microhardness, Strength, Water sorption and solubility.

1. Introduction

The radiopacity of adhesive materials is clinically relevant, mainly in technique-sensitive restorations, where evaluation of the tooth/restorative interface is critical [1, 2]. Unfortunately, the great majority of the commercial adhesives available in the market is radiolucent [3] and they cannot be perfectly detected in radiographs [4] when applied in layers thicker than 40 µm. This is a pertinent clinical concern since adhesive layers should be distinguished from marginal gaps with potential for secondary caries.

The development of radiopaque adhesive systems can avoid inappropriate replacements [5, 6] due to misinterpretations on the diagnosis of secondary caries [2, 5, 7] and detection of gaps near the restoration [4, 7]. Thus, studies should focus on the investigation of bonding features and mechanical properties of radiopaque adhesive systems.

Recently, there has been a great interest in the application of nanotechnology in resin-based materials [8, 9]. Dental composite filling materials with increased hardness and wear resistance were produced by the incorporation of nanofillers [8, 10]. These promising findings led investigators to evaluate the effects of filler addition on the mechanical properties [11-15] as well as bonding features of adhesives [13, 14, 16-18]; however few of them incorporated nano-sized filler particles into the adhesive formulations [8, 10] and evaluated the role of nanofillers on material´s radiopacity [13, 18].

Therefore, the aim of the present investigation was to evaluate the incorporation of varied concentrations of zirconia nanofiller into a two-step etch-and-rinse adhesive on the material´s radiopacity, ultimate tensile strength, microhardness, degree of conversion, water sorption and solubility and immediate and 6-month resin-dentin microtensile bond strength.

2. Material and Methods

This research project was approved by the Institutional Review Board from the local Dental School under protocol # 28/2010.

2.1. Formulation of the experimental adhesives

The experimental adhesive resins from the present study were formulated by using the simplified adhesive system Ambar (FGM Dental Products, Joinville, SC, Brazil) as base. This material was specifically formulated for this study without any filler content. The detailed composition of this adhesive system, as provided by the manufacturer, can be seen in Table 1. The simplified etch-and-rinse adhesive system (Adper Single Bond^{TM} 2, batch no. 8RF, 3M ESPE, St. Paul, MN, USA) was used as commercial reference (Table 1).

Zirconia oxide nanoparticles (20-30 nm average particle size, Transparent Materials, USA) were silanized by gamma-methacryloxypropyltrimethoxysilane (Aldrich Chemical Co., Milwalkee, WI, USA) as reported before [19]. After the silanization process, the nanoparticles were dried for 24 h at 37°C and then disaggregated in a pistil. Five experimental adhesive systems were formulated according to the filler weight percentage (wt%): 0 (EX0), 15 (EX15), 25 (EX25), 35 (EX35) and 50% (EX50).

2.2. Radiopacity

Using a circular stainless steel mold, five specimens measuring 5.0 mm in diameter and 1.0 mm thick were prepared for each material. The adhesive was dispensed in the mold until complete filling. All visible air bubbles trapped in the adhesive solution were carefully removed. The solvent was evaporated by gentle air blowing from a dental syringe for 40 s. Each specimen was polymerized for 80 s with a visible-light curing unit (VIP, Bisco Inc., Schaumburg, IL, USA) with a power density 450 mW/cm^2. Enamel and dentin specimens were obtained from 1.0-mm thick longitudinal sections of human third molars previously stored in 0.5% thymol and used within 6 months after extraction. Slices were prepared using a low-speed diamond blade (Isomet 1000, Buehler; Lake Bluff, IL, USA) mounted in a cutting machine under water cooling.

A total of five radiographs were made. Each radiograph was taken with one specimen of each experimental condition and the enamel-dentin slice positioned on the digital sensor. An X-Ray digital radiography was then taken with an exposure time of 0.2 s. The radiographic position was standardized: the X-ray central beam focusing in a 90° angle with the surface of the image receptor, at a 30 cm focus-object distance and parallelism between the sensor and the specimens with the Heliodent Vario machine (Sirona, Bensheim, Germany). The digital radiopacity (% white) was measured by pixels counting using the UTHSCSA ImageTool 3.0 software (Department of Dental Diagnostic Science, University of Texas Health Science Center, San Antonio, Texas, USA).

2.3. Ultimate tensile strength (UTS)

A metallic matrix 10 mm long, 2 mm wide, and 1 mm deep with an hourglass shape and cross-sectional area of 0.8 mm^2 was employed for the construction of the adhesive specimens. After isolating the matrix, each adhesive solution was dropped into the mold and gently air-dried with an oil and water-free compressed air (40 s) to allow for solvent evaporation. Then, a plastic matrix strip was placed on the top of the adhesive and the surface was light-cured for 80 s at 450 W/cm^2 using the same light curing unit, previously described. Five specimens were constructed for each bonding resin and the specimens were tested in tensile mode in a universal testing machine (Kratos Dinamômetros, São Paulo, SP) at a cross-head speed of 0.5 mm/min.

2.4. KNOOP microhardness

Five resin disks of each material were produced as described for the radiopacity. After preparation, specimens were stored in a dark vial for 24 h before microhardness measurement. Specimens were then taken to a HMV-2 microhardness tester (Shimadzu, Tokyo, Japan) equipped with a Knoop indenter. The measurements were performed on the irradiated surface at three randomized positions with 10 g of load and 15 s dwell time. The values from the same specimen were averaged for statistical purposes.

2.5. Degree of conversion (DC)

The FT-IR analysis was conducted in a FT-IR spectrometer (Spectrum 100, Perkin Elmer, Massachusetts, USA). One drop of the adhesive solutions was placed between acetate strips to achieve a thin film. Before covering the adhesive with the upper acetate strip, they were gently air-dried with oil and water-free compressed air (20 s) to allow for solvent evaporation. Then the specimens were light-cured for 10 s with a power density 450 mW/cm^2 using the same light curing unit previously reported. Each specimen was carefully removed with a narrow surgical knife and stored for 24 h in a dark, dry environment before DC measurement.

The spectrum of the cured and uncured bonding resin was obtained with 32 scans at 4 cm^{-1} resolution in the absorbance method. The percentage of un-reacted carbon–carbon double bonds (% C=C) was determined from the ratio of absorbance intensities of aliphatic C=C (peak height at 1640 cm^{-1}) against internal standard before and after curing of the specimen. The aromatic carbon–carbon bond (peak height at 1610 cm^{-1}) absorbance was used as an internal standard. The DC was determined by subtracting the % C=C from 100%. Five specimens were tested for group.

2.6. Water sorption (WS) and solubility (SL)

WS and SL were determined according to the Malacarne et al. 2006 [20], except for specimens' dimensions (5.0 mm in diameter and 1.0 mm thick) . Ten resin disks of each material were produced as described for the radiopacity. With the adopted energy density (80 s with a power density 450 mW/cm^2) specimens allowed removal from the brass mold without undergoing permanent deformation. Immediately after polymerization, the specimens were placed in a desiccator at 37°C and left undisturbed for 10 days. After this period, specimens were repeatedly weighed after 24 h intervals until a constant mass (m1) was obtained (i.e., variation was less than 0.2 mg in any 24 h period).

Thickness and diameter of the specimens were measured using a digital caliper, rounded to the nearest 0.01 mm, and these measurements were used to calculate the volume (V) of each specimen in mm^3. They were then individually placed in sealed vials containing 10 mL of distilled water (pH 7.2) at 37 °C. After fixed time intervals of 1, 2, 3, 4, 5, 6, 7, 14 and 28 days of storage, the vials (15 mL, Eppendorf of Brazil, São Paulo, SP, Brazil) were removed from the oven and left at room temperature for 30 min. The specimens were washed in running water, gently wiped with a soft absorbent paper, weighed in an analytical balance (m2) and returned to the vials containing 10 mL of fresh distilled water.

Following the 28 days of storage, the specimens were dried in a desiccator containing fresh silica gel in an oven at 37 °C and left undisturbed for 10 days. They were weighed daily until a constant mass (m3) was obtained (as previously described). The initial mass determined after the first desiccation process (m1) was used to calculate the change in mass after each fixed time interval, during the 28 days of storage in water. Changes in mass were plotted against the storage time in order to obtain the kinetics of WS during the entire period of water storage.

WS and SL over the 28 days of water storage were calculated using the following formulae: $WS = (m2 - m3)/V$ and $SL = (m1 - m3)/V$ [20].

2.7. Microtensile bond strength (μTBS)

Forty two extracted human third molars were stored in 0.5% thymol and used within 6 months after extraction. Flat dentin occlusal surfaces were exposed by means of a diamond wheel (Isomet 1000, Buehler; Lake Bluff, IL, USA). The exposed mid-coronal dentin surfaces were further polished on wet # 600-grit silicon-carbide paper for 60 s to standardize the smear layer.

All adhesive systems were applied according to the description in Table 1 and polymerized for 10 s with a power density 450 mW/cm^2 using the same light curing unit previously described. Light intensity was monitored throughout the experiment to ensure that a consistent light intensity was maintained. After bonding procedures (n = 7 teeth), a 4 mm-thick layer of resin composite (Opallis, FGM, Joinville, SC, Brazil) was added to the dentin surface, in 4 increments of 1.0 ± 0.1 mm. Each increment was light-cured for 40 s with a power density 450 mW/cm^2, using the same light curing unit.

The teeth were then bucco-lingually and mesio-distally sectioned through the restoration using with a diamond saw under water cooling (Isomet 1000, Buehler; Lake Bluff, IL, USA) to obtain resin-dentin bonded sticks with a cross-sectional area of about 0.8 mm^2.

Specimens originated from the same tooth were randomly divided to be tested immediately (IM) or after 6 months (6M) of water storage (37°C). The storage solution was not changed over time; however water was added in case water evaporation occurred over time in order to keep the water volume constant.

The resin-dentin sticks, from each adhesive group, were tested in tensile mode until failure in a universal testing machine (Kratos Dinamômetros, São Paulo, SP, Brazil) at a crosshead speed of 0.5 mm/min. The failure modes were evaluated at 40x magnification using a stereomicroscope (Microscopy, Nikon Eclipse E200, Melville, NY, USA) and classified as cohesive in the dental substrate (failure exclusively within dentin or resin composite) or adhesive/mixed (failure at resin/enamel interface or mixed with cohesive failure of the neighboring substrates).

2.8. Statistical analysis

Data from radiopacity, UTS, microhardness and DC was submitted to a one-way ANOVA. Data from WS and SL after 28 days were analyzed by one-way ANOVA. The mean WS of all materials throughout the 28-day period was plotted against time for each adhesive system. Post-hoc multiple comparisons were performed using Tukey's test at a significance level of 5%.

The µTBS values of specimens from the same tooth, in each storage period, were averaged for statistical purposes. Specimens with cohesive and those with premature failures were excluded from the data analysis. The µTBS data were then submitted to a two-way repeated measure ANOVA with the Adhesive and Storage period as the main factors. Tukey's post-hoc test was used for pair-wise comparisons at a pre-set alpha of 0.05.

3. Results

3.1. Radiopacity

One-way ANOVA detected statistically significant difference among groups (Table 2, $p < 0.001$). All experimental bonding adhesives showed radiopacity similar to enamel, except from EX0 and SB. These two adhesives showed radiopacity similar to the dentin substrate.

3.2. Ultimate tensile strength (UTS), microhardness (KHN) and degree of conversion (DC)

No significant difference was observed for the UTS values (Table 3, $p = 0.29$). For KHN and DC, one-way ANOVA detected significant differences between groups (Table 3, $p < 0.0001$ for both tests).

In regard to KHN, the addition of filler loading equal or higher than 25% produced materials with increased microhardness when compared with the commercial SB. The unfilled EX0 and the lightly filled EX15 showed intermediate microhardness between these extremes. Except from EX50 and EX15, all other experimental formulations showed DC means higher than the commercial SB. However, significant differences in terms of DC could be seen among the experimental formulations. The unfilled EX0, and the EX25 produced the higher DC among all experimental bonding resins (Table 3, $p < 0.01$).

3.3. Water sorption (WS) and solubility (SL)

All adhesives tested showed the same pattern of WS and most of the WS occurred within the first day of water storage (Figure 1). The magnitude of WS and SL, however, varied depending on the adhesive formulation (Table 4, $p < 0.0001$ for both tests). All experimental adhesives showed lower WS than the commercial SB. The addition of filler to the experimental solutions did not or affected little the WS of the materials when compared to the unfilled version EX0. On the other hand, the addition of filler reduced the SL of all experimental adhesive solutions, since the filled adhesives exhibited statistically lower SL than the unfilled EX0 and the commercial SB adhesives (Table 4).

3.4. Microtensile bond strength (µTBS)

The mean cross-sectional area ranged from 0.61 to 0.77 mm^2 and no difference was detected among the groups ($p > 0.05$). The percentage of specimens with premature failures (PF) and the frequency of each fracture pattern mode are shown in Table 3. No cohesive failure was observed in the present investigation. Groups EX15, EX25 and EX35 showed a very high percentage of PF compared to SB and Ex0 (Table 5, $p < 0.05$). For the experimental and commercial adhesives, most of the fracture modes were adhesive or adhesive/mixed (Table 5).

Two-way ANOVA detected that the cross-product interaction Adhesive vs. Storage period was not statistically significant ($p = 0.418$), but the main factors Adhesive ($p < 0.001$) as well as Storage period ($p < 0.001$) were. All filled experimental adhesives exhibited lower µTBS than SB and EX0 at both storage periods (Table 6). After six months, significant reductions of µTBS values were observed for all bonding materials, regardless of the adhesive composition (Table 6).

4. Discussion

Dental adhesives are intricate mixtures of components and they are designed to bond composite resins to enamel and dentin [21, 22]. Irrespective of the number of bottles, an adhesive system typically contains resin monomers, curing initiators, inhibitors, stabilizers, solvents and sometimes inorganic filler. Each one of these components has a specific function [21]. Although beneficial effects were observed in favor of filled adhesives [5] this finding is not consensual in the literature [15, 23].

To the extent of the author´s knowledge only one study investigated the impact of filler addition on the adhesive radiopacity [18] and this is therefore a novel study that attempts to investigate this issue. The results of the present study showed that the addition of zirconia nanoparticles yielded enamel radiopacity to the experimental adhesives evaluated. Even the smallest percentage of zirconia nanoparticles evaluated in this study (15%) produced a radiopaque experimental adhesive similar to the radiopacity of the enamel substrate. Similarly Schulz et al. also observed increased adhesive radiopacity after inclusion of agglomerated Ta_2O_5/SiO_2 nanoparticles.

As the addition of filler particles to composite resins has been made in an attempt to improve the mechanical properties of dental composites, [8, 21, 24, 25] one could expect increases in UTS of the filled adhesives, as previously demonstrated by other authors [24]. However, this was not observed in the present investigation. The UTS values of the filled and unfilled adhesives were not statistically different.

A likely explanation for this finding relies on the adequate and balanced monomer blend employed in the experimental adhesive solutions, which may have been responsible for the production of polymeric material with increased properties. Indeed, a positive correlation between the extent of the polymer crosslink and the hardness of polyHEMA were shown in a previous study [26]. The DC findings of present investigation also strengthen this hypothesis. Compared to the commercial SB adhesive, the unfilled experimental adhesive (EX0) showed higher DC and KNH and such difference may be well attributed to compositional differences in monomer blends. While SB contains Bis-GMA, the experimental adhesives do not. Because the aromatic hydroxylated monomer Bis-GMA is more viscous, it presents limited mobility and consequently, the DC of Bis-GMA-matrix has been found to be lower than UDMA-based matrix [27, 28].

It is worth to mentioning that not all experimental adhesives showed high DC. A significant reduction of the DC was observed for the EX50. It was already demonstrated that progressive decreases in DC of composites is observed by increasing the silica particle size, due to light scattering during curing [9]. Thus, the addition of 50 wt% might have induced particle size agglomeration, which in turn, prevented homogeneous light diffusion during curing.

Theoretically, the addition of filler particles to bonding resins reduces the organic matrix fraction of the material, which is the main component responsible for WS. Although reduced WS and SL were expected for all filled adhesives, this was only observed for the formulation with the lowest filler loading (15 wt%). Moderate and highly filled adhesives (EX25, EX35 e EX50) contain reduced organic content; however on the other hand, they have increased interfacial area between the filler particles and the coupling silane agent (3-methacryloxypropyltrimethoxysilane [MPS]). The polar character of the oxane bond (Si–O–Si) that forms between the silane agent (MMP) and the filler is especially vulnerable to hydrolysis, and thus of reduced hydrolytic stability [29, 30]. Thus, it is likely that the benefits of reduced organic matrix were over-weighted by the increase in the interfacial filler area with MPS. Based on this finding, future studies should focus on the use of coupling agents with more hydrophobic features and methods of nanofiller dispersion to guarantee complete disaggregation inside the monomer phase.

The WS of the commercial SB observed in this study is very similar to the values reported in previous one [20, 31]; but it was almost two times higher than the experimental adhesive systems investigated. Dental polymer networks have been shown to be susceptible to hygroscopic and hydrolytic effects to varying extents dependent upon their chemistry and structure and mainly to their hydrophilicity [21, 32-34]. Therefore, the highest WS and SL of SB are suggestive of a more hydrophilic behavior than the experimental adhesives.

The water softening of the polymer by swelling results in the release of unreacted monomers or unbounded oligomers trapped in the polymer network to the surroundings through nanovoids in the material. The magnitude of such finding can be detected by the evaluation of the material´s solubility. The lower the organic fraction of the matrix, the lower is the absolute fraction of unreacted monomers and oligomers that can be released to the surroundings and this may be the reason of why lower SL was observed for the filled experimental adhesives when compared with the unfilled version.

In general, the addition of filler loading in moderate concentration (EX25 and EX35) produced radiopaque materials with mechanical properties that were either improved or remained unchanged compared to the unfilled version. Nonetheless, these positive findings were not observed in terms of dentin bonding. The addition of nanofillers reduced the resin-dentin bond strength of all materials, regardless of the filler loading. It is likely that the aggregation of the nanofillers within the adhesive resulted in filler clusters that were too large to infiltrate the interfibrillar spaces of the hybrid layer preventing their infiltration and also obstructing resin monomer penetration within the interfibrilar collagen fribrils. This was also demonstrated for a material containing a small percentage of nanofiller (3.0 wt%) [35].

The quality of the interface in composites usually plays a very important role in the materials capability to transfer the stress and the elastic deformation from the matrix to fillers. This is true especially for nanocomposites, since the nanoparticles have a high surface area. The silanization of the filler is essential to make the interfaces between filler and polymer compatible. If the nanoparticles aggregate, monomer will not penetrate between the nanoparticles, and thus these regions will be a weak area in the material. When a force is imposed on the nanofilled material with this feature, a stress concentration will be encountered at the interface between nanofiller aggregates and the polymer matrix. As the stress cannot be effectively transferred, it will cause a crack, and finally induce material failure.

This agglomeration can also explain why the addition of nanofillers did not minimize dentin bond degradation. The incomplete penetration of resin monomers into interfibrillar spaces left nanopores within the hybrid layer to which water could infiltrate even, producing hydrolysis and extraction of resinous materials. The exposed collagen fibrils were then susceptible to enzimatic attack by matrix metalloproteinases [36], leading to depletion of collagen fibrils within the hybrid layer [37]. Probably the good dispersion of the nanofillers in the monomer matrix by centrifugal mixing and ultrasonication described in the Schulz et al. study is responsible for the good bond strength results obtained in their study [18].

By adding nanofillers to the experimental adhesive, the relative concentration of methacrylate acidic monomers, with adhesive features, were reduced proportionally. The relatively lower concentration of adhesive monomers by dentin area jeopardizes the bonding of the adhesive film to the dental surface [38], and this might have contributed to the lower bond strength observed in the present investigation for the filled adhesives.

Although reduced bond strength values were found for the filled adhesives, these results cannot discourage further studies on this topic, since other particle with different chemical compositions and sizes could be investigated in order to produce a radiopaque material with adequate mechanical and bonding properties.

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Table 1 – Composition of adhesive systems and application mode.

Adhesive systems	Composition	Application mode	Batch number
Adper Single Bond™ 2 (3M ESPE, St. Paul, MN, USA)	Bis-GMA; polyalkenoic acid co-polymer; dimethacrylates; HEMA; photoinitiators; ethanol; water; nanofiller particles	*1. Acid etching for 15 s* *2. Apply generous amounts of adhesive. Actively scrub for 15 s;* *3. Application of a second coat of adhesive, as above;* *4. Removal of excess solvent by gently drying with an air-stream for 15 s at 15 cm away from the surface, gradually bringing it to within 10 mm of distance;* *5. Light cure for 10 s*	*8RF* *2011-05*
Experimental adhesives* (FGM Dental Products, Joinville, SC, Brazil)	UDMA (5-40), HEMA (5-40), methacrylate acidic monomers (1–20), methacrylate hydrophilic monomers (5-40), silanized silicon dioxide (<1), camphorquinone (<1), 4-EDAMB (<1), ethanol (<20)		*Ex0: 0606231* *Ex15: 080410* *Ex25: 080410* *Ex35: 080410* *Ex50: 080410*

Bis-GMA - bisphenol-glycydil methacrylate; HEMA: 2-Hydroxyethyl methacrylate; UDMA - urethane dimethacrylate; 4-EDAMB: Ethyl-4-dimethyl. (*) To the original composition of the adhesive Ambar, varied concentrations of barium-borosilicate glass particles were added to produce the Ex0, Ex15, Ex25, Ex35 and Ex50 formulations, described in the materials and methods section.

Table 2 – Means and standard deviations of the radiopacity of enamel, dentin and adhesive systems by pixel intensity.

Groups	**Pixel intensity**
Enamel	68.8 ± 15.3 A
Dentin	33.0 ± 8.1 B
SB	26.9 ± 1.2 B
EX0	27.1 ± 1.0 B
EX15	60.5 ± 7.9 A
EX25	71.2 ± 6.7 A
EX35	61.0.9 ± 9.2 A
EX50	73.3.0 ± 7.4 A

Averages identified with the same letters indicate means statistically similar (p > 0.05).

Table 3 – Means and standard deviations of the ultimate tensile strength (MPa), microhardness, and degree of conversion (%) as well as the statistical significance for each method.

Groups	**Ultimate tensile strength (MPa)**	**Microhardness (KHN)**	**Degree of conversion (%)**
SB	20.3 ± 6.9 A	3.3 ± 1.2 C	45.1 ± 2.2 D
EX0	24.8 ± 5.9 A	5.8 ± 0.7 BC	56.4 ± 2.7 AB
EX15	19.9 ± 2.5 A	5.7 ± 0.3 BC	50.1 ± 0.9 CD
EX25	18.2 ± 5.1 A	7.5 ± 1.5 AB	58.6 ± 3.7 A
EX35	18.4 ± 4.0 A	8.8 ± 1.8 A	52.8 ± 1.8 BC
EX50	22.9 ± 2.4 A	8.8 ± 1.8 A	46.8 ± 3.6 D

Comparisons are only valid within columns. Averages identified with the same letters indicate means statistically similar (p > 0.05).

Table 4 - Water sorption (μg/mm^3) and solubility (μg/mm^3) of the adhesives after 28 days of water storage.

Adhesive systems	**Water sorption (μg/mm^3)**	**Solubility (μg/mm^3)**
SB	212.9 ± 16.5 A	65.8 ± 11.6 A
EX0	122.9 ± 10.2 BC	63.9 ± 6.8 A
EX15	107.1 ± 12.5 C,D	18.0 ± 5.4 BC
EX25	113.3 ± 9.1 C	12.4 ± 1.3 C
EX35	130.6 ± 9.5 B	21.9 ± 1.6 B
EX50	130.5 ± 7.8 B	17.7 ± 2.0 BC

Comparisons are only valid within columns. Averages identified with the same letters indicate means statistically similar ($p > 0.05$).

Table 5 – Percentage of specimens (%) according to the fracture pattern* and percentage of premature failures for each experimental condition during specimen preparation.

Adhesive systems	**Fracture mode**			
	A/M	**CR**	**CD**	**PF**
SB	90.3	0	0	9.7
EX0	98.7	0	0	1.3
EX15	46.9	0	0	53.1
EX25	51.1	0	0	48.9
EX35	58.2	0	0	41.8
EX50	71.9	0	0	28.1

** A/M = adhesive or mixed failure; CR = cohesive failure in resin; CD = cohesive failure in dental substrate; PF = premature failures.*

Table 6 – Means, standard deviation (MPa) and statistical significance of resin-dentin bond strength values for each experimental condition.

Adhesive systems	**Immediate**	**6 months**	**Main factor Adhesive**
SB	51.7 ± 4.6	42.0 ± 2.4	46.8 ± 5.9 A
EX0	59.8 ± 1.8	43.2 ± 11.1	49.4 ± 11.3 A
EX15	31.3 ± 10.1	13.5 ± 11.4	39.2 ± 7.6 B
EX25	41.8 ± 9.4	24.4 ± 11.2	36.5 ± 9.1 B
EX35	27.0 ± 7.9	14.3 ± 9.6	35.0 ± 13.2 B
EX50	31.5 ± 16.8	10.3 ± 8.6	20.9 ± 16.0 B
Main factor Storage Period	39.6 ± 14.8 a	24.6 ± 16.0 b	

Groups identified with the same upper or lowercase letter are not significantly different (p > 0.05)

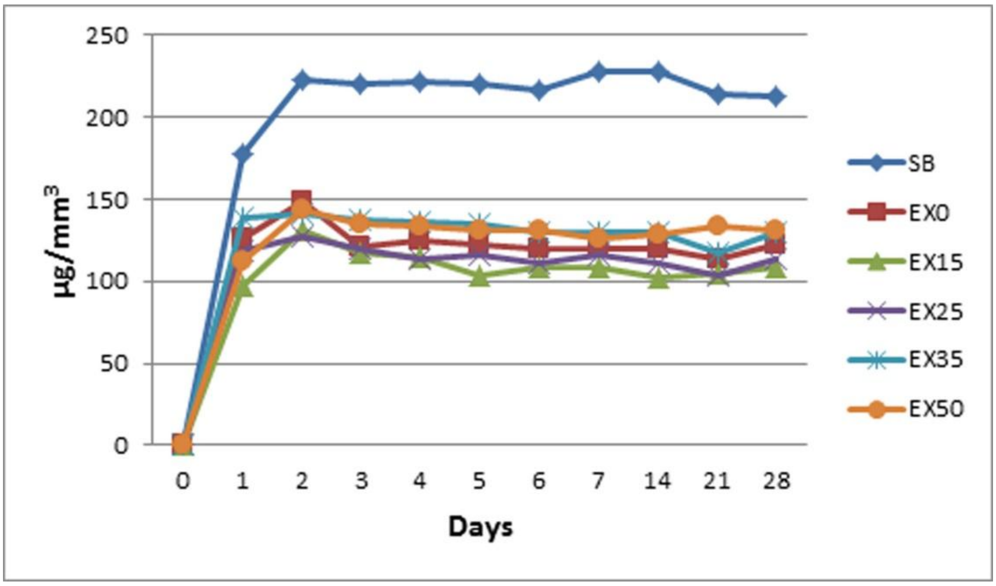

Figure 1 - Changes in mass of a commercial (SB) and experimental adhesives over 28-days of water storage. Symbols represent mean values (*n* = 10).

5 DISCUSSÃO

A adição de partículas de carga (Tani et al.[26] 1994, Miyazaki et al.[20] 1995, Kim et al.[18] 2005, Pongprueksa et al.[27] 2008, Conde et al.[24] 2009, Hota et al.[14] 2009), ou a incorporarção de nanopartículas (Kim et al.[18] 2005, Schulz et al.[25] 2008, Conde et al.[24] 2009, Karabela et al.[28] 2011) em formulações adesivas não é uma questão nova. No entanto, os estudos realizados abordam a adição de carga visando a melhoria das propriedades mecânicas e não em relação ao impacto da adição de carga na radiopacidade do sistema adesivo (Miyazaki et al.[20] 1995, Kim et al.[18] 2005, Conde et al.[24] 2008, Schulz et al.[25] 2008, Giannini et al.[21] 2011). Apesar de efeitos benéficos terem sido observados em adesivos com carga (Miyazaki et al.[20] 1995, Conde et al.[24] 2009) esta conclusão não é unânime na literatura (Tani et al.[26] 1994, Can Say et al.[23] 2006).

Cabe destacar que apenas um estudo avaliou o impacto da adição de carga na radiopacidade do adesivo[25], portanto, este é um estudo novo que busca investigar esta questão. A radiopacidade é um requisito importante que os materiais restauradores devem apresentar para um melhor diagnóstico radiográfico (Tveit, Espelid[5] 1986, Matteson et al.[29] 1989, Espelid et al.[6] 1991, Van Landuyt et al.[19] 2007). Os resultados do presente estudo mostraram que a adição de nanopartículas de zircônia e micropartículas de bário-borosilicato, aos adesivos experimentais avaliados, produziram radiopacidade similar ao esmalte dental.

Em relação ao grau de conversão a adição de carga, nanopartículas ou micropartículas, nos adesivos experimentais não afetou essa propriedade, corroborando com os estudos de Kim et al.[18] 2005 e Conde et al.[24] 2009, que não encontraram diferenças quando adicionaram nanopartículas hidrofílicas de sílica a 0,5-3% e 0-10% ao adesivo. O grau de conversão semelhante dos adesivos com e sem partículas mostrou adequada dispersão no interior da matriz, evitando a formação de aglomerados que poderiam interferir na penetração de luz. Embora, os adesivos com carga mostraram grau de conversão similares, suas médias geralmente foram inferiores ao adesivo sem carga. Isto pode ser devido às diferenças no índice de refração entre o vidro e o polímero radiopaco, o que torna o material mais opaco e menos propenso a penetração de luz. Este problema, no entanto, não é uma preocupação clínica, uma vez que camadas muito finas de material adesivo são geralmente empregadas durante os procedimentos de união.

O sistema adesivo comercial SB mostrou grau de conversão inferior quando comparado com a versão sem partículas dos adesivos experimentais, que pode ser devido a diferenças nas misturas monoméricas. O SB contém Bis-GMA, enquanto os adesivos experimentais não o fazem. Uma vez que o monômero aromático hidroxilado Bis-GMA é mais viscoso, apresenta mobilidade limitada e, por conseguinte, o grau de conversão da matriz do Bis-GMA pode ser inferior ao baseado na matriz de UDMA (Peutzfeldt[30] 1997, Floyd, Dickens[31] 2006).

Embora o teste de microdureza seja geralmente empregado como uma medição indireta do grau de conversão de materiais poliméricos (DeWald, Ferracane[32] 1987), os maiores valores de microdureza foram observados nos adesivos experimentais com partículas, isso não pode ser explicado pelo aumento do grau de conversão, uma vez que esta propriedade não foi afetada pela porcentagem de carga. No entanto, como já foi demonstrado, existe uma correlação positiva entre a fração de volume de partículas e da dureza de Knoop de compósitos (Chung, Greener[33] 1990) porque as partículas de carga são mais duras do que a fase orgânica do material.

A incorporação de partículas inorgânicas é conhecida como um mecanismo de reforço de materiais poliméricos (Kim et al.[34] 2002, Van Landuyt et al.[19] 2007) e, como tal, pode-se também esperar aumento na resistência máxima à tração de adesivos com partículas. Entretanto, neste estudo esse resultado só foi alcançado para a formulação com a adição mais elevada de micropartículas (isto é, 60% em peso). Giannini et al.[21] 2011 avaliaram os efeitos da adição de carga na resistência à flexão biaxial e módulo de flexão de seis adesivos comerciais e não relataram diferenças entre os materiais com ou sem carga. Porém, o que pode ser observado é que o valor absoluto das cargas adicionadas ao adesivo no estudo mencionado ainda era pequena para melhorar esta propriedade mecânica.

A resistência de união é obtida pela adesão dos adesivos às resinas compostas e dos dois a estrutura dentária e, é de fundamental importância para a longevidade da restauração (Sano et al.[35] 1999, De Munck et al.[1] 2003, Abdalla, Feilzer[3] 2008). Teoricamente, a adição de partículas de carga nos sistemas adesivos reduz uma fração da matriz orgânica do material, que é o que sofre a degradação hidrolítica ao longo do tempo (Ferracane[36] 2006). No presente estudo, as partículas de carga foram previamente tratadas com 3-metacriloxipropiltrimetoxisilano (MPS) que deve melhorar a resistência a degradação hidrolítica (De Munck et al.[1] 2003). No entanto, tal fato não foi confirmado no presente estudo, uma vez que, independente da composição adesiva, reduções significativas da resistência de união pode ser observada após 6 meses de armazenamento de água para todos os adesivos avaliados.

Além disso, espera-se que a sorção e solubilidade seja reduzida em adesivos com partículas quando comparados aos sem adição de partículas. No entanto, isso não foi observado no presente estudo, visto que, os adesivos testados absorveram quantidade significativa de água, da mesma forma que em estudos anteriores (De Munck et al.[1] 2003, Reis et al.[37] 2007, Malacarne et al.[38] 2009). Quando empregam-se monômeros hidrofílicos em materiais poliméricos isso pode comprometer a formulação e afetar o comportamento da sorção de água pelo aumento de partículas de cargas. Nos monômeros mais comumente utilizados em sistemas adesivos a presença de hidroxila, grupos carboxila e fosfato (Van Landuyt et al.[19] 2007) tornam seus polímeros mais hidrofílicos e, consequentemente, mais propensos a absorção de água (Ito et al.[39] 2005, Malacarne et al.[38] 2009).

A adição de concentrações de nanopartículas ou de micropartículas para formulações adesivas produziram um material com radiopacidade adequada, onde as micropartículas não comprometeram outras propriedades dos sistemas adesivos. Entretanto, em geral, as propriedades globais mecânicas e absorção de água e solubilidade dos adesivos experimentais com carga melhoraram ou permaneceram inalteradas quando comparada com o adesivo sem carga. No entanto, estudos adicionais devem ser conduzidos a fim de avaliar a eficácia da formulação na união ao substrato dentinário.

6 CONCLUSÃO

Dentro das limitações desse estudo pode-se concluir que tanto a adição de nanopartículas quanto de micropartículas foi capaz de conferir radiopacidade aos adesivos experimentais e, a adição de carga influenciou nas propriedades testadas. De modo geral, pode-se dizer que o melhor desempenho foi para a adição de micropartículas na concentração de 30%.

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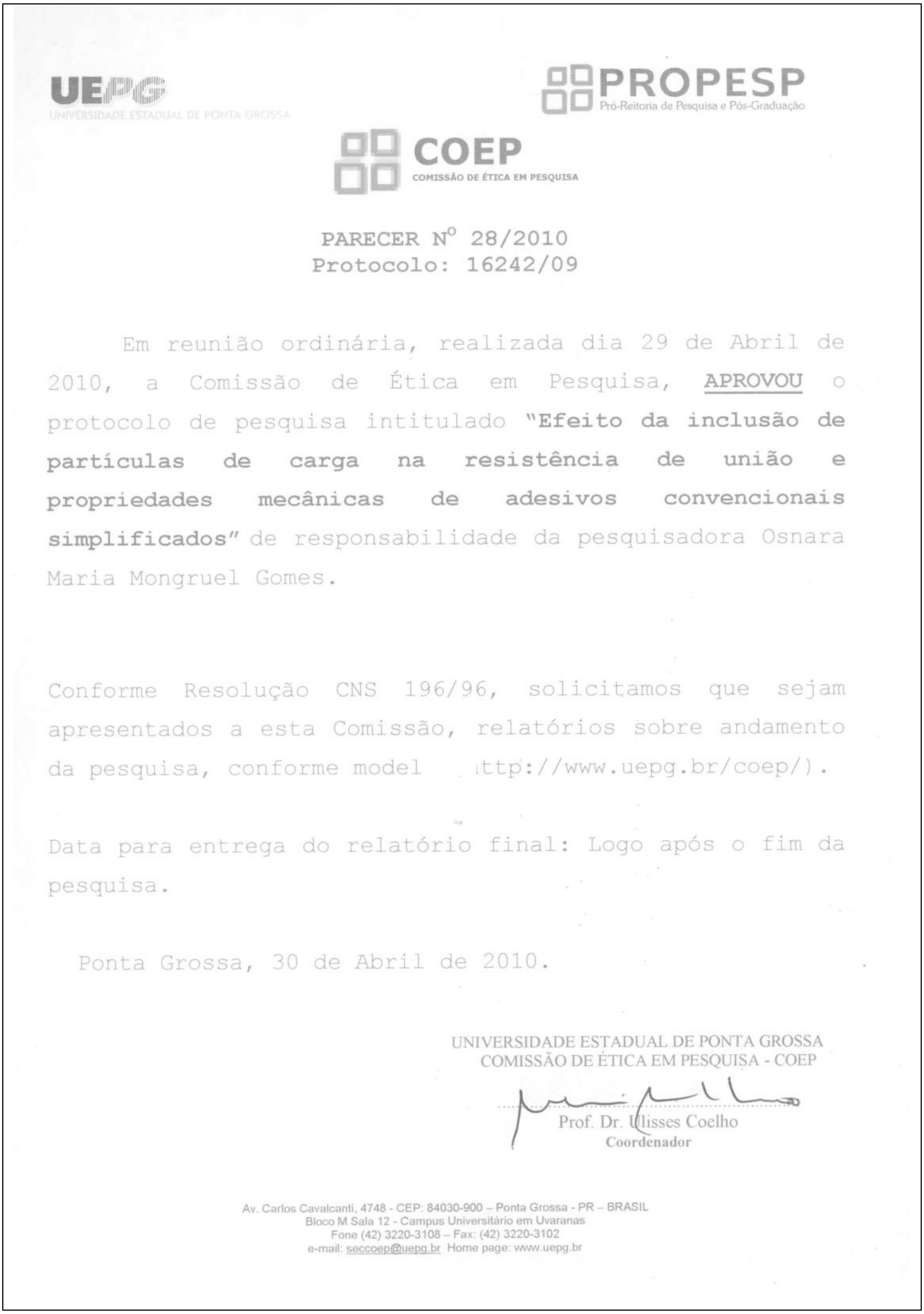
ANEXO A

APROVAÇÃO DO PROJETO PELA COMISSÃO DE ÉTICA EM PESQUISA DA UNIVERSIDADE ESTADUAL DE PONTA GROSSA – COEP-UEPG



UEPG
UNIVERSIDADE ESTADUAL DE PONTA GROSSA

PROPESP
Pró-Reitoria de Pesquisa e Pós-Graduação

COEP
COMISSÃO DE ÉTICA EM PESQUISA

PARECER N° 28/2010
Protocolo: 16242/09

Em reunião ordinária, realizada dia 29 de Abril de 2010, a Comissão de Ética em Pesquisa, APROVOU o protocolo de pesquisa intitulado **"Efeito da inclusão de partículas de carga na resistência de união e propriedades mecânicas de adesivos convencionais simplificados"** de responsabilidade da pesquisadora Osnara Maria Mongruel Gomes.

Conforme Resolução CNS 196/96, solicitamos que sejam apresentados a esta Comissão, relatórios sobre andamento da pesquisa, conforme model ttp://www.uepg.br/coep/).

Data para entrega do relatório final: Logo após o fim da pesquisa.

Ponta Grossa, 30 de Abril de 2010.

UNIVERSIDADE ESTADUAL DE PONTA GROSSA
COMISSÃO DE ÉTICA EM PESQUISA - COEP
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