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ANDERSON CATELAN

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"INFLUÊNCIA DA DENSIDADE DE ENERGIA NAS PROPRIEDADES FÍSICAS E NA RESISTÊNCIA DE UNIÃO DE DOIS SISTEMAS RESTAURADORES"

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Orientador: Prof. Dr. Flávio Henrique Baggio Aguiar

“INFLUÊNCIA DA DENSIDADE DE ENERGIA NAS PROPRIEDADES FÍSICAS E NA RESISTÊNCIA DE UNIÃO DE DOIS SISTEMAS RESTAURADORES”

Doctorate thesis presented to the Piracicaba School of Dentistry of the University of Campinas to obtain the Ph.D. grade in Dental Clinic in the Operative Dentistry area.

Tese de Doutorado apresentada à Faculdade de Odontologia de Piracicaba da Universidade Estadual de Campinas para obtenção do título de doutor em Clínica Odontológica na área de Dentística.

ESTE EXEMPLAR CORRESPONDE À VERSÃO FINAL DA TESE DEFENDIDA PELO ALUNO, E ORIENTADA PELO PROF. DR. FLÁVIO HENRIQUE BAGGIO AGUIAR.

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“The future belongs to those who
believe in the beauty of their dreams”

Anna Eleanor Roosevelt

RESUMO

O propósito deste estudo foi avaliar a influência de diferentes densidades de energia nas propriedades físicas e na resistência de união de sistemas restauradores a base de metacrilato [Clearfil SE Bond (Kuraray) + Filtek Z250 (3M ESPE)] e silorano [sistema Filtek P90 (3M ESPE)], fotoativados com LED de segunda geração de acordo com os grupos experimentais. Espécimes foram confeccionados para o teste de grau de conversão (GC); os espectros de absorção foram obtidos por meio da espectroscopia FT-IR e FT-Raman para os adesivos (n = 10) e compósitos (n = 5), respectivamente. A dureza Knoop (DK) foi avaliada no topo e base dos compósitos (n = 10). Após 24 h de imersão em etanol absoluto, nova leitura de DK foi realizada para obtenção da plastificação (P) pela redução percentual da dureza. Os testes de sorção de água (SA) e solubilidade (S) dos adesivos (n = 5) e compósitos (n = 5) foram realizados de acordo com a norma 4049:2009, exceto para o tamanho dos espécimes e protocolo de fotoativação. Para os testes de resistência de união (n = 7) e nanoindentação (n = 3), cavidades Classe II foram realizadas nas proximais de molares humanos, as quais foram restauradas com os sistemas restauradores avaliados. O teste de microtração foi realizado em uma máquina de ensaio universal sob velocidade constante de 0,5 mm/min. Na técnica da nanoindentação foram mensurados a nanodureza (ND) e o módulo de elasticidade reduzido (Er) da dentina, camada híbrida, adesivo e compósito. Os dados obtidos foram submetidos à análise estatística (alfa = 0,05). Para os adesivos a maior densidade de energia melhorou somente o GC ($p < 0,05$); o “primer” da P90 exibiu maior GC, SA e S comparado ao “bond” do Clearfil e P90 ($p < 0,05$). O compósito metacrilato apresentou maior GC, DK, P e SA ($p < 0,05$) do que o silorano. Não houve diferença na S das resinas compostas ($p > 0,05$). Geralmente a superfície de topo mostrou maior GC e DK do que a base ($p < 0,05$). O sistema restaurador a base de metacrilato, bem como o aumento da densidade de energia mostraram maior resistência de união ($p < 0,05$), sem diferença entre 24 h e 6 meses ($p > 0,05$). Os valores de ND e Er dos materiais a base de metacrilato foram maiores do que os do silorano ($p < 0,05$). A maior densidade de energia não melhorou a ND e Er dos materiais ($p > 0,05$). O envelhecimento diminuiu a maioria das propriedades nanomecânicas dos componentes da interface dente-restauração ($p < 0,05$), exceto a ND e Er do compósito e Er do adesivo ($p > 0,05$). Assim, pode-se concluir que as propriedades físicas e a resistência de união foram material-dependente; a maior densidade de energia melhorou a resistência de união, mas não influenciou, em geral, as propriedades físicas e nanomecânicas; e o envelhecimento diminuiu a maioria das nanopropriedades dos componentes da interface dente-restauração, mas não afetou a resistência de união das restaurações.

Palavras-chave: Materiais dentários, Resinas compostas, Polimerização.

ABSTRACT

The purpose of this study was to evaluate the influence of different energy densities on the physical properties and bond strength of methacrylate- [Clearfil SE Bond (Kuraray) + Filtek Z250 (3M ESPE)] and silorane-based [Filtek P90 system (3M ESPE)] restorative systems, light-cured with a second generation LED according to experimental groups. Specimens were carried out for the degree of conversion (DC) test; the absorption spectra were obtained by FT-IR and FT-Raman spectroscopy for the adhesives (n = 10) and composites (n = 5), respectively. The Knoop hardness (KH) was evaluated at the top and bottom of the composites (n = 10). After 24 h of immersion in absolute ethanol, re-reading of KH was performed to obtain the percentage reduction of the hardness. The water sorption (WS) and solubility (S) tests of the adhesives (n = 5) and composites (n = 5) were performed according to ISO 4049:2009, except for specimens' dimension and light-curing protocol. For the bond strength (n = 7) and nanoindentation (n = 3) tests, Class II cavities were performed on the proximal of human molars, which were restored with the restorative systems evaluated. The microtensile test was carried out in an universal testing machine under cross-head speed of 0.5 mm/min. In the nanoindentation technique were measured the nanohardness (NH) and reduced elasticity modulus (Er) of the dentin, hybrid layer, adhesive, and composite. The data obtained were subjected to statistical analysis (alpha = 0.05). For the adhesives the highest energy density improved only the DC ($p < 0.05$); the "primer" of the P90 exhibited greater DC, WS, and S compared to "bond" of the Clearfil and P90 ($p < 0.05$). The methacrylate composite showed higher DC, KH, P, and WS ($p < 0.05$) than silorane. There was no difference in the S of the composites ($p > 0.05$). Generally the top surface showed greater of DC and KH than base ($p < 0.05$). The methacrylate-based restorative system, as well as increased energy density showed higher bond strength ($p < 0.05$), with no difference between 24 h and 6 months ($p > 0.05$). The NH and Er values methacrylate-based materials were greater than silorane ($p < 0.05$). The higher energy density did not improve the NH and Er materials ($p > 0.05$). The aging decreased the most nanomechanical properties of the components of the tooth-restoration interface ($p < 0.05$), except the NH and Er of the composite and Er of the adhesive ($p > 0.05$). Thus, it can be concluded that the physical properties and bond strength were material-dependent; the highest energy density improved the bond strength, but not influenced, in general, physical and nanomechanical properties; and the aging reduced the most nanoproperties of the components of the tooth-restoration interface, but did not affect the bond strength of restorations.

Keywords: Dental materials, Composite resins, Polymerization.

SUMÁRIO

1. INTRODUÇÃO

A composição química dos materiais resinosos utilizados nas restaurações dentais é complexa, pois eles contêm grande diversidade de monômeros e aditivos (Al-Hiyasat *et al*., 2005) que variam em tipo e concentração. Os monômeros mais utilizados nos compósitos odontológicos são o bisfenol-A glicidil metacrilato (Bis-GMA) e uretano dimetacrilato (UDMA); co-monômeros diluentes: trietileno glicol metacrilato (TEGDMA) e o bisfenol-A glicidil dimetacrilato etoxilado (Bis-EMA), como alternativa aos monômeros existentes (Sideridou & Achilias, 2005; Polydorou *et al*., 2007). Além dos monômeros, outros aditivos como fotoiniciadores (sendo a canforoquinona o mais utilizado), co-iniciadores e inibidores de polimerização estão presentes na composição do compósito (Polydorou *et al.*, 2007). Adesivos dentais contêm monômeros resinosos similares aos encontrados nos compósitos odontológicos, para obter união covalente entre eles e apresentam reação de polimerização semelhante (Miletic *et al.*, 2009).

A reação de polimerização dos compósitos resinosos e sistemas adesivos ocorre pela conversão dos monômeros em uma estrutura de polímeros com ligações cruzadas (Friedl *et al.*, 2000; Feilzer *et al.*, 1990). O desempenho clínico destes materiais resinosos é altamente dependente da conversão monomérica, da estrutura polimérica formada e da densidade de ligações cruzadas entre os polímeros formados para resistir às forças mastigatórias (Moon *et al.*, 2004; Gonçalves *et al.*, 2009). Quando a canforoquinona, molécula responsável por iniciar a reação de polimerização, absorve um fóton de luz (unidade final da energia luminosa) de comprimento de onda de, aproximadamente, 468 nm, um elétron desta molécula é impulsionado para um nível de energia maior, deixando-a em um estado excitado (Lehninguer, 1991). Assim, a canforoquinona colide com uma amina e um radical livre é formado. Este radical pode reagir com uma ligação dupla de carbono (C=C) de um monômero iniciando a reação de polimerização (Price *et al.*, 2002) e os monômeros que tiveram a dupla ligação de carbono quebrada em um ou nos dois extremos desta molécula reagem com outros monômeros na mesma situação, formando-se moléculas de polímeros.

Entretanto, a formação de macromoléculas de polímeros está associada à contração de polimerização dos materiais a base de metacrilato, podendo ocasionar falha da interface dente-restauração e diminuir a longevidade clínica das restaurações (Feilzer *et al.*, 1990; Friedl *et al.*, 2000). Na tentativa de minimizar os efeitos da contração de polimerização, foi desenvolvimento um sistema monomérico obtido a partir da reação das moléculas de oxirano e siloxano, denominado silorano. Este monômero é baseado na polimerização pela abertura do anel das moléculas do silorano através de uma reação de polimerização catiônica, em lugar da polimerização dos radicais livres dos monômeros metacrilato (Tezvergil-Mutluay *et al.*, 2008); propiciando menor contração de polimerização (Guggenberger & Weinmann, 2000; Tezvergil-Mutluay *et al.*, 2008), menos sorção de água e solubilidade (Palin *et al.*, 2005), e propriedades mecânicas similares quando comparado com materiais a base de metacrilato (Weinmann *et al.*, 2005; Ilie & Hickel, 2006).

Apesar da melhoria das propriedades dos materiais resinosos tem se verificado que eles não são totalmente polimerizados, pois apresentam monômeros residuais entre as estruturas de polímeros formadas e grupos pendentes (Asmussen & Peutzfeldt, 2001). Como o grau de conversão é relacionado com as propriedades físicas do compósito (Rueggeberg *et al.*, 1994), a quantidade de monômeros remanescentes é um co-determinante das propriedades do polímero resultante (Asmussen & Peutzfeldt, 2001). Quanto maior a intensidade da energia luminosa (*quantun*) usada no processo de fotoativação, mais fótons irão reagir com as moléculas de canforoquinona dentro da matriz resinosa, aumentando assim o grau de conversão; isto é, a quantidade de monômeros convertidos em polímeros. Dessa forma, a quantidade de energia luminosa é um importante fator que influencia o grau de conversão e contração de polimerização do compósito (Abade *et al.*, 2001).

Há muitos fatores que podem afetar a quantidade de energia luminosa que as superfícies de topo e de base de um incremento de compósito recebem, como tipo e tamanho da ponta do aparelho de fotoativação, distância entre a ponta e a superfície do compósito, irradiância e especificidade de luz da fonte ativadora, interação entre o comprimento de onda da fonte de luz e o agente iniciador da reação de polimerização, tempo de fotoativação, cor, opacidade, espessura e composição do compósito (Shortall *et al.*, 1995; Correr Sobrinho *et al.*, 2000a; Correr Sobrinho *et al.*, 2000b; Yap, 2000; Leloup *et al.*, 2002; Prati *et al.*, 1999). Se o incremento do compósito não receber energia suficiente para adequada reação de polimerização, problemas podem ocorrer, determinando o insucesso clínico da restauração. Entre eles, pode-se citar: alteração das propriedades físicas, aumento na taxa de pigmentação; aumento na taxa de desgaste, aumento do potencial de citotoxidade pela presença do monômero residual; fraca união entre dente, adesivo e compósito; e maior probabilidade de colapso na interface dente-restauração (Ferracane & Grener, 1984; Yap, 2000; Price *et al.*, 2002; Asmussen & Peutzfeldt, 2002; Asmussen & Peutzfeldt, 2003).

Dentre os fatores que podem reduzir a irradiância que atinge o compósito, o único que não pode ser controlado pelo cirurgião dentista durante a realização de uma restauração de uma cavidade profunda é a redução da distância entre a ponta do aparelho de fotoativação e a superfície do incremento do compósito. Em situações clínicas na qual se têm cavidades profundas, é comum a distância entre o primeiro incremento de compósito e a ponta do aparelho de fotoativação ser maior do que 6 mm, o que reduziria a densidade de energia que atinge a superfície do compósito, diminuindo o grau de conversão e/ou levando à formação de polímeros com estruturas lineares (Aguiar *et al.*, 2005). Em ambas as situações, o compósito poderá apresentar propriedades físicas inferiores, manchamento superficial e da interface, e influenciará no desempenho clínico da restauração (Atmadja & Bryant, 1990).

Como a distância entre a ponta do aparelho de fotoativação e a superfície do incremento do compósito é difícil de ser controlada, pois depende da extensão da cárie e da profundidade da cavidade após o preparo cavitário, devese atentar para outros fatores, como: potência óptica da fonte ativadora e a especificidade de luz emitida pelo aparelho de fotoativação na tentativa de se minimizar a redução da irradiância provocada pelo distanciamento da ponta do aparelho de fotoativação. Estudos têm mostrado melhores propriedades mecânicas de materiais resinosos com o aumento do tempo de fotoativação e, consequentemente, da densidade de energia disponível para conversão dos monômeros em polímeros (Yap & Seneviratne, 2001; Aguiar *et al*., 2007). Entretanto, verifica-se a importância em se avaliar as propriedades físicas e a durabilidade da resistência de união desse sistema restaurador a base de silorano com a variação da densidade de energia.

Dessa forma, os objetivos no presente estudo *in vitro*, composto por quatro artigos científicos, foram avaliar:

1) O grau de conversão, a sorção de água e a solubilidade de dois sistemas adesivos, variando a densidade de energia do aparelho de fotoativação (capítulo 1);

2) O grau de conversão, a microdureza Knoop, a plastificação, a sorção de água e a solubilidade de dois compósitos dentais, fotoativados por LED com diferentes densidades de energia (capítulo 2);

3) A resistência de união à microtração e o padrão de fratura de dois sistemas restauradores, variando a densidade de energia da fonte de luz e o armazenamento após 24 h e 6 meses, em cavidade simulada Classe II tipo *slot* vertical (capítulo 3);

4) A nanodureza e o módulo de elasticidade da dentina, da camada híbrida, do adesivo e da resina composta em restaurações Classe II realizadas com dois sistemas restauradores, submetidos a diferentes densidades de energia e armazenamento após 24 h e 6 meses (capítulo 4).

2. CAPÍTULOS

2.1. CAPÍTULO 1

Influence of the energy density on the degree of conversion, water sorption, and solubility of self-etch adhesives

Abstract

The purpose of this study was to investigate the influence of the energy density on the degree of conversion (DC), water sorption (WS), and solubility (S) of the Clearfil SE Bond (CSE) and Filtek P90 (P90) self-etch adhesive systems. The primer of the P90 (P90P), and bond agents of the CSE (CSEB) and P90 (P90B) were tested. Specimens were light-cured by second-generation light-emitting diode (LED) at different energy densities (6.1, 12.2, 13.9, and 27.8 J/cm^2). DC (n = 10) was measured using Fourier-transform infrared spectroscopy (FT-IR). The specimens were kept in a desiccator until that constant mass was obtained (m1); then its volumes were calculated (mm^3), and subsequently immersed in distilled water for 7 days (m2). Specimens were reconditioned to constant mass in desiccator (m3). WS and S (n = 5) were determined using the equations m2-m3/v and m1-m3/v, respectively. Data were subjected to two-way ANOVA and Tukey´s test at pre-set alpha of 0.05. The highest DC was exhibited by P90P, followed by CSEB and P90B, all with statistical difference ($p < 0.05$). The DC was increased with higher energy density and extended light-curing time ($p < 0.05$). P90B and CSEB showed the lower WS followed by P90P, all with statistical difference ($p < 0.05$). CSEB and P90B presented no significance difference on the S values ($p > 0.05$) and were lower than P90 ($p < 0.05$). The WS and S were not influenced by different energy densities evaluated ($p > 0.05$). The increase of the energy density improved only the DC, and P90P exhibited higher DC, WS, and S compared to CSEB and P90B.

Introduction

Currently, conservative restorative procedures can be performed with use of dental adhesives, through the bonding between the restorative material and hard tissues of the tooth.[1] An adequate adhesion to dental tissues is necessary for a long-term durability of the integrity of tooth-restorative material interface. Its failure results in the loss of the retention and marginal adaptation, and is the main reason for adhesive restorations replacement.[2,3]

Contemporary adhesives are classified in etch-and-rinse and self-etch.[3] These adhesives are light-cured and the energy density that reaches the material surface is an important factor that provides better mechanical properties, a low monomer conversion decreases the bonded interface strength and degradation resistance.[4,5] Water sorption (WS) and solubility can be associated to degree of conversion (DC) of resin-based materials.[6]

The increase of the distance between the light guide tip and resinous material surface in deep cavity restoration decreases the irradiance that reaches the restorative material, reducing the DC and/or leading to the formation of more linear polymers, presenting inferior physical properties.[7] The increase of the curing time, and consequently of the energy density available for monomer conversion can improve the physical properties of resin-based materials,[8-10] and thus increase the long-term durability of the adhesive restorations.[11]

The spectroscopy has been extensively used to quantify the remaining double carbon bonds of resin-based materials; high conversion of monomer into polymer is related to improve mechanical behavior[1,6,12] and more clinical longevity. However, the DC is not enough to characterize the 3-dimensional dental composite structure, whereas different C=C bond concentrations coexist in the same polymer.[12] The same DC value may result in different linear polymer content, which is more susceptible to softening than a more cross-linked polymer.[13,14]

Aqueous environment may cause softening of the resin-based materials by swelling of the polymer network and reduction of the frictional forces between polymer chains,[12] affecting the WS and S of resinous materials. Water sorption causes chemical degradation by filler-polymer de-bond and residual monomer release.[6] Moreover, the insufficient cross-linked polymer is more susceptible to plasticization effect by chemical substances that enter during eating and drinking.[15]

The objectives of this investigation were to evaluate the influence of the different energy densities on the DC, WS, and S of the primer of the Filtek P90, and bond agents of the Filtek P90 and Clearfil SE Bond. The null hypotheses tested were: (1) there would be no difference between the materials and (2) there would be no difference between the energy densities on the physical properties evaluated.

Materials and methods

The commercial self-etch adhesive systems investigated were Clearfil SE Bond (CSE) and Filtek P90 System Adhesive (P90). The primer of the P90 (P90P) and bond agents of the CSE (CSEB) and P90 (P90B) were tested. Details of the materials are shown in Table 1.

Table 1 – Materials used.

Material	Composition*
Clearfil SE Bond (Kuraray Medical Inc. Okayama, Japan)	Lot. 01416A bond (CSEB) MDP, Bis-GMA, HEMA, CQ, hydrophobic dimethacrylate, N,N-diethanol p-toluidine, colloidal silica.
Filtek P90 (3M ESPE AG, Seefeld, Germany)	Lot. 9BN primer (P90P) Bis-GMA, HEMA, water, ethanol, silica treated silica filler, CQ, phosphoric acid-methacryloxy-hexylesters mixture, phosphorylated methacrylates, copolymer of acryl and itaconic acid, phosphine oxide.
	Lot. 9BK bond (P90B) Hydrophobic dimethacrylate, phosphorylated methacrylates, TEGDMA, silane treated silica, CQ, stabilizers.

*As informed by manufacturers.

Abbreviations – MDP: 10-methacryloyloxydecyl dihydrogen phosphate; HEMA: 2-hydroxyethylmethacrylate; CQ: camphorquinone; Bis-GMA: bisphenol-A glycidyl dimethacrylate; TEGDMA: triethylene glycol dimethacrylate; and Bis-EMA: ethoxylated bisphenol-A dimetacrylate.

The degree of conversion assessment was obtained using a Fourier Transform Infrared (FT-IR) spectrometer (Spectrum 100 Optica, Perkin Elmer, MA, USA), equipped with an attenuated total reflectance (ATR) device with a horizontal ZnSe crystal (Pike Technologies, Madison, WI, USA). A constant volume of the resinous material (5 µL) was placed on the horizontal face of the ATR cell. Absorption spectra (n = 10) of the cured and uncured materials were obtained in the region between 1800 and 1400 cm^{-1} with 16 scans at 4 cm^{-1} of resolution. To calculate the DC the ratio (R) between the peak heights of the C=C aliphatic (1638 cm^{-1}) and aromatic group (1608 cm^{-1}, used as internal standard) band absorptions for cured and uncured composite was used, according to the formula: DC (%) = [1 – (R polymer / R monomer)] x 100.

Simulating clinical restorative procedure in a cavity of 6 mm of depth, light-curing of the samples were performed at 0 (control) and 6 mm of distance with a second-generation light-emitting diode (LED) Bluephase 16i (Vivadent, Bürs, Austria) device at 1390 mW/cm^2 of irradiance according to experimental groups (Table 2). A low-pressure air stream was gentle applied during 10 s for solvent evaporation of the solvated P90P. A holder coupled to the light source was used to standardize the distance between the light guide tip and material, controlled by digital caliper (Mitutoyo Sul Americana, Suzano, SP, Brazil). The optical power (mW) delivered by the device was measured with a power meter (Ophir Optronics, Har-Hotzvim, Jerusalem, Israel). The tip diameter was measured with digital caliper to determine tip area (cm^2). Irradiance (mW/cm^2) was calculated dividing optical power by tip area, and energy density (J/cm^2) the irradiance multiplied curing time divided by 1000.

Table 2 – Experimental groups.

Group	Material	Curing time, distance of photo-activation, and irradiance	Energy density
G1/G5/G9	CSEB/P90P/P90B	10 s, 6 mm, 610 mW/cm^2	6.1 J/cm^2
G2/G6/G10	CSEB/P90P/P90B	20 s, 6 mm, 610 mW/cm^2	12.2 J/cm^2
G3/G7/G11	CSEB/P90P/P90B	10 s, 0 mm, 1390 mW/cm^2	13.9 J/cm^2
G4/G8/G12	CSEB/P90P/P90B	20 s, 0 mm, 1390 mW/cm^2	27.8 J/cm^2

Clearfil SE Bond “bond” (CSEB); P90 System Adhesive “primer” (P90P); e P90 System Adhesive “bond” (P90B).

The water sorption and solubility were performed in compliance with ISO 4049:2009 standard specifications, except for the specimen dimensions and curing protocol. Silicon mold was used to prepare circular specimens (5 mm diameter and 0.5 mm thickness) of the materials. Solvated P90P was stored in dark room at 37 ^{o}C until constant mass to be obtained, indicating the solvent evaporation. The P90P, P90B, and CSEB materials were placed into mold, covered by Mylar strip, and irradiated according to experimental groups (Table 2).

The specimens (n = 5) were stored in desiccator at 37 ºC containing silica gel. The specimens were weighted daily in an analytical balance (Tel Marke, Bel Quimis, São Paulo, SP, Brazil) accurate to 0.001 mg, constituting a weighing cycle every 24 h. The complete cycle was repeated until a constant mass (m1) was obtained until that the mass loss of each specimen was not more than 0.1 mg per 24 h cycle. Thickness (4 measurements at four equally points on the circumference) and diameter (2 measurements at the right angles) of each specimen were measured using a digital electronic caliper. Mean values were used to calculate the volume (v) of each specimen (mm^3).

Thereafter, the specimens were stored in water at 37 ºC for 7 days, the volume of water for immersion being at less 6 mL per specimen. After this period, the specimens were carefully wiped with an absorbent paper and weighted again; this value was recorded as m2. After this weighting, the specimens were returned to the first desiccators and the entire mass reconditioning cycle was repeated and the constant mass was recorded as m3. The values for WS and S, in micrograms per cubic millimeters, were calculated using the following equations: WS = (m2 – m3) / v and S = (m1 – m3) / v.

The DC and WS data were analyzed by two-way analysis of variance (ANOVA) and Tukey´s test (alpha = 0.05). The S test data were submitted to non-parametric Kruskal Wallis and Dunn tests at the 5 % significance level.

Results

The higher DC was exhibited by P90P, followed by CSEB and P90B, all with statistical difference (p < 0.0001). The DC increased with the greater energy density and extended light-curing time (p < 0.0001). These findings are illustrated in the Table 3.

Table 3 – Degree of conversion (%) of the dental adhesives according to energy density and material.

Energy density (J/cm^2)	Material		
	Clearfil SE bond	Filtek P90 primer	Filtek P90 bond
6.1	59.44 (0.71) Bc	75.09 (0.70) Ab	51.33 (0.68) Cb
12.2	64.98 (0.87) Ba	82.57 (1.46) Aa	54.48 (0.38) Ca
13.9	62.13 (1.25) Bb	74.74 (0.87) Ab	51.00 (0.99) Cb
27.8	64.59 (0.24) Ba	82.80 (1.47) Aa	54.11 (0.48) Ca

Means (S.D.). Distinct letters (capital in the row and lower in the column) are statistically different (p < 0.05).

Table 4 shows water sorption values of the materials. P90B and CSEB showed the lower WS followed by P90P, all with statistical difference (p < 0.0001). There was no difference on the sorption at different energy densities tested (p = 0.9548).

Table 4 – Water sorption (µg/mm^3) of the dental adhesives, according to energy density and material.

Energy density (J/cm^2)	Material		
	Clearfil SE bond	Filtek P90 primer	Filtek P90 bond
6.1	67.70 (7.31)	139.51 (10.60)	18.82 (4.39)
12.2	67.16 (5.41)	137.95 (13.06)	18.32 (3.76)
13.9	66.67 (4.71)	138.88 (12.51)	17.79 (3.91)
27.8	65.88 (5.27)	136.49 (12.46)	18.60 (3.46)
	B	A	C

Means (S.D.). Distinct letters are statistically different among the materials ($p < 0.05$). There is no statistical difference among the energy densities ($p = 0.9548$).

CSEB and P90B presented no significance difference on the S values and were lower than P90P ($p < 0.05$); the solubility of the materials was not influenced by different energy densities evaluated ($p > 0.05$) (Table 5).

Table 5 – Solubility (µg/mm^3) of the dental adhesives, according to energy density and material.

Energy density (J/cm^2)	Material		
	Clearfil SE bond	Filtek P90 primer	Filtek P90 bond
6.10	8.26 (0.00; 8.37)	65.16 (50.88; 70.72)	8.61 (0.00; 8.88)
12.20	7.90 (0.00; 8.05)	55.85 (44.02; 61.93)	8.15 (0.00; 8.67)
13.90	8.04 (0.00; 8.57)	51.87 (50.71; 58.37)	8.01 (0.00; 8.24)
27.80	8.12 (0.00; 8.32)	52.63 (52.23; 55.05)	8.24 (0.00; 8.88)
	B	A	B

Median (minimum value; maximum value). Distinct letters are statistically different among the materials ($p < 0.05$). There is no statistical difference among the energy densities ($p = 0.7158$, 0.1649, and 0.7108 for CSEB, P90P, and P90B, respectively).

Discussion

This study evaluated the influence of the energy density on the DC, WS, and S of the gold standard self-etch adhesive (Clearfil SE Bond) and the specific adhesive system used on the bonding procedures of the low-shrinkage silorane composite (Filtek P90 System Adhesive). Clearfil SE Bond consists in a hydrophilic self-etch primer and hydrophobic bond agent, this viscous hydrophobic resin coating layer improves mechanical properties and increases longevity of the bonding interface.[4] Filtek P90 low shrinkage composite resin has a dedicated self-etching adhesive. The P90 Adhesive System is classified by manufacturer as two-step self-etch adhesive, firstly the hydrophilic P90 primer is applied and light-cured forming the hybrid layer.[16,17] Thus the bifunctional hydrophobic monomer (phosphorylated methacrylate) of the P90 bond applied after the primer cured acts as a low viscosity composite liner of connection between methacrylate monomers (by reaction with acrylate group) and silorane monomer (by reaction of the phosphate group with oxirane).[18] So P90 primer acts as one-step self-etch adhesive.[16,17]

The first null hypothesis was rejected, since the materials showed distinct physical behavior (Tables 3-5). Solvated adhesive (P90P) exhibited the highest DC values than non-solvent-free adhesives (P90B and CSEB). The solvent dilutes the viscous monomers increasing the mobility and improves the DC.[1] However, more amounts of hydrophilic monomers and solvent provided formation of linear chains, less resistant to degradation.[19] Bond agents are composed by solvent-free adhesives, these materials contain more hydrophobic monomers with higher viscosity, which result in lower mobility and more ability to form crosslinks and rigid polymers compared to solvated adhesives; resulting in the auto-deceleration of the polymerization reaction, and causes lower DC by limited conversion rate.[20,21] Thus, although the P90P had showed higher DC, more water sorption and solubility were observed comparable to P90B and CSEB, probably by low resistance to degradation of the solvated adhesive.

The second null hypothesis was partially rejected, once the increase of the energy density and extended light-curing time improved the DC (Table 3), but there is no difference on the WS and S (Tables 4 and 5, respectively). Low light intensity of the curing device results in inferior physical properties.[7] Only 1 mm of air interposed between tip of the light-curing unit and resin-based material decreases the light intensity by approximately 10 %.[22] Several studies have related to improve of the physical properties of resin-based materials with increase of energy density, due the higher DC.[4,8-10]

The light-curing device used in this investigation consists in single peak, second-generation LED, this unit presents a high irradiance (1390 mW/cm^2) and spectrum (between 410 and 530 nm, with a peak on the curve at 454 nm) that includes the maximum energy absorption peak of the camphorquinone at 468 nm, which absorbs a wide spectrum of wavelengths from 360 to 510 nm,[5] photo-initiator included in both adhesive systems tested. At 6 mm of distance, 610 mW/cm^2 of irradiance archived in the adhesive and greater energy density improved the monomer conversion rate. However, similar energy densities (12.2 J/cm^2 - 20 s of light-curing and 6 mm of distance at 610 mW/cm^2; and 13.9 J/cm^2 - 10 s and 0 mm at 1390 mW/cm^2) exhibited different DC values, seems that the extended time of light-curing increased the monomer conversion into polymer, but this difference did not affect the others physical properties tested. Thus, probably differences at the polymer structure can increase the adhesive interface degradation in the oral environment and reduce the clinical longevity of the restorations.

Conclusion

The increase of the energy density and extended light-curing time improved the monomer conversion, but no influenced the WS and S. Despite of the silorane primer had exhibited the highest degree of conversion, a higher water sorption and solubility was observed compared to bond agents of silorane and methacrylate adhesives.

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2.2. CAPÍTULO 2

Effect of the energy density on the physical properties of methacrylate- and silorane-based composites

Abstract

The objective of this study was to evaluate the effect of different energy densities on the degree of conversion (DC), Knoop hardness number (KHN), plasticization (P), water sorption (WS), and solubility (S) of different monomer resin-based. Circular specimens (5 X 2 mm) were carried out of the methacrylate (Filtek Z250, 3M ESPE) and silorane (Filtek P90, 3M ESPE) composite resins, and light-cured at 19.8, 27.8, 39.6, and 55.6 J/cm^2, using second-generation LED at 1390 mW/cm^2. After 24 h, DC (n = 5) was obtained using a FT-Raman spectrometer, KHN (n = 10) was measured with 50-g load for 15 s, and P (n = 10) was evaluated by percentage reduction of the hardness after 24 h immersed in absolute alcohol at top and bottom surfaces. The specimens were kept in a desiccator until that constant mass was obtained (m1), and then its volumes were calculated (mm^3), and subsequently immersed in distilled water for 7 days (m2). Specimens were reconditioned to constant mass in desiccator (m3). WS (n = 5) and S (n = 5) were determined using the equations m2-m3/v and m1-m3/v, respectively. Data were subjected to two-way ANOVA and Tukey´s test (alpha = 0.05). Methacrylate material presented higher DC, KHN, P, and WS than silorane ($p < 0.05$). There was no difference in the S values ($p > 0.05$). In general, top surface showed higher DC and KHN than bottom, for both materials ($p < 0.05$). The increase of the energy density did not improve most physical properties of the composites and were monomer-based dependent.

Introduction

Since the development of the composite resin in the 1960s, numerous improvements in its composition and characteristics were conducted; and with the increased demand by patients for esthetic restorations and simplification of the bonding procedures, light-cured composites have been widely used in the dental practice.[1] Currently dental composites are classified in nanofilled, microfilled or micro/nano hybrid composite resins.[2] These materials are composed basically by polymeric matrix based on the methacrylate monomers, inorganic fillers particles, silane, and photo-initiator system.[3] Bis-GMA is the most monomer used in dental composites, however due to its high molecular weight, high viscosity, and low mobility others monomers with lower viscosity and/or higher mobility, as TEGDMA and UDMA, are used for increase the degree of conversion (DC) and crosslinking of the polymer resultant.[3]

Methacrylate restorative materials exhibit volumetric polymerization shrinkage,[4] ranging from 1.9 to 3.5 vol%,[5] and a significant proportion of unreacted monomer due the incomplete C=C bond conversion.[6] However, a higher DC increases the shrinkage strain.[7,8] Polymerization stress may result in cuspal deflection,[9] de-bonding at adhesive interface, post-operative sensitivity,[10,11] microleakage,[10] marginal staining, secondary caries formation, restoration and dental fractures,[11] affecting the restoration durability. In the attempt to reduce these problems some techniques were proposed to decrease the shrinkage stress effects such as different incremental composite placement, light-curing protocols,[12] and intermediate layer with hybrid glass ionomer and flowable composite.[13]

A low shrinkage monomer, termed silorane, was developed from the reaction of the oxirane and siloxane molecules.[9,14,15] Silorane network is generated by cationic ring-opening polymerization mechanism instead of free radical cure of methacrylate monomers,[9,14] and more light-curing time to form cations is necessary to initiate the polymerization reaction.[4,9,16] It has been show lower polymerization shrinkage,[5,9,14] less than 1 vol%,[5] and mechanical properties comparable to conventional Bis-GMA composites.[5,15]

In deep cavities the reduction of the irradiance reaches in the material due the distance between guide tip and resinous material surface is one factor that cannot be controlled by dentist during the restorative procedure. Thus, the restoration weakening can occur by lower DC and/or formation of more linear polymers, presenting inferior physical properties, such as reduced hardness, increased wear, solubility, and discoloration.[17] The increase of the curing time, and consequently the energy density available for the monomer conversion can improve the physical properties of resin-based materials,[8,18,19] and thus increase the long-term durability of adhesive restorations.[2]

The DC is an important physical property that may have some impact on the restoration longevity, but this property alone is not enough to characterize the 3-dimensional dental composite structure, whereas different C=C bond concentrations coexist in the same polymer.[20] The same DC value may result in different linear polymer content, which is more susceptible to softening than a more cross-linked polymer.[6,21] Thus, the study of others physical properties together with DC measurement are better to knowledge of the performance of dental materials. The objectives of this study were to evaluate the effect of the energy density on the DC, Knoop hardness number (KHN), plasticization (P), water sorption (WS), and solubility (S) of methacrylate- and silorane-based composite resins. The hypotheses tested were that: (1) there would be no difference between the materials and (2) the higher energy density would improve the physical properties tested.

Materials and methods

Table 1 illustrates the material's details. Circular specimens (5 mm diameter and 2 mm thickness) were made for KHN and P (n = 10), and for DC, WS, and S (n = 5). The circular polytetrafluoroethylene mold was filled with the composite resin held between two glass slabs separated by Mylar strips and the pressed with a 500-g load, to compress the material, prevent bubble formation, and remove material excess.

Table 1 – Materials used.

Material	Composition*
Filtek Z250 (A2 shade; 3M ESPE, St. Paul, MN, USA)	Lot. N144001BR Filler: 60 vol%, aluminum oxide, silica, and zirconium oxide (0.01-3.5 µm). Resin: bisphenol-A glycidyl dimethacrylate (Bis-GMA), ethoxylated bisphenol A dimetacrylate (Bis-EMA), and urethane dimethacrylate (UDMA).
Filtek P90 (A2 shade; 3M ESPE, St. Paul, MN, USA)	Lot. N183458 Filler: 55 vol%, silica, and yttrium trifluoride (0.04-1.7 µm). Resin: Bis-3,4-Epoxycyclohexylethyl-Phenyl-Methylsilane and 3,4-Epoxycyclohexylcyclopolymethylsiloxane.

*According to manufacturers.

Cavities were filled with only one increment of composite, which was randomly light-cured set 0 or 4 mm from the top surface of the mold using a second generation light-emitting diode (LED) Bluephase 16i (Vivadent, Bürs, Austria) device at 1390 mW/cm^2 of irradiance according to Table 2. A holder coupled to the light source was used to standardize the distance between the light guide tip and material, controlled by digital caliper (Mitutoyo Sul Americana, Suzano, SP, Brazil).

Table 2 – Experimental groups.

Group	Composite	Curing time, distance of photo-activation, and irradiance	Energy density
G1/G5	Filtek Z250/P90	20 s, 4 mm, 990 mW/cm^2	19.8 J/cm^2
G2/G6	Filtek Z250/P90	20 s, 0 mm, 1390 mW/cm^2	27.8 J/cm^2
G3/G7	Filtek Z250/P90	40 s, 4 mm, 990 mW/cm^2	39.6 J/cm^2
G4/G8	Filtek Z250/P90	40 s, 0 mm, 1390 mW/cm^2	55.6 J/cm^2

The optical power (mW) delivered by the device was measured with a power meter (Ophir Optronics, Har-Hotzvim, Jerusalem, Israel). The tip diameter was measured with digital caliper (Mitutoyo Sul Americana, Suzano, SP, Brazil) to determine tip area (cm^2). Irradiance (mW/cm^2) was calculated dividing optical power by tip area, and energy density (J/cm^2) the irradiance multiplied curing time divided by 1000. Simulating clinical restorative procedure in a cavity of 6 mm of depth, the increment of composite with approximately 2 mm of thickness totalized in the top surface of first composite increment an energy density of 19.8 and 39.6 J/cm^2 at 990 mW/cm^2 (4 mm of distance between tip of curing light device and top surface of first composite increment), when light polymerized during 20 and 40 s, respectively. Control groups were light-cured for 20 and 40 s set 0 mm from restorative material surface at 1390 mW/cm^2, resulting in 27.8 and 55.6 J/cm^2, respectively (Table 2).

After polymerization, the specimens were removed from the matrices, dry stored in light proof containers at 37 ^{o}C for 24 h, and polished with 1200-grit silicon carbide (SiC) grinding paper (CarbiMet 2 Abrasive Discs, Buehler, Lake Bluff, IL, USA). The degree of conversion assessment was recorded in the absorbance mode using a Fourier Transform Raman (FT-Raman) spectrometer (RFS 100/S, Bruker Optics Inc., Billerica, MA, USA). Absorption spectra of the cured and uncured composites were obtained on the top and bottom surfaces with 64 scans at 4 cm^{-1} resolution in the region between 1000-2000 and 600-2000 cm^{-1} for methacrylate and silorane-based resins, respectively. To calculate the DC the ratio (R) between the peak heights of the C=C aliphatic (1638 cm^{-1}) and aromatic (1608 cm^{-1}) for methacrylate, and oxirane (1263 cm^{-1}) and siloxane (1000 cm^{-1}) for silorane band absorptions for cured and uncured composite was used. According to the formula: DC (%) = [1 – (R polymer/R monomer)] x 100.

Initial microhardness (MHi) reading was measured in the top and bottom surfaces of each specimen using a microhardness tester (HMV-2T, Shimadzu, Tokyo, Japan) with a Knoop diamond indenter under 50-g load for 15 s. Five indentations were made in each surface of the specimen, one at the center and others 4 at a distance of 100 µm from the central location. The average of the five KHN values was calculated for each specimen.

Plasticization analysis was evaluated by percentage reduction of the microhardness (%MHred) after absolute alcohol storage.[21] After MHi assessments, all specimens were immersed in the 100 % ethanol for 24 h. Following this period, a second microhardness measurement (MHf) was made as previously described. The same operator did the KHN test, before and after alcohol storage. The results were tabulated, and the P was calculated using the following equation: %MHred = 100 – [(MHf X 100) / MHi].

The water sorption and solubility were performed in compliance with ISO 4049:2009 standard specifications, except for the specimen dimensions and curing protocol. The specimens were stored in desiccator at 37 ºC containing silica gel and daily weighted in an analytical balance (Tel Marke, Bel Quimis, São Paulo, SP, Brazil) accurate to 0.001 mg, constituting a weighing cycle every 24 h. The complete cycle was repeated until a constant mass (m1) was obtained until that the mass loss of each specimen was not more than 0.1 mg per 24 h cycle. Thickness (4 measurements at four equally points on the circumference) and diameter (2 measurements at the right angles) of each specimen were measured using a digital electronic caliper. Mean values were used to calculate the volume (v) of each specimen (mm^3).

Thereafter, the specimens were stored in water at 37 ºC for 7 days, the volume of water for immersion being at less 6 mL per specimen. Specimens were weighted again after being carefully wiped with an absorbent paper; this value was recorded as m2. After this weighting, the specimens were returned to the first desiccators and the entire mass reconditioning cycle was repeated and the constant mass was recorded as m3. The values for WS and S, in micrograms per cubic millimeters, were calculated using the following equations: WS = (m2 – m3) / v and S = (m1 – m3) / v.

The experimental design of this study was constituted of 2 factors (material in 2 levels: methacrylate- and silorane-based micro-hybrid composite resins and, energy density in 4 levels: 19.8, 27.8, 39.6, and 55.6 J/cm^2). For DC, KHN, and P one sub-factor in 2 levels was added: top and bottom surfaces. DC, KHN, and P data were subjected to subdivided parcels 2-way ANOVA and Tukey´s test at a pre-set of 0.05. The factors material and energy density were considered in the parcels and the sub-factor surface (top and bottom) was considered in the sub-parcel. WS was analyzed by two-way ANOVA and Tukey´s test (alpha = 0.05), and S data were submitted to non-parametric Kruskal Wallis, Dunn, and Mann Whitney tests at the 5 % significance level.

Results

Table 3 illustrates the DC of the composite resins. The methacrylate material presented higher curing degree than silorane ($p < 0.001$), the DC of the top surface also was higher than bottom ($p = 0.015$), and no difference was observed to energy density ($p > 0.05$).

Table 3 – Degree of conversion (%) of the composite resins according to material, energy density, and surface analyzed.

Material	Energy density (J/cm^2)	Surface	
		Top$^{\#}$	Bottom
Filtek Z250*	19.8	62.68 (1.67)	61.09 (0.72)
	27.8	63.23 (1.39)	63.27 (1.95)
	39.6	63.90 (2.73)	62.25 (2.45)
	55.6	63.93 (1.83)	62.97 (2.29)
Filtek P90	19.8	45.61 (2.91)	44.82 (2.09)
	27.8	45.63 (1.78)	44.60 (0.78)
	39.6	45.42 (2.36)	44.85 (2.08)
	55.6	46.43 (3.30)	45.04 (1.92)

Means (S.D.). $^{\#}$It differs from the bottom surface ($p < 0.001$). There was no statistical difference for energy density ($p > 0.05$). *It differs from the Filtek P90 ($p = 0.015$).

Silorane material showed lower KHN than methacrylate ($p < 0.001$) as well as bottom compared to top surface ($p < 0.001$). The factor energy density ($p < 0.001$) and the interaction of the factor (composite resin) and sub-factor (surface analyzed) showed statistical differences ($p < 0.001$). In general, the lowest energy density tested presented lower KHN, except for the top surface of the silorane composite, which showed no difference between the energy densities tested (Table 4).

Table 4 – Knoop microhardness number (Kg/mm^2) of the composite resins according to material, energy density, and surface analyzed.

Material	Energy density (J/cm^2)	Surface	
		Top	Bottom
Filtek Z250*	19.8	63.23 (1.91) Ab	60.83 (1.73) Bb
	27.8	64.41 (1.17) Aab	62.85 (1.09) Aab
	39.6	66.17 (3.58) Aa	64.86 (1.55) Aa
	55.6	66.65 (0.95) Aa	64.35 (1.80) Ba
Filtek P90	19.8	52.77 (0.90) Aa	46,42 (0.89) Bb
	27.8	53.18 (1.53) Aa	48.75 (1.41) Ba
	39.6	53.56 (0.96) Aa	47.78 (1.15) Bab
	55.6	52.72 (1.48) Aa	49.23 (0.98) Ba

Means (S.D.). Distinct letters (capital in the row and lower in the column within of each composite) are statistically different ($p < 0.05$). *It differs from the Filtek P90 ($p < 0.001$).

The P test exhibited lower softening after ethanol storage for silorane than methacrylate resin-based composite ($p < 0.001$), no difference for energy density ($p = 0.0586$) and surface analyzed ($p = 0.5504$) was found (Table 5). In the Table 6, silorane also presented lower water sorption than methacrylate material ($p < 0.001$), but no statistical difference for energy density ($p = 0.8368$). There was no difference between the materials and energy densities for S ($p > 0.05$) (Table 7).

Table 5 – Plasticization (%) of the composite resins according to material, energy density, and surface analyzed.

Material	Energy density (J/cm^2)	Surface	
		Top	Bottom
Filtek Z250*	19.8	47.52 (1.90)	45.93 (2.08)
	27.8	47.27 (1.09)	46.19 (1.65)
	39.6	45.93 (2.57)	44.06 (1.72)
	55.6	46.31 (1.36)	44.94 (1.57)
Filtek P90	19.8	15.32 (3.52)	17.09 (3.27)
	27.8	14.93 (3.25)	16.43 (4.42)
	39.6	13.91 (2.53)	16.76 (2.73)
	55.6	13.43 (2.66)	14.98 (3.67)

Means (S.D.). There was no statistical difference for energy density ($p = 0.0586$) and surface analyzed ($p = 0.5504$). *It differs from the Filtek P90 ($p < 0.001$).

Table 6 – Water sorption (μg/mm^3) of the composite resins according to material and energy density.

Energy density (J/cm^2)	Material	
	Filtek Z250*	Filtek P90
19.8	16.41 (2.47)	8.97 (2.48)
27.8	16.61 (2.89)	8.48 (2.16)
39.6	15.53 (2.26)	8.44 (2.25)
55.6	15.46 (2.18)	8.33 (2.09)

Means (S.D.). *It differs from the Filtek P90 ($p < 0.001$). There was no statistical difference for energy density ($p > 0.8368$).

Table 7 – Solubility (μg/mm^3) of the composite resins according to material and energy density.

Energy density (J/cm^2)	Material	
	Filtek Z250	Filtek P90
19.8	0.00 (-4.92; 0.00)	0.00 (-4.55; 0.00)
27.8	0.00 (-4.58; 0.00)	0.00 (-4.29; 0.00)
39.6	0.00 (-4.70; 0.00)	0.00 (0.00; 0.00)
55.6	0.00 (0.00; 0.00)	0.00 (0.00; 0.00)

*Median (minimum value; maximum value). There was no significance difference between the energy densities ($p = 0.4565$ and $p = 0.2544$ for Z250 and P90, respectively) and between the composite resins ($p = 0.9089$, $p = 0.4604$, $p = 0.2126$, and $p = 1$ for 19.8, 27.8, 39.6, and 55.6 J/cm^2, respectively).

Discussion

The composite resins are widely used as restorative material in the dental practice and several clinical studies have reported an adequate durability of resin-based restorations even after an extended period of time.[2,22,23] The first hypothesis that both materials showed similar performance was partially rejected. Methacrylate composite presented higher DC, KHN, P, and WS than silorane (Tables 3-6); only in the S test no difference was found between the materials (Table 7). According to results of this current investigation, higher DC and KHN were found for methacrylate compared to silorane composite.[20] The UDMA monomer contained in the Filtek Z250 composite gives more mobility and has been related to increase DC;[3] and differences in the mechanism of the polymerization reaction can explain these results. Methacrylate is cured by radical intermediates and cycloaliphatic oxirane polymerizes via cationic intermediates.[5] Moreover, the onset of cationic ring-opening polymerization of the silorane is slower due to the necessary formation of sufficient cations to initiate the polymerization, thus more time of light-curing is required compared to radical cure of methacrylate monomers molecules into polymer network.[4,9,16]

Improvements of the mechanical properties have been associated to increase of the conversion of the monomer into polymer,[8,18,19] and also highly correlated to the filler fraction of composite resins.[24] The increase of the filler content has been associated with lower volumetric shrinkage, as it reduces the volume of organic matrix, and can affect negatively the DC by mobility restrictions imposed on the reactive species and light scattering.[25] Low hardness usually results in poor wear resistance[26] and has been related to filler fraction.[27] Silorane exhibits 55 vol% and methacrylate 60 vol% of inorganic filler. A positive correlation between the volume fraction of filler and hardness was found.[27] Thus, the higher

DC and filler content of the methacrylate can be influenced the highest KHN values than silorane composite.

Aqueous environment may cause softening of the resin-based materials by swelling of the polymer network and reduction of the frictional forces between polymer chains, resulting in lower hardness.[20] Moreover, the insufficient cross-linked polymer is more susceptible to plasticization effect by chemical substances that enter during eating and drinking.[28] Silorane represents a merger of siloxane and oxirane species. Siloxane reveals good biocompatibility even in uncured condition and high hydrophobicity and oxirane exhibits low shrinkage and high reactivity.[14] Unchanged in the Knoop hardness was reported for silorane after storage in water due to presence of the siloxane moiety, while the methacrylate composites were susceptible to softening.[20] Thus, this more hydrophobic nature of the silorane may contribute for lower WS and P comparable to conventional methacrylate resin-based.

The plasticization test has been used to evaluate indirectly the polymer cross-linked structure.[6,21] However, with the different hydrophobicity of the monomers tested this property is difficult to be correlated, as a material less susceptible to the deleterious effects and absorption of alcohol and with lower crosslink density could present a smaller hardness decrease after ethanol exposure. The solubility of the composite is strongly influenced by monomer conversion,[29] and high hydrophobicity of the siloxane species may decrease the S of the silorane.[20] Despite of the greater DC of the methacrylate, the higher hydrophobicity of the silorane composite could have compensated its lower monomer conversion and resulted in the same S values.

The light-curing time recommended for silorane composite resin using quartz-tungsten-halogen (QTH) with irradiance between 500-1400 mW/cm^2 is 40 s, as well as LEDs with output between 500-1000 mW/cm^2. For LEDs with irradiance between 1000-1500 mW/cm^2 is indicated an exposure light time of 20 s. A second generation LED was used in this study; this device shows single peak and high irradiance (1390 mW/cm^2), indicating 20 s of polymerization. This curing unit emits a narrow spectrum (between 410 and 530 nm, with a peak on the curve at 454 nm) that includes the maximum energy absorption peak of the camphorquinone at 468 nm, which absorbs a wide spectrum of wavelengths from 360 to 510 nm,[30] photo-initiator included in both composites tested.

The energy density that reaches the material is an important factor that provides better physical properties, the highest distance between the tip of light source and surface irradiated decreases the irradiance and can affect the polymerization effectiveness.[17] Only 1 mm of air interposed between tip of the light-curing unit and material restorative decreases the light irradiance in approximately 10 %.[31] Several studies have related to improve of the physical properties of resin-based materials with increase of energy density, due the higher DC.[8,18,19] In this investigation, the greater energy densities increase only hardness property (Table 4), and the second hypothesis also was partially rejected.

During the restorative procedure is common that the distance between the light guide tip and first composite increment surface placed at bottom of the cavity be 4 mm (cavity depth 6 mm and composite increment 2 mm). In this clinical simulation the irradiance achieved was of 990 mW/cm^2 at 4 mm, very near of the limit for light-cured during 20 s. Maybe the high light power of curing device was sufficient to form more cross-linked polymers,[6] that although of improve the mechanical behavior and polymer resistance to degradation, results in the deceleration of the polymerization reaction and limits the conversion rate.[32] Thus, with the high power LED used, the physical properties were little affected. However, special care should be taken when the polymerization of restorative materials using light-curing units of low irradiance power in deep cavities.

The top surface of composites showed higher DC and KHN than bottom, except for methacrylate at 27.8 and 39.6 J/cm^2 (Tables 3 and 4). The light-curing beneath of the restorative material at 4 mm of distance decreased the irradiance for 380 mW/cm^2 at bottom surface, approximately. The distance increased between the light guide tip and material, light scattering by filler particles, and the thickness of the composite decline the light intensity that reaches in the bottom surface of the restorative material,[17,25] resulting in lower DC and most hardness values of the bottom compared to top surface of the material.

A previous retrospective longitudinal study showed good performance of two posterior composite resins over 22 years; yet a lowest annual failure rate for the higher filler loaded composite was observed, suggesting that physical properties of the material may have some impact on the restoration longevity.[2] So, the principle small differences in the physical properties could result in identical clinical performance after short-term, but not over extended period of time.

Conclusions

The following conclusions were drawn of the current study: (1) the increased energy density improved the hardness; (2) methacrylate composite resin showed higher degree of conversion and microhardness; (3) silorane-based restorative material presented lower plasticization and water sorption; (4) there was no significant difference on the solubility between the different monomer-based composites tested.

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2.3. CAPÍTULO 3

Impact of the energy density and aging on the bond strength of methacrylate- and silorane-based restorative systems

Abstract

The purpose of this study was to evaluate the effect of different energy densities on the microtensile dentin bond strength of methacrylate- and silorane-based restorative systems after 24 h and 6 months of storage. Standardized Class II cavities were prepared in 56 freshly-extracted human molars (n = 7), restored with methacrylate [Clearfil SE Bond (Kuraray) + Filtek Z250 (3M ESPE)] or silorane [P90 restorative system (3M ESPE)] monomer-based materials, and light-cured according to experimental groups using second-generation light-emitting diode at 1390 mW/cm^2. After water storage for 24 h at 37 ^{o}C, the teeth were sectioned to yield a series of 0.8 mm thick slices. Each slab was trimmed into an hourglass shape of approximately 0.64 mm^2 area at the gingival dentin-resin interface. Specimens were tested using universal testing machine at cross-head speed of 0.5 mm/min until failure, after 24 h and 6 months. Fractured specimens were analyzed by scanning electronic microscopy to determine failure modes. Data were statistically analyzed by three-way ANOVA and Tukey´s test (alpha = 0.05). The methacrylate restorative system as well as increase of the energy density showed higher bond strength ($p < 0.05$). There was no statistical difference between 24 h and 6 months ($p > 0.05$). The dentin bond strength was influenced by the material and energy density; however, long-term storage after 6 months did not affect the bond durability of the restorations tested.

Introduction

Polymerization of methacrylate-based composite is characterized by volumetric shrinkage.[1] These photo-activated restorative materials exhibit significant proportion of methacrylate groups unreacted due the incomplete conversion of carbon double bonds.[2] However, as greater the degree of conversion (DC) highest the shrinkage strain.[3] Polymerization stress may result in cuspal deflection,[4] de-bonding at composite-dentin interface, post-operative sensitivity,[5,6] microleakage,[5] secondary caries formation, marginal staining, restoration and dental fractures,[6] all reducing the longevity of the restoration.

A low shrinkage monomer was development from the reaction of the oxirane and siloxane molecules, termed silorane.[4,7,8] Silorane chemistry present a cationic ring-opening polymerization mechanism instead of the free radical cure of methacrylate monomers[4,7] and more light-curing time to form cations is necessary to initiate the polymerization reaction.[1,4,9] It exhibits lower polymerization shrinkage[4,7,10] and mechanical properties comparable to methacrylate dental composites.[8]

In deep cavity the irradiance that reaches on the restorative material surface is decreased by the distance between the guide tip of the light-curing unit and material during the restorative procedure, reducing the degree of conversion, and/or leading to the formation of more polymers with linear structures, presenting inferior physical properties and will result in the weakening of the restoration.[11]

Improvement on the physical properties of resin-based materials with increase of the curing time, and thus of the energy density available for the conversion of monomers to polymers has been reported.[3,12,13] However, few studies have been assessed the bond strength of these new restorative system with the energy density variation and after aging. The objectives of this study were: to evaluate the influence of different monomer systems and energy density on the microtensile bond strength (microTBS) after 24 h and 6 months, as well as analyze the fracture modes. The hypotheses tested were therefore that: (1) there would be no difference between restorative systems, (2) the highest energy density would increase bond strength, and (3) the aging would decrease microTBS values.

Materials and method

This study was submitted and approved by Review Board of Ethics under protocol number 031/2010. Fifty-six freshly extracted non-carious, unrestored human molars were collected and stored in 0.1 % thymol solution at 4 ^{o}C. The teeth were scaled, cleaned, stored in distilled water at 4 ^{o}C, and used within 3 months after extraction.

The roots of the teeth were embedded in polystyrene resin (Piraglass, Piracicaba, SP, Brazil) to facilitate the manipulation, and occlusal surfaces were ground with 320-grit SiC paper under running water using polishing machine (APL-4, Arotec, São Paulo, SP, Brazil) until the distance between the occlusal surface and cementum-enamel junction was 5 mm. Standardized Class II slot cavities were performed in one of the proximal surfaces of human molars with cylindrical diamond bur (no. 3100, KG Sorensen, Barueri, SP, Brazil) using a high speed under water spray. The cavity was 4 mm wide, 6 mm high (1 mm below the cementum-enamel junction), and 2 mm deep. A custom-made preparation device allowed the standardization of the cavity dimensions. The margins were not beveled and burs were every replaced after five preparations.

Table 1 shows the materials' information used in this study. Methacrylate- (Clearfil SE Bond + Filtek Z250) and silorane-based (Filtek P90 system) restorative systems were used in the restorative procedures according to manufacturers' instructions.

Table 1 – Materials used.

Material	Composition*
Clearfil SE Bond (Kuraray Medical Inc. Okayama, Japan)	Lot. 00955A Primer MDP, HEMA, water, CQ, hydrophilic dimethacrylate. Lot. 01416A Bond MDP, Bis-GMA, HEMA, CQ, hydrophobic dimethacrylate, N,N-diethanol p-toluidine, colloidal silica.
Filtek P90 adhesive (3M ESPE, Seefeld, Germany)	Lot. 9BN Primer Bis-GMA, HEMA, water, ethanol, silica treated silica filler, CQ, phosphoric acid-methacryloxy-hexylesters mixture, phosphorylated methacrylates, copolymer of acryl and itaconic acid, phosphine oxide. Lot. 9BK Bond Hydrophobic dimethacrylate, phosphorylated methacrylates, TEGDMA, silane treated silica, CQ, stabilizers.
Filtek Z250 (A2 shade; 3M ESPE, St. Paul, MN, USA)	Lot. N144001BR Filler: 60 vol%, aluminum oxide, silica, and zirconium oxide (0.01-3.5 µm). Resin: Bis-GMA, Bis-EMA, and UDMA.
Filtek P90 composite (A2 shade; 3M ESPE, St. Paul, MN, USA)	Lot. N183458 Filler: 55 vol%, silica, and yttrium trifluoride (0.04-1.7 µm). Resin: Bis-3,4-Epoxycyclohexylethyl-Phenyl-Methylsilane and 3,4-Epoxycyclohexylcyclopolymethylsiloxane.

*As informed by manufacturers.

Abbreviations – MDP: 10-methacryloyloxydecyl dihydrogen phosphate; HEMA: 2-hydroxyethylmethacrylate; CQ: camphorquinone; Bis-GMA: bisphenol-A glycidyl dimethacrylate; TEGDMA: triethylene glycol dimethacrylate; Bis-EMA: ethoxylated bisphenol-A dimethacrylate; and UDMA: urethane dimethacrylate.

The cavities were sequentially randomized in 8 groups (n = 7), illustrates in Table 2, detailed by the following protocol: for methacrylate groups (1, 2, 5, and 6), firstly the primer of the Clearfil SE Bond was vigorously scrubbed with applicator brushes in throughout cavity during 20 s and mild air stream for solvent volatilization, then the bond was applied, gently air stream and light-cured. For silorane groups (3, 4, 7, and 8), Filtek P90 primer (bottle 1) was actively applied for

15 s, mild air stream, and cured. Then bond (bottle 2) was applied, gentle air stream, and cured. After bonding procedures, individual matrices were placed to allow the adequate filling of the proximal preparation. Three horizontal increments of approximately 2 mm of thickness each of the composite resin were inserted and light-cured according to experimental groups (Table 2).

Table 2 – Experimental groups.

Group	Restorative system	Curing time, distance of photoactivation, irradiance[#]	Energy density[#]
G1/G5*	Methacrylate	10/20, 6/4, 610/990	6.1/19.8
G2/G6*	Methacrylate	20/40, 6/4, 610/990	12.2/39.6
G3/G7*	Silorane	10/20, 6/4, 610/990	6.1/19.8
G4/G8*	Silorane	20/40, 6/4, 610/990	12.2/39.6

*Groups 24 h/6 months of water storage, respectively.

[#]Curing time (s), distance of photoactivation (mm), irradiance (mW/cm^2), and energy density (J/cm^2) used to cure the adhesive system and composite resin, respectively.

Resinous materials were light-cured by occlusal surface using a second-generation light-emitting diode (LED) Bluephase 16i (Ivoclar Vivadent) device at 1390 mW/cm^2 of irradiance. The optical power (mW) delivered by the device was measured with a power meter (Ophir Optronics, Har-Hotzvim, Jerusalem, Israel). The tip diameter was measured with digital caliper (Mitutoyo Sul Americana, Suzano, SP, Brazil) to determine tip area (cm^2). Irradiance (mW/cm^2) was calculated dividing light power by tip area, and energy density (J/cm^2) the irradiance multiplied curing time divided by 1000. The distance between tip of light-curing unit and bottom of cavity was 6 mm at 610 mW/cm^2 of irradiance; thus, when the adhesive systems were cured during 10 or 20 s resulted in 6.1 and 12.2 J/cm^2 of energy density, respectively. The increment of composite had 2 mm of thickness, approximately, totalizing in the top surface of first composite increment an energy density of 19.8 and 39.6 J/cm^2 at 990 mW/cm^2 (4 mm of distance between tip of curing light device and top surface of the first composite increment), when light polymerized during 20 and 40 s, respectively (Table 2). The irradiance on the bottom surface at 6 mm (with 2 mm beneath of the composite resin) was 380 mW/cm^2, approximately.

After restorative procedures, specimens were stored in distilled water at 37 ^oC for 24 h. After this period, the proximal surface was finished and polished with Al_2O_3 abrasive discs (Sof-Lex Pop-On, 3M ESPE, St. Paul, MN, USA), from coarse to superfine for 30 s with a handpiece rotating at approximately 10,000 rpm. Then, the restored teeth were vertically serially sectioned to yield 3 series of 0.8 mm thick slices using a diamond saw (Isomet 1000, Buehler, Lake Bluff, IL, USA) at 300 rpm. Each slab was trimmed into an hourglass shape of approximately 0.64 mm^2 area at the gingival resin-dentin interface using a super-fine diamond bur (no. 1090FF, KG Sorensen, Barueri, SP, Brazil). To aged groups (G5-G8, Table 2) the hourglasses were stored in distilled water at 37 ^oC for 6 months, changed weekly. So that all specimens suffer direct exposure to aging, and thus there was no influence of its exposure to direct/indirect to environmental of storage on the bond strength values,[14] and may be considered as a form of accelerated aging.[15]

Twenty-four hours or 6 months after water storage at 37 ^oC, the cross-sectional area of each hourglass was measured with a digital caliper to the nearest 0.01 mm and recorded for the calculation of the dentin bond strength. Each bonded slab was individually attached to a flat grip Geraldeli´s device for microtensile testing with cyanoacrylate instant adhesive (Super Bonder Gel, Loctite, Henkel, Brazil), and subjected to a tensile force using a universal testing machine (EMIC DL 500, São José dos Pinhas, SC, Brazil) at cross-head speed of 0.5 mm/min until failure. The number of slabs prematurely de-bonded during specimen preparation was recorded; however, no bond strength value was attributed for statistical analysis.[16] Means and standard deviations were calculated and expressed in mega Pascal (MPa).

After microtensile test, dentin side of the fractured specimens was dried by silica stored in incubator at 37 ^oC for 48 h, mounted on the aluminum stubs, and gold sputtered-coated under high vacuum (SCD 050, BAL-TEC AG, Balzers, Principality of Liechtenstein). A scanning electron microscope (JSM 5600 LV, JEOL, Tokyo, Japan) was used to evaluate the bond failure modes between 70 and 1000x and classified as follow: (1) cohesive in dentin, (2) adhesive, (3) cohesive in the composite, and (4) mixed. The microTBS data obtained were analyzed by three-way ANOVA and Tukey´s test at a 0.05 level of significance. The main factors were restorative system, energy density, and aging.

Results

In Table 3, it can be observed that methacrylate restorative system showed greater dentin bond strength than silorane ($p < 0.001$), the highest energy density provided higher microTBS values ($p = 0.0034$), and there was no statistical difference between 24 h and 6 months ($p > 0.05$).

Table 3 – Microtensile bond strength values [MPa (SD)] according to restorative system, aging, and energy density.

Restorative system		Energy density (J/cm^2)	
		6.1/19.8*	12.2/39.6*
Methacrylate[#]	24 h	28.01 (4.21) B	30.68 (4.89) A
	6 months	23.84 (3.91) B	28.15 (4.81) A
Silorane	24 h	17.18 (3.86) B	20.06 (3.31) A
	6 months	16.93 (3.20) B	20.37 (3.71) A

Means (S.D.). *Energy density used to cure the adhesive and composite, respectively. [#]Differs of silorane restorative system. Distinct letters in the row are statistically different ($p < 0.05$). There was no statistical difference for aging ($p > 0.05$).

The descriptive failure modes analysis for each restorative system is shown in Table 4.

Table 4 – Fracture pattern analysis.

Group	Pre-testing failure	Failure modes (%)			
		Cohesive in the dentin	Adhesive	Cohesive in the composite	Mixed
G1	3/21	-	76.47	-	23.53
G2	0/21	-	42.86	-	57.14
G3	3/21	-	16.67	-	83.33
G4	2/21	-	26.32	-	73.68
G5	3/21	-	88.24	-	11.76
G6	2/21	-	61.11	-	38.89
G7	3/21	-	27.78	-	72.22
G8	1/21	-	30.00	-	70.00

Discussion

The first hypothesis tested was rejected, since the methacrylate materials presented greater dentin bond strength than low shrinkage restorative system (Table 3); and it is according to previous study that showed higher microTBS to methacrylate than silorane composite regardless of the placement technique.[17] Self-etch adhesives are based on the absence of rinsing and drying steps, maintaining the ideal dentinal humidity and reducing the technique sensitivity.[15] Two-step self-etch adhesive consists of a self-etch primer with acid monomers that demineralize and simultaneously penetrate monomers into dentin subsurface, followed by application of hydrophobic bond agent solvent-free, which provides better mechanical properties.[18] All-in-one adhesive contains a mixture of acid, hydrophilic, and hydrophobic monomers, water and organic in one bottle.[18] This adhesive is more acid and hydrophilic, allowing deeper penetration with water content increases, due acidification of adhesive in the presence of water, and interfering in polymerization which leads to uncured acid and aggressive monomers to continue etching the dentin, affecting negatively the bonding interface.[18,19]

Clearfil SE Bond consists in a hydrophilic self-etch primer and hydrophobic bond agent, this viscous hydrophobic resin coating layer improves mechanical properties and increases longevity of the bonding interface.[18] Filtek P90 low shrinkage composite resin has a dedicated self-etching adhesive. Although of the P90 Adhesive System to be classified by manufacturer as two-step self-etch adhesive, firstly the hydrophilic P90 primer is applied and light-cured forming the hybrid layer.[1,20] Thus, the bifunctional hydrophobic monomer (phosphorylated methacrylate) of the P90 bond applied after the primer cured acts as a low viscosity composite liner of connection between methacrylate monomers (by reaction with acrylate group), and silorane monomer (by reaction of the phosphate group with oxirane).[10] So P90 primer may represent a one-step self-etch adhesive and could explain the lower bond strength values.[1,20]

The self-etch adhesives may be classified in 4 types: strong (pH < 1), intermediately strong (pH ± 1.5), mild (pH ± 2), and ultra-mild (pH ≥ 2.5).[21] The mild self-etch primer of Clearfil SE Bond has a pH of 2.0,[18] and is composed by functional acid monomer MDP, which adhere to hydroxyapatite of the tooth most readily and intensively,[22] this stable chemical bond was left around the collagen fibrils within the hybrid layer.[21] The self-etch P90 primer has a pH of 2.7[6] and is classified as ultra-mild.[1,6,21] Transmission electron microscopy (TEM) of this adhesive shows a thin nano-interaction zone, probably representing the combination of the resin-impregnation within smear layer and actual dentin hybridized.[1,6] The bonding effectiveness of the ultra-mild one-step self-etch adhesive is largely affected by the properties of the smear layer produced, because interacting superficially with the smear layer-covered dentin.[23] It has been reported that two-step self-etch adhesive systems performed better bonding ability than one-step self-etch adhesives.[15,19,21]

Increase of the energy density improved the microTBS of restorative systems tested (Table 3); thus the second hypothesis was validated. Only 1 mm of air interposed between tip of the light-curing unit and material restorative decreases the light intensity by approximately 10 %.[24] Several studies have related the improvement of the physical properties of resin-based materials with increase of energy density, due the higher DC.[3,12,13,18] A significant correlation exists between bond strength and total curing time by greater DC.[25] Special care should be taken when the polymerization of resinous materials using curing units of lower light power and deep cavities.

The onset of cationic ring-opening polymerization of the silorane is slower due the necessary formation of sufficient cations to initiate the polymerization, thus more time of light-curing is required compared to radical cure of methacrylate monomers molecules into polymer network.[1,4,9] The curing device used in this investigation consists in single peak, second generation LED, this unit presents a high optical power and spectrum between 410 and 530 nm with a peak on the curve at 454 nm that includes the maximum energy absorption peak of the camphorquinone at 468 nm, which absorbs a wide spectrum of wavelengths from 360 to 510 nm,[26] photo-initiator included in all resin-based materials tested.

The light-curing time recommended for silorane composite using quartz-tungsten-halogen (QTH) with irradiance between 500-1400 mW/cm^2 is 40 s, as well as LEDs with output between 500-1000 mW/cm^2. For LEDs with irradiance between 1000-1500 mW/cm^2 is indicated an exposure light time of 20 s. An irradiation of 10 s is recommended to cure the primer and bond of P90 Adhesive, without to indicate minimum irradiance. In this study, a LED with irradiance of 1390 mW/cm^2 was used, indicating 20 and 10 s of light polymerization for composite and adhesive, respectively. However, the irradiance achieved on the surface of first composite increment was of 990 mW/cm^2 at 4 mm of tip, and 610 mW/cm^2 at 6 mm for adhesive system. Furthermore, with the distance of 4 mm of the guide tip from the top surface of the composite and light-curing beneath the restorative material, the irradiance at the bottom surface was, approximately, 380 mW/cm^2. Bond strength is influenced by monomer conversion;[25] thus, the greater energy density could have increased the DC of adhesives and/or composites, and improved the dentin microTBS.

The third hypothesis was rejected because the long-term water storage did not affect the bond interface effectiveness of the restorations evaluated (Table 3). Interface components can be degraded by hydrolysis and the water can infiltrate and result in the plasticization of the polymeric matrix, by swelling and reduction of the frictional forces between the polymer chains, reducing the mechanical properties, and consequently bonding interface integrality.[15] However, the 6 months of water storage of this investigation did not decrease the microTBS values; similar result was previously reported[5]. Contrary, others studies showed a significant decrease in the bond strength after more short periods (within 3 months),[27,28] and even longer periods (within 4 years).[29,30]

The MDP contained in the Clearfil SE Bond adhesive system in contact with the tooth form the MDP-calcium salt hardly dissolved in water, therefore the bond between MDP and hydroxyapatite should be stable.[22] Thus, the chemical interaction improves the resistance to hydrolytic breakdown and de-bonding stress, keeping the restoration margins sealed for longer period.[21] Moreover the application of the primer followed by the hydrophobic bonding agent, contained mainly cross-linking monomers, Clearfil's bond provides better mechanical properties,[18] associated to methacrylate Filtek Z250 composite resin and high power density could be resulted long-term stability of the bond interface.

Single-bottle adhesives such as one-step self-etch P90 primer can act as permeable membranes and be more susceptible to aging,[31] and these adhesives are strongly influenced by light intensity of the photo-curing device.[18] Thus the second viscous hydrophobic coating layer (P90 bond) seems to have improved the vulnerable to water sorption resultant of the high HEMA content in the P90 primer, applied and cured previously,[6] after long-term water storage. Moreover, the active application of one-step self-etch adhesives has been related to improve the bonding performance,[32] along with the increased hydrophobicity of the silorane composite resin due to the presence of siloxane species[7,8] and high irradiance could be contributed to the bond longevity of this new restorative system.

The methacrylate restorative system showed more adhesive failures, while silorane exhibited more mixed failures (Table 4). The major of the silorane fractures occurred between the bond agent and composite, remaining bond on the dentin surface, perhaps due possible lower adhesion compared to adhesion between the methacrylate materials. The highest energy density increased the mixed failures and decreased the adhesive failures for methacrylate restorative system, likely by greater monomeric conversion. Water storage increased the adhesive failures percentage for both restorative systems, probably by water plasticization, probably by swelling of the polymer network and reduction of the frictional forces between polymeric chains.

The quality and uniformity of the polymerization reaction is an important parameter that affects the conversion of the monomers into structured polymers, and consequently improves the physical properties and clinical performance; however, this process is dependent of various factors, such as design and size of the tip guide, distance of the light guide tip from the material surface, power density, exposure duration, shade and opacity of the composite, increment thickness, materials' composition, and others.[11] Thus, the manufactures should provide information, such as minimum irradiance and time of light-curing required for optimal polymerization of their adhesive systems,[26] and make clear, in their manual instructions, that the minimum irradiance indicated is the that reaches on the surface of the material and not the optical power of output of the light-curing device, therefore more high irradiance is necessary to cure adequately materials light polymerized in deep cavities, and contribute to the improvement of the longevity of adhesive dental restorations.

Conclusion

The methacrylate restorative system and increase of the energy density exhibited higher dentin microtensile bond strength values; however, long-term storage after 6 months in distilled water did not affect the bond durability of the methacrylate- and silorane-based restorations tested.

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2.4. CAPÍTULO 4

Energy density and aging effects on the nanomechanical properties of methacrylate- and silorane-based restorations

Abstract

The aim of this study was to assess nanomechanically the influence of the energy density on the nanohardness (NH) and reduced elasticity modulus (Er) of the components of the dentin-restoration interface (underlying dentin, hybrid layer, adhesive, and composite) of methacrylate- and silorane-based materials at 24 h and 6 months following restorative procedure. Class II cavities were carried out in molars (n = 3) and restored with methacrylate (Clearfil SE Bond - Kuraray + Filtek Z250 - 3M ESPE) or silorane (P90 restorative system - 3M ESPE) materials, and light-cured according to time recommended by manufacturer´s instruction or double time, using LED at 1390 mW/cm^2. After 24 h, it was obtained one slice of each restoration, which was embedded in epoxy resin and polished. Nanoindentation measurements were performed in the components with fluid tip using TI 700 Ubi-1 nanoindenter (Hysitron). Three regions were selected and at each region, 3 indents were made with maximum load values of 100 and 1200 µN for hybrid layer and others components, respectively. Data were statistically analyzed by ANOVA and Tukey´s test ($\alpha = 0.05$). Generally the NH and Er values of the methacrylate were higher than silorane materials ($p < 0.05$). The greater energy density did not improve the NH and Er of the materials ($p > 0.05$). The aging decreased the most nanomechanical properties of the dentin-restoration interface components ($p < 0.05$). In general, nanomechanical properties decreased over time, methacrylate restorative system exhibited higher NH and Er than silorane, and energy density did not influenced the properties tested.

Introduction

The majority of the current composite resins are methacrylate-based monomer; but its polymerization is characterized by volumetric shrinkage.[1] These light-cured restorative materials exhibit a significant proportion of methacrylate groups unreacted due the incomplete conversion of the C=C bonds.[2] However, a higher monomer conversion rate results in greater the shrinkage strain.[3] Polymerization stress can result in cuspal deflection,[4] de-bonding at adhesive interface, post-operative sensitivity,[5,6] microleakage,[5] secondary caries, marginal discoloration, restoration and dental fractures,[6] all reducing the durability of the restorations.

A low shrinkage monomer was developed from the reaction of oxirane and siloxane molecules, named silorane.[4,7,8] Methacrylate polymerizes by free radical cure, while silorane chemistry present a cationic ring-opening polymerization mechanism,[4,7] and more light-curing time to form cations is necessary to initiate the polymerization reaction.[1,4,9] It exhibits lower polymerization shrinkage[4,7,10] and mechanical properties comparable to conventional methacrylate dental composites.[8]

During the restorative procedure, the distance between the guide tip of the light-curing unit and the resinous material surface in deep cavity reduces the irradiance that reaches in the restorative material and, decreases the monomer conversion and physical properties.[11] The increase of the curing time, and thus the energy density available for the conversion of monomers into polymers of light-cured resinous materials, improving the physical properties has been reported.[3,12,13]

The nanoindentation allows obtain the nanohardness (NH) and reduced elastic modulus (Er) of the resin-dentin interface components.[14] However, few studies have evaluated the effect of the energy density on the nanoproperties after long-term storage through of this technique, principally of the silorane monomer system. So, the objective of this study was to evaluate the influence of different monomers and energy density on the NH and reduced Er after 24 h and 6 months of storage. The hypotheses tested were: (1) there would be no difference between the materials, (2) the highest energy density would increase the NH and Er values of the materials, and (3) the aging would decrease the nanomechanical properties tested.

Materials and method

The Review Board of Ethics approved this study under protocol number 031/2010. Twelve freshly extracted non-carious, unrestored human molars were collected and stored in 0.1 % thymol solution at 4 ^{o}C. The teeth were cleaned, stored in distilled water at 4 ^{o}C, and used within 3 months after extraction.

The roots of teeth were embedded in polystyrene resin (Piraglass, Piracicaba, SP, Brazil) to facilitate the manipulation, and occlusal surfaces were grounded with 320-grit silicon carbide (SiC) grinding paper (CarbiMet 2 Abrasive Discs, Buehler Inc., Lake Bluff, IL, USA) under running water using polishing machine (APL-4, Arotec, São Paulo, SP, Brazil) until the distance between the occlusal surface and cementum-enamel junction was 5 mm. Standardized Class II slot cavities with margin in dentin tissue were performed in one of the proximal surfaces of human molars, with a high speed diamond bur (# 3100, KG Sorensen, Barueri, SP, Brazil), under water spray. The cavity was 4 mm wide, 6 mm high (1 mm below the cementum-enamel junction), and 2 mm deep. A custom-made preparation device allowed the standardization of the cavity dimensions. The margins were not beveled and burs were every replaced after five preparations.

Table 1 shows the materials information’s used in this study. Two composite resins (Filtek Z250 and Filtek P90) and self-etching adhesive systems (Clearfil SE Bond and Filtek P90 Adhesive) were used to restore the cavities.

Table 1 – Materials used.

Material	Composition*
Clearfil SE Bond (Kuraray Medical Inc. Okayama, Japan)	Lot. 00955A Primer MDP, HEMA, water, CQ, hydrophilic dimethacrylate. Lot. 01416A Bond MDP, Bis-GMA, HEMA, CQ, hydrophobic dimethacrylate, N,N-diethanol p-toluidine, colloidal silica.
Filtek P90 adhesive (3M ESPE, Seefeld, Germany)	Lot. 9BN Primer Bis-GMA, HEMA, water, ethanol, silica treated silica filler, CQ, phosphoric acid-methacryloxy-hexylesters mixture, phosphorylated methacrylates, copolymer of acryl and itaconic acid, phosphine oxide. Lot. 9BK Bond Hydrophobic dimethacrylate, phosphorylated methacrylates, TEGDMA, silane treated silica, CQ, stabilizers.
Filtek Z250 (A2 shade; 3M ESPE, St. Paul, MN, USA)	Lot. N144001BR Filler: 60 vol%, aluminum oxide, silica, and zirconium oxide (0.01-3.5 µm). Resin: Bis-GMA, Bis-EMA, and UDMA.
Filtek P90 composite (A2 shade; 3M ESPE, St. Paul, MN, USA)	Lot. N183458 Filler: 55 vol%, silica, and yttrium trifluoride (0.04-1.7 µm). Resin: Bis-3,4-Epoxycyclohexylethyl-Phenyl-Methylsilane and 3,4-Epoxycyclohexylcyclopolymethylsiloxane.

*As informed by manufacturers.

Abbreviations – MDP: 10-methacryloyloxydecyl dihydrogen phosphate; HEMA: 2-hydroxyethylmethacrylate; CQ: camphorquinone; Bis-GMA: bisphenol-A glycidyl dimethacrylate; TEGDMA: triethylene glycol dimethacrylate; Bis-EMA: ethoxylated bisphenol-A dimethacrylate; and UDMA: urethane dimethacrylate.

The cavities were sequentially randomized in 4 groups (n = 3), illustrates in Table 2, detailed by the following protocol: for methacrylate groups (1 and 2), firstly Clearfil SE Bond primer was vigorously scrubbed with applicator brushes in throughout cavity during 20 s and mild air stream for solvent volatilization, then the bond was applied, gently air stream and light-cured. For silorane groups (3 and 4), Filtek P90 Adhesive primer (bottle 1) was actively applied for 15 s, mild air stream, and cured. After, bond (bottle 2) was applied, gentle air stream, and cured. The composite resins were placed in three horizontal increments, approximately 2 mm thickness each, and light-cured according to experimental groups (Table 2).

Table 2 – Experimental groups.

Group*	Restorative system	Curing time, distance of photoactivation, irradiance[#]	Energy density[#]
G1/G5	Methacrylate	10/20, 6/4, 610/990	6.1/19.8
G2/G6	Methacrylate	20/40, 6/4, 610/990	12.2/39.6
G3/G7	Silorane	10/20, 6/4, 610/990	6.1/19.8
G4/G8	Silorane	20/40, 6/4, 610/990	12.2/39.6

*Groups 24 h/6 months of water storage, respectively.

[#] Curing time (s), distance of photoactivation (mm), irradiance (mW/cm^2), and energy density (J/cm^2) used to cure the adhesive system and composite resin, respectively.

Resin-based materials were light-cured by the occlusal surface using a second-generation light-emitting diode (LED) Bluephase 16i (Vivadent, Bürs, Austria) unit at 1390 mW/cm^2 of irradiance. The light power (mW) of device was measured with a power meter (Ophir Optronics, Har-Hotzvim, Jerusalem, Israel). The tip diameter was measured with digital caliper (Mitutoyo Sul Americana, Suzano, SP, Brazil) to determine tip area (cm^2). Irradiance (mW/cm^2) was calculated dividing light power by the tip area; and energy density (J/cm^2) the irradiance multiplied curing time divided by 1000. The distance between tip of light-curing unit and bottom of cavity was 6 mm at 610 mW/cm^2 of irradiance; thus, when the adhesive systems were light activated during 10 and 20 s resulted in 6.1 and 12.2 J/cm^2 of energy density, respectively. The increment of composite resins had 2 mm of thickness, approximately, totalizing in the top surface of first composite increment an energy density of 19.8 and 39.6 J/cm^2 at 990 mW/cm^2 (4 mm of distance between tip of curing light device and top surface of first composite increment), when light polymerized during 20 and 40 s, respectively.

The restoration was cut in half and the two halves of the restoration were embedded in epoxy resin (Buehler Inc., Lake Bluff, IL, USA) and grinded manually with 800-, 1000-, and 1200-grit SiC grinding paper (CarbiMet 2 Abrasive Discs, Buehler Inc., Lake Bluff, IL, USA) under running water. Standardized metallographic polishing technique was used, the samples were polished to a mirror-like finish with polycrystalline diamond suspensions of grades 9, 6, 3, 1 μm (MetaDi Supreme, Buehler Inc., Lake Bluff, IL, USA) and 0.05 μm alumina suspension polish (MasterPrep, Buehler Inc., Lake Bluff, IL, USA) on the soft polishing pads (MicroCloth, Buehler Inc., Lake Bluff, IL, USA). Between each polishing stage specimens were cleaned using an ultrasonic cleaner (Kendal CD 4800) with distilled water for five minutes.

Nanoindentation measurements were performed in the interface components with fluid tip using TI 700 Ubi-1 nanoindenter (Hysitron Inc., Minneapolis, MN, USA). This system operates with load- and displacement-controlled and allows for the simultaneous measurement of the load and displacement during the indentation. Metal disc was glued in the bottom of the block of epoxy resin for fixation on the nanoindenter's test platform. Wax was placed around of the boundary of the block and filled with Hanks' balanced salt solution (BioWhittaker, Lonza Walkersville Inc., Walkersville, MD, USA), in order to keep the specimen hydrated throughout the testing procedure. Three regions were selected visually, using optical microscope coupled to equipment. Attached to microscope a three-axis piezo scanner (TriboScan, Hysitron Inc.) controls the tip positioning as well as in situ imaging and the load-displacement transducer with a probe attached is used to indent the specimen while collect the load-displacement data.

Elongated pyramidal Berkovich fluid diamond probe, approximately 4 mm in length (curvature radius ≈ 100 nm, Hysitron Inc.), allows that the end of the probe to be completely immersed in a fluid, while the probe holder and transducer remain in the air, thus imaging and testing on the hydrated samples are possible. At each region three indentations were made in each interface component (dentin, hybrid layer, adhesive, and composite) with maximum load values of 100 and 1200 μN for hybrid layer and others components, respectively; under a standard trapezoidal load function of 10-40-10 s. Nine indentations were realized per restoration in each component evaluated, and the average of this 9 measurements was used to calculate the NH and Er of the dentin, hybrid layer, adhesive, and composite of each specimen.

The indentation load-displacement data collected were used to calculate the NH and Er by the TriboScope software (version 8.2.0.14, Hysitron Inc.), using Oliver-Pharr method.[15] The samples were stored in Hank's solution for 6 months, to prevent tooth demineralization and keep it hydrated, changed weekly.[16]

Nanomechanical properties readings at 24 h and 6 months were performed in the same sample, and proc-mixed analysis of variance (ANOVA) was used for repeated measures. NH and Er of the bond layer of the Filtek P90 System Adhesive was subjected to 2-way ANOVA and Tukey's test at a pre-set alpha of 0.05. The NH and Er data of the dentin, hybrid layer, adhesive, and composite were analyzed by 3-way ANOVA and Tukey's test (alpha = 0.05).

Results

Nanomechanical properties of the underlying intertubular dentin were not influenced by the material and energy density ($p > 0.05$), decreasing over time ($p < 0.05$) (Table 3). The greater energy density did not improve the NH and Er of the materials ($p > 0.05$) (Tables 4-7).

NH and Er values of the methacrylate were higher than silorane-based materials ($p < 0.05$) (Tables 4, 5, and 7), except Er of the adhesive at 24 h measurement for both energy densities ($p > 0.05$) (Table 5).

The 6 months of the storage aging decreased the NH and Er values of the dentin-restoration interface components ($p < 0.05$) (Tables 4-6), except for Er of the adhesive ($p > 0.05$) (Table 5). The NH and Er of the composite resin did not influenced by the aging ($p > 0.05$) (Table 7).

Table 3 – Nanohardness (NH) and reduced elastic modulus (Er) of the dentin according to energy density, restorative system, and aging.

Energy density (J/cm^2)	Restorative system	NH (MPa)		Er (GPa)	
		24 h	6 months	24 h	6 months
6.1/19.8	Clearfil + Z250	1289.63 (125.56) A	959.96 (48.78) B	23.73 (2.86) A	20.28 (1.61) B
	P90 system	1390.26 (122.44) A	1002,69 (51.63) B	23.83 (1.71) A	20.70 (0.82) B
12.2/39.6	Clearfil + Z250	1301.85 (104.63) A	1030.12 (138.79) B	24.37 (1.88) A	20.34 (2.67) B
	P90 system	1290.56 (112.23) A	993.80 (100.44) B	24.11 (1.54) A	20.78 (0.90) B

Means (S.D.). *Adhesive system/composite resin, respectively. Distinct letters in the row are statistically different ($p < 0.05$).

Table 4 – Nanohardness (NH) and reduced elastic modulus (Er) of the hybrid layer according to energy density, adhesive system, and aging.

Energy density (J/cm^2)	Adhesive system	NH (MPa)		Er (GPa)	
		24 h	6 months	24 h	6 months
6.1	Clearfil	379.18 (106.38) Aa	126.56 (47.62) Ba	6.12 (1.49) Aa	2.40 (0.72) Ba
	P90 primer	252.94 (97.36) Ab	89.02 (13.71) Bb	5.01 (1.51) Ab	1.54 (0.15) Bb
12.2	Clearfil	383.15 (40.25) Aa	292.96 (33.23) Ba	6.08 (0.19) Aa	4.90 (0.67) Ba
	P90 primer	327.26 (124.05) Ab	97.75 (23.67) Bb	5.33 (1.57) Ab	1.90 (0.48) Bb

Means (S.D.). Distinct letters (capital in the row and lower in the column) are statistically different ($p < 0.05$).

Table 5 – Nanohardness (NH) and reduced elastic modulus (Er) of the adhesive according to energy density, adhesive system, and aging.

Energy density (J/cm^2)	Adhesive system	NH (MPa)		Er (GPa)	
		24 h	6 months	24 h	6 months
6.1	Clearfil	258.41 (82.29) Aa	186.74 (19.12) Ba	5.65 (2.07) a	6.18 (0.91) a
	P90 primer	191.62 (34.85) Ab	108.38 (14.32) Bb	4.21 (0.65) a	2.36 (0.20) b
12.2	Clearfil	282.55 (43.85) Aa	211.21 (26.91) Ba	5.89 (0.92) a	5.35 (0.58) a
	P90 primer	204.95 (32.06) Ab	137.65 (10.67) Bb	3.90 (0.70) a	2.80 (0.14) b

Means (S.D.). Distinct letters (capital in the row and lower in the column) are statistically different ($p < 0.05$).

Table 6 – Nanohardness (NH) and reduced elastic modulus (Er) of the bond of the Filtek P90 System Adhesive according to energy density and aging.

Energy density (J/cm^2)	NH (MPa)		Er (GPa)	
	24 h	6 months	24 h	6 months
6.1	338.25 (27.41) A	270.45 (4.21) B	5.29 (0.36) A	4.55 (0.04) B
12.2	332.23 (25.41) A	296.73 (19.17) B	5.56 (0.19) A	4.89 (0.30) B

Means (S.D.). Distint letters in the row are statistically different ($p < 0.05$).

Table 7 – Nanohardness (NH) and reduced elastic modulus (Er) of the composite resin according to energy density and aging.

Energy density (J/cm^2)	Composite resin	NH (MPa)		Er (GPa)	
		24 h	6 months	24 h	6 months
19.8	Filtek Z250	1108.90 (231.02) a	977.41 (23.95) a	16.79 (2.93) a	15.59 (0.80) a
	Filtek P90	777.16 (62.87) b	638.25 (65.45) b	13.16 (1.33) b	12.53 (1.41) b
39.6	Filtek Z250	1123.62 (155.86) a	1089.33 (31.00) a	16.63 (1.67) a	17.72 (0.98) a
	Filtek P90	793.06 (50.74) b	750.52 (74.76) b	13.80 (0.95) b	12.45 (1.48) b

Means (S.D.). Distinct letters in the column are statistically different ($p < 0.05$).

Discussion

Longevity of adhesive restorations is dependent of an adequate and stable adhesion of the restorative materials to dental hard tissues over time. The first hypothesis tested was partially accepted; the methacrylate restorative system showed higher nanomechanical properties than silorane system, except for Er of the adhesive at 24 h measurement (Tables 4, 5, and 7). Self-etch adhesives are less sensitive technically by absence of the rinsing and drying steps, maintaining the ideal dentin humidity and reducing the risk of errors during application.[17] Two-step self-etch adhesive contains an acid primer that demineralizes and penetrates monomers into dentin subsurface simultaneously; followed by application of the solvent-free hydrophobic bond agent that improves the mechanical properties.[18] One-step self-etch adhesive contains a mixture of acid, organic solvents, water, hydrophilic, and hydrophobic monomers in a single bottle.[18]

Clearfil SE Bond consists in a hydrophilic self-etch primer and a solvent-free hydrophobic bond agent, this viscous hydrophobic resin coating layer can increase the mechanical properties for containing monomers with more ability to form crosslinks.[18] A dedicated self-etch adhesive was formulated for Filtek P90 low shrinkage composite, classified by manufacturer as two-step self-etch adhesive, termed Filtek P90 System Adhesive. Firstly the hydrophilic and solvated P90 primer is applied and light-cured creating the hybrid layer.[1,19] P90 bond is applied after the primer cured and acts as a low viscosity liner of connection by bifunctional hydrophobic monomer (phosphorylated methacrylate) between the methacrylate monomers by reaction with acrylate group, and silorane monomer by reaction of the phosphate group with oxirane.[10] So P90 primer may represent an one-step self-etch adhesive.[1,19] The solvated adhesives, such as P90 primer, have been related to worse mechanical properties, despite of the DC improvement by mobility increased of the molecules, than solvent-free adhesives.[20] Thus, the bond agent of the Clearfil applied after the primer may have promoted better mechanical behavior with higher NH and Er, of the hybrid layer and adhesive, compared to P90 primer.

Sufficient cations are necessary to initiate the cationic ring-opening polymerization of the silorane composite, the onset of this reaction is more slower and more time of light-curing is required compared to radical cure of the methacrylate monomers into polymer network.[1,4,9] Higher DC, Knoop microhardness, and depth of cure were found for methacrylate than silorane composite in a previous study.[21] Thus, the superior physical properties of the methacrylate-based composite probably resulted in highest NH and Er values than silorane.

The second hypothesis was rejected, since the energy density did not influence the NH and Er values of the materials (Tables 4-7). Improvements on the physical properties of resin-based materials have been related to increase of the energy density, due the higher DC.[3,12,13,17] Light intensity is reduced approximately in 10 % by 1 mm of air interposed between guide tip of the light-curing unit and material surface irradiated.[22] Special care in deep cavities and curing unit with low light power should be taken during the polymerization of resinous materials.

The light-curing time recommended for silorane composite resin using quartz-tungsten-halogen (QTH) with irradiance between 500-1400 mW/cm^2 is 40 s, as well as LEDs with output between 500-1000 mW/cm^2. For LEDs with irradiance between 1000-1500 mW/cm^2 is indicated an exposure light time of 20 s. An irradiation of 10 s is recommended to cure the primer and bond of P90 System Adhesive, without to indicate minimum irradiance. In this study, a high light power LED of 1390 mW/cm^2 was used, indicating 20 and 10 s of light polymerization for composite and adhesive, respectively. However, the irradiance achieved on the surface of first composite increment was of 990 mW/cm^2 at 4 mm of guide tip and 610 mW/cm^2 at 6 mm for adhesive system.

A second generation LED unit used exhibits a narrow spectrum (between 410 and 530 nm, with a peak on the curve at 454 nm), which includes the maximum energy absorption peak of the camphorquinone at 468 nm that absorbs wavelengths from 360 to 510 nm,[23] photo-initiator included in all resin-based materials evaluated. However, the increase of the energy density available for light polymerization did not improve the NH and Er of the materials, perhaps the high light power was sufficient to form more cross-linked polymers, which are less susceptible to degradation than linear polymers,[2] but results in the deceleration of the polymerization reaction and limits the conversion rate.[24]

The third hypothesis was partially validated because the long-term storage decreased the most nanomechanical properties of the components of the dentin-restoration interface (Tables 4-6). Bonding interface components can be degraded by hydrolysis, the water sorption results in the polymer plasticization by swelling and reduction of the frictional forces between the polymer chains, decreasing the mechanical properties.[17]

The MDP monomer contained in the Clearfil in contact with the dental tissues form the MDP-calcium salt hardly dissolved in water; therefore the bond between MDP and hydroxyapatite should be stable.[25] Thus, the chemical interaction improves the resistance to hydrolytic breakdown and de-bonding stress, keeping the restoration margins sealed for longer period.[26] Moreover the hydrophobic bonding agent application after hydrophilic primer improves the mechanical properties by presence of the cross-linking monomers.[18]

All-in-one adhesives such as one-step self-etch P90 primer acts as permeable membranes and can be more susceptible to aging,[27] these adhesives are strongly influenced by light intensity of the curing unit.[18] The bond of the P90 adhesive also is solvent-free and contains more monomers with more ability to form crosslinks.[18,20] The nanomechanical properties of the components of the adhesive interface (hybrid layer, adhesive, and bond layer of the P90) were reduced after storage, except the Er of the adhesive (Table 5). However, although of the solvated P90 primer has showed the same Er of the Clearfil at 24 h, after aging it exhibited decrease this property, probably by greater susceptible to plasticization due the more amount of hydrophilic monomers and possible residual solvent.

Siloxane species present in the silorane composite exhibit high hydrophobicity,[7,8] the NH and Er of this material was not affected after 6 months of storage, probably due to hydrophobic nature of the siloxane specie (Table 7). The higher conversion rate of the methacrylate composite than silorane[21] may has compensated its lower hydrophobicity and increased the plasticization resistance of the Filtek Z250, which also did not have its properties decreased by aging. The nanomechanical properties of the underlying intertubular dentin were decreased over time (Table 3).

The conversion of the monomers into structured polymers is related to the increase of the physical properties of the resinous material, this polymerization reaction is dependent of various factors, such as design and size of the tip guide, distance of the light guide tip from the material surface, power density, exposure duration, shade and opacity of the composite, increment thickness, composition of the materials; resulting in clinical performance improvement of light-cured materials and more durability of the adhesive restorations.[11]

Conclusion

In general, nanomechanical properties decreased over time, methacrylate restorative system exhibited higher NH and Er than silorane, and energy density were not influenced the properties tested.

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3. CONCLUSÕES

Com os resultados do presente estudo as seguintes conclusões foram obtidas:

1) O aumento da densidade de energia melhorou o grau de conversão dos sistemas adesivos, mas não teve influência na sorção de água e solubilidade. O “primer” do sistema adesivo a base de silorano exibiu maior grau de conversão, mas maior sorção e solubilidade do que o “bond” do mesmo sistema e o “bond” do adesivo a base de metacrilato;

2) A resina composta a base de metacrilato apresentou maior grau de conversão e microdureza, enquanto o compósito a base de silorano mostrou menor plastificação e sorção de água. Os valores de solubilidade não foram influenciados pela densidade de energia e não houve diferença entre os materiais. A maior da densidade de energia aumentou apenas a dureza Knoop;

3) A resistência de união da dentina ao teste de microtração foi melhorada com o aumento da densidade de energia. O sistema restaurador a base de metacrilato exibiu maior resistência de união do que o a base de silorano e esta não foi afetada pelos 6 meses de armazenamento para ambos sistemas restauradores;

4) De uma maneira geral, as propriedades nanomecânicas foram reduzidas com o envelhecimento. O sistema restaurador a base de metacrilato mostrou maiores valores de nanodureza e módulo de elasticidade reduzido do que o sistema a base de silorano e o aumento da densidade de energia não aumentou as nanopropriedades testadas.

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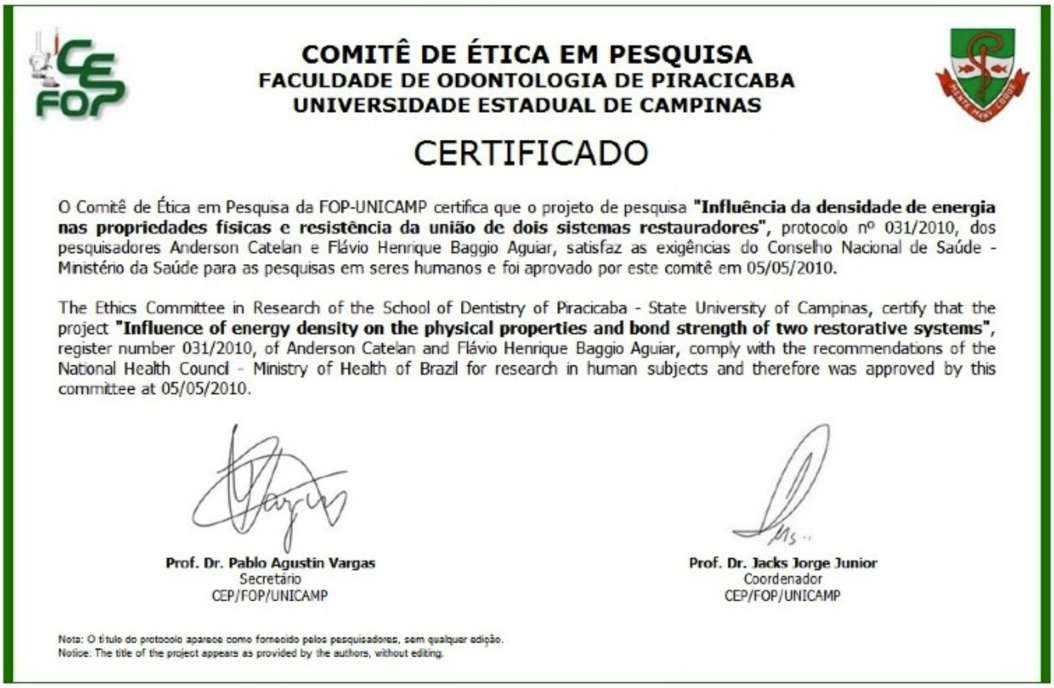
5. ANEXO



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CERTIFICADO

O Comitê de Ética em Pesquisa da FOP-UNICAMP certifica que o projeto de pesquisa **"Influência da densidade de energia nas propriedades físicas e resistência da união de dois sistemas restauradores"**, protocolo nº 031/2010, dos pesquisadores Anderson Catelan e Flávio Henrique Baggio Aguiar, satisfaz as exigências do Conselho Nacional de Saúde - Ministério da Saúde para as pesquisas em seres humanos e foi aprovado por este comitê em 05/05/2010.

The Ethics Committee in Research of the School of Dentistry of Piracicaba - State University of Campinas, certify that the project **"Influence of energy density on the physical properties and bond strength of two restorative systems"**, register number 031/2010, of Anderson Catelan and Flávio Henrique Baggio Aguiar, comply with the recommendations of the National Health Council - Ministry of Health of Brazil for research in human subjects and therefore was approved by this committee at 05/05/2010.

Prof. Dr. Pablo Agustin Vargas
Secretário
CEP/FOP/UNICAMP

Prof. Dr. Jacks Jorge Junior
Coordenador
CEP/FOP/UNICAMP

Nota: O título do protocolo aparece como fornecido pelos pesquisadores, sem qualquer edição.
Notice: The title of the project appears as provided by the authors, without editing.