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FACULDADE DE ODONTOLOGIA DE PIRACICABA

LÍVIA AGUILERA GAGLIANONE

CIRURGIÃ-DENTISTA

INFLUÊNCIA DE DIFERENTES FONTES DE LUZ E DISTÂNCIAS DE ATIVAÇÃO NO GRAU DE CONVERSÃO E PROPRIEDADES MECÂNICAS DE SISTEMAS ADESIVOS

Dissertação apresentada à Faculdade de Odontologia de Piracicaba, da Universidade Estadual de Campinas, para obtenção do Título de Mestre em Clínica Odontológica – Área de Concentração em Dentística.

Orientadora: Profa. Dra. Giselle M. Marchi Baron

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Profa. Dra. PAULA MATHIAS RABELO DE MORAIS

Prof. Dr. CESAR AUGUSTO GALVÃO ARRAIS

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"Foi o tempo que dedicaste à tua rosa
que fez tua rosa tão importante."

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RESUMO

O objetivo do presente trabalho foi avaliar a influência de diferentes fontes de luz e distâncias de ativação no grau de conversão (GC) e nas propriedades mecânicas (módulo de elasticidade - ME e resistência à flexão - RF) de cinco sistemas adesivos (*Scotchbond MP Plus* - SBMP; *Single Bond 2* - SB2; *One-up Bond F Plus* - OUP; *Clearfil Protect Bond* - CP, e *P90 System Adhesive: primer* - P90P e adesivo - P90B). Para realização dos testes, no experimento 1, as amostras de cada sistema adesivo foram divididas em três grupos (n=5), de acordo com as distâncias de ativação (2, 4 e 6 mm), enquanto que, no experimento 2, os espécimes foram divididos em dois grupos (n=5), dependendo da fonte de luz utilizada: halógena de quartzo-tungstênio (QTH) ou luz emitida por diodo (LED). Todos os adesivos foram fotoativados por 10s, exceto OUP cujo tempo de polimerização foi aumentado para 30s. Para avaliação das propriedades mecânicas, foram confeccionadas barras (7 mm X 2 mm X 1 mm) a partir de matrizes de silicone. Após 24 horas, o teste de três pontos foi realizado em Máquina de Ensaio Universal, com velocidade de 0,5 mm/min. O GC dos espécimes foi mensurado através do espectrômetro de raios infra-vermelhos transformada de Fourier (FTIR) e calculado comparando os espectros não-polimerizados e polimerizados dos sistemas adesivos. Os dados obtidos para ambos os experimentos foram analisados estatisticamente através de ANOVA 2-critérios e teste de Tukey ($p \leq 0,05$). No experimento 1, avaliando GC, SB2, P90P e OUP (10s) mostraram diferença significante entre as distâncias testadas. Em todas as condições experimentais, SB2 obteve os melhores resultados de GC e OUP (10s), os piores valores. Contudo, analisando ME e RF, o melhor desempenho foi observado para o SBMP e P90B aos 2, 4 e 6 mm; SB2 foi inferior a todos os demais adesivos. Não houve diferença entre as distâncias de ativação para RF. No experimento 2, SB2, P90P e OUP (30s) mostraram melhor GC com QTH, já com LED, SB2 e P90P obtiveram os piores resultados de GC. Apenas P90B e OUP (30s) não apresentaram diferença estatística entre as fontes de luz. Avaliando ME, somente SBMP e CP mostraram significância estatística entre QTH e LED, enquanto que não houve diferença entre as fontes de luz para RF. Adesivos hidrófobos (SBMP, CP e P90B) obtiveram melhores valores de ME e RF, independentemente da fonte de luz testada. Dessa forma, pode-se concluir que o grau de conversão e as propriedades mecânicas dos sistemas adesivos são influenciados pelos fatores "distâncias de ativação" e "fonte de luz". Entretanto, essa interferência no comportamento do material depende da composição e características de cada sistema adesivo.

Palavras-chave: Adesivos dentinários, Polimerização, Grau de conversão, Propriedades mecânicas.

ABSTRACT

The aim of the present study was to evaluate the influence of different light curing units (LCUs) and distances of light curing tip on the degree of conversion (DC) and mechanical properties (elastic modulus - *E* and flexural strength - FS) of five adhesive systems (*Scotchbond MP Plus* - SBMP; *Single Bond 2* - SB2; *One-up Bond F Plus* - OUP; *Clearfil Protect Bond* - CP, and *P90 System Adhesive:* primer - P90P and bond - P90B). To perform the tests, in experiment 1, samples of each adhesive were divided into three groups (n=5), according to light tip distance (2, 4 and 6 mm), whereas, in experiment 2, specimens were divided into two groups (n=5), depending on LCU evaluated: quartz tungsten halogen (QTH) and blue light emitting diode (LED). All adhesive systems were irradiated for 10s, except for OUP which had its activation time increased to 30s. For evaluation of mechanical properties, specimens were prepared using bar silicon molds (7 mm X 2 mm X 1 mm). After storage for 24h, the three-point flexural test was performed, at a crosshead speed of 0,5 mm/min, using a universal testing machine. DC was measured using Fourier Transform infrared spectroscopy (FTIR) and it was calculated by comparing the polymerized and unpolymerized spectra obtained from adhesive resins. The data were statistically analyzed ($p \leq 0.05$) using a two-way ANOVA and Tukey´s test. In experiment 1, DC was affected by distances of light curing tip and adhesive system. The distances were statistically significant for SB2, P90P and OUP (10s). For all distances tested, SB2 showed the best DC values and OUP (10s), the worst ones. However, for *E* and FS, better performance was obtained for SBMP and P90B at 2, 4 and 6mm, while SB2 presented the lowest values. For FS, there was no difference between distances tested. In Experiment 2, DC was also affected by LCUs and adhesive system. SB2, P90P and OUP (30s) showed better DC values for QTH, and with LED, SB2 and P90P presented the worst ones. Only P90B and OUP (30s) were not statistically significant among LCUs. For *E*, only SBMP and CP showed difference between QTH and LED, whereas, for FS, there was no difference among light sources. Non-solvated adhesives (SBMP, CP and P90B) presented the best *E* and FS values, regardless of light sources tested. It can be concluded that DC and mechanical properties of adhesive systems are influenced by factors “distances of light curing tip” and “light sources”. Nevertheless, this interference is material dependent.

Keywords: Dentin-bonding agents, Polymerization, Degree of conversion, Elastic modulus, Mechanical properties.

SUMÁRIO

INTRODUÇÃO

Sistemas adesivos foram desenvolvidos na Odontologia com o objetivo de promover retenção entre substratos dentários e compósitos ou cimentos resinosos, proporcionando realização de técnicas restauradoras mais conservadoras (Van Landuyt *et al.*, 2007).

O mecanismo básico da adesão ao esmalte e à dentina refere-se ao processo de substituição do conteúdo mineral removido dos tecidos dentais por monômeros resinosos do adesivo, constituindo, assim, uma interligação micro-mecânica entre os dois componentes, caracterizando a hibridização (De Munck *et al.*, 2005).

Os agentes adesivos são divididos em sistemas convencionais (*etch-and-rinse*) e auto-condicionantes (*self-etch*). O primeiro grupo caracteriza-se pela remoção da *smear layer* através do condicionamento ácido do dente, seguido da aplicação do *primer* e adesivo no substrato, em três diferentes passos, ou até mesmo em duas etapas (ácido + *primer*/adesivo), representando os adesivos convencionais simplificados (Toledano *et al.*, 2006; Giannini *et al.*, 2008). A técnica de condicionamento total ainda é considerada a mais eficiente na obtenção de adesão estável em esmalte (Peumans *et al.*, 2005).

Já os adesivos auto-condicionantes possuem monômeros ácidos que desmineralizam os tecidos duros e promovem a infiltração do adesivo, simultaneamente (Cadenaro *et al.*, 2005; Carvalho e Turbino, 2005), reduzindo não só o tempo clínico de aplicação, como também, a dificuldade técnica e o risco de cometer erros durante o procedimento (De Munck *et al.*, 2005). De forma semelhante aos adesivos convencionais, esses sistemas podem ser simplificados, sendo aplicados em uma (adesivos de passo único) ou duas etapas (primer ácido + adesivo).

Nakabayashi & Saimi (1996) formularam a hipótese que, para esse grupo de adesivos, a profundidade de desmineralização deveria corresponder à de infiltração dos monômeros. Porém, estudos morfológicos mostraram que, até nos sistemas auto-condicionantes, existia discrepância entre as zonas de desmineralização e penetração (Tay *et al.*, 2002; Carvalho *et al.*, 2005). De forma geral, os adesivos auto-condicionantes, especialmente os de passo único, podem exibir menor resistência de união em relação à dentina e diminuição no desempenho clínico em longo prazo, quando comparado ao sistema convencional (Cadenaro *et al.*, 2005).

Para que iniciem a sua conversão em polímeros, os monômeros dos sistemas adesivos precisam ser fotoativados, com luz visível, para desencadear a reação entre os grupos metacrilatos, resultando na interligação das moléculas para formar rígidos polímeros (Navarra *et al.*, 2009).

Por muitos anos, a luz halógena de quartzo-tungstênio (QTH) tem sido utilizada como a principal fonte de luz para fotoativação dos materiais resinosos (Moraes *et al.*, 2010). Elas produzem amplo espectro de comprimento de onda, entre 370 e 520nm, que abrange a faixa de absorção da maioria dos fotoiniciadores presentes nos sistemas adesivos, em especial a canforoquinona (CQ), cujo pico de absorção máxima é de 468nm (Nomoto et *al.*, 2004; Guo et *al.*, 2009). Entretanto, alguns fatores podem comprometer seu desempenho, como degradação dos seus componentes devido à grande quantidade de calor emitido e diminuição da densidade de potência com o tempo (Jandt *et al.*, 2000; El-Mowafay *et al.*, 2007). Sendo assim, a tecnologia dos diodos emissores de luz (LED) foi proposta na tentativa de superar os problemas inerentes da luz halógena (Mills, 1995).

Em geral, a fonte de luz LED consome menos energia, não necessita de filtros para produzir luz azul, seus semicondutores de nitrato de índio gálio (InGaN) usados para emissão de luz, ao invés de filamentos metálicos como da QTH, geram menos calor e sofrem menor degradação ao longo do tempo. Os aparelhos LED de segunda geração, além da característica produção de estreito comprimento de onda, entre 440 – 490nm, com pico em torno de 470nm, coincidente ao de absorção da CQ, emitem luz em alta irradiância, acima de 750mW/cm^2 (Burgess *et al.*, 2002; Leonard *et al.*, 2002; Uhl *et al.*, 2004; Jimenez-Planas *et al.*, 2008).

Recentemente, uma terceira geração, que utiliza dois tipos de LEDs, foi desenvolvida com o objetivo de produzir uma faixa espectral mais ampla que a dos LEDs convencionais, entre 370-520nm, para abranger fotoiniciadores alternativos a CQ, sensíveis a comprimentos de ondas não contemplados no estreito espectro produzido pelos outros LEDs (Price *et al.*, 2005; Ilie & Hickel, 2008). Esse amplo espectro deve-se à presença de LEDs adicionais, além do LED convencional central, que emitem luz na região ultra-violeta (UV). Sendo assim, essa fonte de luz apresenta espectro de emissão com picos em dois comprimentos de onda, um em torno de 400nm, produzido pelos LEDs adicionais, e outro em 452nm, associado ao LED convencional central (Price *et al.* 2005; Ilie & Hickel, 2008; Brandt *et al.* 2010). Essa nova geração também caracteriza-se pela emissão de luz em alta irradiância, associada a maior geração de calor (Guiraldo *et al.*, 2008).

Sendo assim, com a constante evolução dos LEDs, estudos tem avaliado a efetividade dessa tecnologia na fotopolimerização dos compósitos odontológicos (Cunha *et al.*, 2009; Mortier *et al.*, 2009). Contudo, adesivos apresentam diferenças de composição em relação às resinas compostas, como alguns co-monômeros e solventes orgânicos, sendo que estes podem afetar a polimerização. Apesar dessas diferenças, há poucos estudos que avaliem o efeito das diferentes fontes de luz no grau de conversão (GC) dos sistemas adesivos (Arrais *et al.*, 2007; Ye *et* al., 2007; Moraes *et al.*, 2010).

A obtenção de altos níveis de conversão dos monômeros e satisfatória infiltração monomérica na rede de colágeno desmineralizada são fatores cruciais no estabelecimento da adesão duradoura entre resina/dentina (Reis *et al.*, 2004). Entretanto, alguns fatores podem influenciar diretamente o grau de conversão, como permanência de água ou solventes orgânicos residuais, e a qualidade da fonte de luz utilizada para fotoativar os sistemas adesivos (Arrais *et al.*, 2007), sendo importante considerar características como irradiância da fonte de luz, direção do feixe luminoso e profundidade da cavidade (Shortall *et al.*, 1995).

Materiais fotopolimerizáveis apresentam desvantagens como limitada profundidade de ativação que se relaciona, de forma relevante, com o desempenho clínico desses materiais, uma vez que o conteúdo de monômeros residuais torna-se maior com o aumento da distância de ativação (Nomoto *et al.*, 2006; Jandt *et al.*, 2000). A adequada polimerização demanda uma distância entre a fonte de luz e a superfície do compósito de, no máximo, 6 mm (Caughman *et al.*, 1995). A distância clínica recomendada entre a ponta da fonte de luz e a superfície da resina/adesivo é de 1 mm, entretanto, em alguns casos, a forma do preparo, como em cavidades Classe II profundas, não torna possível a fotoativação a essa distância (Thomé *et al.*, 2007).

Dessa forma, as propriedades físicas dos materiais fotopolimerizáveis irão variar de acordo com a distância da superfície irradiada (Rueggeberg & Craig, 1988). Alguns estudos já buscaram estabelecer a relação entre a distância de polimerização e as alterações causadas nas resinas compostas (Ruyter & Oysaed, 1982; Kawaguchi *et al.*, 1994; Thomé *et al.*, 2007; Moore *et al.*, 2008); todavia, pouco se sabe a respeito da influência desse mesmo fator no comportamento dos sistemas adesivos.

O grande interesse pela elucidação de fatores que favoreçam a obtenção de melhores resultados de grau de conversão dos adesivos é por acreditar que este afeta as propriedades mecânicas do material, como resistência à flexão, tração e compressão, módulo de elasticidade e dureza (Nomoto *et al.*, 2006). Estudos *in vitro* indicaram boa relação entre o GC e propriedades mecânicas do adesivo com a resistência de união aos tecidos dentais (Kanehira *et al.*, 2006; Bae *et al.*, 2005). Dickens & Cho (2005) afirmaram que a análise do grau de conversão pode ser usada como medida indireta da força inerente dos sistemas adesivos, já que, no complexo da adesão, este material está presente em finas camadas.

Dentre os componentes do complexo de adesão, a camada adesiva possui os menores valores de rigidez, sendo considerada o elo mais fraco do conjunto, depois da camada híbrida. Entretanto, devido a sua capacidade de deformação elástica, consegue resistir às forças da contração de polimerização dos compósitos. Dessa forma, sistemas adesivos com melhores propriedades mecânicas podem evitar o descolamento de certas áreas, favorecendo a resistência de união do complexo (Van Meerbeek *et al.*, 1993; Lin & Douglas, 1994).

Baseado nessas informações, torna-se evidente a necessidade de novos estudos que avaliem a influência de alguns fatores que podem interferir na polimerização e a relação desses com o grau de conversão e propriedades mecânicas dos diferentes sistemas adesivos.

Sendo assim, os objetivos do presente estudo foram avaliar os efeitos de diferentes fontes de luz (QTH ou LED), e de distâncias de ativação (2 mm, 4 mm, 6 mm) sobre o grau de conversão e propriedades mecânicas (resistência à flexão e módulo de elasticidade) de diferentes sistemas adesivos.

Capítulo 1

Influence of distance of light curing tip on the degree of conversion, flexural strength and elastic modulus of dental adhesive systems

Lívia Aguilera Gaglianone - Department of Restorative Dentistry, Piracicaba School of Dentistry, State University of Campinas-UNICAMP, Piracicaba, SP, Brazil
Adriano Fonseca Lima – Department of Restorative Dentistry, Piracicaba School of Dentistry, State University of Campinas-UNICAMP, Piracicaba, SP, Brazil
Luciano de Souza Gonçalves - Department of Restorative Dentistry, Department of Dental Materials, Piracicaba School of Dentistry, State University of Campinas-UNICAMP, Piracicaba, SP, Brazil
Andrea Nóbrega Cavalcanti - Department of Oral Rehabilitation, School of Dentistry, School of Medicine and Public Health of Bahia, Salvador, BA, Brazil
Flávio Henrique Baggio Aguiar – Department of Restorative Dentistry, Piracicaba School of Dentistry, State University of Campinas-UNICAMP, Piracicaba, SP, Brazil
Luís Roberto Marcondes Martins – Department of Restorative Dentistry, Piracicaba School of Dentistry, State University of Campinas-UNICAMP, Piracicaba, SP, Brazil
*Giselle Maria Marchi – Department of Restorative Dentistry, Piracicaba School of Dentistry, State University of Campinas-UNICAMP, Piracicaba, SP, Brazil

***Author to whom correspondence should be addressed. Present address:**

Prof. Dr. Giselle Maria Marchi
Departamento de Odontologia Restauradora – Área Dentística
Faculdade de Odontologia de Piracicaba – UNICAMP
Av. Limeira, 901 – Areião. CEP 13414-903, Piracicaba – SP, Brasil
Tel.: +55-19-2106-5200. Fax: 55-19-3421-0144. E-mail: gimarchi@fop.unicamp.br

ABSTRACT

The aim of this study was to evaluate the degree of conversion (DC) and mechanical properties (elastic modulus – *E* and flexural strength – FS) of five adhesive systems (*Scotchbond MP Plus* - SBMP; *Single Bond 2* – SB2; *One-up Bond F Plus* - OUP; *Clearfil Protect Bond* – CP, and *P90 System Adhesive:* primer - P90P and bond - P90B) photocured using 2, 4 and 6mm distances from light curing tip. DC was measured using Fourier Transform infrared spectroscopy (FTIR) and it was calculated by comparing the spectra obtained from adhesives before and after light activation for 10s (Demetron LC – 650 mW/cm^2), except OUP that was photo-cured for 10s and 30s. For the mechanical properties test, specimens (n=5) were prepared with a bar shape (7 mm X 2 mm X 1 mm). After 24 h, the three-point bending test was performed, at a crosshead speed of 0.5mm/min. Data were statistically analyzed ($p \leq 0.05$) using a two-way ANOVA and Tukey´s test. DC was affected by adhesive system and distances of light curing tip. The distances were statistically significant for SB2, P90P and OUP (10s), with 2/4 mm showing better performance than 6mm. For all distances tested, SB2 showed the best DC values and OUP (10s), the worst ones. However, for *E* and FS, better performance was obtained for SBMP and P90B at 2, 4 and 6 mm, while SB2 presented the lowest values. For FS, there was no difference between distances tested in all groups. It can be concluded that the DC and *E* of adhesive systems are influenced by different distances of light curing tip, in which lower distances were associated to more positive results, nevertheless, this interference is material dependent since hydrophilic adhesives presented the highest DC values while hydrophobic systems were superior in relation to elastic modulus.

Keywords: Dentin-bonding agents, Polymerization, Conversion reaction, Elastic Modulus

INTRODUCTION

Dental adhesives are designed to promote bonding between composite resins and dental hard tissues, providing more conservative restorative procedures (De Munck *et al.*, 2005), and they can be classified in two main groups (Van Landuyt *et al.*, 2007). The etch-and-rinse adhesives require previous phosphoric acid-etching and application of the adhesive after rinsing of the acid (Giannini *et al.*, 2008; De Munck *et al.*, 2005), and self-etching systems are based on acidic monomers, that simultaneously etch and diffuses through dentin, promoting the hybrid layer formation (De Munck *et al.*, 2005).

Bonding agents contain resin monomers, organic solvents, initiators and inhibitors, and each component has a specific function (Van Landuyt *et al.*, 2007). In addition, for light-cured systems, to initiate monomer´s conversion into polymers, adhesive systems need to be light activated.

The mechanical, physical and biological properties of the dental adhesives are significantly influenced by the degree of monomers conversion (DC) (Holmes *et al.*, 2007). Regardless of the light curing unit, the amount of radiation that reaches the material depends on several factors, such as lamp output intensity, exposure time, and distance of light curing tip to material, and these factors can modulate the DC of resin agents (Jimenez-Planas *et al.*, 2008).

Greater distances from the light guide tip to gingival floor must be assumed in a typical Class II preparation, and this fact must be taken as clinically relevant (Ernst *et al.*, 2004). In this context, it is important to recognize that increasing the distance among the light guide tip and the adhesive material surface can cause a significant difference in polymerization, that may reflect changes in resin DC and mechanical behavior of adhesive layer.

It has generally been accepted that the mechanical properties of light curing dental materials is improved with increasing DC (Ferracane & Greener, 1986; Dickens & Cho, 2005), nevertheless, the influence of different distances of light curing tip on mechanical properties of dental adhesives systems is still unknown.

In order to assess the DC and mechanical properties of resin agents, considering the distance of light curing unit tip, this study evaluated the influence of this factor in the performance of different adhesive systems. The null hypothesis tested were: (1) different distances have no effect on DC and mechanical properties of the tested adhesives; (2) DC and mechanical properties performance do not depend on composition of adhesive systems.

MATERIAL AND METHODS

The commercial adhesives investigated in this study were: *Adper Scotchbond Multi-Purpose Plus* (**SBMP**), *Adper Single Bond 2* (**SB2**); *P90 System Adhesive* – primer (**P90P**) and bond (**P90B**) agents; *Clearfil Protect Bond* (**CP**) and One-up Bond F Plus (**OUP**). Classification, manufacturer and composition of these materials are listed in Table 1.

Three curing tip distances were used in this study: 2 mm, 4 mm and 6 mm. Light-activation was performed using a holder coupled to the light sources to standardize the distances between the light guide tip and material. The distances were controlled with an electronic digital caliper (Mitutoyo, Tokyo, Japan). Light intensity that reached specimen surface was also measured, with a calibrated power meter (Ophir Optronics, Jerusalem, Israel), according to evaluated distances 2, 4 and 6 mm - respectively, 650, 410 and 370 mW/cm^2.

For evaluation of DC and mechanical properties, each adhesive system was divided into three groups (n=5), according to the distance of curing device (2, 4 and 6mm).

2.1 Mechanical properties

Twenty microliters (µL) of each adhesive were placed in four increments (5 µL each one) into a silicon mold, to prepare a specimen with a bar shape (7 mm X 2 mm X 1 mm). After each increment, a gentle air was applied for ten seconds using a low-pressure air stream in the solvated adhesives (SB2, P90P and OUP), for the solvent evaporation.

Before light-activation, a Mylar strip was placed over the mold in an attempt to obtain a flat sample surface. Adhesives were irradiated using a conventional quartz-tungsten-halogen light source (Demetron LC; Sybron Kerr, Danbury, CT, USA), for 10 seconds (650 mW/cm^2), according to the manufacturers' instructions, except for OUP that had the activation time increased to 30 s. This procedure was necessary, since after 10 s of light activation, the OUP specimen did not present an adequate consistency for the three-point flexural test.

After storage for 24 h in distilled water, specimens were subjected to three-point flexural test for measuring flexural strength (FS) and elastic modulus (*E*), at a crosshead speed of 0.5mm/min using a universal testing machine (Instron model 4411, Instron Corp., Canton, MA, USA). Before the test, the dimensions of each specimen were inserted in the software Bluehill 2 (Instron Corp., Canton, MA, USA), that calculated the *E* (GPa) and FS (MPa), according to the dimensions and tension.

2.2 Degree of conversion

DC of bonding agents was measured using Fourier Transform infrared spectroscopy - FTIR (Spectrum 100 Optica; PerkinElmer, MA, USA), equipped with an attenuated total reflectance (ATR) device that is composed of a horizontal ZnSe crystal

(Pike Technologies, Madison, WI, USA). Constant volume of the adhesive resin (5 μL) was placed on the horizontal face of the ATR cell.

For SBMP and CP, only the bond agent was evaluated, without use of the primer. For hydrophilic adhesives (SB2, P90P and OUP), solvent evaporation process also consisted in a gentle air applied for ten seconds using a low-pressure air stream.

A preliminary reading for uncured material was taken under the following conditions: 1665–1580 cm^{-1} frequency range, 4 cm^{-1} resolution, Happ-Genzel apodization, in absorbance mode. Additional FTIR spectra were obtained immediately after light-curing. Light curing was then carried out for 10 s for the major of adhesives tested, following manufacturer's instructions, except for OUP that was light cured for 10 s / 30 s.

DC was calculated using a baseline technique (Rueegeberg *et al.*, 1990), based on band ratios of 1638 cm^{-1} (aliphatic carbon-to-carbon double bond) and, as an internal standard, 1608 cm^{-1} (aromatic component group) between the polymerized and unpolymerized samples.

2.3 Statistical analysis

Data from DC, elastic modulus and flexural strength of adhesive systems were analyzed by two-way ANOVA, with main variables "bonding agents" and "distance of light curing tip". All post hoc multiple comparisons were performed using Tukey's test. Statistical significance was preset at a $\alpha = 0.05$.

RESULTS

Means and standard deviations of the DC of all adhesives are summarized in Table 2/ Figure 1. For the monomers conversion evaluation, it was noted an interaction between the variables “adhesive system” and “distance of light curing tip”.

SBMP, P90B, CP and OUP (30s) showed no difference among distances of light curing tip. Instead, for SB2, 2 mm were equal to 4mm, and they were better than 6mm. P90P and OUP (10s) revealed the worst DC values at 6 mm distance.

SB2 showed the best DC results, and OUP (10s) revealed the worst means, regardless of tested distance of light curing tip. OUP (30s) was similar to SBMP, P90B and CP at 2 / 4 mm, however, at 6 mm, it revealed better performance than those adhesives, and similar conversion compared to SB2. There was no statistical difference between P90P and SB2 at 2 / 4 mm, but P90P showed inferior DC means at 6 mm.

Means and standard deviations of the elastic modulus of all adhesives are presented in Table 3/ Figure 2. There was no difference among distances (2=4=6 mm) for P90B, P90P and OUP (30s). For SBMP, 6 mm results were lower than 2 and 4 mm, that presented similar *E* among themselves, while, for SB2, 2 / 6 mm were similar and better than 4 mm. CP system revealed higher means for 2 mm, statistically significant for 4 / 6 mm.

SBMP and P90B presented the highest *E* means compared to other tested adhesives at all distances. At 2 mm, these two systems were followed by CP, and they showed statistically higher values than SB2, P90P and OUP (30s). Related to 4 mm, SBMP/P90B> CP> OUP(30s)≥ P90P≥ SB2. At 6 mm, CP was statistically similar to SBMP and P90B, SB2 and OUP (30s) revealed intermediate values, and P90P presented the lowest values.

Means and standard deviations of flexural strength of all adhesives are summarized in Table 4/ Figure 3. There was no statistical difference among distances of light curing tip for all tested adhesive systems (2=4=6 mm).

SBMP and P90B showed similar performance at 2, 4 and 6 mm, presenting the best FS values. CP was similar to SBMP/P90B only at 2 / 6 mm. At 2 / 4 mm, P90P and OUP (30s) revealed intermediate values, while SB2 showed lower means for FS. However, at 6 mm, P90P, OUP (30s) and SB2 were equal and showed the lowest values.

DISCUSSION

This study evaluated different adhesive systems in an attempt to obtain further information about their mechanical properties behavior when distinct distances of light curing tip are employed. The results showed that this factor was able to modulate the DC and mechanical properties of tested adhesives. In face of this fact, the first null hypothesis tested was rejected. Evaluating the different adhesives, the distinct behavior of these products, in GC and mechanical properties, lead to the second null hypothesis rejection, that assumed the similarity in properties performance regardless bonding agent.

One-Up Bond F Plus presented difficulties in specimen preparation when polymerized according to the manufacturer's instructions (10 s). One hypothesis that might explain this fact is that in addition to HEMA (2-hydroxyethyl methacrylate) or other functional monomers, OUP contains 5–20% methylmethacrylate (MMA), which is known to produce lower polymer stiffness and to form only linear polymers (Kurata *et al.*, 2008). Furthermore, it is a non-camphorquinone (CQ) based adhesive that presents the arylborate catalyst as photoinitiator (Hosaka *et al.*, 2010), which can reduce their efficiency with reduced time of activation. After increasing irradiation time (30 s), the specimens presented adequate stiffness to perform the tests, probably due to higher DC obtained after the change in photo curing protocol.

Silorane adhesive system, a specific bonding agent to be used with the low-shrinkage resin composite, Filtek Silorane, was also evaluated. In contrast to the others two-step self-etching systems, the primer agent of the Silorane Adhesive must be polymerized. In other words, the hybrid layer is formed with the hydrophilic compounds of the primer, and no mixing occurs between these monomers and the hydrophobic bonding layer. For this reason, the primer of the Silorane Adhesive can be classified as a simplified self-etching system, and the hydrophobic coating, provided by the bond agent, promotes additional stability to the bonded interface (Navarra *et al.*, 2009). Thus, the properties were evaluated for the two components in order to analyze the effectiveness of this adhesive system.

According to the results, distances of light curing tip did not interfere with the flexural strength for any adhesive tested, regardless of their composition. On the other hand, there were significant differences among distances for DC and elastic modulus, and they did not present similar behavior for both properties. The DC of hydrophilic adhesives was more affected by the increase in the distance of activation, except to OUP cured by 30 s. In contrast, different distances tested did not affect the monomer conversion of the hydrophobic adhesives. Nevertheless, the increase of distance caused a reduction on the elastic modulus of SB2, SBMP and CP while there was no difference for P90B, P90P and OUP (30s) for all distances tested.

Increasing the distance between the light-guide tip and adhesive surface can cause a significant difference in the polymerization since the actual intensity of light for curing is dependent on the intensity produced by the curing unit and the distance of the light curing tip (Bayne, Heymann & Swift Jr, 1994). In this study, a remaining irradiance of 63% was obtained at a distance of 2mm and of 57% at 6mm, corroborating with a previous study that observed 78% of remaining power density at 2mm and 47% at 6mm (Pires *et al.*, 1993). This reduction in irradiance, due to light scattering, can cause a decrease in the speed of curing reaction, decreasing the crosslink polymers formation, and consequently, may cause a deleterious effect on the elastic modulus, mainly in adhesives with high content of BisGMA, such as SBMP.

As it was observed in this study, greater distances of activation were associated with worse degree of conversion and elastic modulus. However, the variable “distance of light curing tip” influenced these properties differently, depending on the composition of adhesive systems. In DC, only hydrophilic systems were affected by distances, whereas this factor was significant for hydrophobic adhesives in *E*.

Evaluating the results regarding adhesive systems composition, solvated adhesives (SB2 and P90P) presented higher DC. According to manufacturer’s information, Single Bond 2 presents approximately 45% of solvent in its composition (ethanol and water) while primer of Silorane adhesive system has 30% of ethanol/water. The solvent can facilitate the mixing of hydrophilic with hydrophobic monomers (Malacarne-Zanon *et al.*, 2009) and decrease the viscosity of the resins, increasing the molecular mobility and growing polymer chain segments, improving the DC of the materials (Dickens & Cho, 2005; Holmes *et al.*, 2007; Cadenaro *et al.*, 2008). Nevertheless, the presence of large amounts of residual solvent was associated to effects that could inhibit polymerization reaction and compromise polymer structure (Reis *et al.*, 2004; Carvalho *et al.*, 2003; Arrais *et al.*, 2007).

One-Up Bond system presented lower DC, even comparing with solvent-free adhesives, confirming that the DC of bonding agents does not depend solely of the type and amount of organic solvent; instead, it also depends on the monomeric composition and other components of each material (Giannini *et al.*, 2008). As abovementioned, OUP has a monomer that produces less resistant polymers and a photoinitiator different from CQ, which may have contributed to its low DC values when polymerized for 10 s. However, increasing the exposure time to 30 s, higher DC values were obtained, since longer irradiation times can lead to higher conversion rates (Breschi *et al.*, 2007).

This current study also aimed to assess whether higher degree of conversion could be related to better results of adhesive systems mechanical properties, since DC based on the quantity of remaining double bond has been used extensively to characterize and provide a relative assessment of the quality of dentin adhesives. The presence of high content of solvent increases the DC, however, it seems to promote negative effects for the adhesives mechanical properties, confirming that the measurement of polymer conversion does not necessarily provide complete representation of the polymer structure quality (Ye *et al.*, 2007). In this study, it was demonstrated that solvent presence in adhesive systems, despite increasing the degree of conversion, caused substantial differences in mechanical properties.

SBMP and P90B, solvent-free systems, showed better mechanical properties in all experimental conditions. There was no difference among them since the first presents a BisGMA (60-70%) / HEMA (30-40%) mixture while the other has 70-80% of unspecified hydrophobic dimethacrylate diluted in 5-10% of TEGDMA. A higher content of a dimethacrylate may render material to have a greater ability to form crosslinks, which may also form rigid polymers (Bae *et al.*, 2005). CP also showed high values of *E* and FS, nevertheless, this adhesive presents BisGMA in lower concentration than SBMP (25-45%) which could promote lower crosslink density, decreasing the stiffness of the materials in the experimental conditions.

In relation to SB2, P90P and OUP (30s), low values of mechanical properties can be explained, mainly, by the presence of solvent. There is a correlation between effective removal or complete absence of volatile solvent in dental adhesives and increase in their mechanical properties (Paul *et al.*, 1999; Carvalho *et al*., 2003; Ye *et al.*, 2007). This component increases the effective free volume of the resin and can prevent the approximation between reactive pendant species, making the cross-linking reaction more difficult (Ye *et al.*, 2007). Moreover, higher concentrations of hydrophilic monomers and presence of solvents tend to form linear chains (Kurata *et al.*, 2008) that slide over one another, producing a less resistant polymer (Paul *et al.*, 1999).

Thus, the results lead to suggest that solvent presence in small concentrations may be favorable for obtaining a better degree of conversion, whereas in larger amounts, this component would be prejudicial to the polymer formation. For this reason, the influence of factors that could modulate the process of polymeric structure may be related to material composition, since different distances of activation affected only solvated adhesives DC, while for elastic modulus, they were significant for hydrophobic systems.

Therefore, it was evident that more studies should be conducted to the knowledge of the complete relationship among distances of light curing tip, as well as different light intensities, with adhesive systems composition in order to establish the best polymerization conditions and hence, better material performance.

CONCLUSIONS

The effect of distances of light curing tip on degree of conversion and elastic modulus showed that increased distances of activation resulted in a significant decrease of these properties, and that this influence was related to adhesives composition, due to the chemical complexity of these systems, leading to different behaviors in relation to evaluated properties.

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Table 1: Classification, Manufacturer and Composition of the bonding agents tested.

Bonding Agent	Classification*	Manufacturer	Composition
Adper Scotchbond Multi-Purpose Plus**	Three-step, etch&rinse	3M ESPE, St Paul, MN, USA	BisGMA, HEMA, polyalkenoic acid copolymer, CQ, EDMAB, DHEPT
Adper Single Bond 2	Two-step, etch&rinse	3M ESPE, St Paul, MN, USA	BisGMA, UDMA, HEMA, polyalkenoic acid copolymer, CQ, DHEPT, water, ethanol, silica
Silorane adhesive system P90 **PRIMER**	Two-step, self-etch	3M ESPE, St Paul, MN, USA	BisGMA, HEMA, water, ethanol, silane treated silica filler, CQ, Phosphoric acid–methacryloxy-hexylesters mixture, phosphorylated methacrylates, Copolymer of acrylic and itaconic acid, Phosphine oxide
Silorane adhesive system P90 **BOND**			Hydrophobic dimethacrylate, phosphorylated methacrylates, TEGDMA, silane treated silica, CQ, stabilizers
Clearfil Protect Bond**	Two-step, self-etch	Kuraray Medical Inc., Okayama, Japan	10 MDP, BisGMA, HEMA, hydrophobic dimethacrylate, camphorquinone, N,N-diethanol-p-toluidine, silanated colloidal silica, surface treated NaF
One-Up Bond F Plus	One-step, self-etch (two bottles)	Tokuyama Dental Corp., Tokyo, Japan	**Agent A**: MAC-10, MMA, coumarin dye, methacryloylalkyl acid phosphate **Agent B:** HEMA, multifunctional methacrylic monomer, fluoraluminosilicate glass, water, photoinitiator (arylborate catalyst)

*As informed by the manufacturers. **Composition for only the Bond bottle is presented.

Abbreviations - BisGMA: bisphenol-A glycidyldimethacrylate; *HEMA*: 2-hydroxyethylmethacrylate; *CQ*: camphorquinone; *EDMAB*: ethyl4-dimethylaminobenzoate; *DHEPT*: dihydroxyethyl p-toluidine; *UDMA*: diurethane dimethacrylate; *TEGDMA*: triethylene glycol dimethacrylate; *10 MDP*: 10-methacryloyloxydecyl dihydrogen phosphate; *NaF*: sodium fluoride; *MAC-10*: 11-methacryloyloxy-1,1-undecanedicarboxyric acid; *MMA*: methylmethacrylate.

Table 2. Means and Standard Deviations (SD) for DC (%) of Adhesive Systems Testing the Different Distances of Cure with QTH Light-Curing Unit

Adhesive Systems	**QTH**		
	2mm	**4mm**	**6mm**
SBMP	59,6 (0,9) Abc	58,3 (0,6) Ab	55,8 (0,9) Aab
SB2	75,8 (2,9) Aa	73,1 (0,8) Aa	62,9 (1,8) Ba
P90B	56,8 (0,6) Ac	54,0 (0,5) Ab	54,9 (0,3) Aab
P90P	81,0 (1,4) Aa	69,1 (2,9) Ba	50,8 (1,9) Cb
CP	62,7 (0,3) Ab	61,0 (1,3) Ab	58,5 (0,5) Aab
OUP (10s)	35,3 (2,9) Ad	26,6 (1,4) Bc	18,5 (0,7) Cc
OUP (30s)	65,3 (3,2) Ab	58,1 (2,8) Ab	60,8 (2,6) Aa

Means followed by distinct capital letters in the same row and distinct small letters in the same column are significantly different at $p<0.05$.

Table 3. Means (SD) for Elastic Modulus (GPa) of Adhesive Systems Testing the Different Distances of Cure with QTH Light-Curing Unit

Adhesive Systems	**QTH**		
	2mm	**4mm**	**6mm**
SBMP	2,2 (0,1) Aa	2,0 (0,1)Aa	1,5 (0,2) Ba
SB2	1,0 (0,1) Ac	0,5 (0,1) Bd	0,8 (0,1) Ab
P90B	1,8 (0,3) Aa	1,9 (0,2) Aa	1,7 (0,2) Aa
P90P	0,7 (0,1) Ac	0,7 (0,1) Acd	0,6 (0,1) Ac
CP	1,7 (0,2) Ab	1,3 (0,1) Bb	1,4 (0,3) ABab
OUP (30s)	1,2 (0,1) Ac	0,9 (0,1) Ac	1,0 (0,1) Ab

Means followed by distinct capital letters in the same row and distinct small letters in the same column are significantly different at $p<0.05$.

Table 4. Means (SD) for Flexural Strength (MPa) of Adhesive Systems Testing the Different Distances of Cure with QTH Light-Curing Unit

Adhesive Systems	**QTH**		
	2mm	**4mm**	**6mm**
SBMP	108,6 (11,6) Aa	107,5 (11,3) Aa	82,4 (19,7) Aa
SB2	17,8 (3,6) Ac	17,4 (3,2) Ad	25,7 (4,6) Ab
P90B	81,7 (21,0) Aa	99,0 (24,1) Aa	100,2 (16,0) Aa
P90P	33,3 (10,7) Ab	41,0 (2,0) Abc	28,4 (3,4) Ab
CP	71,5 (11,8) Aa	59,8 (14,0) Ab	61,7 (7,7) Aa
OUP (30s)	37,0 (12,2) Ab	31,7 (8,7) Ac	37,0 (5,8) Ab

Means followed by distinct capital letters in the same row and distinct small letters in the same column are significantly different at $p<0.05$.

Capítulo 2

Effect of different light sources on degree of conversion and mechanical properties of etch-and-rinse and self-etch adhesive systems

Lívia Aguilera Gaglianone - Department of Restorative Dentistry, Piracicaba School of Dentistry, State University of Campinas-UNICAMP, Piracicaba, SP, Brazil
Adriano Fonseca Lima – Department of Restorative Dentistry, Piracicaba School of Dentistry, State University of Campinas-UNICAMP, Piracicaba, SP, Brazil
Luciano de Souza Gonçalves - Department of Restorative Dentistry, Department of Dental Materials, Piracicaba School of Dentistry, State University of Campinas-UNICAMP, Piracicaba, SP, Brazil
Andrea Nóbrega Cavalcanti - Department of Oral Rehabilitation, School of Dentistry, School of Medicine and Public Health of Bahia, Salvador, BA, Brazil
Flávio Henrique Baggio Aguiar – Department of Restorative Dentistry, Piracicaba School of Dentistry, State University of Campinas-UNICAMP, Piracicaba, SP, Brazil
Luís Roberto Marcondes Martins – Department of Restorative Dentistry, Piracicaba School of Dentistry, State University of Campinas-UNICAMP, Piracicaba, SP, Brazil
*Giselle Maria Marchi – Department of Restorative Dentistry, Piracicaba School of Dentistry, State University of Campinas-UNICAMP, Piracicaba, SP, Brazil

***Author to whom correspondence should be addressed. Present address:**

Prof. Dr. Giselle Maria Marchi
Departamento de Odontologia Restauradora – Área Dentística
Faculdade de Odontologia de Piracicaba – UNICAMP
Av. Limeira, 901 – Areião. CEP 13414-903, Piracicaba – SP, Brasil
Tel.: +55-19-2106-5200. Fax: 55-19-3421-0144. E-mail: gimarchi@fop.unicamp.br

ABSTRACT

The purpose of this investigation was to evaluate the effect of different light sources on the degree of conversion (DC) and mechanical properties (elastic modulus - *E* and flexural strength - FS) of five adhesive systems (*Scotchbond MP Plus* - SBMP; *Single Bond 2* - SB2; *One-up Bond F Plus* - OUP; *Clearfil Protect Bond* - CP, and *P90 System Adhesive:* primer - P90P and bond - P90B). Two groups *per* adhesive were formed (n=5), according to the light source (quartz tungsten halogen - QTH and light emitting diode - LED). For mechanical properties test, bar shaped specimens (7 mmX2 mmX1 mm) were prepared, stored for 24 h, to be tested using the three-point flexural bending test, at a crosshead speed of 0.5mm/min. DC was measured using Fourier Transform infrared spectroscopy (FTIR) and it was calculated by comparing the spectra obtained from adhesives before and after light activation for 10s (QTH: Demetron LC - 650 mW/cm^2 and LED: UltraLume 5 – 850 mW/cm^2), except OUP that was photo-cured for 10s and 30s. Data were statistically analyzed ($p \leq 0.05$) using a two-way ANOVA and Tukey´s test. DC was affected by adhesive system and light source. Solvated adhesives (SB2, P90P and OUP 30s) showed better DC values for QTH, however, with LED, SB2 and P90P presented the worst results. Light sources were statistically significant for all tested adhesives, except P90B and OUP (30s). For *E*, only SBMP and CP showed difference among QTH and LED whereas, for FS, there was no difference among light sources. Non-solvated adhesives (SBMP, CP and P90B) presented the best *E* and FS values, regardless light sources tested. It can be concluded that DC and *E* can be influenced by different light sources, with halogen unit showing better results when significant differences were obtained. Nevertheless, this interference is material dependent since hydrophilic adhesives presented the highest DC values while hydrophobic systems were superior in relation to elastic modulus.

Keywords: Dentin, Bonding agents, Polymerization, Light curing unit, Conversion reaction, Elastic Modulus

INTRODUCTION

It is widely admitted that the photopolymerization can influence the final properties of resin based material. However, the relationship of polymerization processes and properties in dental resins are complicated (Dewaele *et al.*, 2010), since several factors can modulate the mechanical properties of the resin agents (Ye *et al.*, 2007; Ilie & Hickel, 2008; Malacarne-Zanon *et al.*, 2009; Gonçalves *et al.*, 2009).

Dental adhesives are designed to promote bonding between composite resins and dental hard tissues, providing more conservative restorative procedures (De Munck *et al.*, 2005). Different strategies are used to create dentin bonding: the total-etch bonding systems requiring removal of the smear layer with phosphoric acid, followed by the application of a primer and adhesive in two or even in one step; and the self-etching agents, in which increased concentrations of acidic monomers enable the primer or adhesive to etch and infiltrate the dentin simultaneously, promoting the mechanical interlocking. Despite of bonding strategy, to initiate monomer´s conversion into polymers, the light-cured adhesive systems need to be light activated.

In the last few years, light curing technology has advanced with the introduction of high intensity (600 – 1000 mW/cm^2) halogen lights and light emitting diode (LED), and the light intensity such as the spectrum of wavelength can influence the efficacy of the polymerization process (Moraes *et al*., 2010).

Quartz-tungsten-halogen (QTH) lamps emit light when a tungsten filament is heated to high temperatures, and work at broad spectra of wavelengths between 400 and 500 nm (Dunn & Taloumis, 2002). Some drawbacks of QTH units include bulb overheating and long-term degradation of the bulb and filter (Jimenez-Planas *et al.*, 2008), resulting in a reduction of the light curing unit´s (LCU) effectiveness over time (Jandt *et al.*, 2000).

To overcome the problems inherent to halogen LCUs, the LED technology has been introduced as an alternative source for curing dental restorative materials. LEDs consume little power and do not require filters to produce blue light (Jimenez-Planas *et al.*, 2008), however, emit light with narrow spectra of wavelengths between 450 and 490 nm, with a peak at 470 nm (Leonard *et al.*, 2002).

The monomer conversion after polymerization of light-cured materials affects the mechanical properties such as tensile, compressive and flexural strengths, elastic modulus, wear and hardness (Asmussen, 1982; Ferracane, 1985). However, since mechanical properties are associated with the polymeric structure, it must be considered that polymers that have similar DC, can present different crosslink densities, differing in the strength among the materials (Ye *et al.*, 2007). In this context, the influence of different light sources on polymer formation and, consequently, mechanical properties of dental adhesive systems is still unknown.

In face of these facts, the aim of this study was to investigate the effects of two light sources (QTH/LED) on the elastic modulus (*E*), flexural strength (FS) and degree of conversion (DC) of different adhesive systems. The null hypothesis tested were: (1) the different light curing units have no effect on degree of conversion and mechanical properties of the adhesives tested; (2) DC and mechanical properties performance do not depend on composition of adhesive systems.

MATERIAL AND METHODS

The commercial adhesives investigated were: *Adper Scotchbond Multi-Purpose Plus* (SBMP - 3M ESPE, St. Paul, Min., USA); *Adper Single Bond 2* (SB2 - 3M ESPE, St. Paul, Min., USA); *One-up Bond F Plus* (OUP - Tokuyama Dental Corp., Tokyo, Japan); *Clearfil Protect Bond* (CP - Kuraray Medical Inc., Okayama, Japan); and *P90 System Adhesive* -

primer (P90P) / bond (P90B) (3M ESPE, St. Paul, Min., USA). Adhesive systems composition is presented in Table 1.

Two commercially available LCUs were evaluated: QTH (Demetron LC; Sybron Kerr, Danbury, CT, USA – light intensity: 650 mW/cm^2) and LED (UltraLume 5; Ultradent Products Inc., South Jordan, Utah, USA – light intensity: 850 mW/cm^2). The irradiance of each LCU was measured with a calibrated power meter (Ophir Optronics, Jerusalem, Israel). For evaluation of DC and mechanical properties, each adhesive system was divided into two groups (n=5), according to the LCU´s (QTH/LED).

Polymerization, for both degree of conversion and mechanical properties analysis, was performed with a holder coupled to the light sources to standardize the distance of 4 mm between the light guide tip and material. This process was controlled with an electronic digital caliper (Mitutoyo, Tokyo, Japan).

2.1 Mechanical properties

Twenty micro-liters (µL) of each adhesive were placed in four increments (5 µL each one) into a silicon mold, to prepare a specimen with a bar shape (7 mm X 2 mm X 1 mm). After each increment, a gentle air was applied for ten seconds using a low-pressure air stream in the solvated adhesives (SB2, P90P and OUP), for the solvent evaporation.

Before light-activation, a Mylar strip was placed over the mold in an attempt to obtain a flat sample surface. Adhesives were irradiated for 10 s with the respective light-curing unit of each group, according to the manufacturers' instructions, except for OUP that had the activation time increased to 30 s. This procedure was necessary, since the specimen of OUP does not present an adequate consistency for the three-point flexural test after 10 s of light activation.

After storage for 24 h in distilled water, specimens were subjected to three-point flexural test for measuring flexural strength (FS) and elastic modulus (*E*), at a crosshead speed of 0.5mm/min using a universal testing machine (Instron model 4411, Instron Corp., Canton, MA, USA). Before the test, the dimensions of each specimen were inserted in the software Bluehill 2 (Instron Corp., Canton, MA, USA), that calculated the *E (*GPa) and FS (MPa) according to the dimensions and tension.

2.2 Degree of conversion

The degree of conversion of bonding agents was measured using Fourier Transform infrared spectroscopy - FTIR (Spectrum 100 Optica; PerkinElmer, MA, USA), equipped with an attenuated total reflectance (ATR) device that is composed of a horizontal ZnSe crystal (Pike Technologies, Madison, WI, USA). Constant volume of the adhesive resin (5 μL) was placed on the horizontal face of the ATR cell.

For SBMP and CP, only the bond agent was evaluated, without use of the primer. For hydrophilic adhesives (SB2, P90P and OUP), solvent evaporation process also consisted in a gentle air applied for ten seconds using a low-pressure air stream.

A preliminary reading for the uncured material was taken under the following conditions: 1665–1580 cm^{-1} frequency range, 4 cm^{-1} resolution, Happ-Genzel apodization, in absorbance mode. Additional FTIR spectra were obtained immediately after light-curing. Light curing was then carried out for 10s for the major of adhesives tested, following manufacturer’s instructions, except for OUP that was light cured for 10 s / 30 s.

Degree of conversion (DC) was calculated using a baseline technique (Rueegeberg *et al.*, 1990), based on band ratios of 1638 cm^{-1} (aliphatic carbon-to-carbon double bond) and, as an internal standard, 1608 cm^{-1} (aromatic component group) between the polymerized and unpolymerized samples.

2.3 Statistical analysis

Data from degree of conversion, elastic modulus and flexural strength of adhesive systems were analyzed by two-way ANOVA, with main variables “bonding agents” and “light curing units”. All post hoc multiple comparisons were performed using Tukey’s test. Statistical significance was preset at a $\alpha = 0.05$.

RESULTS

Degree of conversion means and standard deviations of all adhesives are summarized in Table 2/ Figure 1. Evaluating monomers conversion, it was noted an interaction between the main variables “adhesive system” and “light sources”. Only P90B and OUP (30s) showed no difference among light curing units. For the other adhesive systems, better values of DC were obtained with QTH.

With QTH, SB2, P90P and OUP (30s) showed higher DC values, and OUP (10s) revealed the worst means of monomers conversion. However, with LED, solvated adhesives (SB2 and P90P) revealed the worst performance, and only OUP (30s) maintained better DC means. SBMP, P90B and CP presented intermediate values, regardless of LCU tested.

The means and standard deviations of the elastic modulus are presented in Table 3/ Figure 2. There was no difference among light curing units for SB2, OUP (30s), P90P and P90B. For SBMP and CP, QTH revealed better *E* values than LED.

SBMP and P90B presented the highest means for elastic modulus, compared to the other adhesives tested, at both LCUs. When polymerized with QTH, CP was similar to these two systems and statistically higher than SB2, P90P and OUP (30s). While, related to LED, different performance was obtained with SBMP/P90B≥ CP≥ OUP (30s) ≥ P90P/SB2.

Means and standard deviations of all adhesives flexural strength are summarized in Table 4/ Figure 3. There was no statistical difference between light curing units for all adhesive systems tested (QTH = LED).

SBMP, P90B and CP showed similar behavior with QTH and LED, presenting the best FS values. There was no difference between SB2, P90P and OUP (30s), with QTH, and the lowest means were obtained with these adhesives. However, OUP (30s) revealed better performance with LED, showing intermediate values (SBMP/ CP/ P90B > OUP (30s)> SB2/ P90P).

DISCUSSION

Different commercially adhesive systems were evaluated in an attempt to obtain information about their mechanical properties behavior when distinct light curing units are employed. According to the results, light sources can modulate degree of conversion such as elastic modulus, so the first null hypothesis tested was rejected. Evaluating different adhesives, the distinct behavior of these products leads to second null hypothesis rejection that assumed the similarity in properties performance regardless bonding agent.

Some studies have compared LEDs to halogen light performance with composite resins (Jandt *et al.*, 2000; Leonard *et al.*, 2002; Asmussen & Peutzfeldt, 2003). However, adhesives usually present different comonomers compared with dental composites, and they also present organic solvents, which can affect polymerization. Despite these differences, the LCUs effect on the DC of adhesive systems has been scarcely studied (Arrais *et al.*, 2007; Ye *et al.*, 2007; Moraes *et al.*, 2010).

In this current study, light curing units did not interfere with the flexural strength for any adhesive tested, regardless of composition. However, there were significant differences between LCUs for DC and elastic modulus.

Despite the lower irradiance level, QTH presented better DC results for almost all adhesives systems and better *E* values for hydrophobic systems. The LED curing unit evaluated, in addition to present higher irradiance also at 4 mm distance (630 and 410 mW/cm^2 respectively for LED and QTH), was characterized for being a dual-wavelength LED, comprising five light-emitting diodes, with a wavelength range of 370-520nm, in which the central LED produced a stronger peak at 458nm while the other four accessory LEDs, a peak at 400nm (Ilie & Hickel, 2008). However, it comprised a large, oval (11 X 7.5 mm) curing footprint that may have influenced in material polymerization due to the difference in size of curing tip and tested sample. The small distance established between curing tip and adhesive surface may have compromised peripherals accessory diodes action since light emitted by them did not reach the specimen effectively, reducing LCU spectrum of wavelength that was restricted to the produced by central LED, which consequently may explain the decrease of the LED unit efficiency although its higher light intensity.

Another possible explanation for better QTH performance is that, in this case, the lower light scattering associated with this unit and a more effective contact between emitted light and material surface might have increased speed of reaction, promoting better DC values, and this higher reactivity probably favors the increase of non-solvated adhesives crosslink, leading to better *E* values.

Two of the solvated adhesives, SB2 and P90P, showed the greatest significant difference between the LCUs while OUP system presented different LCUs performance depending on exposure time applied. As a solvated adhesive, when polymerized for 10 s, it demonstrated the same DC behavior as SB2 and P90P, however, increasing curing time to 30 s, LED and QTH values for DC and *E* were similar, probably because of higher conversion since free radicals are still created by the illumination (Breschi *et al.*, 2007; Ilie & Hickel, 2008). So, it can be suggested that an increase in exposure time of SB2 and P90P, with this LED, would cause an improvement in the measured characteristics, since the manufacturers indicate one specific curing time for their materials, not taking into account differences among LCUs. A pilot study revealed 76% and 84% of increase in monomer conversion for SB2 with 20 s and 30 s of activation, respectively.

The purpose of this study was also to investigate DC and mechanical properties performance according to commercial dental adhesives composition. It was observed that solvated adhesives (SB2, P90P and OUP 30s) presented higher degree of conversion in relation to non-solvated systems, when polymerized by halogen light unit. This can be explained by the molecules mobility in the system, since the solvent dilutes the viscous monomers, leading reaction to occur in a less restricted environment. The decreased system viscosity allows propagation to continue for longer times without being such diffusion-controlled like non-solvated adhesives systems (Ye *et al.*, 2007).

One-Up Bond system presented lower degree of conversion than the others tested systems. This agent is a non camphorquinone (CQ) based adhesive that presents the arylborate catalyst as photoinitiator, which can reduce their efficiency with reduced time of activation, despite the 10 s of curing be recommended by the manufacturer. However, increasing the exposure time to 30 s, higher DC values were obtained due to longer irradiation times that can lead to higher conversion rates (Breschi *et al.*, 2007).

Hydrophobic bonding agents present a greater ability to form crosslinks (Bae *et al.*, 2005), which can assure polymer stiffness. However, the formation of crosslinking structure also reduces the diffusion of reactants, resulting in auto deceleration of the rate and limiting the final conversion (Dickens *et al.*, 2003).

The DC based on the quantity of remaining double bond has been used extensively to characterize and provide a relative assessment of dentin adhesives quality. However, the measurement of polymer conversion does not necessarily provide complete representation of the quality of the polymer structure (Ye *et al.*, 2007), which is directly related to mechanical behavior of resin-based materials. This current study demonstrates that the chemical complexity associated to solvent presence in adhesive systems composition, despite increasing the degree of conversion, caused substantial differences in the mechanical properties.

Since polymers differ in linearity, and therefore crosslink density, better elastic modulus and flexural strength results were associated to the hydrophobic resins (SBMP, P90B and CP) due to high amount of Bis-GMA and TEGDMA on its composition, which are monomers that have a greater ability to form crosslinks, consequently rigid polymers (Bae *et al.*, 2005), while low values were obtained for the hydrophilic systems (SB2, P90P and OUP 30s). These results corroborate with other study that observed elastic modulus decreasing with an increase in solvent content, suggesting changes in the polymer crosslinking structure (Ye *et al.*, 2007). Higher concentrations of hydrophilic monomers, such as HEMA, and presence of high amount of solvents tend to form linear chains (Kurata *et al.*, 2008) that slide over one another, producing a less resistant polymer (Paul *et al.*, 1999).

The relationship of photopolymerization process, structure and properties in dental resin-based materials is complicated and depends on many factors, such as monomer structure, viscosity, temperature (Bae *et al.*, 2005; Faria-e-Silva *et al.*, 2010) and solvents presence (Guo *et al.*, 2009; Cadenaro *et al.*, 2008). The current results indicate that the impact of QTH and LED lights on the DC and elastic modulus of adhesive systems was material-dependent and that bonding agent-curing unit combination had a significant effect on tested properties.

Therefore, according to results, it is verified that future studies should be conducted for understanding the real relationship among light curing units and each adhesive composition in order to pursue the best polymerization conditions and hence better material performance.

CONCLUSIONS

The effect of light curing units on degree of conversion and elastic modulus showed that halogen light resulted in better properties performance, and that this influence was related to adhesives composition due to the chemical complexity of these systems, leading to different behaviors in relation to evaluated properties.

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Table 1. Bonding agents tested.

Bonding Agent	Composition*
Adper Scotchbond Multi-Purpose Plus**	BisGMA, HEMA, polyalkenoic acid copolymer, CQ, EDMAB, DHEPT
Adper Single Bond 2	BisGMA, UDMA, HEMA, polyalkenoic acid copolymer, CQ, DHEPT, water, ethanol, silica
Silorane adhesive system P90 **PRIMER**	BisGMA, HEMA, water, ethanol, silane treated silica filler, CQ, Phosphoric acid–methacryloxy-hexylesters mixture, phosphorylated methacrylates, Copolymer of acrylic and itaconic acid, Phosphine oxide
Silorane adhesive system P90 **BOND**	Hydrophobic dimethacrylate, phosphorylated methacrylates, TEGDMA, silane treated silica, CQ, stabilizers
Clearfil Protect Bond**	10 MDP, BisGMA, HEMA, hydrophobic dimethacrylate, camphorquinone, N,N-diethanol-p-toluidine, silanated colloidal silica, surface treated NaF
One-Up Bond F Plus	**Adhesive A**: MAC-10, MMA, HEMA, water, coumarin dye, methacryloylalkyl acid phosphate **Adhesive B:** multifunctional methacrylic monomer, fluoraluminosilicate glass, photoinitiator (arylborate catalyst)

*As informed by the manufacturers. **Composition for only the Bond bottle is presented. *BisGMA*: bisphenol-A glycidyldimethacrylate; *HEMA*: 2-hydroxyethylmethacrylate; *CQ*: camphorquinone; *EDMAB*: ethyl4-dimethylaminobenzoate; *DHEPT*: dihydroxyethyl p-toluidine; *UDMA*: diurethane dimethacrylate; *TEGDMA*: triethylene glycol dimethacrylate; *10 MDP*: 10-methacryloyloxydecyl dihydrogen phosphate; *NaF*: sodium fluoride; *MAC-10*: 11-methacryloyloxy-1,1-undecanedicarboxyric acid; *MMA*: methylmethacrylate.

Table 2. Means and Standard Deviations (SD) for Degree of Conversion (%) of Adhesive Systems Testing the Different Light-Curing Units

Adhesive Systems	4mm	
	QTH	LED
SB2	69,1 (1,6) Aa	38,4 (1,9) Db
SBMP	57,4 (0,7) BCa	52,9 (0,5) Bb
CP	59,3 (0,3) Ba	55,4 (1,6) Bb
P90B	54,4 (1,4) Ca	54,0 (1,0) Ba
P90P	69,0 (1,3) Aa	32,9 (1,0) Eb
OUP 10s	48,0 (1,3) Da	45,0 (4,6) Cb
OUP 30s	65,3 (3,7) Aa	64,1 (4,0) Aa

Means followed by distinct letters represent statistically significant differences (2-way ANOVA/Tukey, alfa=5%). Upper case letters compare adhesives in the same column and lower case letters compare light curing units in the same row.

Table 3. Means and Standard Deviations (SD) for Elastic Modulus (GPa) of Adhesive Systems Testing the Different Light-Curing Units

Adhesive Systems	4mm	
	QTH	LED
SB2	0,7 (0,05) Ba	0,5 (0,02) Ca
SBMP	1,9 (0,2) Aa	1,2 (0,2) Ab
CP	1,7 (0,2) Aa	1,0 (0,2) ABb
P90B	1,3 (0,4) Aa	1,4 (0,5) Aa
P90P	0,6 (0,1) Ba	0,4 (0,1) Ca
OUP 30s	0,8 (0,2) Ba	0,8 (0,1) Ba

Means followed by distinct letters represent statistically significant differences (2-way ANOVA/Tukey, alfa=5%). Upper case letters compare adhesives in the same column and lower case letters compare light curing units in the same row.

Table 4. Means and Standard Deviations (SD) for Flexural Strength (MPa) of Adhesive Systems Testing the Different Light-Curing Units

Adhesive Systems	**4mm**	
	QTH	**LED**
SB2	22,4 (8,4) Ba	18,4 (3,0) Ca
SBMP	89,1 (16,0) Aa	75,2 (13,1) Aa
CP	88,9 (11,2) Aa	71,8 (18,6) Aa
P90B	78,0 (16,7) Aa	99,5 (22,6) Aa
P90P	28,4 (3,9) Ba	20,1 (2,8) Ca
OUP 30s	29,7 (6,3) Ba	38,5 (5,8) Ba

Means followed by distinct letters represent statistically significant differences (2-way ANOVA/Tukey, alfa=5%). Upper case letters compare adhesives in the same column and lower case letters compare light curing units in the same row.

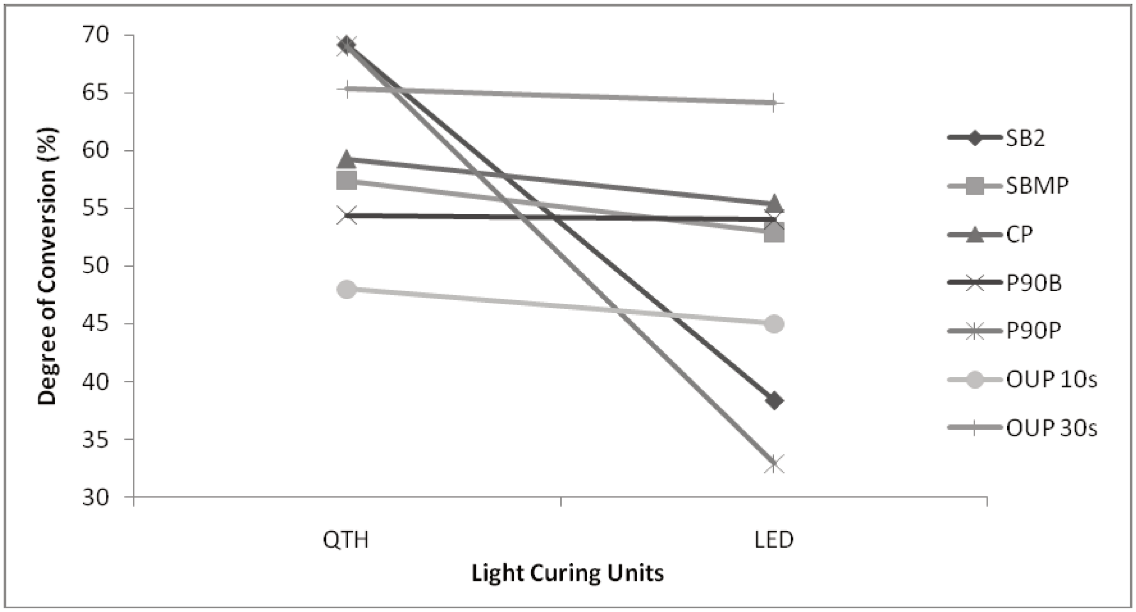

Figure 1. Degree of Conversion (DC) of Adhesive Systems Testing the Different LCUs.

CONSIDERAÇÕES GERAIS

A relação existente entre o processo de fotopolimerização, estrutura e propriedades dos materiais resinosos é complexa e depende de muitos fatores relacionados à própria fotoativação, assim como daqueles intrínsecos ao material, como composição monomérica, quantidade de solvente e viscosidade (Elliot & Bowman, 2002; Ye *et al*., 2007). Sendo assim, este trabalho buscou investigar a importância de fatores como diferentes fontes de luz e intensidades, distâncias de ativação e composição no desempenho dos diferentes sistemas adesivos.

No presente estudo, a influência desses fatores no grau de conversão e nas propriedades mecânicas de adesivos comerciais foi evidente. No Capítulo 1, diferentes distâncias de ativação foram investigadas já que, em condições clínicas, nem sempre é possível posicionar a ponta do aparelho fotoativador o mais próximo da superfície do material. Divergências em relação à eficiência das fontes de luz se tornam mais evidentes com o aumento da distância de ativação (Ilie & Hickel, 2008). No Capítulo 2, uma fonte de luz halógena convencional foi comparada com LED de terceira geração, capaz de produzir picos de emissão de luz em dois comprimentos de onda. Dessa forma, buscou-se elucidar se, além das diferentes intensidades, essa característica poderia influenciar na polimerização dos sistemas adesivos.

A qualidade da fonte de luz aplicada para fotoativar materiais resinosos é fator crucial para obtenção de altas taxas de conversão monomérica (Arrais *et al*., 2007). Neste estudo, foi possível observar que os dois fatores avaliados (distâncias de ativação e fontes de luz) influenciaram o grau de conversão dos adesivos testados, relacionando-se com a composição dos mesmos.

No Capítulo 1, as distâncias foram significantes apenas na conversão de adesivos com maior conteúdo de solvente. Comportamento semelhante foi observado para esses adesivos hidrófilos no Capítulo 2, entretanto, dois representantes hidrófobos (SBMP/CP) também mostraram diferença entre as fontes de luz. Esses dados podem sugerir que a presença de solvente na composição dos adesivos torna a conversão dos monômeros mais susceptível aos fatores ligados ao processo de polimerização.

Outra característica relevante ao grau de conversão é a composição do material uma vez que, em ambos os capítulos, foram obtidos resultados similares. Independentemente da condição experimental, de forma geral, adesivos hidrófilos mostraram valores superiores aos adesivos hidrófobos. Isso pode ser explicado pela redução da viscosidade do material, devido à presença de solvente, a um nível que favoreceria a mobilidade dos radicais livres e formação de sítios de ligação na cadeia polimérica (Dickens & Cho, 2005; Holmes *et al.*, 2007; Cadenaro *et al.*, 2008). Entretanto, associa-se à presença de grande quantidade de solvente residual a efeitos que podem inibir a reação de polimerização e comprometer a formação de adequada matriz polimérica (Reis *et al.*, 2004; Carvalho *et al.*, 2003; Arrais *et al.*, 2007). Dessa forma, pode-se sugerir que a presença de solvente em pequenas concentrações pode ser favorável para obtenção de melhores taxas de conversão, enquanto que, em maiores proporções, este componente seria prejudicial à formação do polímero.

De forma geral, afirma-se que melhores propriedades mecânicas de materiais resinosos fotoativáveis estão associadas a altos valores de grau de conversão (Ferracane & Greener, 1986; Dickens & Cho, 2005). Contudo, essa relação não foi observada no presente estudo, confirmando que o grau de conversão dos monômeros em polímero não representa, necessariamente, informações sobre qualidade ou durabilidade da estrutura polimérica formada (Ye *et al*., 2007).

Nos dois capítulos, independentemente da condição experimental avaliada, melhor módulo de elasticidade foi associado aos adesivos hidrófobos. Esses materiais apresentam grande quantidade de monômeros dimetacrilato que possuem maior capacidade de formação de ligações cruzadas entre as cadeias poliméricas, o que contribui para maior rigidez do polímero resultante (Bae *et al.*, 2005). Nesse caso, a presença de, até mesmo, pequenas concentrações de solvente pode não ser favorável para a formação de polímeros com maior densidade de ligações cruzadas (Malacarne-Zanon *et al.*, 2009).

Há uma correlação entre efetiva remoção de solventes nos sistemas adesivos com o aumento das propriedades mecânicas (Paul *et al.*, 1999; Carvalho *et al*., 2003; Ye *et al.*, 2007). Esse componente é capaz de evitar a aproximação das extremidades reativas, tornando o estabelecimento de ligações cruzadas mais difícil (Ye *et al.*, 2007), além de apresentar tendência a formar cadeias lineares (Kurata *et al.*, 2008), que deslizam uma sobre as outras, resultando em polímeros menos resistentes (Paul *et al.*, 1999). Sendo assim, sugere-se cautela no estabelecimento de uma relação entre GC e propriedades mecânicas no que se refere a materiais resinosos com solvente, uma vez que a presença deste pode estar relacionada com o aumento da conversão dos monômeros, porém, formando polímeros com estruturas menos rígidas.

Diferentemente do obtido para o grau de conversão, os fatores em estudo não influenciaram o módulo de elasticidade dos adesivos hidrófilos, entretanto, foram capazes de afetar os adesivos hidrófobos. Esse fato sugere a confirmação de que estes adesivos, devido à natureza de sua composição, relacionam-se de maneira mais direta com as propriedades mecânicas, sofrendo, inclusive, modulação na polimerização diante de fatores como distâncias de ativação e diferentes fontes de luz. Cabe ressaltar, ainda, que essa mesma influência dos fatores testados sobre os sistemas adesivos não foi observada para resistência à flexão. Em outras palavras, em relação a essa propriedade, melhores valores também foram atribuídos aos adesivos hidrófobos, entretanto não houve diferença significativa entre as distâncias e fontes de luz avaliadas, demonstrando que os fatores ligados ao processo de fotopolimerização não foram capazes de afetar a resistência flexural dos sistemas adesivos testados.

Sendo assim, diante dos resultados obtidos, verifica-se que mais estudos devem ser realizados para o conhecimento da real relação entre os fatores envolvidos no processo da fotoativação com a composição de cada sistema adesivo, de forma a buscar as melhores condições de polimerização e, consequentemente, melhor desempenho do material.

CONCLUSÃO

De acordo com as condições experimentais e com base nos resultados obtidos foi possível concluir que:

- As diferentes fontes de luz e distâncias de ativação avaliadas exerceram influência no grau de conversão e no módulo de elasticidade dos sistemas adesivos testados;
- Não houve influência dos fatores testados na resistência à flexão;
- A luz halógena mostrou melhores resultados de grau de conversão para maioria dos sistemas adesivos, enquanto que, em relação ao módulo de elasticidade, ela foi superior para a maioria dos adesivos hidrófobos testados;
- Não houve diferença entre as distâncias de ativação em relação ao grau de conversão de adesivos hidrófobos, ao passo que, para módulo de elasticidade, igualdade entre as distâncias foi observada entre os adesivos hidrófilos;
- O grau de conversão, módulo de elasticidade e resistência à flexão mostraram-se material dependente;
- Adesivos ricos em solvente apresentaram melhor desempenho de grau de conversão, enquanto que melhores resultados relacionados às propriedades mecânicas foram obtidos para adesivos hidrófobos, independentemente dos fatores testados.

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ANEXO

MATERIAIS E MÉTODOS

Para realização deste estudo, cinco diferentes sistemas adesivos foram utilizados e estão apresentados na Figura 1: *Adper Scotchbond Multi-Purpose Plus* (**SBMP -** 3M ESPE, St. Paul, Min., USA); *Adper Single Bond 2* (**SB2 -** 3M ESPE, St. Paul, Min., USA); *One-up Bond F Plus* (**OUP** – Tokuyama Dental Corp., Tokyo, Japan); *Clearfil Protect Bond* (**CP -** Kuraray Medical Inc., Okayama, Japan); e *P90 System Adhesive – primer* (**P90P**) e adesivo (**P90B**) (3M ESPE, St. Paul, Min., USA).

Figura 1 – (A) Adper Scotchbond MP Plus (componente adesivo); (B) Adper Single Bond 2; (C) One-up Bond F Plus; (D) Clearfil Protect Bond (componente adesivo); P90 Adhesive System: (E) componente *primer* e (F) componente adesivo.

Os grupos foram divididos de acordo com os fatores em estudo de cada experimento. No Capítulo 1, avaliou-se diferentes distâncias de ativação (2, 4 e 6mm), totalizando três grupos (n=5) para cada sistema adesivo (Quadro 1). Já no Capítulo 2, diferentes fontes de luz, ilustradas na Figura 2, foram testadas: luz halógena – **QTH** (Demetron LC, Sybron Kerr, Danbury, CT, USA – intensidade de luz: 650mW/cm2); ou luz emitida por diodo – **LED** (Ultralume 5 – Ultradent Products Inc., South Jordan, Utah – intensidade de luz: 850mW/cm2), totalizando dois grupos (n=5) para cada sistema adesivo (Quadro 2). Essa divisão dos grupos é válida tanto para o teste de grau de conversão como o de propriedades mecânicas.

Quadro 1 – Divisão dos grupos experimentais de acordo com as distâncias de ativação (Capítulo 1).

Sistemas Adesivos	Fonte de Luz	Distância de ativação
SBMP	QTH	2mm 4mm 6mm
SB2	QTH	2mm 4mm 6mm
OUP	QTH	2mm 4mm 6mm
CP	QTH	2mm 4mm 6mm
P90P	QTH	2mm 4mm 6mm
P90B	QTH	2mm 4mm 6mm

Figura 2 – (A) Luz halógena - QTH e (B) Luz emitida por diodo – LED.

Quadro 2 – Divisão dos grupos experimentais de acordo com as fontes de luz avaliadas (Capítulo 2).

Sistemas Adesivos	Distância de ativação	Fontes de Luz
SBMP	4mm	QTH LED
SB2	4mm	QTH LED
OUP	4mm	QTH LED
CP	4mm	QTH LED
P90P	4mm	QTH LED
P90B	4mm	QTH LED

Mensuração do Grau de Conversão

Em ambos os estudos, foram realizadas cinco leituras do grau de conversão (n=5) para cada grupo experimental. Cinco microlitros (5µL) do sistema adesivo foram aplicados em única camada, com o auxílio de pipeta de precisão (Microman Classic, modelo M25, Gilson, FRA), representada na Figura 3, diretamente no elemento de refletância total atenuada acoplado (ATR), do Espectrômetro de raios infra-vermelhos Transformado de Fourier - FTIR (Spectrum 100 Optica; PerkinElmer, MA, USA), o qual possui um cristal horizontal de Seleneto de Zinco (Pike Technologies, Madison, WI, USA) no centro que funciona com substrato ativo para os raios infra-vermelho (Figura 4).

Figura 3 – Pipeta de precisão utilizada para manipulação dos sistemas adesivos com marcação em 5µL.

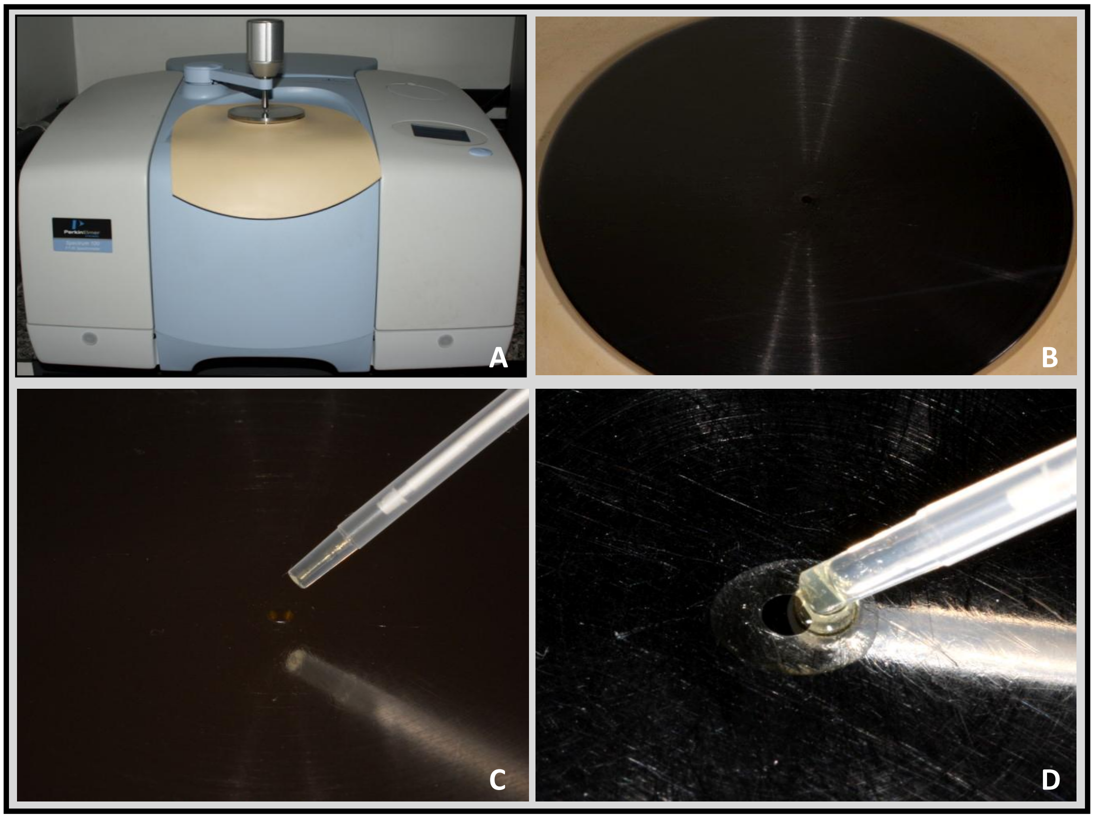


Figura 4 – (A) Espectrômetro de Raios Infra-vermelhos Transformado de Fourier (FTIR); (B) Plataforma de leitura com cristal de seleneto de zinco no centro; (C) Posicionamento da pipeta contendo o sistema adesivo em relação ao cristal do FTIR e; (D) quantidade padronizada de adesivo sendo dispensada sobre o cristal.

Após dispensar o adesivo sobre o cristal, foi aplicado leve jato de ar por 10s, para os adesivos que continham solvente em sua composição (SB2, P90P e OUP), a uma distância de 10 cm. Após volatilização do solvente, procedia-se à fototivação, seguindo o tempo recomendado pelo respectivo fabricante, de acordo com a fonte de luz e distância de ativação respectiva a cada experimento. Foram determinados dois grupos para mensuração do grau de conversão do One-up Bond (OUP), um com tempo de fotoativação de 10 s, sugerido pelo fabricante, e outro com 30 s, uma vez que somente com esse tempo de polimerização foi possível confeccionar os corpos-de-prova para o teste das propriedades mecânicas.

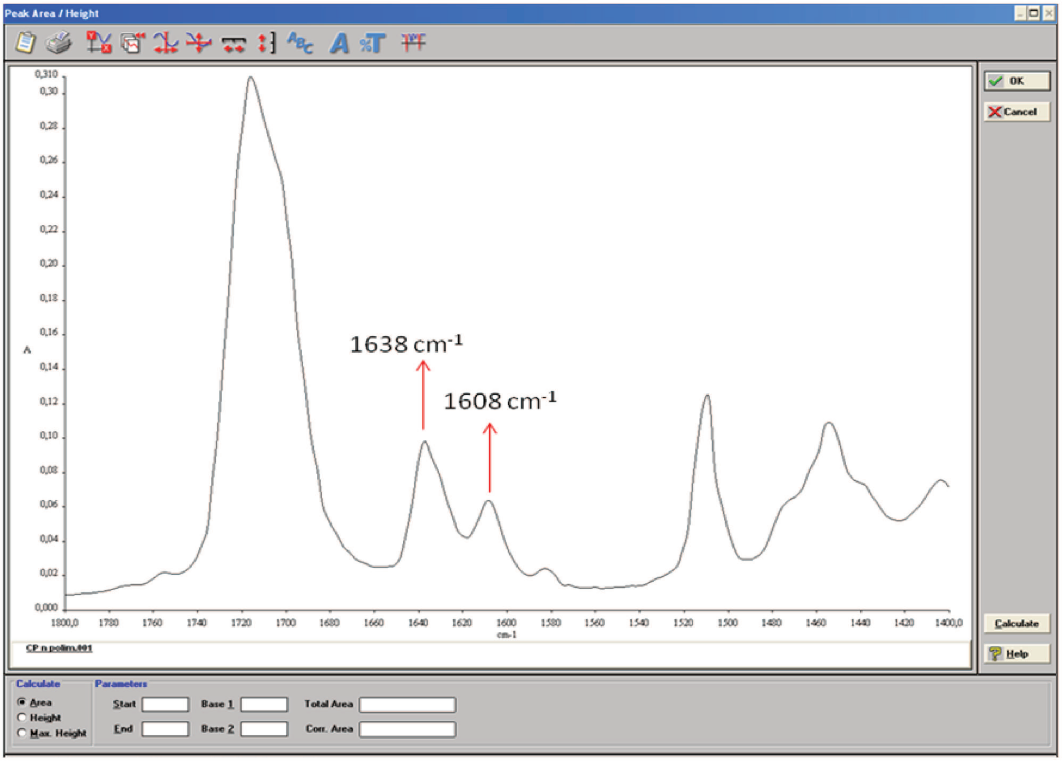
No Capítulo 1, para simular as distâncias de ativação, a polimerização foi realizada com o auxílio de um suporte que foi acoplado à fonte de luz (QTH) de forma a padronizar a distância estabelecida entre a ponta do aparelho fotopolimerizador e a superfície do material. Esse processo foi controlado através de paquímetro digital (Mitutoyo, Tokyo, Japan). O mesmo foi feito no Capítulo 2, porém a distância estabelecida de 4 mm manteve-se constante para as duas fontes de luz que foram acopladas ao suporte uma de cada vez.

O ensaio foi conduzido a partir da leitura inicial de cada sistema adesivo não fotoativado. Esta leitura foi considerada o controle para cada tipo de adesivo, pois fornecia os valores das áreas correspondentes às bandas dos anéis aromáticos e alifáticas previamente à polimerização do material em estudo (leitura do monômero). Durante cada leitura, foram obtidos espectros infravermelhos com auxílio do programa Spectrum (PerkinElmer) presente em microcomputador ligado ao espectrômetro. O programa foi utilizado no modo de monitoramento da varredura, usando a apodização Happ-Genzel, com resolução de 4 cm^{-1} e os espectros sendo coletados no intervalo de 1665 a 1580 cm^{-1}.

O cálculo do grau de conversão foi feito baseado na proporção entre as duplas ligações de carbono alifáticas ($C = C$) e aromáticas, usadas como controle interno por ser considerada inerente à composição do material, nos estados polimerizados e não polimerizados (Ferracane & Greener, 1984) – Figuras 5 e 6. Durante a reação de polimerização, a absorbância das duplas ligações de carbono aromáticas permanece constante, enquanto que há redução da quantidade de duplas ligações alifáticas. A dupla ligação de carbono alifática absorve a energia no comprimento de onda de 1638 cm^{-1}, enquanto que a aromática no comprimento de 1608 cm^{-1}.

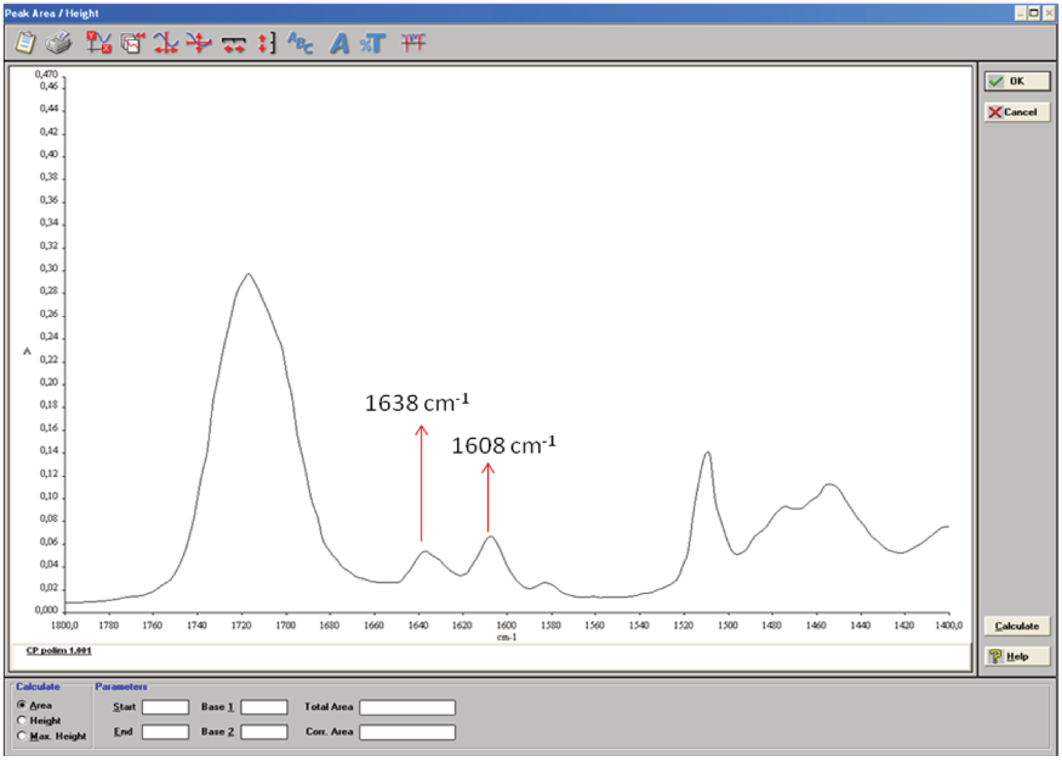
Para o cálculo, foi utilizada a técnica de *baseline* (Rueegeberg *et al*., 1990), traçado pelo próprio programa Spectrum. A partir desta, foram mensurados alguns parâmetros pelo próprio programa. A intensidade corrigida dos picos observados nos comprimentos de onda 1638 e 1608 cm^{-1} foi utilizada na seguinte fórmula: R = intensidade em $1638cm^{-1}$ / intensidade em $1608cm^{-1}$, sendo o grau de conversão (%) calculado da seguinte forma:

$$GC\ (\%) = \left[1 - \left[\frac{\dfrac{1638\ cm^{-1}}{1608\ cm^{-1}}\ \text{polimerizado}}{\dfrac{1638\ cm^{-1}}{1608\ cm^{-1}}\ \text{não polimerizado}} \right] \right] X\ 100$$



● Area
○ Height
○ Max. Height

Figura 5 – Gráfico do programa *Spectrum* ilustrando as duplas ligações alifáticas (1638 cm^{-1}) e aromáticas (1608 cm^{-1}) de um adesivo em seu estado não polimerizado.



Calculate
● Area
○ Height
○ Max. Height

Figura 6 – Gráfico do programa *Spectrum* ilustrando as duplas ligações alifáticas (1638 cm^{-1}) e aromáticas (1608 cm^{-1}) do mesmo adesivo que a figura anterior, porém, em estado polimerizado.

Avaliação das Propriedades Mecânicas

Este ensaio foi realizado conforme descrito na ISO 4049/2000, para o teste de flexão de três pontos, com exceção das dimensões do corpo de prova.

Inicialmente, para confecção das amostras, foram preparados moldes padronizados de silicone de adição (Aquasyl, Dentsply, Petrópolis, RJ, Brasil) a partir da impressão do material de moldagem em matrizes de Teflon que possuem uma elevação interna central em forma de barra medindo 2 mm de largura, 1 mm de altura e 7 mm de comprimento (Figura 7). Uma vez prontos os moldes de silicone, barras foram confeccionadas com os diferentes sistemas adesivos citados (Figura 8).

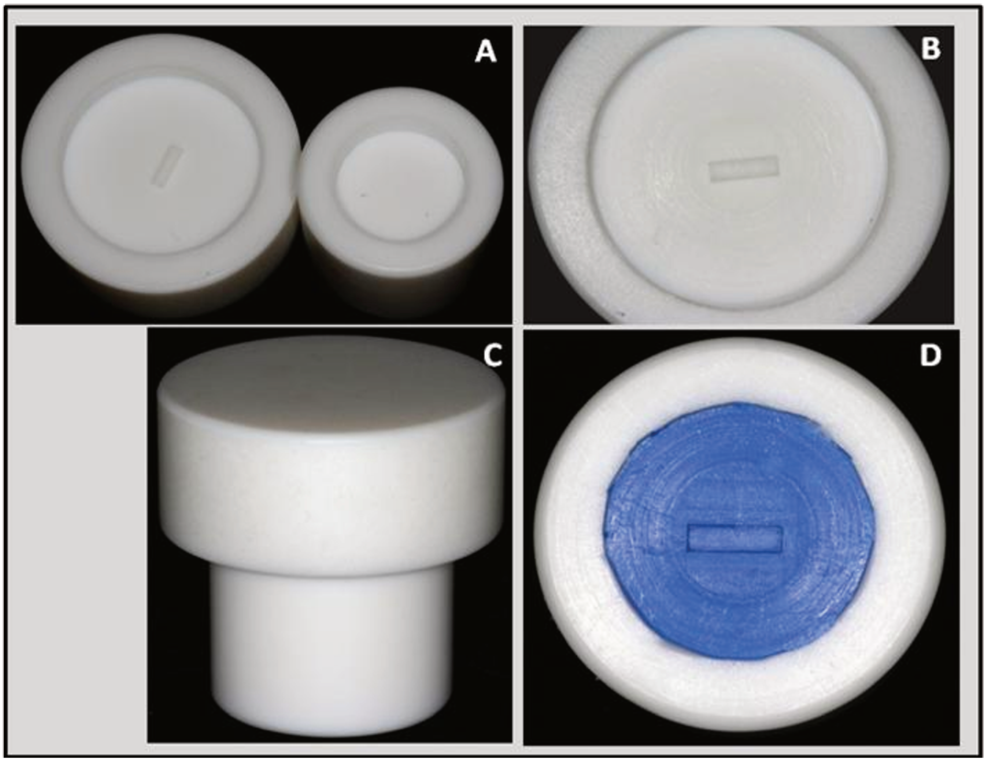


Figura 7 – (A) Partes superior e inferior da matriz de Teflon; (B) Parte superior da matriz com elevação central em forma de barra; (C) Matriz em posição para impressão no material de moldagem; e (D) Molde de silicone de adição confeccionado a partir da matriz de Teflon.

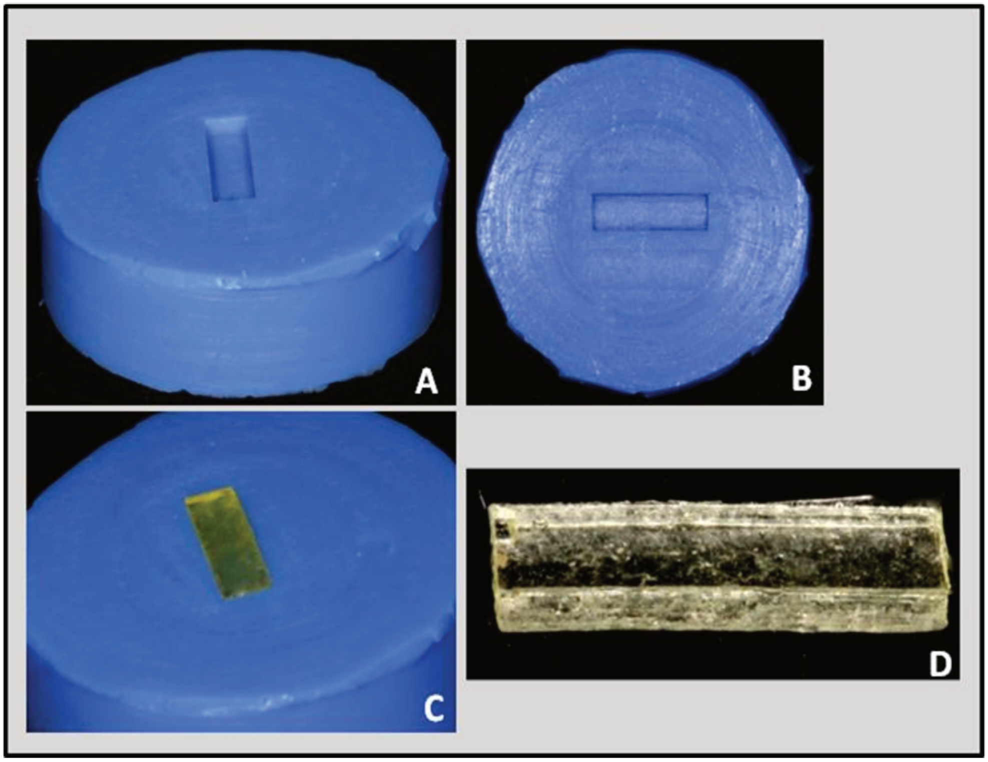


Figura 8 – (A) Vista de perfil da matriz de silicone que foi utilizada para confecção dos corpos-de-prova de adesivos; (B) Vista superior; (C) Adesivo polimerizado após inserção do mesmo em camadas; e (D) Amostra de um adesivo em forma de barra nas dimensões da matriz de silicone (2 mm X 1 mm X 7mm).

Os sistemas adesivos foram dispensados na matriz em quatro camadas, contendo 5µL cada, totalizando 20µL de adesivo por espécime. Cada camada foi inserida com o auxílio de pipeta de precisão (Microman Classic, modelo M25, Gilson, FRA) – Figura 3, aplicado leve jato de ar por 10s, a uma distância de 10 cm, através de seringa tríplice, previamente à aplicação de nova camada ou fotoativação, no caso da última. Após volatilização do solvente da quarta camada, foi colocada sobre este uma tira de poliéster para facilitar a regularização da superfície da amostra. A fotoativação foi realizada pelo tempo de ativação recomendado pelo fabricante (10 s para a maioria dos sistemas adesivos), com exceção do OUP.

O sistema adesivo OUP apresentou falha prematura durante a etapa de confecção dos corpos de prova quando fotopolimerizado pelo tempo recomendado pelo fabricante (10 s). Dessa forma, aumentou-se o tempo de ativação para 30 s, e assim, foi possível obtenção de espécimes para avaliação das propriedades mecânicas.

Os aparelhos fotopolimerizadores foram fixados em máquina padronizadora de preparos e as distâncias entre a ponta da fonte de luz e a superfície da matriz de silicone eram controladas por paquímetro digital (Mitutoyo, Tokyo, Japan) - Figuras 9 e 10.

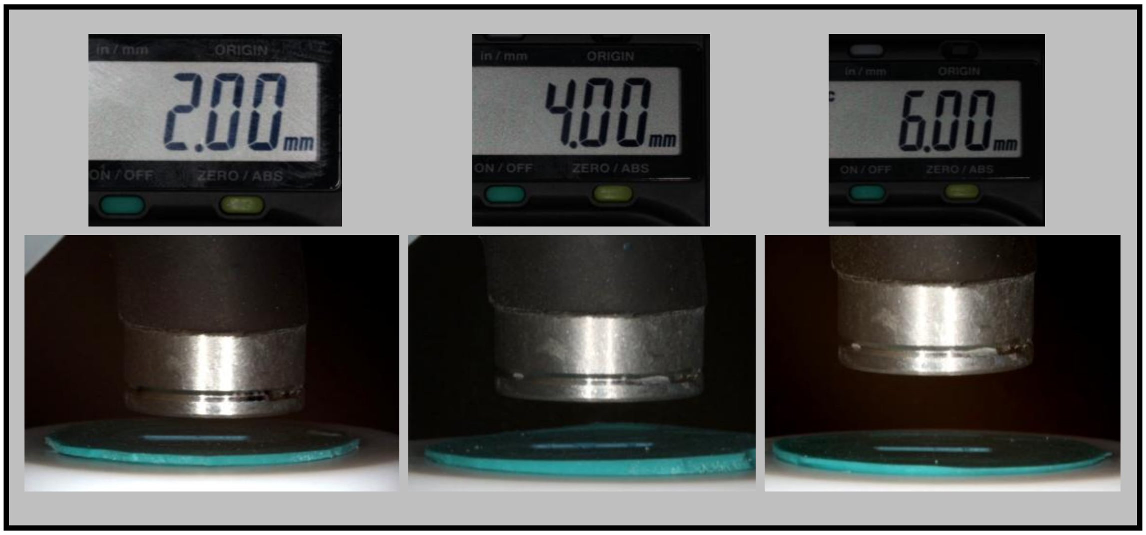


Figura 9 – Distâncias da ponta da fonte de luz (QTH) com a superfície do corpo de prova (Capítulo 1).

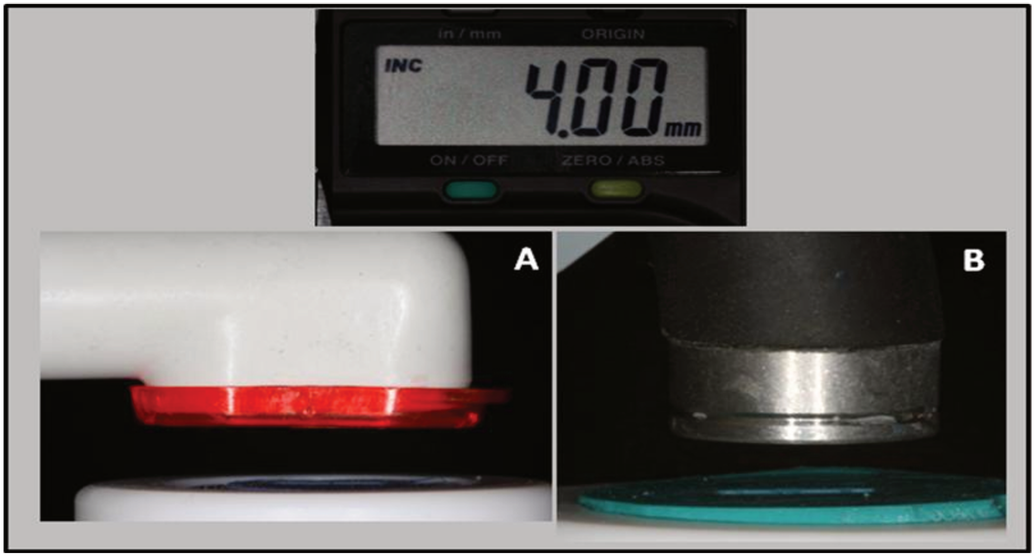


Figura 10 – Relação da ponta das fontes de luz com a superfície do corpo de prova aos 4mm: (A) LED e (B) QTH – Capítulo 2.

Após a confecção, os espécimes foram armazenados em água destilada, a 37˚C, por 24 horas. A mensuração da resistência à flexão e módulo de elasticidade foi realizada depois de percorrido este tempo da confecção dos espécimes, através do teste de três pontos (ISO 4049/2000), conforme a Figura 11, a velocidade de 0,5 mm/min, com célula de carga de 500 N, em Máquina de Ensaio Universal (Instron, model 4411, Buckinghamshire, England) – Figura 12, cujos resultados foram obtidos através do programa Blue Hill II (Instron, model 4411, Buckinghamshire, England). Os valores de Resistência à flexão foram calculados em Megapascal (MPa) e os de Módulo de Elasticidade, em Gigapascal (GPa).

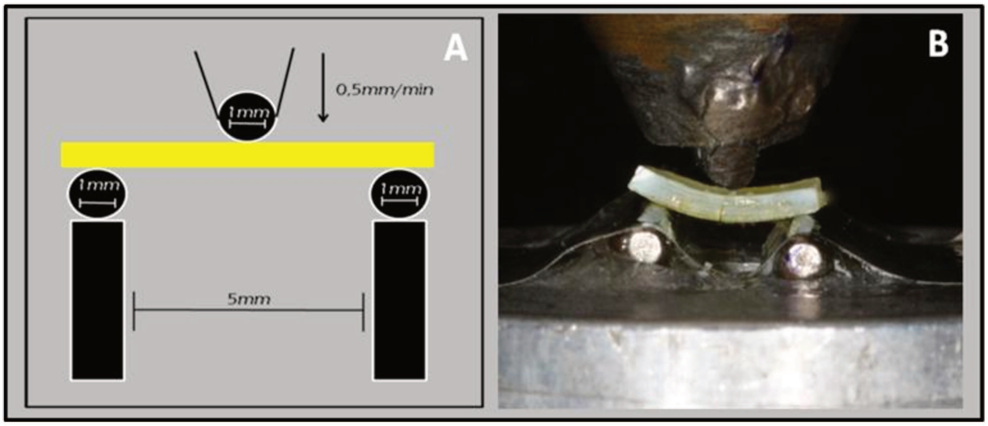


Figura 11 – (A) Representação esquemática do teste de resistência à flexão que foi realizado no presente trabalho; e (B) Teste de flexão sendo executado no corpo de prova de adesivo.

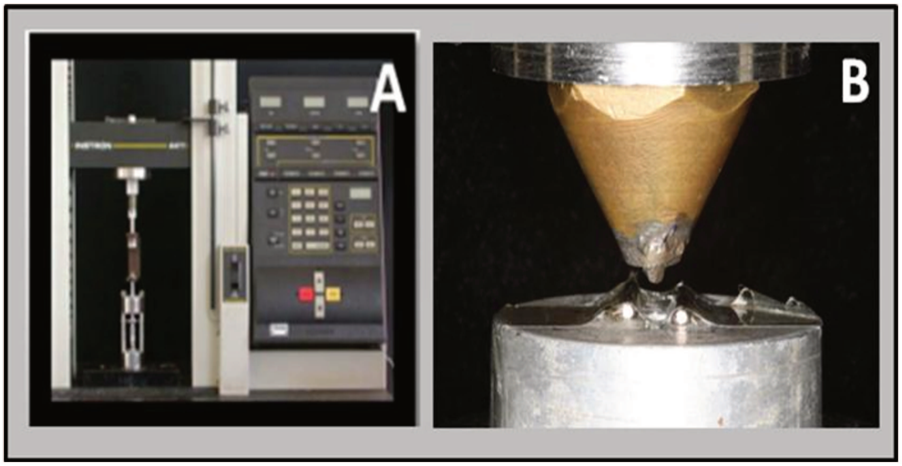


Figura 12 – (A) Máquina de Ensaio Universal; e (B) Vista aproximada do dispositivo de flexão utilizado neste estudo.

Análise Estatística

Os resultados obtidos através da análise do grau de conversão e propriedades mecânicas (módulo de elasticidade e resistência à flexão) foram tabulados, analisados quanto a sua normalidade e comparados conforme as diferentes distâncias (2 mm, 4 mm e 6 mm), avaliadas no Capítulo 1, e fontes de luz utilizadas (LED e QTH) no Capítulo 2.

Para cada experimento, os dados foram submetidos ao teste de Análise de variância (ANOVA) 2-fatores: Capítulo 1 (sistemas adesivos X distâncias de ativação) e Capítulo 2 (sistemas adesivos X fontes de luz) e, após observar diferença estatística significativa entre os grupos, foi aplicado o teste de Tukey. Foi utilizado o programa estatístico SAS e considerado o nível de significância de 5% ($p<0,05$).