# *Brazilian Journal of Development*

## Effects of residual contamination on mechanical properties and real-time conversion of etch-and-rinse adhesive

## Efeitos da contaminação residual nas propriedades mecânicas e na cinética de conversão de adesivos convencionais

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**ABSTRACT**

Introduction: An ideal hybrid layer should have water and solvents completely replaced by resin monomers, thus creating an interdiffusion zone with collagen and resin, and guaranteeing resistance and adequate mechanical properties to resist the challenges incurred in restoration. Objective: To evaluate the influence of residual contamination by different concentrations of water, ethanol and chlorexidine on mechanical properties and conversion of two etch-and-rinse adhesives. Method: Bar specimens of a model adhesive (M1) and a commercial Scotchbond MP adhesive (SBMP) were prepared and submitted to flexural strength (FS), elastic modulus ($E$), conversion degree (DC) and the kinetics of cure (K) evaluation. The real-time polymerization (RP) was monitored for 120 seconds. The data were statistically analyzed by two-way ANOVA and Tukey's test ($\alpha$=0.05). Results: All solutions showed a decrease in FS and $E$ values. For M1 adhesive, this decrease could be noted with increase of all dilutions tested. A decrease in DC values also was noted as dilutions increased, independent of solution tested. For SBMP adhesive, the mechanical properties were affected more by water and chlorexidine solutions and, it was noted an increase in DC with the increase of solution, especially for ethanol. For K test, adding water to adhesives, a progressive decrease could be noted on graphics. Conclusions: So a reduction in mechanical properties of adhesive solutions could be noted when extreme amounts of residual solutions. Nevertheless, at lowest concentrations, ethanol and chlorexidine seems not interfere on K and RP of adhesives.

**Keywords:** Chlorexidine, Dentinal adhesive, Ethanol, Mechanical properties, Water.

**RESUMO**

Introdução: Uma camada híbrida ideal deve ter água e solventes completamente substituídos por monômeros de resina, criando assim uma zona de interdifusão com colágeno e resina, garantindo resistência e propriedades mecânicas adequadas para resistir aos desafios da restauração. Objetivo: Avaliar a influência da contaminação residual por diferentes concentrações de água, etanol e clorexidina nas propriedades mecânicas e na conversão de dois adesivos de condicionamento e enxágue. Método: Amostras de barras de um adesivo modelo (M1) e um adesivo Scotchbond MP comercial (SBMP) foram preparadas e submetidas à resistência à flexão (RF), módulo de elasticidade (E), grau de conversão (GC) e cinética de cura (CC) avaliação. A polimerização em tempo real (PTR) foi monitorada por 120 segundos. Os dados foram analisados estatisticamente por ANOVA a dois fatores e teste de Tukey ($\alpha$ = 0,05). Resultados: Todas as soluções apresentaram uma diminuição nos valores de RF e E. Para adesivo M1, essa diminuição pode ser observada com o aumento de todas as diluições testadas. Também foi observada uma diminuição nos valores de GC à medida que as diluições aumentavam, independentemente da solução testada. Para o adesivo SBMP, as propriedades mecânicas foram mais afetadas pelas soluções de água e clorexidina e, observou-se um aumento no GC com o aumento da solução, principalmente no etanol. Para o teste CC, adicionando água aos adesivos, uma diminuição progressiva pode ser observada nos gráficos. Conclusões: Portanto, uma redução nas propriedades mecânicas das soluções adesivas pode ser observada quando quantidades extremas de soluções residuais. No entanto, em concentrações mais baixas, etanol e clorexidina parecem não interferir no CC e PTR dos adesivos.

**Palavras chaves**: Clorexidina, Adesivo dentinários, Etanol, Propriedades mecânicas, Água.

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## 1 INTRODUCTION

During etching, half of the superficial mineral volume is removed and replaced by water[1] Water fills spaces which were before occupied by inorganic dentin, thus avoiding collagen fibrils collapse and allowing monomer infiltration by solvent and hydrophilic monomers applied.[2,3] An ideal hybrid layer should have water and solvents completely replaced by resin monomers, thus creating an interdiffusion zone with collagen and resin, and guaranteeing resistance and adequate mechanical properties to resist the challenges incurred in restoration.[1] However, independent of adhesive technique used, a complete water and solvent elimination is practically impossible to be achieved[1,4] and located spaces rich in water and poor of monomers are commonly identified,[4] which impairs the restorative stability by hindering the degree hybrid layer monomers conversion.[3] Apart from rendering the polymerized resin matrix more susceptible to subsequent water ingress, leading to resin hydrolysis followed by polymer swelling and leaching of resin components which are account for the deterioration in mechanical properties.[4]

In order to guarantee the substrate adhesion stability, some preventive approaching techniques, e.g. rinse cavity with chlorexidine or with ethanol after etching, are proposed by recent literature.[4-7] Between interfibrilar spaces, after etching and rinse steps, highly hydrated proteoglycans with negative charge forms a hydrogel through the interfibrilar spaces, besides water.[4] Such hydrogel also contains metalloproteinase enzymes that regulate the metabolism of collagen-based tissues.[4,6] The application of Chlorhexidine 2%, a metalloproteinase inhibitor, acts inhibiting the collagenolytic and gelatinolytic activities in partially demineralized dentin that is treated with the etch-and-rinse adhesives[6] decelerating degradation. Meanwhile, the ethanol wet-bonding was developed to enhance the durability of etch-and-rinse adhesives[4] by chemically dehydrate acid-etched demineralized dentin matrices, resulting in lateral shrinkage of collagen fibrils that cause an increase in the width of their interfibrilar spaces and a reduction in the hydrophilicity of the collagen matrix.[4, 7]

Despite the effectiveness of such solutions regarding the improvement of bonding strength and restoration longevity, [4,6] the application techniques of both EtOH and CHX are not well-known in the recent literature.[4, 6] Once the water excess generates complications on hybrid layer[3,4] and the CHX used as cavity rinse are mostly manipulated as an aqueous vehicle, these quantities may influence the degree of conversion as mechanical property of the polymer formed.[8] Further, the EtOH excess causes a gain in organic solvent quantities of adhesive system and may alter the colligative properties of solutions, *i.e.*, lower the freezing point and vapor pressure, and increase the osmotic pressure and boiling point solvents.[9] Also, this EtOH excess may generate a solvent

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saturation at interdiffusion zone, increasing the fluidity of monomeric system applied and defaulting the crosslinking of monomer resin applied after rinse.[10] As consequence, a reduction of degree of conversion may occur, causing a decrease in mechanical properties of the polymer formed. [9,11]

Therefore, as the influence of these solutions on adhesive monomers and the consequences of its excess in the quality of the polymer formed should be better elucidated, the purpose of this study is to evaluate the influence of different concentrations of solutions used as residual cavity rinse on adhesive dilution, evaluating the mechanical properties and kinetic of conversion of different adhesive systems. The first null hypothesis tested was that water, CHX or ethanol solutions have no influence over mechanical properties of adhesives tested independent of dilution concentration and the second null hypothesis was that an increase in dilution concentration of adhesives has no influence at the kinetic of conversion as at the rate of polymerization, independent of adhesive and solution tested.

## 2 METHODOLOGY

### 2.1 ADHESIVE SYSTEMS

Bisphenol-A glycidyl dimethacrylate (Bis-GMA), triethyleneglycol dimethacrylate (TEGDMA), HEMA and camphorquinone (CQ) were generously supplied by Esstech (Essington, PA, USA). 4-dimethylamine benzoate (EDAB) was purchased from Sigma-Aldrich (Milwaukee, WI, USA). All reagents were used without further purification.

Two different formulations of light-cured, model unfilled dental resins were evaluated: M1 (40 wt% Bis-GMA and 60 wt% HEMA) and a commercial adhesive, (Adper Scothbond Multi-Purpose Adhesive – 3M/ESPE, St. Paul. MN, USA).

For M1 manipulated adhesive, Bisphenol A glicidyl dimethacrylate (96% BisGMA), tri-ethyleneglicol dimethacrylate (96.5% TEGDMA), 2-hydroxyethyl methacrylate (99.5%, HEMA) and camphorquinone (97%, CQ) were gently supplied by Esstech, Inc. (Essignton, PA, USA). The 4-dimethylamie benzoate (98% EDAB) were purchase from Aldrich chemical (Milwaukee, WI, USA). All monomers were used without further purification. To blend, 1 mol% of CQ and 2 mol% of EDAB were added as photoinitiation system.[12] The materials were prepared through intensive mixture (Magnetic Misture, MPL Laboratory Products, Piracicaba, Brazil) in dark room with controlled temperature and humidity. All materials are listed in Table 1.

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**Table 1.** Description of materials used and their formulations.

| Description | Composition | Manufactured |
|---|---|---|
| **Adper Scotchbond Multi-Purpose Adhesive*** | - Bis-GMA (60-70%) <br> - HEMA (30-40%) | 3M ESPE Dental Products  St. Paul, MN |
| **M1 Model Adhesive** | - Bis-GMA (40%) <br> - HEMA (60%) | Manipulated adhesive |
| *Manufactures patents protect the exact percentages of monomers. | | |

## 2.2 MECHANICAL PROPERTIES

The experiment was performed according to the ISO 4049/2009 for dental polymers, except to the sample dimensions. Each adhesive were tested mixed with 0; 3 or 9% of primer (n=6). The mix of primer and adhesive were prepared, vigorous agitated to promote a homogeneous solution and then inserted in the silicone mold. Specimens were prepared according to a previous study protocol (Gaglianone *et al.*, 2012). Except for solvent evaporation step. Twenty microliters (µL) of each adhesive/primer solution were placed into a silicon mold, to prepare a specimen with a bar shape (7 mm X 2 mm X 1 mm).

Before light-activation, a Mylar strip was placed over the mold in an attempt to obtain a flat sample surface and prevent the inhibition of cure by the oxygen. Adhesives were irradiated using a light-emitted diode source (LED Elipar FreeLight2; 3M/ESPE, St. Paul. MN, USA) for 60 seconds (850 mW/cm$^2$). This procedure was performed since the aim of the study was to evaluate the effect of primer concentration with the best condition of cure available.

After storage for 24h on dry container, specimens were subjected to three-point bending test for measure the flexural strength (FS) and elastic modulus ($E$), at a crosshead speed of 0.5 mm/min using a universal testing machine (Instron model 4411, Instron Corp., Canton, MA, USA). Prior to the test, the dimensions of each specimen were recorded with Bluehill 2 software (Instron Corp., Canton, MA, USA), which has calculated the E (GPa) and FS (MPa), according to the dimensions and tension.

## 2.3 DEGREE OF CONVERSION

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 10 (Pike Technologies,

Madison, WI, USA). The specimens evaluated were the same tested for mechanical properties (n=5).

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. Specimens were placed on the horizontal face of the ATR cell with a constant weight of 90bar.

DC was calculated using a baseline technique,[13] based on band ratios of 1638 cm$^{-1}$ (aliphatic carbon-to-carbon double bond) and, as internal standard, of 1608 cm$^{-1}$ (aromatic component group) between the polymerized and uncured samples (n=5).

## 2.4 CONVERSION KINETICS AND RATE OF POLYMERIZATION

The real-time polymerization (K) was evaluated by Fourier transform infrared spectroscopy (Spectrum 100 Optica; PerkinElmer, MA, USA) as previously described, using an attenuated total reflectance device composed of a horizontal ZnSe crystal. A constant volume (5 µL) of bonding at neat form, or at 2 or 9% dilution in Water, CHX or Ethanol solution was dispensed immediately after mixture onto the crystal and photo-activated for 120s using a Light Emitted Diode source with 850 mW/cm$^2$ irradiance (LED Elipar FreeLight2; 3M/ESPE, St. Paul. MN, USA). The polymerization reaction was monitored in real time for those 2 min using Happ-Genzel apodization, collecting spectra in the 1680 to 1540 cm$^{-1}$ range, with a resolution of 8 cm$^{-1}$. With this setup, one spectrum (one scan) every two seconds was acquired. Three specimens were tested for each bond/primer concentration.

The DC for each scan was calculated as previously described. Average conversion vs. time data was plotted and Hill's 4-parameter non-linear regressions were used for curve fitting. As the coefficient of determination was greater than 0.99 for all curves, the rate of polymerization (RP) was calculated using these data-fitted plots.

## 2.5 STATISTICAL ANALYSES

The mechanical properties (FS, *E*), as well as as the DC were analyzed by two-way ANOVA and Tukey's test, at a 0.05 level of significance, having "adhesive" and "solution concentration" as the two variables (SAS 9.1 version – The SAS Institute, Cary, NC, USA).

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## 3 RESULTS

### 3.1 FLEXURAL STRENGTH

Decomposition ANOVA has shown significant effect only for isolated variables, adhesive and solution concentration, with no statistical significance for interactions. For M1 adhesive, Ethanol, Water and CHX solutions have shown a decrease of flexural strength as increasing the concentration of solutions on adhesives. For SBMP adhesive, only the ethanol dilution has shown no statistical difference, independent of concentration dilution. For both water and CHX solutions, as the concentration of dilution increased, a decrease in results could be noted (Table 2).

**Table 2.** Means (SD) for Flexural Strength (Mpa) of Adhesive Systems Testing Different Dilutions with Water, Ethanol and Chlorexidine.

| Adhesive | Solution | Concentration | | |
|---|---|---|---|---|
| | | 0% | 2% | 9% |
| **M1** | **Ethanol** | 156,37 (19,03) Aa | 149,87 (15,12) Aab | 121,17 (2,62) Ab |
| | **Water** | 173,26 (30,53) Aa | 153,70 (20,70 Aa | 116,09 (15,62) Ab |
| | **CHX** | 146,10 (9,78) Aa | 134,27 (14,26) Aab | 114,10 (7,40) Ab |
| **SBMP** | **Ethanol** | 142,79 (13,71) Aa | 141,28 (12,75) Aa | 113,91 (19,42) Aa |
| | **Water** | 151,20 (21,79) Aa | 133,72 (7,54) Aab | 103,11 (13,15) Ab |
| | **CHX** | 138,18 (18,40) Aa | 118,60 (10,38) Aab | 90,42 (19,22) Ab |

Each adhesive means followed by distinct capital letters in the same row and distinct small letters in the same column is significantly different at $p < 0.05$ -Two-Way ANOVA and Tukey test comparing means. *Indicate statistical differences between adhesives at same solution concentration.

### 3.2 ELASTIC MODULUS

When the elastic modulus ($E$) was evaluated, the ANOVA decomposition has presented a significant effect for solution, adhesive and concentration and also for the double interactions "solution*adhesive", "solution*concentration" and "adhesive*concentration", with no significance for triple interactions. For M1 adhesive, as the dilution concentration increased, a decrease on $E$ could be noted, independent of solution tested (Table 3). For the Ethanol solution, when SBMP were evaluated, the adhesives have presented worse behavior at 0% and 9% dilution concentration, and best results with statistical significance difference at 2% ($p < 0.05$).

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**Table 3.** Means (SD) for Elastic Modulus (GPa) of Adhesive Systems Testing the Different Dilutions with Water, Ethanol and Chlorexidine

| Adhesive | Solution | Concentration | | |
|---|---|---|---|---|
| | | 0% | 2% | 9% |
| M1 | Ethanol | 2,10 (± 0,38) Aa | 1,95 (± 0,18) ABab | 1,70 (± 0,09) Ab |
| | Water | 2,41 (± 0,23) Aa | 2,25 (± 0,19) Aa | 1,70 (± 0,15) Ab* |
| | CHX | 2,20 (± 0,06) Aa | 1,88 (± 0,16) Bab* | 1,55 (± 0,08) Ab |
| SBMP | Ethanol | 2,04 (± 0,08) Bab | 2,31 (± 0,08) Aa | 1,95 (± 0,26) ABb |
| | Water | 2,53 (± 0,20) Aa | 2,36 (± 0,10) Aab | 2,21 (± 0,21) Ab* |
| | CHX | 2,14 (± 0,09) Ba | 2,14 (± 0,15) Aa* | 1,72 (± 0,12) Bb |

Each adhesive means followed by distinct capital letters in the same row and distinct small letters in the same column is significantly different at p<0.05 -Two-Way ANOVA and Tukey test comparing means. *Indicate statistical differences between adhesives at same solution concentration.

When comparing the solutions for SBMP adhesive, at 0% of dilution the water solution has presented the best results when compared to others solutions at same concentration. For M1 adhesive, only at 2% of water dilutions the adhesive has presented best results when compared to other solutions at same concentration.

For comparisons between adhesives, only for CHX at 2% and water at 9% statistical significance has shown that SBMP has presented the best behavior when compared to M1 adhesive (Table 3).

## 3.3 DEGREE OF CONVERSION

For the degree of conversion (DC) results, only dilutions and solutions of the same adhesive were compared. Comparisons between adhesives were not evaluated, since for DC the comparisons between materials with different compositions were not the best form to demonstrate their best or worse behavior.[14-16]

The M1 adhesive has shown the best results for CHX solutions when comparison between solutions was evaluated (p<0.05) and worse results for water dilutions at 9% . For SBMP adhesive, at 2% of dilution, CHX presented the worse results, with statistical significances, and at 9% of dilution CHX and water have presented similar worse results (p<0.05) when compared to Ethanol dilution (Table 4).

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**Table 4.** Means and Standard Deviations (SD) for DC (%) of Adhesive Systems Testing the Different Dilutions with Water, Ethanol and Chlorexidine.

| Adhesive | Solution | Concentration | | |
|---|---|---|---|---|
| | | 0% | 2% | 9% |
| **M1** | **Ethanol** | 68,97 (± 0,38) Aa | 58,20 (± 0,92) Bb | 55,61 (± 0,36) Bc |
| | **Water** | 58,36 (± 1,00) Ba | 57,52 (± 0,61) Ba | 52,59 (± 1,12) Cb |
| | **CHX** | 68,97 (± 0,38) Aa | 68,74 (± 0,59) Aa | 65,62 (± 0,77) Ab |
| **SBMP** | **Ethanol** | 57,47 (± 0,55) Ac | 60,22 (± 0,29) Ab | 67,97 (± 0,78) Aa |
| | **Water** | 57,47 (± 0,55) Ac | 60,22 (± 0,70) Aa | 60,35 (± 1,33) Ba |
| | **CHX** | 57,47 (± 0,55) Ab | 58,30 (± 0,80) Bb | 61,56 (± 1,67) Ba |

Each adhesive means followed by distinct capital letters in the same row and distinct small letters in the same column is significantly different at $p<0.05$ -Two-Way ANOVA and Tukey test comparing means. *Indicate statistical differences between adhesives at same solution concentration.

For comparisons at same adhesive and same solution, the M1 adhesive has presented a decrease in values as the concentration of dilution increased for all solutions tested, with statistical significance. For SBMP adhesive, the DC increased as ethanol concentration was increased in dilution, showing significant statistical differences at each concentration dilution tested ($p<0.05$). For water solution, the results were increased only with higher level of water in dilution independent of water concentration, and for CHX, an increase with statistical significance difference could be noted only by increasing it to 9% of dilution on SBMP adhesive ($p<0.05$) (Table 4).

### 3.4 KINETIC OF CONVERSION

Independent of the adhesive tested, the groups containing 9% of water or CHX on adhesive dilution were those that had most influence on K peaks, presenting the water solution at worst results and reducing K for a maximum of 40%.

However, the K results have demonstrated an increase in peaks for ethanol solution on dilution for all adhesives tested, with the most noticeable increase for adhesives without solvent on blend, as SBMP, which presented at neat form 44% of conversion, reaching 54% with 9% of ethanol solution in its dilution.

### 3.5 RATE OF POLYMERIZATION

The best Rate of polymerization (RP) results were presented by SBMP adhesive, which has shown an increase in RP for the 9% ethanol solution on adhesive dilutions, a result even better than

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the 2% ethanol solution. Also, for SBMP, the 2% CHX dilution presented the best results when compared to the neat form. The SBMP at neat form has shown the best results only when compared to 2 and 9% of dilution with water and 9% with CHX solutions.

After SBMP, the M1 adhesive was the adhesive that has presented the best Rp, presenting however half of SBMP peaks values. The M1 adhesive has presented the best results at neat form and has shown to be very sensitive to water, with the worst results for 9% of water in dilution, followed by 9% of CHX.

The adhesives with the worst Rp were adhesives with solvent in the formulation, M1/Acetone and M1/Ethanol, presenting the best results at neat form, with 2% of ethanol or with 2% of CHX on dilutions, and the worst results with 2 and 9% of water on adhesives dilution respectively.

## 4 DISCUSSION

The experimental results have denied the first null hypothesis, since the increases in water, CHX or Ethanol have influenced the mechanical properties of resin polymer formed. For both adhesives, the manipulated M1 and SBMP, a decrease on FS and $E$ could be noted by increasing the dilution concentration, independent of the solution tested. For SBMP adhesive, only the ethanol dilution showed no statistical difference independent of concentration dilution. For water and CHX solutions, as the concentration of dilution increased, a decrease of results could be noted (Table 2). These results corroborate some authors[3, 17] who defend that further dilutions of the model resin separate photoactivation components and also dilute radical concentration. Increased dilution also separates resin components from the growing polymer chain, thus decreasing the overall extent of conversion. As increasing solvent increases the physical space between possible reactive species of the polymeric reaction, it leads to decreased monomer conversion, confirmed as DC also decreases with increasing solution concentration. Lastly, as solvent concentration increases, oxygen diffusion into the mixture would increase as a result of the decrease in viscosity. Increasing oxygen content may also contribute to the decline in conversion observed when solvent concentrations of higher amounts were tested.[9]

To SBMP adhesive, the 2% CHX and 9% Water dilution have presented the best results with statistical significance when compared to M1 adhesive. Since M1 formulation contain higher HEMA concentration (60%), a higher mobility chain is predictable, and could hinder the crosslinking process. It is thus different from SBMP, an adhesive with more hydrophobic characteristics, since only the covered monomer bottle was used, containing 65% of BisGMA,

ensuring a higher quality of formed polymer.[18] However, this monomer presents a worse behavior when associated with increased concentrations of water, decreasing the chain quality formed,[1] which is explained since at 9% of water or CHX, a worse *E,* DC and FS result could be noted.

Nevertheless, for SBMP adhesive, when evaluating the DC, for all solutions, CHX, water or EtOH, an increase in results with statistical significance difference could be noted. This increase in DC could be explained by the increase in resin viscosity, since with this system, as already mentioned, only the hydrophobic cover adhesive layer was used in standardizing the hydrophilicity of adhesive, since the primer variable was not an objective at this study (research sent for publication by this group). Increasing the adhesive viscosity, an increase in chain mobility may occur, facilitating radicals diffusion thru chains, and increasing crosslinking.[8] Also, this DC increase indicates that DC increase should not be associated with mechanical properties improvements,[5,6] since adding solvent to the reaction increases the probability of cycling, due to the diluted concentration of monomer and solvent rate of polymerization, causing the local radical on its own chain to remain longer in close proximity to pedant double bonds,[19] creating more linear reactions and decreasing network quality.

Different of SBMP, for M1 adhesives, increasing diluents concentration have caused a decrease on DC results (Table 4). In dental adhesive formulations, hydrophobic components such as Bis-GMA are usually employed to enhance the mechanical properties and compatibility with restorative resin composites.[3,18] Hydrophilic components, such as HEMA, are used to improve water-compatibility and enhance the infiltration of adhesives into wet, demineralized dentin.[18,20] In the presence of water, phase separation of the uncured hydrophobic/hydrophilic components may easily develop.[20] The presence of water and monomer phase separation affects the polymerization rate and the degree of conversion, and induces an inhomogeneous structure of the cured adhesive, which might be a potential mechanism for degradation.[1,4,21] Therefore, the performance of photoinitiator in presence of water becomes very critical, extended by CHX, a solution with an aqueous vehicle.

The second null hypotheses were also denied, since an interference at the K and RP results of all adhesives systems tested could be noted when dilution concentrations were increased. When water and CHX concentration increased, a decrease at peak loaded for K could be noted independent of the adhesive analyzed, resulting at maximum of 35-40% conversion to all adhesive systems tested (Figure 1).

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**Figure 1.** Kinetic Conversion Graphic of water, Ethanol and CHX concentrations dilutions (%) versus time (s).
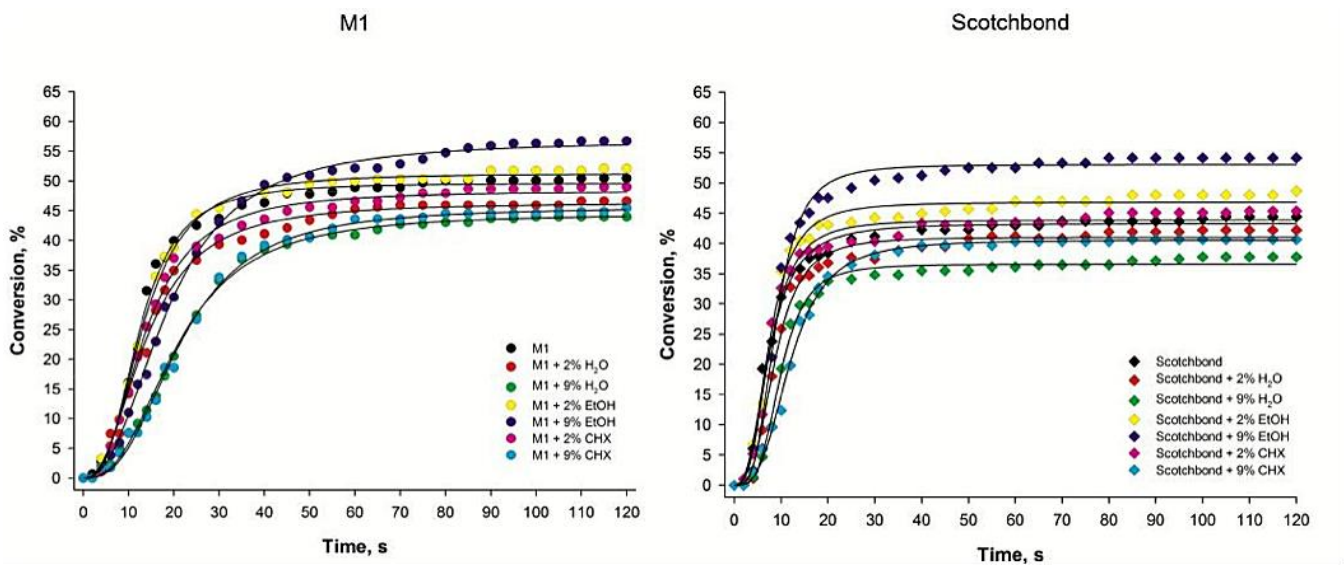


The worsts results, with greatest decrease at load peak, were presented by higher dilutions of water followed by CHX. Water and CHX excess, known as aqueous agents, have generated a high efficacy on polymer plasticization.[7] Hydrogen bridges between water and polar hydroxyl, carboxylate, or phosphate group of polymer networks disrupt interchain hydrogen bonding, altering the molecular structure and increasing the segmental mobility of polymer chain segments.[17,22] These changes are reflected by a reduction in the mechanical properties, and a decline in the glass transition temperatures of the polymer resins hinders the final polymer formation.[23.]

On the other hand, when adhesives where diluted to Ethanol concentrations, all adhesives have presented an increase to K loaded peak, with increasing dilutions presenting increasing peaks (Figure 2). Since in the present study the K loaded peaks suffered an increase with the addition of EtOH, and since it is a very common organic solvent used as vehicle at adhesives systems, ethanol solvent seems to act by decreasing the viscosity of comonomer blends, allowing for radical propagation to continue longer without the reaction being diffusion controlled.[19]

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**Figure 2.** Rate of Polymerization (Rp) Graphics of water, Ethanol and CHX concentrations dilutions (%) versus time (s).
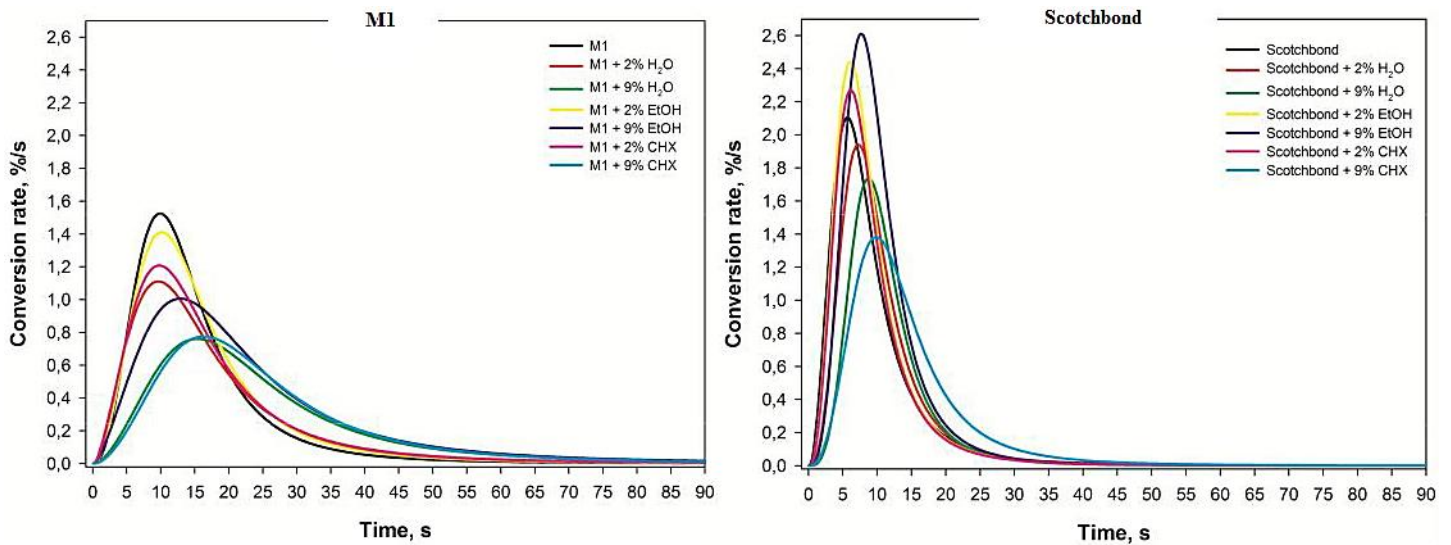


Notwithstanding, this solvent excess, despite increases to K peaks, has a negative influence on the final system conversion (Table 4). It may be hypothesized that the anticipated influence of the higher polarity and hydrogen bonding values of ethanol interfere with free radical formation and lead to a quenching of the polymerization reaction, reducing the temperature of solvent/resin mixture, and reducing the overall conversion. The solvent can also absorb heat generated during the polymeric exothermic reaction, thus also decreasing the overall rate and extend of cure.[24]

When RP were evaluated, a significant decrease in loaded peaks could be noted when maximum dilution concentrations groups where analyzed, independent of adhesive and solution tested. We should hypothesize that adding solvent to the reaction, or in this case water, CHX or EtOH, does increase the probability of cycling, due to the dilution of monomer, slowing the over-all rate of polymerization causing the local radical on its own chain to remain longer in proximity to pedant double bonds. [19] In addition, the dilution concentrations during polymerization will also change the gel-point conversion of polymer because of varying degrees of cyclization, which is demonstrated by the photopolymerization kinetics presented in this study, resulting also in decreasing quality of polymer formed,[8] also confirmed, once FS and *E* values suffered a significant decrease with increasing concentrations dilutions of water, CHX and EtOH on tested adhesives.

Despite significant improvements of adhesive systems, there is a strong trend among manufacturers to simplify the adhesive procedures to satisfy clinicians' demand for adhesive procedures that are faster, less technique-sensitive and more userfriendly[2]. However, resin-tooth interface remains the weakest area of composite resin restorations[8] and any interference with of

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solvents, solvated resins and other solutions with demineralized dentin matrices may compromise the bonding process resulting in the formation of poor quality hybrid layers. Once demonstrated the effectiveness of EtOH and CHX as pre-treatment techniques in reference of longevity and adhesive strength,[25,26,27] the present study has demonstrated that these techniques should be used carefully, with a controlled amount of rinse and controlling the remained solution in cavity, thus avoiding at maximum monomers dilution that may create loss of characteristics of the polymer formed and also decrease the quality of bonding system. With all this study limitations, clinically, the authors should hypothesize that once CHX or EtOH is applied to the cavity before bonding procedure, if a controlled remained humidity is achieved, the clinician guarantees a very stable hybrid layer formation with the formation of a polymer with high quality and satisfactory restorative longevity.

The remained solution in cavity the dilution concentrations during polymerization that may create loss of characteristics of the polymer formed and also decrease the quality of bonding system.

## 5 CONCLUSION

A significant decrease in FS and *E* were observed with increasing concentrations dilutions of water, CHX and EtOH on tested adhesives.

The increase in dilution concentration of adhesives influenced the characteristics of formed blends of tested adhesives. Only EtOH and CHX in low concentration seem do not interfere in K and RP results of the tested adhesives.

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