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Influence of primer and adhesive mixture on the real-time polymerization and mechanical properties of experimental dental adhesives

Influência da mistura de primers e adesivos na polimerização em tempo real e nas propriedades mecânicas de adesivos dentais experimentais

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ABSTRACT
Objective: To evaluate the influence of primer concentration on the physical and chemical properties of model adhesive systems. Materials and methods: Two model adhesives were tested: M1 (40% BisGMA and 60% HEMA) and M2 (40% BisGMA, 40% HEMA and 20% TEGDMA). The mixture of adhesives with four different concentrations of the primer agent (0, 5, 10 and 15%). The properties evaluated were flexural strength (FS), elastic modulus (E), degree of conversion (DC), the kinetics of conversion (K) and the rate of polymerisation (RP). To evaluate the mechanical properties, were prepared specimens using silicone bar moulds (7 mmX2 mmX1 mm), and tested them by the three-point bending test at a crosshead speed of 0.5 mm/min. DC and the kinetics of cure were measured by Fourier Transform infrared spectroscopy (FTIR). Results: The FS and E of all adhesives tested were not affected by different primer concentrations. All adhesives had decreased DC as the primer concentration increased. In the real-time conversion, the model adhesives presented decreased RP according to increases in primer concentration. Conclusions: Mechanical properties of non-solvated adhesives were not affected by the primer concentrations tested and the DC and RP were influenced by concentrations of the agents.

Keywords: Flexural strength, elastic modulus, degree of conversion, adhesive layer, hybrid layer.

RESUMO
Objetivo: Avaliar a influência da concentração do primer nas propriedades físicas e químicas dos sistemas adesivos modelo. Materiais e métodos: Dois modelos de adesivos foram testados: M1 (40% BisGMA e 60% HEMA) e M2 (40% BisGMA, 40% HEMA e 20% TEGDMA). A mistura de adesivos com quatro concentrações diferentes do agente primário (0, 5, 10 e 15%). As propriedades avaliadas foram: resistência à flexão (RF), módulo elástico (E), grau de conversão (GC), cinética de conversão (K) e taxa de polimerização (P). Para avaliar as propriedades mecânicas, foram preparadas amostras usando moldes de barra de silicone (7 mmX2 mmX1 mm) e testadas pelo teste de flexão de três pontos a uma velocidade de 0,5 mm / min. GC e a cinética de cura foram medidas por espectroscopia no infravermelho por transformada de Fourier (FTIR). Resultados: RF e E de todos os adesivos testados não foram afetados por diferentes concentrações de primers. Todos os adesivos diminuíram o GC à medida que a concentração do primer aumentou. Na conversão em tempo real, os adesivos do modelo apresentaram diminuição da P de acordo com o aumento da concentração do primer. Conclusões: As propriedades mecânicas dos adesivos não solvatados não foram afetadas pelas concentrações de primers testadas e as GC e P foram influenciadas pelas concentrações dos agentes.

Palavras-chave: Resistência à flexão, módulo de elasticidade, grau de conversão, camada adesiva, camada híbrida.

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1 INTRODUCTION

The adhesive techniques for dental substrate have developed significantly in recent decades.1 A variety of adhesive systems is available on the market, with different brands and approaches to the treatment of dental tissues.2 Despite progress in the simplification of adhesive techniques, three-step, etch-and-rinse adhesive systems are still considered the gold standard for dentin bonding.1,2 However, dentin hybridization is still not considered ideal, since the multiple steps might also generate a susceptibility to technique sensitivity.3

An important feature of the technique is the dentin priming step.1,4 The function of the primer is to allow monomers to penetrate into the demineralized moist dentin, but the primer might result in reduced mechanical properties in terms of hybridization quality.2,3,5 2-hydroxyethyl methacrylate (HEMA) is a major component of the primer agent of the two-bottle adhesives. HEMA is a low-weight, short-chain monomer, responsible for generating high stress on polymerisation and, consequently, a low flexural strength.5,6 In contrast to dimethacrylate monomers, which present two reactive groups, the monovinyl HEMA is unable to generate polymer crosslinking.1,2 The behavior of the hydroxyl group at the extremity of the molecule is too hydrophilic, even after polymerisation.2 As a result, a polymer is formed by resin materials with high HEMA content, being more prone to hydrolysis in the oral environment, with a potential decrease in the mechanical properties of dental materials. 2,7

It is known that low degree of C=C conversion, presence of water, and excess HEMA can reduce the mechanical properties of adhesive systems, a fact that seems to be the major cause of decreased hybrid layer durability and subsequent restoration failure.4,8,9 Therefore, the aim of this study was to evaluate the influence of primer and adhesive mixture on the conversion and mechanical properties of experimental dental adhesives by testing different primer concentrations. The null hypothesis tested was that different primer concentrations have no influence on the mechanical properties of adhesives, and also that the kinetics and rate of polymerisation will not be influenced, regardless of primer concentration.

2 MATERIALS AND METHODS

2.1ADHESIVE 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.

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Two different formulations of light-cured, model unfilled dental resins were evaluated: M1 (40 wt% Bis-GMA and 60 wt% HEMA) and M2 (40 wt% Bis-GMA, 40 wt% HEMA, and 20 wt% TEGDMA). To both blends, 1 mol% of CQ and 2 mol% of EDAB were added as photoinitiators.10 The materials were prepared by intensive motorized mixing in a dark room with controlled temperature and humidity. The primer of the commercial adhesive system Adper Scotchbond Multi-Purpose (3M ESPE, St. Paul, MN, USA) was used. The Scotchbond primer contains water (40-50%), HEMA (35-45%), and polyacrylic and itaconic acid copolymers (10-20%).

2.2 MECHANICAL PROPERTIES

The experiment was performed according to the ISO 4049/2009 standard for dental polymers, except for the dimensions of the specimens. Each adhesive tested was mixed with 0, 5, 10, or 15% of the primer (n=5). The primer/adhesive volumes were determined by several pilot studies until authors were sure of the best clinical standard with a calibrate laboratory technique control. The primer/adhesive mixture was prepared and vigorously agitated to promote a homogeneous solution, then inserted into a silicone mould. Specimens were prepared according to a protocol previously described,11 except for the solvent evaporation step, placing 20-µL of each adhesive/primer solution in the silicone mold, yielding a bar-shaped specimen (7 mm × 2 mm × 1 mm).

Before light-activation, a Mylar strip was placed over the mold in order to obtain a flat surface and to prevent the inhibition of cure by oxygen. Adhesives were irradiated for 60s using a light-emitting diode curing unit (Elipar FreeLight2; 3M ESPE) with 850-mW/cm2 irradiance. The prolonged photocuring was applied to evaluate primer/adhesive mixture in the best possible curing scenario. After dry storage for 24h, the specimens were subjected to three-point bending tests at a crosshead speed of 0.5 mm/min until failure in a mechanical testing machine (model 4411; Instron Corp., Canton, MA, USA). Flexural strength (FS) and elastic modulus (E) were calculated based on the load-displacement trace.

2.3 DEGREE OF C=C CONVERSION

The degree of C=C conversion (DC) of the primer/adhesive mixtures was measured by Fourier Transform mid-infrared (FTIR) spectroscopy (Spectrum 100 Optica; Perkin-Elmer, Wellesley, MA, USA), equipped with an attenuated total reflectance (ATR) device composed of a horizontal ZnSe crystal (Pike Technologies, Madison, WI, USA). The specimens evaluated were the same as those tested for mechanical properties (n=5). A preliminary reading for uncured material was taken in the absorbance mode under the following conditions: 24 scans, 1665–1580 cm-1

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frequency range, 4 cm-1 resolution, and Happ-Genzel apodisation. Additional spectra were obtained immediately after light-curing. Specimens were placed on the horizontal face of the ATR cell with a constant weight of 90 bar. DC was calculated according to a baseline technique,12 based on band ratios of 1638 cm-1 (methacrylate aliphatic C=C) and, as internal standard, 1608 cm-1 (aromatic C=C) between the polymerised and uncured samples.

2.4 POLYMERISATION KINETICS AND RATE

Real-time polymerisation FTIR spectroscopy as previously described. A constant 5 µL volume of primer/adhesive mixture was dispensed onto the crystal and photo-activated for 120s, and the polymerisation reaction was monitored in real time acquiring one spectrum every 2s. Three specimens were tested for each primer/adhesive concentration. Average conversion vs. time data were plotted, and Hill's 4-parameter non-linear regressions were used for curve-fitting. As the coefficient of determination was higher than 0.99 for all curves, the rate of polymerisation (Rp) was calculated based on these data-fitted plots.

2.5 STATISTICAL ANALYSIS

The mechanical properties (FS, E), as well as the DC, were analysed by two-way ANOVA and Tukey's test at a 0.05 level of significance, with "adhesive" and "primer concentration" as the two factors (SAS 9.1 version; The SAS Institute, Cary, NC, USA).

3 RESULTS

Figures 1 and 2 show the results for FS and E. Irrespective of the primer concentration, M1 and M2 have showed similar results. The DC, however, was influenced by the different amounts of primer, as shown in Table 1. M2 appeared to be the more sensitive to the primer concentration, showing statistically significant differences with 10% of primer on dilution. SBMP has shown less sensitive behavior, with significant results only after 15% primer concentration.

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Fig 1. Results for flexural strength (bars are means±standard deviations).

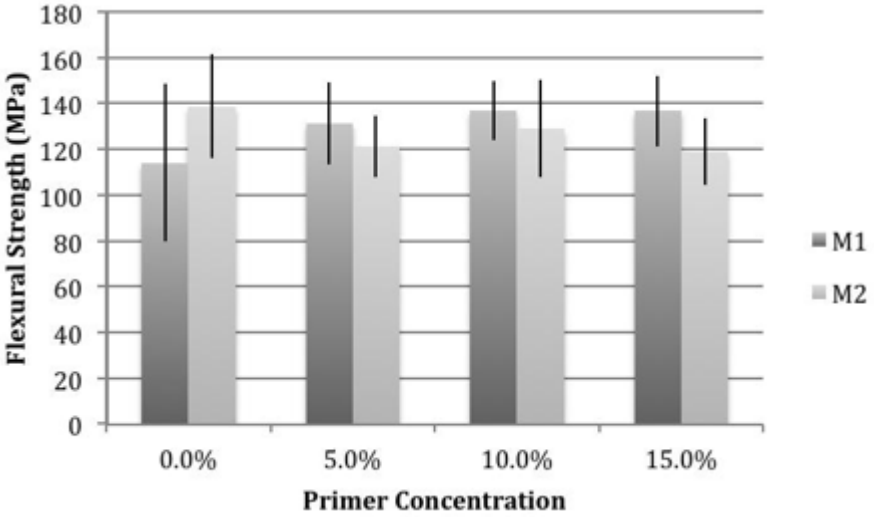

Fig 2. Results for elastic modulus (bars are means±standard deviations).

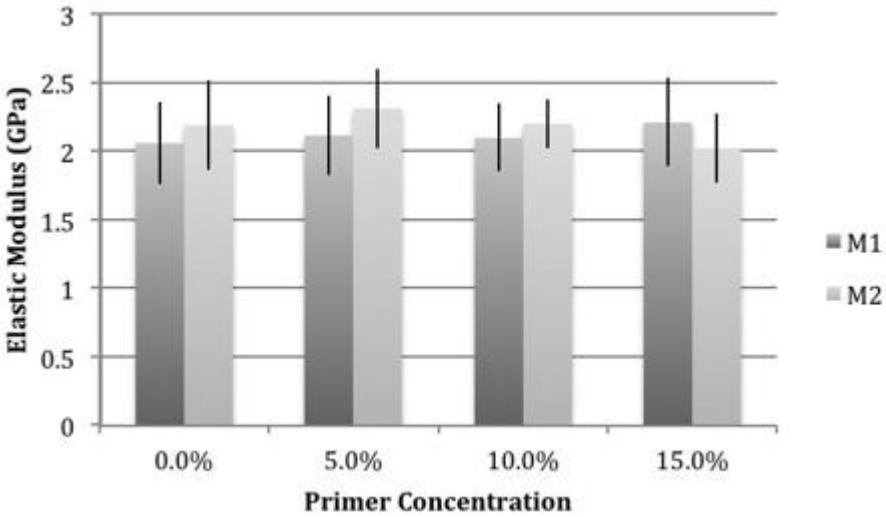

Table 1 - Means (standard deviations) for the DC (%) of the primer/adhesive mixtures

Adhesive	Primer concentration			
	0%	5%	10%	15%
M1	58.4 (1.0) A,a	47.4 (1.0) A,b	46.8 (1.7) A,b	44.2 (1.8) A,c
M2	50.6 (0.5) B,a	47.5 (1.1) A,b	40.6 (1.2) B,c	41.4 (1.3) B,c

Distinct capital letters in the same column and lowercase letters in the line indicate significant differences ($p < 0.05$).

The higher the primer concentration, the worse the K, and again, the M2 adhesive was shown to be the more sensitive adhesive, with final conversion decreasing as the primer

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concentration increased in adhesive dilution (Fig. 3). Also, with the increasing primer concentration on adhesive dilution, RP decreases were noted for manipulated adhesives (Fig. 4).

Fig 3. Polymerization kinetics of the primer/adhesive mixtures.

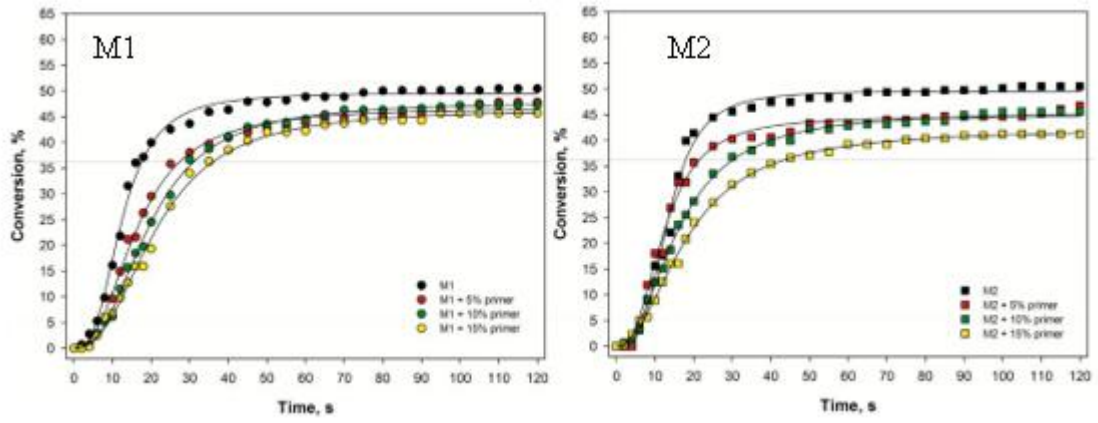
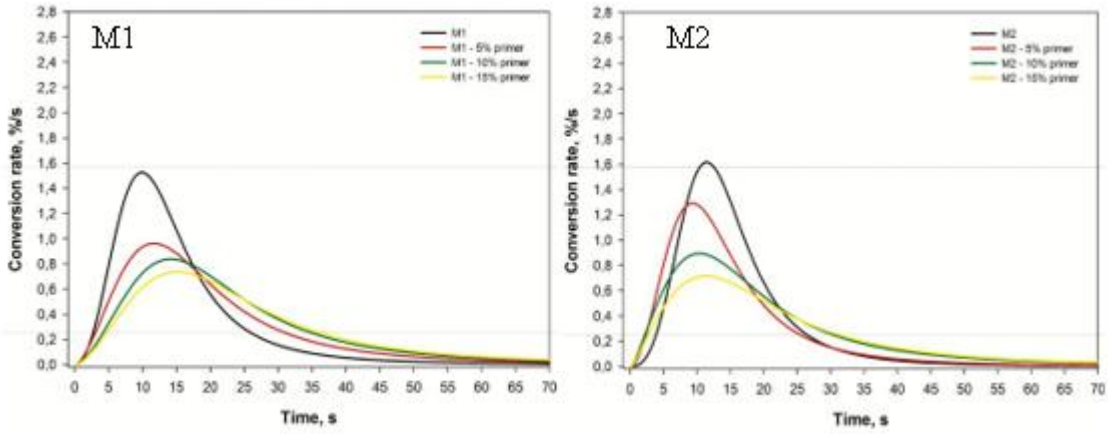


Fig 4. Polymerization rate profiles of the primer/adhesive mixtures.



4 DISCUSSION

The primer agent used in two-bottle dental adhesives allows for the infiltration of hydrophobic monomers into demineralised dentin, in order to re-expand collapsed dentin and coat the wet collagen fibrils with a hydrophilic monomer, such as HEMA.1

However, the amount of primer might lead to excess solvent and functional monomers, resulting in a less effective polymer.6,13 However, in our study, the first null hypothesis was accepted, since the FS and E were similar in all conditions tested, independent of the primer concentration in adhesive dilutions.

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The high content of HEMA and water in adhesives can cause a reduction in their mechanical properties, due to the formation of polyHEMA, a flexible and porous polymer form, thus jeopardizing the clinical performance of the adhesives.2,14,15 However, in the present study the mechanical properties were not influenced, possibly due to the high amount of Bis-GMA and TEGDMA, cross-linking monomers with a high molecular weight used in dental adhesives to provide mechanical strength, forming densely cross-linked polymers.2

Regarding the polymerisation process, the adhesives were activated for 60 seconds. Based on the real-time conversion, it was observed that at approximately 50 seconds, the polymerisation process was almost completed for all formulations. Since the aims of the present study were to evaluate the influence of the primer content on the mechanical and chemical properties of the model adhesives, the authors evaluated the specimens at the maximum possible conversion, to guarantee that the results obtained would be due to the primer addition, and not to reduced irradiation.

Despite the fact that the addition of primer did not influence the mechanical properties of the adhesive formulations tested, the degree of conversion, kinetics and rate of polymerisation were negatively influenced by the different amounts of the hydrophilic agent. Therefore, the second null hypothesis must be rejected.

For DC, independent of the adhesive tested, with the increase of primer concentration on adhesive dilution, a decrease of DC was recorded. The M2 blend was shown to be the adhesive that is more sensitive to primer addition, with the degree of conversion decreasing as the primer concentration on adhesive dilution increased to reduced rates compared with those of M1.The M2 adhesive presented a composition with 20% TEGDMA. The TEGDMA monomer has a flexible aliphatic structure, with, in addition, a free fractional volume, i.e., free space between chains and major lateral groups.16 Such spaces appear to be crucial for molecular movement, leading the TEGDMA with its principal chain characteristic, low viscosity, since its movement also improves linear and cross-link chain formation. However, with the excess water provided by the primer, the TEGDMA monomer, with the free space among chains2,17 and also its hydroxyl group,18 can easily incorporate the water present in the primer agent, compromising the cure of the adhesive.

The M1 adhesive has a high concentration of HEMA on formulation (60%). HEMA, as already mentioned, is a hydrophilic monomer, which guarantees a satisfactory degree of conversion even in aqueous environments when compared with TEGDMA, a monomer with more hydrophobic characteristics,2,16 explaining the high degree of conversion obtained for M1 compared with M2. However, with the hydrophilic behavior after polymerisation,13,18 HEMA continues to suffer hydrolysis even after polymerisation in an aqueous medium, and this characteristic may be a

negative factor for adhesives containing high HEMA content compared with those formulations containing monomers such as TEGDMA.

The excess water due to the primer addition may cause difficulty for cross-link chain formation, generating a decrease in the 'jellification' phase, with a consequent decrease in the RP of adhesives19,20. Also, this excess could cause a phase separation between Bis-GMA and HEMA.19, resulting in difficulty in monomer conversion, thus explaining the negative influence of the primer addition on cure characteristics of the adhesive formulations tested.

The authors remind readers that these findings were obtained under conditions that differ from those found clinically. It must be taken into consideration the controlled temperature, standardised amounts of adhesive and primer, as well as the incorporation of primer into the adhesive as a homogeneous solution. However, even with such controlled variables, the chemical properties of the model adhesives were negatively influenced. This fact should be considered in clinical situations, since, when adhesive procedures are performed, the amount of water after acid-etching, the water present in dentinal tubules, as well as the difficulty in controlling the amount of primer content in dentin, may prejudice the quality of the polymer formed, and, consequently, prejudice the adhesive performance as well as the longevity of the bond.

5 CONCLUSION

Based on the results obtained, it can be concluded that the addition of primer agent did not influence the flexural strength and elastic modulus of the model adhesives tested; however, even low concentrations of primer have jeopardized the degree of conversion of the adhesives, thus modulating the kinetics of cure and reducing the rate of polymerisation of the dentin bonding agents.

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