Long-term bond strength, degree of conversion and resistance to degradation of a HEMA-free model adhesive

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Abstract

Aim: To evaluate the long-term bond strength, degree of conversion and resistance to degradation in ethanol of HEMA-containing and HEMA-free model adhesive resins of a three-step etch-and-rinse adhesive system. **Methods:** The superficial dentin of 16 bovine incisor teeth was exposed, and the teeth were divided in two groups according to the HEMA concentration in the experimental adhesive (0% and 15%). In each tooth were made 6 cylindrical composite restorations. Half of the tooth restorations were submitted to microshear bond strength test after 24 h and the other half after 6 months. Degree of conversion of experimental resins was determined by Fourier transform infrared spectroscopy. Crosslink density was indirectly determined by the Knoop hardness of five specimens per group before and after immersion in ethanol for 6 h. **Results:** The group with 0% HEMA showed no difference in bond strength as compared to the group with 15% HEMA after 24 h or 6 months. There was no difference in degree of conversion and crosslink density between groups. **Conclusions:** HEMA content of the adhesive resin did not influence the bond strength to dentin, degree of conversion or resistance to degradation in ethanol.

Keywords: dental bonding; dentin-bonding agents; light-curing of dental adhesives.

Introduction

The longevity of dental restorations is an important clinical concern[1-2]. Efficient adhesive resin infiltration and polymerization at the tooth/resin interface are related to the preservation of the results of clinical procedures[3]. Improvement of the adhesive systems has been associated with the development of different system formulations, as the incorporation of resin monomers with hydrophilic groups increases the bond strength[4].

Almost all commercial etch-and-rinse adhesive systems include 2-hydroxyethyl methacrylate (HEMA) or other hydrophilic monomer in their composition[5]. This hydrophilic monomer is required to enhance infiltration of hydrophobic components into demineralized dentin to promote micromechanical retention of curable monomers. However, the presence of hydrophilic components in the hybrid layer could promote water penetration and degradation of the polymer over time[6-8] whereas HEMA increases permeability of the adhesive layer, taking up water and decreasing the mechanical properties of hybrid layer. The influence of HEMA on mechanical properties of polymer structure may be attributed to the

low degree of conversion exhibited by polymers containing increased concentration of HEMA[9]. It is known that a low degree of conversion is related to a low crosslink density[10] and decreased mechanical properties of the formed polymer. The bond strength to tooth substrate is directly related to the mechanical properties of the adhesive layer[11].

The effect of HEMA on adhesive resin properties has already been examined in a previous study and showed that an increased ratio of HEMA decreases the degree of conversion and ultimate tensile strength, and increases the water sorption and solubility of polymer[9]. However, more studies are needed to evaluate other properties and the longevity of the adhesive/dentin bond of adhesive resins with or without HEMA, since the presence of a hydrophilic monomer in the adhesive layer could influence the bond strength over time. Hence, the present study tested the null hypothesis that the addition of 15% HEMA in a model adhesive resin will not influence the microshear bond strength, degree of conversion and resistance to chemical degradation.

Material and methods

Materials

The monomers used were bisphenol A glycol dimethacrylate (BisGMA), ethoxylated bisphenol A glycol dimethacrylate 6 (BisEMA), triethylene glycol dimethacrylate (TEGDMA) and 2-hydroxyethyl methacrylate (HEMA). Two blends with different ratios of HEMA were prepared, one with 0% and another with 15% in weight (Table 1). For each group, 1% mol of camphoroquinone (CQ, Esstech, Essington, PA, USA), used as photosensitizer and 1% mol of N,N-Dimethyl-para-toluidine (DMPT, Fluka, Everett, WA, USA) used as a reducing agent were added to transform the mixtures into light polymerizing blends. The photoactivation for all tests was initiated by a light-emitting diode light source (Radii, SDI, Bayswater, Victoria, Australia), and the irradiance value was confirmed with a digital power meter (Ophir Optronics, North Andover, MA, USA) with 1200mW/cm^2.

Table 1. Composition of the adhesive resins.

Group	Composition	%Wt
0% HEMA	Bisphenol A glycol dimethacrylate	42
	Ethoxylated bisphenol A glycol dimethacrylate 6	42
	Triethylene glycol dimethacrylate	16
	2-Hydroxyethyl methacrylate	0
15% HEMA	Bisphenol A glycol dimethacrylate	36.5
	Ethoxylated bisphenol A glycol dimethacrylate 6	36.5
	Triethylene glycol dimethacrylate	12
	2-Hydroxyethyl methacrylate	15

Microshear bond strength

Sixteen bovine maxillary incisor teeth, stored in 4 °C distilled water for no more than 3 months, were used in this study. The teeth were embedded in acrylic resin and the labial enamel was ground down to expose the superficial dentin. The dentin was ground with 600-grit SiC paper for 30 s in running water[12]. The teeth were divided in two groups according to the HEMA presence in the model adhesive resins (0% and 15%). The dentin was conditioned for 15 s with 37% phosphoric acid gel and washed for the same time. The water was gently removed with an absorbent paper. A commercial primer composed by water (40-50%), HEMA (35-45%) and polyalkenoic acid (10-20%) (Primer Scotch Bond Multi Purpose, 3M ESPE, St. Paul, MN, USA) was agitated using disposable applicators on the dentin surface for 10 s and dried for 10 s with an air stream at a distance of 10 cm. Then the model adhesive resins was applied for 5 s using disposable microbrush tips and polymerized for 20 s. In each tooth, 6 cylindrical composite restorations (Z250, 3M ESPE) were made using metallic cylindrical moulds 2 mm high, resulting restorations with 0.88 (± 0.03) mm^2 of adhesive area[13]. Restorations were polymerized for 40 s, and the teeth were stored in 37 °C distilled water. Three of these restorations in each tooth were randomly submitted to a microshear bond strength test after 24 h and the other three after 6 months of storage. The specimens were mounted in a universal testing machine (DL-2000, EMIC, São José dos Campos, SP, Brazil), and shear force was applied at a 1 mm/min cross-head speed using a steel wire (± 0.4 mm). The wire was positioned in the bond line, and the cylinder was pulled. The bond strengths were expressed in MPa. The failure mode of each specimen was determined under a stereomicroscope at 60x magnification and designated as adhesive, mixed or cohesive failure in either adhesive or resin composite. The means and standard deviations of the groups were analyzed for statistically significant differences by two-way ANOVA for microshear bond strength evaluation. To compare the pattern of failure between groups, the Kruskal-Wallis test was used. Statistical significance was defined as $p < 0.05$.

Degree of conversion

Degree of conversion of the experimental adhesives was evaluated using Fourier transform infrared spectroscopy (FTIR) with a Shimadzu Prestige 21 (Shimadzu, Kyoto, Japan) spectrometer equipped with an attenuated total reflectance device with a horizontal ZnSe crystal and a 45° mirror angle (PIKE Technologies, Madison, WI, USA). A support was coupled to the spectrometer to fix the light curing unit and standardize the distance between the fiber tip and sample at 5 mm. IRSolution software in monitoring scan mode was used, with Happ-Genzel appodization in a range of 1750 to 1550 cm^{-1} and resolution of 8 cm^{-1}. Analysis was performed at a controlled room temperature of 23 ± 1 °C and $60 \pm 1\%$ relative humidity after sample (3 µL) polymerization, which was directly dispensed onto the ZnSe crystal and light-activated for 20 s., The test was repeated three times (n = 3). The degree of conversion was calculated as described in a previous study[14], considering the intensity of carbon-carbon double bond stretching vibration (peak height) at 1635 cm^{-1} and using the symmetric ring stretching at 1610 cm^{-1} from the polymerized and unpolymerized samples as an internal standard. The means of the degree of conversion of the groups

were compared using the *t*-test, with $p < 0.05$ indicating statistical significance.

Softening in ethanol

To determine the resistance to degradation, the experimental adhesives were placed in circular elastomeric molds with 4 mm diameter and 2 mm deep, covered with polyester strips and photoactivated for 20 s. Five specimens (n = 5) were prepared for each experimental adhesive and then embedded in a acrylic resin with the top in contact with a glass plate and polished in a polisher (Model 3v; Arotec, Cotia, SP, Brazil) with a felt disc embedded with alumina suspension (Alumina 1.0 µm, Arotec) after the specimens were stored at 37 °C for 24 h. The specimens were subjected to a microhardness test in which 9 indentations (15 g/10 s), 100 µm apart from each other and were assessed using a digital microhardness tester (HMV 2, Shimadzu, Tokyo, Japan). The initial Knoop hardness number (KHN_1) was registered, and then the specimens were subjected to softening in absolute alcohol for 6 h at 37 °C, when the hardness test was repeated, and the post-conditioning hardness value was measured (KHN_2)[15]. The hardness values between groups were compared by *t*-test, and the values before and after ethanol immersion were compared by paired *t*-test, being statistically different if $p < 0.05$.

Results

Microshear bond strength values of experimental adhesive with 0 and 15% of HEMA (0% HEMA and 15% HEMA, respectively) to bovine dentin showed no difference between groups (Table 2). The 0% HEMA group showed no statistical difference to the 15% HEMA group at 24 h or 6 months ($p > 0.05$). The fracture mode of almost all specimens was classified as mixed for all groups (Figure 1) and presented no significant difference in failure pattern when correlated with presence of HEMA and storage times.

The data for degree of conversion and softening in ethanol are shown in Table 3. For the degree of conversion in 20 s, no significant difference between groups was detected ($p = 0.262$). Initial microhardness evaluation showed no statistical difference among 0% HEMA and 15% HEMA adhesive resins ($p = 0.211$). After 6 h in absolute ethanol, the 15% HEMA resin showed no statistical difference in Knoop microhardness to 0% HEMA adhesive resin ($p = 0.346$). However, 15% HEMA and 0% HEMA adhesive resins showed

Table 2. Mean and standard deviation, in MPa, of microshear bond strength of HEMA and HEMA-free adhesive resins in 24 h and 6 months.

Groups	24 h	6 months
0% HEMA	13.77 (± 3.90)[Aa]	12.83 (± 5.02)[Aa]
15% HEMA	14.02 (± 4.13)[Aa]	13.82 (± 3.55)[Aa]

Same capital letter indicates no statistically significant difference in same column ($p > 0.05$). Same small letter indicates no statistically significant difference in same row ($p > 0.05$).
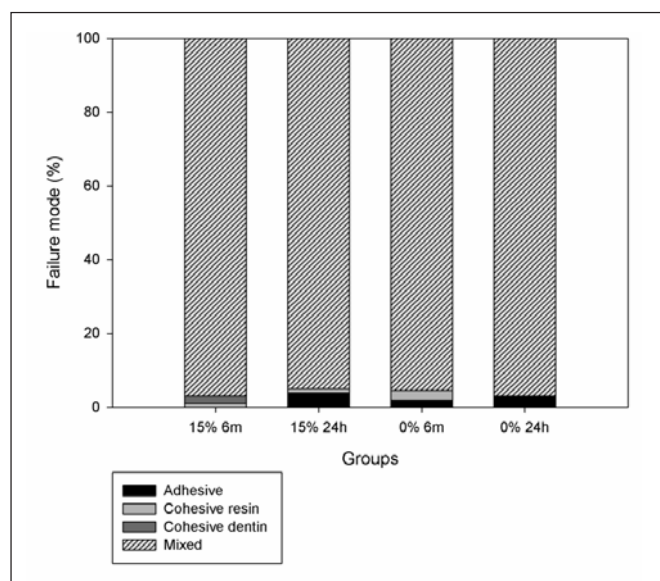

Fig. 1. Failure pattern, in percentage, of debonded specimens of HEMA and HEMA-free groups at 24 h and 6 months.

Table 3. Mean and standard deviation of degree of conversion (%), initial and final Knoop microhardness value (KHN_1 and KHN_2, respectively) of HEMA and HEMA-free adhesive resins

Group	DC (%)	KHN_1	KHN_2
0% HEMA	49.78 (± 0.73)*	16.02 (± 1.15)[Aa]	6.98 (± 0.71)[Bb]
15% HEMA	47.16 (± 3.40)*	17.18 (± 1.54)[Aa]	7.56 (± 1.09)[Bb]

Same symbol (*) indicates no statistical difference in the same column ($p = 0.262$). Same capital letter indicates no statistically significant difference in the same column ($p > 0.05$). Different small letter indicates no statistically significant difference in the same row ($p < 0.05$).

a statistical reduction in Knoop microhardness values after 6 h in absolute ethanol immersion ($p < 0.001$).

Discussion

Immediate and long-term bond strength at the adhesive/resin interface influences the efficiency of the resin bond to dentin. Almost all commercial dental adhesive systems contain HEMA in their composition in order to improve wetting of the dentin substrate, promote hydrophobic monomer infiltration and enhance bond strength. This study evaluated the long-term microshear bond strength of experimental adhesive resins with different ratios of HEMA to bovine dentin and showed no statistical difference between groups despite the presence of HEMA or the storage time. Despite the non-significant difference shown for degree of conversion, the Knoop microhardness of both adhesive resins decreased after immersion in ethanol.

There is morphological evidence that hydrophilic adhesive systems behave as semi-permeable membranes[16-17]. Porous regions in the bonded interface with water-rich and hydrophilic monomer zones could lead to channels for water sorption and leaching of unpolymerized monomers, thus promoting hydrolytic degradation of the polymer. Long-term

hybrid layer degradation is explained by the degradation of polymer matrix[8] and/or collagen fibrils[18] by hydrolysis due to water penetration from the dentin and oral environment through porosities and intermolecular spaces of the polymer network interface with dentin substrate, decreasing the mechanical properties of the polymer formed.

Despite the increase in the percentage of hydrophilic and low molecular weight monomer of the 15% HEMA group, the same adhesive resin compositions showed no difference in ultimate tensile strength between each other, 85.4 and 81.1 MPa for 0% HEMA and 15% HEMA respectively, in a previous study[9]. However, the water sorption and solubility of 15% HEMA adhesive resin presented significantly higher values than 0% HEMA[9]. Nevertheless, in the present study, the bond strength showed no difference between the two groups even in a long-term bond strength test. This could be explained by the low viscosity of HEMA, which increases the penetration of adhesive resin into the demineralized dentin of the 15% HEMA group, thus increasing the proportion of hydrophobic monomers in the hybrid layer.

A previous study shows that the microshear bond strength of adhesive resins to bovine dentin did not differ from human dentin[19]. The same pattern was confirmed in an evaluation using microtensile bond strength test[20]. Moreover, the scanning electronic microscopy images reveal that bovine and human dentin present similar dentinal morphology after phosphoric acid etching[20].

HEMA monomer hydrophilicity contributes to promote bonding to tooth substrate[4]. Due to its low molecular weight and size, HEMA may easily penetrate demineralized dentin tissue[4,21], thus promoting hybrid layer formation. However, increased hybrid layer hydrophilicity could lead to bond interface that is more prone to degradation. In a previous study[21], a transmission electronic microscopy evaluation showed the same pattern of spot and cluster-like nanoleakage for a HEMA-free and a HEMA-containing adhesive systems, whereas the HEMA-free adhesives present lower immediate dentin bond strength than the HEMA-containing adhesives. Despite this difference in initial bond strength, a long-term evaluation is still required to confirm the effects of HEMA-containing adhesives' hydrophilicity on the preservation of bonded interface. In this study, no difference between bond strength of 0 and 15% HEMA adhesive resins were found neither immediately nor after 6 months of water storage.

The failure pattern of specimens was almost all mixed for both groups. The microshear bond strength test revealed a non-homogeneous stress concentration at the dentin substrate[22] which could explain these results. However, no significant difference was observed in the failure pattern when correlated with presence of HEMA and storage times. An explanation for these results may be the presence of BisEMA in the composition of the adhesive resins. The BisEMA molecule is similar to BisGMA, with a phenyl central core without the two hydroxyl groups in the backbone, which decreases the viscosity of the comonomer blend[23]. A decreased viscosity could lead to a higher interpenetration of monomer into the demineralized dentin, proxying the HEMA function in the adhesive resin.

Both adhesive resins evaluated in this study presented a similar degree of conversion. The 0% HEMA showed no difference on softening in ethanol when compared with 15% HEMA. Resistance to degradation after immersion in ethanol is affected by the crosslink density of polymers[24]. Networks with high crosslink density have reduced solvent uptake due to reduced free space between the polymer chains. Therefore, it is expected that organic solvents would cause less softening in these polymers[8]. In polymers with a low crosslink density, alcohol can form strong secondary bonds with the polymer chains, penetrate and replace the interchain secondary bonds, and dissolve the material, causing the softening[25].

The polymerization behaviors could be affected by increased HEMA content, reducing the degree of conversion, due perhaps to lower monomer reactivity. The 0% HEMA adhesive resin's low polymerization ratio in the initial polymerization seconds[9] may result from the high BisGMA content (42% wt). BisGMA has a stiff central core with a hydroxyl group in the backbone that hinders monomer diffusion through the solidifying adhesive and reduces the mobility of unreacted pendant double bonds[9]. It is known that a high ratio of monofunctional/bifunctional monomers may result in a polymer with low crosslink density, due to its less reactive double bonds[26], but this fact was not observed in this study. The crosslink density, indirectly assessed by the softening in ethanol, of the 15% HEMA adhesive resin and of the adhesive resin without monofunctional components showed no significant difference. Nonetheless, the addition of a iodonium salt (e.g. diphenyliodonium hexafluorphosphate) as an alternative photoinitiator could improve the reactivity of methacrylate monomers[27], enhancing the degree of conversion[27] and improving dentin-bond strength[28], and thus offsetting the drawbacks of a high viscosity blend, as the 0% HEMA. An *in vitro* study[29] showed similar results for bond strength of HEMA-free experimental adhesive systems compared to a commercial three-step etch-and-rinse adhesive system. Additionally, a clinical study showed a high retention rate of non-carious class V restorations after 5 years in function that did not differ from a three-step etch-and-rinse adhesive system containing HEMA[30].

The commercial primer (Adper Scotch Bond Multi Purpose, 3M ESPE) used in restorative procedures presents 35-45 wt% of HEMA in its composition, which provide an adequate diffusion of monomers on etched dentin and help to explain the lack of difference in longitudinal microshear bond strength between 0 and 15% HEMA adhesive resins verified in this study. The polymerized HEMA that remained entrapped on the adhesive layer of both tested groups could also make less sensible the detection of long-term bond strength changes promoted by HEMA addition to bonding resin. Even with the significantly higher water sorption rate and solubility of the 15% HEMA adhesive resin used[9], a significant degradation of bond strength was not observed. However, the storage period used could be not long enough for a noticeable degradation to occur and differences in bond strength of the tested adhesive resins to be perceived.

Within the limitations of this study, the content of

HEMA in the adhesive resin showed no influence on the degradation of bond strength to dentin in the three-step etch-and-rinse adhesive system use din this study. It neither influenced the degree of conversion and resistance to degradation of adhesive resin.

Acknowledgements

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