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ORIGINAL ARTICLE

Effects of long-term water storage on the microtensile bond strength of five experimental self-etching adhesives based on surfactants rather than HEMA

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Abstract
Objectives The purpose of this study is to evaluate the hypothesis that replacing 2-hydroxyethyl methacrylate (HEMA) for surfactant dimethacrylates (SD) does not affect the immediate and long-term microtensile bond strength (μTBS) of experimental two-step self-etch HEMA-free adhesive systems applied on dentin.
Materials and methods Five experimental HEMA-free two-step self-etching systems containing different SD (ethoxylated bisphenol A diglycidyl dimethacrylate (Bis-EMA 10, B10), Bis-EMA 30 (B30), poly-ethyleneglycol (400) dimethacrylate (PEG 400, P400), PEG 1000 (P1000), and PEG 400 urethane dimethacrylate (UDMA) (UP400)) and a HEMA-containing system (control) (HA) were formulated. Specimens were subjected to the μTBS test after 24 h and 6 and 12 months of storage. Data (in megapascals) were analyzed by Kruskal–Wallis and Dunn tests (α=0.05).
Results Medians of the μTBS data after 24 h of storage are: HA=57.2^{A}, B10=26.2^{BC}, B30=24.0^{C}, P400=32.6^{BC}, P1000=37.3^{B}, and UP400=57.9^{A}; after 6 months are: HA=47.9^{A}, B10=18.5^{B}, B30=7.8^{C}, P400=16.1^{B}, P1000=14.6^{BC}, and UP400=51.6^{A}; and after 12 months are: HA=31.2^{A}, B10=15.2^{B}, B30=9.0^{B}, P400=9.1^{B}, P1000=13.3^{B}, and UP400=35.7^{A}. Between the HEMA-free groups, the adhesive system formulated with PEG 400 UDMA produced similar μTBS to the HEMA-containing group. Also, the storage of specimens decreased the μTBS (p<0.05).
Conclusion Replacing HEMA for PEG 400 UDMA in an adhesive system formulation generated a satisfactory μTBS to dentin.
Clinical relevance Surfactant dimethacrylates have a potential use in the development of HEMA-free self-etching adhesive systems, which are more chemically stable.

Keywords Dental adhesive · Surfactant · Microtensile bond strength test · Resin–dentin interface · Biodegradation

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Introduction

Dentin-bonding agents are blends of hydrophobic and hydrophilic monomers with a twofold purpose: adhesion between the hydrophobic restorative materials and the intrinsically wet dentin substrate. Generally, hydrophobic monomers are characterized by the presence of at least two polymerizable groups (vinyl groups or –C=C–) [1]. These dimethacrylates can form densely cross-linked polymers [2], providing mechanical strength [3, 4] and reducing the susceptibility to hydrolysis in aqueous solutions [5]. On the

other hand, the hydrophilic monomers act like adhesion-promoting agents, called "functional monomers." These functional monomers have, on one extremity, a polymerizable group that links to the hydrophobic dimethacrylates and, on the other extremity, a hydrophilic functional radical [6].

The 2-hydroxyethyl methacrylate (HEMA) is a hydrophilic functional monomer broadly used in commercial dentin-bonding agents in amounts that vary between 35 and 55 % [6, 7]. Due to the low molecular weight, HEMA acts as a cosolvent, helping to mix hydrophobic and hydrophilic ingredients in a single homogeneous blend [8]. Additionally, its great penetration ability makes this water-soluble monomer an excellent adhesion-promoting agent, leading to an increase in immediate bond strengths [9, 10].

However, HEMA and many other (co)monomers, additives, or polymerization products have been extensively associated to allergenic reactions and are triggers to induce pulp apoptotic cell death when diffusing into dentinal tubules [11–13]. Also, HEMA is a common sensitizer among dentists and dental technicians because it can penetrate through conventional gloves during adhesive handling [14] and may lead to the development of contact dermatitis [15].

As verified by a chemical analysis, HEMA cannot form cross-linking like the dimethacrylate monomers, and it only links in linear space positions, resulting in a polymer more prone to hydrolysis in the oral environment. Thus, a potential decrease in mechanical properties of the adhesive resin can be expected over time [5, 6]. In fact, several in vivo and in vitro studies have shown that resin–dentin interfaces become much weaker over time [16–20]. It was suggested that alterations in resin components, such as the plasticizing effects of water and chemical hydrolysis, may be the first step in the degradation of such interfaces due to rapid loss of the monomers and chemicals from hybrid layers in humid environments [21]. When HEMA concentration was evaluated as an independent variable in experimental adhesive formulations, it was found that the higher HEMA content (30 and 50 % wt) showed lower degree of conversion, rate of polymerization, and microtensile bond strength to dentin when compared with the control group (0 % wt of HEMA) and the group containing 15 % wt [22]. The same study showed that the sorption and solubility properties increase according to the HEMA content.

In an attempt to improve the long-term stability of the adhesion between tooth structure and composite, HEMA-free adhesive systems were recently introduced on the market [23]. Replacing HEMA in adhesive formulations may reduce the hydrolysis phenomenon, but, at the same time, may interfere with the adhesive hydrophilicity, which is important for the hybridization of the dentin substrate [24].

An interesting approach to maintain the hydrophilicity of the adhesive blends and, at the same time, to form more stable cross-linked polymers with reduced adhesive toxicity is to replace HEMA with surfactant dimethacrylates (SD) with high molecular weights (Table 1). Surfactant dimethacrylates are solubility enhancers that facilitate penetration of hydrophobic components into wet demineralized dentin, reducing the phase separation [25, 26] and increasing the bond strengths to dentin [27, 28]. Unlike HEMA, SD presents two polymerizable groups (–C=C–) that form cross-linked polymers that are less susceptible to hydrolysis in humid environments [1, 5]. Additionally, the high molecular weight may impair the monomer diffusion through non-sclerotic dentin [13], and, theoretically, a reduction of the adhesive toxicity and pulp reactions by steric impedance would be expected [29].

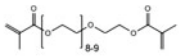
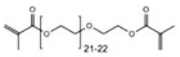
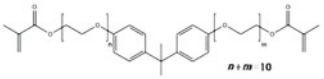
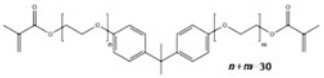
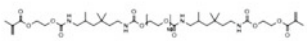
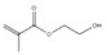
Considering the potential and advantages of using SD, the aim of this study was to test the hypothesis that replacing HEMA for different SD does not affect the immediate and long-term microtensile bond strength (μTBS) of experimental two-step self-etch HEMA-free adhesive systems applied on dentin.

Material and methods

Experimental HEMA-free self-etching adhesive system formulation

Six experimental two-step self-etching primers evaluated in the study were formulated by mixing the components described in Table 2. The respective resin bonds were formulated through an intensive mixture of components described in Table 3. To make the resin bond light curing, a binary light-curing system consisting of 0.4 wt% camphorquinone (CQ, Esstech) and 0.8 wt% ethyl 4-dimethylaminebenzoate (EDAB, Fluka, Milwaukee, WI, USA) was dissolved in the mixture. All the primers and adhesives were ultrasonicated for 15 min each. Ethoxylated bisphenol A diglycidyl dimethacrylate, with 10 and 30 ethylene oxide units (Bis-EMA 10 and Bis-EMA 30, respectively), poly-ethyleneglycol (400) dimethacrylate (PEG 400), poly-ethyleneglycol (1000) dimethacrylate (PEG 1000), poly-ethyleneglycol (400) extended urethane dimethacrylate (PEG 400 UDMA), HEMA, 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropyl)-phenyl]-propane (Bis-GMA), and triethyleneglycol dimethacrylate (TEGDMA) were purchased from Esstech (Esstech Inc., Essington, PA, USA). GDMA-P is an equimolar mixture of glycerol dimethacrylate dihydrogen phosphate and glycerol tetramethacrylate hydrogen phosphate, produced according to a previous investigation [30]. The reagents were used as received, without further purification.

Table 1 Description of surfactants used in this study

Surfactant	Lot number	Molecular weight (g/mol)[a]	Molecular formula	Molecular structure
Poly-ethyleneglycol (400) dimethacrylate (PEG 400)	# 614-07-02	550–594	$C_{26-28}H_{46-50}O_{12-13}$	
Poly-ethyleneglycol (1000) dimethacrylate (PEG 1000)	# 615-50	1,124–1,168	$C_{52-54}H_{98-102}O_{25-26}$	
Ethoxilate bisphenol A diglycidyl dimethacrylate (Bis-EMA 10)	# 560-05	805	$C_{43}H_{64}O_{14}$	
Ethoxilate bisphenol A diglycidyl dimethacrylate (Bis-EMA 30)	# 568-10-02	1,686	$C_{83}H_{144}O_{34}$	
Poly-ethyleneglycol (400) extended urethane dimethacrylate (PEG 400 UDMA)	# 621-13	1,139	$C_{54}H_{98}N_4O_{21}$	
2-hydroxyethyl methacrylate (HEMA)	# S3201-475	130	$C_6H_{10}O_3$	

[a] Data supplied by Esstech, Inc

Specimen preparation

Forty-eight extracted bovine incisors were used in this study. After pulp and periodontal tissue removal, the teeth were stored frozen at −4 °C for less than 3 months. Specimens were stored in CloramineT 0.5 % before specimen preparation. The teeth were randomly allocated into six experimental groups. The vestibular enamel was removed with a model trimmer to form a flat, superficial, coronal dentin surface. The exposed dentin surface was wet polished with 600-grit silicon carbide paper to create a standardized smear layer.

The water excess of the prepared surface dentine was removed with a piece of absorbent paper. One coat of each experimental self-primer was applied for 20 s and gently air-dried for 10 s. If a lightly wet and glossy surface was not observed, the same protocol was repeated. Then, one coat of resin bond was applied and light activated for 20 s using a

Table 2 Composition of the experimental self-etching primers

Primers (groups)	Surfactant monomer	Composition (% wt)			
		Surfactant	Ethanol	Water	GDMA-P
P400	PEG 400	30	20	20	30
P1000	PEG 1000	30	20	20	30
B10	Bis-EMA 10	30	20	20	30
B30	Bis-EMA 30	30	20	20	30
UP400	PEG 400 UDMA	30	20	20	30
HA[a]	HEMA	30	20	20	30

PEG 400 poly-ethyleneglycol (400) dimethacrylate, *PEG 1000* poly-ethyleneglycol (1000) dimethacrylate, *Bis-EMA 10* ethoxylated bisphenol A diglycidyl ether dimethacrylate with ten ethylene oxide units, *Bis-EMA 30* ethoxylated bisphenol A diglycidyl ether dimethacrylate with 30 ethylene oxide units, *PEG 400 UDMA* poly-ethyleneglycol (400) extended urethane dimethacrylate, *HEMA* 2-hydroxyethyl methacrylate, *GDMA-P* an equimolar mixture of glycerol dimethacrylate dihydrogen phosphate and glycerol tetramethacrylate hydrogen phosphate

[a] Control group

Table 3 Composition of the experimental resin bonds

Resin bond (groups)	Surfactant monomer	Composition (% wt)				
		Surfactant	Bis-GMA	TEGDMA	CQ	EDAB
P400	PEG 400	25	49	24.8	0.4	0.8
P1000	PEG 1000	25	49	24.8	0.4	0.8
B10	Bis-EMA 10	25	49	24.8	0.4	0.8
B30	Bis-EMA 30	25	49	24.8	0.4	0.8
UP400	PEG 400 UDMA	25	49	24.8	0.4	0.8
HA[a]	HEMA	25	49	24.8	0.4	0.8

PEG 400 poly-ethyleneglycol (400) dimethacrylate, *PEG 1000* poly-ethyleneglycol (1000) dimethacrylate, *Bis-EMA 10* ethoxylated bisphenol A diglycidyl ether dimethacrylate with ten ethylene oxide units, *Bis-EMA 30* ethoxylated bisphenol A diglycidyl ether dimethacrylate with 30 ethylene oxide units, *PEG 400 UDMA* poly-ethyleneglycol (400) extended urethane dimethacrylate, *HEMA* 2-hydroxyethyl methacrylate, *Bis-GMA* 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropyl)-phenyl]-propane, *TEGDMA* triethyleneglycol dimethacrylate, *CQ* camphorquinone, *EDAB* ethyl 4-dimethylaminebenzoate

[a] Control group

light-emitting diode light-curing unit (Radii SDI, Bayswater, Victoria, Australia). The irradiance was measured with a digital power meter (Ophir Optronics, Danvers, MA, USA) and was approximately 1,400 mW/cm^2. After adhesive light activation, two increments of at most 2 mm of resin composite (Charisma, color shade C2, Heraeus Kulzer, Germany) were placed, completely covering the dentin surface, and then were light cured in close contact for 20 s each. The specimens were stored for 24 h in distilled water at 37 °C. The specimens were sectioned in two perpendicular directions to the bonded interface using a water-cooled diamond saw at low speed (Isomet 1000, Buehler Ltd, Lake Bluff, IL), producing beams with a cross-sectional surface area of approximately 0.5 mm^2 for microtensile bond testing. The beams of each adhesive system were allocated in three groups according to storage period (24 h, 6 months, and 12 months), staying in distilled water at 37 °C. Water was changed weekly to make it fresh.

μTBS evaluation and fracture analysis

The prepared beams had their ends covered and individually fixed to a custom-made testing jig using a cyanoacrylate glue (Super Bonder Gel, Loctite, Diadema, SP, Brazil) and were tested in tension until failure in a mechanical testing machine (DL-500, Emic, São José dos Pinhais, Brazil) at a crosshead speed of 1 mm/min. μTBS were calculated and expressed in megapascals. Half of each specimen corresponding to dentin was removed from the device and was examined in an optical microscope at a magnification of ×100 and ×500. The failure patterns were classified as on the adhesive interface, cohesive in adhesive resin, cohesive in dentin, or mixed.

Statistical analysis

Due to different sample sizes and data that did not fulfill normality and equal variance requirements, statistical analysis was performed using Kruskal–Wallis one-way of variance on ranks and Dunn's method as multiple comparison procedures (α=5 %). All the premature failures were registered, but they were not included for statistical comparisons.

Results

Median values for μTBS in megapascals, the number of specimens tested (*n*), failure distribution (in percentages), and premature failures (p.f.) according to adhesive groups and storage time are shown in Table 4.

Statistical analysis revealed that the μTBS median values after 24 h of storage were statistically higher for all groups tested compared to median values after 6 and 12 months of storage. No difference was found between μTBS of 6 and 12 months of storage for each group (p>0.05). The μTBS of groups HA (control) and UP400 were similar; however, both groups showed statistically higher median values for the three storage times evaluated.

Regarding the distribution of failure patterns at 24-h storage, the B10, B30, P400, and P1000 groups presented higher adhesive failure percentages (above 80 %) with few mixed and/or cohesive resin failures. In the HEMA-free UP400 group, equal percentages of mixed and adhesive failures were observed (41 %), with some cases of cohesive dentin and cohesive resin failures. The HA control group showed few adhesive failures with a predominance of cohesive resin and mixed failures.

In all the groups, no premature failures were observed in this period. After 6 months of storage, an increase in adhesive failure percentages was observed in the HA, UP400, and B30 groups, with 100 % observed in B30. Additionally,

Table 4 Median values for microtensile bond strength in megapascals, number of specimens tested (*n*), premature failures (p.f.) according to groups and storage time and failure distribution (in percentages)

Groups tested according to storage times		Median (MPa)	*n*	p.f.	Failure distribution (%)			
					AD	CD	CR	MI
24 h	HA[x]	57.2 $^{A\ a}$	25	–	8	20	44	28
	B10	26.2 $^{A\ bc}$	28	–	93	–	–	7
	B30	24.0 $^{A\ c}$	24	–	92	–	–	8
	P400	32.6 $^{A\ bc}$	22	–	82	–	–	18
	P1000	37.3 $^{A\ b}$	21	–	80	–	10	10
	UP400	57.9 $^{A\ a}$	29	–	41	7	11	41
6 months	HA[x]	47.9 $^{B\ a}$	25	–	50	–	15	35
	B10	18.5 $^{B\ b}$	23	–	64	–	10	26
	B30	7.8 $^{B\ c}$	15	7	100	–	–	–
	P400	16.1 $^{B\ b}$	26	–	77	8	2	13
	P1000	14.6 $^{B\ bc}$	22	–	69	–	5	26
	UP400	51.6 $^{B\ a}$	24	–	55	13	12	20
12 months	HA[x]	31.2 $^{B\ a}$	25	–	50	–	15	35
	B10	15.2 $^{B\ b}$	23	2	77	–	–	23
	B30	9.0 $^{B\ b}$	14	9	100	–	–	–
	P400	9.1 $^{B\ b}$	20	3	70	5	–	20
	P1000	13.3 $^{B\ b}$	16	8	67	6	–	27
	UP400	35.7 $^{B\ a}$	23	1	48	17	4	31

Different superscript capital letters represent differences statistically significant between median values at different storage periods. Different superscript small letters represent differences statistically significant between adhesive groups. Failure distribution observed at ×100 and ×500 magnifications

CD cohesive in dentin, *MI* mixed, *AD* adhesive interface, *CR* cohesive in the adhesive resin

[x] Control group

some premature failures were observed in the B30 group. In this period, HA and UP400 showed similar failure patterns. Concerning the specimens tested after 12 months of storage, in general, the failure patterns were similar to those observed after 6 months of storage. In this period, except for HA, all the groups showed some premature failures, mainly for the B30 and P1000 groups (Table 4).

Discussion

The surface active agents (surfactants) are used to improve formulations and functionalities of many daily products and generally can be classified into four primary groups according to the charge characteristic: anionic, cationic, nonionic, and zwitterionic (dual charge) [31]. In this study, five different nonionic SD were tested in the experimental HEMA-free self-etching adhesive formulations. The composition of the adhesive systems was identical, except for the kind of amphiphilic monomer, thus allowing for an indisputable evaluation of the effect of HEMA substitution on adhesion performance.

The SD employed are basically characterized by the presence of two methacrylate radicals corresponding to hydrophobic groups and long oxiethylene chain extenders ($[–CH_2–CH_2–O–]_n$) or urethane radicals ($R^1–O–(CO)NR^2–R^3$) corresponding to hydrophilic groups [31]. These hydrophilic radicals improve wettability, diffusibility, and penetrability of the resin blend, which are crucial properties to reaching an effective hybridization on the wet demineralized dentin [27, 28].

According to data of the immediate and long-term μTBS rejections, the hypothesis was partially refuted. Thus, replacing HEMA with different SD affects the immediate and long-term μTBS of experimental two-step self-etch HEMA-free adhesive systems applied on dentin. The exception occurs when UP400 was used in the formulation. The immediate μTBS data showed that UP400 and HA (control, HEMA-containing) produced the highest μTBS ($p<0.05$). Additionally, a predominance of mixed failures was observed in both groups (Table 4).

Group UP400 was formulated with PEG 400 UDMA, a urethane-containing SD with a high molecular weight. This molecule acts as a hybridization agent into the collagen fibrils due to the presence of a long chain extender of ethylene oxide units and four urethanes between the two hydrophobic unsaturated radicals. Thus, a bipolar behavior is created, allowing at the same time monomer diffusion into the collagen fibrils and the formation of the cross-linked polymer [26]. Also, the four –NH– present in the urethanes (Table 1) can bind the monomers by hydrogen bonding (H-bonding), leading to a more rigid polymer network with increased mechanical properties [2]. Considering that SD increased the hydrophobic dimethacrylate concentrations into the collagen fibrils [26], this adhesive system probably produced a very strong hybrid layer, making the adhesive–dentin interface more resistant [27, 32].

The HEMA-free experimental groups B10, B30, P400, and P1000 produced μTBS values significantly lower than UP400 and HA in all storage periods (Table 4). Additionally, high adhesive failure rates were observed in the fractured specimens at 24 h (above 80 %). These findings can be explained by the hydrophilic groups that characterize the SD employed in these experimental adhesives, which are composed of one or two very long chain extenders of ethylene oxide units. These long chain extenders can act as an aprotic solvent [33], increasing the wettability and the degree of conversion of the resin blend [34, 35], and also can determine a higher network parameter and consequently a more flexible polymer, acting as a rubber solid [35]. The formation of the polymer with high flexibility and high network parameter may result in a weak resin–dentin interface that is more susceptible to swelling [5] with high appearance flaws inside the incompletely infiltrated zones, which could be the reason for the low μTBS on dentin and the high adhesive failure rates [16, 28, 32].

In relation to the storage time, the μTBS values after 24 h were statistically higher for all groups tested when compared to values after 6 and 12 months of storage. No statistical difference was found between μTBS of 6 and 12 months of storage for each group. After 12 months of storage, except for HA, all the groups showed some premature failures, mainly for the B30 and P1000 groups (Table 4). These findings can be explained by the adhesive resin degradation that probably occurs because of adhesive displacement by water into the adhesive–dentin interface, as a result of hydrolysis [36]. Although the degradation of naked collagen fibril by MMPs occurs into adhesive–dentin interfaces [37], in the case of self-etching adhesives, the hydrolysis of adhesive resin may be more damaging to long-term bonding effectiveness due to their bond structure having less demineralized dentin [36]. In fact, the evaluation of the μTBS in in vivo specimens after long-term functional restorations demonstrated a severe hydrolysis of adhesive resin within the hybrid layer created by a self-etching adhesive system [38]. Additionally, physical changes such as plasticization, softening, and chemical changes such as oxidation alter permanently the mechanical properties of the polymer network in the adhesive–dentin interface [5].

Furthermore, the hygroscopic and hydrolytic effects in dental polymers are dependent on the extent and water uptake rate that is determined by the density of the polymer network and the potential for hydrogen bonding and polar interactions [5]. Thus, the low μTBS observed in groups B10, B30, P400, and P1000 after 6 and 12 months of storage can be related to the presence of several ether groups

(R–O–R′) into the long chain extenders of ethylene oxide present in the SD employed. Venz et al. [39] reported that the hydrophilic ether linkage is the main group related to water sorption, following by hydroxyl groups and, in the end, urethane linkages. Hence, the chemical nature of the cross-linking agent may overcome the effect of higher molecular density [40].

The increased water sorption will result in a polymer plasticization, thereby reducing interchain interactions, such as entanglements and secondary bonds. Consequently, this sponge effect results in reduction of the polymer mechanical properties [5]. However, when μTBS data at 6 and 12 months of storage were compared, no statistical differences were observed (Table 4). The probable reason lies in the full saturation of the network, which reaches a maximum within 1 or 2 months [41]. Additionally, the elution of the unreacted monomers, oligomers, by-products, and polymerization promoters occurs mainly in the first weeks, creating initial chemical polymer stabilization. But the chemical polymer degradation through oxidation, chain scission, and attack of functional groups remains over time, resulting in the increased porosity in the hybrid in specimens produced in vivo after long-term function [42].

Finally, the possible biological adverse effects of HEMA alternatives have not been well understood. There are few studies which have evaluated the biocompatibility of polyethyleneglycol dimethacrylates. Moreover, to the best of our knowledge, there are no studies evaluating its biological effects in dental adhesives. However, poly(ethylene glycol) dimethacrylate (PEGDMA) did not produce any toxic effect when used in the formulation of inorganic–organic hybrid resin films developed for biomedical applications [43]. In that study, PEGDMA exhibited an excellent biological performance in cell cultures and mice.

Considering the potential and advantages of SD and the lack of information available in literature, further studies of issues such as cytotoxicity and new formulations testing are necessary for better understanding of SD usage as adhesion promoters in dental adhesives.

Conclusions

Surfactant dimethacrylates have a potential use in the development of HEMA-free self-etching adhesive systems. The experimental system containing PEG 400 UDMA presented satisfactory immediate and long-term bond strengths, demonstrating a performance similar to the HEMA-containing control system.

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Conflict of interest The authors declare that they have no conflict of interest.

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