International Journal of Adhesion & Adhesives 62 (2015) 78–84

Contents lists available at ScienceDirect

International Journal of Adhesion & Adhesives

journal homepage: www.elsevier.com/locate/ijadhadh

Incorporation of inorganic fillers into experimental resin adhesives: Effects on physical properties and bond strength to dentin

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ARTICLE INFO

Article history:
Accepted 6 July 2015
Available online 20 July 2015

Keywords:
Self-etch adhesive
Durability
Nanofillers
Ytterbium trifluoride

ABSTRACT

This study investigated the effect of different monomeric systems and inorganic fillers on the physical properties of experimental resin adhesives and on the immediate and 6-month bond strength to dentin. Two, 2-step self-etch adhesive systems were prepared: two primers (constituted of GDMA-P, ethanol, water, and HEMA or PEG(400)-UDMA) and two adhesives (constituted of Bis-GMA, TEGDMA, and HEMA or PEG(400)-UDMA). Next, the adhesives were allocated into three groups according to filler incorporated: unfilled (control), silica (SiO_2), or ytterbium trifluoride (YbF_3). Degree of conversion (DC, after 30 and 60 s of light-activation), water sorption (WS) and solubility (SL), and flexural strength (σ) and modulus (E_f) tests were performed for all adhesives. A microtensile bond strength (μTBS) test to dentin was evaluated after 24 h (immediate) and 6 months (6-month) of water storage using a universal testing machine (DL500, EMIC). Data were analyzed using statistical tests ($\alpha = 5\%$). The adhesives showed similar DC at a same light exposure time, although light-activation for 60 s improved conversion of monomers. The unfilled HEMA-containing adhesive showed higher WS, SL, σ and E_f compared to others. The incorporation of fillers into the adhesives did not affect negatively the immediate μTBS results; however, after 6 months the presence of SiO_2 impaired in complete premature failures, and the presence of YbF_3 reduced the μTBS in the PEG(400)-UDMA-based group. The unfilled HEMA-containing group also reduced bond strength after 6 months of water storage. In conclusion, depending on the resin matrix composition, YbF_3 seems to be a good option for reinforcing adhesive systems.

1. Introduction

Dental adhesive systems are polymer-based biomaterials used to bond restorative materials to the teeth substrates (i.e., enamel and dentin). The adhesion process can be easily achieved by the application of three different components: one with an acidic nature, one primer solution, and one resin-based material (adhesive). The former helps with the demineralization process of the substrate, creating micro-porosities on the surface; the second (primer) turns the substrate receptive and/or chemically compatible to the adhesive; and the latter is the component that infiltrates in and firmly adheres to the substrate [1]. After the application of these materials, a strong adhesive interface is obtained, which is commonly named as 'hybrid layer' [2].

Even though adhesive systems have already been long-term evaluated as dental bonding agents by several in vivo and in vitro studies [3–7], they still present some limitative aspects that should be taken into consideration. For example, the 2-hydroxyethyl methacrylate (HEMA) is a highly hydrophilic monomer commonly present in dental adhesives. Nevertheless, recent studies have been demonstrating the fast bonding degradation that HEMA-containing adhesives undergo when submitted to a wet environment, mainly because this monomer is more sensitive to hydrolysis when compared to less hydrophilic monomers (e.g., Bis-GMA, TEGDMA, Bis-EMA, UDMA) [8–10]. As a consequence, current research in dental biomaterials has been focused on the replacement of HEMA by more hydrolytically stable monomers. Indeed, a recent study has investigated the mechanical and physical properties of experimental adhesives containing alternative dimethacrylates rather than HEMA [9]. The authors demonstrated that some of these monomers could be potentially used for the development of HEMA-free adhesive systems, and after reviewing

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http://dx.doi.org/10.1016/j.ijadhadh.2015.07.001
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some important aspects involved in dental adhesion processes, the polyethyleneglycol (400) extended urethane dimethacrylate [PEG (400)-UDMA] was selected as a good option for the replacement of HEMA.

Despite of all the potential benefits that a HEMA-free composition may bring to the durability of the adhesive treatment [11,12], the decrease in hydrophilicity may on the other hand modify the physical stability and chemical interaction between the adhesive and some inorganic compounds (fillers) that may be present in the material. Indeed, the loading of adhesives with different types of fillers has been increasingly evaluated since a significant reinforcement of the material can be achieved [13–16]. In addition, some properties (e.g., radiopacity) that may be absent in unfilled adhesives may be interestingly obtained by the incorporation of fillers [14,17]. However, there is little information regarding the effect that hydrophilic and/or hydrophobic resin compositions loaded or not with inorganic fillers may have on physical properties as well as on bond strength to tooth substrates.

Hence, the aims of this study were: (1) to prepare experimental filled and unfilled adhesive systems containing HEMA or PEG (400)-UDMA; and (2) to investigate the effect of different monomers/fillers on physical properties of the adhesives and on their bond strength to dentin. The following hypotheses were tested: (1) adhesives constituted of different monomeric systems would present different physical properties; (2) filled adhesives would present better physical properties compared to unfilled adhesives; and (3) PEG(400)-UDMA-based adhesives would not decrease dentin bond strength after 6 months evaluation.

2. Materials and methods

2.1. Preparation of the experimental adhesive systems

Two-step self-etch adhesive systems were prepared in this study varying the monomeric system and the type of fillers incorporated into the resin matrix. First, two primers were formulated by mixing 30 wt% of HEMA (Sigma-Aldrich, St. Louis, MO, USA) or PEG(400)-UDMA (Esstech Inc., Essington, PA, USA), 30 wt% of 1,3-glycerol dimethacrylate (GDMA-P), which was synthesized as previously described [18], 20 wt% of ethanol (Vetec, Duque de Caxias, RJ, Brazil) and 20 wt% of distilled water. Next, two adhesives were formulated based on a 2:1:1 mass ratio of the monomers 2-bis[4-(2-hydroxy-3-methacryloyloxypropyl)phenyl]-propane (Bis-GMA, Evonik, Essen, Germany), triethyleneglycol dimethacrylate (TEGDMA, Esstech), and HEMA or PEG(400)-UDMA. To make the resin bonds light-sensitive, 0.4 wt% of photoinitiator (camphorquinone, CQ, Esstech) and 0.8 wt% of co-initiator (ethyl 4-dimethylamino benzoate, EDAB, Sigma-Aldrich) were added.

Each adhesive was then separated into three groups according to the type of filler added: unfilled – no fillers added (control); SiO_2–10 wt% of nanosilica fillers (7 nm average particle size, Aerosil 380, Degussa, Weiss-Fraunenst, Germany); and YbF_3–10 wt% of ytterbium trifluoride (Stanford Materials, Aliso Viejo, USA). Prior to their incorporation, the fillers were silanized using a 10 wt% solution of gamma-methacryloxypropyltrimethoxysilane (γ-MPTS, Sigma-Aldrich) and acetone (Vetec); the resultant slurry was stored for 24 h at 37 °C to assure complete solvent removal. The fillers were sieved and finally incorporated into their respective adhesive formulations, followed by mechanical mixing (motorized mixer) and ultrasonication for 1 h.

2.2. Physical properties of the adhesives

The degree of conversion (DC) was evaluated using Fourier Transform mid-infrared spectroscopy (Prestige21, Shimadzu, Japan). First, a standard adhesive volume (~3 μl) was dispensed on the crystal and a preliminary reading (uncured material) was taken. The absorbance intensities used were the following: peak around 1635 cm^{-1} (aliphatic C=C) and peak around 1608 cm^{-1} (aromatic C–C). Light-activation was then performed with a light-emitting diode (LED) light-curing unit (Radii®, Bayswater, VIC, USA) for 30 and 60 s (s) ($n=5$); next, another reading was carried out (cured material) using the same aforementioned absorbance intensities. The DC was calculated as previously described [19], and using the following formula:

$$DC = \frac{1-\left(1635\ \mathrm{cm}^{-1} \div 1608\ \mathrm{cm}^{-1}\right)\mathrm{cured}}{\left(1635\ \mathrm{cm}^{-1} \div 1608\ \mathrm{cm}^{-1}\right)\mathrm{uncured}} \times 100\%$$

The water sorption (WS) and solubility (SL) tests were performed according to ISO 4049:2009 [20]. Each resin bond was placed into a metallic mold and light-activated for 30 s at both top and bottom surfaces. Next, the specimens ($n=5$) were placed into a desiccator containing freshly dried silica gel and calcium chloride, weighed after a constant mass (m_1) was obtained, measured about their diameter and thickness, and immersed in distilled water for seven days at 37 °C. All specimens were then blotted dry with lint-free absorbing papers, weighed again (m_2), and placed inside the desiccator until a constant third mass was obtained (m_3) [9]. For each specimen, the WS and SL data, in μg/mm^3, were calculated using the following formulas:

$$WS = \frac{m_2 - m_3}{V} \qquad SL = \frac{m_1 - m_3}{V}$$

where V is the volume (in mm^3) of each specimen, which was calculated using the diameter and thickness measurements.

Bar-shaped specimens ($10 \times 2 \times 2\ mm^3$, $n=10$) were prepared for each adhesive using a metallic mold. Light-activation was performed for 30 s on two consecutive points of the top and bottom surfaces. The specimens were then stored in distilled water for 24 h at 37 °C. Next, they were submitted to three-point bend test (span length of 6 mm) in a universal testing machine (DL500, EMIC, São José dos Pinhais, PR, Brazil) at a crosshead speed of 1 mm/min. Flexural strength (σ) and flexural modulus (E_f) were calculated in MPa using the following formulas:

$$\sigma = \frac{3Fl}{2bh^2} \qquad E_f = \frac{Ll^3}{4bh^3d}$$

where F is the peak load (N); l is the span length (mm); b is the width of the specimen (mm), h is the thickness of the specimen (mm), and d is the deflection of the specimen at load L during the straight line portion of the load-displacement trace. All data were expressed in MPa.

2.3. Bond strength to dentin

Forty-eight extracted bovine incisors were obtained, stored in 0.5 wt% Chloramine T solution for seven days, and randomly allocated into six groups ($n=8$), according to the adhesive system investigated (2 primers × 3 adhesives). The enamel present in the buccal surface of each tooth was removed, resulting in flat dentin surfaces, which were wet polished with 600-grit silicon carbide paper to standardize the smear layer. Next, each primer was applied for 20 s and gently air-dried for 10 s until a lightly wet and glossy surface was achieved [21]. In the sequence, one coat of the respective adhesive was applied and light-activated for 30 s, followed by two 2 mm-thick increments of resin composite (Filtek™ Z350 XT, 3M ESPE, St. Paul, MN, USA), which were also light-activated for 20 s each. The exact combination of primers and adhesives used in the study is shown in Fig. 1A. The samples were then stored in distilled water (24 h at 37 °C), sectioned in two perpendicular directions to the adhesive interface using a water-cooled diamond saw at low speed (Isomet 1000, Buheler Ltd., Lake Bluff, IL, USA), resulting in beam-shaped specimens with a cross-sectional surface area of approximately 0.8 mm^2, which were stored in distilled water for 24 h or 6 months, at 37 °C. The

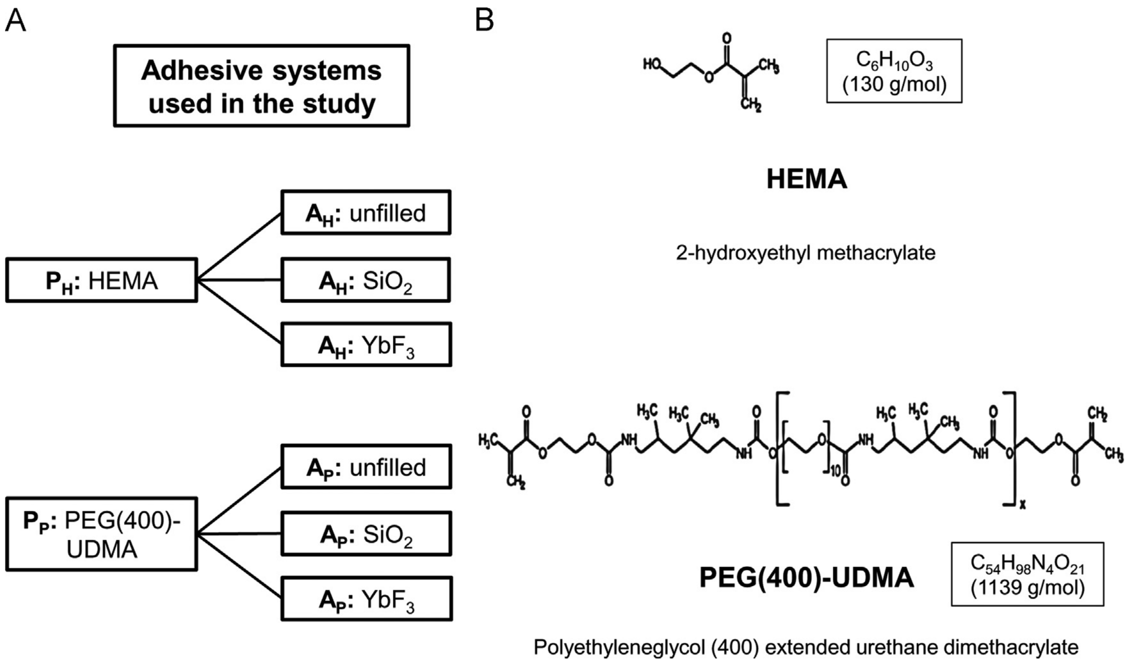


Fig. 1. Adhesive systems used in the study, which were obtained by combining primers containing HEMA or PEG(400)-UDMA and the respective filled and unfilled adhesives (A). Molecular formula, weight and structure of the HEMA and PEG(400)-UDMA molecules.

Table 1
Composition of primers and adhesives prepared in the study.

Primer	**Composition (wt%)**				
	HEMA	PEG(400)-UDMA	GDMA-P	Ethanol	Water
P_H: HEMA	30	0	30	20	20
P_P: PEG(400)-UDMA	0	30	30	20	20

Adhesive	**Composition (wt%)**					Filler (10 wt%, related to total polymer weight)
	Bis-GMA	TEGDMA	HEMA	PEG(400)-UDMA	CQ/EDAB	
A_H: unfilled	50	25	25	0	0.4/0.8	–
A_H: SiO_2	50	25	25	0	0.4/0.8	SiO_2
A_H: YbF_3	50	25	25	0	0.4/0.8	YbF_3
A_P: unfilled	50	25	0	25	0.4/0.8	–
A_P: SiO_2	50	25	0	25	0.4/0.8	SiO_2
A_P: YbF_3	50	25	0	25	0.4/0.8	YbF_3

HEMA: 2-hydroxyethyl methacrylate; PEG(400)-UDMA: polyethyleneglycol (400) extended urethane dimethacrylate; GDMA-P: 1,3-glycerol dimethacrylate; Bis-GMA: 2-bis [4-(2-hydroxy-3-methacryloyloxypropyl)phenyl]-propane; TEGDMA: tryethyleneglycol dimethacrylate; CQ: camphorquinone; EDAB: ethyl 4-dimethylaminebenzoate; SiO_2: nanosilica; and YbF_3: ytterbium trifluoride.

specimens were finally submitted to microtensile bond strength test (DL500) at a crosshead speed of 1 mm/min [22], and data were expressed in MPa. After testing, the specimens were individually analyzed using a stereomicroscope for determining their mode of failure, which was classified as adhesive failure (when no resin composite remained on the dentin surface), cohesive in dentin or cohesive in resin composite failures (when the failure occurred at the respective substrates), and mixed failure (when the surface presented at least 25% of two different modes).

2.4. Statistical analysis

Data were analyzed with the statistical program SigmaPlot version 12.0 (Systat Software Inc., San Jose, CA, USA) using two-way Analysis of Variance (ANOVA) for homoscedastic data (DC, WS, SL, σ, and E_f) and ANOVA on Ranks for heteroscedastic data (bond strength). Tukey test was used for multiple comparisons. Within the degree of conversion and bond strength results, *t*-tests and Mann–Whitney test were used, respectively, to compare data at the different periods of time tested. The significance level of all analyses was set at $\alpha = 5\%$ Table 1.

3. Results and discussion

The first property evaluated in this study was the DC of the adhesives since the incorporation of fillers can affect the optical density of the resin matrix [23], which may lead to higher scattering and light reflection phenomena, hampering the material's polymerization. According to results shown in Table 2, and considering them at the same light exposure time, all adhesives resulted in similar DC ($p \geq 0.090$), corroborating with previous studies that found no detrimental effect on the polymerization of resin adhesives containing 0.530 wt% of fillers [13,14,23]. However, the increase in light-activation time from 30 to 60 s significantly improved the DC of all adhesives ($p \leq 0.040$). Indeed, the two highest gains in conversion were observed within the YbF_3-based adhesives (16.7% for that containing HEMA and 17.4% for that containing PEG(400)-UDMA), suggesting that the increased light exposure allowed higher excitement of the photoinitiator/CQ, leading to better radical polymerization of monomers. In Fig. 2 it is possible to clearly observe the effective polymerization obtained with the HEMA-containing and PEG(400)-UDMA-based adhesives prepared in the study.

In adhesive dentistry, the physical stability of resin adhesives against hydrolysis is one of the most important issues related to bond strength degradation [7]. Taking this into consideration, WS and SL tests were performed, since they can simulate hygroscopic and hydrolytic phenomena of degradation [24], thus helping to predict the behavior of the prepared adhesives after direct contact with a wet environment. According to results displayed in Table 3, the HEMA-containing adhesives demonstrated higher WS than those constituted of PEG(400)-UDMA ($p < 0.001$). This confirms that the former have a more hydrophilic behavior than the latter, which may be easily explained by the pendant hydroxyl group (-OH) present in HEMA molecule (Fig. 1B), which attracts water to the polymer system by hydrogen bonding interactions. By contrast, PEG(400)-UDMA has a long chain molecule and no hydroxyls, resulting in a more hydrophobic system [9,24]. An interesting finding was that filled adhesives showed similar WS when compared to their unfilled counterparts, suggesting the fillers were uniformly distributed and co-polymerized with the organic matrix [25,26]. With regard to the solubility results, also shown in Table 3, the unfilled HEMA-containing adhesive demonstrated the highest SL (21.2 $\mu g/mm^3$), which was approximately four times higher than the other HEMA-containing groups and almost 20 times higher than those based on PEG(400)-UDMA ($p < 0.001$). The hydrophilic nature of HEMA has probably made the polymer network more prone to hydrolysis, resulting in the break of intermolecular chains and consequently in the elution of free/unreacted components from the adhesive [23,24]. Surprisingly, the presence of SiO_2 or YbF_3 reduced the SL produced by the HEMA-containing adhesive, once again suggesting that they were co-polymerized to the organic matrix, reducing the occurrence of hydrolysis. It should be noted that all specimens were light-activated for a total time of 60 s (30 s on each side) in an attempt to achieve better polymerization (as discussed before) and a more physically stable material [24].

Table 2
Degree of conversion (mean ± standard deviation) of all adhesives tested in the study, after 30 or 60 s (s) of light-activation.

Groups	Time of light-activation (s)			
	30		60	
	HEMA	PEG(400)-UDMA	HEMA	PEG(400)-UDMA
Unfilled	49.9 (±1.5)	51.6 (±4.4)	61.1 (±8.0)	60.2 (±1.7)
SiO_2	54.0 (±2.7)	51.6 (±6.1)	62.2 (±3.9)	60.5 (±5.3)
YbF_3	48.1 (±6.7)	44.0 (±1.3)	64.8 (±7.6)	61.3 (±4.2)

There was no statistically significant differences between adhesives at the same time of light-activation ($p > 0.05$); however, adhesives light-activated for 60 s presented higher DC than adhesives light-activated for 30 s ($p < 0.05$).

Regarding the mechanical properties, the unfilled HEMA-containing adhesive was stronger than the others ($p < 0.001$) (Table 3), probably due to the formation of strong intermolecular hydrogen bonds among HEMA molecules [9]. Considering that PEG(400)-UDMA is not able to form these intermolecular bonds, it impaired lower σ and E_f properties compared to HEMA. In addition, PEG(400)-UDMA has a long monomeric chain when compared to HEMA molecule, which may also cause plasticization. Interestingly, a dual effect was observed regarding to the incorporation of fillers: when they were added into the HEMA-containing adhesive the mechanical properties were significantly reduced, whereas their incorporation into those adhesives based on PEG(400)-UDMA did not cause any detrimental effect. Although agglomeration or heterogeneous dispersion of fillers in the resin phase may contribute to reduction in polymer strength [23], it has been already assumed that the fillers were uniformly distributed into the adhesives since no detrimental effects on the DC, WS and SL properties were observed. Therefore, other reasons may have played a role on the strength reduction within the HEMA-containing adhesives containing fillers. Indeed, silanized fillers can co-polymerize with methacrylate monomers via the methacrylate functional group present in silane molecule. This is important to create a stable C=C covalent bond between silane and the polymer structure [25]. Considering that HEMA is a monomethacrylate (Fig. 1B), it is able to form a C=C bond only once, which may have occurred during the polymerization process with the silanized fillers, other HEMA molecules, or other monomers linked to the main polymer network. This could have resulted in several unreacted/unbounded compounds into the polymer, reducing the mechanical strength of the system. On the other hand, PEG(400)-UDMA is a dimethacrylate (i.e., it has two methacrylate functional groups per molecule, Fig. 1B), making it possible to link simultaneously with both the silanized fillers and the main polymer network, resulting in a more uniform system. These foregoing inferences can therefore explain why the filled PEG(400)-UDMA-based adhesives were as strong as the unfilled adhesive and why the incorporation of fillers into the HEMA-containing adhesive decreased the mechanical properties of the latter system.

Taking together the DC, WS, SL, σ, and E_f results, the first and the second hypotheses of the present study can be only partially accepted.

The main purpose of an adhesive agent in dentistry is to bond two surfaces/substrates to each other. Therefore, the bond strength of the formulated adhesive systems to dentin was also investigated. According to Fig. 3A, the immediate bond strength results showed that the HEMA-containing adhesives produced similar adhesion values, regardless of the presence of fillers ($p \geq 0.065$). Differently, the PEG(400)-UDMA-based adhesive reinforced with SiO_2 resulted in higher bond strength than its unfilled and YbF_3-based counterparts ($p \leq 0.002$), which have not differed between each other ($p = 0.996$). The failure mode analysis corroborates the present findings, with a satisfactory equilibrium between adhesive and mixed failures (inset table in Fig. 3A). The adhesion process to dental substrates involves basically three steps: surface etching, priming and bonding [1]. Self-etch adhesives are characterized by the simultaneous etching and priming of

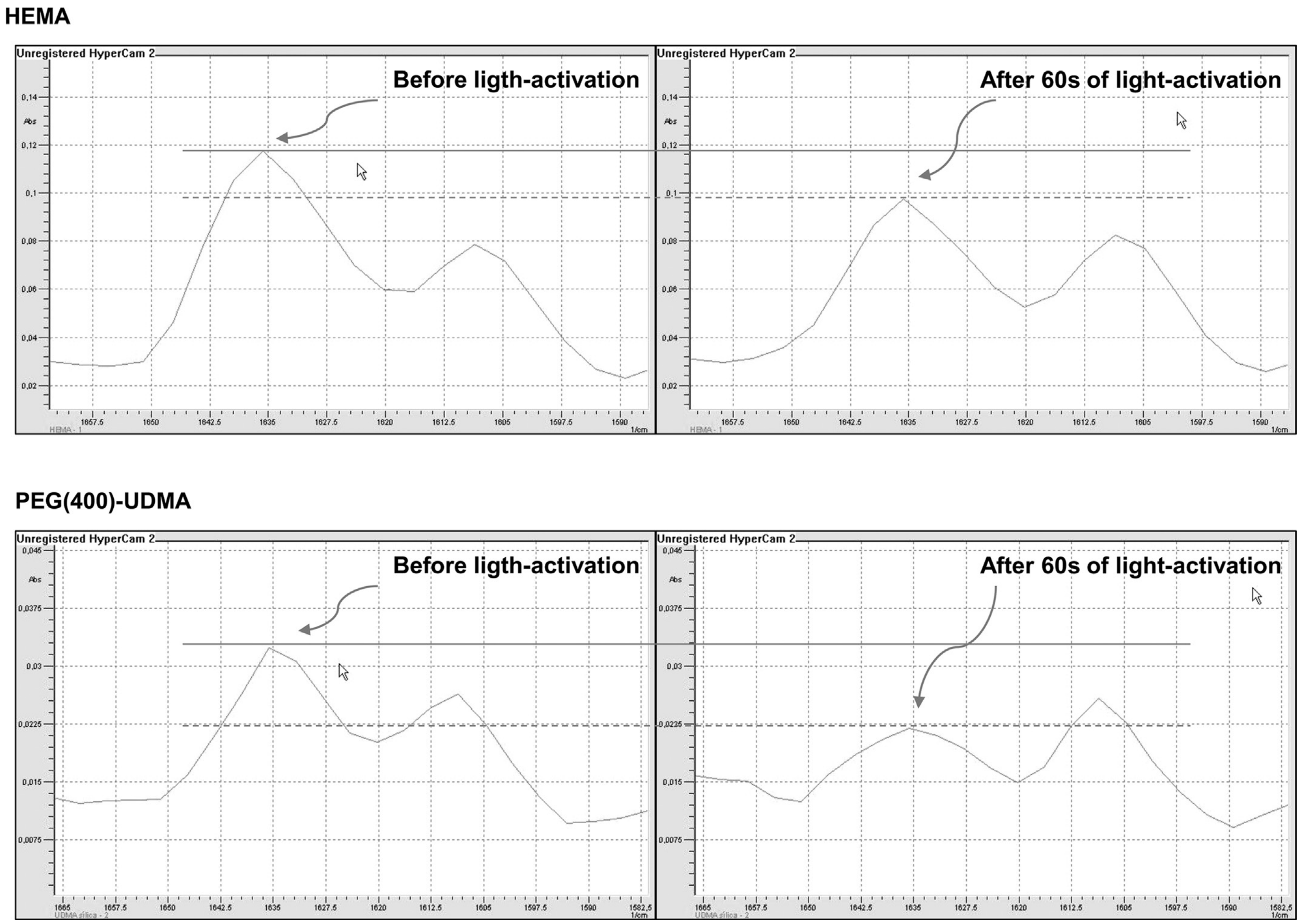


Fig. 2. Representative infrared spectra of HEMA- and PEG(400)-UDMA-containing adhesives before and after light-activation for 60 s (s). In each pair of images (before and after light-activation), note the reduction in peak intensity around the 1635 cm^{-1} peak, related to the aromatic ring.

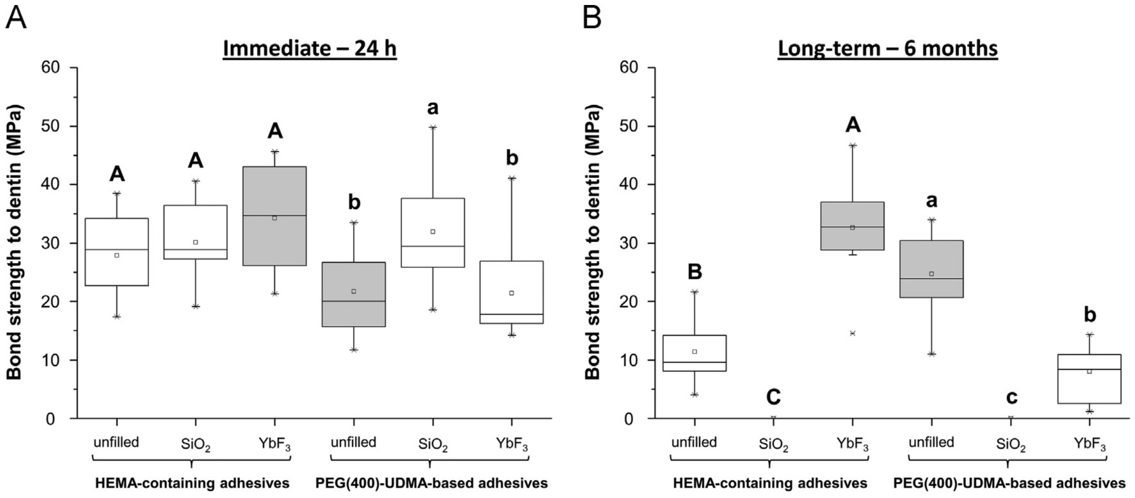
Table 3
Physical properties of all resin bonds investigated in the study with means and standard deviation (SD).

Groups	WS (μg/mm^3)		SL (μg/mm^3)		σ (MPa)		E_f (GPa)	
	HEMA	PEG(400)- UDMA	HEMA	PEG(400)-UDMA	HEMA	PEG(400)-UDMA	HEMA	PEG(400)-UDMA
Unfilled	^{A} 59.2^a (13.0)	^{A} 36.6^b (4.2)	^{A} 21.2^a (10.5)	^{A} 1.1^b (1.2)	^{A} 168.7^a (23.2)	^{A} 94.2^b (4.8)	^{A} 2.7^a (0.5)	^{A} 1.0^b (0.1)
SiO_2	^{A} 50.9^a (1.9)	^{A} 34.3^b (4.3)	^{B} 5.1^a (4.0)	^{A} 1.6^a (1.2)	^{B} 101.6^a (14.1)	^{AB} 98.5^a (15.1)	^{B} 1.2^a (0.1)	^{A} 1.1^a (0.3)
YbF_3	^{A} 57.3^a (7.9)	^{A} 37.7^b (1.3)	^{B} 4.9^a (3.2)	^{A} 2.3^a (1.2)	^{B} 92.3^a (11.0)	^{B} 79.8^b (4.8)	^{B} 1.1^a (0.1)	^{A} 1.0^a (0.1)

WS: water sorption; SL: solubility; σ: flexural strength; E_f: flexural modulus; HEMA: 2-hydroxyethyl methacrylate; PEG(400)-UDMA: polyethyleneglycol (400) extended urethane dimethacrylate; SiO_2: sílica; and YbF_3: ytterbium trifluoride.
Similar uppercase letters before means and in a same column indicate similarity among filled and unfilled groups ($p > 0.05$); different lowercase letters after means and in a same raw represent statistically significant differences between groups containing HEMA or PEG(400)-UDMA ($p < 0.05$).

the substrate, which allows the formation of a homogeneous hybrid layer and uniform monomer infiltration [7]. The primers used in this study have already demonstrated efficacy when bonding to dentin [18,21]; conversely, the resin adhesives containing SiO_2 or YbF_3 have not been yet investigated.

The presence of SiO_2 or YbF_3 did not affect negatively the bonding ability of the adhesives (Fig. 3A), which at a first sight could indicate an advantageous characteristic over the unfilled adhesives. Nonetheless, after 6 months of water storage, a significant reduction in bond strength occurred for some groups investigated (Fig. 3B). Indeed, both groups containing SiO_2 resulted in complete premature failures (adhesive failures, see in the inset table shown in Fig. 3B), thus suggesting that hydrolysis was very aggressive into the hybrid layer formed with these adhesives. According to Antonucci et al. [27], the oxane bond (Si–O–Si) formed between silane and SiO_2 is very prone to hydrolysis, and considering the specimens were stored in water for 6 months, hydrolytic degradation occurred within these oxane bonds, leaching the fillers out of the polymer. Consequently, water migration has probably occurred into the debonded interphases, increasing the hygroscopic and hydrolytic degradation of the polymer network [24]. With regards to the unfilled HEMA-containing group, it reduced bond strength after water storage ($p < 0.001$), which was already expected since HEMA makes the



Groups	HEMA-containing adhesives		PEG(400)-UDMA-containing adhesives	
	Adhesive	Mixed	Adhesive	Mixed
unfilled	63%	37%	71%	29%
SiO_2	52%	48%	63%	37%
YbF_3	60%	40%	65%	35%

Groups	HEMA-containing adhesives		PEG(400)-UDMA-containing adhesives	
	Adhesive	Mixed	Adhesive	Mixed
unfilled	93%	7%	57%	43%
SiO_2	100%	-	100%	-
YbF_3	55%	45%	89%	11%

Fig. 3. Box-plots showing the immediate (A) and 6-months (B) bond strength results. The inset tables represent the failure mode distribution (adhesive or mixed) of each group investigated at each period of storage tested.

polymer hydrophilic due to the pendant hydroxyl group, and thus susceptible to degradation [9,11,12,21]. However, the presence of YbF_3 surprisingly protected the HEMA-containing adhesive against hydrolysis, as observed by the stable bond strength results ($p=0.654$), although the same pattern was not seen for the PEG (400)-UDMA-based group. It can be suggested that YbF_3, which is constituted by fluorine (i.e., an electronegative atom and excellent hydrogen bond acceptor) [28], formed strong intermolecular hydrogen bonds with the hydroxyl groups of HEMA molecules, impairing lower hydrophilicity to the polymer system containing HEMA. Considering that no hydrogen bond interactions were possible to occur within the PEG(400)-UDMA-based polymer since no pendant hydroxyls were present, YbF_3 was not able to protect this polymer system against hydrolysis. Lastly, the other group that resulted in stable bond strength after 6 months of water storage was the unfilled PEG(400)-UDMA-based group (Fig. 3B), probably because it was less hydrophilic than the HEMA-containing group (Table 3). Therefore, the third hypothesis of the study was also only partially accepted.

4. Conclusions

Silica (SiO_2) and ytterbium trifluoride (YbF_3) fillers were successfully incorporated into resin adhesives, with no detrimental effect over most of the physical properties investigated. The immediate bond strength to dentin was also not affected by addition of fillers, although a significant reduction was achieved after 6 months of water storage, except for the group containing HEMA and YbF_3. With regard to the unfilled adhesives, the more hydrophobic PEG(400)-UDMA-based group showed stable bond strength over time compared to the more hydrophilic HEMA-containing group. The incorporation of fillers into resin adhesives should be performed with caution in order to avoid detrimental effects on the bonding ability of the material over time.

References

[1] Alex G. Is total-etch dead? Evidence suggests otherwise Compend Contin Educ Dent 2012;33(12–4):6–22 4–5; quiz 6, 38.

[2] Nakabayashi N, Kojima K, Masuhara E. The promotion of adhesion by the infiltration of monomers into tooth substrates. J Biomed Mater Res 1982;16:265–73.

[3] Marchesi G, Frassetto A, Mazzoni A, Apolonio F, Diolosa M, Cadenaro M, et al. Adhesive performance of a multi-mode adhesive system: 1-year in vitro study. J Dent 2014;42:603–12.

[4] Ozer F, Blatz MB. Self-etch and etch-and-rinse adhesive systems in clinical dentistry. Compend Contin Educ Dent 2013;34(12-4) 6, 8; quiz 20, 30.

[5] Pashley DH, Tay FR, Breschi L, Tjaderhane L, Carvalho RM, Carrilho M, et al. State of the art etch-and-rinse adhesives. Dent Mater 2011;27:1–16.

[6] van Dijken JW, Sunnegardh-Gronberg K, Lindberg A. Clinical long-term retention of etch-and-rinse and self-etch adhesive systems in non-carious cervical lesions. A 13 years evaluation. Dent Mater 2007;23:1101–7.

[7] Van Meerbeek B, Yoshihara K, Yoshida Y, Mine A, De Munck J, Van Landuyt KL. State of the art of self-etch adhesives. Dent Mater 2011;27:17–28.

[8] Liu Y, Tjaderhane L, Breschi L, Mazzoni A, Li N, Mao J, et al. Limitations in bonding to dentin and experimental strategies to prevent bond degradation. J Dent Res 2011;90:953–68.

[9] Munchow EA, Zanchi CH, Ogliari FA, Silva MG, de Oliveira IR, Piva E. Replacing HEMA with alternative dimethacrylates in dental adhesive systems: evaluation of polymerization kinetics and physicochemical properties. J Adhes Dent 2014;16:221–8.

[10] Ogliari FA, Ely C, Zanchi CH, Fortes CB, Samuel SM, Demarco FF, et al. Influence of chain extender length of aromatic dimethacrylates on polymer network development. Dent Mater 2008;24:165–71.

[11] Collares FM, Ogliari FA, Zanchi CH, Petzhold CL, Piva E, Samuel SM. Influence of 2-hydroxyethyl methacrylate concentration on polymer network of adhesive resin. J Adhes Dent 2011;13:125–9.

[12] Takahashi M, Nakajima M, Hosaka K, Ikeda M, Foxton RM, Tagami J. Long-term evaluation of water sorption and ultimate tensile strength of HEMA-containing/-free one-step self-etch adhesives. J Dent 2011;39:506–12.

[13] Conde MC, Zanchi CH, Rodrigues-Junior SA, Carreno NL, Ogliari FA, Piva E. Nanofiller loading level: influence on selected properties of an adhesive resin. J Dent 2009;37:331–5.

[14] Leitune VC, Collares FM, Trommer RM, Andrioli DG, Bergmann CP, Samuel SM. The addition of nanostructured hydroxyapatite to an experimental adhesive resin. J Dent 2013;41:321–7.

[15] Nuvoli D, Alzari V, Sanna R, Scognamillo S, Alongi J, Malucelli G, et al. Synthesis and characterization of graphene-based nanocomposites with potential use for biomedical applications. J Nanopart Res 2013:15.

[16] Xia LJ, Xu ZH, Sun LM, Caveney PM, Zhang MJ. Nano-fillers to tune Young's modulus of silicone matrix. J Nanopart Res 2013:15.

[17] Carreno NLV, Oliveira TCS, Piva E, Leal FB, Lima GS, Moncks MD, et al. YbF_3/SiO_2 fillers as radiopacifiers in a dental adhesive resin. Nano-Micro Lett 2012;4:189–96.

[18] Leal FB, Madruga FC, Prochnow EP, Lima GS, Ogliari FA, Piva E, et al. Effect of acidic monomer concentration on the dentin bond stability of self-etch adhesives. Int J Adhes Adhes 2011;31:571–4.

[19] Moraes RR, Faria-e-Silva AL, Ogliari FA, Correr-Sobrinho L, Demarco FF, Piva E. Impact of immediate and delayed light activation on self-polymerization of dual-cured dental resin luting agents. Acta Biomater 2009;5:2095–100.

[20] ISO 4049:2009. Dentistry-Polymer-Based Filling, Restorative and Luting Materials.

[21] Zanchi CH, Munchow EA, Ogliari FA, de Carvalho RV, Chersoni S, Prati C, et al. Effects of long-term water storage on the microtensile bond strength of five experimental self-etching adhesives based on surfactants rather than HEMA. Clin Oral Investig 2013;17:833–9.

[22] Munchow EA, Bossardi M, Priebe TC, Valente LL, Zanchi CH, Ogliari FA, et al. Microtensile versus microshear bond strength between dental adhesives and the dentin substrate. Int J Adhes Adhes 2013;46:95–9.

[23] Reis LO, Kaizer MR, Ogliari FA, Collares FM, Moraes RR. Investigation on the use of triphenyl bismuth as radiopacifier for (di)methacrylate dental adhesives. Int J Adhes Adhes 2014;48:80–4.

[24] Ferracane JL. Hygroscopic and hydrolytic effects in dental polymer networks. Dent Mater 2006;22:211–22.

[25] Karabela MM, Sideridou ID. Effect of the structure of silane coupling agent on sorption characteristics of solvents by dental resin-nanocomposites. Dent Mater 2008;24:1631–9.

[26] Sideridou ID, Karabela MM. Effect of the amount of 3-methacyloxypropyltrimethoxysilane coupling agent on physical properties of dental resin nanocomposites. Dent Mater 2009;25:1315–24.

[27] Antonucci JM, Dickens SH, Fowler BO, Xu HH, McDonough WG. Chemistry of silanes: interfaces in dental polymers and composites. J Res Natl Inst Stand Technol 2005;110:541–58.

[28] Dalvit C, Invernizzi C, Vulpetti A. Fluorine as a hydrogen-bond acceptor: experimental evidence and computational calculations. Chemistry 2014.