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Mineral precipitation, polymerization properties and bonding performance of universal dental adhesives doped with polyhedral oligomeric silsesquioxanes

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Mineral precipitation, polymerization properties and bonding performance of universal dental adhesives doped with polyhedral oligomeric silsesquioxanes

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Keywords: Nanofillers; POSS; novel adhesives; structure property relations

Declaration of interest: Four universal adhesives (Adhese Universal, Futurabond U, iBOND Universal, Scotchbond Universal) were provided by the manufacturers. The providers were not involved in any research activity nor consultations regarding this study.

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Abstract

Objectives: To investigate the effect of methacrylate polyhedral oligomeric silsesquioxane (POSS-8) particles on the polymerization process, dentin bond strength, and mineral precipitation of universal dental adhesives.

Methods: Five universal adhesives (Adhese Universal, CLEARFIL Universal Bond, Futurabond U, iBOND Universal, Scotchbond Universal) were filled with POSS-8 particles (10 wt%, additionally 2 wt% and 5 wt% in Scotchbond Universal). The particle size and dispersion in ethanol and acetone were examined by dynamic light scattering. Degree of conversion, linear shrinkage, and shear bond strength to dentin treated with the filled and pure adhesives (controls) were measured. Growth of calcium phosphate (Ca/P) precipitates on the adhesive specimens immersed in artificial saliva for up to 28 days was analyzed by energy-dispersive X-ray spectroscopy and scanning electron microscopy. Statistical analyses were performed using ANOVA and Tukey's post-hoc tests ($p < 0.05$).

Results: The hydrodynamic radius of the particles in acetone (1.4 ± 0.4 nm) and ethanol (1.1 ± 0.4 nm) revealed their good dispersion. POSS-8 did not change the degree of conversion and dentin bond strength of any adhesive. Ca/P precipitates formed on iBOND Universal specimens doped with POSS-8 after 4 weeks of immersion, but were not detected on the unfilled adhesive. The mineral precipitation of all other adhesives was not improved by POSS-8.

Significance: POSS-8 particles did not compromise polymerization and bonding of universal adhesives. Ca/P precipitation was stimulated by POSS-8 only in iBOND Universal.

Keywords: Bioactive nanofillers; POSS; novel adhesives; structure-property relations

1. Introduction

Dental adhesives are available for decades and underwent various and ongoing product developments with the aim to make them less technique-sensitive, faster and easier to use. Recently, particular attention is paid to the universal or multi-mode adhesives, which are designed for different adhesion strategies (self-etch-, etch&rinse-, or selective-etch mode) and various substrates (enamel, dentin, ceramics, metal). Versatility of universal adhesives is clinically highly beneficial, but these products undergo the same hydrolytic and enzymatic degradation processes as previous generations of dental adhesives [1–4].

One approach to prevent hybrid layer degradation is the incorporation of nanoparticles, which might improve the mechanical properties of the adhesive and, consequently, reinforce the hybrid layer [5–9]. Some studies focus on the searching for suitable bioactive particles/glasses that could improve bonding through remineralization of the hybrid layer, and thus prevent its degradation [10]. The main challenge is to make the particles small enough to fit in between the collagen fibrils. The incorporation of nanosized hydroxyapatite, zirconia or glass fillers has been shown to increase dentin bond strength of adhesive resins depending on the concentration of fillers [5–7]. On the other hand, particle reinforcement of dental adhesives is also associated with possible adverse effects, such as agglomeration of particles [6,7,11,12] and increased viscosity [12,13], which could result in detrimental effects on bond strength [6,14].

Recently, polyhedral oligomeric silsesquioxanes (POSS) were suggested as alternative fillers for adhesive resins, as their hybrid character allows for good dispersion and particle mobility in organic substances. While monofunctional methacryl POSS particles were unable to improve the network structure of an acetone-based dental adhesive, the incorporation of multifunctional methacryl POSS particles led to enhanced properties without affecting viscosity [12]. Such particles may also act as crosslinkers and thus improve the conversion of the matrix and mechanical properties. Furthermore, POSS particles were shown to induce bioactive properties of a dental adhesive [12] and other composite materials [15].

Therefore, this study aimed to systematically analyze the effect of infiltrating different universal adhesives with multifunctional POSS particles at a concentration of 10 wt% on mineral precipitation, polymerization properties, and dentin bonding performance. Additionally, lower POSS concentrations were tested in one universal adhesive.

The null hypothesis was that the POSS particles would not affect the degree of conversion, linear shrinkage, dentin bond strength, and mineral precipitation of the universal adhesives.

2. Materials and methods

Five commercial universal adhesives (Table 1) were used as base materials to test the effect of adding 10 wt% multifunctional methacryl polyhedral oligomeric silsesquioxanes (POSS-8, Methacryl POSS Cage Mixture, Hybrid Plastics Inc, Hattiesburg, USA). Additionally, the effect of POSS-8 at different concentrations (2 wt%, 5 wt%) was studied on Scotchbond Universal. The adhesive groups with POSS-8 and controls were mixed using a magnetic stirrer for 5 min in a dark environment to avoid polymerization.

2.1. Dispersion and size of the particles

As the medium for the dynamic light scattering (DLS) experiment two solvents of the respective adhesives (ethanol or acetone) were used. The contribution from other small molecules of the adhesives in the range of particle scattering makes such experiment in adhesive system not possible. A homogenous solvent is necessary to achieve a constant background. The DLS experiment was carried out with Zetasizer Nano-ZS (Malvern, Worcestershire, Great Britain) which estimates the size distribution from the measured correlation function by non-negative least square (NNLS) analysis. The scattered light was monitored at an angle of 173° and at 25°C. Each test (consisting of 13 x 10 s measurements) was repeated three times.

For each solvent, seven concentrations (ϕ_x) of the POSS-8 particles were measured. The diffusion coefficient D_0 was estimated from the extrapolation to $\phi \rightarrow 0$ of the measured, concentration-dependent diffusion coefficients D_x. The hydrodynamic radius R_h of the

POSS-8 particles was determined from the diffusion coefficient D_0 according to the Stokes-Einstein equation:

$$D_0 = k_B T / 6\pi\eta R_h \quad (1)$$

with the Boltzmann constant k_B, temperature T (K), and viscosity of the solvent η.

2.2. Degree of conversion

A thin layer of adhesive (~0.3 mm thickness, n = 3) was applied on the attenuated total reflectance (ATR) crystal of a Fourier transform infrared spectrometer (TENSOR 27, Bruker, Billerica, USA). During a delay time of 3 min for acetone, and 5 min for ethanol, the solvents were allowed to evaporate. After this time, the specimens were light cured for 10 s with an LED curing light (Bluephase G2, Ivoclar Vivadent, Schaan, Liechtenstein, 1090 mW/cm^2), and infrared spectra were collected between 900 and 4000 cm^{-1} and with a resolution of 4 cm^{-1}. All spectra were corrected for a background, scanned prior to each measurement.

The DC in the Bis-GMA-containing adhesives was estimated from the ratio of peak heights of aliphatic C=C stretching vibrations at 1638 cm^{-1} (H_{al}) and aromatic C=C stretching vibrations at 1608 cm^{-1} (H_{ar}) of cured and uncured specimens:

$$\mathrm{DC} = 1-(\mathrm{H_{al}}/\mathrm{H_{ar}})_{\mathrm{cured}}/(\mathrm{H_{al}}/\mathrm{H_{ar}})_{\mathrm{uncured}} \quad (2)$$

For iBOND Universal, a carbonyl peak at 1730 cm^{-1} (H_{carb}) was used as reference instead of the aromatic C=C, and in that case H_{ar} in eq (2) was replaced with H_{carb}.

2.3. Linear polymerization shrinkage

Linear polymerization shrinkage of the adhesives was measured using a custom-made linometer, developed following de Gee et al. [16] and described in detail previously [17,18]. Briefly, the device comprised a solid metal frame on which a thin aluminum platelet was loosely placed. The rear side of the platelet featured a perpendicular diaphragm that extended into a recess of the infrared measuring sensor of the linometer. A standardized amount of adhesive (20 μl) was applied on the aluminum platelet using a pipette, and compressed to a thickness of 0.8 mm by means of a 1-mm-thick glass slide (Thermo Scientific Menzel X50, Gerhard Menzel B.V&Co.KG, Braunschweig, Germany). Light curing of the adhesives was performed for 20 s through the glass slide using an LED curing unit (Bluephase G2, Ivoclar Vivadent). The vertical movement of the diaphragm induced by polymerization shrinkage of the adhesives was recorded by the infrared measuring sensor at a sampling frequency of 5 Hz. Measurements (n = 5 per group) were performed for 10 min from the start of photoactivation at ambient room temperature.

2.4. Shear bond strength

Rectangular dentin specimens (6 x 6 mm, n = 140) were prepared from freshly extracted, non-damaged bovine incisors. The specimens were then embedded in chemically cured acrylic resin (Paladur, Heraeus Kulzer GmbH, Hanau, Germany) and ground flat with P500 paper (Hermes Abrasives, Hamburg, Germany). Specimens were randomly divided in 14 groups with n = 10 each. The universal adhesives were applied according to the manufacturers' information in self-etch mode and light cured for 10 s (Bluephase G2, Ivoclar Vivadent, 1090 mW/cm^2). A customized holding device was used to fix a transparent acrylic cylinder (inner diameter: 3 mm; height: 4 mm) vertically on the flat surface. A nano-hybrid composite (Venus Diamond, Heraeus Kulzer GmbH) was filled in 2 x 1.5-mm increments into the acrylic cylinder. Each increment was light cured for 20 s at 1090 mW/cm^2 (Bluephase G2, Ivoclar Vivadent). The specimens were stored in water at 8 °C for 24 h prior to the measurements.

Shear bond strength was tested with a universal testing machine (Zwick 1446, Zwick GmbH & Co. KG, Ulm, Germany). A chisel-shaped loading device applied shear force vertically to the adhesive interface at a speed of 1 mm/min. The shear bond strength was determined from the maximal force applied before failure. For failure mode analysis, all debonded surfaces were microscopically examined with a stereomicroscope (Stemi SV 11, Carl Zeiss Microscopy GmbH, Göttingen, Germany). Failures were classified as cohesive (failure within dentin), adhesive (failure at the dentin-composite interface), or mixed (shared cohesive and adhesive failures).

2.5. Mineral precipitation

The crystal precipitation was studied on disk-shaped specimens (diameter: 5 mm, height: 1 mm, n = 6), which were cured in a Teflon mold from both sides for 30 s (ethanol-based adhesives) or 120 s (aceton-based adhesive) at 1090 mW/cm^2 (Bluephase G2, Ivoclar Vivadent). Prior to curing, the solvents were removed from the adhesive mixtures by vacuum (10 min).

After the immersion in 15 ml artificial saliva [19] (37 °C for 14, 21 and 28 days (n = 2) without changing of the medium), the impurities and fallen precipitates were gently removed from the surfaces of the specimens by distilled water and the specimens were kept at room temperature in a desiccator with silica gel for drying. The presence and ratio of calcium and phosphate groups in the precipitated crystals was evaluated using energy-dispersive X-ray (EDX) spectroscopy at 20 kV (Cryo-FE-SEM, FEI Quanta 200 FEG with Edax, FEI Company, Hillsboro, USA). The morphology of crystals was analyzed on the Platinum-Palladium sputtered specimens (28 days group) by scanning electron microscopy (SEM) at 5 kV (Ultra Plus, Carl Zeiss GmbH, Jena, Germany).

2.6. Statistical analysis

The data from shear bond strength, degree of conversion, and linear shrinkage were tested for normal distribution using Quantil-Quantil plots and showed normal distribution for all groups and tests. Two-way ANOVA followed by Tukey post-hoc tests was applied considering the kind of universal adhesive and the concentration of POSS-8 as factors ($p < 0.05$). The distribution of failure modes in the filled and unfilled groups was analyzed by χ^2-test ($p < 0.05$). The data of four groups with various POSS-8 concentrations in Scotchbond Universal were analyzed by one-way ANOVA and Tukey post-hoc test applying the POSS concentration as a factor ($p < 0.05$). All statistical analyses were conducted using Dell Statistica software (Dell Inc., Tulsa, USA).

3. Results

3.1. Dispersion and size of the particles

According to eq (1) and considering the viscosity of acetone (0.311 mPas) and ethanol (1.0 mPas), the extrapolation of the measured diffusion coefficient to $\phi = 0$ resulted in the hydrodynamic radius of POSS-8 particles $R_h = 1.4 \pm 0.4$ nm in acetone and 1.1 ± 0.4 nm in ethanol.

The interaction between particles in a solution can be expressed through the interaction parameter k_D that is directly proportional to the second virial coefficient B_2 and can be obtained from the slope of the diffusion coefficient versus concentration based on the equation $D_\phi/D_0 = 1+k_D\phi$. A positive value of k_D in ethanol solution (0.039) indicates repulsive interactions between the particles which promotes dispersion. In the case of acetone, a minimally negative, however almost neutral value (-0.0008) was found. This indicates a slightly better dispersion of the POSS-8 particles in ethanol than in acetone. In both cases, however, the interactions seem to be relatively weak.

3.2. Degree of conversion

The measured degrees of conversion (DC) of all studied groups are given in Table 2. No significant differences were detected between the unfilled groups. Also, the incorporation of the POSS-8 particles did not significantly affect the DC. However, a tendency to lower DC by adding particles at 10 wt% concentration can be seen in all groups.

A similar or slightly decreased apparent degree of conversion in the composites filled with POSS-8 particles does not necessarily mean a similar or lower crosslink density and similar or worse mechanical properties. Each POSS-8 particle brings ideally 8 vinyl groups, but for steric reasons and because of the distribution of the radicals during initiation and propagation stage, not all groups are available for polymerization. Thus, even partially polymerized particles may form a crosslink point with high functionality, but still reduce the DC measured by FTIR [12]. Assuming a similar density of the components and that the monomers react in a similar manner independently of the presence of particles, we can estimate the ratio of residual vinyl groups on the particles after curing to those before curing, X/P, as described in the previous study [12]. Also assuming absolutely no reaction of particles, X/P would equal 1, which can be expressed for the ratios of vinyl to benzene or carbonyl groups, R, as follows:

$$(R_f^u - R_a^u) = (R_f^c - R_a^c) \tag{3}$$

where *u* and *c* denote the uncured versus cured state and subscripts *f* and *a* refer to filled adhesive or control adhesive. With this approximation, one can estimate the DC of solely functional groups on POSS-8, $DC_{POSS} = (1-X/P)$ [12], and also the expected DC measured in the case that no reaction between particles and monomers or between particles itself took place in the filled adhesives (eq. 3 applies), DC_0:

$$DC_0 = (1-R_f^c/R_f^u) = (R_a^u-R_a^c)/R_f^u \tag{4}$$

We point out that this is only a very rough estimation and serves solely to bring a better understanding of the polymerization process in the studied systems.

The results show that particles worsen the DC in Scotchbond Universal at a concentration of 10%, where the measured DC (66.9 ± 2.6%) was slightly lower than the estimated DC_0 (69.3%). Contrary, at lower concentrations, the measured DC (84.9 ± 8.6% and 83.6 ± 10.1% for 2% and 5% loading, respectively) was higher than the estimated DC_0 (77.1% and 74.8% for 2% and 5% loading, respectively). Similarly, CLEARFIL Universal Bond, iBOND Universal, and Futurabond U showed a strong interconnection of particles with DC_{POSS} of 65.1%, 65.5% and 54.6%, respectively, and improvement of DC versus DC_0 of 10.4%, 16.0% and 6.2%, respectively. In Adhese Universal, only roughly 10% of functional groups on the particles reacted.

3.3. *Linear polymerization shrinkage*

iBOND Universal showed the significantly lowest linear shrinkage (LS, Table 2) of all studied adhesives with and without POSS-modification. POSS-8 significantly increased LS only of CLEARFIL Universal Bond, while LS of the other adhesives remained unchanged. A slight, yet not significant, reduction of LS could be observed for Futurabond U.

3.4. *Shear bond strength*

No significant difference in shear bond strength (SBS) was found between the POSS-8-filled and control groups of all adhesives (Table 2). Nevertheless, differences in SBS were observed between the commercial adhesive systems. The only acetone-based adhesive, iBOND Universal, performed as the worst of the studied universal adhesives. A significantly lower SBS of iBOND Universal was found compared to Adhese Universal, Scotchbond Universal and Futurabond U.

The majority of failures were mixed failures, and the distribution of the failure modes was significantly influenced by adding 10 wt% POSS-8 only in Scotchbond Universal, where more adhesive and less cohesive failures occurred in the POSS-8-filled adhesive. Nevertheless, the SBS of Scotchbond Universal was not affected by the addition of POSS particles (Table 2).

3.5. *Effect of POSS-8 concentration on SBS, DC and LS*

Fig. 1 reveals the SBS, DC and LS of Scotchbond Universal mixed with POSS-8 at various concentrations. All variables were normalized to the values of the control group (0% POSS) to show the change brought by the particles. The differences were small and the Tukey test revealed no significant differences between the groups.

3.6. *Mineral precipitation*

Calcium phosphate (Ca/P) precipitates were observed after 2 weeks of immersion in all groups except the iBOND Universal groups, where the first crystals appeared after 4 weeks and only in the POSS-8-loaded specimens. SEM images of these precipitates are shown in Fig. 2. Only small differences in the formation of Ca/P precipitates were observed between the POSS-containing groups and control groups. The POSS-filled adhesives showed a slightly increased density of crystals compared to the control groups.

EDX analysis confirmed the Ca/P nature of the crystals formed on the specimens and revealed the molar ratios of Ca and P in the precipitates. Fig. 3 shows the increase of this ratio over 4 weeks of immersion in each group. The values at 2 weeks were slightly higher in the POSS-filled groups than in the controls for most of the adhesives except Futurabond U, but the rate of increase was mostly higher during the observation times of 2-4 weeks in the control groups.

4. Discussion

The methacryl-functionalized hybrid POSS-8 particles could be successfully incorporated in the commercial universal adhesive systems. By adding 10 wt% POSS-8, the physico-chemical properties of the adhesives were only mildly modified or remained stable, and thus the application of the POSS-8-filled adhesives would not be hindered, taking into account the studied properties. However, POSS-8 did not provide any relevant benefit regarding mineral precipitation for most of the tested adhesives. For the improvement of structural properties of adhesive systems, one could profit from the multifunctionality of the POSS-8 particles at lower concentrations, such as 2 or 5%. The null hypothesis can thus only be partially rejected.

The particle size obtained from the light scattering experiment is in good agreement with a recent study [12]. The slightly smaller, yet not significantly different size of POSS-8 in ethanol than in acetone might be due to a thinner solvent layer around POSS-8 in ethanol.

The POSS-8 particles had no significant effect on the final conversion of the universal adhesives. The monomer conversion is closely related to polymerization shrinkage of resin-based composites [20]. No change of LS was observed through addition of POSS-8 particles in most of the studied universal adhesives, which is beneficial for the application of such particles in dental materials. Similarly, no significant change in shrinkage strain was observed through addition of 1,2,3-triazolium-functionalized POSS particles into a dental composite, while an improved conversion was detected [21]. The increase of conversion was attributed to the plasticization effect of the functionalized POSS. The significant increase of LS of CLEARFIL Universal Bond on the other hand implies a possible negative effect when too much crosslinker-like particles are used.

Contrary to the shrinkage and DC results, iBOND Universal showed the worst SBS of all studied adhesives. The relatively high SBS values of Scotchbond Universal may be due to the additional polyalkenoic acid copolymer, Vitrebond, which has been shown to increase dentin bond strength of adhesives [22], even though the hydrophilicity of this monomer may contribute to reduced bonding with dental restorative composites. Table 2 also shows that higher conversion and lower shrinkage cannot effectively predict the performance in dentin bonding of the studied adhesive systems.

The methacryl POSS particles did not significantly change SBS of any adhesive. It has been shown that the non-functionalized particles can lead to a reduced bond strength and conversion, particularly at higher loadings [23–25], even though an increase in bond strength has also been observed [26,27]. However, the functionalized or silanized filler particles have been found to be more promising for improvement of mechanical properties of adhesives [27,28]. The missing effect of POSS-8 on the SBS of the studied universal adhesives may be due to various factors, such as lower reactivity and mobility of the multifunctional particles or high concentration.

Multifunctional methacryl POSS particles are known to improve the mechanical properties of composites mainly at relatively low concentration, and worsening of the material characteristics follows if too high concentrations are applied. Depending on the application, loadings between 2% and 10% showed the best performance [29–32]. Similarly, we observed a small, however not significant increase of DC and SBS when adding 5% POSS-8 to Scotchbond Universal, followed by a trend of decreased DC and SBS at higher concentration (10%). This is in line with results of Fong et al. [29] indicating that 2% POSS particles did not visibly alter the DC, while at 10% loading, a slight reduction of DC could be seen. Similarly, the POSS-8 particles did not significantly reduce the DC up to a concentration of 5% in a methacryl-based composite. Only at 10% loading, a significant DC reduction was found by Wang et al. [11]. Their study also showed that shrinkage of the nanocomposite remained unchanged up to 5% of POSS-8 and was reduced at 10% loading due to reduced conversion at this concentration.

The growth of the Ca/P precipitates in all control groups except iBOND Universal was most probably stimulated by the original fillers in the adhesives. Scotchbond Universal, CLEARFIL Universal Bond, and Adhese Universal contain silica particles according to the material safety sheets, information from the producer or the literature [33,34], but no fillers are listed in the safety sheets of Futurabond U and iBOND Universal. The lack of fillers may be the reason why no mineral precipitation occurred in the iBOND Universal control group at all investigated immersion times. The appearance of precipitates after 4 weeks of immersion in the POSS-8-filled iBOND Universal adhesive confirms that POSS-8 particles can promote mineral precipitation in this adhesive system. However, more measurements with higher concentrations and longer immersion times (e.g. up to one year) shall be performed in future studies to test whether such mineral precipitation may have a sufficient bioactive effect for the application. The bioactivity of POSS-8 particles has been shown in previous studies [12,15]. The nucleation points in the studied adhesive systems consist mainly of the Si-OH groups on the silica fillers or as unreacted groups on POSS-8 particles [31].

The Ca/P crystals present a cauliflower- or plate-like structure in all groups with detected precipitation. Similar crystals were also observed in other studies [35–39]. This structure is similar to natural hydroxyl apatite in enamel and therefore the development of dental materials stimulating the growth of such Ca/P crystals is of high interest [13,38,40].

The Ca/P molar ratios show for almost all groups and immersion times that precipitates with lower amount of Ca than in the stoichiometric hydroxyapatite HA -10:6 [41] grew on the specimens. This suggests the presence of both, HA and calcium phosphate or even more complex mixtures of calcium- and phosphate-based crystals, such as tri- or octa-calcium-phosphate phases, which can reform to a more stable bioactive HA phase if mixed with simulated body fluid [40]. These crystals undergo a transformation at longer immersion times (Fig. 3), where more precipitates close to HA and with higher amount of calcium are formed [38]. The lower Ca/P ratios at 2 weeks in all control groups except Futurabond U indicate a faster nucleation during the first 2 weeks of immersion in the presence of POSS-8 particles. Consequently, the reduction of free ions in the solution after the initial precipitation might cause the later reduction of the growth rate in the POSS-8-filled adhesives [42].

5. Conclusions

The POSS-8 particles did not significantly affect the physico-chemical properties of most universal adhesives at 10% loading, while they could stimulate mineral deposition when mixed with iBOND Universal. Among the tested universal adhesives, Scotchbond Universal and Adhese Universal showed the best combination of degree of conversion, linear shrinkage and bonding ability for applications in dental medicine. Although iBOND Universal exhibited the lowest shrinkage and relatively high degree of conversion with and without POSS-modification, poor bonding performance was measured using this adhesive.

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Figures and Tables

Table 1

Composition (wt%) and pH of the universal adhesives according to manufacturers' information.

Universal adhesive	Composition	Etching monomer	pH
Adhese® Universal (Ivoclar Vivadent, Schaan, Liechtenstein)	2-hydroxyethyl methacrylate (10-25%), Bis-GMA (10-25%), ethanol (10-25%), 1,10-decandiol dimethacrylate (3-10%), methacrylated phosphoric acid ester (3-10%), camphorquinone (1-2.5%), 2-dimethylaminoethyl methacrylate (1-2.5%), silica fillers	10-MDP	2.7
CLEARFIL™ Universal Bond (Kuraray, Tokyo, Japan)	Bisphenol A diglycidylmethacrylate (15-35%), 2-hydroxyethyl methacrylate (10-35%), ethanol (<20%), 10-methacryloyloxydecyl dihydrogen phosphate, hydrophilic aliphatic dimethacrylate, colloidal silica, dl-camphorquinone, silane coupling agent, accelerators, initiators, water	10-MDP	2.3
Futurabond® U (VOCO GmbH, Cuxhaven, Germany)	Bisphenol A diglycidylmethacrylate (25-50%), 2-hydroxyethyl methacrylate (25-50%), 1,6-hexanediylbismethacrylate (10-25%), acidic adhesive monomer (5-10%), urethandimethacrylate (5-10%), ethanol, catalyst (≤2.5%), initiator	Acidic adhesive monomer	2.3
iBOND® Universal (Heraus Kulzer, Hanau, Germany)	Acetone (25-50%), 4-methacryloxyethyltrimellitic acid anhydride (10-25%), diurethandimetracrylate	4-META	1.6 - 1.8
Scotchbond™ Universal (3M ESPE, Maplewood, USA)	2-hydroxylethyl methacrylate (15-25%), bisphenol A diglycidyl ether dimethacrylate (15-25%), decamethylene dimethacrylate (5-15%), ethanol (10-15%), 2-propenoic acid, 2-methyl-, 3-(trimethoxysilyl)propylester, reaction products with vitreous silica (5-15%), water (10-15%), 2-propenoic acid, 2-methyl-, reaction products with 1,10-decanediol and phosphorous oxide (P2O5) (10-20%), copolymer of acrylic and itaconic acid (1-5%), dimethylamino ethyl methacrylate (<2%), camphorquinone (<2%), dimethylaminobenzoat(-4) (< 2%), 2,6-di-ter-butyl-P-cresol (<0.5%)	10-MDP	2.7

Table 2

Degree of conversion (DC), linear shrinkage (LS), shear bond strength (SBS), and failure modes (A: adhesive, C: cohesive, M: mixed) of all studied groups. Different superscript letters show significant differences between the groups within each measuring parameter.

Universal adhesive	**POSS-8 [wt%]**	**DC [%]**	**LS [%]**	**SBS [MPa]**	**Failures [%]**		
					A	**M**	**C**
Adhese Universal	0	75.5 ± 10.8^{ab}	6.8 ± 0.4^{ab}	21.4 ± 5.9^{a}	10	90	0
	10	68.2 ± 3.1^{ab}	6.8 ± 0.4^{ab}	20.3 ± 3.6^{ab}	0	100	0
CLEARFIL Universal Bond	0	79.9 ± 9.5^{a}	5.3 ± 0.5^{c}	15.0 ± 4.9^{bc}	20	80	0
	10	78.2 ± 4.5^{ab}	7.0 ± 0.2^{a}	13.2 ± 3.8^{c}	30	60	10
Futurabond U	0	62.9 ± 9.0^{ab}	7.0 ± 0.2^{a}	20.5 ± 4.7^{ab}	0	100	0
	10	60.0 ± 8.4^{b}	6.3 ± 0.3^{ab}	14.8 ± 4.9^{bc}	30	70	0
iBOND Universal	0	80.5 ± 13.4^{a}	4.0 ± 0.6^{d}	12.5± 2.5^{c}	90	10	0
	10	79.0 ± 2.1^{ab}	4.2 ± 0.2^{d}	10.9 ± 2.8^{c}	70	30	0
Scotchbond Universal	0	78.5 ± 1.3^{ab}	6.1 ± 0.3^{bc}	20.6 ± 4.5^{ab}	0	50	50
	10	66.9 ± 2.6^{ab}	6.6 ± 0.5^{ab}	20.7 ± 5.0^{ab}	10	90	0

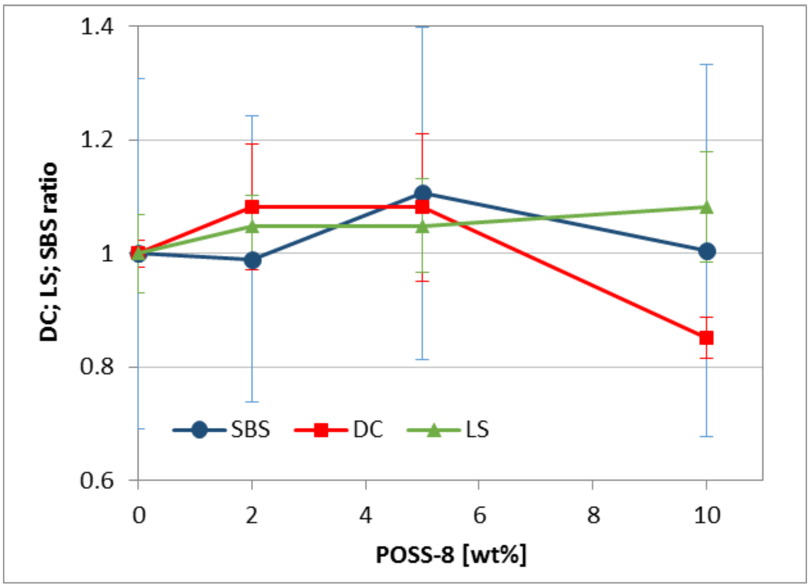

Fig. 1. Effect of POSS-8 concentration on the shear bond strength (SBS, blue circles), degree of conversion (DC, red squares), and linear shrinkage (LS, green triangles) of Scotchbond Universal. All values are normalized to those measured at 0% POSS-8 concentration.

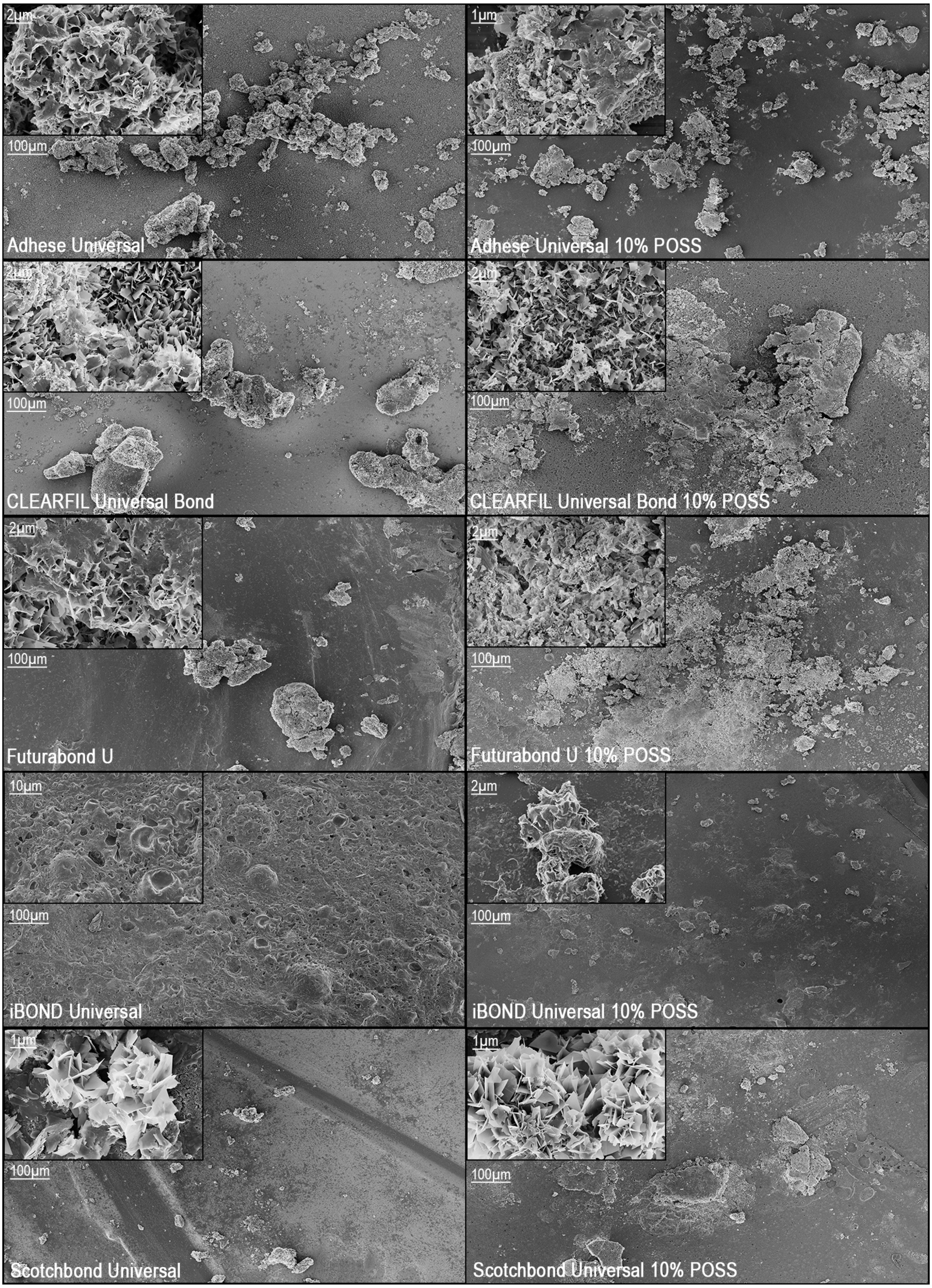

Fig. 2. Ca/P precipitates on the surfaces of pure adhesives (left) and adhesives filled with 10 wt% POSS-8 (right) after storage for 28 days in artificial saliva.

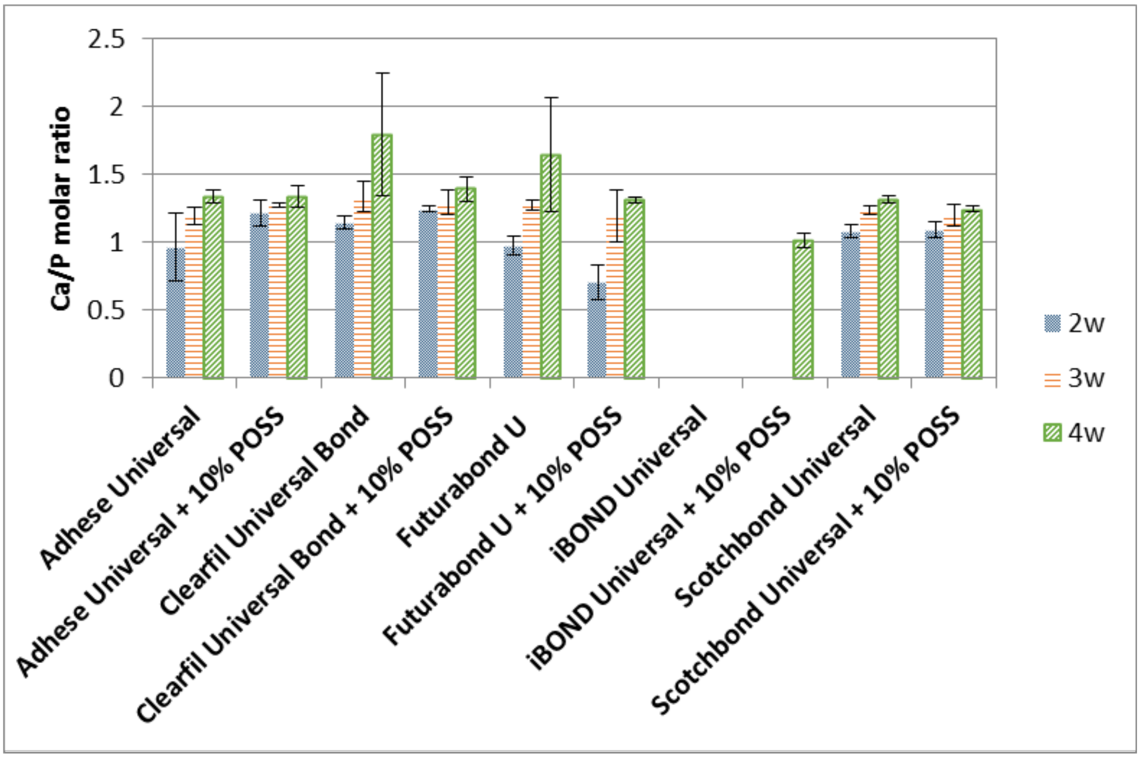

Fig. 3. EDX results of the molar Ca/P ratio for different times of immersion (2 weeks, 3 weeks, and 4 weeks) of all studied groups. The error indicators show standard deviations.