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The role of spacer carbon chain in acidic functional monomers on the physicochemical properties of self-etch dental adhesives

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ABSTRACT

Objectives: To evaluate the effects of acidic functional monomers with different hydrophilicity and spacer carbon chain length on the degree of conversion (DC), wettability (contact angle), water sorption (WS) and ultimate tensile strength (UTS) of experimental one-step self-etch adhesives (1-SEAs).

Methods: A series of standard resin blends was prepared with each formulation containing 15 mol% of each acidic monomer. The structural variations of the acidic monomers were MEP (spacer chain with 2 carbons), MDP (10-carbons), MDDP (12-carbons), MTEP (more hydrophilic polyether spacer) and CAP-P (intermediate hydrophilicity ester spacer). Dumbbell-shaped and disc specimens were prepared and tested for UTS and WS, respectively. DC was assessed by FTIR, while the wettability of each 1-SEA was evaluated on glass slides and flat dentine surfaces. Results were analysed with one-way ANOVA and Tukey's test ($p < 0.05$).

Results: The outcomes showed lower UTS for CAP-P, control blend and MEP than MTEP, MDDP and MDP ($p < 0.05$). The degree of conversion was statistically similar for all resins ($p = 0.122$). On dentine, the wettability was higher (lower contact angle) with the most hydrophilic monomer MTEP. Higher WS was attained using MTEP. Different lengths of the spacer chains did not result in different wettability and WS ($p > 0.05$).

Conclusion: At similar molar percentage, different acidic functional monomers induced similar degree of conversion and different UTS when included in a 1-SEA. However, the inclusion of highly hydrophilic monomer may increase the wettability on dentine and the WS.

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1. Introduction

Dentine bonding agents (DBAs) used in dentistry are the results of well-homogenised resin monomers and solvents (e.g. alcohols, acetone and/or water).[1,2] Most of the resin monomers used for the formulation of such DBAs present two terminal groups separated by a spacer chain.[1] One of the terminal groups constitute the polymerisable site of the monomer,[1,3] which is predominately represented by methacrylate or in some cases functionality. Dental restorative resin composites are mainly formulated using cross-linking di-methacrylates, whereas DBAs may be formulated using a variety of different monomers which can also contain specific functional groups.[1] Functional monomers accomplish specific roles such as dentine/enamel etching, phase separation stabilisation, improvement of the penetration of cross-linking monomers and antibacterial effects.[3] The carbon chain of a monomer may be composed by hydrophobic alkanes as in the 10-methacryloxy-decyl-dihydrogen-phosphate (MDP) or by relatively hydrophilic polyethylene glycols as in the tri-ethylene-glycol-di-methacrylate (TEGDMA).

Acidic functional monomers play an essential role on the bonding performance and on the physicochemical properties of self-etch adhesives, as they may be capable of conditioning enamel and/or dentine substrates. MDP may be considered nowadays as a gold-standard monomer[4–6] in the formulation of high-performance DBAs due to its effectiveness in chemical interaction and durability with hard dental tissues; the excellent performance of MDP is also attributed to its hydrophobic spacer carbon chain. Indeed, its chemical structure relies on a polymerisable methacrylate group separated from an acidic di-hydrogen-phosphate functionality by a relatively hydrophobic ten-carbon spacer chain.[1]

However, self-etching acidic functional monomers in DBAs should also fulfil some specific requirements such as high degree of polymerisation conversion, optimal wetting on the tooth surface, minimal water sorption and adequate mechanical strength.[3,7] The length and composition of the spacer chain between the polymerisable and the functional/acidic groups may influence these physicochemical properties.[3]

Unfortunately, there is little information regarding the effects of different spacer carbon chains on the physicochemical properties of self-etch adhesives. Furthermore, there is no investigation which specifically investigated the effect of different spacer carbon chains with standardised polymerisable methacrylate and acidic dihydrogen-phosphate groups similar to MDP. In other words, the role of the spacer carbon chain of MDP on the physicochemical properties of self-etch adhesives is not clear and would be of high interest to investigate.

This study aimed to assess the influence of length and hydrophilicity of the spacer linkage in acidic functional monomers on the degree of conversion, ultimate tensile strength (UTS), water sorption (WS) and wetting of experimental self-etch adhesives. Two null hypotheses were tested: (1) the monomers composed by more hydrophilic spacer chains display no differences on the selected physicochemical properties; (2) monomers composed by spacer chains with different lengths attain no differences on the selected physicochemical properties.

2. Materials and methods

2.1. Synthesis of functional monomers

The functional monomers were synthesised as described by Ogliari et al.[8] Briefly, 1,10-decanediol [$HO(CH_2)_{10}OH$], 1,12-dodecanediol [$HO(CH_2)_{12}OH$] and tetra ethylene glycol [$HO(CH_2CH_2O)_3CH_2CH_2OH$] (all from Sigma–Aldrich, St. Louis, USA) were esterified using methacrylic acid in order to attach the methacrylate group in one extremity of the molecule. Caprolactone 2-methacryloyloxy-ethyl ester [$HO(CH_2)_5CO_2CH_2CH_2O_2CC(CH_3)=CH_2$] was used after this process as it is available as the methacrylate-functionalised intermediate. The synthesis of 10-methacryloyloxy-decyl-dihydrogen phosphate (MDP), 12-methacryloyloxy-dodecyl-dihydrogen phosphate (MDDP), methacryloyloxy-tetraethylene-glycol-dihydrogen phosphate (MTEP) and methacryloyloxy-caprolactone dihydrogen phosphate (CAP-P), respectively, was accomplished by reaction of methacrylate-attached intermediates with phosphorus pentoxide and methylene chloride in an ice bath for 48 h. Subsequent to reactions and purification,[8] the isolated products were characterised using FTIR to confirm the synthesis of the MDP, MDDP, MTEP and CAP-P. The monomer referred to as HEMA-P, 2MP or 2-methacryloyloxy-ethyl-dihydrogen phosphate (MEP) was purchased from Esstech (Essington, PA, USA) and used without further purification. The chemical structures of the monomers evaluated in the present investigation are displayed in Fig. 1.

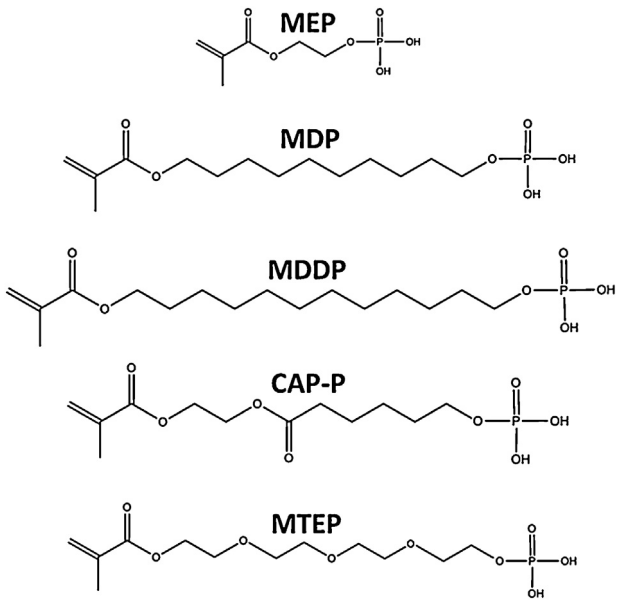

Fig. 1 – Chemical structures of the five acidic functional monomers evaluated. 10-Methacryloyloxy-decyl-dihydrogen phosphate (MDP), 12-methacryloyloxy-dodecyl-dihydrogen phosphate (MDDP), 2-methacryloyloxy-ethyl-dihydrogen phosphate (MEP), methacryloyloxy-tetraethylene-glycol-dihydrogen phosphate (MTEP) and methacryloyloxy-caprolactone dihydrogen phosphate (CAP-P).

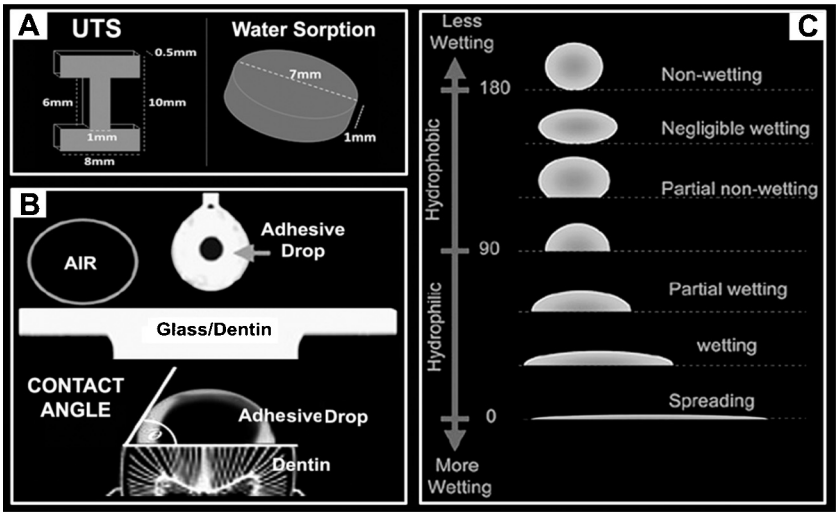

Fig. 2 – Schematic drawing of the specimens used for ultimate tensile strength (A, left) and water sorption (A, right). (B) The lateral view of the FTA software. (C) The sorts of wetting and spreading of the resins and water droplets onto the dentine surface.

2.2. *Formulation of experimental adhesives*

A base resin blend (control) was prepared by mixing 30 wt% urethane-dimethacrylate (UDMA), 10 wt% bisphenol-A-diglycidyl-methacrylate (BisGMA), 7 wt% triethylene-glycol-dimethacrylate (TEGDMA), 5 wt% hydroxyethyl-methacrylate (HEMA), 15 wt% deionised water, 30 wt% absolute ethanol and 3 wt% photoinitiation system. The photosensitive molecule used was camphoroquinone (CQ, 0.5 wt%). The ethyl 4-dimethylaminebenzoate (EDAB, 1 wt%) was the coinitiator and the onium salt[9,10] was the diphenyliodonium hexafluorophosphate (DPIHP, 1.5 wt%).

The acidic functional monomers were added in 15 mol% to the base resin blend to create a series of experimental one-step self-etch adhesives (1-SEA). Therefore, the number of functional monomer molecules was standardised rather than to standardise their weight percentage which would afford differences due to strikingly different molar masses.

2.3. *Degree of conversion*

The degree of conversion (DC) of the experimental 1-SEAs and base resin blend (control) was undertaken following a protocol previously described.[11] Briefly, a small drop (3 μL) of each adhesive resin (without solvent evaporation) was analysed using the Attenuated Total Reflection Fourier-Transform Infrared spectrophotometer (Nicolet 5700, Thermo Fisher Scientific, Loughborough, UK) equipped with an ATR crystal. The spectra were assessed before and subsequent to light-activation (40 s; 600 mW/cm^2, Optilux VLC, Demetron Kerr, Orange, USA). All spectra were obtained in a range of 1800–1500 cm^{-1}, with 12 scans at 4 cm^{-1} resolution in transmission mode and 2.8 mm/s mirror speed. The peak height was determined subsequent to baseline subtraction and normalisation process using the FTIR software. The residual unreacted carbon–carbon double bond content (% C═C) in the polymer film (thickness 800 ± 200 μm) was determined from the ratio of absorbance intensities of aliphatic C═C (peak at 1637 cm^{-1}) against an internal standard (aromatic carbon–carbon bond peak at 1608 cm^{-1}) before and 120 s after starting the photo-curing. Degree of conversion was determined by subtracting the C═C% from 100%. The analyses were performed in triplicate. Data were statistically analysed using one-way ANOVA ($p < 0.05$).

2.4. *Ultimate tensile strength*

Dumbbell-shaped specimens of the 1-SEAs containing the different functional monomers and the base resin blend (control) were created using silicone moulds ($n = 10$). The specimens had the dimensions of 0.5 mm thickness, 10 mm length, 1 mm constriction and 8 mm width[12] as shown in Fig. 2A. The UTS assessment was realised following a protocol similar to that of Loguercio et al.[13] The resins were poured into the moulds without solvent evaporation and gently air-blasted for 20 s. A polyester strip covered the resins and the light-activation using the Optilux VLC (Demetron) with 600 mW/cm^2 irradiance was realised for 40 s with the light tip in contact with strip (on the top of the specimen). The light tip diameter was 10 mm; thus, it covered the entire specimen allowing a single light-activation for each specimen. Thereafter, the specimens were carefully removed from the moulds and stored in a dark environment with 100% relative humidity for 24 h.

The specimens were fixed to a metal jig using cyanoacrylate glue (Super Bonder Gel, Loctite, Henkel Co., Rocky Hill, USA) and stressed to failure in a universal testing machine EZ-test (Shimadzu Co., Kyoto, Japan) with a 500-N load cell and a cross-head speed of 0.5 mm/min to measure the force to break the specimens. The exact cross-sectional area of each tested specimen was measured before testing using a digital calliper. The UTS data were transformed to MPa by dividing the tensile force at failure (N) by the cross-sectional area of the specimen (mm^2). The results were statistically analysed using one-way ANOVA and Tukey's test ($p < 0.05$).

2.5. Water sorption

The water sorption evaluation was undertaken strictly according to the method outlined in ISO specification 4049 except for specimen dimensions which were reduced in order to allow a single light-activation. The self-etch adhesives and the control resin blend had the solvents completely evaporated using a 3 bar air-stream from an oil-free triple syringe until a constant mass was achieved. Such procedure was undertaken only to follow ISO specification even possibly causing phase separation before polymerisation. The solvents were initially mixed to the blend in order to improve its homogeneity and to facilitate the mixture of monomers with different viscosities. Ten disc-shaped specimens with 7 mm diameter and 1 mm thickness (Fig. 2A) were prepared for each adhesive using standard silicone moulds. A polyester strip covered the resins poured into the moulds and the light-activation for 40 s using the halogen lamp (Optilux) was performed with the light tip in contact with the strip. The specimens were removed from the moulds and weighed on an analytical balance (JK-180: Chyo, Tokyo, Japan) every 5 min up to the stabilisation of the mass.

The specimens were subsequently stored in a silica-containing desiccator at 37 °C and weighed after 24 h intervals up to the stabilisation of the constant mass (M_1), (variation less than 0.2 mg in three weight measures). The volume (V) of the specimens (mm^3) was calculated by measuring the thickness and diameter with a digital calliper (±0.01 mm). The specimens were immersed in 1.5 mL of distilled water at 37 °C and weighed after 14 days storage (M_2). Subsequently, the specimens were dried in the desiccator and weighed daily until a final constant mass was obtained (M_3). Water sorption (WS) was calculated using the equation: $WS = M_2 - M_3/V$.[13] Data were statistically analysed by one-way ANOVA and Tukey's test at $\alpha = 5\%$.

2.6. Wettability/contact angle assessment

The wettability survey followed a similar protocol to that published by Grégoire et al.[14] The 1-SEAs' contact angle as a function of time was assessed using a FTA Drop shape instrument (FTA Instruments, Cambridge, UK). A highly hydrophobic resin blend (negative control) with 30 wt% BisGMA, 20 wt% TEGDMA, 50 wt% UDMA was prepared for this survey. The wettabilities of each 1-SEA, the negative control and the control blend were evaluated.

One small calibrated drop (3 μL) of each resin was carefully applied onto an untreated glass slide using a micropipette. After 3 s (initial accommodation), the transverse contact angle (direct lateral view)[14] of the droplet on the glass slide was measured by the FTA equipment during 120 s with 1 picture (analysis) per second (Fig. 2B and C). The right and left angles were measured and averaged by the FTA software which automatically calculates the tangent of the droplet shape and the mean contact angle. Five droplets per group ($n = 5$) were tested in different glass slides. The real-time analysis during 120 s allowed the detection of the spreading which was considered as the percentage reduction (%Red) from the maximum contact angle (Max) at time 0 s to the minimum contact angle (Min) at 120 s. The wettability analysis on the glass slides was performed in order to evaluate the contact angles on a relatively inert substrate which has no water content unlike dentine.

For the dentine wettability/contact angle measurements, ten extracted human molars were selected after extraction. The teeth were used after approval by the appropriate institutional ethics committee (protocol 127/2011). They were sectioned longitudinally with two parallel cuts (1.5 and 3 mm above the cemento-enamel junction) in the occlusal crowns. One slab per tooth was obtained with a flat medium dentine surface. In a pilot study, the slabs were wet-polished with 600-grit silicon carbide papers for 30 s in order to create a clinically relevant smear layer. The surface roughness was assayed by profilometry in order to ensure surfaces with standardised roughness. One droplet (3 μL) of distilled water was applied onto the smear-layer covered dentine surface and the contact angle measured as aforementioned. This procedure was realised in triplicate for each dentine slab. One-way ANOVA and Tukey's test ($p < 0.05$) were used in this pilot study to select the five dentine slabs with most similar wettability. The profilometry test was used adjunctively only to ensure similar roughness before the actual wettability survey, these results were not added to the investigation once they are not referring to the functional monomers or self-etch adhesives tested. The five selected slabs with similar water contact angles (hydrophilicity) and roughness were selected in order to standardise the dentine substrate. They obtained statistically similar wettability ($p = 0.874$) and roughness ($p = 0.143$).

The contact angle of each resin (five 1-SEAs, negative control and control blend) was assessed as described with the glass slides with resin drops of 3 μL onto the dentine slabs ($n = 5$). The dentine slabs were vigorously rinsed with acetone for 30 s in order to completely remove the resins and the dentine surfaces and re-abraded using a 600-grit silicon carbide paper to re-create the smear-layer. The results of adhesive wettability on the glass slide were statistically analysed with three separate one-way ANOVA (maximum angle at 0 s, minimum angle at 120 s and percentage reduction from the maximum to the minimum angles) and Tukey's test at $\alpha = 5\%$. Similarly, further three one-way ANOVA tests (Max, Min and %Red) and Tukey's tests ($p < 0.05$) were used to analyse the outcomes of adhesive wettability on the dentine surfaces.

3. Results

The outcomes (means and standard deviations) of the degree of conversion (DC) analysis are presented in Fig. 3A. The statistical results generated by the comparison of the experimental adhesives showed no difference ($p = 0.122$) in the DC. The mean values varied from the lowest (82.7%) degree of conversion using MEP to the highest (91.5%) DC using MDDP.

The UTS results are depicted in Fig. 3B. Important statistically significant differences ($p < 0.001$) were found between the different monomers tested in this study. The control blend obtained the lowest UTS (mean 6.13 MPa) whereas MEP (8.42 MPa) and CAP-P (8.09 MPa) presented intermediary outcomes. The adhesives containing MTEP (10.9 MPa), MDP (10.24 MPa) and MDDP (10.39 MPa) achieved the highest ultimate tensile strengths ($p < 0.01$).

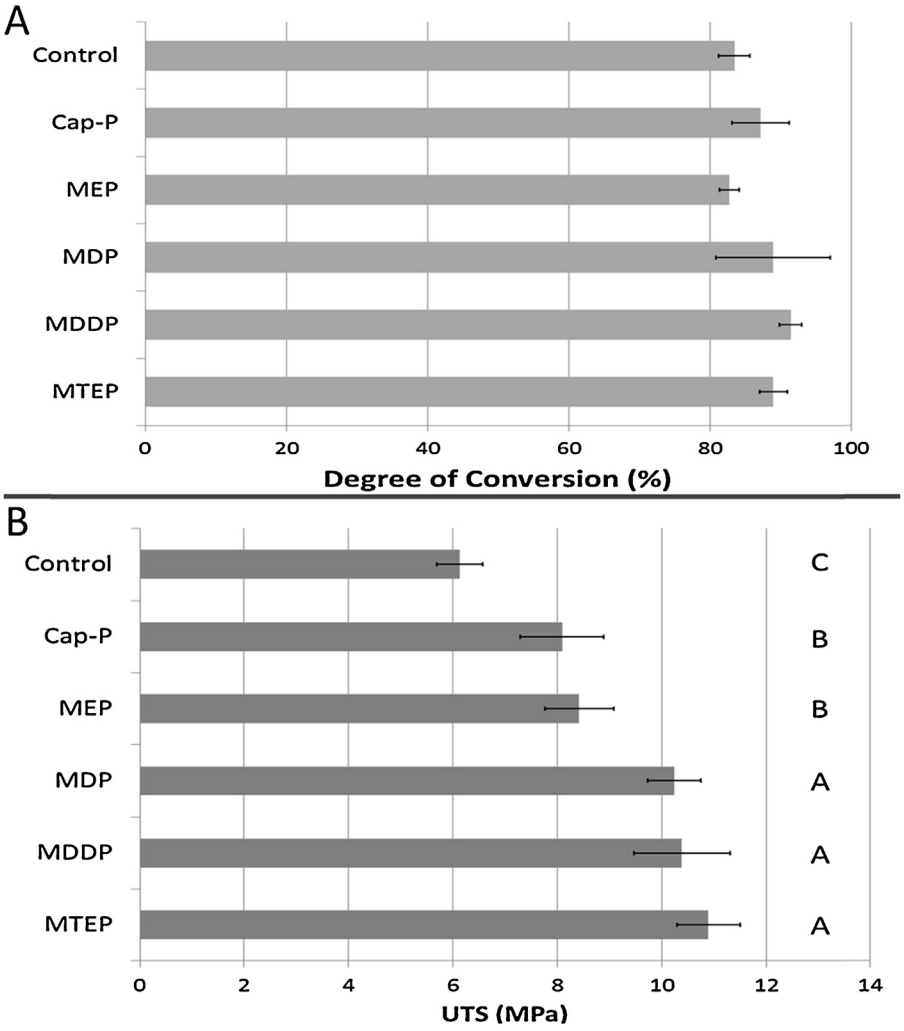

Fig. 3 – (A) Outcomes of the degree of conversion (%) analysis represented by means and standard deviations. No statistical difference was detected among all groups ($p = 0.122$). (B) Means and standard deviations obtained from the ultimate tensile strength survey. Different letters at right position represent statistically significant different UTS outcomes ($p < 0.05$).

Significant differences ($p < 0.001$) were also attained subsequent to the water sorption study (Fig. 4). The most hydrophilic functional monomer MTEP (mean 100.9 μg/mm^3) and the intermediate hydrophilic monomer CAP-P (mean 85.5 μg/mm^3) obtained higher water sorption than the other functional monomers and the control blend. The water sorption of CAP-P and MTEP were similar ($p = 0.093$). The results of Control (mean 62.7 μg/mm^3), MDP (mean 61.0 μg/mm^3), MEP (mean 67.1 μg/mm^3) and MDDP (mean 59.4 μg/mm^3) were statistically similar ($p > 0.05$).

Representative images of the droplets (contact angle measurement) on the glass slide or dentine surface are shown in Fig. 5A and B, respectively. The contact angle was notably higher on the dentine surface than the glass slide (Fig. 5) for the control blend, negative control and all functional monomers, except for the MTEP (mean 22.1° maximum angle on glass slide; mean 24.1° maximum angle on dentine). The wettability results for the glass slide and dentine are shown in Fig. 6A and B, respectively. The statistical analysis of contact angles (Max and Min) and spreading (%Red) on the glass slides showed highest maximum angle for the negative control (mean 37.6°) and the lowest with the 1-SEA containing CAP-P (mean 17.7°). The highest minimum angle after 120 s was obtained also with negative control (mean 33.2°) and the lowest with CAP-P (mean 12.0°) which was statistically similar to MTEP (mean14.3°, $p = 0.309$) and MDP (mean 14.5°, $p = 0.236$). The percentage reduction was similar between the control blend and all functional monomers ($p > 0.05$) but the negative control (11.6%) presented lower percentage reduction than all other resins ($p < 0.001$).

The statistical analysis performed on the results of dentine wettability showed higher maximum angle for the negative control (mean 49.0°) than all the other resins ($p < 0.001$). MTEP and CAP-P obtained the best initial dentine wettability (lower maximum contact angle). Similarly, the final (minimum) contact angle was higher for negative control (mean 42.7°) and lower for MTEP (mean 13.9°) which was similar to CAP-P (mean 17.2°, $p = 0.749$). The spreading (%Red) on dentine was statistically higher for the most hydrophilic functional monomer MTEP (mean 42.6%) than all other resins except

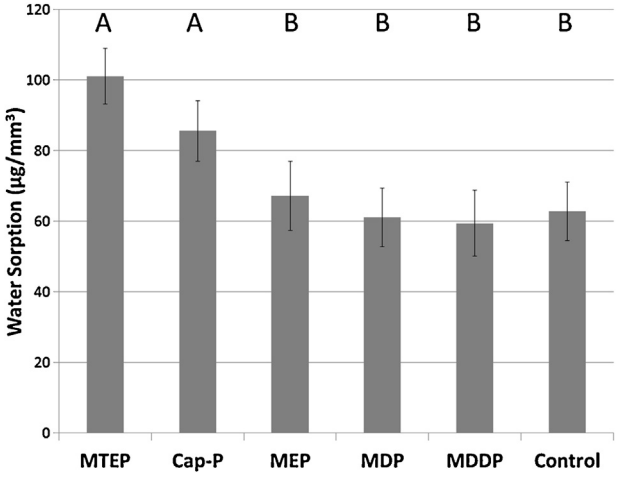

Fig. 4 – Graphic showing the outcomes (means and standard deviations) of water sorption examination. Same letters above the columns depict statistical similarity ($p > 0.05$).

CAP-P (mean 39.0%, $p = 0.778$). The percentage reduction of the negative control (mean 12.9%) was lower than all other resins ($p < 0.001$). No statistical differences were observed among MEP, MDP and MDDP ($p > 0.05$) on the maximum and minimum contact angles as well as on the spreading (percentage reduction) both onto the glass slide and the dentine.

4. Discussion

The present results demonstrated that the five functional monomers tested in this *in vitro* study induced remarkable differences in terms of ultimate tensile strength, water sorption and dentine wettability. Furthermore, this study also demonstrated that the degree of conversion was similar regardless the functional monomer included within the formulation of a standard one-step self-etch adhesive.

The first null hypotheses must be rejected as the UTS of CAP-P was lower than MDP's UTS, the water sorption of both MTEP and CAP-P were higher than that of MDP, and the glass slide and dentine wettabilities of MTEP and CAP-P presented

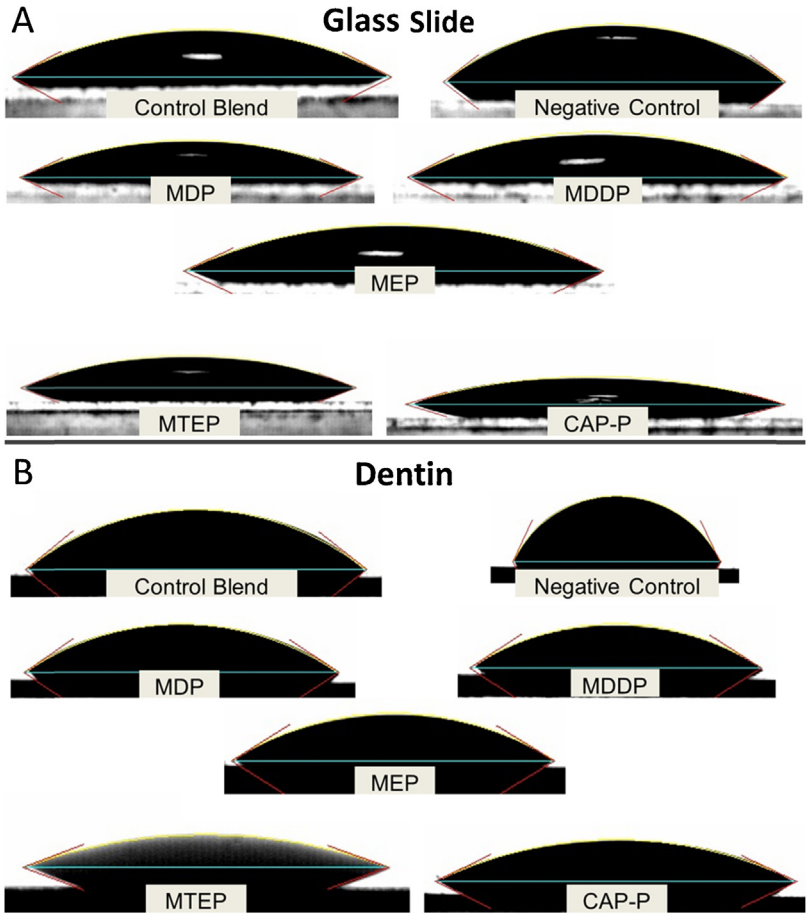

Fig. 5 – Images of resin drops obtained from the FTA software. All images are related to droplets with the maximum contact angles (time 0 s) on glass slide (A, upper board) and dentine (B, lower board). The left and right margins of the droplets in contact with the substrates may not be observed due to reflective effects of the equipment. Note the higher contact angle (lower wettability) on dentine than on the glass slide except for MTEP which obtained similar wettability on both substrates.

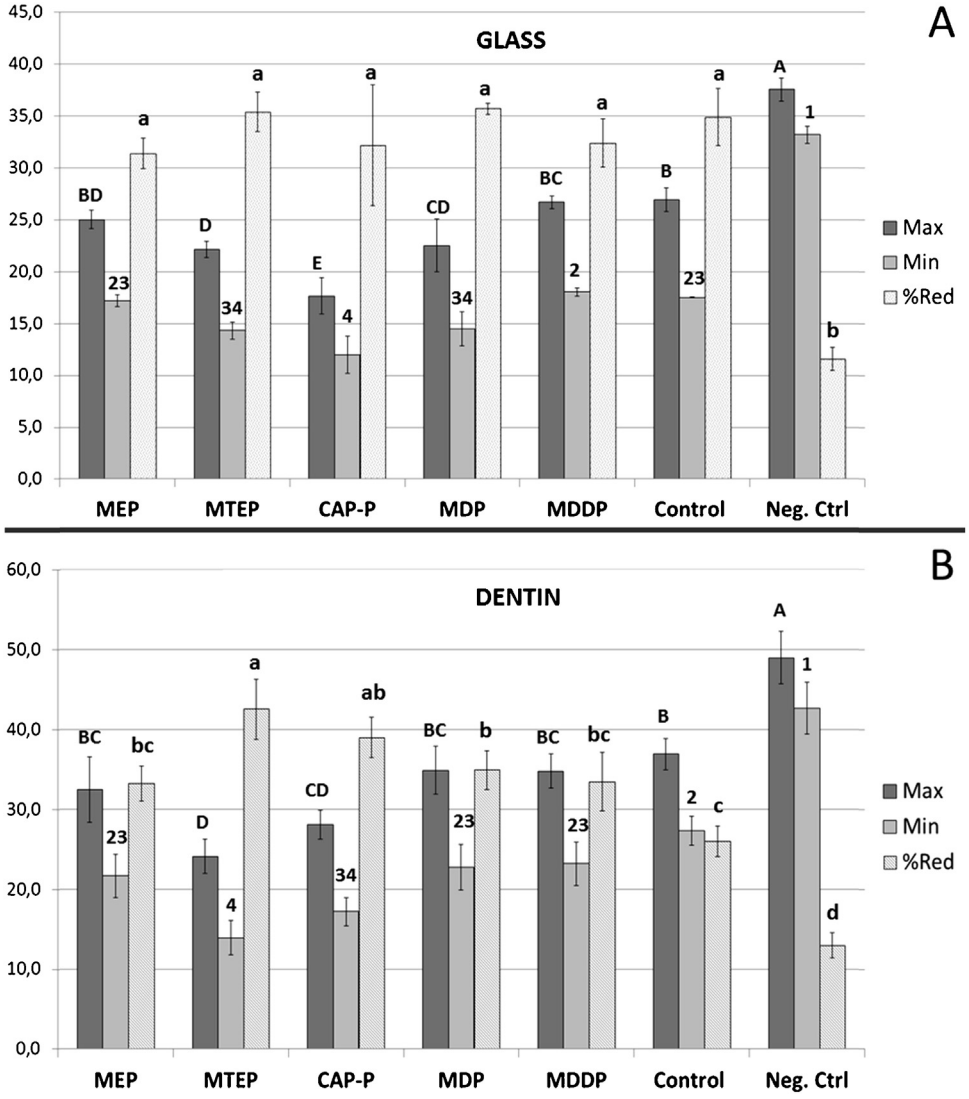

Fig. 6 – (A) Graphic depicting the results of the wettability assessment on glass slide. The means and standard deviations of maximum (Max), minimum (Min) contact angles and percentage reductions (%Red) are presented with the statistical outcomes above the columns. Different lower-case letters indicate statistical difference ($p < 0.05$) on the spreading (%Red). (B) Graphic showing the outcomes of the dentine wettability. Means and standard deviations of Max and Min angles as well as the spreading (%Red) are exhibited with the statistical results above the columns. Different capital letters indicate statistical difference ($p < 0.05$) on the maximum contact angles. Same numbers (i.e. 34 and 23) obtained statistically similar ($p > 0.05$) minimum contact angles and different lowercase letters indicate statistical difference ($p < 0.05$) on the percentage reduction.

significant differences compared to the 1-SEA containing MDP. As MEP showed lower UTS than MDP and the degree of conversion, water sorption, glass slide wettability and dentine wettability were similar for MEP, MDP and MDDP, the second null hypotheses must be partially rejected.

In the present investigation, the tested functional monomers were added to a standardised resin blend in the same mole percentage; in other words, the number of molecules of each functional monomer added to the resin blend was identical, and since all monomers are mono-methacrylates, the number of groups was the same in all the experimental DBAs formulated in this study. In fact, the differences in monomer structures would be expected to contrast differences in the limiting conversion as the short chain monomers could afford early vitrification with lower level of conversion. For instance, if MEP was homopolymerised, the polymer would certainly have higher glass transition temperature than MDP and the other longer chain monomers.

The degree of conversion of DBAs is generally related to the photo-initiation system[15] and the light-curing exposure times.[16] The light-curing unit (LED or halogen lamp) may also play an important role depending on the wavelengths and irradiance emitted during the procedure.[17,18] The solvent content and rate of evaporation also promote discrepancies in

the degree of conversion. However, the standardised amounts of both solvents added prevented such effects. The present degree of conversion outcomes showed that different spacer carbon chains in acidic functional monomers induced no effect on the monomer conversion when included in the same molar percentage. Nevertheless, most of the prior investigations did not use equivalent molar concentrations but rather they add the acidic functional monomers in similar weight percentage which could induce differences in the polymerisation and final conversion due to more polymerisable groups included with lower molecular weight monomers.

Despite the similarities in the degree of conversion, significant differences were observed in the ultimate tensile strength (UTS) of the tested DBAs. França et al.[19] showed similar UTS and different degree of conversion with pre-heated resin cements. Conversely, no correlation between the degree of conversion and UTS for self-etch and etch-and-rinse adhesives was also reported.[18] The control blend had higher ethanol and water percentage than the DBAs containing the experimental functional monomers; hereby, this might explain the lower UTS (Fig. 3B) of the control group even with similar degree of polymerisation (Fig. 3A). More non-evaporated solvent may have remained entrapped into the specimens compromising the mechanical strength due to reduced cross-link density and the softening effects even with not large differences in the solvent content. The findings of previous investigations[20,21] corroborate with the present outcomes showing that model adhesives may present similar degree of conversion and lower UTS when increasing the solvent content. A possible reason for increased UTS of MDP- and MDDP-based adhesives may be due to the Van der Waals forces between the long and apolar spacer carbon chains of these monomers. Similarly, the dipole–dipole interactions between two tetra-ethylene glycol chains[22] of MTEP may also have contributed with the higher UTS of this monomer. The short spacer chain of MEP and the ester group in the spacer chain of CAP-P may not favour such intermolecular interactions.

Water sorption survey showed similar outcomes for control blend, MEP, MDP and MDDP, whereas the more hydrophilic functional monomers (CAP-P and MTEP) obtained higher results. These outcomes are contrasting from the UTS results due to the different solvent evaporation in the water sorption (total) and UTS (partial) surveys. The most rational explanation for the higher water sorption attained with CAP-P and MTEP may be attributed to the higher hydrophilicity of their spacer carbon chains.[23] The length of the spacer carbon chain provided no difference in water sorption. The hypothetical addition of similar weight percentage of functional monomers instead of similar molar percentages would have included more hydrophilic phosphate groups for the lower molecular weight monomer MEP and triggered higher water sorption. However, with the present experimental design, this effect was avoided and only the hydrophilicity of the spacer carbon chain could affect the water sorption. It is important to take into account that the water sorption and the resin hydrophilicity are negatively correlated with the bonding durability.[23]

Another physicochemical property strongly correlated with the bonding performance is the wettability,[3,14] which is often measured by the contact angle.[14] Fig. 5 illustrates the initial wettability of the experimental self-etch adhesives, the control blend and the highly hydrophobic negative control blend. By comparing Fig. 5A and B, one may observe the noteworthy higher contact angle (lower wettability) of most of the resins applied onto dentine surfaces in comparison to the glass slide. However, the most hydrophilic monomer MTEP presented similar contact angles on both substrates (Fig. 6A and B). Therefore, one may conclude that the smear-layer covered dentine surface possess hydrophilic features[24] in comparison with the relatively inert glass slide substrate. It is well known that the polishing procedure performed on the dentine under running water may create the standardised smear-layer and promote water uptake within the smear debris yielding to a relatively high wet/hydrophilic surface.[24]

The use of a high hydrophobic negative control resin was advocated in order to assess the wettability of a solvent-free hydrophobic solution. This allows contrasting differences in terms of substrate hydrophilicity and spreading non-related to the solvent evaporation. It is possible to note that the spreading ability of the negative control resin (Fig. 6A and B) on the glass slide (mean 11.6% reduction) was very near to that on the dentine surfaces (mean 12.9% reduction). In addition, the spreading of the negative control was very much lower than the spreading of solvated resins whilst the maximum and minimum contact angle of the negative control was higher than those of control blend and 1-SEAs in both substrates. This might be explained by the notable difference in the viscosity as the negative control resin is far more viscous than the other resins due to absence of solvent and low-viscosity hydrophilic monomers such as HEMA.

On the glass slides, the maximum and minimum contact angle varied following the viscosity of the functional monomers used within the formulation of the standardised blend. The hydrophilicity of the spacer carbon chain exhibited significant changes in the contact angles whereas few differences were observed with spacer carbon chains with different length (Fig. 6A). However, the spreading represented by the percentage reduction was similar for all the tested monomers and control blend due likely to the similar solvent content and solvent evaporation rate.

Onto the smear-layer covered dentine, the maximum and minimum contact angle of MTEP (most hydrophilic monomer) was lower than the other tested monomers, while, the spreading ability of MTEP was higher (Fig. 6B). The unique functional monomer statistically similar (Fig. 6B) to MTEP in the three parameters was CAP-P (intermediary hydrophilic spacer chain) which presented outcomes that fall between the hydrophilic and hydrophobic monomers. Indeed, the hydrophilicity of the smear-layer covered dentine contributed to the better outcomes of MTEP. Furthermore, the higher contact angles onto the dentine surface with the hydrophobic monomers in comparison with the glass slide show the hydrophilic nature of the smear-layer covered dentine surface.[24] This may have jeopardised the wettability of more hydrophobic monomers. Therefore, the contact angles and spreading are proportional to the interaction between the adhesive and the dentine substrate.[14] Furthermore, the surface energy of substrates and the superficial tension of the experimental adhesives are strictly correlated with the wettability and spreading.[14] Indeed, the more hydrophilic

spacer chains may reduce the surface tension of experimental adhesives, improving their wetting ability.

The different length of spacer carbon chains plays no apparent role on the dentine wettability (Fig. 6B) due to the similar hydrophilicity of the functional monomers and respective DBAs (Fig. 4). The smear-layer produced by different burs (i.e. cross-cut carbides, finishing carbides and diamond rotary burs) present different surface roughness which may influence the dentine wettability.[25] The smear-layer plays an important role in the self-etch adhesive dentistry[26] and in the dentine wettability of 1-SEAs.[27] Therefore, the caries removal, excavation procedures and cavity finishing should be regarded as important factors that may affect the dentine wettability.[25]

Overall, important findings were observed in the present investigation regarding the physicochemical behaviour of self-etch adhesives related to the spacer carbon chain of acidic functional monomers. The monomers with hydrophilic spacer chains presented better wetting but also increased water sorption. Indeed, the wetting behaviour of self-etch adhesives may afford different interactions with the dental hard tissues. Several commercial adhesives employ more hydrophilic functional monomers in order to improve the dentine wettability; on the other hand, they may induce more water uptake and accelerate the degradation processes within the resin–dentine interface. Therefore, the higher the hydrophilicity of the adhesive resins generally the lower the bonding durability.[13,23] Indeed, different composition and length of the spacer group can additionally affect the pH and steric ability of the acidic functionality to interact with the dentine and any remaining mineral. This might change the formation and stability of the monomer-calcium salts. Further experiments are already in progress in order to evaluate the microtensile bond strength, micropermeability and chemical interaction of these monomers.

5. Conclusion

By the present results, one may conclude that the different spacer chains of acidic functional monomers do not afford different degrees of polymerisation conversion when the monomers are included in same molar percentage. Nevertheless, both the length and hydrophilicity of the spacer chain provide different mechanical properties whereas only more hydrophilic spacer carbon chain induces more water sorption and better dentine wettability. More hydrophilic functional monomers (CAP-P and MTEP) might be recommended considering only initial physicochemical properties (dentine wettability) and potential initial bond strength. Nevertheless, regarding the durability of the resin blend and potential bonding stability (low water sorption), more hydrophobic functional monomers (MDDP and MDP) are more adequate to avoid the effects of hydrolytic degradation.

Authors' contributions

Dr. V.P. Feitosa is responsible for the idea of the investigation, wrote the manuscript, synthesised part of the functional monomers and performed the UTS experiment. Prof. S. Sauro contributed substantially for the experimental design and performed the degree of conversion analysis. Prof. F.A. Ogliari synthesised and purified the acidic functional monomers. Prof. J.W. Stansbury proofread the manuscript and contributed significantly for the Discussion section. Prof. G. Carpenter performed the wettability survey. Prof. T.F. Watson proofread the manuscript and performed the English review. Prof. M.A. Sinhoreti realised all statistical analyses. Dr. A.B. Correr performed the water sorption experiment and proofread the manuscript.

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