Role of the functional monomer 10-methacryloyloxydecyl dihydrogen phosphate in dentin bond durability of universal adhesives in etch-&-rinse mode

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This study aimed to determine the role of the 10-methacryloyloxydecyl dihydrogen phosphate (MDP) in dentin bond durability of universal adhesive in etch-&-rinse mode through bond strength tests after different degradation conditions. This study used the MDP-containing universal adhesive, Clearfil Universal Bond Quick (CU), and an experimental adhesive (NM) made with the same ingredients as CU, excluding MDP. Shear bond strength (SBS) to dentin were obtained in etch-&-rinse mode with or without MDP. CU in self-etch mode was used as a comparison. The groups were divided into three types: 1) subjected to thermal cycling; 2) subjected to long-term water storage; and 3) stored in water for 24 h, as a baseline. The discrepancies in the mean SBS of the CU and NM groups become prominent with prolonged degradation periods. This study indicates that the MDP in universal adhesive might play a key role in enhancing dentin bond quality even when etch-&-rinse mode is used.

Keywords: Dentin bond durability, MDP, Universal adhesive, Etch-&-rise mode

INTRODUCTION

Functional monomers in self-etch (SE) adhesives can serve various purposes, such as wetting, demineralization, and chemical interaction with tooth substances. In particular, creating chemical bonds between mineralized tissues and functional monomers is important to secure immediate bonding and enhance bonding durability. Various types of functional monomers have been employed in different conventional two- or single-step SE adhesive systems, with phosphoric acid ester, carboxylic acid, and alcohol functional monomers. Among these functional monomers, 10-methacryloyloxydecyl dihydrogen phosphate (MDP) is one of the most promising for chemical bonding to hydroxyapatite (HAp). MDP can create a calcium salt within a clinically realistic time and this chemical bonding shows stability even after ultrasonication. Furthermore, the formed calcium salts are hydrolytically stable, leading to long-term bond durability through self-assembled nano-layers at the MDP/HAp interface. The benefits of MDP have already been demonstrated bonding to enamel. Tsuchiya et al. investigated the effect of MDP on the enamel bond durability of single-step SE adhesives by integrating fatigue testing and long-term water storage (WS). They concluded that although similar bond strength values were obtained for adhesives both with and without MDP in etch- &-rinse (ER) mode at 24 h WS, the MDP-containing adhesive showed significantly higher enamel bond strength values than the MDP-free adhesive after long-term WS. In addition, some investigations have shown that MDP-containing adhesives can form an acid-base resistant zone, which plays a key role in the prevention of secondary caries, the sealing of restoration margins, and the promotion of restoration durability.

MDP is a common component of most universal adhesives, which can be classified as SE adhesive systems, due to their being one-bottle adhesives and having similar compositions to those of single-step SE adhesives. However, universal adhesives have unique characteristics in that they can be used in ER, selective etch, or SE mode. Although new types of universal adhesives with different emphases, for instance, reducing adhesive application times, using a chemical cure adhesive, or including metal or ceramic primer, have been constantly introduced to the clinic, many of these contain MDP in combination with other types of functional monomers. Several laboratory studies have found that the enamel and dentin bond performance of universal adhesives is similar to or better than those of the conventional single-step SE adhesives, thanks to optimizing adhesive composition and adopting MDP. There are important open questions concerning the dentin bond durability of universal adhesives, as several studies found that the dentin bond performance of some universal adhesives did not decline even when phosphoric acid pre-etching was performed on dentin, unlike conventional single-step SE adhesives. It is not clear why etching mode does not appear to influence dentin bond performance. In general, considering the chemical bonding between functional monomers and HAp, dissolving the smear layer and the HAp on the dentin surface through phosphoric acid etching may reduce chemical interactions. In addition, remnant collagen fibrils in ER mode that are incompletely encapsulated by resin monomers may be vulnerable and thus more easily undergo structural deterioration due to hydrolytic degradation. Thus, given the known mechanism of action of MDP, we might expect it to have little influence in ER mode. That is, the improved performance of universal adhesives in ER...
mode to dentin may be due to their other components. Therefore, it is important to investigate the dentin bond mechanism of universal adhesives in ER mode and the role of functional monomers when phosphoric acid pre-etching is performed on dentin.

Based on these considerations, the aim of this study was to determine the dentin bond durability of two universal adhesives in ER mode, with and without MDP, under simulated in vitro degradation. Two different simulated degradation methods, thermal cycling (5,000, 10,000, 20,000, or 30,000 thermal cycles) and long-term WS (3 months, 6 months, or 1 year), were applied before shear bond strength (SBS) testing. The null hypotheses to be tested were: (1) the functional monomer MDP would not affect the dentin bond strength after in vitro degradation; and (2) phosphoric acid pre-etching would not affect the dentin bonding durability of the MDP-containing adhesive.

MATERIALS AND METHODS

Study materials
The materials used in this study are shown in Table 1. The universal adhesive used was Clearfil Universal Bond Quick (CU; Kuraray Noritake Dental, Tokyo, Japan). An experimental adhesive made with the same ingredients as CU but excluding MDP (NM; supplied by Kuraray Noritake Dental) was also used. The phosphoric acid pre-etching agent employed was Ultra-Etch (Ultradent Products, South Jordan, UT, USA). The resin composite used for bonding to dentin was Clearfil AP-X (Kuraray Noritake Dental). A halogen-quartz-tungsten visible light curing unit (Optilux 501, sds Kerr, Danbury, CT, USA) was used, and the light irradiance (average 600 mW/cm²) of the curing unit was checked during the course of the experiment.

Specimen preparation
Specimen preparation was performed in accordance with ISO 29022. Extracted mandibular bovine incisors stored frozen for up to 2 weeks were used as substitutes for human teeth. Approximately two-thirds of the apical root structure of each tooth was removed with a diamond-impregnated disk in a low-speed saw (IsoMet 1000, Precision Sectioning Saw, Buehler, Lake Bluff, IL, USA). The labial surfaces were ground with wet 240-grit silicon carbide (SiC) paper (Buehler) to create a flat dentin surface. Each tooth was then mounted in self-curing acrylic resin (Tray Resin II, Shofu, Kyoto, Japan) to expose the flattened area. The dentin bonding surfaces were polished using a water coolant and 320-grit SiC paper (Fuji Star Type DDC, Sankyo Rikagaku, Saitama, Japan).

Table 1  Materials used in this study

| Code  | Adhesive (Lot No.)                  | Main Components                                                                 | pH          | Manufacturer                      |
|-------|------------------------------------|---------------------------------------------------------------------------------|-------------|-----------------------------------|
| CU    | Clearfil Universal Bond Quick       | bis-GMA, MDP, HEMA, hydrophilic amide monomer, colloidal silica, ethanol, water, NaF, CQ, silane coupling agent, chemical polymerization accelerator | 2.3 (0.03)* | Kuraray Noritake Dental, Tokyo, Japan |
|       | (4483016)                          |                                                                                  |             |                                   |
| NM    | Experimental Adhesive (451192)      | bis-GMA, HEMA, hydrophilic amide monomer, colloidal silica, ethanol, water, NaF, CQ, silane coupling agent, chemical polymerization accelerator | 7.5 (0.04)* | Kuraray Noritake Dental          |
|       |                                    |                                                                                  |             |                                   |
|       | Pre-Etching Agent Ultra-Etch (G017) | 35% phosphoric acid                                                             |             | Ultradent Products, South Jordan, UT, USA |
|       |                                    |                                                                                  |             |                                   |
|       | Resin composite Clearfil AP-X       | bis-GMA, TEGDMA, silanated barium glass filler, silanated silica filler, silanated colloidal silica, catalysts, accelerators, CQ, pigments, others |             | Kuraray Noritake Dental          |
|       | (9B0035)                           | Filler load: 83.5 wt%                                                            |             |                                   |

MDP: 10-methacryloyloxydecyl dihydrogen phosphate, HEMA: 2-hydroxyethyl methacrylate, bis-GMA: 2,2-bis[4-(2-hydroxy-3-methacryloxy-propoxy) phenyl] propane, TEGDMA: triethylene glycol dimethacrylate, CQ: dl-camphorquinone.

*pH measurement was conducted five times for each adhesive using a compact pH meter (LAQUAtwin-pH-33, Horiba, Tokyo, Japan)
curing unit.

The total of 360 bonded specimens were subjected to thermal cycling (TC group) or storage in distilled water at 37°C for a long period (WS group). For the TC groups, bonded assemblies were stored in distilled water at 37°C for 24 h and were then treated with 5,000; 10,000; 20,000; or 30,000 thermal cycles between 5 and 55°C, with a dwell time of 30 s. For WS groups, bonded specimens were stored in distilled water at 37°C for 3 months, 6 months, or 1 year before the SBS tests. The storage water, which did not contain any anti-bacterial agents and was maintained at 37°C, was changed every week during the course of the experiment. Baseline specimens were stored in distilled water at 37°C for 24 h before the SBS tests (baseline group).

The SBS was measured using an Ultradent Bonding Assembly (Ultradent Products) as described by ISO 290222. The bonded specimens were loaded to failure at 1.0 mm/min using a universal testing machine (Type 5500R, Instron, Canton, MA, USA). The SBS values (in MPa) were calculated from the peak load at failure divided by the bonded surface area. After testing, the bonded tooth surfaces and resin composite cylinders were observed under an optical microscope (SZH-131, Olympus, Tokyo, Japan) at a magnification of ×10 to determine the failure mode. Based on the percentage of substrate area (adhesive–resin composite–tooth) observed on the de-bonded cylinders and bonded tooth sites, the types of bond failure were recorded as: 1) adhesive failure, 2) cohesive failure in composite, 3) cohesive failure in dentin, or 4) mixed failure–partially adhesive and partially cohesive.

Scanning electron microscopy (SEM) observations
Representative resin/dentin interfaces and de-bonded fracture sites were observed by field emission SEM (ERA-8800FE, Elionix, Tokyo, Japan). For ultrastructural morphological observations of the restorative-dentin interfaces to determine the penetration of the adhesives, bonded specimens stored in 37°C distilled water for 24 h were embedded in epoxy resin (Epon 812, Nissin EM, Tokyo, Japan) and then longitudinally sectioned using a low-speed saw (IsoMet 1000). The sectioned surfaces were polished to a high gloss with a sequence of SiC papers (400, 800, 1500, 2000, and 4000 grit, Buehler) followed by diamond pastes of 6, 3, 1, and 0.25 μm particle size (DP-Paste, Struers, Ballerup, Denmark). The resin/dentin interface specimens were dehydrated in ascending grades of tert-butyl alcohol (50% for 2 h, 75% for 2 h, 95% for 2 h, and 100% for 24 h), and then transferred to a critical-point dryer (Model ID-3, Elionix) for 1 h. The resin/dentin interfaces of the specimens were subjected to argon-ion beam etching (EIS-200ER, Elionix) for 40 s using an ion beam (accelerating voltage 1.0 kV, ion current density 0.4 mA/cm²) directed perpendicular to the polished surfaces. Finally, all SEM specimens were coated with a thin film of gold in a vacuum evaporator (Quick Coater, Type SC-701, Sanyu Electron, Tokyo, Japan). De-bonded samples were not treated in any way prior to coating with a gold. Observations were performed at an operating voltage of 10 kV.

Statistical analysis
Before analysis of variance (ANOVA), the data for each group were tested for homogeneity of variance (Bartlett’s test) and normal distribution (Kolmogorov-Smirnov test). To analyze the effect of factors on bond strength, a two-way ANOVA and subsequent Tukey’s honestly significant difference (HSD) test (α=0.05) were used separately for analysis of the full data sets for TC and WS groups (Factors were as follows: 1) with or without MDP adhesive and 2) storage period), excluding the data for CU in SE mode. One-way ANOVA followed by Tukey’s HSD test (α=0.05) was used to make comparisons within subsets of the data, as described later. The statistical analysis was performed using the statistical software SigmaPlot (ver. 11.0, SPSS, Chicago, IL, USA).

RESULTS
Comparison of SBS after thermal cycle treatment
Results for the SBS under TC conditions are shown in Table 3. The two-way ANOVA revealed that the factor of MDP significantly influenced dentin SBS values (p=0.001), but the number of thermal cycles did not influence them significantly (p=0.07). The interaction between factors was not significant (p=0.998). Defining the baseline dentin SBS value for each tested adhesive as 100%, we found that the SBS values under TC ranged from 92.4 to 99.6% in the CU in SE mode group, from 85.5 to 90.8% in the CU in ER mode group, and from 25.7 to 74.3% in the NM in ER mode group (Table 3). When

Table 2  Application protocol for pre-etching and self-etching adhesives

| Method code | Pre-etching protocol | Adhesive application protocol |
|-------------|----------------------|------------------------------|
| ER          | Dentin surface was phosphoric acid conditioned for 15 s. Conditioned surface was rinsed with water for 15 s (three-way dental syringe) and air-dried. | Adhesive was applied to the air-dried tooth surface for 10 s, followed by medium air pressure for 5 s. Adhesive was light-cured for 10 s. |
| CU and NM   |                      |                              |
Table 4 Influence of long-term water storage on SBS (MPa, SD)

|                  | Baseline | 5,000 TC | 10,000 TC | 20,000 TC | 30,000 TC |
|------------------|----------|----------|-----------|-----------|-----------|
| CU-SE            | 33.0 (3.8)\textsuperscript{aA} [100\%] | 30.5 (3.5)\textsuperscript{aA} [92.4\%] | 32.9 (6.1)\textsuperscript{aA} [99.6\%] | 30.9 (6.1)\textsuperscript{aA} [93.6\%] | 31.2 (5.1)\textsuperscript{aA} [94.5\%] |
| CU-ER            | 32.5 (5.4)\textsuperscript{aA} [100\%] | 29.5 (3.5)\textsuperscript{aA} [90.8\%] | 28.9 (4.9)\textsuperscript{aA} [88.9\%] | 29.0 (4.8)\textsuperscript{aA} [89.2\%] | 27.8 (4.2)\textsuperscript{aA} [85.5\%] |
| NM-ER            | 10.1 (1.5)\textsuperscript{aA} [100\%] | 7.5 (2.8)\textsuperscript{AB} [74.3\%] | 6.4 (1.5)\textsuperscript{AB} [63.4\%] | 5.2 (2.9)\textsuperscript{BC} [51.5\%] | 2.6 (1.9)\textsuperscript{C} [25.7\%] |

Same lower case letter in vertical column indicates no difference at a 5\% significance level.

Same upper case letter in horizontal rows indicates no difference at a 5\% significance level.

$n=15$; SBS: shear bond strength, SD: standard deviation, CU: Clearfil Universal Bond Quick, SE: self-etching mode, ER: etch & rinse mode, NM: MDP-free experimental adhesive based on CU

Table 5 Failure mode analysis of de-bonded specimens

|                  | TC       | WS       |
|------------------|----------|----------|
|                  | 24-h     | 5,000 TC | 10,000 TC | 20,000 TC | 30,000 TC | 3-month | 6-month | 1-year |
| CU-SE            | [80/0/10/10] | [80/0/10/10] | [70/0/10/20] | [80/0/10/10] | [80/0/0/20] | [80/0/20/0] | [80/0/10/10] | [90/0/0/10] |
| CU-ER            | [70/0/20/10] | [80/0/10/10] | [70/0/10/20] | [80/0/10/10] | [80/0/10/10] | [70/0/20/10] | [80/0/10/10] | [90/0/0/10] |
| NM-ER            | [100/0/0/0] | [100/0/0/0] | [100/0/0/0] | [100/0/0/0] | [100/0/0/0] | [100/0/0/0] | [100/0/0/0] | [100/0/0/0] |

Failure mode is presented as the percentages of each failure mode (adhesive failure/cohesive failure in resin composite/cohesive failure in dentin/mixed failure).

Comparing CU in SE mode and ER mode, although CU in ER mode groups showed lower mean SBS than in SE mode groups at all TC periods, there were no significant differences between them. Comparing CU in ER mode and NM in ER mode, CU showed significantly higher SBS values than NM, regardless of the TC period. CU did not show any significant differences in mean SBS between treatment groups, for either ER or SE modes. On the other hand, NM showed decreased SBS values with increased TC periods, while most of the TC groups showed significantly lower SBS values than the baseline groups.

Comparison of SBS after WS treatment

The results for the SBS under WS conditions are shown in Table 4. The two-way ANOVA revealed that both factors MDP ($p<0.001$) and WS periods ($p<0.001$) significantly influenced dentin SBS values. However, interaction between factors was not significant ($p=0.61$). Defining the baseline dentin SBS value for each tested adhesive as 100\%, we found that the SBS values under WS ranged from 110.9 to 113.0\% in the CU in SE mode group, from 90.5 to 96.3\% in the CU in ER mode group, and from 59.4 to 84.2\% in the NM in ER mode group (Table 4). Comparing CU in ER mode and NM in ER mode, CU had significantly higher SBS than NM, just as for the TC condition. CU did not show any significant
differences in SBS between WS periods, regardless of the etching mode. However, CU in SE mode had significantly higher SBS than in ER mode, for all the WS periods. NM tended towards lower SBS with increased WS periods. The 1-year NM groups had significantly lower SBS values than the baseline groups.

**Failure mode analysis of de-bonded specimens**
A comparison of the frequencies of different failure modes between CU groups and NM groups under different degradation conditions is shown in Table 5. For CU groups, although 10 to 20% of cohesive failure in dentin or mixed failure was observed, no significant differences were detected in failure modes between degradation conditions or periods. For NM groups, all the failure modes were adhesive failures.

**SEM observations**
Representative SEM images of restorative/dentin interfaces are shown in Figs. 1 to 3. MDP containing CU showed excellent adaptation between dentin substrate and adhesive, regardless of etching mode (Figs. 1 and 2). However, the morphological appearance of CU was notably different between SE and ER modes. For the SE mode, the smear layer remained and formed a hybrid smear layer in which the resin monomers penetrated beyond the smear layer into intact dentin surface (Fig. 1). In contrast, a hybrid layer of 1 to 2 μm and formed resin tags were found in ER mode (Fig. 2). NM showed a similar appearance to CU in ER mode (Fig. 3).

Representative SEM observations of de-bonded specimens of resins after SBS testing are shown in Fig. 4. For the baseline groups (Figs. 4A–C), CU in SE and ER modes predominantly showed adhesive failure at lower magnification (Figs. 4Aa and Ba). The higher magnification images show similar failure features, with evidence of resin tags, cracks, and cleavages (Figs. 4Ab and Bb). Longer resin tags can be seen for CU in the ER mode than the SE mode. NM in ER had longer and clearer resin tags than the other treated groups (Fig. 4Cb). For the WS treatments (Fig. 4D–F), although CU groups (Figs. 4D and F) showed similar failure features to the baseline CU groups regardless of the etching mode, NM groups (Figs. 4F) showed different morphological appearances when compared to each group of the baseline. In particular, NM at 1-year WS showed flatter detached surfaces and fewer resin tags than the baseline of NM. SEM images of the TC treatment groups were similar to those of the WS groups.
**DISCUSSION**

For universal adhesives, it may be advantageous to select the optimal etching mode in accordance with cavity configuration, size, depth, and ratio of enamel and dentin in the cavity. However, little information is available about the role of functional monomers in dentin bond durability of universal adhesives in ER mode. Therefore, we used an experimental adhesive made with the same ingredients as the commercial universal adhesive, but without MDP. Our results show that the MDP-containing adhesive CU had significantly higher SBS than the experimental MDP-free adhesive NM, regardless of the etching mode or degradation method. When comparing the CU groups and NM group at 24 h, the CU groups showed bond strengths almost three times higher than those of NM group, while the differences in SBS values between the CU groups and NM group increased with increased degradation period for both conditions tested, under different TC and different WS treatments. These results support our hypothesis that the functional monomer MDP does indeed affect dentin bond quality in ER mode after in vitro degradation, and allow us to reject the first null hypothesis stated earlier.

In order to evaluate deterioration status or to predict the longevity of resin composite restorations, clinical studies observing restored teeth are clearly the best method. However, it is difficult to standardize clinical studies for many reasons. Therefore, it may be beneficial to establish simulated testing of the oral environment that can obtain rapid outcomes and provide a standardized way to determine bond durability among materials, thus helping to predict expected clinical effectiveness. However, there are limits to how well the complex degradation process of resin composite restorations can be simulated in vitro. Therefore, observing multiple different degradation methods and integrating the outcomes may be helpful in grasping the deterioration process that occurs under intra-oral conditions.

Although there were no significant differences in SBS between CU in SE and ER modes at any thermal cycle periods, significant differences in SBS were observed between the two etching modes at all the WS periods. The difference between these degradation conditions might be caused by their different degradation mechanisms and progression rates. In the thermal cycle treatment, degradation is accelerated by differences in thermal expansion of the materials composing the bonded interfaces. The discrepancies in thermal expansion between tooth substrate and adhesive can lead to cracks and percolations at bonded interfaces due to mechanical stress. On the other hand, degradation under the WS treatment is accelerated not only by hydrolysis of hydrophilic resin components, but also by host-derived proteases with collagenolytic activity.

CU in SE mode did not show any significant differences in SBS values between treatment periods in either treatment condition. However, when looking at each test condition of SBS as a percentage, CU in SE mode under TC ranged from 92.4 to 99.6%, and under WS from 110.9 to 113.0%. The reasons for increased SBS in CU with SE mode in WS may be related to post-polymerization strengthening of the adhesive in the early phase and retarded degradation. Comparing the thermal cycle and WS treatments, SBS at 5,000 TC was similar to that at 6 months WS, while the SBS at 10,000 TC was similar to that at 1 year WS. This is consistent with previous reports. However, the different trends in CU in ER mode were found, that is, the ranges of SBS reductions were higher for the ER mode than the SE.
mode, regardless of the degradation method. Hence, it can be inferred that although the functional monomer MDP played an important role in enhancing dentin bond quality in both SE and ER mode, dissolving the smear layer and the HAp in the dentin surface through pre-etching might be disadvantageous for early phase enhancement of chemical bonding and long-term dentin bond durability.

In this study, the commercially available universal adhesive CU was employed as a positive control. In order to assess the role of MDP, the adhesive was applied to the dentin surface for 10 s, followed by a medium air blow for 5 s. This universal adhesive can be used without any wait time, requiring just air-blowing on the adhesive-applied surface. A previous study showed that while reduced application time had a negative impact on enamel bond strength in some universal adhesives, CU did not show any significant differences in enamel and dentin SBS values under all the experimental conditions. However, universal adhesives induce larger changes in surface free energy with prolonged application time, suggesting increased chemical interactions. For NM in our study (without MDP), a demineralization effect in SE mode would not be expected given its pH of 7.5, while no chemical bonding was expected due to the lack of a functional monomer. However, NM showed measurable SBS values under all the experimental conditions. NM contains HEMA and a newly developed amide monomer. Both of these compounds are highly hydrophilic and mobile as monomers, and the amide monomer can polymerize to form a hydrophobic polymer. Thus, it might be reasonable to suppose that the monomers penetrate deeply into the dentin structure and polymerize there, giving rise to strong micro-mechanical interlocking. This hypothesis was supported by the SEM images of the de-bonded surfaces, which appeared to show many resin tags that had partially pulled out of the dentinal tubules in the testing process. Though the adhesive did not have an ability to chemically bond to dentin, the resin monomers employed in this adhesive could penetrate to deeper areas of dentin.

In contrast to CU, the SBS of NM decreased significantly with longer degradation, regardless of the degradation method. Although CU in ER mode tended to have lower SBS with longer periods of degradation, there were no significant differences observed for either treatment. However, we did observe significant differences between etching modes for CU in the WS treatments, suggesting that the second null hypothesis (that phosphoric acid pre-etching would not affect the dentin bonding durability of the MDP-containing adhesive) should be rejected, despite the lack of significant differences from or between the baselines. From the SEM observations of de-bonded specimens, although the baseline NM in ER showed longer and clearer resin tags than the other treated groups (Fig. 4Cb), flatter detached surfaces and fewer resin tags than the baseline were observed at 1 year of WS (Fig. 4Fb). On the other hand, CU in ER mode at 1 year WS showed a similar failure appearance to that at 24 h baseline CU in ER, with evidence of resin tags, cracks, and cleavages. The difference in SEM images between CU and NM in ER may also indicate the chemical bonding ability of MDP. NM had sufficient ability to penetrate into demineralized dentin without creating a chemical bond to HAp, resulting in simple failure patterns. Therefore, in the case of CU in ER mode, it can be speculated that MDP and the newly developed amide monomer might have the ability to carry sufficient resin monomers, and that the functional monomer MDP penetrated deeply into demineralized dentin and could form chemical bonds with HAp.

A previous study explained the role of MDP in enhancing bond durability by observing that the MDP-treated surface becomes hydrophobic because the methacrylate group of MDP is directed away from the surface, while the long carbon spacer group can create neighboring MDP molecules to align parallel to each other as they form the water-insoluble MDP-Ca salt. Although the degradation process is different for TC and WS, in both cases hydrolytic degradation occurs in the vicinity of the interface between dentin and adhesive. Therefore, the water-resistant hydrophobic layer formed by MDP might contribute to bond durability. Our study indicates that MDP plays an important role in enhancing the dentin bond durability of universal adhesive in ER mode. In particular, even when dentin surface is etched by phosphoric acid, the MDP containing adhesive CU could sustain bond strength regardless of the degradation method. Although the details of the mechanism of MDP to dentin bonding in ER mode are unclear, it can be speculated that a certain interaction might occur between exposed collagen fibrils and MDP, in addition to effective penetration of the tested adhesive into deeper, etched regions of dentin. On reconsidering the dentin bond durability of universal adhesives in ER mode, optimized adhesive components that focus on monomer penetration ability, sufficient polymerization of the resin matrix, functional monomer quality, and solvent and water evaporation may have resulted in an improvement over single-step SE adhesives.

CONCLUSION

Within the limitations of this in vitro study, although the ranges of SBS reductions were higher for CU in ER mode than CU in SE mode, the MDP-containing adhesive we tested showed significantly higher dentin bond strength than an experimental MDP-free adhesive, irrespective of the degradation method. This suggests that the functional monomer MDP in universal adhesives might play an important role in enhancing the dentin bond quality even when ER mode is used.

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