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Effect of the demineralisation efficacy of MDP utilized on the bonding performance of MDP-based all-in-one adhesives

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ABSTRACT

Objectives: The amounts of calcium salt of 10-methacryloyloxydecyl dihydrogen phosphate (MDP-Ca salt) and dicalcium phosphate dihydride (DCPD) with an amorphous phase produced by the demineralisation of enamel and dentin were determined using commercial MDP-based 2-hydroxyethyl methacrylate (HEMA)-containing and HEMA-free all-in-one adhesives. The effect of the amount of MDP-Ca salt produced on bonding performance to enamel and dentin was then characterized.

Methods: Three types of commercial HEMA-containing adhesives (Scotchbond Universal Adhesive, Clearfil Tri-S Bond ND, Clearfil Tri-S Bond ND Quick), a commercial HEMA-free adhesive (G-Bond Plus) and an experimental HEMA-free adhesive were used. The reactant residues of each adhesive were prepared after interacting with enamel and dentin samples for 60 s. The amounts of MDP-Ca salt and amorphous DCPD produced were determined using a phosphorous-31 nuclear magnetic resonance technique. Enamel and dentin bond strengths were measured for each adhesive, with and without thermocycling.

Results: The amounts of MDP-Ca salt and amorphous DCPD formed after interacting with enamel and dentin differed among the five adhesives and were independent of their pH values. Enamel showed a strong positive-correlation of the bond strength of the all-in-one adhesives to the amount of MDP-Ca salt produced, however, the dentin showed a weak negative-correlation.

Conclusion: The HEMA-free all-in-one adhesives showed a greater efficacy to demineralise the enamel and dentin than the HEMA-containing all-in-one adhesives. The dentin showed a different effect of the amount of MDP-Ca salt produced on the bonding performance compared with enamel.

Clinical significance: The enamel bond strength of MDP-based all-in-one adhesives strongly contributes to the demineralisation efficacy by the incorporation of MDP, in contrast to the dentin bond strength. However, the efficacy of MDP-based all-in-one adhesives to demineralise the enamel and dentin is not directly related to the pH value of the MDP-based all-in-one adhesive.

1. Introduction

To simplify bonding procedures and reduce technique sensitivity, two- and one-step self-etch adhesive systems have been developed [1]. These adhesives are widely accepted by dentists since they show excellent enamel and dentin bonding performance [2–4]. This is because the acidic monomer utilized in these adhesives plays a key role in ensuring consistent high quality bonding performance [5–14] and interfacial morphology [15,16]. In addition, the water contained in these adhesive systems acts as an ionizing medium for the acidic group in the acidic monomer.

Previously, self-etch adhesives have been classified into four categories based on the initial pH value: “strong” (pH < 1), “intermediately strong” (pH ≈ 1.5), “mild” (pH ≈ 2) and “ultra-mild”

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(pH ≥ 2.5) adhesive [17,18]. It is accepted that the pH value of the self-etch adhesive strongly affects the ability to solubilize the smear layer and the depth of demineralisation of the underlying dentin [19,20], as well as the actual interaction depth of the self-etch adhesive on the dentin [17].

However, Poggio et al. [21] have reported that the pH value of one-step self-etch (all-in-one) adhesives does not significantly influence shear bond strengths to enamel and dentin surfaces. This may be due to the pH value being strongly affected by the composition and concentration of the 10-methacryloyloxydecyl dihydrogen phosphate (MDP)-based all-in-one adhesive [22].

On the other hand, Nishiyama and coworkers [11–14] quantitatively evaluated the efficacies of MDP incorporated into experimental MDP-based 2-hydroxyethyl methacrylate (HEMA)-free all-in-one adhesives used to demineralise enamel and dentin by varying the amount of MDP or water using nuclear magnetic resonance (NMR) techniques. NMR is used to analyse enamel and dentin reactant residues of the adhesives, which provides information about the type and amount of molecular species of calcium salts of MDP (MDP-Ca salts) that have been produced during the application of the MDP-based all-in-one adhesives to enamel and dentin. Such information is very useful to understand the mechanism by which MDP-based all-in-one adhesives demineralise the enamel and dentin and the mechanism by which MDP-based all-in-one adhesive adhere to enamel and dentin [11,23].

In this study, we characterized the effect of the amount of MDP-Ca salt produced during demineralisation of the smear layer and underlying enamel and dentin on the bonding performance of MDP-based all-in-one adhesives. The null hypotheses tested were that: 1) the efficacy of the HEMA-containing all-in-one adhesives to demineralise the enamel or dentin surface differs from that of HEMA-free all-in-one adhesives, and 2) the amount of MDP-Ca salt produced by the demineralisation of the enamel or dentin has no effect on bonding performance to enamel and dentin.

2. Materials and methods

2.1. Materials and chemicals

In this study, we used three types of commercial MDP-based HEMA-containing all-in-one adhesives, Scotchbond Universal Adhesive (SUA), Clearfil Tri-S Bond ND (ND), Clearfil Tri-S Bond ND Quick (ND Quick), and a commercial MDP-based HEMA-free, 4-methacryloyloxyethyl trimellitic acid (4-MET)-containing all-in-one adhesive, G-Bond Plus (GBP) (Table 1). The pH values of each adhesive are listed in Table 1 [24–26]. Furthermore, a previously formulated MDP-based HEMA-free all-in-one adhesive was used as a positive control for GBP, so as to objectively evaluate the demineralisation capacity of commercial MDP-based all-in-one adhesives.

Other chemical reagents were purchased from Wako Pure Chemical Industries (Osaka, Japan) unless otherwise indicated.

2.2. Preparation of an experimental MDP-based HEMA-free all-in-one adhesive

The components and compositions of the experimental MDP-based HEMA-free all-in-one adhesive (DA) are described in the previous studies [11,12,14]. In brief, 6.0 g MDP (purity = 97.0%) was mixed with the base monomer, consisting of 10.0 g urethane dimethacrylate (Negamikogyo, Ishikawa, Japan), 10.0 g triethylene glycol dimethacrylate (Shin-Nakamura Chemical Co, Wakayama, Japan) and 9.4 g 4-methacryloyloxyethyl trimellitic anhydride (purity = 97.0%). One mass% of camphorquinone and dimethylamino benzoic acid ethyl ester, and 2000 ppm of hydroquinone monomethyl ether were then dissolved in the mixed monomer as a photo-initiator, an accelerator and an inhibitor, respectively. Colloidal silica (4.26 g, R-972, Nihon Aerosil, Tokyo, Japan) was added to 35.4 g of the mixed monomer.

The DA was then prepared by diluting 39.66 g of the filled resin with 80.5 g acetone aqueous solution consisting of 11.2 g water and 69.3 g acetone. The quantities of MDP and water included in DA were 49.9 mg/g and 93.2 mg/g, respectively.

2.3. Preparation of enamel and dentin reactant residues of commercial and experimental adhesives

In accordance with previous studies [11–14], the enamel and dentin reactant residues of each adhesive were prepared. In brief, 0.200 *g* of enamel or dentin particles that had been prepared by cutting bovine crown teeth (2–2.5 years old) using a high-speed handpiece with a diamond bur (Bur No.105R, Shofu, Kyoto, Japan) were suspended in each adhesive (1.000 *g*), and the suspensions were then mixed for 1 min at 20 °C. After the reaction, 30 mL of ethanol was added to each adhesive-enamel or -dentin suspension to stop further reaction of the MDP with the enamel or dentin. Each suspension was centrifuged at 3500 rpm for 20 min, and the supernatant was decanted. Thereafter, the enamel and dentin reactant residues of each adhesive were rinsed 3 times with 30 mL of ethanol to remove residual MDP and other monomer components included in each adhesive, and were then dried at 20 °C. The enamel and dentin reactant residues were prepared 3 times for each adhesive.

2.4. Observation of ^{31}P NMR spectra

The ^{31}P NMR spectra of enamel and dentin reactant residues of each adhesive were observed using an NMR spectrometer (EX-270, JEOL, Tokyo, Japan). The contact, repetition and accumulation times were 2000 μsec, 20.05 s and 120 times respectively. Ammonium dihydrogen phosphate was used as an external reference and ^{31}P NMR chemical shifts are expressed in ppm.

The curve-fitting analyses of the corresponding ^{31}P NMR spectra were performed by assuming that DCPD with an amorphous phase was also produced along with several types of MDP-Ca salts as described previously [12–14]. To curve-fit the respective ^{31}P NMR spectrum, we used OriginPro® 9.1 Data Analysis and Graphing Software (OriginLab Co., Northampton, MA, USA). The intensity of each simulated peak used for the curve-fitting analyses of enamel and dentin reactant residues was then determined for each adhesive.

2.5. Determination of amounts of MDP-Ca salt and DCPD with an amorphous phase produced by demineralisation of enamel or dentin

The peak intensity of MDP that had been consumed yielding several types of MDP-Ca salts was determined by totaling the relative intensity ratios of the simulated peaks for each MDP-Ca salt in each experimental group. Based on a previous study [13], the amount of MDP consumed was then determined by assuming that the peak intensity for MDP-Ca salts was 2.641 when 116.1 mg MDP placed in 1.0000 g of DA had completely yielded several types of MDP-Ca salts. The amount of MDP that had been consumed yielding several types of MDP-Ca salts was then determined as the amount of MDP-Ca salt produced.

On the other hand, the peak intensity of DCPD with an amorphous phase was determined as the relative intensity ratio of the simulated peak for DCPD. The amount of amorphous DCPD produced was calculated by assuming that the peak intensity for MDP-Ca salts was 2.641 when 116.1 mg MDP placed in 1.0000 g of the DA had completely yielded a mono-calcium salt of the MDP monomer as described previously [13,14]. The following equation was used for this calculation: 116.1 mg × the peak intensity for amorphous DCPD determined in each experimental group / 2.641 × 172.09 (molecular weight of DCPD) / 378.25 (molecular weight of mono-calcium salt of the MDP monomer).