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Demineralization capacity of commercial 10-methacryloyloxydecyl dihydrogen phosphate-based all-in-one adhesive

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ABSTRACT

Objective. We determined the amounts of calcium salt of 10-methacryloyloxydecyl dihydrogen phosphate (MDP-Ca salt) and dicalcium phosphate dihydride (DCPD) with an amorphous phase developed during the application of commercial MDP-based all-in-one adhesives to enamel and dentin. This is because the demineralization by MDP and following calcium salt formation of MDP may be limited by an ionic bond formation of MDP to hydroxyapatite in the enamel and dentin and following intermediary layer formation of MDP, since MDP forms a chemically-stable adsorption layer.

Methods. Scotchbond Universal Adhesive, Clearfil Tri–S Bond ND, Clearfil Tri–S Bond ND Quick, G–Bond Plus and our designed MDP-based all-in-one adhesive were used. Enamel and dentin reactant residues of each adhesive were prepared by varying the adhesive application periods: 1, 30 and 60 min, and were analyzed using phosphorous-31 nuclear magnetic resonance and X-ray diffraction.

Results. Increasing the adhesive application period to enamel and dentin led to the increased amount of MDP-Ca salt in contrast to amorphous DCPD. In the dentin, each adhesive showed a saturated value on the production amount of MDP-Ca salt when the adhesive was applied more than 30 min. In contrast, in the enamel, each adhesive showed an intermediate value on the saturated production amount of MDP-Ca salt that the respective adhesive exhibited. This is due to MDP employed demineralizes the enamel and dentin until MDP was completely consumed yielding MDP-Ca salt.

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Conclusion. Commercial MDP-based all-in-one adhesives would not form an intermediary layer of MDP on hydroxyapatite throughout their application period to enamel and dentin.
Clinical relevance. The rate of MDP-Ca salt produced by the demineralization of enamel and dentin depends on the components that constitute commercial adhesive more strongly than on the concentrations of MDP and water in the respective adhesive. This is because HEMA-containing adhesive shows a slower production rate of MDP-Ca salt than HEMA-free adhesive in the enamel and dentin samples.

1. Introduction

Studies have been performed to understand the adhesion mechanism of two-step self-etch adhesives to the enamel and dentin through acidic monomers, such as 10-methacryloyloxydecyl dihydrogen phosphate (MDP), 2-methacryloyloxyethyl phenyl hydrogen phosphate (Phenyl-P) or 4-methacryloyloxyethyl trimellitic acid (4-MET), [1–12].

Van Meerbeek et al. [1–4,6,8,9] have focused on an interaction of an acidic monomer with calcium of hydroxyapatite constituted the enamel and dentin structure. The MDP ionically bonded to calcium of hydroxyapatite is accompanied by the formation of an intermediary layer of MDP, since MDP forms an ionic bond to calcium of hydroxyapatite more stable than Phenyl-P and 4-MET. They have concluded that the intermediary layer formation of MDP on the MDP ionically bonded to hydroxyapatite in the enamel and dentin and its thickness directly contributes higher bonding performance of MDP-based two-step self-etch adhesive.

On the other hand, Nishiyama et al. [13–24] have so far quantitatively evaluated the efficacies of acidic monomers employed in two- and one-step self-etch adhesives to demineralize the enamel and dentin using carbon-13 (^{13}C) and phosphorous-31 (^{31}P) nuclear magnetic resonance (NMR) techniques. This is because the NMR analysis results give us information on the type of the molecular species of calcium salts of acidic monomer and their amounts, which have been produced during the application period of self-etch adhesives to the enamel and dentin. They concluded that the NMR analysis result is very useful to understand the mechanism by which self-etch adhesive demineralizes the enamel and dentin surfaces and the mechanism by which self-etch adhesive adheres to the enamel and dentin. This is due to the amount of calcium salts of acidic monomer being a useful indicator for predicting not only the degree of demineralization of enamel and dentin by the adhesive but also the enamel and dentin bonding performance of the adhesive.

In this study, to gain an insight on whether commercial MDP-based 2-hydroxyethyle methacrylate (HEMA)-containing and HEMA-free one-step self-etch (all-in-one) adhesive forms an intermediary layer of MDP on hydroxyapatite in the enamel and dentin or not, the amount of MDP-Ca salt and DCPD with an amorphous phase produced were determined by varying the application period of commercial MDP-based all-in-one adhesives to the enamel and dentin surfaces. This is because the ionic bond formation of MDP to hydroxyapatite in the enamel and dentin structure and/or following intermediary layer formation of MDP may limit further demineralization of the enamel and dentin by MDP and thus production of MDP-Ca salt, since MDP forms a chemically-stable adsorption layer.

The null hypotheses were that (1) commercial HEMA-containing and HEMA-free all-in-one adhesives form an intermediary layer of MDP on hydroxyapatite during their application periods to the enamel and dentin, and (2) commercial HEMA-containing all-in-one adhesive shows faster production rate of MDP-Ca salt produced during their application period to the enamel and dentin sample than commercial HEMA-free all-in-one adhesives.

2. Materials and methods

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) and Clearfil Tri–S Bond ND Quick (ND Quick), and a commercial MDP-based HEMA-free, thus 4-methacryloyloxyethyl trimellitic acid (4-MET)-containing all-in-one adhesive, G–Bond Plus (GBP) as shown in Supplemental Table 1. Here, we used a previously deigned MDP-based HEMA-free all-in-one adhesive for verifying the analysis results on the MDP and water concentrations included in commercial adhesives. This is because we have known the components and their compositions that constitute our designed adhesive.

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

2.1. *Preparation of deigned MDP-based HEMA-free all-in-one adhesive*

The components and compositions of deigned MDP-based HEMA-free all-in-one adhesive (DA) were described in previous studies [19–21,23,24]. In brief, 6.0 g MDP (purity = 97.0%) was mixed with the base monomer, which consists 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, respectively. Colloidal silica (4.26 g, R-972, Nihon Aerosil, Tokyo, Japan) was then added to the 35.4 g mixed monomer. The DA was then prepared by diluting 39.66 g of the filled resin with

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