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Chemical interaction of glycero-phosphate dimethacrylate (GPDM) with hydroxyapatite and dentin

Kumiko Yoshihara [a,*], Noriyuki Nagaoka [b], Satoshi Hayakawa [c], Takumi Okihara [d], Yasuhiro Yoshida [e], Bart Van Meerbeek [f]

[a] Center for Innovative Clinical Medicine, Okayama University Hospital, 2-5-1 Shikata-cho, Kita-ku, Okayama 700-8558, Japan

[b] Advanced Research Center for Oral and Craniofacial Sciences, Okayama University Dental School, 2-5-1 Shikata-cho, Kita-ku, Okayama 700-8558, Japan

[c] Biomaterials Laboratory, Graduate School of Interdisciplinary Science and Engineering in Health Systems, Okayama University, 3-1-1, Tsushimanaka, Kita-ku, Okayama 700-8530, Japan

[d] Division of Applied Chemistry, Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushima-Naka, Kita-ku, Okayama 700-8530, Japan

[e] Department of Biomaterials and Bioengineering, Faculty of Dental Medicine, Hokkaido University, Kita 13, Nishi 7, Kita-ku, Sapporo, Hokkaido, 060-8586 Japan

[f] KU Leuven (University of Leuven), Department of Oral Health Research, BIOMAT, & University Hospitals Leuven, Dentistry, Kapucijnenvoer 7, Block A — Box 7001, BE-3000 Leuven, Belgium

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ABSTRACT

Objectives. Although the functional monomer glycero-phosphate dimethacrylate (GPDM) has since long been used in several dental adhesives and more recently in self-adhesive composite cements and restoratives, its mechanism of chemical adhesion to hydroxyapatite (HAp) is still unknown. We therefore investigated the chemical interaction of GPDM with HAp using diverse chemical analyzers and ultra-structurally characterized the interface of a GPDM-based primer formulation with dentin.

Methods. HAp particles were added to a GPDM solution for various periods, upon which they were thoroughly washed with ethanol and water prior to being air-dried. As control, 10-methacryloyloxydecyl dihydrogen phosphate (MDP) was used. The molecular interaction of GPDM with HAp was analyzed using X-ray diffraction (XRD) and solid-state nuclear magnetic resonance (NMR) spectroscopy. Crystal formation upon application of GPDM onto dentin was analyzed using thin-film XRD (TF-XRD). Its hydrophobicity was measured using contact-angle measurement. The interaction of GPDM with dentin was characterized using transmission electron microscopy (TEM).

Results. XRD revealed the deposition of dicalcium phosphate dihydrate (DCPD: $CaHPO_4 \cdot 2H_2O$) on HAp after 24 h. NMR confirmed the adsorption of GPDM onto HAp. However, GPDM was easily removed after washing with water, unlike MDP that remained adhered to HAp. Dentin treated with GPDM appeared more hydrophilic compared to dentin treated with MDP.

* *Corresponding author.*
E-mail addresses: k-yoshi@md.okayama-u.ac.jp (K. Yoshihara), nagaoka@okayama-u.ac.jp (N. Nagaoka), satoshi@okayama-u.ac.jp (S. Hayakawa), okihara@cc.okayama-u.ac.jp (T. Okihara), yasuhiro@den.hokudai.ac.jp (Y. Yoshida), bart.vanmeerbeek@kuleuven.be (B. Van Meerbeek).

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TEM disclosed exposed collagen in the hybrid layer produced by the GPDM-based primer formulation. Significance: Although GPDM adsorbed to HAp, it did not form a stable calcium salt. The bond between GPDM and HAp was weak, unlike the strong bond formed by MDP to HAp. Due to its high hydrophilicity, GPDM might be an adequate monomer for an etch-and-rinse adhesive, but appears less appropriate for a 'mild' self-etch adhesive that besides micro-retention ionically interacts with HAp, or for a self-adhesive restorative material.

1. Introduction

Current adhesive restorative protocols involve either an 'etch-and-rinse' or 'self-etch' approach to bond resin-based composite (RBC) to tooth tissue [1]. The newest generation of 'universal' or 'multi-mode' adhesives provide the dentist an adhesive that can be used following both the etch-and-rinse or self-etch mode, or even by combining selective enamel etching with a self-etch adhesive approach [2].

Self-etch and the newer universal adhesives contain acidic (bi-)functional monomers [2,3]. Many different functional monomers have been synthesized and utilized in dental adhesives [4,5]. In general, such a functional monomer presents with a threefold molecular structure, consisting of an acidic functional group separated from a (metha)crylate group by a spacer group [3–5]. The polymerizable (meth)acrylate group will co-polymerize with other monomers to be build in the resin matrix of the adhesive and adjacent RBC. The spacer group, when sufficiently long, effectively separates the polymerizable (meth)acrylate group from the acidic functional group and provides some hydrophobicity to the functional monomer. Potential acidic functional groups are phosphate, phosphonate or carboxyl groups [3–5], which will either demineralize HAp or chemically bond to HAp, as defined by the adhesion-decalcification (AD) concept [6,7]. According to this AD concept, acidic molecules adhere first to HAp by electrostatic interaction and either remain bonded through stable monomer-Ca salt formation following the 'adhesion route' or readily de-bond when no stable monomer-Ca salt is produced, resulting in abundant demineralization following the 'decalcification route' [6,7]. Previous studies demonstrated that the AD route followed by the functional monomer depends on its molecular structure with the acidic functional group inducing different etching abilities [3]. Following the decalcification route, a several micrometers thick hybrid layer is formed, in which substantial collagen is deprived from its surrounding HAp; the produced calcium phosphates are embedded within the exposed collagen fibril network. Otherwise, the adhesion route will typically result in a submicron HAp-rich hybrid layer without much collagen exposure. Besides the actual acidic functional group, the spacer group's chemical structure and its length co-determine the chemical interaction potential with HAp and dentin [8,9]. Among many functional monomers, 10-methacryloyloxydecyl dihydrogen phosphate or MDP (Fig. 1) is today considered one of the most effective monomers to strongly bind to HAp, thereby forming stable MDP-Ca salts [10,11]. Moreover, MDP was chemically and ultra-structurally demonstrated to self-assemble in nano-layers [11–14]. The

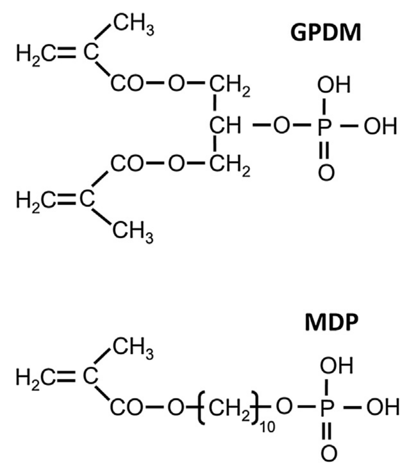

Fig. 1 – Molecular structure of the functional monomers GPDM and MDP.

chemically stable bond between MDP and HAp was shown to contribute to bond durability, this based on laboratory [15,16] as well as clinical research [17], in particular on the long term for the MDP-based so-called gold-standard (2-step) self-etch adhesive Clearfil SE Bond (Kuraray Noritake, Tokyo, Japan) [18]. The regularly structured monomer nanolayers are also thought to contribute to bond stability, although definitive evidence should still be provided. Currently, the functional monomer MDP is very commonly utilized in adhesives, lately in particular in universal adhesives.

Another functional monomer that has been used in dental adhesive technology since a long time, is glycerophosphate dimethacrylate or GPDM (Fig. 1). GPDM is one of the first chemical compounds proposed to bond to human dentin [4,19,20]. GPDM has one phosphate acidic functional group and two polymerizable methacrylate groups. Initially, GPDM was utilized in etch-and-rinse adhesives, among which the so-called etch-and-rinse gold-standard adhesive Optibond Fl (Kerr, Orange, CA, USA). High bond strength, immediately and upon accelerated aging, was repeatedly shown in laboratory research [21]. Superb laboratory data for OptiBond FL (Kerr) were substantiated by outstanding long-term clinical data, among which a 94% retention rate recorded for Class-V restorations at 13 years [17,22]. More recently, GPDM was also used as functional monomer in the self-etch adhesive OptiBond XTR (Kerr), which also showed comparatively high bond strength onto enamel and dentin *in vitro* [23–26]. In addition, GPDM is also used as functional monomer in self-adhesive composite cements like Maxcem Elite Chroma (Kerr)

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