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Chemical affinity of 10-methacryloyloxydecyl dihydrogen phosphate to dental zirconia: Effects of molecular structure and solvents

Ying Chen[a,b,1], Zhicen Lu[a,b,1], Mengke Qian[a,b], Huaiqin Zhang[a,b], Chen Chen[a,c,1], Haifeng Xie[a,b,*], Franklin R. Tay[d,**]

[a] Jiangsu Key Laboratory of Oral Diseases, Nanjing Medical University, China
[b] Department of Prosthodontics, Affiliated Hospital of Stomatology, Nanjing Medical University, Nanjing, China
[c] Department of Endodontics, Affiliated Hospital of Stomatology, Nanjing Medical University, Nanjing, China
[d] Department of Endodontics, The Dental College of Georgia, Augusta University, Augusta, GA, 30912, USA

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ABSTRACT

Objectives. To examine whether solvents and changing the molecular structure of 10-Methacryloyloxydecyl dihydrogen phosphate (10-MDP) affect its chemical affinity to Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP).

Methods. The present work investigated the chemical affinity between Y-TZP and 10-MDP dissolved in different solvents (acetone/ethanol/water or mixture) using X-ray photoelectron spectroscopy, Fourier-transform infrared spectroscopy, and thermodynamic calculations. Shear bond strength (SBS) tests were used to evaluate the influence of different solvents on 10-MDP bonding. In addition, several phosphate ester monomer variants were created by changing the 10-MDP molecular structure. Changes included extending/shortening the spacer chain-length, and installing hydroxyl or carboxyl groups as side chains at different positions along the spacer chain. The thermodynamic parameters of the complexes formed between the 10-MDP variants and tetragonal zirconia were evaluated.

Results. The acquired data indicated that solvent is necessary for the formation of Zr–O–P bonds between 10-MDP and Y-TZP. Solvents affected the chemical affinity of 10-MDP to Y-TZP; acetone facilitated the best bonding, followed by ethanol. Changing the molecular structure of 10-MDP affected its chemical affinity to Y-TZP. The variants 15-MPDP, 12-MDDP, 6-hydroxyl-10-MDP and 6-carboxy-10-MDP all exhibited higher thermodynamic stability than 10-MDP when coordinated with tetragonal zirconia. In contrast, 2-MEP, 5-MPP, 10-hydroxyl-MDP, 10-carboxy-MDP, 5,6-dihydroxyl-10-MDP and 5,6-dicarboxy-10-MDP exhibited lower thermodynamic stability.

Significance. 10-MDP coordinates with zirconia through dissociating in solvents. Changing the molecular structure of 10-MDP theoretically affects its chemical affinity to Y-TZP.

* *Corresponding author at*: Han Zhong Road 136th, Stomatological Hospital of Jiangsu Province, Nanjing 210029, China. Fax: +86 25 8651 6414.
** *Corresponding author*. Fax: +1 706 721 021.
E-mail addresses: xhf-1980@126.com (H. Xie), tayfranklin7@gmail.com (F.R. Tay).
[1] These authors contributed equally to this work.

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1. Introduction

Phosphate ester monomers are frequently used clinically for coupling of Yttria-stabilized tetragonal zirconia polycrystals (Y-TZP) to methacrylate-based resin composites. This chemical coupling procedure is simple, noninvasive to ceramic substrates, and results in excellent bonding outcomes [1–5]. Because phosphate ester monomers contain methacryloyloxy functional groups, they also support the adhesion of methacrylate-based resins to tooth structures [6–8]. Hence, there has been growing interest in developing new phosphate ester monomers for chairside applications in restorative dentistry.

10-Methacryloyloxydecyl dihydrogen phosphate (10-MDP) is currently the most widely-used phosphate ester monomer applied for the coupling of Y-TZP. Chemical bonding between 10-MDP and Y-TZP has been extensively studied [1–5]. However, pure 10-MDP is a sticky colloid and its molecular structure is too crowded for it to be optimally dispersed in non-solvated form on the surface of Y-TZP. Accordingly, a solvent, such as ethanol or acetone, is required to facilitate optimal dispersion of 10-MDP. A recent study reported that the most effective concentration range of 10-MDP for optimal interaction between 10-MDP and hydroxyapatite is 5–10% [7].

The 10-MDP molecule retains a phosphoric-acid group at an end of the molecule, which serves as an adhesion promoting agent for hydroxyapatite or metal oxides such as alumina and zirconia. The molecule also contains a vinyl group at another end, which facilitates polymerization with unsaturated carbon bonds in the resin matrix. These two active groups are separated by a spacer ester chain comprised of ten carbons. As 10-MDP is a polar molecule, a polar solvent has to be used for dissolving the molecule to create primer solutions. For biological safety reasons, the polar solvents most commonly used for preparing dental primers and adhesives are water, ethanol, and acetone. For commercially available 10-MDP-containing primers and adhesives, water (Panavia F2.0 ED primer, Clearfil Protect Bond, and Clearfil SE bond, all from Kuraray Noritake Dental Inc., Tokyo, Japan; G-Premio Bond, GC Corp., Tokyo, Japan) and ethanol (Clearfil Ceramic Primer, Kuraray Noritake Dental Inc.; Z-Prime Plus, Bisco Inc., Schaumburg IL, USA; Danville Z-Bond, Danville Materials, Carlsbad, CA, USA) are the most commonly used solvents, while acetone (Alloy Primer, Kuraray Noritake Dental Inc.), or a mixture of ethanol and water (Clearfil S3 BOND, Single-step Clearfil Tri-S Bond (3S), Ex-3, all from Kuraray Noritake Dental Inc., All-Bond Universal, Bisco Inc.; Scotchbond Universal, 3M ESPE, St. Paul, MN, USA) are less frequently used. Nevertheless, the influence of polar solvents on the chemical affinity of 10-MDP to Y-TZP remains unclear.

Previous studies indicate that 10-MDP exhibits favorable adhesive performance when incorporated into primers, adhesives, or resin cements [2,3,9]. Different chemoanalytical techniques have been used to elucidate the chemical reaction between 10-MDP and Y-TZP, including Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), time of flight-secondary ion mass spectrometry (ToF-SIMS), ^{1}H and ^{31}P magic angle spinning (MAS) nuclear magnetic resonance spectroscopy (NMR), and two dimensional $^{1}H \rightarrow {}^{31}P$ heteronuclear correlation (HETCOR) NMR [10–14]. Based on these techniques, the phosphoric-acid group in 10-MDP was found to be responsible for its chemical bonding ability with non-polar and chemically-inert Y-TZP surfaces. To date, it is not clear why all compounds with dihydrogen phosphate functionalities cannot react with Y-TZP at room temperature. It has been speculated that the phosphate group does not form coordination bonds with Y-TZP when it is not incorporated into the molecular structure of a phosphate ester [4]. Although several commercially available phosphate ester monomers also possess polymerizable vinyl groups and functional phosphate groups, their chemical affinity with dentin apatite is drastically different from 10-MDP [15,16]. Because different phosphate ester monomers have different ester chain structures, the authors hypothesize that alteration of the ester chain structure may strengthen or weaken the ability of 10-MDP to chemically bond with Y-TZP. Clarification of this issue may result in the development of novel phosphate ester monomers with better chemical activity for Y-TZP.

Accordingly, the chemical interactions between 10-MDP dissolved in different solvents and Y-TZP were examined in the present study. In addition, the chemical affinities of several 10-MDP variants to tetragonal zirconia were also evaluated. Variants of 10-MDP included molecules with extended or shortened ester chain lengths, or versions with one or two hydroxyl or carboxyl group side chains at different positions. The null hypotheses tested were: (1) there is no difference in the chemical affinity of 10-MDP to Y-TZP, irrespective of whether the molecule is solvated or used without dissociation in a solvent; and (2) the chemical affinity of phosphate ester monomers to tetragonal zirconia is not affected by alterations in their molecular structure.

2. Materials and methods

2.1. *Modeling of complexes between tetragonal zirconia and 10-MDP (and its variants) and thermodynamic calculations*

Derivatives of 10-MDP were designed that comprised variations of the spacer ester chain or side chains of the 10-MDP molecule (Fig. 1). Variations included extending or shortening the length of the spacer ester chain (2-carbon, 5-carbon, 12-carbon, or 15-carbon), adding a hydroxyl or a carboxyl group, or two hydroxyl or two carboxyl groups as side chains at different positions on the spacer chain (distal to the phosphoric-acid group or at a middle position).

Models of tetragonal zirconia crystals and the 10-MDP molecule and its variants were created and geometrically optimized. Dissociation of 10-MDP and its variants was simulated in the aqueous phase. Interactions between the monomers and tetragonal zirconia crystals were analyzed by thermodynamic calculations in the vacuum phase. The Gibbs free energy was determined for the reaction pathway based on a previous study [17].

High level calculations were performed using the density functional theory (DFT) method. The C and H in the carbon chain were studied at the 3-21G level, while the remain-

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