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Functional monomer impurity affects adhesive performance

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ABSTRACT

Objective. The functional monomer 10-MDP has been considered as one of the best performing functional monomers for dental adhesives. Different adhesives containing 10-MDP are commercially available, among which many so-called 'universal' adhesives. We hypothesize that the quality of the functional monomer 10-MDP in terms of purity may affect bonding performance.

Methods. We therefore characterized three different 10-MDP versions (10-MDP_KN provided by Kuraray Noritake; 10-MDP_PCM provided by PCM; 10-MDP_DMI provided by DMI) using NMR, and analyzed their ability to form 10-MDP_Ca salts on dentin using XRD. The 'immediate' and 'aged' micro-tensile bond strength (μTBS) to dentin of three experimental 10-MDP primers was measured. The resultant interfacial adhesive-dentin ultra-structure was characterized using TEM.

Results. NMR disclosed impurities and the presence of 10-MDP dimer in 10-MDP_PCM and 10-MDP_DMI. 10-MDP_PCM and 10-MDP_DMI appeared also sensitive to hydrolysis. 10-MDP_KN,

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on the contrary, contained less impurities and dimer, and did not undergo hydrolysis. XRD revealed more intense 10-MDP_Ca salt deposition on dentin induced by 10-MDP_KN. The adhesive based on the experimental 10-MDP_KN primer resulted in a significantly higher 'immediate' bond strength that remained stable upon aging; the μTBS of the experimental 10-MDP_PCM and 10-MDP_DMI adhesives significantly dropped upon aging. TEM revealed thicker hybridization and more intense nano-layering for 10-MDP_KN.

Significance. It was concluded that primer impurities and the presence of 10-MDP dimer affected not only hybridization, but also reduced the formation of 10-MDP_Ca salts and nano-layering. 10-MDP in a high purity grade is essential to achieve durable bonding.

1. Introduction

Phosphate functional monomers are designed to chemically interact with dentinal hydroxyapatite, being thought of importance for bond durability. Among many functional monomers, 10-MDP was most shown to improve bonding effectiveness in laboratory and clinical research [1–6]. In our previous research, 10-MDP's chemical interaction with hydroxyapatite (HAp) of tooth tissue was proven using diverse chemical analytical tools, such as XRD, XPS and NMR [7–9]. Furthermore, 10-MDP was documented to self-assemble into so-called 'nano-layering', a process driven by the deposition of 10-MDP_Ca salts with low solubility [8,10–12]. Each nano-layering consists of two sublayers of parallel oriented 10-MDP monomers in opposite direction. 10-MDP's methacrylate group is directed inwards, enabling mutual co-polymerization between two opposed monomers. Its functional phosphate group is directed outwards, capturing Ca released from dentin thanks to the etching effect of 10-MDP and so coupling adjacent nano-layers. Further in-depth research into the process of nano-layering is warranted to assess the relevance and actual contribution of this compact 3D structure to the stability of the adhesive interface.

The functional monomer 10-MDP was originally synthesized by Kuraray (today Kuraray Noritake, Tokyo, Japan) and has been introduced in 1981 (following 'Clearfil SE Bond' Technical Information from Kuraray Noritake). The actual 10-MDP patent expired in 2011, and has led other companies to develop and launch 10-MDP adhesives, many of them have been referred to as so-called 'universal' adhesives, such as Adhese Universal (Ivoclar Vivadent, Schaan, Liechtenstein), All-Bond Universal (Bisco, Schaumburg, IL, USA), Clearfil Universal Bond (Kuraray Noritake), Futurabond U (Voco, Cuxhaven, Germany; although the MSDS document does not specify what the 'acidic adhesive monomer' is), G-Premio Bond (GC, Tokyo, Japan) and Scotchbond Universal (3M ESPE, Seefeld, Germany). Besides indicated for direct and indirect restorative procedures, universal adhesives allow the dentist to opt for either an etch-and-rinse (E&R) or self-etch (SE) application protocol.

Bonding effectiveness of the different commercial 10-MDP-based adhesives was found to vary [13,14]. Self-evidently, difference in composition is the most plausible reason. Bond strength was shown to depend on the actual concentration of 10-MDP [12]. The interfacial interaction potential of 10-MDP with HAp was found to be inhibited by other monomers like HEMA [15]. 10-MDP's performance may also degrade with time, as the monomer is sensitive to hydrolytic degradation [16].

To date, the effect of 10-MDP's purity on bonding effectiveness is unknown, although several chemical companies (PCM, Krefeld, Germany; DMI, San Diego, CA) commercially offer the functional monomer to be used for dental purposes. Different purities are reported in the accompanied technical documentation. Moreover, patent literature not clearly describes the synthesis process and actual purification process [17,18]. We therefore investigated in this study three different 10-MDP versions, provided by three different companies, on their purity and their chemical interaction potential as well as bonding effectiveness to dentin. The null hypothesis tested was that the adhesive performance of experimental primers varying for the 10-MDP version was not different when they were used as part of a 2-step SE adhesive protocol.

2. Materials and methods

Three different 10-MDP monomers were selected, as they were provided by DMI (further referred to as '10-MDP_DMI'), by Kuraray Noritake (referred to as '10-MDP_KN'), and by PCM (referred to as '10-MDP_PCM'). The purity grade of 10-MDP_DMI was reported by DMI to be 90%, versus 83% reported by PCM for 10-MDP_PCM. The purity grade of 10-MDP_KN was not released by Kuraray Noritake, but was informed to be higher than that of the other 10-MDP's tested and to be the same as that of 10-MDP included as functional monomer in the commercial adhesive Clearfil SE Bond (Kuraray Noritake).

Three respective experimental primers were prepared to consist of a 15:45:40 wt% solution of 10-MDP/ethanol-D6/water-D2 and were stored for 1 month at 37 °C. The pH of the experimental primers was 2.66 for 10-MDP_DMI, 2.03 for 10-MDP_KN, and 2.73 for 10-MDP_PCM.

2.1. *Nuclear magnetic resonance spectrocopy (NMR)*

NMR is a research technique that exploits the magnetic properties of atomic nuclei and can provide detailed information about the electronic structure of a molecule. In order to investigate the molecular structure of 10-MDP and potential impurities, we analyzed the three 10-MDP experimental primers using ^{1}H (with respect to hydrogen), ^{13}C (with respect to carbon) and ^{31}P (with respect to phosphorus) NMR spectroscopy. The three experimental primers were disposed