

Hybrid Interface of Dentistry and Inorganic Chemistry

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Perspective

Historical changes of adhesive resin systems [1]

In the 1970s and 1980s, total etching system (2-Step), namely etching + bonding phosphoric acid, was developed. When a tooth is drilled, its fine fragments are gathered and a layer called a smear layer is formed. In order to eliminate the layer, phosphoric acid treatment is carried out to dissolve the smear layer and to melt the enamel in a jagged shape, whereby resin and made it easy to adhere. Etching is decalcification, which is a process of dissolving a smear layer (a layer formed by cutting a tooth) and eroding the enamel and dentin with an acid, and the adhesive monomer chemically bonds to the demineralized enamel. It is a setup to make it easier. Citric acid, maleic acid, phosphoric acid, etc. were used. The dentin is etched to leave the collagen fibers and the hydroxyapatite is decalcified. Bonding refers to curing, and a resin monomer is flowed at the place where it is adapted by priming and light curing is performed. Polymerization of primer and bonding. This bonding surface needs to be hydrophobic to firmly adhere to the primer and composite resin.

In 1990s, dentin bonding system (3-Step), namely etching (citric acid maleic acid phosphate) + priming (HEMA (2-hydroxyethylmethacrylate) hydrophilic monomer) + bonding (photopolymerization catalyst), was developed. In addition to etching with acids such as citric acid, maleic acid, phosphoric acid, etc., priming with hydrophilic monomers by HEMA (Scheme 1), and bonding using photopolymerization catalyst are three steps. Because it uses three different chemicals for each of the three steps, it is easy to make mistakes, it is difficult to operate, the patient's jaw with the mouth opened is hard, so we aim to reduce the stage and develop it was wrong. Priming is permeation, which is a setup to make flowing a highly flowable resin monomer (primer) to the surface roughened by etching. Since dentin contains a large amount of moisture in a capillary structure, the primer needs to be hydrophilic, and HEMA is often used. When the primer penetrates into the dentin, it coagulates with collagen fibers exposed by etching together with light curing to form a resin impregnated layer.

HEMA, a limber, needs to be hydrophilic because it wants to get into the capillary structure of dentin containing much water. However, since it is hydrophilic even after polymerization, water enters. Then, water accumulates at the bottom of the resin impregnated layer. Hydrolysis and this moisture will cause the enzyme, called matrix metalloproteinase (MMP) containing Ca^{2+} and Zn^{2+} , to enter and degrade collagen fibers at the interface and deteriorate. It is said that the resin impregnated layer remains semi-permanently unless water enters in, and it is a problem to create an adhesive surface without using HEMA, which causes water to enter.

Around 1995, Self-etching system (2-Step) self-etching priming (etching and priming one start with +) Bonding, which need no washing with water nor drying was developed in Japan. While, in USA, wet-bonding system (2-Step) etching + priming & bonding reported by J. Kanca (practitioner) by wet-priming to find strong adhesion, was used. Separate methods have become mainstream in Japan and the United States. In Japan, "Self-etching system" was carried out with etching and priming together. This does not require water washing and drying, and the content is "self-etching priming + bonding". In USA, "Wet-bonding system" was done from the flow that we wanted to

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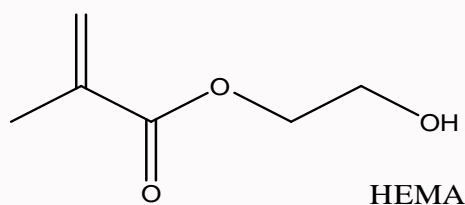
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Scheme 1: Structure of HEMA.

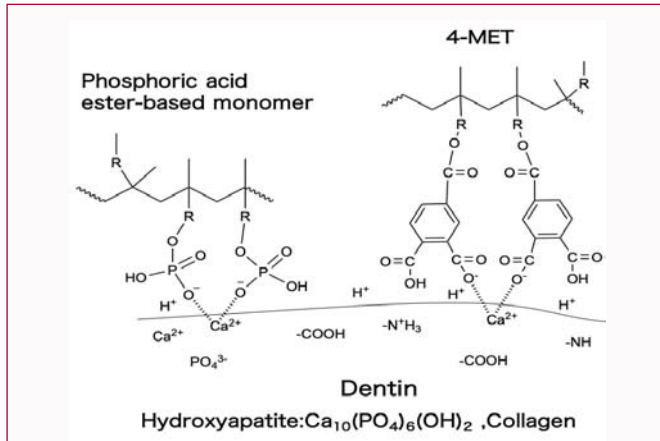


Figure 1: Typical features of a dentin adsorbing terminal (left) phosphoric group or (right) carboxylic group (4-MET).

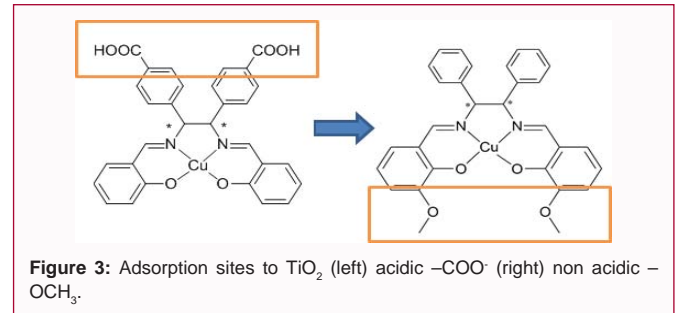


Figure 3: Adsorption sites to TiO_2 (left) acidic $-COO^-$ (right) non acidic $-OCH_3$.



Figure 2: Coating agents containing (a) hydroxyapatite nanoparticles, (b) phosphoric buffer for MI, and (c) NaF against tooth decay.

do etching by all means. This content was "Self-etching + Priming bonding".

The GC company developed G-bond which does not contain HEMA. HEMA degrades the resin impregnated layer. That is, the filling becomes easy to remove. By using acetone as a solvent instead of HEMA, water contained in a synergistic effect with highly volatile acetone at the time of air blowing can be effectively eliminated from the bonding layer. Furthermore, although the strength differs depending on the doctor, this air blow can reduce the difference in strength due to the difference of the doctors by instructing the most intense pressure air blow.

Before G - Bond Plus was released, G - bond was circulating. In G-Bond, effective adhering monomer "phosphate ester monomer"

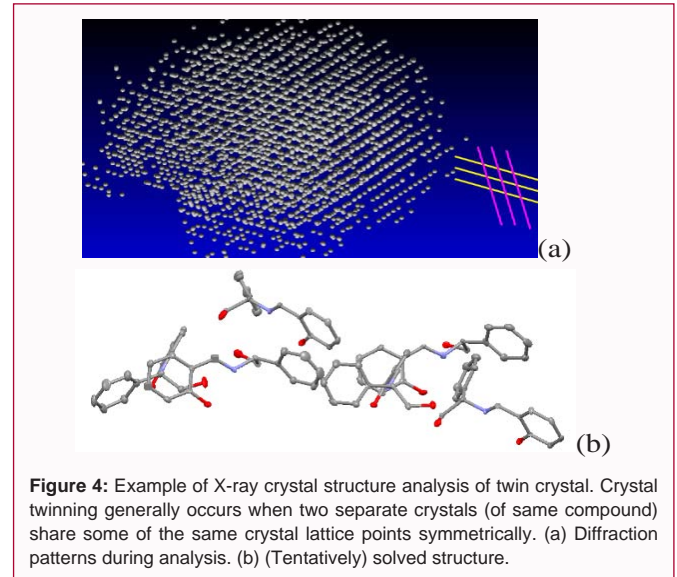


Figure 4: Example of X-ray crystal structure analysis of twin crystal. Crystal twinning generally occurs when two separate crystals (of same compound) share some of the same crystal lattice points symmetrically. (a) Diffraction patterns during analysis. (b) (Tentatively) solved structure.

and "4-MET" was blended to enamel and dentin, respectively (Figure 1), but by changing this blending balance, decalcification to enamel strengthened and strengthened adhesion to enamel. From these facts, it is considered that strength and durability of this product can be expected as compared with conventional products.

In the conventional resin impregnated layer, the hydroxyapatite was scarcely contained and the primer was familiar to the exposed portion of the collagen fiber portion. However, in G-bonds, apatite of collagen fiber was retained by suppressing decalcification, and chemically reacted with hydroxyapatite to form insoluble calcium salt. As a result, a chemical reaction layer as thin as 500 nm was made instead of the conventional resin impregnated layer, and the durability was improved. This slight thinness is thought to have a large influence on the filling of a few chips such as front teeth.

After 2000-present, one system (1-Step) self-etching priming bonding was employed generally. "All in-one system" became mainstream, finally it became one step, which may be a goal of minimum intervention (MI) [2].

Hints for/by inorganic chemistry

From these facts, chemical reactions caused by acids and adhesion of molecules may also be important for inorganic chemistry. Ashing is the reaction of calcium in hydroxyapatite (Figure 2(a)) and acids. Both phosphoric acids ($pK = 2.15, 7.20, \text{ and } 12.38$ for each deprotonation step) (Figure 2(b) for MI) and carboxylic acid ($pK = 4.75$ for acetate's deprotonation). NaF (Figure 2(c)) can induce remineralization against ashing ($Ca^{2+} + F^- \rightleftharpoons CaF^+ \text{ } pK = -1.04; CaF_2 \rightleftharpoons Ca^{2+} + 2F^- \text{ } pK = 10.31; Ca^{2+} + CH_3COO^- \rightleftharpoons CH_3COOCa^+ \text{ } pK = -0.77$).

Indeed, we have compared adsorption onto TiO_2 surface with (acidic anion) carboxylic groups [3,4] and (non-acidic) methoxy group [5] (Figure 3). Of course binding by neutral methoxy group was weaker due to the lack of electrostatic interaction.

Accumulation of further atoms or ions onto the substrate to grow “crystals” may be suitable situation from the viewpoint of biomineralization [6]. In extreme terms, it seems like a situation that grows “twin crystal” (Figure 4) on the surface of hydroxyapatite. In this way, the synergistic effect of dental medical application and basic science (inorganic chemistry) is expected to contribute to further improvement of technology. Different fields should have more exchanges (in other words, interaction on “hybrid interface”!).

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