Bonding strength of glass ionomers to dense synthetic hydroxyapatite and fluoroapatite ceramics

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The bonding strength of two glass ionomers, a resin-modified and a conventional one, to dense synthetic hydroxyapatite (HA) and fluoroapatite (FA) ceramics was compared by measuring the shear strength between the ionomers and the apatites. Before the glass ionomers were applied on the apatites, the surfaces of HA and FA plates were either fine-polished or acid-etched after fine polishing. Commercially pure titanium (CP Ti) plates were used as a control. The effects of polyacrylic acid (PAA) surface preconditioning on bonding strength were also studied. The results show that the ionomers bind to HA significantly more strongly than to FA in all cases. The resin-modified material showed a significantly higher shear strength to apatites than the conventional one. Acid etching increased the shear strength significantly for the conventional glass ionomer to both HA and FA, and 25% PAA preconditioning increased the shear strength significantly for the resin-modified glass ionomer to both HA and FA. It was concluded that glass ionomers seemed to bind to apatite chemically, and the bonding strength was influenced by the cohesive strength of the ionomers and the surface roughness of the apatites. The dense synthetic apatites seemed to be good test materials for bonding evaluations of glass ionomers to mineral tissue. ☐ *Adhesion; apatites; glass ionomers; polyacrylic acid*

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The bonding ability of polyacrylic acid (PAA), the main organic component in dental glass ionomer materials, to tooth substance is one of the advantages of the glass ionomer materials used as dental cement and dental filling materials. The bonding mechanism is, however, still a subject of research (1). Wilson et al. (2) postulated that carboxyl groups in PAA replace the phosphate groups in apatite, by which a strong chemical bonding is established between PAA and apatite. Skinner et al. (3) concluded that stereochemical factors are of importance in the adsorption of PAA to hydroxyapatite (HA) and indicated that there is an ion exchange between PAA and apatite.

One of the problems of using human teeth for bonding testing is that the results vary significantly owing to variations in the tooth structures (4). Such variations may be avoided by using a dense synthetic HA or fluoroapatite (FA) ceramic, whose surface structure is homogeneous. Since apatites are the main mineral constituents of the teeth, the high bonding strength between a material (cement) and a dense, synthetic, and well-polished apatite ceramic should reflect the bonding strength of the same material to the apatite surface of teeth.

The low strength of the conventional glass ionomers has been one of the limitations to their application in dentistry. Recently, however, resin-modified ionomers have been developed, in which a light-curing system is introduced in the conventional glass ionomers, and the strength of the glass ionomers has been significantly improved (5). The advantages of the conventional glass ionomers remain, including the release of fluoride and adherence to tooth surfaces (6, 7). It has also been reported that the resin-modified glass ionomers bind to dentin significantly more strongly (twofold) than the conventional glass ionomers (8, 9). Obviously, the strength of the materials plays an important role in the bonding strength when the glass ionomers bind to tooth substance chemically. The purpose of this investigation was to compare bonding strength between resin-modified and conventional glass ionomers to the dense synthetic apatites HA and FA and to study the underlying mechanism of such bonding.

Material and methods

Two glass ionomer materials were used (Table 1): a resin-modified one, Photac-Fil, and a conventional one, Ketac-cem. The powders and liquids of the conventional cement were mixed in accordance with the manufacturer's instruction. Plates (5 × 5 × 1 mm) of dense apatite ceramics, HA and FA, were cut from bulk-sintered ceramics and embedded in a metallic holder with an auto-cured dental resin. The ceramic plates were polished in a polishing machine (Pedemin, PAD-7, Struers, Denmark) under running water. The control plates (5 × 5 × 1 mm) of commercially pure titanium (CP Ti) were cut from a large plate, and the surfaces were used as received or acid-etched. Then the prepared surfaces of all the specimens were covered with plastic tape with

Table 1. Materials used in this study

Materials	Batch no.	Manufacturer	Strength* (MPa)
Photac-Fil	Lot 0012 × 265 Aplicap	ESPE, Germany	29.5 ± 5.2
Ketac-cem	MD v325	ESPE, Germany	7.2 ± 0.5

* Three-point bending strength of the glass ionomers 24 h after setting.

a punched hole (3 mm in diameter) in the middle of the surface, to limit the adhesion area.

The prepared specimens were divided into the following groups in accordance with the pretreatment of the surfaces: I) fine polishing with sandpaper (silicon carbide) no. 4000; II) 37% H_3PO_4 etching for 1 min after fine polishing; III) 25% PAA aqueous solution (MW 50,000; Polyscience, USA) preconditioned for 1 min after fine polishing; IV) 25% PAA preconditioned for 1 min after fine polishing and kept in air for 2 h at 37 °C, 60 °C, or 100 °C; and V) 25% PAA preconditioned for 1 min after fine polishing, kept in air for 2 h at 37 °C, 60 °C, or 100 °C, and reimmersed in deionized water overnight at room temperature.

Plates of CP Ti were used as a control. Surface profiles of the polished and etched surfaces (groups I and II) were measured with a surface profilemeter (T1000, Hommelwerke, Germany) before the bonding test.

The newly mixed Ketac-cem and Photac-Fil pastes were filled into a polyethene tube, 3 mm in diameter and 2 mm in height, and placed on the apatite and CP Ti surfaces. Photac-Fil paste was cured with a lamp (VLC 400, Demetron, USA) for 40 sec from the top of the tube. The newly mixed Ketac-cem was cured by its acid-base reaction only. The specimens were kept in a humidity chamber (100% relative humidity) at 37 °C for 1 h and then immersed in deionized H_2O for 23 h at 37 °C before the bonding test.

Bonding test

The specimen was fixed in a universal material testing machine (Alwetron TCT 50T, AB Lorentzen & Wettre, Sweden). A shear force was applied to the edge of the disc with a hard-metal tip (Fig. 1) at a crosshead speed of 1 mm/min. Six to nine specimens were used for each glass ionomer at each condition. The results were statistically analyzed (*t* test and ANOVA), and $P < 0.05$ was used as the statistically significant level.

Fracture surface examination

After the shear strength testing, the fracture surfaces of the specimens were examined in a Jeol JSM-820 SEM. A 10-nm Au–Pd alloy layer was coated by ion sputtering.

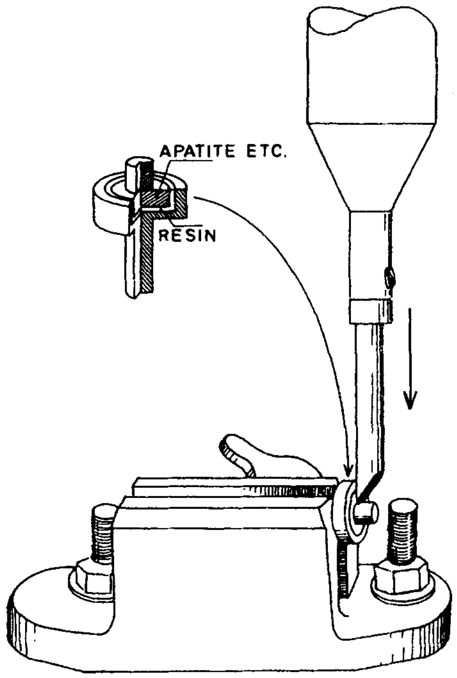

Fig. 1. The set-up for measuring the shear strength.

Results

Table 2 presents some properties of the dense apatites and CP Ti used in this study (some of the results were adapted from our previous studies and from the literature (10, 11)). The apatite plates were dense ceramics with a theoretical density of HA and FA of about 3.156 g/cm^3. FA and HA had similar surface smoothness after polishing. HA became rougher than FA after phosphoric acid etching. The surface of CP Ti was rougher than that of apatites before etching and was not affected by the acid etching.

Bonding strength

The bonding strengths of the two glass ionomers to HA, FA, and CP Ti are shown in Table 3. Photac-Fil had a significantly higher shear strength to HA and FA than Ketac-cem with and without acid etching (groups I and II). Acid etching increased the bonding strength significantly for the conventional ionomer, but the increase was not significant for the resin-modified ionomer. Both glass ionomers bound significantly more strongly to HA than to FA in groups I, II, and III. The shear strengths of the glass ionomers to CP Ti were low.

Table 2. Properties of dense synthetic apatite ceramics and commercially pure (CP) titanium

	Hydroxyapatite (HA)	Fluoroapatite (FA)	CP Ti
Density (g/cm^3)	3.15	3.15	4.54
Hardness (GPa)	3.7	3.8	1.40
E-modulus (GPa)	100	100	110
Bending strength (MPa)	110	100	530*
Surface profile (Ra)			
Polished	0.05 ± 0.01	0.07 ± 0.01	0.60 ± 0.23†
Etched (37% H_3PO_4)	0.61 ± 0.11	0.15 ± 0.06	0.61 ± 0.18

Some of the results were collected from References 10, 11. HA and FA powders were purchased from Merck, Germany, and Cam Implants bv, the Netherlands, respectively.

* Tensile strength.

† Commercially pure titanium as received from the manufacturer (grade 1, Permascand AB, Sweden).

Table 3. The shear strength (MPa) of glass ionomers to dense apatites and commercially pure (CP) titanium before (group I) and after etching with 37% H_3PO_4 (group II) (mean ± SD)

	Ketac-cem		Photac-Fil	
Materials	Group I	Group II	Group I	Group II
HA	3.4 ± 0.35	4.9 ± 0.44	7.0 ± 1.4	7.4 ± 0.59
FA	2.1 ± 0.37	3.2 ± 0.14	5.0 ± 0.52	5.5 ± 0.63
CP Ti	0.75 ± 0.45	0.66 ± 0.34	0.67 ± 0.59	0.72 ± 0.45

Table 4. Comparison of the shear strength (MPa) between Photac-Fil and the dense apatites with different surface conditions (mean ± SD)

Groups	Hydroxyapatite	Fluoroapatite
I	7.0 ± 1.4	5.0 ± 0.52
II	7.4 ± 0.59	5.5 ± 0.63
III	12.5 ± 2.3	8.3 ± 1.7
IV	Loss*	Loss*
V	9.3 ± 0.47 (37°C)** 9.2 ± 0.58 (60°C) 9.2 ± 0.40 (100°C)	8.9 ± 2.2 (37°C)** 7.5 ± 1.1 (60°C) 8.1 ± 2.1 (100°C)

* Loss means that the cement fell off before the shear strength was measured. The specimens treated at different temperatures showed the same results.

** The temperatures used after 25% polyacrylic acid preconditioning.

The effects of 25% PAA aqueous solution preconditioning on the bonding strength are illustrated in Table 4. Groups III and V showed significant increases in shear strength compared with groups I and II. Photac-Fil bound most strongly to PAA-treated HA (group III). In group IV the cement cylinders fell off the ceramic surface before the load was applied, and thus the shear strength was too low to be recorded. No significant increases in shear strength were found at different temperatures in group V.

Fracture surface

The initiation of the fracture occurred mostly at the interface and grew into the cement layer for Ketac-cem (Fig. 2). However, for Photac-Fil combined with PAA preconditioning, the fracture originated from the interface and often grew into the apatite (Fig. 3) at shear strengths greater than 8 MPa.

Discussion

One of the significant advantages of the glass ionomers is that they bind to the mineral component of tooth tissue, which has also been shown in this experiment. The chemical bonding between HA and carboxyl groups of PAA has been proposed (2, 12). The increase of the surface roughness increases the retention strength, particularly in the case of tooth enamel on which a comparatively large surface area can be obtained by acid etching (13). Therefore, the bonding tests on teeth may reflect the combination effects of chemical and mechanical retention of the glass ionomer. That may explain the large difference between our results and those of others measured using extracted teeth, both on dentin and on enamel (14). A well-polished, dense, synthetic apatite surface limits the mechanical retention. Thus, the high bonding strength obtained between the glass ionomers and the HA or FA ceramic plates reflects probably the chemical bonding. However, the increased retention due to a rougher surface was also seen in the conventional glass ionomer, particularly on HA ceramics, on which acid etching is more effective than on FA or CP Ti. It may be possible that 25% PAA solution and unset glass ionomer paste will have an etching effect on the apatites. However, considering the increased bonding strength after preconditioning with 25% PAA aqueous solution (group III) and the lower etching capacity of PAA than of H_3PO_4, the chemical bonding between the PAA and apatite seems to be obvious. Furthermore, the shear strength between the

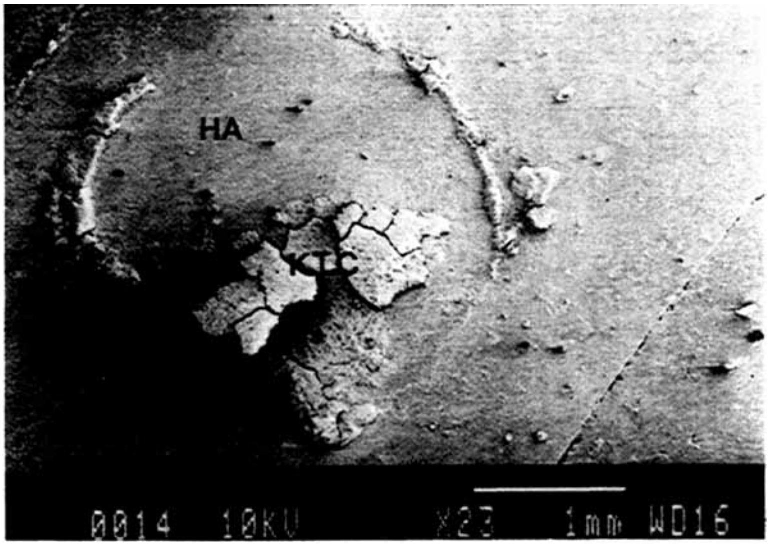

Fig. 2. Scanning electron micrograph of the fracture surface of Ketac-cem (KTC) and hydroxyapatite (HA). The fracture was initiated from the interface, and the cracks grew into the ionomer body. HA remains intact.

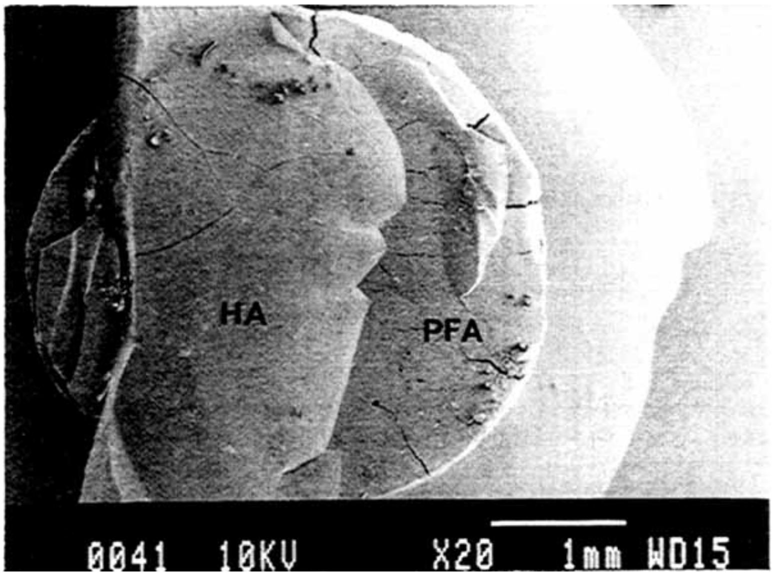

Fig. 3. Scanning electron micrograph of the fracture surface of Photac-Fil (PFA) and hydroxyapatite (HA). The fracture originated from the interface, and cracks grew into the HA ceramic body.

glass ionomers and CP Ti was low even though the CP Ti had a rougher surface (Table 2), indicating a pure mechanical retention in this case. Etching increases the surface area; this may, as has been shown, give an increased retention, which may be due to an increased chemical bonding possibility and, possibly to some extent, a mechanical retention. The mechanical retention obtained by means of etching probably plays a minor role, at least with regard to glass ionomer retention to enamel.

The resin-modified glass ionomer binds significantly more strongly to apatite than the conventional ionomer in group I, suggesting the importance of the cohesive strength of the glass ionomer cement (Table 1) for the bonding strength because the fracture propagated into the glass ionomers of the conventional type (Fig. 2). It seems that the bonding strength between PAA and apatite could be even higher, because the fraction was often initiated and grew in the apatite ceramics when the shear strengths were more than 8 MPa (Fig. 3). The improved mechanical strength of the resin-modified glass ionomer may improve the retention of these restorative materials clinically.

Results of bonding tests from different laboratories are difficult to compare, because the variations can be as great as 100%. One of the causes of the divergence is the variation in tooth structure (8). The mineral content differs between teeth and within the same tooth. We suggest that the dense synthetic apatite be used as a testing material for measuring the bonding between PAA-based materials and mineral tissue in addition to extracted teeth.

It seems that at least a monolayer of PAA binds to the apatite surface of HA and FA. In Table 4 preconditioning with 25% PAA solution for 1 min (group III) resulted in a significantly higher bonding strength than that of other surface preparations (groups I and II), which suggests that the interaction between PAA and HA or FA occurred rapidly at room temperature. This PAA monolayer functioned as a coupling agent and will bind to the glass ionomer matrix both mechanically and chemically. It may be that parts of the unreacted carboxyl groups in the PAA on the apatite surface may react with calcium or aluminum ions released from the newly mixed glass ionomers. In group IV the dried PAA formed a thin film, which prevented the freshly prepared cement from direct contact with the PAA monolayer. The PAA film was slowly dissolved while the specimens were kept in water for 23 h at 37 °C; as a result, the cement cylinders fell off the apatite surface. In group V a stable monolayer of PAA on the apatite surface was exposed when unbonded PAA was dissolved after being reimmersed in water, which improved the bonding strength between the cement and the apatite. Again, the reaction between PAA and apatites was very fast and occurred at room temperature. Further studies are needed with regard to the status and stability of this monolayer and to the molecular weight and the concentration of the PAA.

The differences between HA and FA in shear strength to glass ionomers were significant in these experiments. The shear strength of the glass ionomers to HA was significantly higher than that to FA in groups I to III. This may be due to the difference in acid resistance between HA and FA (15). However, these results should be carefully applied in the interpretation of the influence of the fluoride on the bonding strength of glass ionomer cement to teeth, because the amount of pure FA in teeth is much lower than that of FA used in this experiment. We believe that the differences in shear strength between HA and FA to glass ionomer are most likely due to the differences in chemistry rather than due to the differences in surface roughness caused by the PAA etching effects.

It is concluded that the dense synthetic apatite is a reliable testing material to evaluate the bonding between PAA-based materials and tooth mineral. The improved mechanical strength of the resin-modified glass ionomer increased the bonding to apatite; preconditioning the apatite surface with a PAA aqueous solution increased the bonding strength of the resin-modified glass ionomer to apatites significantly, provided that the cement was applied on the PAA film before it became dry, whereas the effect of acid etching on the shear strength between apatite and the glass ionomer cement was significant for the conventional ionomer.

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