

The Effect of Acidic Pretreatment Solutions on the Direct Bonding of Orthodontic Brackets to Enamel

R. D. MULHOLLAND, D.D.S., M.S.

D. O. DESHAZER, D.D.S., M.S.

INTRODUCTION

Several investigators^{1,2,3,4,5,6} have worked with the adhesive properties of various materials on dental enamel. Also, numerous surface active agents have been employed to make the apatite surface more receptive to bonding.^{7,8,9,10} Although phosphoric acid¹¹ and other acids and alkalies¹² have been employed in pretreating enamel prior to bonding, the pH and the molarity were not independently controlled. The concentrations were expressed as percentages and consequently do not permit a correlation between bond strength and type of acid, pH, or molarity. In considering the effect of acidic pretreatment it was believed necessary to evaluate such parameters more systematically.

The purpose of this study was to explore the effects of acidic pretreatment solutions, varying in molarity and pH, on the direct bonding of an orthodontic bracket to the enamel surface with Addent 35.¹³ Four acids were chosen, two of which were monovalent (hydrofluoric and hydrochloric) and two of which were polyvalent (phosphoric and aspartic). Moisture contact with the bonded specimens was eliminated as a variable from this study; however, the specimens were stored in one hundred per cent humidity.

MATERIALS AND METHODS

Freshly extracted, human, maxillary anterior teeth were obtained from var-

ious dental sources in the area. Teeth having restorations, marginal cracks or other defects were eliminated. The teeth were cleaned with pumice, numbered and stored in distilled water. No effort was made to determine the age of the teeth; most of them were from adult patients.

Medium siamese edgewise brackets were welded to an 0.25 cm² stainless steel wire mesh.

The support system to measure the mean vertical tensile strength was composed of a commercial jar lid, an attachment bracket, two sections of 0.040 inch wire, a number five swivel and a small metal bucket. The jar lid served as a support platform for the tooth and was mounted on an adjustable aluminum rod assembly. A 7 x 8 mm hole in the lid allowed for the connection between the attachment bracket and assembly and the bonded bracket from the underside of the lid. To insure a true tensile force, the hole was of sufficient size to allow for bracket clearance and any needed adjustment of the labial surface after load application.

The attachment bracket was constructed by longitudinally sectioning a bracket through the edgewise slot and soldering the two pieces together so that the "wings" faced each other (Fig. 1). Connection was accomplished by simply sliding the attachment bracket "wings" over those of the bonded bracket.

The connection of the number five swivel with the attachment bracket

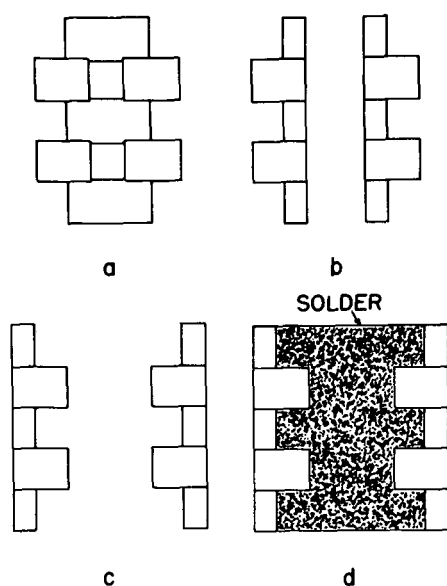


Fig. 1 Construction of the attachment bracket, a) a normal siamese edgewise bracket, b) siamese bracket sectioned longitudinally through the edgewise slot, c) sectioned bracket repositioned so the "wings" face each other, and d) repositioned bracket soldered together so the wings face each other to form the attachment bracket.

and the bucket was done with 0.040 inch wire (Fig. 2). Number one buck-shot and/or gram weights were added to the foam-lined bucket until the bond broke.

The maximum number of teeth that could be bonded ideally with one mix was four. With more than this the Addent began to set and lose some of its better adhesive and flow properties.

The teeth were then pumiced for approximately fifteen to twenty seconds, washed with tap water, and dried. Carding wax was used to support each tooth so that the labial surface was level while the solutions were applied with a cotton swab. The solutions were left on the surface for one minute, blown off with compressed air, and the carding wax removed.

A film of catalyst was spread on the

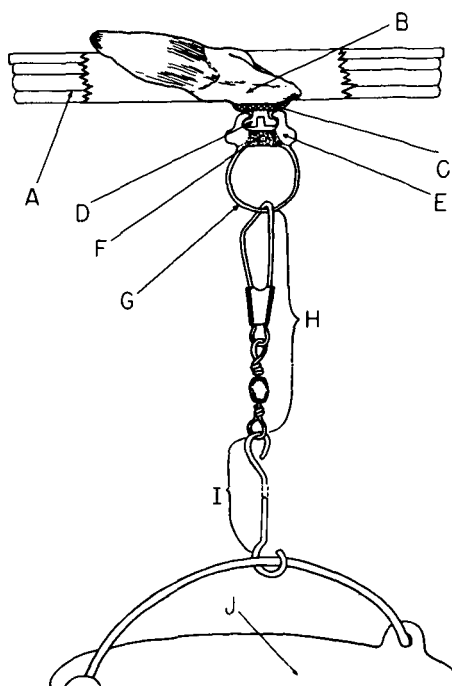


Fig. 2 The entire loading mechanism connected to the bonded bracket, A) a commercial jar lid with a hole (7mm x 8mm), B) crown portion of a maxillary central incisor, C) wire mesh and Addent, D) bonded bracket, E) attachment bracket, F) solder, G) .040 inch wire ring, H) no. 5 swivel, I) .040 inch wire hook, and J) metal bucket.

labial surface of the teeth and a drop was added to the Addent resin. Recommended mixing procedures were followed. After mixing, the Addent was applied to the wire mesh of the bonding bracket and then placed on the labial tooth surface with moderate finger pressure. After removing the excess Addent material, the bonds were covered with Addent protective wax and stored at one hundred per cent humidity at room temperature. The bonded teeth were not submerged in water at any time.

Bond strength was measured by placing the tooth on the loading platform and connecting the attachment bracket and accessories as shown in Figure 2.

Buckshot was slowly added, by hand, until the bond broke.

The support system and the weights in the bucket were weighed on the torsion balance to determine the total force in grams required to break the bond. These data were later converted to kilograms per square centimeter and statistically evaluated for the standard error of the mean and with the "t" test for probability.

RESULTS

Before the various pretreating solutions could be evaluated it was deemed necessary to establish optimum and standardized conditions under which bond strength could be measured.

During the course of preliminary investigations, differences were found between teeth from the same person as well as between individuals, as would be expected from clinical experience. Because of the variance between teeth, results were recorded on individual teeth. Bowen¹⁴ has shown that teeth can be used repeatedly without affecting the values of subsequent tests provided the substrates are resurfaced between tests. The resurfacing procedure used in this study consisted of pumicing the enamel for fifteen to twenty seconds followed by a water wash and drying.^{15,16}

Since it was possible that the cavity liner might aid in bond strength, experiments with and without liner were conducted. The control and the experimental values were 6.82 kg/cm² and 8.10 kg/cm², respectively. A "t" value of 1.14 indicated no significant difference between the two values; consequently the cavity liner was eliminated as a variable.

Investigations on bond strength were conducted to find the effect of adding a drop of catalyst to the enamel surface prior to cementation. The average

value of 14.02 kg/cm² with catalyst was significantly increased over the 8.46 kg/cm² for the control ($t = 3.99$, $p < 0.025$). All subsequent experiments used one drop of catalyst on the enamel surface prior to cementation. Bonds were stored in one hundred per cent humidity and broken at intervals ranging from one hour to four days. No appreciable difference was noted in bond strength. In general, the bonds were broken after approximately five hours.

Monovalent Acids

The bond strength of the control (pH = 6.0) was 14.02 kg/cm², of the pH 4 HCl, 17.74 kg/cm²; that of the pH 2 HCl was 37.27 kg/cm² (Table 1). Both values are significantly increased above the control average of 14.02 kg/cm². The teeth were then resurfaced and evaluated again under pH 6.0 control conditions. A value of 14.95 kg/cm² was obtained which is not a statistically significant increase. Hydrofluoric acid, pH 4, resulted in a bond strength of 23.82 kg/cm² (Table 1) which is significantly higher than the control of 14.02 kg/cm² and the pH 4 HCl value of 17.74 kg/cm².

Polyvalent Acids

Phosphoric acid (H₃PO₄) and aspartic acid (HOOC-CH₂-CHNH₂-COOH) were used in the series. Molarities of 0.1 and 0.01 at pH 4 were tested with phosphoric acid as well as pH 4 and 2 at a molarity of 0.1. Aspartic acid was evaluated as a 0.01 M pretreating solution at pH 4 and 2. Higher concentrations with aspartic acid exceeded the solubility limit.

The results of phosphoric acid treatment on bond strength are shown in Table 2. At pH 4 there is essentially no difference between samples treated with 0.1 and 0.01 M phosphoric acid, i.e., a bond strength of 13.42 kg/cm² and a value of 12.09 kg/cm², respectively.

TABLE I
The Effect of Monovalent Acids on Bond Strength

| Tooth No. | Control pH 6 kg/cm ² | HCl pH 4 kg/cm ² | HCl pH 2 kg/cm ² | HF pH 4 kg/cm ² |
|-----------|------------------------------------|--------------------------------|--------------------------------|-------------------------------|
| 20 | 16.73 (2) | 17.83 (2) | 32.12 (2) | 25.09 (2) |
| 22 | 17.34 (2) | 19.78 (2) | 37.57 (2) | 28.80 (2) |
| 23 | 12.61 (2) | 18.09 (2) | 50.17 (2) | 21.76 (2) |
| 25 | 9.38 (2) | 15.25 (2) | 29.23 (2) | 19.64 (2) |
| Aver. | 14.02 ± 1.86 | 17.74 ± 0.92 | 37.27 ± 4.64 | 23.82 ± 2.01 |

Control:HCl(pH 4) t = 3.19 p < 0.025

HCl(pH 4):HCl(pH 2) t = 4.57 p < 0.010

HCl(pH 4):HF(pH 4) t = 4.84 p < 0.010

() = no. of determinations

± S.E.M.

TABLE II
The Effect of Polyvalent Acids on Bond Strength

| Tooth No. | 0.01 M H ₃ PO ₄ pH 4 kg/cm ² | 0.10 M H ₃ PO ₄ pH 4 kg/cm ² | 0.10 M H ₃ PO ₄ pH 2 kg/cm ² | 0.01 M Asp. pH 4 kg/cm ² | 0.01 M Asp. pH 2 kg/cm ² |
|-----------|---|---|---|---|---|
| 20 | 10.32 (2) | 10.37 (2) | 30.12 (1) | 5.99 (3) | 29.02 (3) |
| 22 | 21.92 (2) | 10.58 (2) | 34.34 (1) | 12.61 (3) | 28.03 (3) |
| 23 | 13.99 (2) | 17.63 (2) | 36.53 (1) | 12.44 (3) | 23.39 (3) |
| 25 | 7.43 (2) | 9.74 (2) | 26.42 (1) | 9.36 (3) | 24.40 (3) |
| Aver. | 13.42 ± 3.13 | 12.09 ± 1.86 | 31.85 ± 2.26 | 10.10 ± 1.56 | 26.21 ± 1.37 |

0.01M H₃PO₄(pH 4):0.10M H₃PO₄(pH 4) t = 0.39 p = not significant

0.10M H₃PO₄(pH 4):0.10M H₃PO₄(pH 2) t = 13.29 p < 0.005

0.10M Asp.(pH 4):0.10M Asp.(pH 2) t = 6.40 p < 0.005

() = no. of determinations

± S.E.M.

Holding phosphate molarity constant at 0.1 M, there was a significant change in bond strength with a lowering of pH. At pH 4, the 0.1 M phosphoric acid value was 12.09 kg/cm² and at pH 2 the strength increased to 31.85 kg/cm².

These data relating increased bond

strength with a lowered pH correspond to the data obtained with hydrochloric acid. The value for phosphoric acid at pH 2 (31.85 kg/cm²) is not significantly different than that obtained with hydrochloric acid at pH 2, namely, 37.27 kg/cm².

After a few tests with phosphoric

acid, small to moderate numbers of irregularly shaped voids began to appear in the Addent adjacent to the enamel surface. Evaluation with fresh Addent, using phosphoric acid pretreatment, again resulted in void formation.

New teeth and fresh phosphoric acid were also evaluated, but the voids remained. Deletion of phosphoric acid resulted in an essentially smooth bond surface. Therefore, the presence of phosphoric acid at either concentration (0.1 or 0.01 M) and at either pH of 4 or 2 was in some way responsible for the formation of voids.

The presence of voids with phosphoric acid is not apparent with the first pretreatment. At least two to three pretreatments with the acid are needed in order for void formation to appear consistently. The data presented in Table 2 are from bond strength measurements recorded after voids began to appear.

Judging from the previous results, aspartic acid was expected to give an increase in bond strength with a decrease in pH. Small to moderate numbers of irregularly shaped voids began to appear consistently after the aspartic acid preliminary pretreatments. Data were then recorded.

Table 2 depicts the effects of aspartic acid pretreatment on bond strength. Aspartic acid at pH 4 had a bond strength of 10.10 kg/cm² and at pH 2 a value of 21.21 kg/cm². The difference was statistically significant. As with phosphoric and hydrochloric acids, the bond strength is inversely proportional to pH.

No significant degree of difference could be noted between the number, shape or size of the voids with aspartic acid as compared with those with phosphoric acid. A random sample of bonds, with voids, from either acid, was collected, photographed and en-

larged on graph paper. The average amount of surface area lost for attachment was calculated to be seven per cent.

A final control experiment after hydrochloric, hydrofluoric, phosphoric, and aspartic acid pretreatments had a value of 14.52 kg/cm², slightly but not significantly higher than the original control of 14.02 kg/cm².

Figure 3 is a bar graph depicting the effects of pH on bond strength for the four acids used in this study. Since molarity had no significant effect on bond strength, it was not necessary to include this variable.

With the monovalent acids there appears to be a direct relationship between bond strength and a lowering of pH. The polyvalent acids demonstrated no significant increase in bond strength until a pH of 2 was attained.

Although a bar graph is useful for presenting these data, it does not effectively encompass the rather large changes in hydrogen ion concentration in relationship to the changes in bond strength.

A change from pH 6 down to pH 4 represents a 200 fold increase in hydrogen ion concentration. With this change, the hydrochloric acid bond strength increased from 14.02 kg/cm² or about twenty-five per cent. The corresponding increase with hydrofluoric acid to 23.82 kg/cm² was about seventy per cent.

Similarly, from pH 6 to pH 2 the hydrogen ion concentration increases 400 fold. The bond strength over this same range for hydrochloric acid and for the polyvalent acids increases about 150 per cent and 100 per cent, respectively.

DISCUSSION

A definite correlation has been shown, by this investigation, between

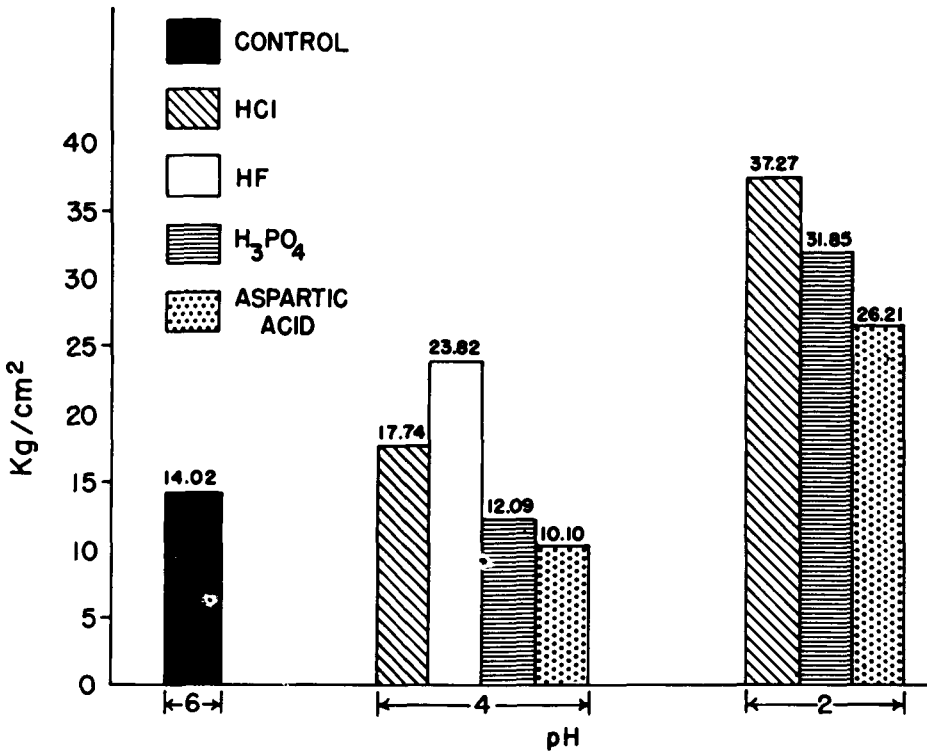


Fig. 3 Bar Graph of the effects of pH on bond strength, the value at the top of each bar is the mean bond strength.

an increase in bond strength and a decrease in pH of acidic pretreatment solutions.

The possibility of acid pretreatments increasing bond strength by exposing organic matter would seem to apply more to dentin than to enamel since enamel is mostly inorganic. The organic substance that might be exposed in the enamel would not contribute much to the bond strength because of its relative scarcity. Bowen¹⁰ has shown that the reason NPG-GMA surface-active comonomer increases bonding is due to the inorganic portion and not the organic constituent of enamel.

Hydrofluoric acid gave rise to a very significant increase in bond strength at pH 4 when compared with hydrochloric acid at the same pH. Recent investi-

gations by Glantz and Nyquist¹⁷ have shown that the application of an eight per cent stannous fluoride solution to the tooth surface has increased the wettability of the surface. This may be the reason for the significant increase in bond strength with hydrofluoric acid. These investigators referred to the ability of fluoride to increase wettability by reducing the free surface energy.

Both hydrochloric and hydrofluoric acid can increase the wettability of the enamel surface by removing adhesive contaminating materials such as organic plaques. They also have an etching effect which is proportional to a decrease in pH. The additional presence of fluoride in hydrofluoric acid is apparently of great importance for in-

creasing the wettability of the surface because the strengths of the bonds with hydrofluoric acid are significantly higher than those with hydrochloric acid. Consequently, the presence of fluoride appears to be beneficial in adhesive bonding.

One possible explanation for the failure of more concentrated solutions to increase bond strength is that the more concentrated the solution, the more likely it is to form ionic aggregates on the enamel surface and prevent the cleansing and etching effect by protons. Also, the ionic aggregates on the surface could be responsible for the formation of the voids, thus reducing bond strength. Whether it is the ionic aggregates that inhibit wettability and produce voids, or if it is a characteristic of all polyvalent acids to produce voids with Addent, is not known. Newman,¹⁸ however, has shown that phosphoric acid treatments increase wettability with water drops. This indicates that wettability is not inhibited by phosphoric acid and that the voids might be produced from a reaction between Addent and the polyvalent acids.

The reduction in bond strength below the control value with the polyvalent acid pretreatments at pH 4 can be attributed to the presence of voids in combination with the relatively small etching effects of these acids at pH 4. When the pH is lowered to 2, however, a very significant increase in bond strength is recorded. The finding of Koulourides and Buonocore¹⁹ that some of the polyvalent acids dissociate at a pH of approximately 2.6 to act essentially like a monovalent acid may be the reason for the increase in bond strength. The presence of the voids at pH 2 with the polyvalent acids is apparently the reason the bond strengths are so much lower than those of the monovalent acids, although the de-

crease is not significant. The voids will weaken the joint by crack propagation and the "built in zipper" effect as referred to by Zisman.²⁰

Using the same four teeth throughout the acidic pretreatment experiments and not having any visible deleterious effects occur on the enamel surface indicates that hydrochloric acid can be used in pretreatments at the pH levels attained in this study. Percentage solutions of hydrochloric and phosphoric acid, comparable to those used in other studies, have been found to have a pH range of -0.5 to 0.5. The lowest pH used in this study was 2.0.

A final observation is that the zinc phosphate cements used in orthodontics have been found to have a pH of about 1.6 during band cementation and that this may be maintained for fifteen to forty-five minute periods after cementation.²¹ Objections by some investigators to the use of pH 2 monovalent acids as pretreatment solutions should be reconsidered in view of the pH of zinc phosphate cements.

*College of Dentistry
University of Nebraska
Lincoln, Nebraska 68508*

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