Storage stability of solutions of pyruvic acid/glycine used in adhesive bonding

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The rate of deterioration of pyruvic acid/glycine solutions used as common pretreatment of enamel and dentin in the Gluma bonding technique was investigated. Bond strengths between composite resin and enamel/dentin were measured. The bonds were mediated by pyruvic acid/glycine solutions, applied from 0 to 6 months after the time of manufacture. Bond strengths to enamel varied between 8.6 and 13.5 MPa and to dentin between 6.2 and 18.0 MPa. The pH of the solutions rose slightly during the experimental period, but no statistically significant change in bond strengths was observed. □ *Composite resin materials; dental materials; dentin adhesives; operative dentistry*

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The Gluma dentin-bonding system has proven effective in mediating a bond between composite resin and dentin. Bond strengths as high as 18 MPa (1) and the ability to reduce considerably marginal gap formation (2) have been reported. The system, however, is somewhat complicated owing to the many steps involved in the technique: acid etching of enamel, ethylenediaminetetraacetic acid (EDTA) treatment of dentin, and application of Gluma Bond, followed by resin and composite.

Hansen (3) found that the effect of the Gluma system in reducing the width and extent of marginal contraction gaps in dentin cavities was impaired when the cavity walls had been etched with phosphoric acid. Deductively, a prerequisite for the effectiveness of the system is a limitation of acid etching to enamel only. Since this is not always easily controlled practically, a common pretreatment of enamel and dentin constitutes one way of advantageously simplifying the current technique.

In a study by Asmussen & Bowen (4) a solution of pyruvic acid and glycine proved effective as a common pretreatment. The solution, however, might be expected to decompose gradually and therefore to lack storage stability and practicability. It was the purpose of the present work to test the rate with which pyruvic acid/glycine solutions deteriorate.

Materials and methods

The materials used in the investigation are listed in Tables 1 and 2.

Human extracted teeth that had been kept

Table 1. List of proprietary materials used in the investigation

Material	Manufacturer	Batch no.
Danbond	B-W Dental ApS, Frederiksberg, Denmark	—
Durafill	Kulzer & Co., GmbH, Wehrheim, FRG	Aug. 86, 135
Scotchbond Etching Gel	Dental Products/3M, St. Paul, Minn., USA	8 CH
Silux Enamel Bond	Dental Products/3M, St. Paul, Minn., USA	8 A

Table 2. List of materials used to prepare Gluma, EDTA, and pyruvic acid/glycine solutions

Material	Manufacturer
Glutardialdehyde	E. Merck, Darmstadt, FRG
Glycine	E. Merck, Darmstadt, FRG
2-hydroxyethyl-methacrylate	Merck, Schuchardt, FRG
Pyruvic acid	Fluka AG, Buchs, Switzerland

in 1% chloramine solution since extraction were embedded in epoxy resin (Epofix, Struers, Denmark) and left for 24 h for the resin to polymerize. The teeth were then ground on carborundum paper no. 1000 until a flat enamel or dentin surface had been obtained.

Two aqueous solutions of pyruvic acid were prepared, with concentrations of 10% w/w and 20% w/w. Glycine was added to adjust the pH of both solutions to 2.2. The ground tooth surfaces were then treated as described in the following.

Dentin surfaces

The procedure included the following steps: 1) Pyruvic acid/glycine solution (PA/gly) was applied and gently rubbed with a swab for 20 sec and then left untouched for 40 sec. 2) The surface was rinsed with water for 15 sec and dried with compressed air. 3) Gluma was applied and gently rubbed with a small soft brush for 20 sec and then left untouched for 40 sec. 4) Excess reagent was removed with a blast of air. 5) The specimens were mounted in an assembly enabling a plug of filling material to be bonded to the treated surface. 6) A drop of enamel bonding resin (Danbond or Silux Enamel Bond) was applied and distributed with a blast of air. 7) Composite resin (Durafill) was packed into the hole of the mold (height = 2.5 mm; diameter = 3.5 mm) and pressed in contact with the resin-treated tooth surface and polymerized for 60 sec (Translux CL, Kulzer & Co. GmbH, FRG). 8) The bond test specimens were removed from the assembly and stored in water at 37°C for 24 h.

Enamel surfaces

For treatment of the enamel surfaces, steps 3 and 4 of the above procedure were omitted.

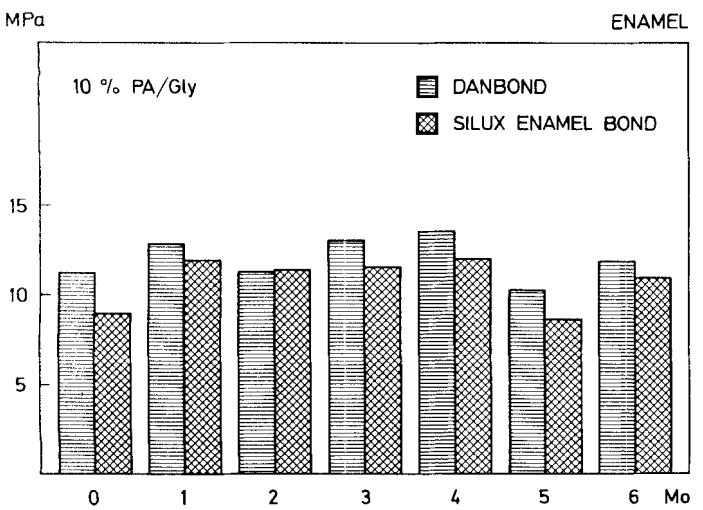

Fig. 1. Shear bond strengths (MPa) between enamel and composite resin. The enamel was etched with 10% pyruvic acid/glycine and treated with either Danbond (horizontally lined bars) or Silux Enamel Bond (cross-hatched bars). The abscissa indicates age of the pretreatment solution. Mean values. Pooled standard deviation = 2.25.

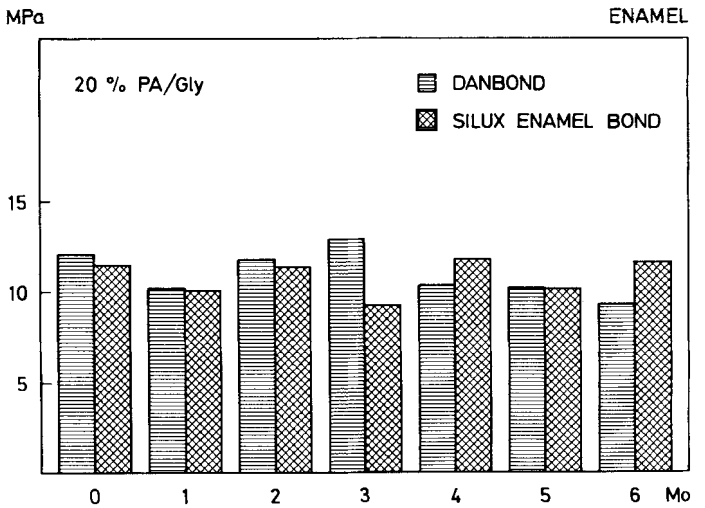

Fig. 2. Shear bond strengths (MPa) between enamel and composite resin. The enamel was etched with 20% pyruvic acid/glycine and treated with either Danbond (horizontally lined bars) or Silux Enamel Bond (cross-hatched bars). The abscissa indicates age of the pretreatment solution. Mean values. Pooled standard deviation = 2.39.

After the 24-h storage the shear bond strength was measured by use of a Universal Testing Machine (Instron Ltd., U.K.) at a cross-head speed of 1.0 mm/min, as previously described (5). Each series of experiments consisted of six specimens. The described set of experiments was performed on the day of manufacture of the PA/gly solutions (month 0) and once every month for another 6 months (months 1–6). At month 0, a control series was tested on enamel and dentin, in which phosphoric acid (Scotchbond Etching Gel) or 0.5 M EDTA, pH 7.4, was used instead of PA/gly in step 1 of the above procedure. At month 6, another control series was tested on dentin.

In connection with the monthly manufacture of bond test specimens, the pH of the PA/gly solutions was determined (pH/ion meter 135, Corning Medical & Scientific, U.K.).

The results were analyzed by use of Student's *t* test, analysis of variance, and linear regression analysis (6).

Results

The results of the shear tests are depicted in

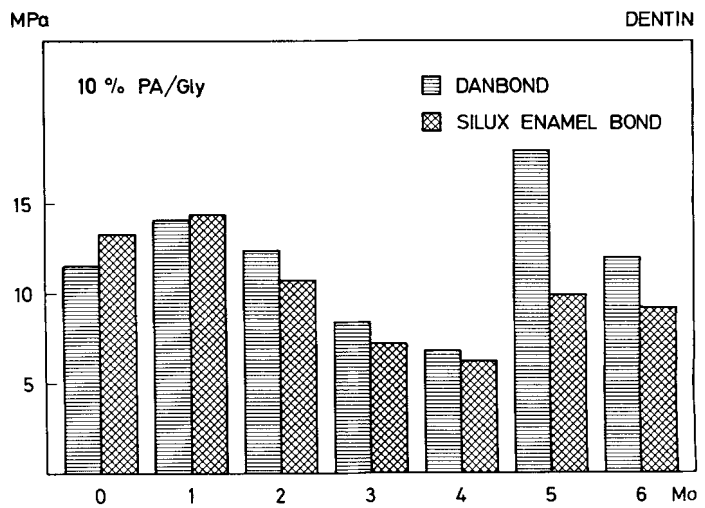

Fig. 3. Shear bond strengths (MPa) between dentin and composite resin. The dentin was treated with 10% pyruvic acid/glycine, Gluma, and either Danbond (horizontally lined bars) or Silux Enamel Bond (cross-hatched bars). The abscissa indicates age of the pretreatment solution. Mean values. Pooled standard deviation = 4.45.

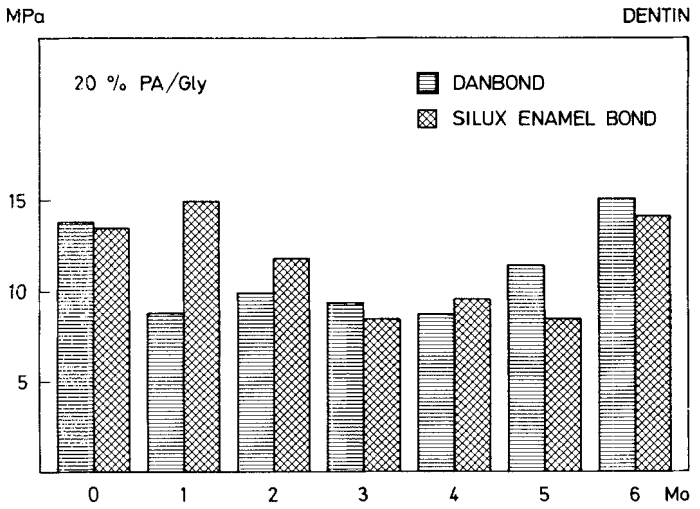

Fig. 4. Shear bond strengths (MPa) between dentin and composite resin. The dentin was treated with 20% pyruvic acid/glycine, Gluma, and either Danbond (horizontally lined bars) or Silux Enamel Bond (cross-hatched bars). The abscissa indicates age of the pretreatment solution. Mean values. Pooled standard deviation = 4.44.

Figs. 1–5. For each of the five figures, the standard deviations of all values measured were pooled. The pooled standard deviations are given in the legends to the illustrations. The results of the pH measurements are listed in Table 3.

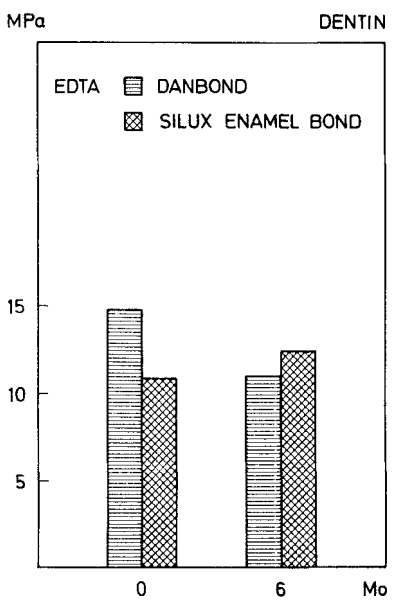

Fig. 5. Shear bond strengths (MPa) between dentin and composite resin. The dentin was treated with 0.5 M EDTA, Gluma, and either Danbond (horizontally lined bars) or Silux Enamel Bond (cross-hatched bars). Tests were performed at the beginning and end of the experimental period. Mean values. Pooled standard deviation = 3.85.

The mean bond strengths measured on enamel varied between 8.6 and 13.5 MPa and on dentin between 6.2 and 18.0 MPa. For each combination of tooth surface, PA/gly solution, and storage time (Figs. 1–4), the bond strengths obtained with Danbond and Silux Enamel Bond were compared by use of Student's t test. With one exception (Fig. 3, month 5) ($P < 0.05$), no statistically significant differences were found between the bond strengths of the two resins ($P > 0.05$). Accordingly, for each storage time, the results for the two resins were pooled, to give a new mean value and standard deviation (5).

For each of Figs. 1–4, linear regression analysis was carried out on the data obtained by the above pooling. In none of the four groups did the analysis show a decrease in bond strength during the experimental

Table 3. The pH values for the two solutions of pyruvic acid/glycine measured each month

Month	10% PA/Gly	20% PA/Gly
0	2.20	2.20
1	2.25	2.22
2	2.21	2.18
3	2.45	2.39
4	2.39	2.33
5	2.39	2.28
6	2.41	2.36

period ($P > 0.05$). In each of the four cases, then, the values may be assumed to be of equal magnitude. A new mean value and standard deviation was then computed from all the bond strengths measured for each of the four combinations of tooth surface and PA/gly solution. The pooled bond strengths and standard deviations obtained in this manner were 11.3 ± 2.49 MPa (Fig. 1), 10.9 ± 2.32 MPa (Fig. 2), 11.0 ± 5.20 MPa (Fig. 3), and 11.3 ± 4.77 MPa (Fig. 4).

Student's *t* test showed no statistically significant difference between the two control values measured at month 0 on enamel etched with phosphoric acid and treated with either Danbond (17.7 ± 2.80 MPa) or Silux Enamel Bond (17.3 ± 2.54 MPa) ($P > 0.05$). For the two enamel bond resins a joint mean value and standard deviation was calculated (17.6 ± 2.65 MPa). Compared with this enamel control value, the bond strengths obtained between composite resin and enamel etched with either of the two PA/gly solutions (11.3 ± 2.49 MPa and 10.9 ± 2.32 MPa) were significantly lower ($P < 0.0005$).

In Fig. 5, analysis of variance was performed on the four control values measured at month 0 and at month 6 on dentin surfaces treated with EDTA and either Danbond or Silux Enamel Bond. No statistically significant difference was found ($P > 0.05$). The bond strengths were then pooled to a joint mean value and standard deviation (12.7 ± 4.09 MPa). The bond strengths obtained between composite resin and dentin treated with either of the two PA/gly solutions (11.0 ± 5.20 MPa and 11.3 ± 4.77 MPa) were not statistically significantly different from this dentin control value ($P > 0.05$).

The pH values of the two PA/gly solutions measured each month and given in Table 3 were subjected to regression analysis, and in both cases a statistically significant increase in pH was found ($P < 0.05$).

Discussion

Gradually increasing the pH of a 10% w/w PA/gly solution from 2.2 to 2.8, Asmussen & Munksgaard (7) found an increase in bond strength to dentin and a decrease in bond strength to enamel. In the present study a pH of 2.2 was chosen so that bond strengths to enamel and dentin would be of similar magnitude. This was achieved at the expense of the bond strength to enamel, which was higher with phosphoric acid as enamel etchant. It is our opinion, however, that ensuring an optimal bond to dentin fully compensates for the decrease in bond strength to enamel.

Since concentrations of 10% w/w and 20% w/w gave similar bond strengths, the lower concentration is recommended because it has less tendency to form crystals at the screw cap.

The rise in pH registered over the 6 months supports the anticipation that a decarboxylation of the pyruvic acid takes place. The deterioration of the acid was not, however, manifested in the strengths of the bonds to either dentin or enamel within the experimental period. Thus, the storage stability of the PA/gly solutions may be considered to be of adequate length. It may be concluded that the solutions of pyruvic acid and glycine proved serviceable as common pretreatment of enamel and dentin in the Gluma technique.

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