Effect of resin cure mode and fluoride content on bracket debonding

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Abstract: Enamel decalcification around brackets is sometimes observed during and after orthodontic treatment. Reports in the literature suggest that the preventive advantage of fluoride-releasing adhesive resins may be compromised by an increased incidence of bond failure. The purpose of this study was to determine the effects on shear debonding of incorporating fluoride into the bracket bonding system. Another purpose was to determine the effect of polymerization mode on debonding. Orthodontic brackets were bonded to bovine enamel using one of three types of adhesive resin—no-mix, chemically cured, or light-cured—each formulated with and without fluoride. The teeth were stored in artificial saliva for 24 hours or 30 days and then debonded in shear. Data analysis was performed using ANOVA followed by post-hoc multiple comparison between group pairs. It was found that: (1) fluoride had either no effect or it increased the bond value; (2) the no-mix adhesive demonstrated the lowest bond value; (3) the duration of storage in artificial saliva had no effect on the bond value of the chemically cured and light-cured adhesives but did affect the no-mix adhesive; and (4) the no-mix adhesive released significantly less fluoride than the two other products. Thus, the presence of fluoride in the bonding adhesive does not reduce the force required to debond in shear, and chemically or light-cured adhesives provide consistently higher bond values over extended immersion times than the no-mix product.

Key Words: Orthodontic resin, Polymerization mode, Shear debond, Fluoride

The use of direct-bonded orthodontic brackets has increased rapidly since the procedure was first described by Newman[1] in 1965. Most of the predicted advantages of bonding over banding, including time savings and increased patient comfort, have been realized. Bonded brackets are considered easier for the patient to keep clean, which could reduce the risk of enamel decalcification. However, Gorelick et al.[2] found white-spot formation or decalcification of enamel in 50% of the patients examined, regardless of whether they had bonded or banded attachments. More recently, Ogaard et al.[3] reported that even a regimented program of brushing with a fluoride toothpaste did not prevent enamel decalcification around orthodontic brackets.

Fluoride-releasing adhesives were developed to help prevent decalcification around orthodontic appliances. Early attempts to incorporate fluoride into composites, however, resulted in significantly lower bond strengths in vitro.[4-6] In an in vivo study, Underwood et al.[7] found that fluoride had no effect on bond values, while it significantly reduced formation of early carious lesions.

When selecting an adhesive resin, the clinician must consider several important issues pertaining to the durability of bracket adhesion, including the effect of fluoride on initial bond strength and the effect of fluoride release over time. A search of the literature revealed no studies that directly and simultaneously address these issues.

The primary purpose of this study was to test the shear debond strength of brackets bonded to bovine enamel using three different orthodontic adhesives. The adhesives represented three different modes of resin polymerization: no-mix, chemically cured, and light-cured. Each adhesive was formulated with and without fluoride-releasing components. The effect of short- and long-term storage in artificial saliva on bond

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value was also examined. In addition, this study compared the time courses and quantities of fluoride released from the three adhesives.

Materials and methods

The six orthodontic resins used to bond mandibular incisor brackets to bovine incisors are listed in Table 1. These resins were specifically chosen because they represent three distinct types of cure mechanisms; the two resins of each cure type differed only by the presence or absence of fluoride-releasing components.

Bovine mandibular incisors (n=360) were debrided of periodontal attachment and refrigerated in 0.2% sodium azide (an antimicrobial agent). The facial surface of the enamel was flattened using silicon carbide abrasive to a final grit of 600 on a laboratory polishing device (Model 48-1581, Buehler Ltd, Lake Bluff, Ill). Care was taken to not expose the underlying dentin. A flat surface was required to minimize forces other than shear during the bracket debonding procedure. All teeth were stored in distilled water for 24 hours prior to bonding. After the brackets were bonded, the teeth were randomly divided into two groups and stored in artificial saliva for either 24 hours or 30 days. It was determined that the 30-day period was sufficient to allow a substantial amount of the diffusible fluoride to be released from the adhesives.

Table 1
Adhesives tested

Product	Lot number	Type	Fluoride
Rely-a-Bond	129073	No-mix	No
Rely-a-Bond	129173	No-mix	Yes
Phase II	169309	Chemical-cure	No
Phase II	161289	Chemical-cure	Yes
Light-Bond	69093	Light-cure	No
Light-Bond	129153	Light-cure	Yes

All products manufactured by Reliance Orthodontic Products, Inc, Itasca, Ill.

Bracket bonding

The flattened enamel surfaces were etched with 32% phosphoric acid gel (Ultradent Products, Inc, Salt Lake City, Utah) for 30 seconds, rinsed with a forced stream of water for an additional 20 seconds, then dried using a stream of oil-free air for 15 seconds. Lower incisor brackets (Cat. #563-418, American Orthodontics, Sheboygan, Wisc) were then bonded to the teeth following the manufacturer's directions. A 5-minute period was allowed for the initial set before the teeth were placed in the artificial saliva, where they were held for either 24 hours or 30 days prior to testing. The composition of the artificial saliva (g/L) was: methyl p-hydroxybenzoate, 2.00; carboxymethyl cellulose, 10.0; KCl, 0.625; $MgCl_2 \cdot 6H_2O$, 0.059; $CaCl_2 \cdot 2H_2O$, 0.166; K_2HPO_4, 0.804; KH_2PO_4, 0.326; sorbitol, 42.75.

Bracket debonding

The bonded teeth were mounted in a cylindrical brass jig using quick-setting dental stone[8] and secured in position so that the flattened facial surface was parallel to the flat area on the jig side, which oriented the facial surface perpendicular to the bottom of the cylinder. This arrangement permitted facile alignment of the specimen with respect to the debonding plane of the shearing fork. After the stone was set, the entire assembly was placed on a surveyor table on the lower platen of a universal testing machine (Model TTB, Instron Corp, Canton, Mass). The surveyor was adjusted so that the shearing blade was parallel to the flattened enamel surface and positioned in the bracket base close to the tooth surface to minimize bending moments (Figure 1). The shearing fork was lowered at a speed of 1.27 mm/min, and the load applied to the bracket was plotted on a calibrated strip chart recorder. The force applied at the moment of debonding was then measured from the chart. The results are presented in kg rather than MPa because it was not possible

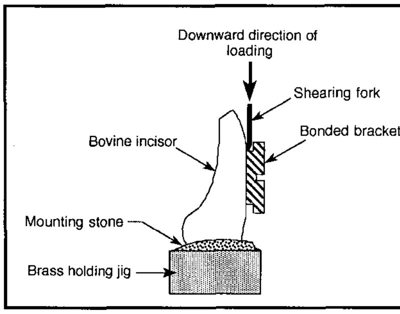

Figure 1
Schematic representation of the debonding apparatus

to determine the exact surface area of the meshwork at the base of the brackets. This measurement would be necessary to calculate the exact surface area of the resin at the interface in order to convert the data into units of stress. However, readers who want an estimate of the results in units of stress can multiply the debond load by a conversion factor of 0.985 to derive units of stress corrected for bracket surface area and expressed in megapascals.

Time course of fluoride release

The release of fluoride from the three fluoride-containing adhesives was determined during 30 days of immersion in artificial saliva. Three cured disks of each adhesive were fabricated by placing the material in a mold. Despite use of the mold, the thickness of the cured disks ranged from 0.243 to 0.480 mm. The top and bottom surfaces of each disk were coated with a single layer of nail polish so that fluoride release occurred

Table 2
Effects of fluoride and storage duration in artificial saliva on shear debond values of three orthodontic adhesives

Cure type	Storage Duration 1 Day	30 Days
No-mix		
without fluoride	9.8 ± 4.3	15.7 ± 5.1
with fluoride	8.0 ± 3.9	17.4 ± 4.5
Chemically cured		
without fluoride	20.0 ± 7.5	19.6 ± 3.9
with fluoride	22.1 ± 5.3	22.5 ± 4.8
Light-cured		
without fluoride	15.0 ± 5.9	16.7 ± 4.4
with fluoride	20.4 ± 5.4	22.2 ± 4.5

Data expressed as mean ± SD (n = 30). Horizontal and vertical bars indicate significant differences ($p < 0.05$) in mean debond values (kg) between pairs. There also were significant differences in values among the products (see text).

only from the edges. A lower incisor bracket, identical to those used in the bonding study, was adapted to the disk using sticky wax. Excess adhesive was removed using a high-speed handpiece. This method simulated the clinical environment of a bracket attached to a thin layer of adhesive the size of the bracket base, with only the peripheral edges exposed to saliva. The exposed adhesive surface area was calculated from its thickness and peripheral distance around the bracket base sides. After a 5-minute period to allow the initial set, the specimens were placed in individual test tubes containing 0.5 ml of artificial saliva. The tubes were sealed and placed on a rotary shaker set at 60 rpm. The control tube contained only artificial saliva.

Fixed volumes of artificial saliva (50 μL) were removed from the test tubes after 24 or 48 hours, or 5, 7, 11, 22, or 30 days. These samples and appropriate sodium fluoride standards were analyzed using an ion-specific electrode (Model 9409, Orion Research, Cambridge, Mass) after adjusting the pH to 5.0 by adding 50 μL TISAB buffer (Orion Research). The amount of fluoride released into the artificial saliva during each time interval was calculated by multiplying the fluoride concentration by the volume of artificial saliva remaining in the test tube. The cumulative amounts of fluoride released at each time point were calculated by adding the amounts removed from the test tubes with each previous sample.

Determination of fluoride content of the uncured adhesives

The fluoride concentrations of the uncured adhesive components were determined using the HMDS-facilitated diffusion method of Taves[9] as modified by Whitford.[10] This method quantitatively transfers the fluoride from the samples and standards into an alkaline trap, which is subsequently buffered and then analyzed using an ion-specific electrode. In the present application, a known mass of uncured adhesive sealant or paste was added to the bottom of a non-wettable, polystyrene diffusion dish. The alkaline trap (50 μL 0.05 N NaOH) was placed on the inside of the lid, which was then sealed to the bottom with petroleum jelly. Four mL of 1.5 N H_2SO_4 saturated with HMDS (hexamethyldisiloxane, Eastman Kodak, Rochester, NY) were then injected into the dish and the diffusion process was allowed to continue overnight to ensure complete fluoride recovery. The lid was then removed and 25 μL of 0.20 N acetic acid was added to the NaOH trap to adjust the pH to 5.0 immediately prior to analysis.

Statistical analyses

The data are presented as mean ± SD. Analysis of variance (ANOVA) was used to test for statistically significant differences among the mean shear debond values, with the independent variables being the presence of fluoride at two levels and resin curing type at three levels. Tukey's hsd post-hoc procedure was used to compare specific pairs of mean debond values to identify those comparisons that differed significantly from one another. Fisher's PLSD post-hoc test was used to detect significant differences among the mean fluoride release values after a one-way ANOVA. All statistical testing was performed using statistical software packages (StatView™ II, v 1.03, Abacus Concepts, Berkeley, Calif; SuperANOVA v 1.11, Abacus Concepts) at the 0.05% level of confidence.

Results

Shear debond values

The results of a three-way ANOVA among cure method, presence of fluoride, and storage time indicated that all main factors had a significant p-value. All interaction terms were also significant, with the exception of fluoride and storage time and the combination of all factors. Thus, a series of two-way ANOVAs were performed testing the effect of the presence of fluoride and storage time on bond values for each of the three methods of cure. Also, two-way ANOVAs were performed for the two different storage times testing the effect of cure type and presence of fluoride on shear debond value.

The debond values of the six adhesives are shown in Table 2. Compared with the corresponding products without fluoride, a statistically significant increase (p=0.01) was noted for the chemically cured product with fluoride after 30 days of storage in artificial saliva and for the light-cured product with fluoride at both time points (p<0.001). Storage time had no effect on the bond values of these two products but it was associated with a significant increase in bond value for the no-mix adhesive both with and without fluoride (p<0.0001).

There also were significant differences in shear debond values among the products. After one day of storage in artificial saliva, the values of the no-mix products with and without fluoride were weaker than those of the other two products (p=0.0001). Among the products without fluoride stored for 30 days, the bond strength of the chemically cured adhesive was greater than that of either of the other two adhesives (p=0.0035). Among the products with fluoride that were stored for 30 days, the chemically cured and light-cured adhesives had equivalent debond values, which were greater than that of the no-mix adhesive (p = 0.0001).

Fluoride release

Table 3 shows the fluoride concentrations of the uncured resin components as determined analytically after HMDS diffusion and as stated by the manufacturer. The concentrations determined in our laboratory were considerably lower than the stated concentrations. In the no-mix system, only the sealant contained fluoride. In the chemically cured system, one of the two liquids and one of the two pastes contained fluoride. In the light-cured system, both the sealant and the paste contained fluoride.

Figure 2 shows the 30-day time courses of fluoride release into artificial saliva from the cured fluoride-containing products. The data are normalized in terms of the surface area of the product exposed to solution. There was no evidence of a measurable release of fluoride from the no-mix product. Release from the other products showed an early burst, followed by a marked slowdown after day 2. The mean cumulative amount of fluoride released into artificial saliva from the chemically cured product was 0.18 and 0.25 μg/mm^2 after the first and 30th days, respectively. Mean fluoride release from the light-cured product was 0.20 and 0.28 μg/mm^2 after the first and 30th day, respectively. The amounts released from these two products did not differ with statistical significance, but they were greater ($p < 0.05$) than those of the no-mix product except on days 5, 7, and 30 ($p < 0.07$). Based on these findings, it was judged that a 30-day storage period in artificial saliva was sufficient to deplete the resins of the majority of diffusible fluoride; the potential effect of fluoride depletion on bond value could be tested after that period.

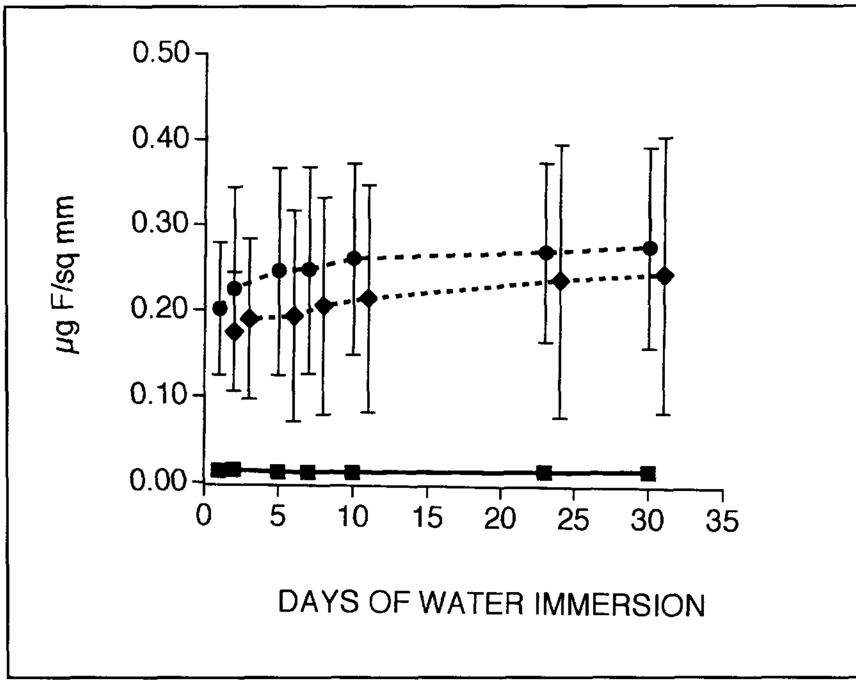

Figure 2
Time course of fluoride release (mean ± SD) from the cured fluoride-containing resins into artificial saliva: ♦ chemically cured; • light-cured; ▪ no-mix. (Chemically cured data has been advanced 1 day so that standard deviation values would not overlap those of the light-cured values.)

Discussion

The primary objective of this research was to determine whether the incorporation of fluoride into orthodontic adhesives had an effect on shear debond value. The no-mix product was not affected by fluoride after one day of storage in artificial saliva, nor was the chemically cured product (Table 2). However, fluoride incorporation increased the bond strength of the chemically cured product after 30 days of storage, and of the light-cured product at both time points. The reason for the increased bond strength is not known, but it may be related to increased wettability of the fluoride-containing resins caused by the presence of fluoride at a specific concentration during polymerization. It is believed that sodium fluoride is added to the resin phase of the bonding agents. Such incorporation may alter the surface tension of the liquid, enabling better coverage of the enamel (lower contact angle), and thus enhanced wettability.

The second objective of this study was to determine whether debond force would change as a function of the duration of storage (aging) in artificial saliva. It was anticipated that the bond values of the fluoride-containing adhesives might decrease with time due to the depletion of fluoride and its possible replacement with water. However, the only time-related change occurred in the no-mix product, which required increased force for debonding. The increase was not related to fluoride, as it was noted whether or not the adhesive contained fluoride.

The type of polymerization significantly affected the shear debond value of the adhesives (Table 2). Among the products without fluoride, the chemically cured adhesive demonstrated the highest debonding load. Among the products with fluoride, the chemically cured and light-cured systems were equivalent in value, and both were greater than that of the no-mix adhesive. These findings can be explained primarily by the extent of cure for each system. The greater debond value for chemically cured resins may be due to a more complete polymerization resulting from better mixing of the components. Polymerization of the light-cured resin was largely restricted to the bracket base periphery where the intensity of light was greatest. The no-mix systems were weakest under all conditions. This polymerization mechanism relies on diffusion of components into successive layers. A gradient in the extent of cure is established, with the maximum cure occurring at the primer-adhesive interface and progressively less cure on either side. Thus, the smaller the resin thickness, the more uniform the cure and the greater the bond strength.

Clinically, when ease of use and debond force reliability of an adhesive are valued equally, a fluoride-releasing, light-cured adhesive may be the resin of choice. This resin system would be indicated for use in high occlusal load regions in caries-prone patients. The no-mix system would be indicated in low-stress areas, such as the maxillary anterior teeth, and where ease of use is an advantage. The chemically cured adhesive, both with and without fluoride, showed consistently higher debond values after both short- and long-term storage in artificial saliva, indicating that it would have universal applications.

Table 3
Fluoride concentrations of resin components as determined analytically and as stated by the manufacturer

Product	Component	Fluoride concentration (mg/kg) By analysis	Manufacturer
No-mix	Primer	930	2200
	Paste	0	0
Chemical-cure	Primer	1520	2600
	Paste	960	4200
Light-cure	Primer	1080	2600
	Paste	1640	2800

The minimal debond loads required for a successful orthodontic adhesive have been reported in the range of 8 to 20 lbs or 3.6 to 9.1 kg.[11,12] Bond values as high as 50 lbs (22.7 kg) or more require special care in bracket removal to prevent damage to the enamel surface.[13] After 30 days of storage in artificial saliva, the debond values of the adhesives used in this study ranged from 15.7 kg for the no-mix product without fluoride to 22.5 kg for the chemically cured product with fluoride. Thus, all the materials tested had clinically-acceptable bond values.

The no-mix adhesive released almost no fluoride during the 30-day observation period. Fluoride was found only in the liquid sealant of this product (Table 3). In addition, by placing the no-mix components together, the sealant is diluted by a factor of 1:6 (one part sealant to six parts paste by weight), which reduces the amount of fluoride available for release. The other two products released similar amounts of fluoride, which were easily measured (Figure 2).

The measured fluoride concentrations of the adhesive components were lower than those stated by the manufacturers (Table 3). One company representative reported that fluoride concentrations are not verified analytically by the manufacturer, so there may be some variability from batch to batch. Nevertheless, the products contained considerable amounts of fluoride, some of which diffused from the chemically cured and light-cured adhesives into the artificial saliva. The percentage of fluoride released during the 30-day observation period ranged from 0.005% for the no-mix product to 0.09% for the light-cured product. These findings are consistent with slow diffusion and maintenance of composite structural integrity.

Conclusions

Based on the limitations imposed by the design of this study, the following conclusions can be drawn:

1. The presence of fluoride had either no effect or was associated with an increase in debond value for each of the adhesive resins tested.
2. Fluoride release rates from the chemically cured and light-cured adhesives into artificial saliva were greater than those from the no-mix adhesive. The rates were reduced to low values after the first week.
3. After 30 days immersion in artificial saliva, the majority of fluoride available for release remained in the adhesives.
4. Among the adhesives without fluoride, debond load was greatest for the chemically cured product.

5. Among the adhesives with fluoride, debond values of the chemically cured and light-cured products were equivalent to each other and greater than that of the no-mix product.

6. Thirty-day storage in artificial saliva nearly doubled the debond load value of the no-mix adhesive compared with one-day storage, but had no effect on the chemically cured or light-cured adhesives.

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Commentary: Effect of cure rate and fluoride content on bracket resin debonding

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This paper should put to rest forever the concept that adding fluoride to bonding resins, as we now know them, is effective. The authors point out that fluoride is generally added to resins to minimize the possibility of white spot lesions/ decalcification, and there has been a concern as to decreased bond strength.

The authors show very convincingly that neither tenet is valid: (1) fluoride is bound in the polymerization process and the amount of fluoride needed to prevent demineralization during orthodontic treatment is simply not released; and (2) the bond strength of the chemically cured and light-cured resins may be slightly enhanced.

The obvious question is: Why do we need fluoride that is not released effectively as a component of bonding resins? I submit that a slight increase in bond strength is insufficient reason.

There is no doubt that clinical orthodontists would be eager to have stronger bonding resins that could legitimately minimize demineralization in the noncompliant patient. Surely the manufacturers of these products know that the amount of fluoride released is negligible over the long-term, and therefore, ineffective for the purpose it was intended. Maybe it's time for manufacturers of these products to take a new look at developing a more effective method of preventing decalcification, or at least to openly disclose the amount of fluoride released over time from the polymerized resins.

The significance of this paper is that bond strength is one thing, and prevention of decalcification is another. My compliments to the authors.