

Moisture-insensitive adhesives: reactivity with water and bond strength to wet and saliva-contaminated enamel

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SUMMARY The purpose of this study was to investigate the reactivity with water of a moisture-insensitive orthodontic primer (Transbond MIP), in conjunction with a no-mix orthodontic adhesive (Unite), and a moisture-insensitive adhesive (Smartbond), and to assess their bond strength to wet and saliva-contaminated enamel relative to the conventional application of the no-mix adhesive. The reactivity of the moisture-insensitive products with water was investigated by micro-multiple internal reflectance Fourier transform infrared spectroscopy (micro-MIR FTIR). Sixty premolars were divided into two groups of 30 teeth each and, on the buccal enamel surfaces, a standardized volume (0.1 ml) of water or fresh whole saliva was applied. Standard edgewise stainless steel brackets were then bonded to enamel surfaces as follows: (a) Unite, (b) Unite with the Transbond MIP, and (c) Smartbond. The brackets were debonded under shear force at a speed of 2 mm/min and the debonded enamel surfaces were subjected to fractographic analysis. The statistical analysis of the bond strength values was performed by two-way ANOVA with condition (water, saliva) and adhesive type serving as discriminating variables ($n = 10$, $\alpha = 0.05$). The results of the fractographic analysis were evaluated by χ^2 test ($\alpha = 0.05$).

FTIR analysis showed that only Smartbond set in the presence of water. Application of water in Transbond MIP increased the extent of carboxyl ionization without inducing any setting reaction. Transbond MIP did not improve bond strength values when combined with the no-mix adhesive. Most adhesive-enamel condition combinations showed a trend to present lower bond strength in the presence of saliva; however, this was not confirmed statistically. Fractography of enamel and bracket base surfaces showed that Unite + Transbond MIP resulted in the most adhesive fractures (leaving no resin on enamel surface), whereas Smartbond presented the highest frequency of cohesive fractures (adhesive left on bracket and enamel surfaces).

Introduction

During recent years manufacturers have sought to enhance the performance of bonding systems in the presence of moisture by introducing novel materials (Kahl *et al.*, 1993).

The inefficiency of adhesive systems in the presence of moisture has long been known through studies showing substantial decreased bond strength for adhesive systems bonded to wet substrates (Bishara *et al.*, 1975). The detrimental effect of moisture on orthodontic

bonding may relate to water adsorption and exertion of a plasticizing effect in the polymer network from the creation of hydrated zones at polar monomer sites, and oxidation of pendant C=C bonds attached to the network which release by-products such as formaldehyde, so producing a plasticizing effect (Cook, 1984).

It must be noted, however, that the use of the terms 'moist' or 'wet' implies the presence of water, whilst saliva or crevicular fluid are considered 'contaminants'. Although the presence of

water can be prevented by adopting moisture-control precautions during bonding procedures, the orthodontist is often faced with the problem of bonding in an environment with increased contamination risk from saliva (Cacciafesta *et al.*, 1998a). This may be a particular concern in bonding partially erupted premolars, especially in the mandibular arch, where the majority of bracket failures are usually located (Cacciafesta *et al.*, 1998b). Problems arise because of the proximity of the adhesive to the cervical portion of the crown, the presence of crevicular fluid, the complex occlusal and masticatory loads, as well as the contour of the crown, which varies substantially for premolars (Eliades and Brantley, 2000).

While some manufacturers claim acceptable performance for their moisture-insensitive products in a wet environment, others have introduced moisture-active adhesives. The former type of product, which may be termed a moisture-resistant adhesive, is available in a primer formulation that replaces the conventional bonding agents applied to the enamel surface, and consists of an aqueous solution of methacrylate-functionalized polyalkenoic acid co-polymer and hydroxyethyl-methacrylate. This product has originally been used as a hydrophilic primer in dentine bonding systems marketed by the same manufacturer.

In contrast to the moisture-insensitive primer, moisture-active adhesives require rather than tolerate the presence of moisture to induce polymerization initiation. The moisture-active adhesive represents a distinct material available

as a cyanoacrylate-based paste formulation, applied to intentionally-wetted etched enamel without the use of a primer.

The purpose of this investigation was to study the reactivity of moisture-insensitive adhesives with water and to assess their shear bond strength to wet and saliva-contaminated enamel relative to a conventional no-mix, chemically-cured orthodontic adhesive.

Materials and methods

The moisture-insensitive primer, adhesive and the no-mix adhesive used in the study are shown in Table 1.

The reactivity of the moisture-insensitive primer and the moisture-active adhesive with water was studied by micro-multiple internal reflectance Fourier transform infrared spectroscopy (micro-MIR FTIR). An aliquot (10 μ l) of each product was applied onto a 2 \times 3-mm sampling surface of a refractive mini-crystal and spectra were acquired on an FTIR spectrometer (PE 1760 X, Perkin-Elmer Corp. Norwalk, CT, USA) equipped with a micro-MIR attachment operated under the following conditions: 4000–400 cm^{-1} range, 4 cm^{-1} resolution, 50 scans co-addition, KRS-5 mini-crystal of 45 degrees edge and seven internal reflections. To simulate the clinical application of the products in a wet environment, 3 μ l of tap water were brushed on the mini-crystal sampling surface, then the primer or the adhesive was applied, and spectra were again recorded and compared with the original spectra of the products.

Table 1 Polymerization initiation and compositional characteristics for the materials used in the study.

Material	Polymerization initiation and application	Resin compositional characteristics
Unite (3M Unitek) Chemically-cured (no-mix)	Paste-primer formulation. Application of liquid component on enamel and bracket base. No mixing is involved	Bis-GMA/TEGDMA monomers
Smartbond (Gestenco) Moisture-active	Paste formulation only. Initiation through exposure to water	Cyanoacrylate
Transbond MIP (3M Unitek) Hydrophilic factor	Primer formulation applied to enamel surface	Methacrylate-functionalized polyalkenoic acid co-polymer

Sixty premolars extracted for orthodontic purposes with sound buccal surfaces were used in the study. The teeth were stored in distilled water with 0.02 per cent sodium azide to inhibit bacterial growth. One week prior to bonding the teeth were stored in normal saline at 37°C. All buccal surfaces were cleaned with a rubber prophylaxis and fluoride-free pumice (3M Unitek, Monrovia, CA, USA), rinsed with water and acid etched with a 37 per cent orthophosphoric acid liquid (3M Unitek) for 30 seconds. Following water-rinsing and air-drying the teeth were divided into three groups (A–C), comprising 20 samples each. In half of the specimens of each group, the etched enamel surfaces were wetted with 0.1 ml of tap water applied with a syringe (Pronto Siringa, Artsana, Italy), whereas in the rest, the enamel was coated with 0.1 ml of whole saliva taken from one volunteer of good oral health receiving no medication *per os*. Standard edgewise (0 degree torque, 0 degree tip) premolar brackets (Ultra-Minitrim, Dentaaurum, Phorzheim, Germany) of 0.022-inch slot width, were used to minimize the implication of bracket face design in the modification of force application during testing (Katona and Moore, 1994). The brackets were bonded to the three groups of enamel specimens as follows:

1. *Group A:* The saliva- or water-coated enamel surface and the bracket base were coated with a thin layer of Unite primer (3M Unitek), the Unite paste was applied to the base, and the bracket was pressed firmly onto the etched enamel surface.
2. *Group B:* A thin layer of Transbond MIP (3M Unitek) was applied on the saliva- or water-coated enamel surface, the base of the bracket was coated with Unite primer, the Unite paste was applied as previously, and the bracket was pressed firmly onto the etched enamel surface.
3. *Group C:* The bracket base was covered with Smartbond adhesive (Gestenco International AB, Sweden), and bonded to the water-wetted or saliva-coated enamel surface.

The excess resin was carefully removed for all materials prior to polymerization. Following

setting, all teeth were mounted on acrylic blocks. For standardization purposes, a segment of a 0.019 × 0.025-inch stainless steel wire (ORMCO, Glendora, CA, USA) was ligated in the slot of each bracket, to provide a means for orientation and levelling of the buccal surface parallel to the direction of the applied force. The specimens were stored in normal saline at 37°C for one week and then were debonded under a shear force applied by a universal testing machine (Model 6022, Instron Corp., Canton, MA, USA) at a crosshead speed of 2 mm/min. The results of the bond strength study were analysed by two-way ANOVA with the type of adhesive (Unite, Unite with Transbond MIP, and Smartbond) and enamel condition (water wetting and saliva contamination) serving as discriminating variables. Differences among groups were further investigated using Scheffé multiple range test at $\alpha = 0.05$ level of significance.

The debonded enamel surfaces were examined with a scanning electron microscope (JXA 733 Superprobe, JEOL Ltd, Tokyo, Japan) to characterize the type of failure as resin adhesive (no resin remnants left on enamel surface), resin cohesive (enamel completely covered by fractured resin) or mixed (combination of the two). The statistical evaluation of the fractographic results was performed with the use of the Yates corrected χ^2 test with a 6 × 3 contingency table, at $\alpha = 0.05$ level of significance.

Results

Figure 1 illustrates the FTIR spectrum of Transbond MIP before and after water application. In the presence of water, the intensity of the hydrogen-bonded O-H vibrations (3500–3250 cm^{-1} stretching and 1642 cm^{-1} bending) increased. However, the intensity of the hydrogen-bonded unionized carboxyl dimer vibrations (2700–2500 cm^{-1} stretching) was reduced and the complex ester peak (1720 cm^{-1}) was shifted to lower frequency due to partial ionization of carboxyl groups. No differences were observed in the relative intensity of C=C stretching vibrations (1638 cm^{-1}) of the methacrylate moieties, which are related to

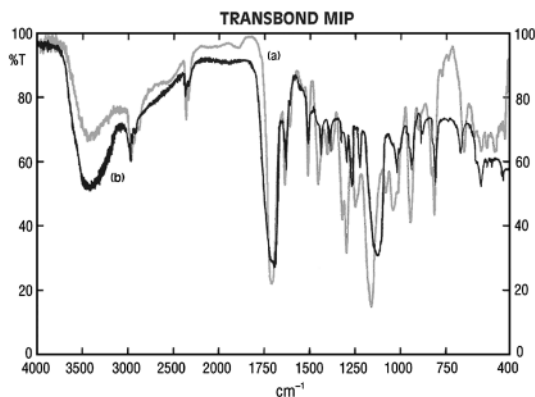


Figure 1 FTIR spectra of the Transbond MIP before (a) and after (b) addition of water.

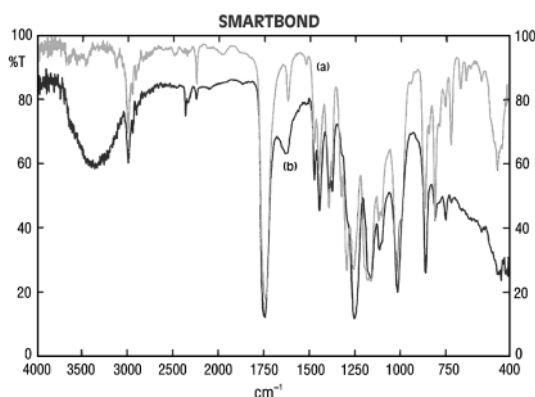


Figure 2 FTIR spectra of Smartbond adhesive before (a) and after (b) addition of water.

free-radical polymerization. The primer remained liquid.

In Figure 2 the FTIR spectrum of Smartbond before and after water addition is shown. The intensity of the original isocyanate group (NCO stretching at 2239 cm^{-1}) was reduced in the set film due to the formation on the polyurethane amide backbone. The adhesive was set producing a film rich in hydrogen-bonded water (O-H stretching at 3400 cm^{-1}), amine (N-H stretching at 3300 cm^{-1}), and CO_2 (2364 cm^{-1}).

Table 2 presents the ANOVA for the bond strength values obtained from the adhesive formulations and the conditions used. The results indicated that both material and condition had significant effects; the interaction term was also significant, precluding the assignment of effects to individual parameters, i.e. adhesive and condition (Sokal and Rohlf, 1995).

The differences among groups with respect to adhesive formulation and condition (water coating and saliva contamination) used are shown in Table 3. The conventional Unite and Smartbond adhesives presented the highest values, whilst the use of Transbond MIP resulted in significantly lower bond strengths. Although there was an apparent trend for the groups bonded to saliva-coated enamel to show decreased bond strength, this was not, as noted previously, verified statistically.

Figure 3 depicts two representative scanning electron images of debonded enamel surfaces demonstrating an enamel adhesive (Figure 3a) and a cohesive type of failure (Figure 3b). The results of the failure mode analysis are summarized in Table 4. The presence of saliva increased the frequency of adhesive failures in all the groups tested. Nevertheless, the highest frequency

Table 2 ANOVA for the bond strength values obtained with respect to the adhesive formulations (conventional Unite, Unite with MIP, and Smartbond) and enamel condition (water-wetted, saliva contaminated) employed in the study.

Source of variation	DF	Mean square	<i>F</i>	Probability > <i>F</i> *
Model	3	9731.5	24.6	0.000
Adhesive (A)	2	3769.2	9.5	0.000
Enamel condition (C)	1	21656.2	54.7	0.000
Interaction A × C	2	5738.3	14.5	0.000
Error	54	395.4		

*The value in this column represents the probability that the observed results could have occurred by random chance.

Table 3 Group differences for the three adhesive formulations (Unite, Unite with MIP, and Smartbond) at the two enamel conditions (water wetted, saliva contaminated) employed in the study ($n = 10$, $\alpha = 0.05$).

Material-condition group	Bond strength (n , mean \pm 1 SD)	Scheffé grouping*
Unite-(w)	89.8 \pm 26.9	A
Smartbond-(w)	70.3 \pm 24.1	A
Unite + MIP-(w)	29.7 \pm 20.7	B
Unite-(s)	28.3 \pm 14.9	B
Smartbond-(s)	26.2 \pm 11.7	B
Unite + MIP-(s)	21.4 \pm 13.5	B

*Means with same letter are not significantly different at the $\alpha = 0.05$ level.

(w), water; (s), saliva.

of adhesive failures was observed in the groups where Transbond MIP was used.

Discussion

The results of the FTIR study showed that the moisture-insensitive primer and adhesive tested demonstrate completely different reactivity with water. In Transbond MIP, water induces partial ionization of carboxyl groups, and an inert dilution effect without activating any setting mechanism. On the contrary, in Smartbond, water initiates a setting mechanism via

Table 4 Failure rates of the adhesives used in the study*.

Groups	Type of failure		
	Adhesive	Cohesive	Mixed
Unite-(w)	2	2	6
Unite + MIP-(w)	4	3	3
Smartbond-(w)	2	6	2
Unite-(s)	2	3	5
Unite + MIP-(s)	5	2	3
Smartbond-(s)	3	5	2

*Yates corrected χ^2 value = 42.8. DF = 10. $\alpha < 0.001$.

nucleophilic attack to isocyanate groups leading to a polyurethane film formation. This is a key difference in understanding the bonding mechanisms involved and the interfacial performance of these products in bond strength testing.

By applying a layer of Transbond MIP onto acid-conditioned enamel, in addition to micro-mechanical retention, a reversible hydrolytic bond mechanism may be established by breaking and reforming of carboxylate salt complexes formed between the ionized carboxyl groups of the methacrylate functionalized-polyalkenoic acid co-polymer and residual enamel calcium, providing some stress relaxation capacity. Besides, co-polymerization of the methacrylate

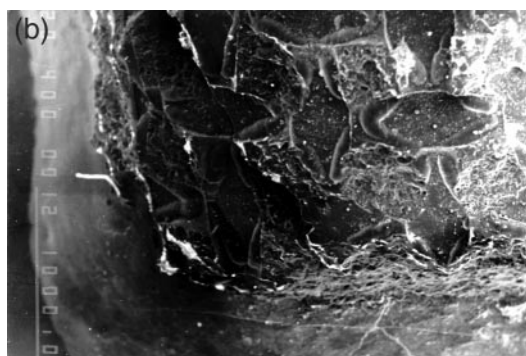
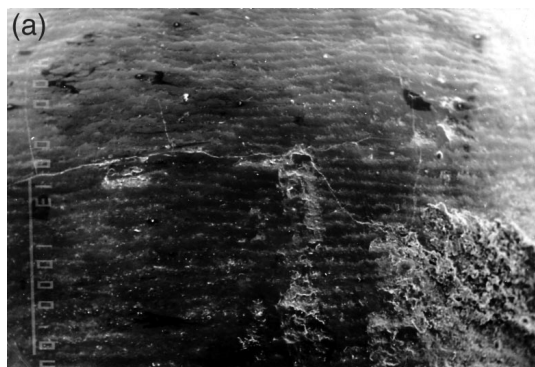


Figure 3 Scanning electron microscopic images of enamel following bracket debonding. (a) Adhesive resin failure of a bracket bonded to water-wetted enamel with Unite + Transbond MIP (original magnification $\times 40$; bar 1 mm). (b) Cohesive resin failure of a bracket bonded to water-wetted enamel with Unite (original magnification $\times 40$; bar 1 mm).

moieties of the co-polymer with the resin, the adhesive is mediated by the presence of the rapid responding monomer hydroxyethylmethacrylate. This may counterbalance the reduced extent of conversion of the methacrylate groups attached to the high molecular weight polyalkenoic acid co-polymer caused by steric hindrance (Eliades, 1994). In this manner, a dynamic equilibrium is set at the interface, incorporating the otherwise detrimental plasticizing effect of water into the bonding mechanism (Peters *et al.*, 1974).

Nevertheless, the findings of the present study suggest that Transbond MIP was ineffective in raising the bond strength of Unite no-mix adhesive in the presence of water. This result is in agreement with previously reported low bond strength values for this primer when combined with other orthodontic adhesives in the presence of moisture (Littlewood *et al.*, 2000). The fact that conventional formulation of Unite was found to be more effective than Unite-Transbond MIP may be explained by the presence of the very sensitive setting reaction of no-mix adhesives. Setting of these materials involves diffusion of the liquid resin brushed onto the bracket base and enamel surface into the paste through the application of pressure during bracket placement. Therefore, it seems that the application of Transbond MIP interferes with the polymerization process of the adhesive.

The poor performance of Transbond MIP seems to be associated with its highly hydrophilic nature, along with its participation in two interfaces possessing dissimilar characteristics. The presence of a hydrophilic factor may allow for improved wetting of etched enamel and possible involvement of the stress relaxation bonding mechanism discussed above. However, the interface with the adhesive paste seems to be disturbed due to incompatibility between the hydrophilic primer and the hydrophobic adhesive resin. This may result in poor diffusion of the liquid primer into the adhesive paste and inadequate co-polymerization. The increased frequency of resin adhesive failures observed in Transbond MIP treated groups supports such a mechanism.

The original dentine bonding system, where a primer similar to Transbond MIP was introduced,

incorporated the additional step of bonding resin placement prior to composite application. This resin consisted of a mixture of hydrophilic and hydrophobic monomers (i.e. Bis-GMA, HEMA) to improve compatibility. Thus, inter-mixing of the primer and bonding resin components facilitated homogeneity of free radical production, and effective co-polymerization of the primer and bonding resin components. However, this was not the case with Transbond MIP with the Unite no-mix adhesive system, where inter-mixing of the components seems difficult due to monomer incompatibility and viscosity difference. A potential improvement could involve inter-mixing of Transbond MIP and Unite Primer before application to etched enamel surface.

Smartbond is a single-phase, particle-filled adhesive based on cyanoacrylate chemistry, which sets in the presence of water, and this may be considered as an inherent advantage of the material. The setting reaction of this product involves two steps. First, isocyanate groups react with water, forming an unstable carbamic acid component, which rapidly decomposes to carbon dioxide and the corresponding amine, and secondly, the amine reacts with residual isocyanate groups, cross-linking the adhesive through substituted urea groups (Turner, 1980). However, in the presence of excess water, the first step of the reaction, namely the formation of amine and carbon dioxide, is enhanced, resulting in reduced film fracture toughness (Eliades and Eliades, 2000). An additional problem with these systems relates to the release of carbon dioxide during the prolonged setting reaction. The carbon dioxide formed is only capable of limited diffusion through the adhesive film as polymerization proceeds and may become entrapped, forming gaps or voids with possible detrimental effects on the interface strength as reported previously (Korbmacher *et al.*, 2000). The high frequency of cohesive failures of Smartbond in the presence of water may be explained by the presence of reduced network connectivity and bulk discontinuities due to void inclusion.

In the present study, the results of bond strength testing are expressed in force units (N)

as opposed to pressure units (Pa) since the transformation of force to pressure requires the estimation of the actual surface contact area, which is far from being approximated by the surface area of the rectangular base because of the base mesh design patterns (Eliades and Brantley, 2000). Moreover, dividing the force values by the base surface area to estimate the pressure values implies that the distribution of the load applied is homogeneous across the entire bracket base, a hypothesis that was proved to be erroneous (Katona and Chen, 1994). Finally, the practicality of reporting pressure units, which are irrelevant clinically, is questionable (Brantley *et al.*, 2000).

The effect of saliva on the alteration of polymeric material properties has not been investigated in the broader dental materials literature. It could be postulated that the presence of a high mucous protein content and enzymes would result in increased degradation reactions in the adhesive. While enzymatic degradation of dental polymers has been shown previously (Freud and Munksgaard, 1990), no documented evidence exists regarding saliva-induced alterations. Since material degradation reactions constitute a long-term process, their results may be masked by the immediate and more invasive action of water.

Although the overall poor strength of the adhesive combinations in the presence of saliva is clearly shown in Table 2, the statistical analysis precludes the extrapolation of this conclusion due to the significance of the interaction term at the 95 per cent confidence level (Sokal and Rohlf, 1995). Thus, the null hypothesis established in this study could not be rejected. This may be partly due to the high standard deviations obtained for all the material-enamel condition combinations, which led to the identification of a limited number of differences. Such a high standard deviation range, which reached 60 per cent of the mean, has been presented in previous studies (Korbmacher *et al.*, 2000) and may be attributed to various uncontrolled variables, such as differences in enamel topography and composition (Wheatherell *et al.*, 1972), or variations in the extent of enamel wetting from water and saliva.

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