Original article

Effects of composition on the hardness of orthodontic adhesives

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Abstract: Although there have been improvements in bracket systems precoated with adhesive, removal of adhesive remnants continues to be problematic. This study compared the hardness and maintainability of precoated adhesive with other commercial adhesives. Knoop hardness values were measured after light- or chemical-induced initial curing, immersion in distilled water at 37°C for 24 h and 1,000 and 10,000 thermal cycles after 24 h. Additionally, the forces required to move brackets by 0.5 mm were measured during bracket positioning, and brackets bonded to bovine enamel were examined by field-emission scanning electron microscopy. The Knoop hardness values of the precoated adhesives were lower than those of commercial resin composite adhesives, and hardness was dependent on the amount of filler in the resin matrix. The ability to maintain the device position may depend on the resin matrix composition. Precoated adhesives with less filler and more matrix material are light curable, and remnant resin may be easily removed.

Keywords; composite resins, dental bonding, hardness tests

Introduction

Orthodontic brackets and adhesives must be removed following treatment. Remnant adhesive on the teeth is removed using carbide bars and pliers; however, these instruments may damage the teeth [1]. Dimethacrylate resin composites are commonly used as orthodontic adhesives, and most can be light cured. However, the removal of any remnant resin is difficult and time consuming. The remnants exhibit high elastic coefficients and high hardness values due to the inclusion of inorganic fillers. Resins of the 4-methacryloyloxyethyl trimellitate anhydride/methyl methacrylate-*n*-butylborane (4-META/MMA-TBB) type (with no inorganic filler) have been widely adopted in Japan [2], not only as orthodontic adhesives [3,4] but also as a luting material for resin-bonded fixed partial dentures [5-8]. These resins are easy to remove because of the lack of filler but are inconvenient to handle due to the chemical curing required.

Adhesive-precoated brackets have been used widely in clinical orthodontics [9] as the tooth-bonding time is short [10]. Recently, systems precoated with “flash-free” adhesives have become available. The adhesive resin matrix is maintained on non-woven polypropylene on the bracket base. In addition, adhesive overflow is greatly reduced. Inorganic fillers are contained not only in conventional resin composite adhesives but also in precoated adhesives. However, the degree of hardness of precoated adhesive cured under brackets has not been determined. This study compared precoated adhesive with adhesives of differing composition relative to the degree of adhesive hardness and the ease of maintaining bracket position during the positioning process. The null hypothesis was that the degree of hardness of the precoated adhesive and the ability to maintain bracket position would not differ from adhesives with varying proportions of adhesive and filler.

Materials and Methods

Materials

The adhesives used are listed in Table 1. Two adhesives (XT adhesive: Transbond XT; 3M Unitek, Monrovia, CA, USA and 4-META/MMA-TBB adhesive: Super-Bond Orthomite; Sun Medical, Moriyama, Japan) were used to bond the ceramic brackets (Clarity Advance, 3M Unitek), and their hardness was also measured. Additionally, adhesive-precoated brackets (Precoated adhesive: APC Flash-Free Adhesive-Coated Appliance; 3M Unitek) were studied. With the brackets being held in position, 0.5 µg polyurethane sponges soaked in bonding agent (unfilled adhesive: Transbond XT primer; 3M Unitek) were pressed to the base of the brackets and bonded (cured) by light from a curing unit.

Knoop hardness

The brackets and adhesives were held with a polyester matrix tape between the movable tip of a height gauge (HDS-H30C; Mitutoyo, Kawasaki, Japan) and a metal slab. The adhesive thickness was 100 µm (Fig. 1). Light-cured adhesives were irradiated for 20 s by a hand-held curing unit (Optilux 501; SDS Kerr, Danbury, CT, USA). The brackets were removed from the height gauge and then re-exposed to light from the curing unit for an additional 20 s (initial curing). The 4-META/MMA-TBB adhesive, which is chemically cured, was held in place for 10 min until initial curing was achieved. Brackets with cured adhesives were immersed in distilled water at 37°C for 24 h following initial curing and then subjected to 1,000 and 10,000 thermal cycles between water baths at 4°C and 60°C (30 s dwell times in each bath). For each specimen in each period ($n = 8$), the Knoop hardness at the center of the adhesive bond to the bracket was measured using a microhardness tester (HMV-2; Shimadzu, Kyoto, Japan) after application of a 245.2 mN load for 15 s. Mean values were then calculated.

Bracket mobility

Bovine tooth crowns were embedded in self-curing acrylic resin (Tray Resin; Shofu, Kyoto, Japan) and adjusted so that the bracket-bearing surface lay parallel to the blade tip of a universal testing machine (5567; Instron, Norwood, MA, USA). The enamel surfaces were flattened and polished with waterproof silicon-carbide paper (#400, #600) to ensure that the experimental conditions remained constant. Immediately following the placement of adhesive on the bracket base, or immediately following the removal of a self-adhesive device from its package, the bracket was placed, in contact with the blade tip, onto a tooth surface treated according to the manufacturer's instructions (Fig. 2). The maximum force required to move the adhered bracket by 0.5 mm at a crosshead speed of 1 mm/min with a 1 kN load cell was measured. All measurements were performed at $23 \pm 1^\circ\text{C}$ and relative humidity of $50 \pm 5\%$.

Scanning electron microscopy

Ceramic brackets bonded to bovine enamel surfaces were examined using field-emission scanning electron microscopy (SEM; ERA-8800FE, Elionix Ltd., Tokyo, Japan). Each enamel surface was treated as recommended in the manufacturer's instructions. Next, ceramic brackets were bonded onto the enamel surfaces. Following immersion in distilled water for 24 h at 37°C, the bonded specimens were embedded in an epoxy resin (Epon 812; Nisshin EM, Tokyo, Japan) and sectioned longitudinally with a diamond

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Table 1 Adhesive composition

Adhesive/trade name, manufacture	Composition (wt%)
Unfilled/Transbond XT light cure adhesive primer, 3M Unitek, Monrovia, CA, USA	
[2-hydroxy-3-[4-[2-[4-[2-hydroxy-3-(2-methylprop-2-enoyloxy)propoxy]phenyl]propan-2-yl]phenoxy]propyl] 2-methylprop-2-enoate	45-55
2-[2-[2-(2-methylprop-2-enoyloxy)ethoxy]ethyl 2-methylprop-2-enoate	45-55
triphenylstibane	<1
2-(4-(dimethylamino)phenyl)ethanol	<0.5
<i>d,l</i> -camphorquinone	<0.3
hydroquinone	<0.03
Precoated/APC Flash Free Adhesive Coated Appliance, 3M Unitek	
2-[4-[2-[4-[2-(2-methylprop-2-enoyloxy)ethoxy]phenyl]propan-2-yl]phenoxy]ethyl 2-methylprop-2-enoate	30-45
[2-hydroxy-3-[4-[2-[4-[2-hydroxy-3-(2-methylprop-2-enoyloxy)propoxy]phenyl]propan-2-yl]phenoxy]propyl] 2-methylprop-2-enoate	30-45
polypropylene	10-20
silane treated ceramic	5-15
4-META/MMA-TBB/Super-Bond Orthomite, Sun Medical, Moriyama, Japan	
Super-Bond Catalyst V:	
partially oxidized tri- <i>n</i> -butylborane (TBB)	60-95
<i>n</i> -hexane	5-40
Super-Bond C&B Quick Monomer:	
methyl methacrylate (MMA)	70-99
2-(2-methylprop-2-enoyloxy)ethyl 1,3-dioxo-2-benzofuran-5-carboxylate (4-META)	3-20
Super-Bond Polymer brush-dip F3:	
poly(methyl methacrylate) (PMMA)	balance
sodium fluoride	<10
Super-Bond teeth primer:	
4-META	10-30
sodium sulfite	1-5
acetone	20-40
water	40-80
XT/Transbond XT light cure adhesive, 3M Unitek	
Transbond XT Adhesive in Syringes:	
dioxosilane;3-trimethoxysilylpropyl 2-methylprop-2-enoate	70-80
[2-hydroxy-3-[4-[2-[4-[2-hydroxy-3-(2-methylprop-2-enoyloxy)propoxy]phenyl]propan-2-yl]phenoxy]propyl] 2-methylprop-2-enoate	10-20
2-[4-[2-[4-[2-(2-methylprop-2-enoyloxy)ethoxy]phenyl]propan-2-yl]phenoxy]ethyl 2-methylprop-2-enoate	5-10
dioxosilane	<2
diphenyliodonium;hexafluorophosphate	<0.2
Etching gel:	
water	55-65
phosphoric acid	30-40
amorphous silica	5-10

Obtained from safety data sheet for each material

Fig. 1 Schematic image of specimen preparation for the Knoop hardness test. Specimens were held between the movable tip of a height gauge and a metal slab (adhesive thickness was 100 µm), followed by curing.

Fig. 2 Force required to maintain position. The force applied prior to perpendicular movement was measured.

saw (Isomet Low-Speed Saw; Buehler, Lake Bluff, IL, USA). The sectioned surfaces were polished to a high gloss with abrasive discs (Fuji Star Type DDC; Sankyo Rikagaku Co. Ltd., Okegawa, Japan), followed by diamond paste (DP-Paste; Struers, Ballerup, Denmark) to a particle size of 0.25 µm. All specimens were dehydrated in a series of tert-butyl alcohol baths (50% [v/v] for 20 min, 75% for 20 min, 95% for 20 min, and 100% for 2 h) and then transferred to a critical-point dryer (Model ID-3; Elionix Ltd., Tokyo, Japan) for 30 min. They were then subjected to argon-ion beam etching (EIS-200ER; Elionix Ltd.) for 40 s (acceleration voltage 1.0

kV, ion current density 0.4 mA/cm²) perpendicular to the polished surfaces. Finally, all specimens were coated with a thin film of gold in a vacuum evaporator (Quick Coater Type SC-701; Sanyu Denchi Inc., Tokyo, Japan) and examined using an operating voltage of 10 kV.

Statistical analysis

Descriptive statistics, including means and standard deviations were calculated for each group using SPSS software (SPSS Inc., Chicago, IL, USA). The Kolmogorov-Smirnov and Levene tests were used to verify

Table 2 Knoop hardness values (HK) by time

Adhesive	Time point			
	Initial curing	24 h after initial curing	1,000 thermal cycles after 24 h	10,000 thermal cycles after 24 h
Unfilled	3.0 (0.5) ^a	5.2 (0.5) ^a	8.2 (1.6) ^{b,c,f}	5.9 (1.1) ^{a,f}
Precoated	5.2 (0.4) ^a	6.8 (1.1) ^{a,b}	10.8 (1.0) ^{c,i}	10.0 (0.6) ^{c,d,j}
4-META/MMA-TBB	8.5 (1.2) ^{b,d,i}	13.0 (3.2) ^{c,i,j}	13.9 (2.6) ^j	9.4 (1.1) ^{c,i,j}
XT	25.6 (1.5) ^e	27.6 (4.2) ^e	36.3 (2.9) ^b	40.8 (5.1) ^b

Values are given as mean (SD) all in HK.

Superscript letters indicate significant differences ($P < 0.05$) between different letters, determined by the Games-Howell test.

Table 3 Force (N) required to maintain position of the adhesives

Adhesive	Mean force
Unfilled [†]	-
Precoated	0.54 (0.66) ^a
4-META/MMA-TBB	0.94 (1.03) ^{a,b}
XT	1.21 (0.48) ^b

Values are given as mean (SD) all in N.

Superscript letters indicate significant difference ($P < 0.05$) between different letters, determined by the Scheffé test.

[†]For unfilled adhesive, maintenance force could not be measured because the adhesive was cured while holding the bracket with dental tweezers.

the normality and homogeneity of variance. Differences in Knoop hardness values between groups were evaluated using the Games-Howell test, followed by two-way analysis of variance (ANOVA). To evaluate bracket mobility, the Scheffé test, followed by one-way ANOVA, was used to compare adhesives. P -values < 0.05 were considered to be statistically significant.

Results

Knoop hardness

Knoop hardness values (HK) of all adhesives are listed in Table 2. Two-way ANOVA was not performed because the Levene test revealed no homogeneity of variance even though the Kolmogorov-Smirnov test revealed normality. Multiple comparisons were performed among all groups. In all tests, the Knoop hardness values of the XT adhesive were highest, whereas those of the unfilled adhesive were lowest. For the precoated and XT adhesives, the hardness values at 1,000 and 10,000 thermal cycles were significantly higher than at initial curing and 24 h following initial curing. The hardness values of the unfilled resin and 4-META/MMA-TBB adhesives peaked at 1,000 thermal cycles and decreased at 10,000 thermal cycles to values similar to those at initial curing. For all of the adhesives, there was no significant difference between hardness at 1,000 and 10,000 thermal cycles.

Maintenance forces and bracket displacement

Maintenance forces (N) and bracket displacement are noted in Table 3 and Fig. 3. Maximum forces were attained at the initiation of force loading for all adhesives (Fig. 3). One-way ANOVA, based on the results in which the Levene and Kolmogorov-Smirnov tests revealed homogeneity of variance and normality, were statistically significant. The forces for precoated adhesives were significantly lower than those for the XT adhesive. When the 4-META/MMA-TBB adhesive is brushed on, the powder/liquid mixture is heterogeneous; therefore, the force required to maintain bracket position was rather wide. The force required to maintain the position of the unfilled adhesive could not be measured because the adhesive was cured while holding the bracket with dental tweezers.

SEM findings

Representative SEM images of ceramic brackets bonded to bovine enamel are shown in Fig. 4. All tested materials exhibited excellent adaptation between the enamel and adhesive. Although all adhesive layers were of similar thickness (approximately 100–200 μm ; Fig. 4a, c, e, g), their appearance was material dependent. A homogenous adhesive layer that appeared to be composed of dimethacrylate was observed for the unfilled adhesive (Fig. 4a). Additionally, gaps formed by the urethane sponges were apparent

Fig. 3 Typical curves of force required to maintain position for each adhesive. The curves peak at the initiation of displacement.

(Fig. 4b). For the precoated adhesive, irregularly sized filler particles were observed in the adhesive layers (Fig. 4d). With the 4-META/MMA-TBB adhesive, poly(methyl methacrylate) resin particles, 10–50 μm in diameter, were observed in the adhesive layers (Fig. 4f). For the XT adhesive, some plucking of irregularly shaped fillers was evident (Fig. 4h).

Discussion

Significant differences in Knoop hardness and bracket position stability of the tested adhesives were noted in this study. The null hypothesis was rejected as the grinding and immobilizing capacities of the adhesives differed. The Knoop hardness differed not only among adhesives but also among time periods. Freeman et al. used 1,000 thermal cycles during testing [11], more than the ISO standard of 500 cycles [12]. Approximately 10,000 cycles correspond to 1 year of clinical use [13,14]. Wattanawongpitak et al. examined the effect of thermal stress (0; 500; and 5,000 cycles) on resin composites, finding that marginal and cavity gap numbers depended on the number of cycles [15]. Jurubeba et al. reported that the bond strength of orthodontic adhesives was affected after $> 7,000$ thermal cycles [16]. In this study, Knoop hardness values did not change between 1,000 and 10,000 cycles. Therefore, grinding properties may not change over the course of several days to 1 year following treatment. Amato et al. recorded the Knoop hardness values of 1 mm thick samples of orthodontic adhesives, including Transbond XT, with the hardness of Transbond XT averaging 30 HK [17]. The values in this study for Transbond XT were similar, 25.6–40.8 HK, although the specimen size differed.

The proportion of filler affects the hardness of resin composites [18]. Of the adhesives in this study, the filler proportion was greatest in the XT adhesive (70–80%) and lowest in the precoated adhesive (5–15%). The Knoop hardness of the precoated adhesive was approximately 4-fold that of the XT adhesive, indicating that hardness depends on the relative proportions of filler and resin. The hardness of the precoated adhesive was 1.32–1.74-fold that of the unfilled adhesive and 0.52–1.06-fold that of 4-META/MMA-TBB, indicating the hardness of the precoated adhesive was similar to or less than that of 4-META/MMA-TBB.

On SEM of the unfilled adhesive, filler was absent from the methacrylate matrix resin supported by the polyurethane sponge ([a] scaffold; Fig. 4b). In the precoated adhesive, filler was sparsely scattered throughout

Fig. 4 Representative SEM images of ceramic brackets bonded to bovine enamel surfaces. An unfilled adhesive at magnifications of $\times 50$ (a) and $\times 200$ (b); a precoated adhesive at magnifications of $\times 50$ (c) and $\times 200$ (d); the 4-META/MMA-TBB adhesive at magnifications of $\times 50$ (e) and $\times 200$ (f); and the XT adhesive at magnifications of $\times 50$ (g) and $\times 200$ (h). Arrowheads indicate gaps created by the urethane sponge in the unfilled adhesive (b), inorganic fillers are scattered sparsely throughout the resin matrix of the precoated adhesive (d), poly methyl methacrylate particles in the 4-META/MMA-TBB adhesive (f), and plucking of inorganic fillers in the XT adhesive (h).

the methacrylate matrix resin. In the XT adhesive, filler distribution was uniform. The shape of the precoated adhesive filler differed from that of the XT filler. On SEM of 4-META/MMA-TBB resin, spherical methyl methacrylate polymers were absent from the adhesive layer. Resin composites change depending on the filler material. De Moraes et al. evaluated the material properties of nanofilled and nanohybrid flowable composites, finding those of nanohybrids were inferior [19]. In this study, SEM revealed differences in filler size among the adhesives containing inorganic fillers (Fig. 4d, h). The Knoop hardness values also differed significantly among these adhesives.

The maintenance forces of all adhesives peaked at the initiation of force loading. The resistance to loading of the XT adhesive was the highest among all of the adhesives tested, reflecting its high viscosity. Beun et al. found no correlation between rheological properties and filler proportion or particle shape [20]. Therefore, the ability to maintain position may

depend on the matrix resin proportion but not that of the filler. As the precoated adhesive specimens were too small to allow viscosity assessment, the ability to maintain position of the thin specimens was measured. The mean force required to maintain position of the precoated adhesive was approximately 0.5 N, significantly lower than that of the XT adhesive. Additionally, as the unfilled adhesive could not maintain bracket position until after being cured, the force required to maintain position could not be studied. Precoated adhesives are more readily removed, and the low-level Knoop hardness facilitates their placement onto brackets and convenient bracket positioning.

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Conflict of interest

The authors declare that there is no conflict of interest regarding the publication of this article.

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