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-tri-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 pressured 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 ± 1°C and relative humidity of 50 ± 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; Nissin EM, Tokyo, Japan) and sectioned longitudinally with a diamond...
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 1 Adhesive composition | Composition (wt%) |
|-----------------------------|-------------------|
| Adhesive/trade name, manufacture | Composition (wt%) |
| --- | --- |
| Unfilled/Transbond XT light cure adhesive primer, 3M Unitek, Monrovia, CA, USA | [2-hydroxy-3-[4-[2-[2-hydroxy-3-(2-methylprop-2-enoyloxy)propoxy]phenyl]propan-2-yl]phenoxy]propyl] 2-methylprop-2-enate 45-55 |
| 2-[2-[2-(2-methylprop-2-enoyloxy)ethoxy]ethyl] 2-methylprop-2-enate 45-55 |
| triphenylsilane <1 |
| 2-(4-(dimethylamino)phenyl)ethanol <0.5 |
| 4,4’-camphorquinone <0.3 |
| hydroquinone <0.03 |
| Precoated/AC Flash Free Adhesive Coated Appliance, 3M Unitek | 30-45 |
| 2-[4-[2-[2-(2-methylprop-2-enoyloxy)ethoxy]phenyl]propan-2-yl]phenoxy]ethyl 2-methylprop-2-enate 30-45 |
| [2-hydroxy-3-[4-[2-[2-hydroxy-3-(2-methylprop-2-enoyloxy)propoxy]phenyl]propan-2-yl]phenoxy]propyl] 2-methylprop-2-enate 30-45 |
| polypyrrole 10-20 |
| silane treated ceramic 5-15 |
| 4-META/MMA-TBB/Super-Bond Orthomite, Sun Medical, Moriyama, Japan | 60-95 |
| Super-Bond Catalyst V: partially oxidized tri-n-butylborane (TBB) | 60-95 |
| n-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 |
| Precoated tooth primer: | 10-30 |
| 4-META | 10-30 |
| sodium sulfite | 1-5 |
| acetone | 20-40 |
| water | 40-80 |
| XT/Transbond XT light cure adhesive, 3M Unitek | 70-80 |
| Transbond XT Adhesive in Syringes: dioxsilane;3-trimethoxysilylpropyl] 2-methylprop-2-enate 70-80 |
| [2-hydroxy-3-[4-[2-[2-hydroxy-3-(2-methylprop-2-enoyloxy)propoxy]phenyl]propan-2-yl]phenoxy]propyl] 2-methylprop-2-enate 10-20 |
| 2-[4-[2-[2-(2-methylprop-2-enoyloxy)ethoxy]phenyl]propan-2-yl]phenoxy]propyl] 2-methylprop-2-enate 5-10 |
| 2-methylprop-2-enate | <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

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**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.
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 (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 peaked at 1,000 thermal cycles and decreased at 10,000 thermal 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.

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 sponge were apparent (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]. Wattanasangpatik 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]. Juribe 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 hardness of Transbond XT (70-80 HK) and lowest in the precoated adhesive (5-15 HK) and 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 the XT adhesive (70-80 HK) and lowest in the precoated adhesive (5-15 HK).

On SEM of the unfilled adhesive, filler was absent from the methacrylate matrix resin supported by the polyurethane scaffold (Figs. 3b, d, f). For the precoated adhesive, filler was sparsely scattered throughout
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 particles in the 4-META/MMA-TBB adhesive (f), and plucking of inorganic fillers in the XT adhesive (h).

**Fig. 4** Representative SEM images of ceramic brackets bonded to bovine enamel surfaces. An unfilled adhesive at magnifications of ×50 (a) and ×200 (b); a precoated adhesive at magnifications of ×50 (c) and ×200 (d); the 4-META/MMA-TBB adhesive at magnifications of ×50 (e) and ×200 (f); and the XT adhesive at magnifications of ×50 (g) and ×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 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.

**References**

1. Boyer DB, Engelhardt G, Bishara SE (1995) Debonding orthodontic ceramic brackets by ultrasonic instrumentation. Am J Orthod Dentofacial Orthop 108, 262-266.
2. Miura F, Nakagawa K, Masuhara E (1971) New direct bonding system for plastic brackets. Am J Orthod 59, 330-361.
3. Sirinungsing S, Saito K, Hayakawa T, Kasi K (2004) Efficacy of using self-etching primer with a 4-META/MMA-TBB resin cement in bonding orthodontic brackets to human enamel and effect of saliva contamination on shear bond strength. Angle Orthod 74, 251-258.
4. Tsuruoka T, Namura Y, Shimizu N (2007) Development of an easy-debonding orthodontic adhesive using thermal heating. Dent Mater J 26, 78-83.
5. Shimizu H, Takahashi Y (2004) Retainer design for posterior resin-bonded fixed partial dentures: a technical report. Quintessence Int 35, 653-654.
6. Matsumura H, Shimizu H, Tanoue N, Koizumi H (2011) Current bonding systems for resin-bonded restorations and fixed partial dentures made of silver-palladium-copper-gold alloy. Jpn Dent Sci Rev 47, 82-87.
7. Minami H, Minesaki Y, Suzuki S, Tanaka T (2012) Twelve-year results of a direct-bonded partial prostheses in a patient with advanced periodontitis: a clinical report. J Prosthet Dent 108, 69-73.
8. Nakamura M, Matsumura H (2013) Fifteen-year clinical performance of a resin-bonded fixed partial denture sealed with a thione primer and a tri-n-butylboranate-initiated luting agent. J Oral Sci 55, 263-266.
9. Verstrynge A, Ghesquiere A, Willems G (2004) Clinical comparison of an adhesive precoated vs. an uncoated ceramic bracket system. Orthod Craniofac Res 7, 15-20.
10. Lee M, Kanavakis G (2016) Comparison of shear bond strength and bonding time of a novel flash-free bonding system. Angle Orthod 86, 265-270.
11. Freeman R, Varanasi IA, Meyers LA, Symons AL (2012) Effect of air abrasion and thermocycling on resin adaptation and shear bond strength to dentin for an etch-and-rinse and self-etch resin adhesive. Dent Mater J 31, 180-188.
12. International Standard for Organization (1994) Dental materials-guidance on testing of adhesive to tooth structure. ISO/TR 11405:1994 Geneva.
13. Gale MS, Darvell BW (1999) Thermocycling procedures for laboratory testing of dental restorations. J Dent 27, 89-99.
14. Moresi AL, D’amario M, Capogreco M, Gatto R, Marzo G, D’arcangelo C et al. (2014) Thermal cycling for restorative materials: does a standardized protocol exist in laboratory testing? A literature review. J Mech Behav Biomed Mater 29, 395-398.
15. Wattanawongpitak N, Yoshikawa T, Burrow MF, Tagami J (2007) The effect of thermal stress on bonding durability of resin composite adaptation to the cavity wall. Dent Mater J 26, 445-450.
16. Jurubeba JEP, Costa AR, Correr-Sobrinho L, Tubel CAM, Correr AR, Vedovello SA et al. (2017) Influence of thermal cycles number on bond strength of metallic brackets to ceramic. Braz Dent J 28, 206-209.
17. Amato PA, Martins RP, dos Santos Cruz CA, Capella MV, Martins LP (2014) Time reduction of light curing: Influence on conversion degree and microhardness of orthodontic composites. Am J Orthod Dentofacial Orthop 146, 40-46.
18. Suzuki S, Ori T, Saimi Y (2009) Effects of filler composition on flexibility of microfilled resin composite. J Biomed Mater Res B Appl Biomater 74, 547-552.
19. de Moraes RR, Gonçalves Lde S, Lancellotti AC, Consani S, Correr-Sobrinho L, Sinhoreti MA. Nanohybrid resin composites: nanofiller loaded materials or traditional microhybrid composites? Oper Dent 34, 551-557.
20. Beun S, Bailly C, Devaux J, Leloup G (2008) Rheological properties of flowable resin composites and pit and fissure sealants. Dent Mater 24, 548-555.