# **ORIGINAL ARTICLE**

# A New Acrylic-based Fluoride-Releasing Cement as a Potential Orthodontic Bonding Agent

# LI SU<sup>1</sup>, YUXING BAI<sup>1</sup>, SONG LI<sup>1</sup>, OMAR T. AL-NAIMI<sup>2</sup> & JOHN F. MCCABE<sup>2</sup>

<sup>1</sup>School of Stomatology, Capital Medical University, Beijing, People's Republic of China, and <sup>2</sup>Dental Materials Science Unit, School of Dental Sciences, Newcastle University, Newcastle upon Tyne, UK

#### Abstract

**Objective.** To develop a fluoride-releasing, acrylic-based 'easy on, easy off' bracket cement as a potential orthodontic bonding agent. **Material and methods.** Three experimental cements were prepared in powder/liquid forms by mixing different ratios of methylmethacrylate (MMA) and 2-hydroxyethyl methacrylate (HEMA) to form the liquid (L) and sodium fluoride (NaF) and polymethylmethacrylate (PMMA) to form the powder (P). The resultant materials were tested for setting characteristics, fluoride release, hardness, strength, shear bond strength (SBS) and adhesive remnant index in comparison with resin composite and glass ionomer, which were used as control materials. The data were analyzed using ANOVA and the Kruskal–Wallis and Mann–Whitney tests. **Results.** The experimental groups had satisfactory setting characteristics. Fluoride release of the group containing P (10% NaF, 90% PMMA) and L (60% MMA and 40% HEMA) was similar to that of glass ionomer. When experimental materials were stored in water for 7 days, their hardness was reduced and stabilized at a value lower than those for composite and PMMA. Strength was only slightly affected by water storage. The SBSs of the experimental groups were considered clinically acceptable at both 30 min and 1 month. The group containing P (10% NaF, 90% PMMA) and L (90% MMA and 10% HEMA) had a higher mean SBS than the other two experimental groups. At 1 month, there were significantly less adhesive remnants observed on the surface of enamel after debonding for the experimental groups compared with the composite. **Conclusion.** The new cement could potentially be useful as an orthodontic bonding agent.

Key Words: Fluoride release, hardness, setting characteristic, shear bond strength, shear punch strength

# Introduction

Direct bonding of orthodontic attachments using the acid etch technique has been carried out routinely in orthodontic practice for many years. However, in contrast to the bonding technique used in restorative dentistry, the orthodontic adhesive will be removed upon the completion of treatment, so there is a need to preserve the integrity of the tooth as much as possible, both during treatment and after debonding. However, loss of enamel may occur in one of four ways: after etching; enamel fracture at debonding; enamel damage during the post-debonding cleanup procedure [1,2]; and decalcification during the course of orthodontic treatment. Much research has focused on the reliability of the adhesive system and to some extent on preventing decalcification during the course of orthodontic treatment by using fluoride-releasing materials as well as oral hygiene measures. However, less research has focused on the possibility of reducing enamel damage during and after bracket removal. The clean-up procedure of the adhesive following debonding is not only time-consuming for the operator and uncomfortable for the patient, but may also remove up to 55.6  $\mu$ m of surface enamel [1] and sometimes may even cause enamel cracks [3].

Currently, composite resins are the most widely used bonding agents in fixed orthodontic treatment. They combine high adhesion values with easy handling; however, enamel fracture and enamel lesions during debonding of the brackets remain the most frequently encountered problems. Unlike the rigid cross-linked network of bisphenel-a-Glycidyl. Methacrylate (bis-GMA)-based systems, polymers of acrylic resins are linear or only lightly cross-linked, which results in a softer, more flexible and potentially weaker

(Received 14 November 2009; accepted 26 February 2010)

ISSN 0001-6357 print/ISSN 1502-3850 online © 2010 Informa UK Ltd. (Informa Healthcare, Taylor & Francis AS) DOI: 10.3109/00016351003745522

Correspondence: John F. McCabe, Dental Materials Science Unit, School of Dental Sciences, Newcastle University, Framlington Place, Newcastle upon Tyne, NE2 4BW, UK. Tel: +44 191 2228294. Fax: +44 191 2226137. E-mail: j.f.mccabe@ncl.ac.uk

material [4]. However, the comparatively poorer physical properties may aid the removal of the bonded bracket at the end of treatment and tends to leave a clean tooth surface and results in a reduced clean-up time [2,5]. This study was, therefore, designed to improve the properties of acrylic resin as a potential orthodontic adhesive by formulating an acrylic-based material containing sodium fluoride (NaF) and 2-hydroxyethyl methacrylate (HEMA). Fluoride is a well-documented anti-caries agent, which can enhance remineralization of early enamel caries and produces enamel which is more resistant to subsequent demineralization [6]. The water-soluble HEMA is a vinyl monomer frequently used as a hydrophilic polymerizable component and as a hydrophilic primer in dental bonding resins [7]. Its hydrophilicity and associated water absorption are considered to have the potential to gradually make the acrylic resin softer and weaker, which may aid debonding at the end of treatment and may also facilitate fluoride diffusion.

The purpose of the present work was to assess the characteristics of the new acrylic-based cement as a potential orthodontic bonding agent. Key properties to be considered were: setting characteristics, fluoride release, hardness, shear punch strength, shear bond strength and adhesive remnants index. A resin-based composite and glass ionomer cement (GIC) were used as controls and the null hypothesis for statistical purposes was that the properties of the experimental material would not differ significantly from those of the controls.

# Material and methods

# Materials

Three experimental groups (EX1–3; see Table I) were prepared by mixing different ratios of HEMA, methylmethacrylate (MMA), NaF and polymethylmethacrylate (PMMA). For all groups, 2 g of powder was mixed with 1 ml of liquid. For assessing setting characteristics, unmodified PMMA was used as a control. For assessing fluoride release, GIC was prepared as a control. For assessing hardness and

Table I. Composition of the experimental and control groups.

strength, PMMA and a light-cured composite were used as controls. For assessing shear bond strength, a light-cured composite was used as a control (Table I).

## Setting characteristics

A differential scanning calorimeter (DSC 823<sup>e</sup>; Mettler Toledo, Zürich, Switzerland) was used to determine the time of polymerization and the relative heat generated during polymerization at both 23°C and 37°C. Throughout the experiments, the differential scanning calorimeter (DSC) unit was operated isothermally at 23°C or 37°C. The test material was mixed and packed into a standard aluminium crucible (2 mm deep, 5 mm diameter). The crucible containing the test material was inserted into the chamber of the DSC and the reaction monitored. After completion of the test, each specimen was weighed and the net weight of the material used was determined by subtraction of the weight of the crucible. Three separate determinations were made for each material at both 23°C and 37°C. The heat of polymerization and the time of polymerization, as indicated by the time to reach the maximum temperature during the exothermic reaction, were measured automatically using version 9.0x of the STAR<sup>e</sup> software, Mettler Toledo, Zurich, Switzerland.

# Fluoride release and weight changes

Three disc specimens of each material were prepared in a plastic mould (15 mm inner diameter, 3 mm thickness) which was supported on a glass plate and polyester strip. A second strip and glass plate were then applied to the top surface of the mould and the material compressed using a screw clamp (50 N). For EX1–3, the specimens were removed from the moulds after 20 min and ground using dry 1200-grit silicon carbide paper. Then, the diameter and thickness of the specimens were measured, and weight was recorded using a digital balance. They were placed horizontally into plastic containers containing 5 ml of distilled and deionized water and

Twee T composition of the experimental and control groups						
	Powder		Liquid			
Group	PMMA (wt%)	NaF (wt%)	MMA (vol%)	HEMA (vol%)		
Ex1	90	10	60	40		
Ex2	95	5	60	40		
Ex3	90	10	90	10		
Control group 1 (PMMA)	100	0	100	0		
Control group 2 (GIC)	Ketac <sup>™</sup> Fil Plus (3M	Ketac <sup>™</sup> Fil Plus (3M ESPE, Germany), glass ionomer cement				
Control group 3 (Composite)	Transbond XT (3M Unitek, USA), composite luting material					

stored at  $37^{\circ}$ C. The preparation of specimens of GIC controls was similar except that they were allowed to set in their mould for 24 h at  $37^{\circ}$ C and 100% relative humidity before being removed.

The water in the containers was changed daily for the first week, then every 3 days up to 1 month and weekly thereafter. Fluoride ion released over a 24-h period was measured using an ion-selective electrode (Orion Research, Thermo Scientific, Waltham, MA, USA) daily for 7 days, then weekly up to 28 days and finally monthly up to 112 days. The final results were reported as fluoride-release rate ( $\mu g/cm^2/day$ ).

Each of the specimens were weighed at regular intervals by removing them from the storage water, drying with a soft tissue, waving in the air for 15 s and then weighing on a digital analytical balance.

#### Martens hardness evaluation

Preparation of the specimens was the same as for fluoride release. For EX1-3 and PMMA, the specimens were removed from the moulds after 20 min. For composite, the specimens were irradiated for 40 s from each side with a Visilux<sup>TM</sup>2 Visible Light Curing Unit (3M ESPE, Seefeld, Germany). All specimens were ground using dry 1200-grit silicon carbide paper to ensure parallel surfaces. The test was made on a Zwick Universal testing machine with a hardness measurement head (Zwick Z 2.5; Zwick GmbH & Co., Ulm, Germany). The distance between the specimen's top surface and the hardness measurement head was initially 9 mm for all tests. The initial head speed approaching the specimen was 0.1 mm/min. After the head sleeve touched the specimen, the approach speed of the diamond indenter until initial contact with the specimen was 0.025 mm/min. Three indentations were made on one side of each specimen. The determined values were averaged to represent the Martens Hardness (HM) of the specimen. The tests were carried out at an indenter load of 200 g. HM was measured automatically using TestXpert<sup>®</sup> software (Zwick GmbH & Co.)and was expressed as newtons per square millimetre. The test was conducted 30 min after the specimens were made and at 7 and 28 days after storage in water at 37°C.

# Shear punch strength test

The materials were sandwiched between two glass plates covered with polyester film, with the thickness and diameter being controlled using a plastic mould. After 20 min, disc specimens of EX1–3 and PMMA were removed from the moulds. The specimens of composite were irradiated for 40 s from each side with a Visilux2 Visible Light Curing Unit. All specimens were polished with 1200-grit silicon carbide dry paper. Ten specimens were prepared for each group. All the specimens were nominally 0.5-mm thick and 10 mm in diameter, although the actual thickness and diameter were measured with a micrometer just before testing. Strength was determined using a punch test by means of the Instron (High Wycombe, UK) universal testing machine. The testing equipment and procedure have been described in detail before [8]. The punch displacement rate was 1.0 mm/min. The shear punch strength (MPa) was calculated as follows:

> force (N)/specimen thickness (mm) × punch circumference (mm)

The tests were conducted at 30 min after the specimens were made and at 7 and 28 days after the specimens were stored in distilled water at  $37^{\circ}$ C.

#### Shear bond strength test

A total of 144 sound premolars, without visible caries, decalcification, fractures or other defects and extracted for orthodontic purposes from patients aged <18 years were collected and stored, refrigerated, in 0.5% aqueous chloramine. All teeth were used within 6 months of extraction. The teeth were divided randomly into four groups, each consisting of 18 upper and 18 lower premolars. The roots were notched and embedded in cold-cure acrylic denture base blocks with the long axis of the tooth vertical. Care was taken to ensure that the sides of the mount-ing blocks were parallel to the vertical axis of the tooth. The specimens were then stored in distilled water and refrigerated before bonding.

The buccal enamel surface was polished for 10 s with oil/fluoride-free pumice, followed by rinsing with distilled water for 10 s and then dried with compressed air for 10 s. The enamel surface was etched for 30 s with a gel containing 37% phosphoric acid solution (Transbond XT etching gel, 3MESPE, Seefeld, Germany), followed by rinsing for 30 s with water and drying with compressed air for a further 30 s. Victory Series<sup>™</sup> premolar brackets (3M Unitek, Monrovia, CA, USA) with a foil mesh base and average base areas of 9.10  $\pm$  0.21 and  $9.20 \pm 0.15 \text{ mm}^2$  for upper and lower brackets, respectively were used. Light-cured composite adhesive (Transbond XT) was used as a control according to the manufacturers' instructions, being photopolymerized with a Visilux2 Visible Light Curing Unit for 20 s from the mesial and distal sides of the bracket separately. For EX1-3, a separate mixture of power and liquid was used for each test specimen. Following bracket bonding, the specimens were placed in a humidity chamber for 10 min to allow curing. For all groups, half the brackets were debonded after 30 min and half at 1 month.

An Instron universal testing machine was used to determine shear-peel bond strength. The specimens were positioned in a vice clamp so that the bracket base, judged by line of sight, was vertical and directly below the load cell. A 0.4-mm diameter round steelwire loop was attached via a universal joint to the load cell at one end and under the gingival tie wings adjacent to the bracket base at the other end. This ensured that the force vector was parallel to the bracket base as far as possible. The debonding force (newtons) was recorded for each specimen with the Instron operating at a crosshead speed of 1.0 mm/min. Shear bond strength (SBS; MPa) was calculated using the following formula:

force (newtons)/bracket base area  $(mm^2)$ .

#### Assessment of adhesive remnants

Debonded enamel surfaces were examined at a magnification of  $\times 30$  using a stereomicroscope. A modified adhesive remnant index (ARI) analysis was carried out to quantify the amount of adhesive on the enamel surface [9,10]. The modified ARI scale has a range between 1 and 5 as follows: a score of 1 was assigned when no adhesive remained on the enamel; 2, when <10% of the base area of enamel was covered with residual adhesive; 3, when 10%– 90% of the surface was covered with residual adhesive; 4, when >90% of the enamel base area was covered with adhesive; and 5 when all the adhesive remained on the enamel surface, along with a clear imprint of the bracket base. A score of 10 was recorded if enamel fracture had occurred.

#### Statistical analysis

One-way ANOVA was used to examine differences in setting characteristics, fluoride release and weight changes between groups. The hardness, shear punch strength and shear bond strength were analyzed with a two-way ANOVA, using the material composition and ageing as independent factors. Kruskal–Wallis and Mann–Whitney tests were used to determine significant differences in ARI scores between groups. Significance for all statistical tests was predetermined at P < 0.05.

#### Results

#### Setting characteristics

There were no significant differences in heat of polymerization among all groups at both  $23^{\circ}$ C and  $37^{\circ}$ C. The time for completion of polymerization of EX1–3 was significantly shorter than that for PMMA at both temperatures (Table II).

#### Fluoride release and weight change

EX1 had a similar level of fluoride release to that of GIC (Figure 1). EX2 and EX3 had lower levels of fluoride release. The greatest weight increases in all groups were observed within the first week, followed by gradual increases in weight over time. EX1 and EX2 gave higher weight increases due to water absorption than EX3 (Figure 2).

# Hardness

There was a significant decrease in hardness for EX1-3 after storage in water for 1 week. After that, hardness became relatively stable, with specimens showing only small increases or decreases. Overall, the hardness of EX1-3 was significantly lower than those of



Figure 1. Mean daily fluoride release (log) from GIC and EX1–3 over a period of 16 weeks.

Table II. Mean (SD) of heat and time of polymerization<sup>a</sup> of all groups at 23°C and 37°C.

Group	$Time_{23^{\circ}C}$ (s)	$Time_{37^{\circ}C}$ (s)	Heat <sub>23°C</sub> (mJ/mg)	Heat <sub>37°C</sub> (mJ/mg)
PMMA	496.6 (14.47)	175.4 (5.38)	120.67 (8.33)	125.33 (6.51)
EX1	404.6 (9.94)	150.8 (0.92)	109.17 (9.25)	135.33 (6.51)
EX2	380.60 (34.50)	156.8 (2.42)	121.00 (4.00)	141.33 (12.06)
EX3	414.4 (21.14)	158.2 (2.42)	114.67 (2.08)	134.67 (4.01)

<sup>a</sup>ANOVA showed that there were no statistically significant differences in heat of polymerization among all groups (P > 0.05). The time of polymerization of PMMA was significantly longer than that of the experimental groups (P < 0.05).



Figure 2. Weight increase plotted against time<sup>1/2</sup> for 16 weeks.

composite and PMMA after storage in water for 1 week. The hardness of the composite material increased with time during the first week, and then remained stable (Table III).

#### Shear punch strength

The strengths of both composite and PMMA increased significantly after storage in water for 1 week; after that they remained stable. The strengths of EX1 and EX2 decreased significantly after storage in water for 7 days, but did not decrease further between 7 and 28 days (Table IV). The strength of EX3 remained unchanged over the whole test period.

#### SBS and ARI

EX1–3 had a higher mean SBS than Transbond XT at 30 min. The SBS for Transbond XT increased significantly between 30 min and 1 month. The SBS of experimental adhesives was significantly lower than that of Transbond XT at 1 month. Of the experimental materials, EX3 had a significantly higher mean SBS at 1 month (Table V). At 1 month, EX1–3 had

Table III. Mean (SD) of Martens hardness of composite, PMMA and experimental groups with  $age^{a}$ .

Group	30 min (N/mm <sup>2</sup> )	7 days (N/mm <sup>2</sup> )	28 days (N/mm <sup>2</sup> )	
Composite	415.67 (23.31)	564.00 (38.76)	509.17 (27.21)	
PMMA	101.33 (3.18)	110.44 (3.27)	103.11 (3.08)	
EX1	129.00 (8.95)	81.33 (1.89)	83.17 (1.18)	
EX2	117.67 (8.95)	83.78 (5.87)	76.44 (11.24)	
EX3	123.56 (4.17)	101.11 (0.69)	92.89 (5.36)	

<sup>a</sup>ANOVA showed that material composition and age had a significant effect on hardness (P < 0.001). The interaction of material composition and age was also significant (P < 0.001).

Table IV. Mean (SD) of shear punch strength of composite, PMMA and experimental groups with age<sup>a</sup>.

Group	30 min (MPa)	7 days (MPa)	28 days (MPa)
Composite	50.24 (5.17)	65.76 (7.30)	69.01 (7.14)
PMMA	51.04 (1.52)	61.67 (3.74)	64.03 (2.64)
EX1	53.24 (3.67)	43.42 (1.98)	48.07 (2.33)
EX2	55.94 (3.39)	46.73 (2.73)	44.61 (2.11)
EX3	50.60 (2.05)	50.08 (2.55)	50.86 (4.21)

<sup>a</sup>ANOVA showed that material composition and age had a significant effect on hardness (P < 0.001). The interaction of material composition and age was also significant (P < 0.001).

Table V. Mean (SD) of SBS of composite and EX1-3 at 30 min and 1 month<sup>a</sup>.

	Bracket removal time	SBS (MPa)			
Group		Mean (SD)	Minimum	Maximum	
Composite	30 min	13.26 (3.79)	7.68	19.37	
	1 month	25.81 (5.62)	12.54	35.75	
EX1	30 min	15.41 (2.92)	10.89	20.83	
	1 month	15.09 (3.19)	9.30	20.52	
EX2	30 min	17.11 (3.46)	10.72	23.42	
	1 month	14.85 (2.89)	8.63	19.29	
EX3	30 min	17.12 (2.80)	13.41	23.53	
	1 month	19.78 (3.93)	13.57	28.02	

<sup>a</sup>ANOVA showed that material composition and age had a significant effect on SBS (P < 0.001). The interaction of material composition and age was also significant (P < 0.001).

significantly lower ARIs than Transbond XT and the debonding of the latter resulted in four instances of enamel fracture (Table VI).

# Discussion

For polymerization reactions, the extent of conversion of monomer to polymer and the rate of reaction can be studied by a number of methods. Amongst these, calorimetry is one of the most convenient and most commonly used. Compared to other methods such as Fourier Transform Infra Red spectroscopy (FTIR), differential scanning calorimetry has the advantage of simplicity, although it does give a rather general view of the process of setting which is not related to the specific nature of the reaction itself. A comprehensive kinetic/structure/property relationship would require both approaches. The results of this study showed that the heat generated during setting was similar amongst all groups at both 23°C and 37°C, which indicated that the polymerization process was largely unaffected by the changes in composition. One explanation for this can be found in the similar heats of polymerization for

	ARI score					
	1	2	3	4	5	10
30-min ARI score <sup>a</sup>						
Composite	0	4	5	9	0	0
EX1	1	6	3	8	0	0
EX2	1	5	6	6	0	0
EX3	1	10	3	4	0	0
1-month ARI score <sup>b</sup>						
Composite	0	3	7	4	0	4
EX1	2	10	2	3	1	0
EX2	3	10	4	1	0	0
EX3	4	7	4	3	0	0

Table VI. Frequency distribution and results of Kruskal-Wallis and Mann-Whitney tests of ARI scores.

<sup>a</sup>Kruskal–Wallis test showed no significant difference at 30 min (P = 0.15).

<sup>b</sup>Kruskal–Wallis test showed highly significant difference at 1 month (P = 0.001). Mann–Whitney tests showed that all EX groups gave a significantly lower ARI than Transbord (P < 0.01).

MMA (54.8 kJ/mol) and HEMA (50 kJ/mol). The replacement of part of the PMMA with NaF will have reduced the initiator concentration slightly, but this seems to have had an insignificant effect on reaction rate. The time of polymerization was the time from the start of mixing the liquid and powder to the time when the material completely set at either 23°C or 37°C, as indicated by the achievement of maximum exotherm. The results showed that the time of polymerization for EX1-3 at 23°C was sufficient to manipulate the material outside the mouth and to initially seat the bracket. The time of polymerization at 37°C allows time for final bracket positioning on the tooth combined with a rapid development of stiffness, which will maintain the desired bracket position very shortly after placement.

Attempts have been made to incorporate fluoride into composite resins but studies have normally reported that the quantity and duration of fluoride release are poor [11,12]. In general, simply adding an organic fluoride salt, such as NaF, only yields initial high fluoride release of short duration [13]. However, the results of the current work showed that EX1-3 produced both an initial burst, followed by a longer period of sustained release. Even though the release does decline slowly over the course of 1 month, the rate is maintained at a similar level to that of the GIC used as a control, particularly for EX1. This indicates that HEMA seems to facilitate sustained fluoride release by promoting rapid diffusion of water. The fluoride release of EX1 was as high as  $0.98 \,\mu g/cm^2/day$ , even at the 16th week. Protection of the enamel can result from such a sustained slow release of fluoride ions [14], or the higher concentrations resulting from the initial burst or, most likely, by a combination of both processes [15]. However, the precise level of fluoride release which is required for a preventive effect remains an unanswered question. Dubroc et al.

[16] reported that an adhesive releasing fluoride at a rate of as little as  $0.5-1.0 \ \mu g/cm^2/day$  could reduce white spot demineralization by 38% over 38 days in rats on a cariogenic diet. Another study [17] has shown that the level of fluoride release thought to inhibit caries initiation in sound enamel in the immediate vicinity of a resin-based dental material is in the range  $0.65-1.3 \ \mu g/cm^2/day$ . Our specimens were soaked in water in order to produce a comparative profile of release under standard conditions. Further evaluation incorporating release into saliva and regular recharging will be required for a thorough understanding.

The incorporation of HEMA renders the acrylic resin softer and weaker after a period of soaking in water. This may aid debonding at the end of treatment. The results showed that the hardness of EX1-3 was significantly lower than that of control groups, especially Transbond XT, after they were stored in water. This result explains the finding that the acrylic-based materials were more easily and safely debonded, with a reduced risk of enamel damage and with little or no 'clean-up' required at the end of orthodontic treatment. Incorporation of HEMA into acrylic resin (EX1-3) resulted in a material which gave a bond strength as high as the composite material after 30 min. However, whilst the composite bond strength increased over time up to 1 month, the bond strength for the EX1-3 materials remained quite constant. This implies that if all materials have bond strength great enough to resist early debonding they should survive a course of treatment, with the HEMA-containing materials being easier to debond at the end of treatment. The results showed that although the strength of most experimental groups reduced during the first 7 days, they reached a plateau after 7 days. The decreased hardness and strength during the first 7 days can be explained by water sorption. It was interesting to note that although weight increased with time, the hardness and strength of EX1–3 did not decrease further after 7 days. A likely explanation for this is that, during the first week, water is absorbed by the resin matrix but, during the following days, water is absorbed into porosities, instead of the resin matrix, through capillary action and such an action may produce minimal mechanical changes. This result confirmed that the precise effect of water sorption depends not only on the rate and amount of water absorbed but also the mechanism of absorption [18].

Bond strength was evaluated in the current study after 30 min and 1 month. In most studies on dental adhesives [19], bond strength is measured after 24 h, because such timing is convenient and adhesives are considered to be completely set at 24 h. However, most orthodontists activate appliances within 10-15 min after bonding. In order to simulate the time at which the initial archwires are ligated, bracket bond strength determinations were initially made at 30 min from the time the teeth were bonded. Since HEMA is known to have a hydrophilic character, it was considered to be appropriate to also assess the bond strength after a longer period of water storage. Hence, bond strengths were also evaluated for specimens which had been stored in water for 1 month. At 30 min, the SBS of EX1-3 was higher than that of Transbond XT, which was thought to be achieved through an ability of HEMA to act as an adhesion promoter, enhancing diffusion into the etched tooth surface. However, at 1 month, Transbond XT gave a significantly higher bond strength value compared with EX1-3. The ideal bond strength should be sufficiently high to withstand the whole duration of orthodontic treatment, yet be sufficiently low to allow removal without harm at the end of treatment. Also relevant to this is the reliability of the bond as indicated by the reproducibility of the bond strength, for which the standard deviation and maximum and minimum values may give an indication. The lowest recorded bond strengths at 30 min were obtained for the composite material (Table V), with a value of 7.7 MPa, whilst minimum values at 1 month ranged from 8.6 to 13.6 MPa. The minimum bond strength adequate for orthodontic purposes has been reported by Reynolds [20] and by Whitlock et al. [21] to be 6-8 MPa. Furthermore, the SBS recommended for successful clinical bonding was estimated by Lopez [22] to be 7 MPa. Hence, although the SBS of materials EX1-3 is significantly lower than that of Transbond XT at 1 month, they still possess sufficient strength to be recommended for consideration for clinical use.

It has been reported that the etching of enamel may affect enamel surface roughness and colour change by the retention of resin tags [23–25], whilst other studies [26,27] have found that the surface structure and

optical properties of enamel were affected mainly by the debonding process instead of by the infiltration of enamel by resin. After 1 month, significant differences in ARI scores were observed for EX1-3 compared with the composite control material. EX1-3 had a preponderance of scores 1 and 2 (no adhesive or <10% adhesive retained on the enamel surface). By contrast, Transbond XT was likely to leave adhesive on at least 10% of the bonded area of the tooth. This was also the only group in which enamel fracture was experienced during debonding. Both bond strength and the nature of the adhesive, particularly its hardness and stiffness, can affect the ease of debonding. The high bond strength for Transbond XT, combined with its higher hardness, resulted in greater forces being required to debond the brackets, leading to some enamel damage.

In the present study, different ratios of HEMA and NaF have been blended with acrylic resin to produce a new acrylic-based cement. The tested experimental material had clinically acceptable setting characteristics. The group containing powder (10% NaF, 90% PMMA) and liquid (60% MMA and 40% HEMA) released fluoride at a rate comparable to a GIC. All experimental groups provided acceptable bond strengths at both 30 min and 1 month. The group containing powder (10% NaF, 90% PMMA) and liquid (90% MMA and 10% HEMA) had higher bond strength than the other two groups. After debonding, the experimental groups were likely to leave adhesive on <10% of the bonded area of the tooth. This suggests that this new acrylic-based fluoride-releasing cement may potentially be useful as an orthodontic bonding agent.

#### Acknowledgements

The authors acknowledge Mr. Andrew Yates for his technical assistance during this study. This investigation was supported in part by the China Scholarship Council. The authors report no conflicts of interest.

**Declaration of interest:** The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the paper.

# References

- Fitzpatrick DA, Way DC. The effects of wear, acid etching and bond removal on human enamel. Am J Orthod 1977;72:671–81.
- [2] Pus MD, Way DC. Enamel loss due to orthodontic bonding with filled and unfilled resins using various clean-up techniques. Am J Orthod 1980;77:269–83.
- [3] Joseph VP, Rossouw E. The shear bond strengths of stainless steel and ceramic brackets used with chemically and lightactivated composite resins. Am J Orthod Dentofacial Orthop 1990;97:121–5.

- [4] Gorelick L, Masunaga GM, Thomas RC, Zachrisson BU. Round table: bonding. Part 1. J Clin Orthod 1978;12: 695–714.
- [5] Everett MS. Debonding orthodontic adhesives. Dent Hyg 1985;59:364–70.
- [6] Featherstone JD. Fluoride, remineralization and root caries. Am J Dent 1994;7:271–4.
- [7] Gladys S, Van Meerbeek B, Braem M, Lambrechts P, Vanherle G. Comparative physico-mechanical characterization of new hybrid restorative materials with conventional glass-ionomer and resin composite restorative materials. J Dent Res 1997;76:883–94.
- [8] Nomoto R, Crrick TE, McCabe JF. Suitability of a shear punch test for restorative materials. Dent Mater 2001;17: 415–21.
- Årtun J, Bergland S. Clinical trials with crystal growth conditioning as an alternative to acid-etch pretreatment. Am J Orthod 1984;85:333–40.
- [10] Summers A, Kao E, Gilmore J, Gunel E, Ngan P. Comparison of bond strength between a conventional resin adhesive and a resin-modified glass ionomer adhesive: an in vitro and in vivo study. Am J Orthod Dentofacial Orthop 2004;126:200–6.
- [11] Chadwick SM, Gordon PH. An investigation into the fluoride release of a variety of orthodontic bonding agents. Br J Orthod 1995;22:29–33.
- [12] Cacciafesta V, Sfondrini MF, Tagliani P, Klersy C. In-vitro fluoride release rates from 9 orthodontic bonding adhesives. Am J Orthod Dentofacial Orthop 2007;132:656–62.
- [13] Xu X, Ling L, Wang R, Burgess JO. Formulation and characterization of a novel fluoride-releasing dental composite. Dent Mater 2006;22:1014–23.
- [14] McNeill CJ, Wiltshire WA, Dawes C, Lavelle CL. Fluoride release from new light-cured orthodontic bonding agents. Am J Orthod Dentofacial Orthop 2001;120:392–7.
- [15] Evrenol BI, Kucukkeles N, Arun T, Yarat A. Fluoride release capacities of four different orthodontic adhesives. J Clin Pediatr Dent 1999;23:315–9.
- [16] Dubroc GC, Mayo JA, Rankine CA. Reduction of caries and of demineralization around orthodontic brackets: effect of a

fluoride-releasing resin in the rat model. Am J Orthod Dentofacial Orthop 1994;106:583–7.

- [17] Erickson RL, Glasspoole EA. Model investigations of caries inhibition by fluoride-releasing dental materials. Adv Dent Res 1995;9:315–23; discussion 324–31.
- [18] McCabe JF, Rusby S. Water absorption, dimensional change and radical pressure in resin matrix dental restorative materials. Biomaterials 2004;25:4001–7.
- [19] Armas GH, Sadowsky PL, Vlachos C, Jacobson A, Wallace D. An in vivo comparison between a visible light-cured bonding system and a chemically cured bonding system. Am J Orthod Dentofacial Orthop 1998;113:271–5.
- [20] Reynolds IR. A review of direct orthodontic bonding. Br J Orthod 1975;2:171–8.
- [21] Whitlock BO 3rd, Eick JD, Ackerman RJ Jr, Glaros AG, Chappell RP. Shear strength of ceramic brackets bonded to porcelain. Am J Orthod Dentofacial Orthop 1994;106: 358–64.
- [22] Lopez JI. Retentive shear strengths of various bonding attachment bases. Am J Orthod 1980;77:669–78.
- [23] Eliades T, Gioka C, Heim MV, Eliades G, Makou M. Color stability of orthodontic adhesives. Angle Orthod 2004;74: 391–3.
- [24] Øgaard B, Larsson E, Henriksson T, Birkhed D, Bishara SE. Effects of combined application of antimicrobial and fluoride varnishes in orthodontic patients. Am J Orthod Dentofacial Orthop 2001;120:28–35.
- [25] Czochrowska E, Øgaard B, Duschner H, Ruben J, Arends J. Cariostatic effect of a light-cured, resin-reinforced glassionomer for bonding orthodontic brackets in vivo. A combined study using microradiography and confocal laser scanning microscopy. J Orofac Orthop 1998;59:265–73.
- [26] Eliades T, Kakaboura A, Eliades G, Bredley TG. Comparison of enamel colour changes associated with orthodontic bonding using two different adhesives. Eur J Orthod 2001;23: 85–90.
- [27] Eliades T, Gioka C, Eliades G, Makou M. Enamel surface roughness following debonding using two resin grinding methods. Eur J Orthod 2004;26:333–8.