

A new use for self-etching resin adhesives: Cementing bone fragments

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ABSTRACT

Objectives: To evaluate the bond capacities of four self-etching resin cements and the selfetching adhesives of the same manufacturer when used to cement bone fragments and compare them with a well-known N-butyl-2-cyanoacrylate bone adhesive.

Methods: 125 cylindrical bone specimens from pig mandibular ramus bone were prepared using terphane burs and cemented to the corticals of 125 other specimens obtained from pig mandibular body bone using the following bond systems: Group A: Adper PLP/Relyx; group B: Optibond/Maxcem; group C: Hystoacryl; group D: AdheSE/Multilink; group E: G-Bond/G-Cem. Shear bond strength was measured 15 min after cement application using a universal testing machine.

Results: Shear bond strength results: group A 2.54 \pm 0.23 MPa; group B 4.83 \pm 0.4 MPa; group C 2.90 \pm 0.24 MPa; group D 2.10 \pm 0.17 MPa; group E 4.22 \pm 0.24 MPa. Values for shear bond strength were significantly greater for group B and E compared to groups A, C and D (p < 0.005, test Mann–Whitney). SEM images showed the presence of a hybrid layer similar to that formed by these bond systems when used on dentine.

Conclusion: Within the limitations of an in vitro investigation, results show that self-etching resin cements together with self-etching adhesives may be used for cementing bone fragments.

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1. Introduction

The use of rigid fixation devices, miniplates and microplates, has transformed the treatment of maxillofacial bone fractures. Their use is problematic when fixing fine bone or whenever there is a risk of the perforations made by fixing screws or pins damaging important soft tissue. Other drawbacks in clinical use consist of extrusion, palpability, bone resorption by stress shielding, revascularisation from exposure, and growth disturbances in the developing craniofacial skeleton.^{1,2}

A perfect adaptation of bone fragments often takes up a lot of time and may be particularly difficult in some areas where metal implants of the types mentioned above are used. It is for this reason that a method of bone fixation is badly needed, a method capable of providing a level of stability similar to that provided by metal osteosynthesis devices but without the negative effects that they can produce.³

Various bond systems have come into use as alternatives. Butyl-2-cyanoacrylate glue has been shown to be useful for the treatment of craniofacial and mandibular bone fractures, and even for talar osteochondral fixings, achieving good clinical results.^{4–6}

Due to the similarity between bone and dentine, the use of dental adhesives for joining bone fragments and for fixing

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metal devices to bone instead of using screws is a possibility which has already been studied by various researchers.^{1,2,7} Many of the primers used in dental adhesives contain active organofunctional groups such as isocyanato, amino, methacrylate, which may attach satisfactorily to collagen and to bone minerals.³

The use of liquid adhesives, cianoacrylate and other dental adhesives, is limited because of the lack of co-adaptability between the surfaces of some bone fragments and the surface rigidity of metallic devices and bone. For this reason, the conventional resin cements have been shown to provide a greater bond strength on bone than when bone is glued using a dentine adhesive.^{7,8}

Recently developed self-etching resin cements might prove to be the ideal material for providing a good union between bone fragments, providing a level of stability comparable to the conventional methods employed by traumatologists and maxillofacial surgeons. These are materials with body, easily malleable during the adaptation phase and then becoming rigid at the fixation stage. Although these cements contain active groups that are identical to self-etching primers and could be capable of forming a union with the components of bone, preliminary experiments carried out in our laboratories showed inadequate bond strength values when using a selfetching resin cement on its own.

The reologic properties of the material probably impede penetration of the monomers into the bone surface producing a limited decalcification/infiltration, which is necessary to obtain a satisfactory bond. Monticelli et al.,⁹ observed that the use of self-etching resin cements on its own produced a limited depth of infiltration in dentine.

The purpose of this study was to evaluate in vitro the shear bond strength of four self-etching resin cements and four selfetching adhesives used to cement bone fragments, comparing these with a cyanocrylate bone adhesive.

2. Materials and methods

2.1. Bone

12 mandibles from freshly sacrificed pigs were used. The pigs had been slaughtered in an abattoir for reasons unrelated to the objectives of this study.

The mandibles were used to prepare 250 specimens. 125 specimens with a length of 42 ± 3.10 mm, a total thickness of 18 ± 2.60 mm and a cortical layer of 4.55 ± 0.96 mm were obtained from the mandibular body. 125 cylinders were obtained from the mandibular ramus using trephane burs (8 mm diameter) under constant water cooling.

2.2. Bonding procedure. Experimental design

100 specimens from the mandibular body were mounted in a 4 cm long copper cylinder with an internal diameter of 30 mm inserting half the length in plaster IV. They were divided at random into five groups. The cylinders obtained from the mandibular ramus were also divided at random into five groups and bonded to those from the mandibular body. The following bonding procedures were carried out: Group A (n = 20): AdperTM PrompTM L-PopTM (Adper PLP)/ RelyxTM UnicemTM AplicapTM (Relyx) (3 M ESPE Dental Products, St. Paul, MN, USA, lot Adper PLP 242179, lot Relyx 311681). Adper PLP was gently brushed onto both bone surfaces for 15 s with the disposable applicator supplied with the system. A moisture-free air source was used to deliver a gentle burst of air to the primer. The self-etch cement was light-cured for 10 s. Relyx cement was applied to the bone obtained from the mandibular ramus, which was then placed onto the mandibular body bone. Excess cement was removed and the cement was light-cured positioning the light guide above, below, to the left and to the right of the adhesive bond for 10 s in each position. The lamp used was an Elipar Classic (3 M ESPE) with 450 mW/cm² light intensity.

Group B (n = 20): Optibond[®] ALL-IN-ONE (Optibond)/MaxcemTM (Maxcem) (Kerr Corporation, Orange, CA, USA, lot Optibond 2733196, lot Maxcem 061104). A generous amount of Optibond was applied onto both bone surfaces with the disposable applicator, brush scrubbing the surface with a brushing motion for 20 s. Then a second layer of the adhesive was applied in the same way. The adhesive was dried with a gentle burst of air first and then a medium air jet for 5 s. Afterwards it was light-cured for 10 s. Maxcem was applied to the bone surface and light-cured in the same way as Relyx in group I.

Group C (n = 20): Hystoacryl[®] (Hystoacryl) (B. Braun, Melsungen, Germany, lot 2-4041). A layer of Hystoacryl was applied to the bone obtained from the mandibular ramus, which was then placed onto the mandibular body bone and held in place for several seconds until they had bonded.

Group D (n = 20): AdheSE[®] (AdheSE)/Multilink[®] Automix (Multilink) (Ivoclar Vivadent, Schaan, Lienchestein, lot AdheSE H2396, lot Multilink K04727). Two layers of the AdheSE were applied to the bone surfaces brushing each layer for 15 s. Then the adhesive was dispersed with a gentle burst of air and lightcured for 10 s. Multilink was applied to the bone surface and light-cured in the same way as Relyx in group I.

Group E (n = 20): GC G-BondTM (G-Bond)/ GC G-Cem Capsule (G-Cem) (GC Corporation, Tokyo, Japan, lot G-Bond 0607111, lot G-Cem 0704161). G-Bond was applied to the bone surfaces with the disposable applicator and left undisturbed for 10 s. Then it was dried for 5 s with a jet of air at maximum air pressure and light-cured for 10 s. G-Cem was applied to the bone surface and light-cured in the same way as Relyx in group I.

The composition of each material appears in Table 1. Each bond system was used according to the manufacturers' specifications.

2.3. Bond strength test

Shear bond strength was measured 15 min after bonding the specimens using a universal test machine (Autograph AGS-1KND, Shimadzu, Kyoto, Japan) with a 1 kN load cell connected to a metal rod with one end angled at 30°. The cross-head speed was 1 mm/min.

The specimens were set at the base of the machine so that the sharp end of the rod incised perpendicularly between the two bonded specimens, exerting a force parallel to the bonded surface.

system).		
Material	Manufacturer	Composition
Adper TM Prompt TM L-Pop TM	3M ESPE Dental Products, St. Paul, MN, USA	Part A. Di-HEMA phosphate 75–90%, bisphenol A diglycidyl ether dimethacrylate 10–15%, ethyl 4-dimethyl aminobenzoate <2%, pl-camphorquinone 1–1.5% Part B. Water 70–80%, 2-hydroxyethyl methacrylate 17–28%
Relyx [™] Unicem [™] Aplicap [™]	3M ESPE Dental Products, St. Paul, MN, USA	<i>Powder</i> . Silanised glass powder 85–95%, silane treated silica 5–10%, calcium hydroxide 1–5%, substituted pyrimidine 1–5%, sodium persulphate <1% <i>Liquid</i> . Methacrylated phosphoric acid esters 40–50%, triethylene glycol dimethacrylate 25–35%, substituted dimethacrylate 22–34%
Optibond [®] ALL-IN-ONE	Kerr Corporation, Orange, CA, USA	Acetone 35–45%, ethyl alcohol 4–9%, uncured methacrylate ester monomers 33–43%.
Maxcem TM	Kerr Corporation, Orange CA USA	Uncured methacrylate ester monomers 20–35%
	orango, ori, oori	Other ingredients. Inert mineral fillers, activators, stabilisers and colorants
Hystoacryl®	B. Braun, Melsungen, Germany	N-butyl-2-cyanoacrylate
AdheSE®	Ivoclar Vivadent, Schaan, Lichtenstein	Primer. Mixture of dimethacrylates, phosphonic acid acrylate <40%, water, initiators and stabilisers Bond. Mixture of dimethacrylates <75%, hydroxyethyl methacrylate <25%, SiO ₂ , initiators and stabilisers
Multilink [®] Automix	Ivoclar Vivadent, Schaan, Lichtenstein	Base and catalyst. Pastes of dimethacrylates 22–26%, hydroxyethyl methacrylate 6–7%, inorganic fillers, ytterbiumtrifluoride, benzoylperoxide <1%, stabilisers and pigments
$GC G-Bond^{TM}$	GC Corporation, Tokyo, Japan.	Propanona 40%, 4-methacryloxyethyltrimellitate anhydride 11%, dimethacrylate 10%, urethane dimethacrylate 9%
GC G-Cem Capsule	GC Corporation, Tokyo, Japan.	4-Methacryloxyethyltrimellitate anhydride 6–10%, urethane dimethacrylate 1.5–3%, alumino-silicate glass 65–70%, pigment 1%, dimethacrylate 15–20%, water 1.5–3%, phosphoric ester monomer 1–2%, initiator <1%

Table 1 - Composition of adhesive systems used (data taken from the Material Safety Data Sheet for each bonding

The force required to debond each sample was registered in Newtons (N), and converted into Mega-Pascals as a ratio of Newtons to area of bonding (50.26 mm²).

2.4. FE-SEM observation

25 specimens from the mandibular body and 25 from the ramus were each divided randomly into five groups and bonded following procedures described above.

The bonded interface was sectioned longitudinally with a water-cooled diamond saw (Horico, Berlin, Germany) thus providing 3 sections per specimen. In order to eliminate possible residues caused by the cutting process they were washed and dried with compressed air. When dry they were affixed to SEM stubs, sputter-coated with gold and examined on a JSM-6100 JEOL SEM operating at 20 kV. Digital images representatives of each group was taken at magnification $2000 \times$ for further study.

2.5. Statistical analysis

The Kolmogorov–Smirnov normality test and the Levene variance homogeneity test were applied to the bond strength

data. As the data did not show a normal distribution nor homogeneity of variances, significant difference were evaluated using the Kruskal–Wallis test (p < 0.05), finding those groups which were significantly different with the Mann–Whitney test for two independent samples. In order to avoid an accumulation of errors due to multiple comparisons, the significance level was modified dividing this (p < 0.05) between the number of comparisons made (Bonferroni Correction) and p < 0.005 was considered significant.

3. Results

3.1. Bond strength values for the different groups tested are shown in Table 2

The Kruskal–Wallis test detected significant differences (p = 0.00) and the Mann–Whitney test identified these differences between the two groups with the greatest bond strength Optibond/Maxcem and G-Bond/G-Cem and the rest of the groups evaluated (AdperPLP/Relyx p = 0.000 and p = 0.000 respectively, Hystoacryl p = 0.001 and p = 0.000 respectively, AdheSE/Multilink p = 0.000 and p = 0.000 respectively).

Table 2 – Shear bond strength (MPa). Groups marked by different superscript letters showed significant differences with one another (*p* < 0.005). Group n Mean Median Range Standard deviation 95% C.I. 3.12 AdperPLP/Relyx^b 20 2.54 2.39 1.04 2.00, 3.07 Optibond/Maxcem^a 20 4.83 5.20 6.32 1.78 4.00, 5.67 p < 0.005 Hystoacryl^b 20 2.90 3.01 4.64 1.07 2.40, 3.40 AdheSE/Multilink^b 20 2.10 1.79 2.59 0.79 1.73, 2.48 G-Bond/G-Cem^a 20 4.12 1.08 3.70, 4.74 4.22 3.70 p < 0.005



Fig. 1 – SEM images at magnification 2000× of the cement-mandibular body interface: (a) Adper PLP/Relyx. (b) Optibond/ Maxcem. (c) Hystoacryl. (d) AdheSE/Multilink. (e) G-Bond/G-Cem. In all groups, except the Hystoacryl group, a perfect union between cement and bone was observed, with an area of greater refringence, similar to the hybrid zone formed between dentine cements and dentine.



Fig. 2 – SEM images at magnification 2000× of the cement-mandibular ramus interface: (a) Adper PLP/Relyx. (b) Optibond/ Maxcem. (c) Hystoacryl. (d) AdheSE/Multilink. (e) G-Bond/G-Cem. In all groups a perfect union between cement and bone was observed with an area of greater refringence, similar to the hybrid zone formed between dentine cements and dentine.

The scanning electron microscope (SEM) evaluation revealed homogenous images in the five groups both at the cement/body interface and at the cement/ramus interface (Figs. 1 and 2). No correlation could be detected between shear bond strength and the SEM findings.

4. Discussion

This study was designed to show that new self-adhesive resin dental cements used together with a self-etching adhesive from the same manufacturer may be used to bond bone under in vitro conditions. We have been unable to find any other study that has tested these bond systems in this way. However there are previous studies that have shown that dentine adhesives can be used for bonding bone to bone¹ and composite to bone.^{2,3,7,8}

We decided to use self-etching resin cements because, even though the bone fragments used for testing had flat and adaptable surfaces, the bone fragments which are produced by real life fractures, particularly in the craniofacial area, are irregular, anfractuous and so tend not to be easily adaptable. Under such circumstances dentine adhesives, which are liquid, are not capable of forming a satisfactory bond. However, resin adhesive cements, which are viscose and highly malleable during the adaptation phase and solid and



Fig. 3 – SEM images at magnification $20 \times$ which show irregularities on the surfaces to be cemented and the lack of adaptability between them. A full-bodied cement facilitates bonding.

rigid after polymerisation, can bond two surfaces that are not co-adaptable (Fig. 3).

When Meechan et al.⁸ studied bone bonding for the dental adhesive All-bond-2, it was saw that as the irregularity of the surface was increased by means of a surgical bur, bond strength increased, whilst modifying the bone surface by acidetching reduced bond strength.

In order to facilitate and augment bond strength for selfetching resin cements, we used self-etching adhesives from the same manufacturer.

Preliminary experiments carried out in our laboratories showed that a cement used on its own did not achieve adequate bond strength values. The reologic properties of the material probably impede penetration into the bone surface which is necessary to obtain a satisfactory bond. However, as can be seen in SEM images of all the study groups (Figs. 1 and 2), when self-etching adhesive was applied, this produced a hybrid layer similar to that formed on dentine. Sakai et al.¹⁰ have shown the existence of a hybrid zone between bone and bone adhesive made up of 4-methacryloyloxyethyl trimellitate anhydride (4-META) and methylmetacrylate (MMA), which is located in the bone sub-surface and formed by the infiltration of monomers into the bone tissue. These types of organofunctional monomers, or similar ones (metacrylates, carboxylates), are present in all the self-etching adhesives (see Table 1) tested in this study. As Sakai et al.,¹⁰ we observed (Fig. 4) in the bone sub-surface a similar infiltration of the self-etching adhesive.

The chemical composition of bone is similar to dentine: 67% hydroxiapatite, 28% collagene type I and 5% noncollagenic proteins.¹¹ The bond mechanisms of self-etching adhesives on bone are probably very similar to those on dentine with the difference that bone does not have a tubular structure and so there are no tags.²

To explain how bonding with self-etching adhesives works on bone, we would put forward the following hypothesis: The self-etching adhesives demineralise bone partially creating irregularities and so augmenting the effective bond surface. This demineralisation involves the removal of hydroxiapatite from the surface leaving the collagene exposed, allowing hybridisation of the area when collagene mixes with the



Fig. 4 – SEM image at magnification 2000× which show the self-etching monomers infiltration in the bone subsurface. To obtain this image the slides were decalcified with 37% phosphoric acid during 5 min. The image belongs to B group (Optibond)/Maxcem). Groups A, D, and E showed similar patterns.

adhesive's monomers.¹² In addition to this micromechanical union, on the basis of Yoshida's adhesión–decalcification concept,¹³ phosphate and carboxylate groups of the specific monomers functionals in the self-etching adhesives forming a chemical union with hydroxiapatite.^{14,15}

In our study the binomial Optibond/Maxcem and G-Bond/G-Cem showed higher shear bond strength values than the rest of the bond systems tested. Therefore, they produced greater stability than N-butyl-2-cycianoacrylate (Hystoacryl[®]) glue.

Cianoacrilato's bonding capacity on bone has been investigated previously^{1,2,5,16} showing a performance equal to that of traditional metallic fixing systems.^{6,17} Amarante et al.¹⁶ showed that fixation of craniofacial osteotomies using cianoacrylate in minipigs produced enough stability to allow the bone to cure satisfactorily without necrosis or bone resorption, all the glue having been reabsorbed into the osteotomy.

The biocompatability of N-butyl-2-cyanoacrylate has been evaluated in earlier studies,^{4,16} in fact documentation of its use in treating maxiofacial fractures commenced as early 1997.¹⁸ Nevertheless, further studies of long-term biocompatibility of the bond systems we have used are needed. Heiss et al.¹⁹ studied tissue response to an alkylene bis(dilactoyl)-methacrylate bone adhesive with promising results, finding that bond degradation (over time) did not interfere with the physiological processes of fracture healing. Morita et al.²⁰ have shown that a bone cement based on 4-META/MMA does not alter bone growth and moreover new bone makes direct contact with new bone. The presence of phosphoric acids and phosphate groups in dental phosphorilate cements are seen to facilitate in vitro the nucleation and growth of hydroxiapatite crystals on the cement surface,²¹ and for this reason the cement might in vivo facilitate the formation of osseous callus.

5. Conclusion

Our study's results show that a combination of self-etching adhesives and self-etching resin cements may be used, in certain cases, to fix bone fragments to one another or to metallic devices. An in vivo study is necessary to prove that the bond strength that this study achieved is adequate and that bone regeneration at the fracture interface may be produced normally.

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