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Comparison of failure mechanisms for cements used in skeletal luting applications

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Abstract Glass Polyalkenoate Cements (GPCs) based on strontium calcium zinc silicate (Sr–Ca–Zn–SiO_2) glasses and low molecular weight poly(acrylic acid) (PAA) have been shown to exhibit suitable compressive strength (65 MPa) and flexural strength (14 MPa) for orthopaedic luting applications. In this study, two such GPC formulations, alongside two commercial cements (Simplex® P and Hydroset™) were examined. Fracture toughness and tensile bond strength to sintered hydroxyapatite and a biomedical titanium alloy were examined. Fracture toughness of the commercial Poly(methyl methacrylate) cement, Simplex® P, (3.02 MPa $m^{1/2}$) was superior to that of the novel GPC (0.36 MPa $m^{1/2}$) and the commercial calcium phosphate cement, Hydroset™, for which no significant fracture toughness was obtained. However, tensile bond strengths of the novel GPCs (0.38 MPa), after a prolonged period (30 days), were observed to be superior to commercial controls (Simplex™ P: 0.07 MPa, Hydroset™: 0.16 MPa).

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1 Introduction

Luting cements are materials used for fixation, binding and sealing applications. Traditionally, luting cements have been used in dental and orthodontic applications for the purposes of adhering crowns, brackets and other prostheses. However, luting cements also have potential for use in surgical applications such as cranioplasty and vertebroplasty. Cements for orthopaedic luting applications have some very specific requirements. High radiopacity [1], low curing temperature [2], non-toxic nature [3], a sufficient working time (6–10 min) [1], a rapid setting time (15 min) [1], a suitable viscosity (required for injection and interpenetration of trabecular spaces) [4], sufficient strength [5–8], a modulus of elasticity similar to surrounding bone [9–11], good biocompatibility/bioactivity [1], adhesive properties to both bone and surgical metals [12] and good resistance to fracture [13].

Poly(methyl methacrylate) (PMMA) is the primary bone cement used in orthopaedic applications [1]. However, PMMA has been shown to cause both chemical and thermal necrosis of bone, due to the leaching of unreacted monomer and its high reaction exotherm (120°C), respectively [14]. Additional concerns with PMMA cements include: lack of a chemical bond to surrounding bone [15], elastic modulus mismatch with trabecular bone [9] and fibrous encapsulation in vivo. In cranioplasty applications, PMMA cements have had limited success, one study (of 36 patients) showed increased intracranial pressure, infection and traumatic bone destruction occurred in a number of cases resulting in four subject deaths, and 14 severely disabled [16]. Vertebroplasty using PMMA cements has had similarly limited success, with adjacent vertebral fracture [12], cement leakage [17] and bone necrosis [3] most commonly occurring. These problems and

disadvantages have focused the search for alternative materials for use in luting applications.

One such alternative are self-setting calcium phosphate cements (CPCs), which are osteoconductive and have the ability to resorb over time being replaced with new bone as part of the natural bone remodelling cycle without provoking an inflammatory response [18–21]. Such biocompatibility is not matched by PMMA bone cements, however CPCs suffer from poor mechanical properties and even in non-load bearing applications such as cranioplasty, implant fracture has been observed [13]. Other complications associated with the use of CPCs in cranioplasty are leakage of cerebrospinal fluid (CSF) and pneumocranium (air entrapment between the cranium and the dura mater) [22], also fibrous tissue formation has been observed surrounding brushite forming CPCs in cranioplasty applications [23].

Glass polyalkenoate cements (GPCs) were developed in the 1960s [24]. They are used in luting and restorative applications in dentistry [25]. However, due to their suitable elastic modulus [26], excellent biocompatibility [27], ability to adhere to bone and surgical metals, as well as their lack of volumetric shrinkage and heat evolution [28], they have potential for skeletal luting applications. GPCs set via an acid-base reaction involving an ion leachable glass (base), and a polyalkenoic acid, usually PAA. The acid degrades the glass structure releasing metal cations. The released ions form chelates with the carboxylate groups of the polymer. The metal cations serve to crosslink the polyacrylate chains resulting in a hard composite material. The resulting cements consists of residual glass particles with a surrounding siliceous layer embedded in a polysalt matrix [29, 30]. The setting of these cements is continuous which is evinced by the increase in mechanical strength over time [29]. GPCs can also be formulated to release beneficial ions over time such as calcium, which is incorporated into teeth and bones [31], and zinc (Zn), which plays a significant role in healthy bone metabolism [32]. Fluoride, though shown to be beneficial in dental GPCs for preventing bacterial degradation of teeth, due to potential problems in bone such as osteomalacia was not included in these GPC formulations [33, 34].

In 1998, Geyer et al. showed that Ionocem®, a commercial GPC, could be used successfully in the frontobasal and laterobasal regions as well as at the skull cap and petrous apex [35]. The study was carried out on 76 patients, with a follow up time of up to 6.5 years. No complications arose and functional (and cosmetic) results were deemed promising. In this study the GPC formed a durable, watertight, mechanically stable bond with the underlying bone with no evidence of inflammation. However, aside from these promising result reported by Geyer et al., concerns with the use of conventional GPCs in orthopaedics were voiced due to the presence of the trivalent aluminium ion (Al^{3+}) in the glass phase and the use of such cements for skeletal application were contraindicated. Aluminium (Al) has been implicated in the pathogenesis of the degenerative neurological disorder, Alzheimer's disease [36], and has been identified as the cause of a patient's death in a case of reconstructive otoneurosurgery using Al-based GPC [37]. However, the authors have previously shown that it is possible to produce aluminium free GPCs based on calcium–zinc silicate glasses [28]. In these glasses the Zn has been shown to act as a network modifier [38], whilst having a beneficial effect on bone metabolism [32] and imparting an antibacterial nature to the cements [39]. The authors have also developed a second generation of these cements where strontium (Sr) has been incorporated into the glass network to improve both the radiopacity and bioactivity of resultant GPCs produced from these glasses. It has already been shown that these Sr–Ca–Zn–SiO_2 GPCs can exhibit sufficient strength for orthopaedic arthroplasty applications [26]. The working time, setting time and flow properties of such cements can also be tailored, making them effective in luting applications [40].

Conventional GPCs have, in shear bond strength tests to HA, been deemed to fail cohesively rather than adhesively [41–43]. However, in a study by Della Bora and Van Noort it has been shown that this type of failure is due to the localised tensile forces acting non-uniformly on surface flaws, which may result in crack propagation through the cement mantle [44]. The aforementioned study suggests the use of a tensile bond strength test for analysis of interfacial bond strengths. Failure of the cement in vivo, however may occur adhesively, due to tensile forces, or cohesively, due to crack propagation through the cement layer [45, 46]. In this study the tensile bond strength, of two commercial cements and two novel GPCs will be systematically evaluated using a novel testing technique. Also analysed will be the fracture toughness of the luting cements, to determine if cohesive failure is likely in vivo.

2 Material & methods

2.1 Glass synthesis

One glass composition, 0.04SrO/0.12CaO/0.36ZnO/0.48SiO_2 (mol. fraction), was synthesised. Appropriate amounts of analytical grade calcium carbonate, strontium carbonate, zinc oxide and silicon dioxide (Sigma Aldrich, Dublin, Ireland), were weighed out in a plastic tub and mixed in a ball mill for 1 h, then dried (100°C, 1 h). The pre-fired glass batch was then transferred to a platinum crucible for firing (1,480°C, 1 h). The glass melt was subsequently quenched into water and the resulting frit was

dried, ground and sieved to retrieve a <25 μm glass powder. The glass was then annealed (645°C, 3 h) to relieve internal stresses within the glass network, such that Zn-GPC specimen preparation was possible.

2.2 Commercial bone cements

The following commercial bone cements were evaluated:

1. Surgical Simplex^{TM} P (Stryker Orthopaedics, Limerick, Ireland). Powder lot # 110BO, liquid lot # 944KO.
2. Hydroset^{TM} (Stryker Orthopaedics, Limerick, Ireland). Lot # IC06276A.

2.3 Cement preparation

Four Zn-GPCs formulations were prepared by mixing the glass with 50 wt.% PAA; E6 (MW, 12,700) and E7 (MW, 25,700) (Advanced Healthcare Ltd., Kent, UK), with and without 10 wt.% trisodium citrate dihydrate (TSC) (Reagecon, Shannon, Ireland), which was added in dry particulate form (<90 μm). TSC was added as a modifying agent and has been previously shown to be effective in modifying rheology of Zn-GPCs [40]. A powder-liquid ratio of 2:1.5 was used, as shown in Table 1. Mixing of GPCs was carried out on a clean glass slab with a dental spatula and was completed within 20 s. All commercial materials were produced in strict compliance with manufacturer's instructions.

2.4 Determination of tensile bond strength

Discs (20 mm Ø, 6.5 mm thick) were produced from mixing 4.5 g of hydroxyapatite (HA) powder (Stryker International, Limerick, Ireland) with 0.7 ml of distilled water. Slurries were cold pressed (10 tonnes, 20 s) before being sintered at 1200°C by an accepted regime [47].

A biomedical titanium alloy (Ti6Al4V) was formed into circular discs (25 mm Ø, 1.7 mm thick) and a hole was drilled in their centre (10 mm Ø). Titanium discs were ground using 1200 grit silica carbide paper (150 rpm for 30 s). Discs were then placed in a 1 M sodium hydroxide solution (60 ± 2°C, 24 h). Discs were subsequently removed from the sodium hydroxide solution, gently rinsed with distilled water and placed in a furnace (600°C, 1h) and subsequently allowed to furnace cool. Sodium hydroxide treatment and heating of discs is an accepted regime which resulted in a uniform growth of an oxide layer on the surface of the discs [48, 49].

Using a layer of cement, applied with a dental spatula, HA and titanium discs were bound together and excess material was removed using a scalpel. All bound discs were placed under a mass of 750 g to produce a cement layer of uniform thickness and discs were placed in an oven at 37 ± 2°C for 1 h to harden. Each set of discs ($n = 5$) were then placed in 25 ml of distilled water and incubated (37 ± 2°C) for 1, 7 and 30 days before being removed and their tensile bond strength tested using the plunger apparatus in Fig. 1, to ensure an even loading, at a constant rate (1.0 mm min^{-1}). Maximum tensile forces were collected using an Instron 4082 Universal testing machine (Instron Ltd., High Wycomb, Bucks, UK) and converted into bond strength using Eq. 1.

$$\sigma = \frac{F}{A} \tag{1}$$

where σ is the bond strength (MPa), F is the maximum force applied (N) and A is the bound area (mm^2).

Table 1 Zn-GPC formulations examined in this study

Formulation	Glass (g)	Acid (g)	TSC (g)	Water (ml)
A	1.00	E6−0.37	0.000	0.37
B	1.00	E7−0.37	0.000	0.37
C	1.00	E6−0.37	0.075	0.37
D	1.00	E7−0.37	0.075	0.37

2.5 Determination of double torsion fracture toughness

The double torsion (DT) test is performed by an accepted regime [50–53], using an Instron 4082 Universal Testing Machine (Instron Ltd., High Wycomb, Bucks, UK) and some specially made fixtures for the support and loading of the samples. These consisted of two parallel rollers of 3 mm Ø, spaced 20 mm apart and load applied at a constant rate (0.1 mm min^{-1}) to the slotted end via two 3 mm Ø ball bearings spaced 10 mm apart (Fig. 2). The specimen is therefore subjected to four-point bend loading, during which the crack initiated and propagated, along the centre of the specimen, within the groove.

DT specimens (3.0 × 65 × 25 mm) are produced in the form of rectangular plates using stainless steel moulds. Mixed cements were placed into the moulds, which were sandwiched between two stainless steel plates and clamped. The moulds were then stored (37 ± 2°C, 1h) in a preheated oven. The samples were then removed and placed in distilled water (37 ± 2°C) prior to testing. The tests were carried out after 1, 7 and 30 days. A sharp groove 1.0 mm deep is cut down the centre of the specimen. A slot was cut at one end of the specimen using a diamond wafer blade. A minimum of three specimens are used for each measurement with three values being taken from each specimen.

In a DT test the mode I stress intensity factor, K_{IC} is independent of crack length and is given by:

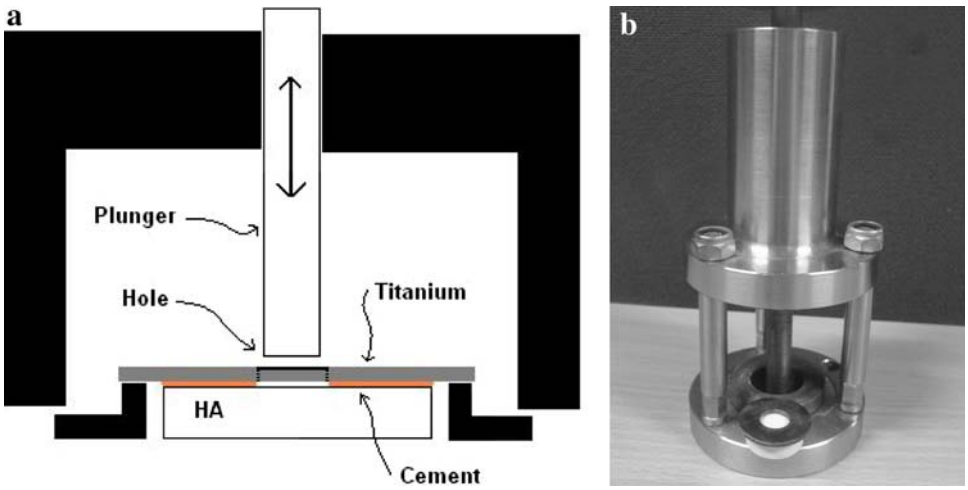

Fig. 1 Tensile bond strength test apparatus. **a** Schematically, **b** photographically

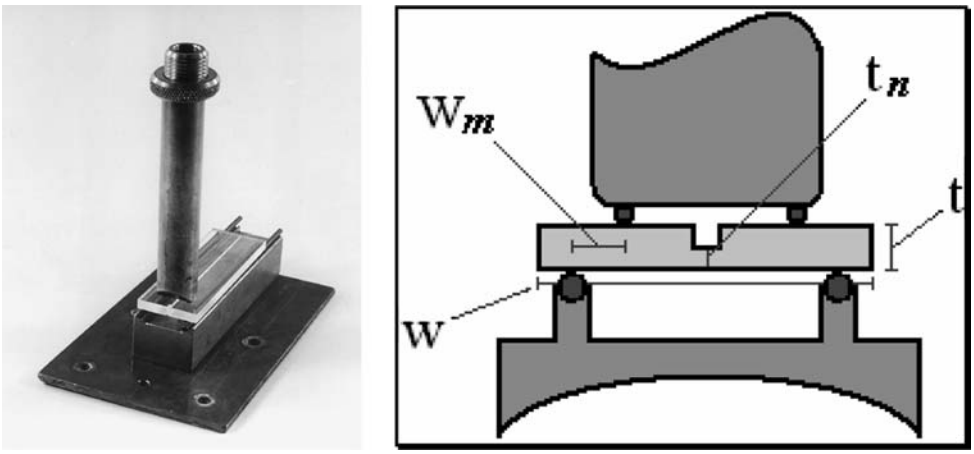

Fig. 2 Double torsion fracture toughness test apparatus

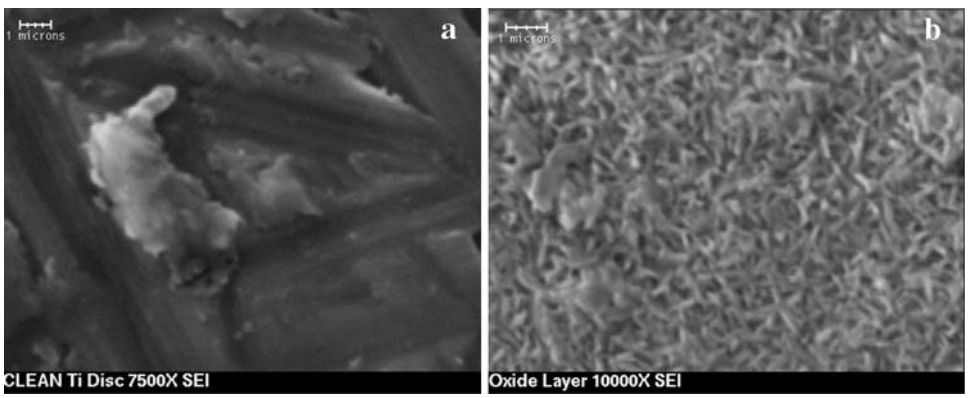

Fig. 3 **a** SEM image of titanium substrate at 7500× and **b** SEM image of oxide layer grown on the titanium substrate at 10,000×

$$K_1 = P_c W_m \left(\frac{3(1+v)}{W t^3 t_n} \right)^{1/2} \quad (2)$$

where Wm is the moment arm, W the specimen width, t the specimen thickness, t_n is the thickness in the crack plate and υ Poisson's ratio (assumed to be 0.33) [50, 51].

Values for K_{IC}, the fracture toughness, were obtained by substituting the appropriate specimen dimensions along with the load at fracture P_c in Eq. 2.

2.6 Surface analysis of titanium and HA discs

Disc surfaces were analysed before adhesion by glancing angle X-ray Diffraction (G-XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) analysis. After tensile bond strength testing discs were analysed by SEM. A Phillips Xpert MPD Pro 3040/60 X-ray Diffraction Unit (Philips, Amsterdam, Netherlands) was used to perform G-XRD on the surface of the discs. A

JEOL JSM-840 scanning electron microscope (JEOL Ltd., Tokyo, Japan) equipped with a Princeton Gamma Tech (PGT) Energy Dispersive X-ray (EDX) system (Princeton Gamma Tech UK, Peterborough, UK) was used to obtain secondary electron images and carry out chemical analysis of the surface of discs. All EDX spectra were collected at 20 kV, using a beam current of 0.26 nA.

3 Results

One glass, composition 0.04SrO/0.12CaO/0.36ZnO/0.48SiO_2 (mol. fraction) was synthesised and cements were produced based on 50 wt.% PAA (E6 and E7), with and without 10 wt.% TSC. Cements were evaluated and compared to commercial controls in terms of double torsion fracture toughness and tensile bond strength.

3.1 Surface analysis of titanium discs

G-XRD of the surface of the titanium disc before and after treatment (Fig. 4a) reveals the presence of an oxide layer before treatment. This oxide layer alters phase during the surface treatment and results in the formation of a mixed crystalline oxide layer, comprising of anatase (TiO_2), rutile (TiO_2) and a sodium titanium oxide ($Na_2O_7Ti_3$) (Fig. 4b). The relative quantity of oxide, as compared to the background titanium peaks is similar in both treated and untreated samples.

Secondary electron imaging of the surface of the titanium disc before surface treatment, as observed in Fig. 3a does not show a continuous oxide covering, however in Fig. 3b it can be seen that an oxide layer has entirely covered the titanium surface after surface treatment. EDX analysis of the surface of both samples reveals only titanium, aluminium and vanadium with no oxide peaks evident. Oxygen detection by EDX however, can be problematic and often remains undetected [54].

3.2 Tensile bond strength testing

Tensile bond strength results of Zn-GPC formulations A and B, as well as both commercial cements can be seen in Fig. 5. Zn-GPC formulations C and D did not form an adhesive layer and delamination occurred prior to testing at the cement-HA interface after all incubation periods.

As can be seen from Table 2, Simplex^{TM} P and Hydroset^{TM} consistently fractured away from the titanium interface, whereas the Zn-GPC formulation B consistently fractured away from the HA disc interface, leaving no residual cement attached, as can be seen from Fig. 6a. Zn-GPC formulation A fractured by a mixture of cohesive failure and adhesive failure from the HA surface, as can be seen from Fig. 6b.

3.3 Double torsion fracture toughness testing

Double torsion fracture toughness results of Zn-GPC cement formulation D as well as Simplex^{TM} P can be observed in Fig. 7. Zn-GPC formulation C and Hydroset^{TM} did not display fracture toughness values by the current test method. Zn-GPC formulations A and B had working times which were too short to allow placement of the cements into the double torsion moulds.

4 Discussion

4.1 Surface analysis of titanium discs

Though an oxide layer was present on titanium discs without surface treatment, due to the formation of the passive oxide layer in an oxygen rich air environment, surface treatment resulted in the formation of a more uniform surface oxide layer which is likely to result in a more even stress distribution for the purposes of the tensile bond strength test. The oxide layer formed is similar in composition and morphology to oxide layers formed in other studies and has been shown to increase the biocompatibility of the alloy in vivo [55–58].

4.2 Tensile bond strength

Controlled TSC additions to Zn-GPCs have been shown to lengthen the working and setting times of cements without adversely affecting their compressive or biaxial flexural strengths [40]. However, delamination of TSC containing cements was observed in tensile bond strength tests prior to testing. This observation considerably undermines the use of TCS containing Zn-GPCs for numerous applications, not least of all in luting applications. Such delamination may result from the reduction of available carboxylate groups as a result of neutralisation with sodium ions from the TSC, as it is these carboxylate groups which are said to be the key to GPC's ability to bond chemically with the HA [59, 60].

Both Zn-GPC formulations without TSC additions (A and B) exhibited superior tensile bond strength to commercial cements examined, over all time intervals studied. Tensile bond strength of GPCs did not vary significantly with maturation time, however a significant increase in tensile bond strength was observed for formulation B after 7 days incubation. This may be an anomaly resulting from variation in application time of cement to the HA disc or reduction of film thickness, both of which are difficult to accurately control. However, it may also be a real effect with reduction of bond strength after 30 days being attributed to an over-crosslinking effect [61], resulting in a more brittle cement, which is more

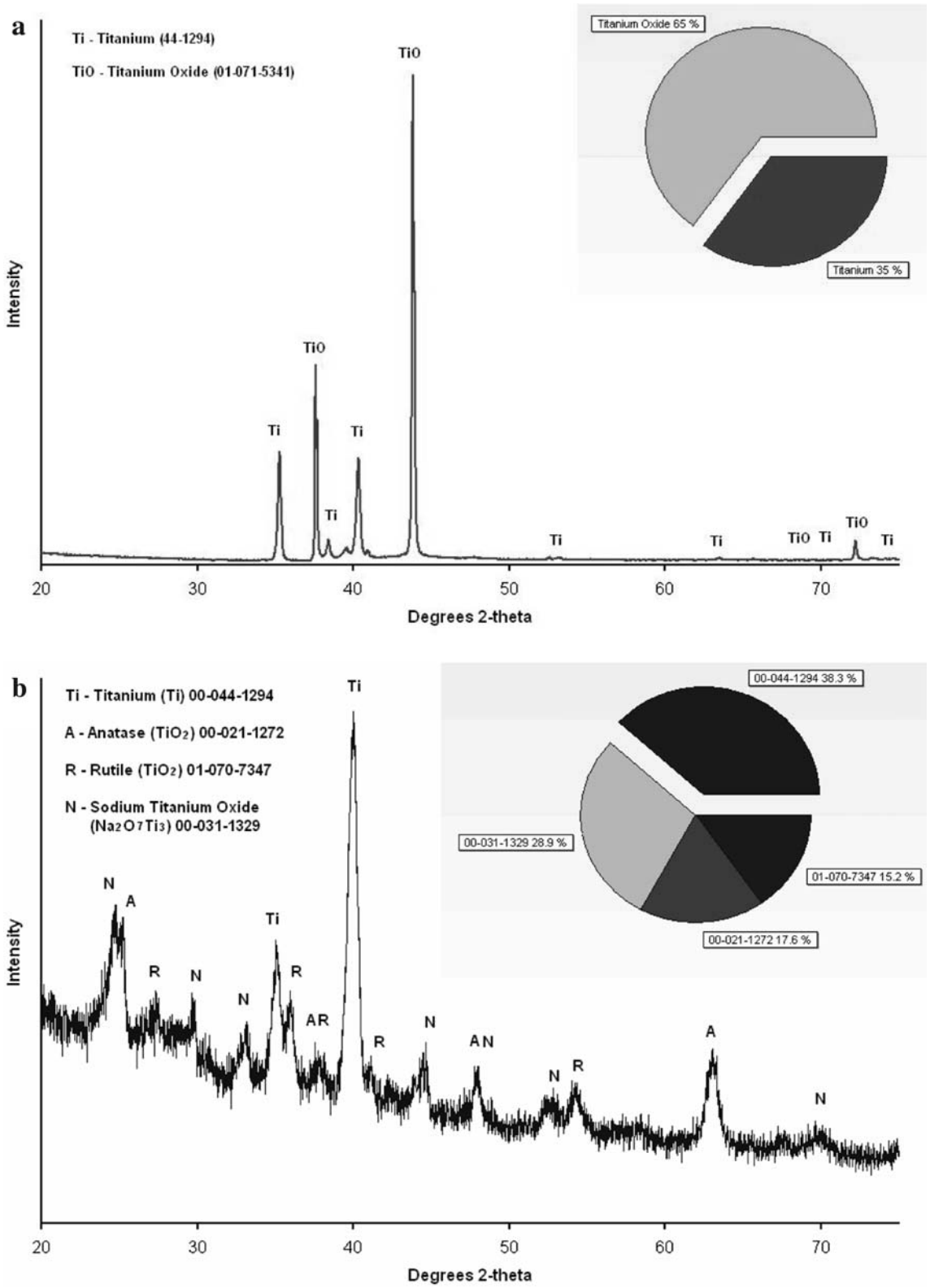

Fig. 4 G-XRD of **a** oxide layer on untreated disc and **b** oxide layer on titanium disc after surface treatment

susceptible to failure initiation due to crack propagation close to the HA interface. After 1 and 7 days, no significant difference is observed between the tensile bond strengths of Simplex^{TM} P and Hydroset^{TM}, however after 30 days of maturation, Hydroset^{TM} exhibited superior bond strength to that of Simplex^{TM} P. From Table 2 it can be seen that both

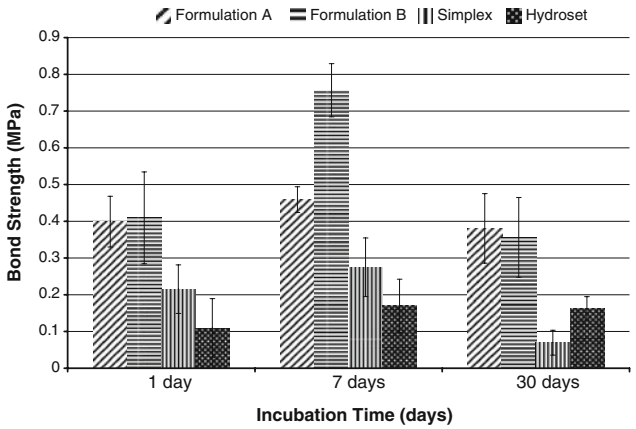

Fig. 5 Tensile bond strength of two GPC formulations and two commercial cements

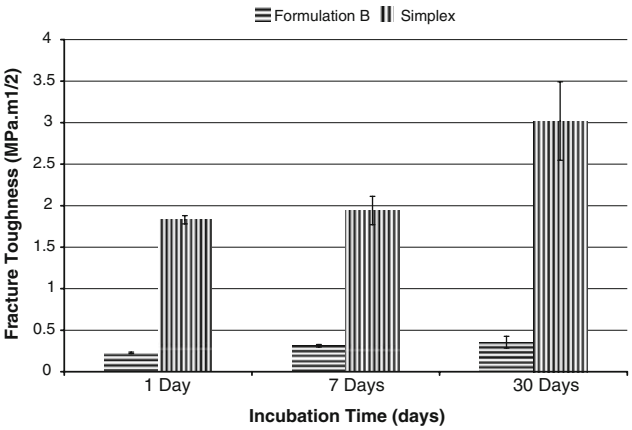

Fig. 7 Double torsion fracture toughness of two GPC formulations and two commercial cements

Table 2 Mode of failure in bond strength samples

Cement	1 day	7 days	30 days
Simplex™ P	Adhesive Ti	Adhesive Ti	Adhesive Ti
Hydroset™	Adhesive Ti	Adhesive Ti	Adhesive Ti
Zn-GPC A	Cohesive/ Adhesive HA	Cohesive/ Adhesive HA	Cohesive/ Adhesive HA
Zn-GPC B	Adhesive HA	Adhesive HA	Adhesive HA

Simplex™ P and Hydroset™ failed at the titanium surface's interface with the cement, this is likely due to a better mechanical interlock with the HA microstructure than with the titanium oxide surface coating. As can be seen from Figs. 6a and 3b, voids present on the surface of the HA disc are considerably larger (around 5 μm) than those present on the surface treated titanium disc (0.5 μm); this may affect the amount of cement which can penetrate the surfaces and result in a better cement adhesion to the HA interface. Both Zn-GPC formulations failed from the HA interface, however formulation A also exhibited some cohesive failure, this is likely due to poor tensile strength as a result of the low molecular weight of PAA used in the formulation. GPCs are known to chemically bond to HA, it is therefore somewhat of a surprise that adhesive failure occurred at the HA interface. From such a result it may be inferred that chemical bonding also occurred between the GPC and the surface treated titanium. Conventional GPCs have been used in orthodontics for many years, to adhere surgical metal to teeth, resulting in good adhesive bonds [62]. Good bond strengths have also been achieved between conventional GPCs and surgical titanium [63]. These results indicate that the Zn-GPCs exhibit better adhesion to the surface treated Ti6Al4V than to the HA. This may occur as a result of the sodium inclusion in the titanium alloy's surface layer which would be expected to increase its reactivity [64, 65]. Also, inclusion of sodium in titanium oxide surface layers has been shown to result in increased oxygen incorporation which would increase the basicity of the layer [66].

Both Zn-GPC formulations without TSC additions (A and B) exhibited superior tensile bond strength to the commercial cements examined, over all time intervals studied. It should also be noted that adhesion to bone is

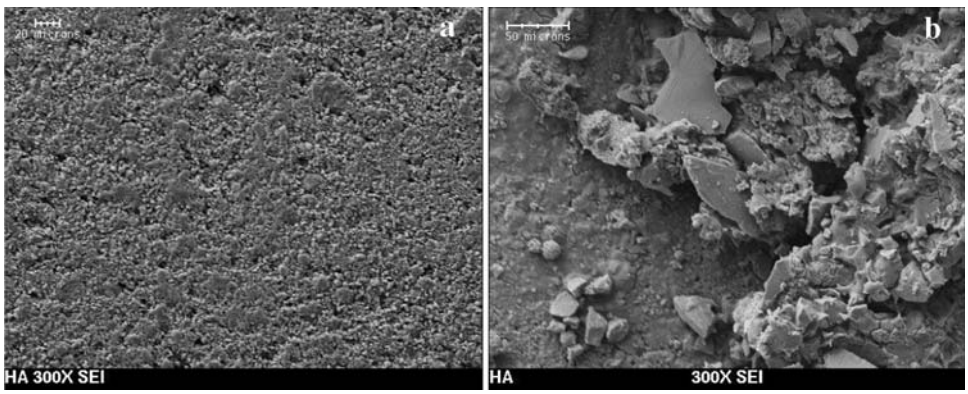

Fig. 6 **a** SEM image of HA disc after a adhesive and **b** cohesive failure, at 300×

likely to result in a stronger bond than to the HA disc in this study due to hydrogen bonding which has been postulated to occurring between the GPC and collagen [67].

4.3 Double torsion fracture toughness

According to ASTM E399-06, which describes a similar test for fracture toughness measurements of metallic materials, under plane-strain conditions, the minimum fracture toughness measurable is deemed to be 0.22 MPa$\sqrt{m}$ [68]. This is not necessarily applicable to double-torsion testing however the lowest mean result recorded in this study is 0.23 MPa$\sqrt{m}$, for Zn-GPC formulation B after 1 day of incubation. Zn-GPC formulation A, as well as Hydroset™ did not record any fracture toughness results due to rapid fracture and it can be assumed that results are below 0.23 MPa$\sqrt{m}$. In another study, fracture toughness of a similar carbonate apatite forming calcium phosphate cement, Norian® SRS (Synthes Inc., West Chester, Pennsylvania, USA), was measured by means of a chevron-notched bar test and was found to be 0.06–0.14 MPa$\sqrt{m}$, this test method may be more suitable for measuring such small fracture toughness values. Fracture toughness of Simplex™ P is significantly greater than that of the Zn-GPCs observed in this study and both cements observed appear to increase fracture toughness with incubation time, as has been observed in some other studies [61, 69].

In this comparative study of adhesive cements, Zn-GPCs fare well and exhibit potential when compared with leading commercial products. Though Simplex™ P has much larger fracture toughness values, as a skeletal luting cement, it is likely to fail in adhesion. Simplex™ P has comparatively poor adhesion to titanium alloys and, due to its lack of bioactivity and formation of a fibrous layer in vivo, is unlikely to bond well to bone. Hydroset™ on the other hand has both low fracture toughness and poor tensile bond strength to biomedical titanium alloys. The poor fracture toughness and bond strength associated with Hydroset™ is not likely to be problematic in its present application as a bone-void filler. Bone void fillers are not designed for adhesion or load-bearing capacity and Hydroset™ is used in such applications for its injectability, biocompatibility and osteoconductive properties. Though Zn-GPCs do exhibit potential for skeletal luting applications such as cranioplasty and vertebroplasty; low fracture toughness values and the reduction of bond strength following rheological modification with TSC may limit their potential. Development of a suitable modifying agent, which lengthens working times and facilitates the use of higher molecular weight PAA, without altering the cements ability to bond to bone or biomedical alloys, would increase their potential for such applications.

5 Conclusion

The PMMA commercial control was found to have superior fracture toughness to the novel cements however, failure it tension was found to occur adhesively in most incidences. The novel Zn-GPCs exhibited superior bond strength to HA and a surface-treated biomedical titanium alloy over prolonged periods. These advantages, as well as more suitable elastic modulus, excellent biocompatibility, bioactivity, lack of volumetric shrinkage and heat evolution infer that aluminium free, zinc-based GPCs exhibit potential for use in skeletal luting applications and remain limited, largely by short working times.

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