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LETTER

Biofilm inhibitory coatings formulated from glass polyalkenoate cement chemistry: an evaluation of their adhesive nature

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Glass polyalkenoate cements (GPCs), are formed by the reaction between an ion-leachable glass and an aqueous solution of polyacrylic acid (PAA) [1]. GPCs may also be formed from a combination of polyalkenoaic acids and various fillers such as those based on the use of additional fillers like N,N′-methylenebisacrylamide to increase their strength and toughness [2]. These materials can be formulated to be anticariostatic [3] by the inclusion of fluoride in the glass phase of GPCs which subsequently releases beneficial amounts of the F^- ion into the oral environment [4, 5]. Commercially available GPCs are all based on calcium alumino silicate glass chemistry [6]. Aluminium is present in the glass because it can isomorphically replace the SiO_4 tetrahedra within the glass structure. This causes a local charge imbalance within the structure, resulting in the acid degradability of the glass [7]. More importantly, aluminium is essential for the mechanical integrity of the cement as the ions undergo cement forming [8]. However, the presence of aluminium retards the medical and surgical applications of such cements as aluminium ions (Al^{3+}) released in vivo can cause demineralisation of the bone [9] and has been implicated in the pathogenesis of degenerative brain diseases including Parkinson's and Alzheimer's disease [10, 11].

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The authors have developed GPCs based on calcium zinc silicate, rather than calcium alumino silicate glasses [3, 12–14], where the zinc ion (Zn^{2+}) replaces Al^{3+}, as it can act as a network modifying oxide in the glass phase [9, 15]. A serendipitous effect of developing zinc-based GPCs was that these cements have antimicrobial ability [3] as the release of zinc ions inhibits bacterial growth. The silver ion (Ag^+) also has an acknowledged antibacterial effect [16, 17] and the authors have recently developed coatings based on silver/zinc-based GPCs which have proven bactericidal efficacy against *S. aureus* and *P. aeruginosa*, common aetiological agents of hospital-acquired infections [18]. In that study, the authors also reported that these GPC coatings adhere to Ti6Al4V titanium alloy. Conventional GPCs are inherently capable of chemically bonding to metal substrates [19] with the assistance of the oxide layer which forms on the alloy surface [20]. However, the authors have not yet reported on the extent of this bonding between these silver/zinc-based GPC coatings and metal. There have been previous studies to create novel testing modalities to evaluate the bond strength of luting cements some of which have been previously reported by the authors [21]. One in-house study involved sandwiching the GPC between hydroxyapatite (HA, a material comparable to the mineral phase of bone) and hardened steel discs [21]. However, the possible applications of these silver/zinc-based GPC coatings include a range of clinical applications where biofilms can proliferate, such as on hard surfaces (surgical stainless steel) [22] and flexible surfaces (tubing for catheters and aspirators) [23], and so the objective of this study is to modify the conventional T-peel test [24], historically employed to determine resistance of a bonded assembly of two adherents when at least one adherent is flexible [24], to quantify the bond between tape and a surgical metal substrate bonded by a luting GPC. There are two types of peel

testing, 90° angle [24] and 180° angle [25], but the new test would be based on the 90° angle modality because the force of the peel test directly relates to the angle of the peel test; the smaller the angle, the larger the strength measured for the cement [26], resulting in a lower margin of error [27].

Bond strength is defined as 'the force per unit area required to break a bonded assembly with failure occurring in or near the adhesive interface' [28]. The literature is devoid of any in vitro studies for determining what force or stress causes a construct to de-bond, and so any in vitro tests are unlikely to directly replicate the clinical situation.

The type of GPC used also affects bond strength. Conventional GPCs tend to fail cohesively [29], whereas resin modified GPCs (RMGPCs) fail adhesively [30], the reason being that the RMGPC matrix is more integral than a matrix in a conventional GPC, resulting in the interfacial layer yielding in advance of the failure of the bulk material [31].

Peel testing of GPCs in the literature has employed diverse test methods, many where one of the substrates is tooth structure [32–36], but some consider alternative substrates such as Teflon [37]. Bond strengths recorded ranged from 1.4 MPa [37] to 13.57 MPa [34]. Samples in these previous studies were tested at room temperature (20 °C) and the test conditions (i.e. rate of peeling) varied. The materials being developed herein have potential as coatings in a wide range of clinical applications, such as antibacterial coatings for surgical implements and as glazes on hard surfaces in hospitals. The authors report here on preliminary work developing a peel test, based on the International Standard test, ISO:8510-1:1990 [24], for these purposes.

Two glass formulations, A and B, were synthesised by melt quenching. Their compositions are reported in Table 1. Full details of the synthesis procedure have previously been reported [18].

Following quenching, the resulting frit underwent grinding in a gyromill (15 mins) and the glass powder was subsequently passed through a 25 μm sieve. All further work was undertaken on the <25 μm particles. The glass transition temperatures (T_g's) of the glasses were evaluated by combined differential thermal analyser-thermal gravimetric analyser (DTA-TGA, Stanton Redcroft STA 1640, Rheometric Scientific, Epsom, UK) and reported as 597 °C. Their amorphous nature was confirmed by X-ray diffraction (Philips Xpert MPD Pro 3040/60 X-ray Diffraction Unit, Philips, Netherlands). Full methodology has been reported previously [18].

Table 1 Glass compositions (mol. fraction)

Glass	SiO_2	ZnO	Ag_2O	Na_2O
A	56.04	32.98	0.11	10.87
B	56.04	32.76	0.33	10.87

Two GPCs, A and B, were prepared by mixing 0.5 g glass, A and B, respectively, with 0.2 g polyacrylic acid (PAA) and 0.2 mL distilled water. Ciba specialty polymers (Bradford, UK) supplied the PAA (M_w, 210,000) in aqueous solution (25 vol.%). The PAA was subsequently freeze dried and ground (maximum particle size, 90 μm). Mixing was undertaken on a clean glass plate with a dental spatula in ambient laboratory conditions. The long working and setting times of these cements (reported previously [18], repeated in Table 2, for completeness) facilitates the coating of the cement onto the Ti6Al4V substrate prior to onset of setting.

In accordance with ISO:8510-1:1990 [24], a T-bar with specific measurements (Fig. 1) was fabricated from Ti6Al4V alloy (James Healy Ltd, Limerick, Ireland).

After mixing, each cement was coated onto the top surface of different T-bars using a clean spatula. A glass fibre tape (3 M^{TM}, Texas, USA) was placed on top of the cements as shown in Fig. 2 and overhung one end of the construct by 20 mm.

Identical constructs, with the exception of the luting cement, were stored in an oven (24 h, 37 °C), prior to being mechanically tested by a 4310 Universal Testing Machine (Instron Ltd., High Wycombe, Bucks, UK) fitted with a 1 kN load cell. A sample size of three was undertaken for both cements. For each construct, the end of the tape was secured in the top jaws of the Instron, and was pulled at 90° from the horizontal at a cross head speed of

Table 2 Working (W_t) and setting times (S_t) of the cement formulations

Cement	W_t	S_t
A	4m12s	16h07m41s
B	5m22s	16h15m23s

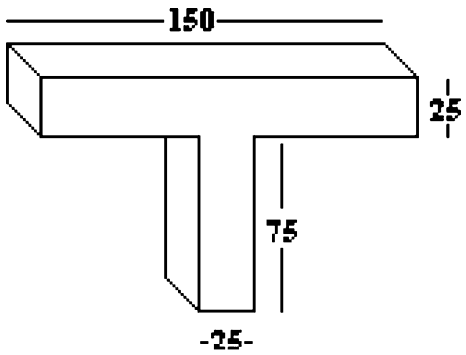

Fig. 1 T-bar specifications for peel test in mm

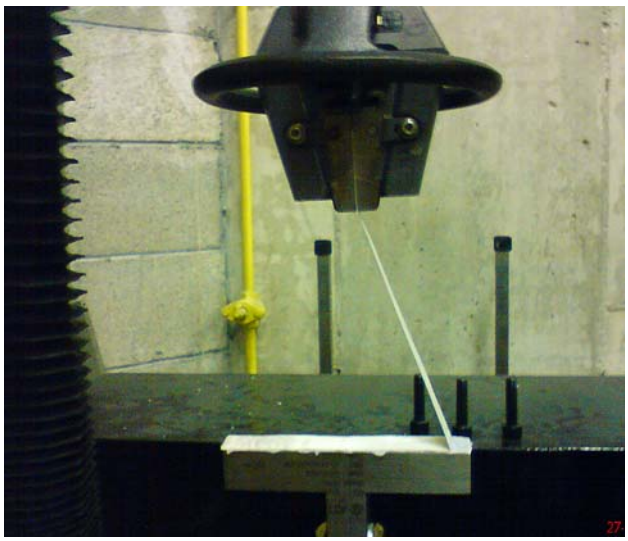

Fig. 2 Image of novel peel test

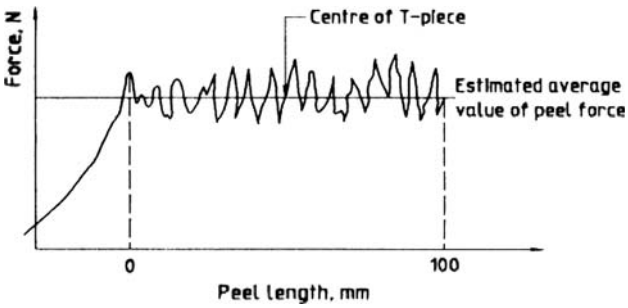

Fig. 3 Typical peel force graph

5 mm min^{-1} in order to cause delamination (Fig. 2). The peel strength of the bond was calculated by recording the average peel force from the moment the peel test plateau (Fig. 3).

The tape surface that was delaminated from the constructs was examined by scanning electron microscopy (SEM) with an accelerating voltage of 20 kV to determine whether failure of the bond was adhesive or cohesive in nature. The samples were prepared for SEM analysis by sputter coating with gold. Secondary electron images (SEI) were obtained from both secondary and back-scattered electrons using a JEOL JSM-840 SEM (JEOL, Japan).

It can be seen from Fig. 4 that the construct using cement A exhibits an average bond strength of 5502 Pa (SD = ±0.00032). The construct using cement B exhibits an average bond strength of 5930 Pa (SD = ±0.00046). Thus, there is no significant difference between the bond strength calculated for the cements based on the two different glasses.

These bond strengths are low compared to those reported for GPCs in the literature [32–36], but most of these previous reports [32, 33, 35, 36] consider at least one of the substrates to be tooth structure. Teeth are composed of crystalline calcium phosphate embedded in a protein matrix. These calcium and phosphate groups undergo displacement in the tooth structure upon attack by the GPC's carboxylate ions. The mechanism of adhesion of GPCs to tooth surfaces has been previously studied with polyacrylic acid, representing the reactive part of the cement, and HA, the main constituent of enamel as a model system. Binding was achieved by carboxylate groups penetrating the apatite matrix and displacing calcium and phosphate ions. Literature shows that efficient binding requires treatment of the dental surface by conditioners (e.g. polyacrylic acid) able to improve its wet-ability and smoothness [38, 39].

The cements in this report were tested against Ti6Al4V, not tooth structure, as they are designed as surgical coatings.

Visual inspection was also employed to examine the surface of the metal substrate and the glass fibre tape

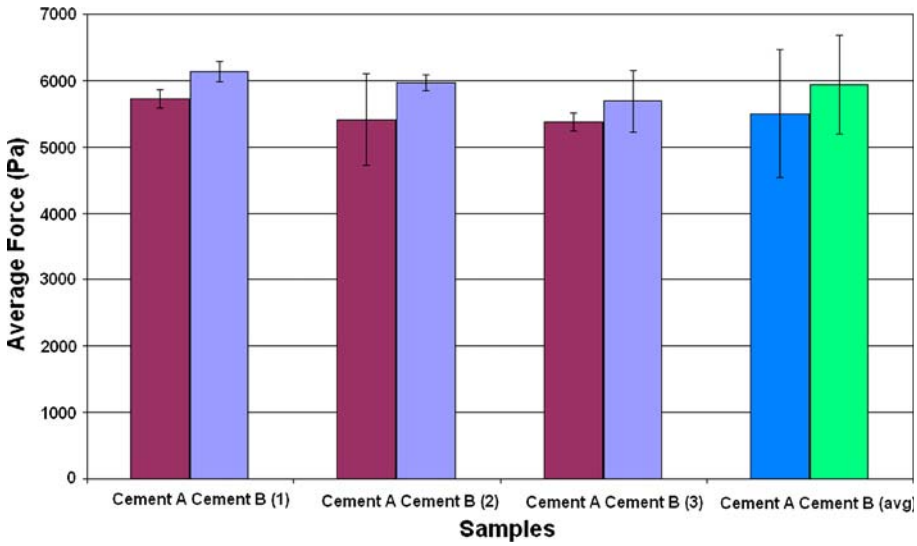

Fig. 4 Peel test results using constructs based on cements A and A

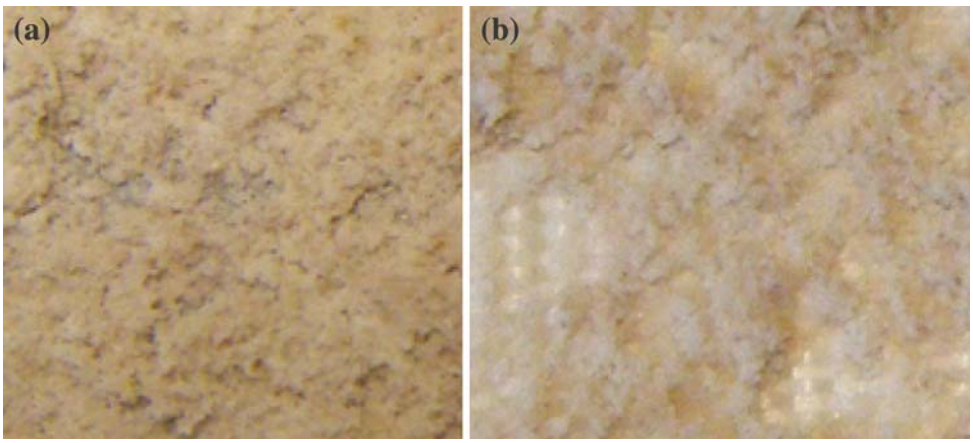

Fig. 5 Optical images of Cement B adhering to **a** Ti6Al4V alloy and **b** glass fibre tape

substrate post-testing (Fig. 5). It was not possible to undertake electron microscopy of the Ti6Al4V substrate due to its size. From both microscopical and visual inspection, it is evident that the cement remained partially attached to both substrates, indicating cohesive failure.

The objective of this study was to create a novel test modality to evaluate the adhesive nature of biofilm inhibitory coatings based on novel silver/zinc GPC coatings. This study showed that the novel GPCs adhered to both rigid and flexible substrates and, upon testing to loads in excess of 5500 Pa, failed in a cohesive manner. Bond strengths reported are low compared to those in the literature, but this may be due to previous studies employing at least one biological substrate, resulting in considerable chemical adhesion. The test methodology developed herein may have potential for measuring bond strengths between cements and substrates where at least one of the substrates is flexible.

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