Characterisation of mechanical and surface properties of novel biomimetic interpenetrating alumina-polycarbonate composite materials

1 Introduction

There is a growing demand for aesthetic fixed orthodontic appliances, most probably linked to the increasing number of adults who wish to undergo orthodontic treatment, both in the UK [1] and Worldwide [1-5]. Orthodontic materials currently used to fabricate aesthetic orthodontic brackets include ceramics, e.g. polycrystalline and monocrystalline alumina, and polymers, e.g. polycarbonate and polyurethane. Since their introduction in the 1980s, ceramic brackets have become very popular, with their use in the USA reportedly increasing during the period 1986 to 2014, from 6% to 70%. At the same time the use of polymeric orthodontic brackets has declined significantly [6]. This is because polymeric brackets suffer from low wear resistance, creep, and discolouration due to water absorption within the oral environment [7-10]. Although ceramic orthodontic brackets are more popular due to their improved wear resistance and good colour stability [11-13], they also have undesirable properties. These include a relatively high hardness, which can lead to excessive wear of the enamel of opposing teeth, their brittle nature, which can lead to unwanted in-service bracket failure, and their high compressive strength, which can result in enamel surface fracture at completion of treatment during bracket removal [8, 14-16].

Attempts have previously been made to introduce hybrid ceramic/ polymeric brackets, comprising two bulk phases joined at a single interface, in order to create a more durable aesthetic bracket that is easier to debond. The bulk polymer comprises the bonding base and the bulk ceramic the remainder of the bracket. However, the weak link is the single interface between the two bulk materials that often leads to delamination and poor clinical performance [17, 18]. More recently, using the technique of freeze-casting, Alrejaye, Pober and Giordano II [19] fabricated an interpenetrating composite material of alumina and polycarbonate, with toughness and strength values comparable to commercially available alumina ceramic orthodontic bracket materials. This novel composite material shows promise as an aesthetic orthodontic bracket material, not only as a result of the interpenetrating nature of the polymer within the porous ceramic framework, but also because freeze-casting can be used to control the degree of porosity in different parts of the structure during fabrication. The ideal aesthetic orthodontic bracket should be strong enough to withstand the oral environment, be efficient at transferring the applied orthodontic forces to initiate tooth movement during orthodontic treatment, maintain a good appearance/colour and be easy to remove at the completion of treatment with little risk to the enamel surface. The use of a ceramic framework with a graduated porosity interpenetrated by a second polymeric phase has the potential to fulfil these requirements

The aim of the present study was to characterise novel biomimetic alumina-polycarbonate (Al_2O_3-PC) interpenetrating phase composites, produced using the freeze-casting technique followed by heat-pressing infiltration of the polycarbonate (PC) polymer phase. The wear

performance of these composite materials was evaluated and compared with their raw constituent materials (alumina and PC polymer), along with human enamel.

2 Materials and methods

Four materials were characterised as part of this investigation. These included, two biomimetic composites produced by freeze-casting aqueous suspensions with either 20% or 30 vol.% initial solid ceramic loadings (Al_2O_3-PC-20% and Al_2O_3-PC-30%), pure polycarbonate polymer (PC polymer) and densely sintered alumina ceramic. In the case of abrasion testing human enamel was also used for comparison.

In the first step, sintered porous alumina ceramic preforms with different ceramic volume fractions were produced using the freeze-casting method. Initially, ceramic powder was dispersed in water, a dispersant and gelatine and then freeze-cast to create porous green scaffolds. These were then sintered to create ceramic scaffolds with differing porosities, according to the initial solid ceramic loading within the aqueous suspension, as described by Al-Jawoosh et al. 2018 [20].

In the second step, the sintered porous ceramic scaffolds were infiltrated with PC polymer. PC films (Density: 1.20 g/cm³, Goodfellow, UK) were hot-heat-pressed into the ceramic preforms at a temperature of 250°C for 4 hours in an oven (Heratherm, Thermo Scientific, UK), using a load of 400N and a stainless-steel cylindrical mould. In each case the weight of the PC polymer was equal to the weight of the porous ceramic preform. Following loading and heat treatment the specimens were left in the oven overnight to cool down before being removed for testing.

Prior to characterisation the Al_2O_3-PC composites, pure PC and dense alumina specimens were cut to size using an Accutom-50 (Struers, UK) cutting machine and a diamond saw (Beuhler, USA). The specimen size prepared was dependent on the characterisation test. Once cut, the specimens were polished using a polishing machine (Tegra Pol 15, Struers, UK) with sequential silicon carbide papers under water cooling down to a final 2400 grit. The samples were then placed in an ultrasonic water bath for 30 minutes (Grant Scientific, UK) to remove any debris and unwanted particles.

For the enamel specimens, third molar teeth were used. Their surfaces were inspected for imperfections and any teeth with cracks, caries, discoloration or loss of hard tissue were excluded. Prior to use the teeth were stored in 0.7% sodium chloride solution containing 0.1% thymol. They were initially sectioned using an Accutom-50 water-cooled high-speed diamond saw (Struers, UK) to separate the crown from the root. Following this step, the pulp chamber was removed from the crown using a high-speed rotatory hand air motor (NSK, Japan). The enamel was then sectioned to produce 2x3x2mm sized specimens. Each enamel block was then mounted in epoxy resin (Stycast; Hitek Electronic Materials, Scunthorpe, UK), polished using a polishing machine (Struers, UK) with p1200 silicon carbide discs (Struers, UK), followed by final hand polishing with Al_2O_3 powder (0.3 µm) as a suspension in deionised water on a glass slab. They were ultrasonicated in deionised water between each polishing stage to remove any debris. The teeth were sourced from an ethically approved tooth tissue bank (REC REF 16/NI/0192) held under HTA licence 12200, project reference: 75.

Once all the composite, alumina and polycarbonate specimens had been prepared, they were characterised as (with the enamel specimens only being used during abrasion and hardness testing) shown in Table 1.

2.1 Density

Six rectangular blocks (4 × 4 × 2 mm) of each of the four material types were prepared and their densities obtained using Archimedes' method, according to ASTM standard, C373−16, USA.

2.2 Compressive strength

Six specimens (4x4x2mm) of each of the materials were compression tested using a universal testing machine (Zwick Roell Z020, Ulm, Germany). Once maximum load was reached, the samples were removed and checked to make sure that the fracture point was at the centre of the sample in each case. For this test the composite material samples were divided into two groups. In one group the force was directed parallel to the direction of freeze-casting, with the ceramic-rich layer at the top and the polymer-rich layer at the bottom, and in the second group the force was applied perpendicular to the direction of freeze-casting.

Flexural strength and elastic modulus

A three-point bend test was used to determine the flexural strength and elastic modulus of each material and in the case of the composite samples this was parallel to the freezing direction with the ceramic rich layer at the top. Each sample (1.8x4x18mm) was placed into a

computer-controlled universal testing machine according to British Standard, BS EN ISO 6872, 2008 [19].

2.3 Fracture toughness

Six rectangular specimens of each composite sample (4x8x32mm) were polished and pre-notched with a high-speed cutting machine according to the standards for a single-edge-notched beam, ASTM 1820.15.A,USA [21]. A razor blade and diamond paste were then employed to sharpen the notch and extend it an additional 200–350 μm. The final length of the notch was measured with an optical microscope. All the samples were tested using a universal testing machine (Zwick Roell Z020, Ulm, Germany) in the direction parallel to the freeze casting. The notch was made through both the ceramic-rich and polymer-rich surfaces.

2.4 Hardness

Vickers hardness tests were performed at a constant load with a calibrated Vickers indenter in a micro-based indentation system (Duramin Ver 0.08, Struers, UK) according to the standards of Advanced Technical Ceramics, EN843-4: 2005 [22]. Six rectangular specimens (4x10x12mm) were subjected to a maximum load for 20 seconds parallel to the direction of freeze casting on the ceramic-rich surface. Thirty determinations were made for each material using the test method parameters as illustrated in Table 2.

Indentation diagonals were measured by light microscopy. Any indentations with an irregular shape were rejected. The lengths of the two resultant diagonals of the surface indentations were measured and averaged for each measurement and the hardness calculated.

2.5 Abrasion testing

The aim of abrasion testing was to determine the predicted maximum wear of an orthodontic appliance constructed of a composite material over two years. A custom-made brushing machine (Bristol University) was utilised for brushing the samples using a linear motion (West et al., 2002). Prior to abrasion testing, adhesive tape was used with each specimen to provide two control areas and an approximate 1.5 mm^2 wide surface window exposed to the toothbrushing. A toothpaste suspension was prepared using a ratio of 25 g toothpaste (Colgate Total Everyday, 1450 ppm.F-, 27.6 µmol/L.F-, Colgate-Palmolive Ltd, Guilford, Surrey, UK) to 40g deionised water, mixed using a stirrer and magnetic flea (Fisher Scientific, Loughborough, UK) until a homogenous suspension was obtained. This was then poured into the brushing machine reservoir to ensure that each specimen was covered by at least 3 mm of dentifrice suspension. The toothbrushes (Oral B, standard medium, size 35, Procter & Gamble, Egham, Surrey, UK) were mounted such that the toothbrush filament tip plane moved back and forth across the specimen. Each test group was allocated a new toothbrush head to avoid contamination between groups. A weight of 200 g was added to the brushes to simulate the everyday brushing force according to International Standard, ISO 11609:2017. The suspension was replaced every hour to ensure adequate coverage of the specimens. The composite specimens were oriented with the ceramic-rich layer at the top, in contact with brush filaments. All samples were brushed for 2 hrs and 50 mins to simulate normal toothbrushing over an average 2-year course of orthodontic treatment. The surface roughness values were evaluated before and after toothbrushing. After brushing, any remaining dentifrice suspension was removed using

deionised water before the specimens were then stored in deionised water prior to measurement.

2.6 Surface loss

Non-contact profilometry (Proscan 2100 non-contact profilometer, Scantron Industrial Products Ltd, Taunton, Somerset, UK) and Proscan software (Scantron Industrial Products, Ltd, Taunton, Somerset, England) were used to measure the surface roughness before and after toothbrushing, along with total surface loss after brushing. A dark reference background check was performed each time prior to scanning to achieve optimum sensitivity during measurements.

To determine the amount of surface loss, a 1.5x1.5mm² area of each specimen was scanned. The Proscan software was used to highlight three areas in each case, one in the centre across the brushed area (treated) and two from the specimen shoulder areas that were covered and protected initially with tape (controls). This allowed for direct comparison between the brushed and unbrushed areas. Differences in height were calculated using the simulation of the area trace method [23]. The measurements were repeated 3 times and the mean value was considered as the surface loss value of the specimen. Six specimens from each material were investigated. Surface loss was measured by scanning the area that had been brushed (treated) along with the unbrushed areas (control) that had previously been protected by taping.

2.7 Surface roughness

To determine the initial surface roughness before toothbrushing, surface scanning was performed on a scan area of 2x2mm². The optimal step size for the scan area was 0.01 mm in

both the horizontal and vertical scan directions and with 200 steps. A reference line was placed on one edge of each specimen in order to record the start position, which was used for all scans with pre-brushing and post-brushing. Six specimens from each material were examined. Surface roughness (Ra, Rz, Rmax and Rq) was measured by scanning the test materials before and after toothbrushing. A S11 chromatic sensor was used for all measurements, with surface filter and auto levelling functions at a sampling rate of 30 Hertz.

Sample imaging

Samples of the ceramic frameworks and the novel biomimetic composites were imaged using SEM (FEI Quanata 400, FEI, USA) after splutter coating with a gold palladium mixture (Emitech K575X, Quorum Technology Ltd, UK). Samples were also imaged using a MicroCT scanner (Nikon XTH225, Tungsten target, 225 reflection head, Japan) at 120 kV, 300 µA and an exposure rate of 1.4 µm/sec, with no filter applied. VGstudio software (VGstudio MAX 3.1, Japan) was used to produce 3D models of the scaffolds from the 2D images obtained by the MicroCT. Rendered 3D images were subsequently obtained using Avizo Standard (version. 8.1, Thermo Fisher Scientific, UK) with isotropic voxels and a spatial resolution of 4 µm.

2.8 Statistical Analysis

The data were analysed using Stata version 14 (Stata Corp, College Station, Texas, USA) with a predetermined significance level of alpha = 0.05 and are described in terms of summary statistics.

3 Results

3.1 Microstructure of ceramic preforms and composites

The SEM images in Figure 1 show the porous ceramic preform made using a 20% initial ceramic loading, before and after infiltration with PC. The pores are characterised by a honeycomb-like structure with good polymer infiltration and no closed pores. Different sizes and shapes of pores were successfully infiltrated with PC.

MicroCT examination was also performed to get a more in depth image of how the polymer phase had infiltrated the porous ceramic scaffolds in all three dimensions. The anisotropic structure can be clearly seen (Figure 2) with a polymer rich layer at the top and a ceramic rich layer at the bottom with full interpenetration of the polymer into the pores of the ceramic preform.

Figure 3 shows 3D images of the scanned composite materials. It is clear that the composite comprises a fully interconnected network of a ceramic network phase with almost total interpenetration by the polymer phase. It would seem that increasing the initial solid ceramic loading results in a significant change in the microstructure of the interpenetrating Al_2O_3-PC phase composite material. The pores are bigger and more rounded in shape when the initial solid ceramic loading was 20 vol.% compared with the composites produced with 30 vol.% initial solid ceramic loading.

3.2 Density measurements

The mean and SD of the densities of the Al_2O_3-PC interpenetrating phase composite materials are illustrated in Table 3. As might be expected, there is a clear trend of increasing density with increasing initial ceramic content, and between the densities of pure alumina (3.90 g/cm^3) and PC (1.20 g/cm^3).

3.3 Compressive strength

Similar to density, the compressive strength of the novel biomimetic composite increased as the fraction volume of ceramic in the composite increased. When materials with anisotropic characteristics are produced, as in the case of freeze-casting, it is important they are tested with respect to their orientation. In other words, they should be tested both parallel and perpendicular to the direction of freeze-casting. When considering the compressive strength we can see that there was a slight increase when tested perpendicular to the direction of freeze-casting, as opposed to parallel to the direction of freeze-casting for both Al_2O_3-PC-30% (274.91 to 285.15 MPa) Al_2O_3-PC-20% (192.43 to 198.26 MPa) (Table 3). For the non-anisotropic dense alumina and PC the compressive strength values were 2358.08 MPa and 131.4 MPa respectively.

3.4 Flexural strength

Flexural strength was measured parallel to the direction of freeze casting and increased with increasing initial ceramic volume from 105.54 to 148.47 MPa for Al_2O_3-PC-20% and Al_2O_3-PC-

30% respectively. The same was true for Elastic Modulus with mean values of 10.72 and 15.17. For alumina and PC, the flexural strength values were 249.3 and 122.49 GPa, while the modulus of elasticity values were 118.5 and 1.5 GPa.

3.5 Fracture Toughness

Once again there was a trend for an increase in the observed mean fracture toughness from 2.17 to 3.11 GPa as the ceramic solid loading increased from 20 vol.% to 30 vol.% in the initial aqueous suspension.

3.6 Hardness

Alumina showed the highest hardness values (8.76 GPa) followed by human enamel (2.45 GPa), and with PC (0.13 GPa) demonstrating the lowest value among all the materials tested. The hardness values of the composites were between the two constituent materials (Table 3).

3.7 Surface loss

All materials showed surface loss following simulated brushing (Table 4). Enamel and alumina showed the least amount of surface loss of all specimens (0.05 and 0.13 µm respectively). PC showed the highest loss (5.94 µm) and Al_2O_3-PC-20% demonstrated higher surface loss compared to Al_2O_3-PC-30% (1.40 and 0.71 µm respectively). Therefore, surface loss is less with increasing ceramic phase volume fraction within the composite materials.

3.8 Surface roughness

Table 4 summarises the results of the roughness parameters before and after simulated toothbrushing. Toothbrushing resulted in increased roughness values for almost all specimens. Prior to brushing, human enamel and PC showed the lowest roughness for all parameters. When looking at the composite materials, Al_2O_3-PC-20% demonstrated higher Ra values when compared to those of Al_2O_3-PC-30%. Interestingly, the surface roughness values for the dense alumina specimens were slightly lower following brushing.

Using SEM to examine the specimens after simulated toothbrushing once again shows the distinct honeycomb-like structure of the Al_2O_3-PC composite samples. However, closer examination of the SEM images in Figure 4 show that the polymer fraction in each case has surface striations that would correspond with the direction of toothbrushing. No such surface effects are visible within the ceramic fractions.

These results are also confirmed by the 3D profilometry images in Figure 5, where there are obvious differences between the post-brushing surface profile for the ceramic and polymer samples. Following brushing, the ceramic samples had a much smoother profile without the brushing grooves observed with the pure polymers.

4 Discussion

The ideal material for use as an orthodontic bracket should provide adequate strength and toughness to resist the forces applied by the archwires and during normal mastication. It should

be able to be bonded easily to the tooth surface and remain in place for the duration of the treatment, and equally importantly should be able to be removed without affecting the tooth surface. It should also not be so hard that it leads to wear of opposing teeth, but so soft that it cannot resist toothbrush abrasion. It is also important the initial aesthetic appearance is maintained throughout the duration of the treatment.

In the present study novel biomimetic Al_2O_3-PC interpenetrating phase composite materials were evaluated and compared with their constituent materials and human enamel. In order to fabricate a biomimetic material inspired by nature, material architecture is of considerable importance, as this will be directly linked to its ultimate performance [24]. The SEM (Figure 1) and MicroCT images (Figures 2 and 3) illustrate how the porous ceramic preforms comprise an anisotropic 3D honeycomb-like structure with almost complete polymer interpenetration. Within the ceramic phase, the polymer phase occupies the space created by the original ice crystals during the freeze-casting process. However, a third lesser phase, namely entrapped air is also occasionally seen, which might represent an area of potential weakness. Such air inclusions may well be due to air bubbles trapped during the polymer heat-press process, or they maybe as a result of closed pores within the porous ceramic preform. Although unwanted, even within more traditional interpenetrating phase composites used as dental restorations, the formation of some areas of void, or air inclusion, is almost inevitable [25].

In order to produce the Al_2O_3-PC interpenetrating phase composites, PC was heat-pressed into the porous ceramic preforms. PC is an amorphous thermoplastic, with a glass transition temperature of approximately 147°C, above which it softens before flowing at approximately

155°C [26]. This infiltration process can be affected by a number of parameters including the porosity and the thermal conductivity of the second phase, and the heat and load applied during processing. An incorrect combination of these parameters may result in incomplete infiltration. The process of *in situ* infiltration of PC into a porous ceramic preform utilised in this study has not been reported elsewhere in literature. The infiltration procedures were performed in an oven, with the ceramic and PC sitting in a mould, on top of which was a stainless-steel weight applying a force of 400 N. A disadvantage of this technique was the difficulty in manipulating both the weights and specimens at such high temperatures within the oven. In this study, we were only able to infiltrate the PC to a depth of approximately 4mm into the porous ceramic preforms. This was probably due to the viscous nature of the high molecular weight PC [27], but this is still greater than the thickness of an orthodontic bracket.

Furthermore, the MicroCT images illustrate that Al_2O_3-PC-20%, was characterised by larger pores (originally ice crystals), when compared to Al_2O_3-PC-30%. This illustrates the possibility of increasing initial solid ceramic loading in the aqueous suspension to control the final structure of the ceramic preform and the resultant interpenetrating phase composite.

The compressive strength values of the Al_2O_3-PC composites were 192.43 to 274.91 MPa, when the initial ceramic solid contents increased from 20 to 30 vol.%. Although lower than the value for alumina (2358.08 MPa), they were higher than that of PC (131.4 MPa) and enamel (62 to 89 MPa), and were comparable to that of dentine (194 to 224 MPa) and resin composite (265 to 290 MPa) [28, 29]. This may be attributed to the combination of the properties of alumina and PC and the complex composite microstructure. The compressive strength values demonstrated

anisotropy dependant on the direction of freeze-casting, i.e. whether it was parallel or perpendicular to the direction of freeze-casting. A slightly higher strength was observed when the load was applied perpendicular to the direction of freeze-casting. These results can be attributed to the alignment of the ceramic walls and therefore polymer infiltrate within the composite, which resembles the effect seen in enamel and dentine [30, 31], and which is different from the pure ceramics or polymers found in currently available monolithic aesthetic orthodontic brackets.

The flexural strengths of the Al_2O_3-PC composites tested were found to be 105.54 MPa and 148.47 MPa for Al_2O_3-PC-20% and Al_2O_3-PC-30% respectively (Table 3). This would suggest that the greater the inorganic ceramic content in the novel composite material, the higher its flexural strength. This is in agreement with previous studies on dental composite materials [32, 33]. The flexural strength observed was part way between the values of the pure polymer and the dense ceramics, which implies a reinforcement mechanism of the multi-phase material compared to the single monolithic components. These results are comparable to the results for experimental UDMA-TEGDMA infiltrated porous sintered ceramic networks (97.73 to 160 MPa) [20, 34], but they were slightly lower than the values reported by Li et al. (2017) for BisGMA-TEGDMA-infiltrated zirconia networks (110 to 240 MPa) [35], probably due to the high strength of the zirconia [36]. However, zirconia has poor aesthetics when used as an orthodontic bracket material [37, 38] when compared to the alumina used in the present study. The flexural strengths observed in the current study were higher than that found for feldspathic porcelain (69 MPa) [39] and slightly higher than traditional dental composites (103 to 107 MPa) [40], but lower than commercially sintered polycrystalline alumina brackets (280 MPa) [41, 42].

The modulus of elasticity was found to range from 10.72 to 15.17 GPa, which is comparable to those of dentine 11 to 19 GPa, lower than those of experimental UDMA-TEGDMA infiltrated porous sintered feldspar ceramic networks 16 to 28 GPa [34], comparable to those of hybrid filler resin composite restorative materials 6-21 GPa [43] , and slightly higher than the values reported for other polymer-infiltrated-ceramic material (9 GPa) [44]**.** This can be attributed to differences in the microstructure of the materials, the volume fractions of the porous ceramic scaffolds, the polymers used and the fabrication methods.

The reported fracture toughness values for enamel and dentine are approximately 0.72 to 1.28 and 2.20 to 3.10 MPa.m^{½} respectively [45-47]. The mean values for the fracture toughness of the biomimetic Al_2O_3-PC interpenetrating phase composites in the present study ranged between 2.17 MPa.m^{½} and 3.01 MPa.m^{½}. Previous studies have reported the fracture toughness of polycrystalline alumina to be 3.5 MPa.m½ [48, 49] and for monocrystalline alumina to be 2.1 to 2.5 MPa.m^{½} [50, 51]. Ceramic brackets have historically shown a tendency for tie wing fracture [52] and the addition of a more flexible second polymer phase, as in the case of the biomimetic composites described here, might reduce the stress concentration at this site and therefore the tendency to in-service failure. The interaction of the physical properties of the two different phases and the resultant reduced stress concentration give these novel composites superior fracture toughness [53]. The fracture toughness values reported in the present study were comparable to those reported by Launey et al. (2009) (3.1 MPa.m^{½}) [54], Chaiyabutr et al. (2.80 MPa.m^{½}) (2009) [55], Li et al. (2017) (1.5 to 3.6 MPa.m^{½}) [35], higher than those reported by Della Bona et al. (2014) (1.09 MPa.m^{½}) [56], but lower than those reported previously by ourselves (3.91 to 4.86 MPa.m^{½}) for Al_2O_3-UDMA-TEGDMA

composite [20]. This may be explained by the difficult infiltration process with the highly viscous PC polymer, which could have resulted in closed pores around the crack tip area and have led to faster crack propagation and more immediate failure. The observed fracture toughness values for the Al_2O_3-PC interpenetrating phase composites in this study, being at the higher end of values previously reported for the polycrystalline alumina most commonly used in orthodontic brackets, would suggest the tie wings of a bracket made from the novel composite might meet the basic requirement for their use in service.

In the present study, Vickers hardness testing results indicate that Al_2O_3-PC interpenetrating phase composite has a tuneable hardness. The hardness values were 0.82 and 1.62 GPa for Al_2O_3-PC-20% and Al_2O_3-PC-30% respectively, falling between those of the dense alumina (8.76 GPa) and pure PC (0.13 GPa). When the hardness of a composite is better matched to that of enamel (2.45 GPa), it would suggest the use of such materials as orthodontic brackets would cause little or no wear to the opposing teeth. This is unlike other commercial and non-commercially available ceramics and composites such as Enamic (3.31 GPa), polymer-infiltrated zirconia (3.93 GPa), zirconia (13.94 GPa) and lithium disilicate glass ceramics (10 GPa) [47, 57, 58], or commercially available ceramic brackets, which are much harder than enamel [42]. In the case of the latter there are reports of adverse wear of opposing tooth surfaces [59]. However, a lower surface hardness compared to stainless steel and nickel titanium alloys, used as bracket and archwire materials, has been suggested to result in inadequate slot-wire engagement [60] during orthodontic tooth movement. Indeed, the fact that teeth move with currently available polymeric brackets would suggest this would be same in the case of brackets made from these novel composite materials.

During orthodontic treatment, orthodontic attachments and arch wires act as barriers and trap food, which makes maintenance of good oral hygiene more challenging [61-63]. It is therefore recommended that patients toothbrush at least twice daily for two minutes [64]. However, toothbrushing can lead to a gradual loss of hard dental tissue [65] and adverse wear of polymeric orthodontic brackets due to their relatively lower hardness [66]. In the present study, the toothbrushing regimen mimicked a twice daily oral hygiene pattern of a two-minute toothbrushing cycle on twenty teeth in total. The force applied was standardised at 200g, as was toothpaste concentration, brushing technique and model of brush. The 200g force was chosen as it simulates the applied force during everyday toothbrushing [67, 68] and because any higher force has been shown to be of little significance for plaque removal [69, 70]. Colgate® Total was chosen as it is a commonly used toothpaste in the UK [71] and an Oral-B manual toothbrush was used due to its standardised shape and previous utilisation [72]. The amount of toothpaste suspension used in each cycle was prepared in accordance with the study by Schemehorn, Moore and Putt [73].

The characterisation and measurement of hard tissue loss due to oral environmental factors is important in dental research [74]. This process is equally important for interpenetrating phase composites, as their surfaces are characterised by unique microstructures with irregular peaks and valleys that cannot easily be defined [75]. Toothbrushing has an abrasive effect on the teeth and can result in tooth tissue loss [76, 77]. Polymeric orthodontic brackets, such as polycarbonate brackets, are characterised by a low resistance to wear compared to human enamel [66, 78], and in the current study, surface loss was greatest in the case of pure PC. For the Al_2O_3-PC interpenetrating phase composites, surface loss decreased as the ceramic volume

fraction increased. This can be explained by the fact that ceramic is more resistant to surface loss caused by toothbrushing.

Surface roughness influences clinical performance, aesthetic characteristics and can affect bacterial accumulation [79-82]. For dental composite materials, the surface roughness characteristics will depend on factors such as type of monomer, filler content, filler size, filler type and preparation methods [83-85]. It is also possible that in orthodontics surface roughness can affect friction [86] and potentially orthodontic tooth movement [87-89]. In the present study, the roughness parameters assessed were Ra, Rmax, Rp and Rq, as these parameters have been previously used to determine the surface characteristics of orthodontic raw materials [66]. When looking at the surface roughness results before brushing, the mean Ra value for the dense alumina specimens and PC were 0.84 µm and 0.23 µm respectively, which is lower than that found previously for polycrystalline alumina (2.69 µm) and for PC (0.94 to 1.20 µm) [66]. However, this might be due to the use of different measuring methods (contact vs. non-contact surface profilometry as used in the present study) and subsequent specimen preparation procedures. When considering enamel specimens before brushing, the Ra value was found to be 0.09 µm, which is comparable to the values obtained by previous research by (0.05 to 0.07 µm) [90]. The Al_2O_3-PC interpenetrating phase composite Ra surface roughness values ranged from 0.69 to 1.71 µm, while the Rmax results ranged from 4.02 to 12.74 µm, which corroborates the findings of the study by Grossman, Rosen and Cleaton-Jones [91], who evaluated and compared Ra and Rmax surface roughness values obtained with a profilometer for six aesthetic resin based restorative materials. The Ra results ranged from 0.35 to 1.51 µm, while the Rmax results ranged from 1.60 to 16.1 µm.

When considering the surface roughness values following simulated toothbrushing, all of the materials under test showed an increase in all surface roughness parameters except for the dense alumina. This is in accordance with the findings of other studies [90, 92, 93]. However, unlike the present study, Heintze and Forjanic [83] found the roughness of the enamel decreased after simulated toothbrushing, and by as much as 40%. This might be attributed to their use of different sample polishing procedures, brushing regimes, tooth paste and brushing force, for example 170 g versus the 200 g used in the current study.

When looking at the Ra results for the novel Al_2O_3-PC interpenetrating phase composites, the mean difference for surface roughness after the simulated toothbrushing ranged from 0.18 to 0.65 µm, which is unlikely to be clinically significant. The roughness observed is likely as a result of the direct contact of the bristles of the brush with the material surface, as well as the effect of the toothpaste [94]. The gradual polishing of the ceramic fraction of the composites and the more rapid abrasion of the polymer phase might lead to this increase in the material roughness (Figure 4). Heintze and Forjanic [83] also found that dental hybrid composite materials showed the greatest increase in mean roughness after toothbrushing when compared with 21 other dental materials. For conventional composite resin materials, Kamonkhantikul et al. (2014) showed a variable surface roughness which increased after toothbrushing, dependant on the filler particle size [85].

In vivo aging can adversely affect the structure and mechanical properties of orthodontic brackets [95]. It has been reported that immersion in water affects the strength characteristics of traditional dental composite materials [96-99] and their fracture toughness [100, 101] as a

result of water absorption into the polymer matrix and subsequent enlargement and softening [102-104]. Moreover, previous studies have demonstrated that in vitro aging using water at 37˚C decreased the strength and toughness of polymer-infiltrated ceramic networks such as Enamic [105-108]. However, polymer infiltrated ceramic networks are very different from ceramics or glass ceramics. The crack propagation in these materials may not follow the Griffith theory as applied to elastic materials that fracture in a brittle manner. The integration of the brittle ceramic and the compliant polymer phases may result in different initial critical crack sizes, hence decelerating failure [106, 109, 110]. Furthermore, we believe that the novel biomimetic ceramic/polymer interpenetrating phase composites may have less water uptake than the traditional dental composites due to the unique structural architecture achieved by gelation and freeze-casting.

Additionally, the effects of aging on the mechanical properties the novel biomimetic ceramic/polymer interpenetrating phase composites could be less significant for orthodontic bracket material compared to dental restorative material due to relatively shorter period of clinical performance time. To simulate the oral situation, future studies should investigate the mechanical properties of the novel biomimetic ceramic/polymer interpenetrating phase composites when subjected to aging in a wet environment both in vitro and in vivo.

Commented [s1]: Added.

5 Conclusion

In the present study, novel Al_2O_3-PC interpenetrating phase composites with a good combination of strength and fracture toughness have been developed, taking inspiration from natural dental tissues. The results of this characterisation study demonstrated the novel Al_2O_3-

PC interpenetrating phase composites to have values for each parameter part way between those of dense ceramic and PC, with the precise value affected by the initial solid loading of the ceramic fraction.

These novel Al_2O_3-PC interpenetrating phase composites, produced using the technique of freeze-casting, show promise as orthodontic bracket materials. The polymer-rich surface could aid in safe bonding and debonding, whilst the relatively ceramic-rich surface will provide wear resistance. The combination of the two materials in the bulk of the bracket should reduce in-service failures and eliminate creep. Further research to optimise their properties, in particular, their bonding properties to human enamel and the ease of debonding should be investigated along with the fracture characteristics of the final Al_2O_3-PC interpenetrating phase composite.

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