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Cost-effective fabrication of bio-inspired nacre-like composite materials with high strength and toughness

Hongbo Wan¹, Nathanael Leung², Sana Algharaibeh^{1,5}, Tan Sui², Qiang Liu³, Hua-Xin Peng⁴, Bo Su^{1*}

¹Biomaterials Engineering Group (bioMEG), Bristol Dental School, University of Bristol, UK

²Department of Mechanical Engineering Sciences, University of Surrey, Guildford, GU2 7XH, UK

³School of Material Science and Engineering, Harbin Institute of Technology (HIT), Harbin, Heilongjiang, China

⁴Institute for Composites Science Innovation (InCSI), School of Materials Science and Engineering, Zhejiang University, Hangzhou, China.

⁵Prosthodontics Department, Faculty of Dentistry, Jordan University of Science and Technology, Jordan

*corresponding author: b.su@bristol.ac.uk

Abstract

A cost-effective one-step densification process based on bi-directional freeze casting was investigated to produce nacre-like alumina/poly(methyl methacrylate) (PMMA) composites with a unique micro-layered (μL) architecture. This method has the advantage of shorter processing time, as it requires only sintering once instead of twice as in the fabrication of conventional brick-and-mortar (BM) composites via freeze casting. By tuning the processing parameters, composites with different ceramic content and layer thickness were obtained. The resultant mechanical properties of μL composites showed that ceramic content and wall thickness affected mechanical properties significantly. The μL composite with fine ceramic walls (8 μm) and relatively high ceramic fraction (72 vol.%) exhibited an exceptional combination of high flexural strength (178 MPa) and fracture toughness (12.5 MPa m^{1/2}). The μL composites were also compared with the conventional BM composites. Although the fracture behaviour of both composites exhibited similar extrinsic toughening mechanisms, the μL composites with longer ceramic walls displayed superior mechanical properties in terms of strength and fracture toughness in comparison with the BM composites comprising short ceramic walls (i.e. bricks), due to the effectiveness of stress transfer of load-bearing ceramic phase within the composites.

Keywords

Bio-inspired composites, brick-and-mortar (BM), micro-layered (μ L), alumina/PMMA, bi-directional freeze casting, toughness

Graphical abstract

1. Introduction

It has always been a technical challenge to design and fabricate synthetic materials with both high strength and toughness because they are often mutually exclusive [1]. Nevertheless, some natural composite materials such as bone, wood, and shells, exhibit remarkable mechanical properties with a good combination of both high strength and toughness [2, 3]. Nacre, also known as the outer layer of abalone shell, has been proven to be an excellent example of biological composite material with both high strength and high toughness because of its unique layered architecture of organic and inorganic phases [4-6]. Nacre is composed of ~95 vol.% highly aligned inorganic aragonite platelets (bricks) and ~5 vol.% of organic biopolymer or protein (mortar) filled the gaps between bricks. In general, the typical architecture of nacre has been known as the “brick-and-mortar” (BM) structure, the “brick” is the major load-bearing constituent which provides strength, while the “mortar” acts as the lubricant for bricks. In the case of appropriate interface [7], the aragonite/protein nacre composite material could be at least one order of magnitude tougher than the monolithic aragonite and protein [8].

To mimic the structure and achieve similar mechanical behaviour of nacre, synthetic composite materials with nacre-like architecture were synthesised via a variety of fabrication techniques such as freeze casting [9, 10], 3D printing [11, 12], magnetic assisted alignment [13], biomineralization [14], hot pressed assisted slip casting [15], and gravitational sedimentation [16]. The resultant nacre-like composite materials with multi-layered architecture display extraordinary flexural or tensile strength and a rising *R*-curve performance due to their unique nacre-mimicking architecture. There are a variety of nacre-inspired architectures such as BM [9, 13], lamellar [10], or laminate BM [17] based on multi-layered system with high energy dissipation owing to layer-by-layer crack propagation.

Freeze casting is a versatile method to create composite materials with nacre-like architecture by assembling the particles suspended in liquid into ordered microstructure. Currently, freeze casting is attracting an increasing interest because of its simplicity and flexibility [18]. By freeze-casting different suspensions containing particles such as ceramic powder [9, 19], platelet [13, 20], and graphene [21], this method could be exploited to generate nacre-like scaffolds through an ice-templating mechanism. Bi-directional freeze casting is a modified technique which can control lamellar orientation of scaffolds

by freezing suspension from two different directions and it could be used to create ceramic scaffolds with highly aligned architecture [19, 22, 23]. With further densification and second phase (e.g. polymer or metal) infiltration, nacre-like ceramic-based composites could be created [24-26]. Mechanical properties of these nacre-like composites could be controlled by composition [24], interface [25], and microstructure [26]. However, current fabrication route to such nacre-like composites via freeze casting are generally time-consuming and expensive, which generally requires more than one sintering steps or use of relatively costly platelets or hot isostatic pressing equipment.

The aim of this work was to develop a more cost-effective fabrication route based on bi-directional freeze casting but via a simple one-step densification to generate nacre-like alumina/PMMA composites. This not only helped shorten the fabrication processing time but also enabled the easy control of microstructure of the resultant nacre-like composites with a unique micro-layered (μL) architecture. The effects of processing conditions on microstructure and mechanical properties of the μL composites were investigated, and compared with the BM composites having similar wall thickness and ceramic fraction using a two-step densification. *In situ* Scanning Electron Microscopy (SEM) mechanical testing was used to determine the fracture toughness (R-curves) and elucidate possible toughening and strengthening mechanisms of the composites.

2. Results

2.1 Fabrication process

Fabrication of nacre-like ceramic/polymer composite materials normally includes three steps: ceramic scaffolds preparation, densification and polymer infiltration. Firstly, bi-directional freeze casting was employed to assemble the nano-scale ceramic particles in a water-based suspension into highly aligned ceramic scaffolds. Since nacre has a high mineral content (96 vol.%), densification process was needed to densify highly porous scaffolds to mimic the microstructure of nacre. Herein, two different densification methods based on the simple uniaxial pressing and pressureless sintering were employed to build up nacre-like ceramic scaffolds (**Fig. 1**). The first method was a conventional two-

step method where ceramic scaffolds were sintered twice. The green body ceramic scaffolds from bi-directional freeze casting were first sintered at a lower temperature (e.g. 1400°C) before uniaxially pressed and then finally sintered at 1550°C. The second method was a newly developed one-step densification method in this work where green ceramic scaffolds from the bi-directional freeze casting were infiltrated with a wax directly without pre-sintering followed by uniaxial pressing and sintering at 1550°C (**Fig.1**). No further increase in ceramic density was observed above this sintering temperature.

The two-step method is a mostly reported fabrication method for the BM structured ceramic scaffolds [24]. The key distinction between these two methods is that partially sintered ceramic scaffold was uniaxially pressed in the two-step method, while ceramic scaffold was unsintered in the one-step method before uniaxial pressing, which had significant implication not only to their overall fabrication time (a typical sintering cycle takes approximately 24 hours) but also to their resultant microstructure and mechanical properties. During the conventional uniaxial pressing, the pre-sintered ceramic layers in scaffolds were broken down into small ceramic platelets (bricks) since they were relatively weak and brittle (**Fig. 1**). Consequently, the densified scaffolds displayed an assembly of aligned ceramic bricks. After infiltration of polymer (mortar), the typical BM composite materials were obtained. Conversely, the objective of one-step method was to better preserve the lamellar (layered) structure in the final densified ceramic scaffolds, in addition to saving time. The uniaxial pressing was further employed to control the spacing between ceramic layers which were intact after the densification of green ceramic scaffolds. Owing to the relatively high plasticity of the green scaffolds with polymeric additives like dispersant and binder (PVA), the ceramic layers plastically deformed instead of brittlely fractured under uniaxial pressing load. Uniaxial pressing was carried out at 90 °C, slightly above the glass transition temperature, T_g of PVA (~80 °C)[27]. It is worth noting that, in the one-step method, even though the ceramic layers were cracked or broken during uniaxial pressing, the broken ceramic walls could still be healed and sintered during the high-temperature sintering process since the ceramic powders in the green scaffolds maintained a high sintering activity. After uniaxial pressing, the scaffolds underwent a single de-binding/sintering step, this means

that the fabrication time for the one-step densification route is significantly shortened compared to the two-step method.

2.2 Microstructure of μ L composite

It is interesting to note that the microstructure of nacre-like μ L composite materials show a distinct layer-by-layer microstructure with various layer thickness (8 – 40 μ m) and ceramic fraction (50 - 85 vol.%) under different solid loadings and pressing conditions, respectively (**Fig. 2**). In the one-step method, two processing parameters i.e. solid loadings of slurry and degree of densification (determined by compression distance) were the two important parameters that affected primarily the microstructure of composites. **Fig. 2d** shows that an increasing in solid loading results in thicker ceramic walls. Specifically, alumina slurries with solid loadings from 10 to 40 vol.% generated nacre-like μ L composites with wall thickness from 8 to 40 μ m as shown in **Fig. 2a and b**. Generally speaking, for freeze casting, the slurry solid loading has a significant influence on microstructure such as lamellar thickness of the scaffolds [28].

The final composites with different ceramic fractions from 50 to 85 vol.% were produced by altering the compressive distance as shown in **Fig. 2e**. It is clear that there was a maximum compression distance for the μ L composites. It was possible to achieve a maximum ceramic fraction up to 85 vol.%, however, the distinctive layered microstructure was lost when the ceramic fraction was above 85 vol.%, because the adjacent ceramic walls were too close after pressing, that fused together during the high temperature sintering stage.

2.3 Mechanical properties of μ L composite

The mechanical properties of μ L composite materials are shown in **Fig. 3**. The flexural strength of the μ L composite materials is strongly dependent on the wall thickness of lamellar layers and the ceramic fraction. The stress-strain curves for μ L composites exhibit some degree of plastic deformation prior to failure, except the one containing 85 vol.% alumina, which displays a brittle failure (**Fig. 3a**). This may be attributed to the difference in their microstructure.

At the same ceramic wall thickness, composites with different ceramic fractions show a similar failure strain ($\sim 0.35\%$) but different stiffness and strength, where higher ceramic fraction results in higher flexural strength and modulus (**Fig. 3b**).

At the ceramic fraction of 72%, the μ L composites with different ceramic layer thickness (from 8 to 40 μm) exhibit similar initial stiffness when strain $< 0.05\%$, but composites with thicker ceramic walls of 40 μm start to yield earlier compared to those with thinner ceramic walls (**Fig. 3d**). The composite with the thinnest ceramic walls (8 μm) has the highest strength of 178 MPa. Decreasing the ceramic wall thickness leads to the increase of flexural strength (from 101 to 178 MPa). It is known that the mechanical properties are sensitive to the size and number of flaws in ceramic phase. On the fractured surface in **Fig. 4**, compared to the thicker walls, the composite with thinner ceramic walls contains fewer flaws per unit area. Moreover, there is a bigger chance to find large pores within the thicker ceramic walls, which explains the negative impact to the flexural strength and fracture toughness.

The R -curves were employed to evaluate the resistance to crack propagation. The loading-unloading curves were converted to relations between crack extension and fracture toughness K_{I} and all the R -curves are shown in **Fig. 3c and f**. According to the ASTM E1820 [29], while all measurements were ‘valid’ before $a_{\text{valid}} = 0.25 \times b_0 = 0.625\text{ mm}$ (where a is crack length and b_0 is uncrack ligament before testing, $b_0 = 2.5\text{ mm}$), the results were ‘invalid’ above it. Hence, although the crack still propagates stably after this limit, this work will focus on the maximum ASTM “valid” toughness value at $a_{\text{valid}} = 0.625\text{ mm}$. The R -curves shown in **Fig. 3c and f** are for composites with different ceramic fractions at the same wall thickness (8 μm) and ceramic wall thickness at the same ceramic fraction (72 vol.%), respectively.

Similar to flexural strength (**Fig. 3e**), the fracture toughness K_{I} demonstrates a strong dependence on the ceramic wall thickness, where the stress-intensity factor K_{I} increases with the decrease of ceramic wall thickness (**Fig. 3f**), probably due to their microstructure and flaw density (**Fig. 4**). In addition to defect reduction in the thinner ceramic layers, the microfracture-accumulating mechanisms may also

significantly contribute to the effect of layer thickness on fracture toughness [30]. When the ceramic layer thickness was decreased, the amount of interface between the ceramic and polymer phases in the composites was increased. This could provide significant benefit to fracture toughness by having more micro-delamination, crack deflection and layer sliding, leading to more energy dissipation.

When the ceramic wall thickness was 8 μm , the composite revealed a rising R -curve or fracture toughness K_{I} when crack was extended, at $a_{\text{valid}}=0.625$ mm, the ‘valid’ fracture toughness K_{I} reached 7.8, 7.2 and 12.5 $\text{MPa m}^{1/2}$ for 50, 60 and 70% ceramic fraction, respectively. However, the composite with 85 vol.% alumina failed catastrophically and illustrated a flat R -curve with a constant fracture toughness K_{I} at 5.8 $\text{MPa m}^{1/2}$. This is not unexpected, previous studies showed that the fracture toughness (in energy terms) of nacre-like composites decreased when the volume fraction of polymer phase decreased because the soft polymer phase allowed more extensive plastic deformation [10]. Nevertheless, for the μL composites, there are other competing toughening factors i.e. ceramic bridging and sliding.

2.4 Toughening mechanism of μL composite: ceramic bridges

In the one-step method, not only ceramic fraction, but also the morphology of ceramic scaffolds such as ceramic bridges, were directly affected by compression distance during uniaxial pressing. In careful examination of the microstructure of μL composites (**Fig. 5**), it becomes apparent that there is a correlation between ceramic bridges and ceramic fraction. The density of bridges, ρ_b is used to quantify the connections between layers. **Fig. 5e** shows that ρ_b increases drastically with the ceramic fraction, from $\sim 8 \times 10^8$ to $\sim 100 \times 10^8/\text{m}^2$ as the ceramic fraction increases from 50 to 85 vol.%. The formation of ceramic bridges is due to asperities formed on the sidewalls of ceramic layers during freeze casting, which connect during pressing and sintering stages because of their high sintering activity. When the layer distance decreases, these asperities are more likely to form bridges.

It is well known that ceramic bridges play a key role in mechanical behaviours of nacre-like composites. Previous studies showed that, by introducing ceramic bridges in nacre-like composites [10, 31, 32], the strength and toughness could be enhanced concomitantly. The first role of ceramic

bridges is stress transfer between layers. The stiff alumina bridges readily redistribute stresses over the connections between ceramic layers, and ceramic bridge breakage may also result in energy dissipation via deformation and fracture. During crack propagation, the nacre-like composite (both μL and BM) may lead to two possible fracture scenarios, i.e. bridge breakage with crack deflection and layer breakage without crack deflection. There is a competition between these two crack propagation paths depending on the relative strength of ceramic bridges and layers. If the stress transferred is lower than the bulk strength of ceramic layers, fracture requires pull-out of the stiff phase (ceramic) from the soft phase (polymer), leading to energy dissipation. By contrast, when the transferred stress exceeds the strength of the ceramic layers, fracture takes place within the stiff ceramic phase, resulting in a catastrophic failure of composites. To quantify the effect of stress transfer provided by ceramic bridges in the μL composite materials, ceramic bridge density (ρ_b) between ceramic layers were estimated. When fracture toughness increased from $7.8 \text{ MPa m}^{1/2}$ (for the 50 vol.% Al_2O_3 composite) to $12.5 \text{ MPa m}^{1/2}$ (for the 72% Al_2O_3 composite), the ceramic bridge density increased from 8×10^8 to $35 \times 10^8 \text{ m}^{-2}$, more ceramic bridges provided larger energy dissipation during their breakage. On the other hand, when the bridges broke, the ceramic layers became disconnected; the bridges lost the efficiency of stress transfer, but the broken bridges could still act as asperities on the surface of ceramic walls which could enhance the frictional sliding of the individual ceramic layers. Nevertheless, when the ceramic bridges density exceeded $35 \times 10^8 \text{ m}^{-2}$, the fracture toughness dropped down to $5.8 \text{ MPa m}^{1/2}$, meaning that the stress transfer surpassed ceramic layer strength, the crack went through the ceramic layers directly without much deflection.

Another factor is the frictional sliding between layers, one of the most important toughening mechanisms in natural nacre [33] and synthetic nacre-like composite [34]. This could be found in the present μL composites comprising >72 vol.% alumina. At a low ceramic fraction (<72 vol.%), the PMMA polymer phase is thick and separates each ceramic layer, the ceramic is rarely allowed to attach to the adjacent layers. In this case, the polymer is also a load-bearing phase offering extensive plastic deformation, contributing to the fracture toughness of composites. As the ceramic fraction increases, the spacing between ceramic layers reduces, the polymer layer becomes relatively thin or

discontinued, it starts to act as a non-load-bearing lubricant which relieves stresses in the μ L composites by offering frictional sliding between ceramic layers thereby increasing the crack resistance.

2.5 Micro-layered vs. brick-and-mortar composites

Fig. 6 shows the cross-section of nacre-like alumina/PMMA composite materials with μ L and BM architectures, fabricated by the one-step and two-step method, respectively. Both have multi-layered structure with ceramic bridges between layers. However, the μ L composite shows a better connectivity and more continuous ceramic walls (**Fig. 6a and c**) compared to the BM composite (**Fig. 6b and d**). In the BM composites, the length of ceramic layers is ranged from 20 to 690 μ m, depending on the processing conditions. While the ceramic layers in the μ L composites are almost continuous since the lamellar structure created in bi-directional freeze casting is well maintained in the one-step method. This will have significant implications to their corresponding mechanical properties.

Fig. 7 shows the comparison of mechanical properties of nacre-like composites with the same ceramic fraction (72 vol.%) and ceramic wall thickness (15 μ m) but different architectures. As can be seen from **Fig. 7a**, the strength and fracture toughness K_{I} of the μ L composites are approximately 15% higher than those of the BM composites owing to their distinct microstructure. The longer and more continuous ceramic walls in the μ L composites have larger load-bearing capacity, thereby higher strength. In terms of the *R*-curves in **Fig. 7b**, both composites initiate at a similar point at around 4 MPa m^{1/2} and display a rising *R*-curve. However, the μ L composite shows a steeper slope for crack propagating as it has the load-bearing ceramic phase resulting in better capability of resisting crack propagation. Notwithstanding, they still show a typical crack deflection behaviour (**Fig. 8a and b**). It is clear from Fig.8 that there will be more micro-delamination and ceramic layer sliding at the interface in the μ L composite with high ceramic fraction and thin ceramic layers, resulting in more zigzagged crack path. Additionally, because ceramic layers in the μ L composites are not perfectly flat and uniform in thickness during freeze casting, relatively thinner part in each ceramic layer acted as a weak phase leading to crack attraction. Furthermore, we reasonably assume that the thinner parts of

ceramic walls played a role of ceramic bridges and offered effective stress transfer between the ‘ceramic bricks.’ In this case, stresses will be predominantly transferred through these thinner parts (similar to mineral bridges in natural nacre) and redistribute stresses over the entire ceramic layers. Herein, the impact of stress transfer is less than the reinforcement effect, therefore the cracks preferred to deflect along the interface leading to energy dissipation. Consequently, the presence of certain ceramic bridges resulted in an improvement in both strength and fracture toughness, thereby the μ L composites could be seen as the ceramic-bridges enhanced BM composites.

3. Discussion

The motivation to design and fabricate the μ L composite is inspired by the microstructure of natural nacre which illustrates the assembling of mineral platelets and the narrow spacing between platelets filled by a biopolymer. As from the structural characterization of nacre, the typical spacing between mineral platelets is only several tens of nm [35]. Therefore, to mimic the microstructure of nacre, ceramic bricks in the nacre-like scaffolds should be densely packed with narrow gaps surrounded them from all directions. Thereby, this microstructure could potentially offer more chances of both frictional sliding and stress transfer, resulting in desirable mechanical properties of high strength and high fracture toughness. Launey *et al.* showed that, when applying an extra pressing process i.e. isostatic pressing, at a high pressure of 1.4 GPa, they effectively reduced the distance between ceramic layers and promoted the formation of inorganic (ceramic) bridges between the bricks after sintering, resulting in a high fracture toughness [9]. In both natural and synthetic nacre-like composites, the secret of such a high toughness has been revealed as multi-crack initiation at a weak layer followed by crack bridging in a tough layer [36]. Both experimental results and theoretical analysis suggested that the unique heterogeneous architecture in these composites improved toughness by creating property variations to slow down crack propagation and prevent crack penetration, as well as guiding cracks along weak interfaces to promote progressive damage [12]. The novelty of the one-step densification process developed in this work is that it can produce the μ L composites with short inter-layer distance and even bridges to connect the ceramic bricks in the continuous ceramic layers

without the use of isostatic pressing at a high pressure and additional sintering stages. The resultant mechanical properties of the μ L composites have displayed both high strength and fracture toughness (Fig. 9).

Three-point bending and loading-unloading compliant method under *in situ* SEM characterization of crack extension on flexural strength and fracture toughness measurement have provided crucial information on how changes in the architecture of the nacre-like alumina/PMMA composites can influence their mechanical behaviours (Fig. 9). When the ceramic wall thickness became thinner (from 40 to 8 μ m), the strength and toughness of the composites increased because the size and density of defects in ceramic phase decreased and microfracture-accumulating mechanisms were enhanced. Ultimately, the ceramic layer thickness was limited by the freezing rate and alumina particle size ($\sim 0.5\ \mu\text{m}$ in the present work). It was found that faster freezing rate and lower solid loading may result in thinner ceramic walls [22]. However, it was restricted by the freeze casting set-up and achievable sample size. In order to further optimise the microstructure and mechanical properties of the μ L composite materials, it is worth using more sinterable ceramic powders with nanoscale particle size or sintering aid to reduce the porosity in the ceramic layers in future work. This not only stops crack penetration through the strong ceramic layers but also diverts crack propagation along soft polymeric interfaces that facilitate progressive damages, resulting in both high strength and toughness. Ceramic fraction made positive contribution to the flexural strength, but the fracture toughness varies when ceramic fraction is increased from 50 to 85 vol.%, with a maximum toughness at 72vol.%. Both intrinsic and extrinsic toughening mechanisms will affect the fracture toughness instantaneously as the volume fraction of constituent phase changes. Consequently, in the composite material containing 50 vol.% ceramic, the compliant phase, polymer is load-bearing and allows extensive inelastic deformation. Therefore, the mechanical characterisation of toughness illustrates a rising *R*-curve and a valid K_{I} of 7.8 MPa m^{1/2}. When the ceramic fraction is increased to 60 vol.%, although extra ceramic bridges are formed, resulting in an increased contribution of extrinsic toughening, the fracture toughness K_{I} is slightly reduced because it contains less polymer which leads to inelastic deformation. As the ceramic fraction is increased further to 72 vol.%, more

ceramic bridges are formed and the polymer phase starts to act as a stress-relieving ‘lubricant’, which is the main toughening mechanism in natural nacre [30], thus the toughness increases dramatically. However, if there are too many ceramic bridges as in the 85 vol.% composite, where polymer loses its functions, becoming neither lubricant nor load-bearing phase, the composite failures catastrophically at the onset of crack initiation, albeit it is the strongest composite in this work. **There is a trade-off between the surface roughness and bridges formed on ceramic layers or bricks in order to achieve both high strength and toughness in nacre-like composites. The number of ceramic bridges or interfacial asperity between ceramic bricks should be controlled so long as they can still maintain the crack deflection along the ‘weak’ interface to have maximum energy dissipation. Otherwise, the composites will fracture in a brittle fashion.**

Therefore, it is possible to obtain both strong and tough nacre-like composites through synergistic actions of layered microstructure and appropriate interfacial properties such as ceramic bridges and micro-asperities. These strengthening and toughening mechanisms have also been adopted to other nacre-like composites including ceramic/glass [37], hard glassy polymer/soft rubbery polymer [12], and graphene/metal or graphene/ceramic/metal [38, 39].

4. Conclusions

Inspired by nature, nacre-like alumina/PMMA composite materials were fabricated via bi-directional freeze casting. A cost-effective one-step densification method was developed to create composites with a unique μL architecture and controlled structural features of ceramic wall thickness (8-40 μm) and ceramic content (50-85 vol.%). The conventional nacre-like composites with BM architecture were also fabricated via a two-step densification method for comparison. The novel one-step method with only one sintering step has the advantage of shorter process time by eliminating the second sintering step. Moreover, it has shown more flexibility in controlling the microstructural features and mechanical properties of the composites.

The mechanical behaviours of the nacre-like alumina/PMMA composites with μ L architecture were strongly dependent on ceramic content, ceramic wall thickness and density of ceramic bridges. These structural features affected intrinsic toughening mechanisms of both compliant polymer phase and stiff/strong ceramic phase, coupled with typical extrinsic toughening mechanisms in the nacre-like composites including ceramic layer pull-out, crack bridging, crack deflection and ceramic bridges breakage. Finer ceramic walls with fewer defects exhibited enhanced mechanical strength and fracture toughness for composites. Higher ceramic content resulted in improvement in initial strength and fracture toughness. The bridging connections between ceramic layers acted as effective stress transfer and hindered premature layer breakage. However, when the ceramic fraction was above a threshold, i.e. >85 vol.%, ceramic bridges became predominant with diminished polymer phase alongside their unique deformation and crack deflection mechanisms, the μ L alumina/PMMA composite exhibited a brittle fracture behaviour. By contrast, the BM composites fabricated by a two-step densification method showed shorter bricks in each ceramic layer. At the same ceramic fraction (72 vol.%) and wall thickness (15 μ m), the μ L composite materials exhibited better structural integrity in each ceramic layer and superior mechanical properties to those of the BM composite materials due to better load-bearing and stress-distributing capacity of the more continuous ceramic phase in the μ L composites.

5. Experimental Methodology

5.1 Materials

Following materials were used as received: alumina powder (CT3000SG, Almatis GmbH, Germany), Dolapix CE 64 (ZSCHIMMER&SCHWARZ Germany), polyvinyl alcohol (PVA powder, MW: 30,000-70,000, Sigma Aldrich), Octanol-1 (Fisher Scientific), paraffin wax, methyl methacrylate (MMA, Sigma Aldrich), γ -methacryloxypropyl trimethoxy silane (γ -MPS, Sigma Aldrich), azobisisobutyronitrile (AIBN, Sigma Aldrich), hydrogen peroxide (35 wt.% solution in water, stabilized, Sigma Aldrich) sulfuric acid (97.5+%, A.R. Grade, Sigma Aldrich) and toluene (99.85%, extra dry, AcroSeal).

5.2 Bi-directional freeze casting

Aligned green scaffolds were fabricated by freezing the water-based suspension of alumina. The suspensions were prepared by dissolving 10 - 40 vol.% vol. of Al_2O_3 powder, 0.02 wt. % MgO respect to alumina as sintering aid, 4 wt.% PVA as binder, and 0.6 wt.% Dolapix CE64 as dispersant into water. After 24 h ball milling, the suspension was poured into a bi-directional freeze casting mould as previously reported [22].

The alumina slurry was frozen completely in 60 mins once the mould was transferred into the copper cold finger located in a liquid nitrogen cold bath. The cooling rate on the bottom of slurry was measured as 35 °C/min. Next, the ice in frozen samples was sublimated in a freeze dryer (Edwards, Modulyo freeze dryer, UK) at -60 °C under vacuum for at least 24 h. The green ceramic scaffolds were obtained.

5.3 Densification

To acquire the scaffolds with higher ceramic fractions, two densification methods based on uniaxial pressing were employed as schematically shown in **Fig. 1**. In the two-step densification method, as-prepared ceramic scaffolds were fired at low temperature to de-binder (550°C /2 h) and then sintered into partially sintered ceramic scaffolds (1400°C /2h), which were subsequently infiltrated by paraffin

wax. To increase the ceramic content and reduce the spacing between ceramic layers further, the wax-infiltrated and partially sintered ceramic scaffolds were subject to second densification under 100 MPa uniaxial pressure perpendicular to lamellar layer direction at 90°C and sintered again at 1550 °C for 2 h. In the one-step densification method, paraffin wax was infiltrated into green ceramic scaffold without pre-sintering. Well-aligned green ceramic scaffolds were fabricated from slurries via bi-directional freeze casting with different solid loadings (10 to 40 vol.%). A universal mechanical testing machine (Zwick/Roell Universal testing machine Z020, Germany) was used to control the compression distance to alter the ceramic fraction and spacing between ceramic layers at 90°C. The relation of compressive distance and ceramic fraction was determined by the following formula:

$$D = T - (T \times C_b)/C_a$$

where D is the compression distance; T is the thickness of green scaffold/wax before compression, C_b and C_a are ceramic fraction before and after compression, respectively. Finally, the compressed ceramic scaffolds with wax were fired in a furnace at 550 °C for 2 h and sintered at 1550 °C for 2 h.

5.4 Polymer infiltration

Sintered alumina scaffolds were grafted with a silane coupling agent (γ -MPS) before polymer infiltration. They were cleaned and hydroxylated in piranha solution (50 vol.% H_2O_2 , 15 vol.% H_2SO_4 , 35 vol.% deionised water) for 20 min at 90 °C, then immersed into a solution of γ -MPS (50% MPS, 50% acetone) for 12 h. After grafting process, the scaffolds were rinsed with acetone to remove the unreacted coupling agent. The grafted scaffolds were immersed in a solution of methyl methacrylate (33 wt.% MMA) and AIBN initiator (1 wt.% respect to MMA) in 66 wt.% toluene at 70 °C for 2 h. In this step, the MMA monomers were initiated AIBN to undergo a free radical polymerization to form covalent bond between PMMA and grafted scaffold surface. The as-prepared scaffolds were then immersed into MMA with 0.5wt.% AIBN initiator at 70 °C for another 20 mins to active the initiator prior to the polymerization in water bath at 45 °C for 24 h. Following an annealing procedure at 90 °C for 2 h, the nacre-like alumina/PMMA composite materials were obtained. Prior to

mechanical testing and SEM imaging, composite specimens were grinded using 2000# sandpaper and polished using 1- μ m diamond suspension.

5.5 Microstructural characterisation

The ceramic fraction of ceramic scaffolds was characterised by Archimedes method. The microstructure of ceramic/polymer composite materials were characterised using scanning electron microscopy (SEM) (Quanta 400 - FEI Scanning Electron Microscope). Everhart-Thornley electron detectors (ETD) and back-scattering electron detect (BSE) were both used to observe the composites. The SEM images were statistically analysed by ImageJ to quantify the ceramic wall thickness and the occurrence and frequency of bridges connecting the ceramic layers. The number of ceramic bridges between adjacent layers were counted per unit area. Over 3 different images were used to estimate the ceramic wall thickness and density of ceramic bridges.

5.6 Mechanical testing

Due to the anisotropic nature of nacre-like composite materials, the loading applied during mechanical testing was in the direction perpendicular to ceramic/polymer lamellar layers. At least three samples were used in each measurement.

Three-point bending test was performed to evaluate the flexural strength using a universal testing machine with a 500N load cell (Zwick/Roell Universal testing machine Z020, Germany). According to the ASTM standard D790 [40], the support span was 12.5 mm and the displacement rate was 0.6 mm/min.

Fracture toughness of samples was measured using three-point bending on single-edged notched bending specimens (SENB). In accordance with the ASTM E1820 [29], composite materials were cut into 5 mm by 2.5 mm by 30 mm with a low-speed, water-cooled diamond saw. The as-prepared specimens were notched by a low-speed diamond saw and then sharpened by a custom-made micro-notching machine, where a razor blade was sliding on the notch tip under a loading of 10 N at a speed of 3 times/s and was immersed in 1- μ m diamond suspension for 2 h for each sample. The radius of sharpened notch was about 25 μ m. As-prepared SENB samples were tested *in-situ* in an SEM using a

Deben MicroTest 150 N bending stage (Deben, UK), with a 20 mm support span. Prior to loading-unloading process, the sample was preloaded to around 20 N. SEM was used to observe the real-time crack propagation and record images with high resolution after each loading-unloading cycle by slow scanning. The displacement rate for loading/unloading is 0.1 mm/min.

To evaluate the fracture toughness resistance regarding the J -integral as a function of crack extension, nonlinear–elastic fracture mechanics measurements were utilised to determine stress intensities, K_J .

The crack-resistance curves (R -curve) which represented an energy dissipation rate as a function of crack extension was a trend line attained by accumulating points for at least three samples [10].

Fracture toughness K_J were determined by the back-calculated from these measured J values using the standard mode I J – K equivalence ($K_J = \sqrt{J E'}$).

In according with the ASTM E1820, the J was composed of both elastic and plastic component, i.e.

$J = J_{el} + J_{pl}$, the elastic component J_{el} was evaluated using $J_{el} = K_I^2 / E'$. In this equation, $E' = E$ in plane stress and $E' = E / (1 - \nu)^2$ in plane strain where ν is the Poisson's ratio and E is the Young's modulus of composites. The values of E were determined using the rule of mixtures, giving 174 GPa for CF85 composite, 150 GPa for CF72 composite, 124 GPa for CF60 and 104 GPa for CF50 composite etc., with $\nu = 0.3$ for all composites.

Using the loading P and specimen size, the mode I stress-intensity factor was calculated, $K_{el} = PS / BW^{1.5} f(a/w)$ (B : Thickness; W : Width; a : Crack length; P : Loading; S : Support span), where f is a non-dimensional function of the crack length a :

$$f(a/w) = 3(a/w)^{0.5} [1.99 - (a/w)(1 - a/w)(2.15 - 3.93(a/w) + 2.7(a/w)^2)] / 2(1 + 2a/w)(1 - a/w)^{1.5}$$

Considering the load-displacement, J_{pl} for plastic portion was determined by

$J_{pl} = 1.9A_{pl} / Bb$ (b : uncrack ligament), where the A_{pl} was the area under load vs. plastic

displacement (V_{pl}) curve, i.e. $A_{pl(i)} = (P_{(i)} + P_{(i-1)})(V_{pl(i)} - v_{pl(i-1)}) / 2$ and the V_{pl} was given by

$v_{pl(i)} = v_{(i)} - (P_{(i)} C_{(i)})$ in terms of loading-unloading curve. $C_{(i)}$ is compliant of unloading part and $v_{(i)}$ is the displacement of load cell.

By coupling the decreasing b with the crack propagation, the incremental definition of J_{pl} calculation was obtained:

$$J_{Pl(i)} = [J_{pl(i-1)} + 1.9(A_{pl(i)} - A_{pl(i-1)})/b_{(i-1)}B] \times [1 - 0.9(a_{(i)} - a_{(i-1)})/b_{(i)}]$$

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Fig. 1. Flow chart illustrating the fabrication processes of ceramic scaffolds for nacre-like composites. The green ceramic scaffolds from bi-directional freeze casting undergo two different densification routes: two-step method and one-step method, to obtain the nacre-like ceramic scaffolds with different architectures.

Fig. 2. SEM images and microstructure-processing relations of μL alumina/PMMA composite materials fabricated via the one-step method with different processing parameters. The composites (72 vol.% alumina fraction) with different layers thickness **a)** 8 μm , **b)** 40 μm were fabricated from 10 and 40 vol.% solid loading, respectively. The composites with **a)** 72 vol.% and **c)** 85 vol.% ceramic fraction were obtained by freezing 10 vol.% slurry and pressed at different compression distance. **d)** is the relation of mean ceramic wall thickness and slurry solid loadings. **e)** is the relation of average ceramic fraction and compressive distance during ceramic scaffold densification. The maximum ceramic fraction in the μL composites is about 85 vol. % as indicated in the graph, above which the layered architecture is diminished. Scale bars for **a)**, **b)** and **c)**: 50 μm .

Fig. 3. Flexural strength and fracture toughness of the μ L composite materials. Effects of ceramic fraction (at the same wall thickness of 8 μ m) and ceramic wall thickness (at the same ceramic fraction of 72 vol.%) on flexural behaviour, strength and fracture toughness KJ are shown in a)-c) and d)-f), respectively. CF: ceramic fraction, WT: wall thickness.

Fig. 4. Fracture surface of μ L composite with 40 μ m a) and 8 μ m b) ceramic wall thickness. Larger and more closed pores are observed within the thicker ceramic walls as indicated by arrows in the inserts in c) and d). Scale bars for a) and b): 10 μ m, c) and d): 5 μ m.

Fig. 5. Cross-section SEM micrographs of the μL composites produced from 10% slurry and pressed at an increasing compression distance, resulting in different ceramic fractions: **a)** 50%, **b)** 60%, **c)** 72% and **d)** 85%. With a decrease in inter-layer distance, ceramic layers are getting closer to each other and more likely to form ceramic bridges (as indicated by yellow arrows) after subsequent sintering, **e)** the density of bridges (number of bridges per m^2) obtained from image analysis vs. ceramic fraction. Scale bar: $10 \mu\text{m}$

Fig. 6. SEM images of alumina/PMMA composite materials containing 72 vol.% alumina with different architecture: **a)**, **c)** μL and **b)**, **d)** BM, produced from the one-step and two-step method, respectively. Scale bar: $500 \mu\text{m}$ in **a)**, **b)**, $50 \mu\text{m}$ in **c)**, **d)**.

Fig. 7. Mechanical properties of nacre-like alumina/PMMA composites, both having 72 vol. % alumina and 15 μm lamellar thickness but with the μL and BM architecture, respectively. **a)** Fracture toughness R -curves, **b)** average of flexural strength and fracture toughness K_J (at $a_{\text{valid}}=0.625$).

Fig. 8. SEM images taken after failure showing the crack propagation behaviour of nacre-like composite **a)** BM and **b)** μL , both composites exhibit similar toughening mechanisms: crack deflection, frictional sliding and ‘pull-out’. Scale bar: **a)** and **b)**: 100 μm

Fig. 9. Mechanical performance map of flexural strength vs. fracture toughness of the μL Al_2O_3 /PMMA composites with different ceramic fractions (CF) and wall thicknesses (WT). The blue dash line indicates the increasing in wall thickness and the red dash line represent increasing alumina content.