



Complex ceramic architectures by directed assembly of ‘responsive’ particles



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ARTICLE INFO

Article history:

Received 26 April 2016

Received in revised form 27 June 2016

Accepted 30 June 2016

Available online 22 July 2016

Keywords:

Directed assembly

Surface functionalization

Responsive polymers

Macro porous ceramics

Emulsion templating

ABSTRACT

Surface functionalization of alumina powders with a responsive surfactant (BCS) leads to particles that react to a chemical switch. These ‘responsive’ building blocks are capable of assembling into macroscopic and complex ceramic structures. The aggregation follows a bottom up approach and can be easily controlled. The directed assembly of concentrated suspensions leads to highly dense (~99%) ceramic components with average 4-point bending strength of ~200 MPa. On the other hand, the emulsification of suspensions with concentrations from 7 to 43 vol% and 50 vol% decane results in emulsions with different properties (stability, droplet size and distribution). The oil droplets provide a soft template confining the alumina particles in the continuous phase and at the oil/water interfaces. Aggregation of these emulsions followed by drying and sintering leads to macroporous (pore sizes ranging from 30 to 4 μm) alumina structures with complex shapes and a wide range of microstructures, from closed cell structures to highly interconnected foams with total porosities up to 83%. Alumina scaffolds with ~55% porosity can reach crushing strength values above 300 MPa in compression and ~50 MPa in 4-point bending.

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1. Introduction

Based on lessons from nature, scientists have been designing materials that respond to stimulus in the same way that living systems respond to subtle changes on their environment [1]. Applications of synthetic ‘responsive’ polymers in drug delivery, tissue engineering or cell mediation have been studied extensively and numerous papers and patents evidence a rapid growing field [1,2]. Responsive polymers are characterized by a reversible response to external stimuli; they are capable of changing their configuration or properties under a change of pH, stress, light or temperature [3–5]. Recent works on surface engineering describe responsive surfaces that, for example, switch from super hydrophobic to super-hydrophilic in response to light, temperature, pH or stress [1,3,6]. However, these advances have not been applied before in wet processing of ceramics.

On the other hand, the design and manufacturing of cellular structures is a widely investigated area in materials science. Thanks

to their unique combination of properties and functionalities (for example they can be light and strong), porous materials are used in many applications for engineering and medicine. From catalysis supports, filters, separation membranes, thermal insulators, reinforcement of composites to scaffolds for bone replacement [7–9]. However, shaping bulk materials in porous hierarchical structures with practical dimensions, controlled morphological features at multiple scale lengths and multifunctional properties, is still a challenge in materials science. Freeze casting, foaming, emulsion and sacrificial templating are some of the techniques currently available to create cellular materials. Freeze casting uses the complex structure of ice to create materials that exhibit bio-inspired hierarchical structures and promising properties [10]. Foaming of colloidal particles functionalized with short chain amphiphile molecules leads to very ultra-stable wet ceramic foams, that can be consolidated into highly porous foams [11]. Sacrificial templating uses natural or synthetic hard templates (for example polymeric foams, wood or coral) and impregnation of colloidal suspensions to create ceramic foams with the same structure as the original template [9]. Emulsion templating is another path used to fabricate cellular ceramics, metals and polymers [12–20]. Although particle stabilised emulsions are known for more than a century [21], many authors have

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delved into their understanding and application to build cellular materials in recent studies [13,15,22,23]. The oil droplets act as a temporary template and determine the morphological features in the final porous structures.

Despite the availability of these wet-processing techniques, there are still some challenges to overcome. For example, these approaches are often limited to the fabrication of monoliths with very simple shapes, like cubes or cylinders. Another disadvantage is their limited flexibility. Some of these techniques are specifically optimized for certain materials and additives, also making difficult the scaling up in a manufacturing process. It is necessary to formulate and integrate new basic science into practical manufacturing techniques to overcome some of the current processing limitations.

In this work we aim to integrate a bottom-up particle assembly approach inspired by natural processes – such as the directed assembly of DNA molecules and other proteins in living organisms – into traditional (“top-down”) processing technologies. This combination enables building hierarchical ceramic structures with complex shapes at the macro scale [12]. The objective is to develop a novel manufacturing route based on the design of ‘responsive’ particles that ‘self-assemble’ on-demand into hierarchical architectures. We use a responsive polymer – namely branched copolymer surfactant (BCS) – to functionalise the surface of alumina particles and make them react to pH changes [12,24]. Here we delve into the basic science involved in this processing approach: from the basic mechanisms involved in surface functionalization, interface stabilisation and emulsification and their effects in the final microstructures, to the effects of different parameters in aggregation kinetics and network stiffness. We describe how to create highly dense and porous ceramic components with a wide range of morphological features (total porosities varying between 50 and 83% with open porosities between 55 and 70% and pore size from 30 to $<4\ \mu\text{m}$) and provide additional results of their mechanical performance.

2. Experimental section

2.1. Particle functionalisation

BCS with a composition of PEGMA₅/MAA₉₅-EGDMA₁₀-DDT₁₀ was synthesized following the protocol described in Refs. [24,25]. BCS solutions with compositions between 0.5 and 5 wt/vol% were prepared in distilled water at pH 8 (adjusted with NaOH). Alumina powders (Al₂O₃, Baikolox B-series SMA6, D₅₀ = 0.3 μm , Baikowski, France) were sieved through 100 μm mesh to break down aggregates. Alumina suspensions (from 7 up to 43 vol%) were prepared by mixing the powders with BCS stock solutions and ball milling for at least 24 h. The suspensions were subsequently conditioned with 2.5 wt% of 1-octanol and stirring under a light vacuum.

2.2. Particle-BCS interactions

BCS functionalised-ceramic suspensions with 10 vol% of particles and increasing concentrations of BCS (from 0.25 to 5 wt/vol%) were prepared and analysed by dynamic light scattering (DLS) to measure the effective average particle size. The results were compared with the real average particle size (0.3 μm as given by the supplier) and also with the particle size distribution of alumina suspensions stabilised with an electro steric dispersant commonly used in ceramic processing, Dolapix CA (Zschimmer & Schwarz GmbH & Co). Additionally, to determine the BCS adsorption isotherm, the equilibrated alumina/BCS suspensions were subjected to centrifugation to sediment the particles. By quantifying the amount of sulphur in the supernatants (coming from the DDT chain ends) using inductive coupled spectroscopy (ICP), we

could quantify the amount of BCS free molecules in the solution and determine the degree of adsorption of BCS onto the particles. Sulphur standard solutions (with concentrations between 0 and 100 ppm) were measured prior the analysis of BCS pattern solutions and supernatants. By measuring the sulphur contents of BCS solutions with concentrations ranging from 0 to 5 wt/vol% BCS, we obtained a calibration fitting to then determine the free BCS amounts in the supernatants.

2.3. Emulsification

Ceramic suspensions with solid loads between 7 and 43 vol% were emulsified with 50 vol% of decane, at stirring speeds ranging from 2000 to 24,000 rpm, by using either an IKA stirrer or IKA Ultraturrax homogenizer.

2.4. Interfacial energy measurements (IFT)

The interfacial (oil/continuous phase) energy of the emulsions was measured using the pendant drop method in a Dataphysics, Contact Angle System OCA (software SCA 20). First, the IFT of oil/BCS solutions (with increasing BCS concentrations, from 0.5 to 5 wt/vol%) were measured from a drop of BCS solution (volumes between 5 and 20 μL) inside an optically clear glass cuvette containing decane. Afterwards, droplets of alumina suspensions containing the same BCS concentrations and fixed solid loading (17 vol%) were also measured using the same method. Additionally, we evaluated the effect of the solid loading on the IFT for a fixed BCS concentration (1 wt/vol%) and increasing particle content.

A fluorescent molecule, Rhodamine, was incorporated into the branched BCS architecture in order to look at the segregation of polymer at the oil/water and oil/continuous phase (for the suspensions) interfaces. Images of emulsions and emulsified suspensions containing rhodamine modified BCS were taken with a Axio Scope.A1 ZEISS optical microscope, using an immersion 100 \times ocular (N-Achroplan 100 \times /1.25 Oil iris WD0.29M27), fluorescence free immersion oil and rhodamine fluorescence filter (FL Filter Set 43 CY 3 Shift free).

2.5. Assembly

We use a pH trigger, glucono- δ -lactone (G δ L, $\geq 99\%$, Sigma Aldrich) to homogeneously drop the pH and control the assembly of particles in alumina suspensions and emulsions. G δ L lowers the pH in a homogeneous two-step process, first dissolution and subsequent hydrolysis of the G δ L to gluconic acid. Amounts of G δ L ranging from 0.5 to 12 wt/vol% were added to drop the pH below the pK_a (6.46 [25]) of BCS and subsequently trigger the establishment of multiple inter- and intra- hydrogen bonds between the BCS molecules. For the production of dense components, concentrated alumina suspensions (43 vol%) were mixed with G δ L, poured into the moulds and left until aggregation is completed inside a vacuum cast device (up to 90 min). In the case of porous materials, G δ L was added to the emulsified suspensions by gently shaking the vials. The emulsions were then poured into the moulds and left setting at room temperature for at least 24 h before drying in a convective oven at 37 °C.

2.6. Rheology

Viscosity and viscoelasticity measurements were performed using a Discovery Hybrid Rheometer HR1 (TA Instruments). Viscosity measurements of alumina suspensions and emulsions were done with a conical (\varnothing 60 mm) geometry and a solvent trap cover under steady sensing. Viscoelastic fingerprints and assembly processes were measured with a parallel plate (\varnothing 40 mm) and solvent

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