Ceramics International 43 (2017) 16727–16735

Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Guar gum: A novel binder for ceramic extrusion

M. Elbadawi[a,*], M. Mosalagae[b], I.M. Reaney[b], J. Meredith[a]

[a] Department of Mechanical Engineering, University of Sheffield, Mappin Street, Sheffield S1 3JD, United Kingdom
[b] Department of Material Science and Engineering, University of Sheffield, Mappin Street, Sheffield S1 3JD, United Kingdom

ARTICLE INFO

Keywords:
Extrusion (A)
Strength (C)
Biomedical application (E)
Guar gum

ABSTRACT

Ceramic honeycomb extrusion is a technique capable of attaining high strength, porous ceramics. However, challenges prevent the realisation of its potential. These include the design of an intricate honeycomb die and the formulation of an extrudable paste. The present study addresses the latter by using guar gum (GG) as a binder. GG was rationally selected because hydrogels thereof exhibit strong shear-thinning and high stiffness properties, which are required for extrusion. Rheological analyses demonstrated ceramic pastes with similar qualities were achieved, with hydroxyapatite (HA) used as the model ceramic. The shear stiffness modulus of HA pastes was determined as 8.4 MPa with a yield stress of 1.1 kPa. Moreover, this was achieved with GG as the sole additive, which further facilitates the overall fabrication process. The binder extraction notably occurred at relatively low temperatures when other high molecular weight polymers demand temperatures above 1000 °C; therefore the latter precludes the use of ceramics with low sintering onset. The process culminated in a porous HA scaffold with similar porosity to that of a commercial HA graft, but with higher compressive strength. Lastly, the study notes that the biological and water-soluble properties of GG can broaden its application into other ceramic fabrication processes.

1. Introduction

Porous ceramics continue to be a subject of interest for many functional ceramic applications. In the field of bioceramics, a porous bone graft is required due to the benefits elicited by the pores, which include new bone formation, vascularisation and oxygen nutrient transport [1–4]. However, given that porosity and mechanical strength are mutually exclusive, it has proven difficult to form porous bioceramic scaffolds with sufficient strength using traditional fabrication methods [5,6].

Ceramic honeycomb extrusion is one technique capable of achieving high mechanical properties [7,8], which is partly attributed to its periodic porous architecture [9,10]. Hence, there is potential for the technique in the fabrication of synthetic bone grafts. Like other fabrication techniques, including solid free-form fabrication, which are considered as state of the art, ceramic extrusion necessitates the use of binders. Methylcellulose (MC), and other cellulose-derived polymers are heavily relied on as the primary binder [11–16]. One concern with using MC is its thermal gelation property [17], whereby the polymer crosslinks at high temperatures and hardens. Thermal gelation of MC occurs typically at ~ 50 °C, and as the processing temperature nears the thermal gelation point, the viscosity increases exponentially. Thus, fabrication techniques using MC require additional control to preclude processing above 50 °C that can lead to defects, such as crack formation [18].

Guar gum is another water-soluble polysaccharide capable of forming a gel network ideal for the suspension of ceramic particles. Guar gum (GG) is an industrial gum with a number of applications [19]. GG has a molecular weight ranging from 0.2 to 5.0 million, the highest of the water-soluble polysaccharides, and hence are able to impart high viscosity. This can be achieved at low concentrations [20], which is desirable in ceramic extrusion as high viscosity is needed to impart green strength whilst low binder concentrations ensures a high ceramic solids loading can be achieved. This will lower the probability of defects appearing post-extrusion, particularly during shrinkage. Moreover, in bioceramics, GG is attractive as it is nontoxic, biocompatible and biodegradable [21], and thus can be used in cell-laden processes. In contrast to MC, GG is not affected by thermal gelation [22], thus facilitating processing of ceramics when selected as the binder.

The aim of this article is to examine the suitability of GG as a binder for ceramic honeycomb extrusion, using hydroxyapatite as the model ceramic. The central part of the study seeks to explore its potential through rheological characterisation, as well as determining a suitable thermal debinding profile. The characteristics of the hydroxyapatite scaffolds, with respect to mechanical, porosity and microstructural properties are also reported.

* Corresponding author.
E-mail address: melbadawi1@sheffield.ac.uk (M. Elbadawi).

http://dx.doi.org/10.1016/j.ceramint.2017.09.066
Received 23 May 2017; Received in revised form 9 September 2017; Accepted 9 September 2017
Available online 11 September 2017

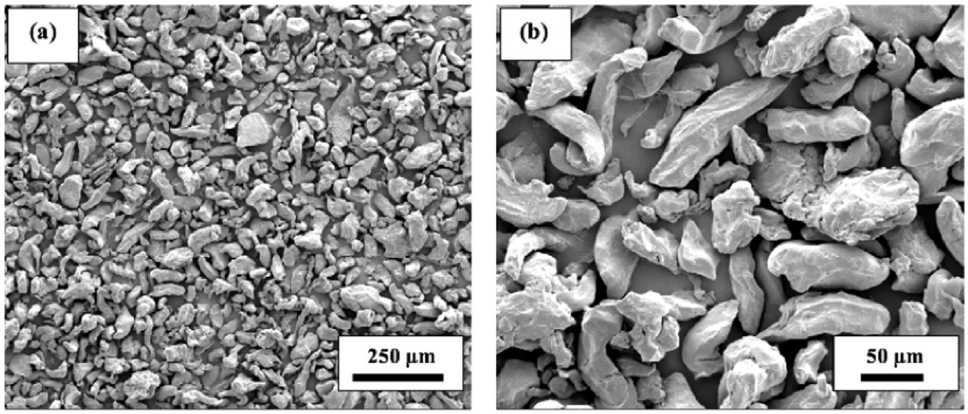

Fig. 1. SEM (SE) micrographs depicting the powder morphology of guar gum, at low **(a)** and high **(b)** magnification.

2. Materials and method

2.1. Raw materials

Commercially available hydroxyapatite powder (Purum grade, Sigma Aldrich) pre-calcined at 1000 °C, and GG (Lot no.: SLBH5231V; Sigma Aldrich) were used for this study. Fig. 1 depicts the powder morphology of the GG powder. Distilled water was used as the solvent.

2.2. Fabrication procedure

Mixing was carried out in two stages. First, the dry components (ceramic and binder) were weighed and then mixed using a high-energy speed mixer (Speedmixer™ DAC 300FVZ, Synergy Devices Limited) to ensure a homogenous distribution of the ceramic component and polymer. Solvent was then added in two minute intervals, until a single coalesced paste was obtained. Mixing was continued for a further 5 min following coalescence of the ceramic paste. Once a suitable paste was obtained, it was extruded using an *in-house* ram extruder and honeycomb die (Fig. 2). The die comprised feed holes of 1.2 mm and distance of 1.52 mm apart; and die pins with a width of ~ 1 mm. The pastes were next loaded into the barrel of the extruder, and placed under vacuum (i.e. deaired) prior to extrusion. A servo-hydraulic press (Schenck 250 kN) was employed to actuate the piston. The extrudates were dried for twenty-four hours, at ambient temperatures. The extrudates were then thermally debound in a muffle furnace (Elite Thermal Systems Ltd). The thermal debinding process is detailed in the results section. The extrudates were subsequently sintered in a muffle furnace at 1250 °C using a heating rate of 5 °C/min. For further characterisations, the extrudates were sectioned into ~ 4.5 mm^3 cubes (Isomet® 250, Buehler), and ground flat using silicon carbide grinding paper. A total of ten scaffolds were fashioned from three extrudates.

2.3. Characterisation

2.3.1. Rheological

Viscosity measurements of the pastes were performed using Malvern's Rosand RH200 15 mm twin bore capillary rheometer, and the experimental procedure was selected using the Flowmaster™ software. A tungsten carbide die with a diameter, length and angle of 1 mm, 16 mm and 180°, respectively, was used. Before each measurement, the samples were kneaded by hand and loaded into the barrel at ambient temperature, followed by manual compaction using a piston to a reference point (95–110 mm).

To compliment the capillary rheometry analysis, a rotational rheometer was employed in oscillatory mode, also referred to as dynamic mechanical analysis (DMA), to elucidate the mechanical behaviour of pastes. By performing an amplitude sweep test, whereby subjecting samples to increasing oscillatory forces, a shear stress-strain curve was obtained. From the data, the shear modulus and the plastic behaviour of samples were determined. The former is akin to the elastic modulus, however, as the instrument applies a torsional force, rather than an axial force, it is the shear characteristics that were analysed. The DMA data was used in correlation to the capillary rheometer data to determine the quality of the extrudates. The rotational rheometer (MCR 302, Anton Paar) was equipped with an 8-mm parallel plate geometry, and controlled using Rheoplus software. As ceramic pastes are classified as high-viscous materials, an 8-mm plate geometry was selected, capable of generating high rheological stresses. The speed of the test was empirically determined to ensure that measurements can be recorded before the paste ages. Care was taken not to omit key transition points. When working with relatively low solvent slurries, ageing can occur if the test is unnecessarily prolonged, consequently leading to erroneous measurements. Accordingly, the following parameters were selected: the initial and final strain were 0.001% and 20%, respectively; the frequency was set to 50 rad/s; and the plate gap was set to 0.5 mm.

The MOOG SmarTEST ONE controller, which was used to control the servo-hydraulic press was also used to record the force feedback as a

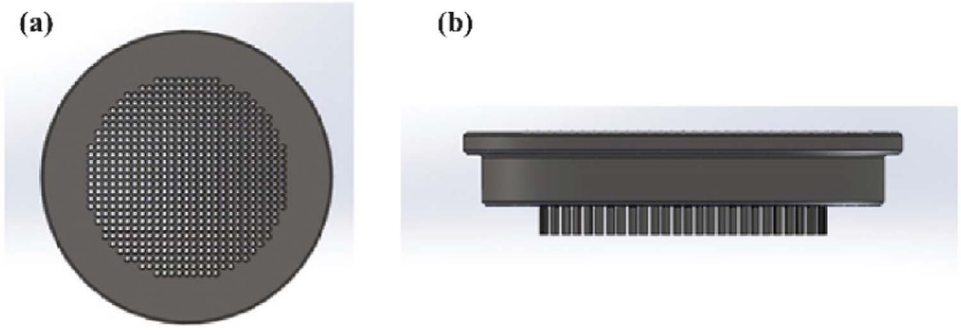

Fig. 2. CAD model of the honeycomb die used.