Applied Clay Science 105–106 (2015) 60–65

Contents lists available at ScienceDirect

Applied Clay Science

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

Research paper

Porous hollow tubes processed by extrusion of ceramic emulsions

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ARTICLE INFO

Article history:
Received 29 July 2014
Received in revised form 24 November 2014
Accepted 10 December 2014
Available online 2 January 2015

Keywords:
Ceramic emulsions
Extrusion
Hollow tubes
Porous materials

ABSTRACT

The processing of ceramic materials by extrusion is widely used to obtain products with constant cross section. Most of them are framed with applications as catalysis, filtration, building, fuel cells, isolators, etc., mainly if they are porous with special designed microstructural characteristics as pore size/distribution, liquid and gas permeability, mechanical properties, etc. Thus, in this work we combine a cellular ceramic preparation strategy based on a synergy of emulsification process and gel casting, with the extrusion process to obtain porous hollow tubes. Tree ceramic emulsions were extruded under different ram speeds and its effect was studied using Benbow-Bridgwater model.

1. Introduction

In recent years a lot of strategies have been developed for cellular ceramics preparation. These materials are characterized by properties as high permeability, low relative density, high specific area, low thermal conductivity and high thermal shock resistance. All of these properties are dependent on microstructural features of the cellular ceramic as porosity, mechanical strength, shape, cavities size and distribution, and also thickness/connectivity between the cells (Acchar et al., 2008; Vitorino et al., 2013), Table 1.

According to their properties, cellular ceramics can be used in specific applications, being average cellular size one of the strongest microstructural characteristics as shown in Fig. 1. This characteristic is highly dependent on the conditions and preparation methods which used for cellular ceramics production (Studart et al., 2006). Nevertheless, rather than cellular ceramics preparation, their processing is also important. In this context, extrusion is a valid shape strategy to process bodies with constant cross section to be applied in different applications like catalysis, catalytic supports, refractories, and filtration. However relevant literature show that the success of the extrusion shaping process is dependent on the material ability to be deformed without rupture, through the application of the stress, and keep the desirable deformation, after stress be removed or reduced, i.e. the plasticity of the extruded paste (Ribeiro et al., 2006; Andrade et al., 2011).

In a recent study we develop a methodology to prepare porous cellular ceramics based on a emulsification of ceramic suspensions in melted paraffin (Vitorino et al., 2013; Sanches et al., 2014), and plasticity studies to assess the extrudability of ceramic emulsions as alumina, kaolin and red clay were also performed (Vitorino et al., accepted for publication).

Thus, the purpose of this work is to assess the potential of ceramic emulsions extrusion to process in large scale porous hollow tubes to be used in representative applications.

2. Materials and methods

2.1. Materials preparation: ceramics emulsions preparation

The ceramic emulsions (kaolin, red clay and alumina, with the mineralogical composition already presented in a previous study (Vitorino et al., accepted for publication)) used to extrude hollow tubes were prepared based on a methodology and in conditions presented in previous works (Vitorino et al., 2013; Table 2). Dolapix PC–67 (chemical basis: Polycarboxylic acid, sodium salt, according to the data sheet from Zschimmer-Schwarz) was used as dispersion agent to stabilize the suspension and to adjust its viscosity close to 0.5 Pa·s. These ceramic suspensions were combined with melted paraffin (80 °C) to obtain emulsions with paraffin:suspension volume ratio of 1.5. The resulting emulsions were naturally cooled down to room temperature, and dried (below the paraffin melting point to prevent the coarsening of paraffin droplets) during different times to adjust the green ceramic emulsion humidity.

2.2. Ceramic emulsions characterization: plasticity

The plasticity characterization was performed by plastic compression of three samples per composition using a Lloyd Instruments LR

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http://dx.doi.org/10.1016/j.clay.2014.12.014
0169-1317/

Table 1
Typical properties of cellular porous ceramics.

Property		Range	Reference
Cell size, D		3–300 μm	Barg et al. (2009), Sepulveda and Binner (1999)
Mechanical strength, σ		<30 MPa	Barg et al. (2012), Bartuli et al. (2009), Sarkar et al. (2012), Sepulveda and Binner (1999)
Densification		<50%	Khattab et al. (2012), Peng et al. (2000)
Permeability	Gas	10^{-11}–10^{-14} m^2	Innocentini et al. (2009)
	Liquid	10^{-4}–10^{-5} m s^{-1}	Belouatek et al. (2008), Lee M. et al. (2014), Lee et al. (2002), Sarkar et al. (2012)

30 K with a compression rate of 2.0 mm min^{-1} until a maximum deformation of about 70% (Andrade et al., 2011; Ribeiro et al., 2005; Vitorino et al., submitted for publication).

2.3. Materials processing: ceramics emulsions extrusion

Two dies of different die-land length, 30 L and 120 L (30 and 120 mm respectively of their die length) were used to extrude the emulsions (ram extruder). During the extrusion process different ram velocities were tested (1, 2, 5, 10, 20, 50, 100 and 200 mm min^{-1}) in order to study the contribution pressure drop along the die length (p_0, p_1, …, p_7) as schematically is illustrated in Fig. 2.

2.4. Materials consolidation: sintering

After drying, the extruded bodies were sintered at 2 °C min^{-1} from room temperature up to 200 °C, followed by 3 h of dwell time. Low heating rate (2 °C min^{-1}) was also used for up to 500 °C, to ensure that all paraffin was eliminated under controlled conditions. The sample was then heated at 5 °C min^{-1} to the final sintering temperature (Table 2), with 2 h of dwell time.

2.5. Materials characterization

2.5.1. Structural and microstructural characterization

Scanning electron microscopy (SEM – Hitachi SU1510) was used to perform the microstructural characterization of the fired bodies, to check the most relevant microstructural features of the bodies processed by extrusion. Structural characterization of raw materials was performed by X-Ray diffraction (Bruker D8 Advance DaVinci) to identify the presented mineral phases.

2.5.2. Bigot curves

Drying is an important step in the processing of ceramic products, to remove the water used in the shaping step. Usually, the drying studies are performed through the evolution of water content as a function of linear shrinkage of green ceramic bodies called Bigot curves. These studies are very useful to obtain the critical water content (CWC), i.e. the humidity from which the drying rate can be increased.

Bigot curves were obtained by weighing and measuring of extruded bodies every 30 min of drying, initially in air, followed by drying in oven at 110 °C.

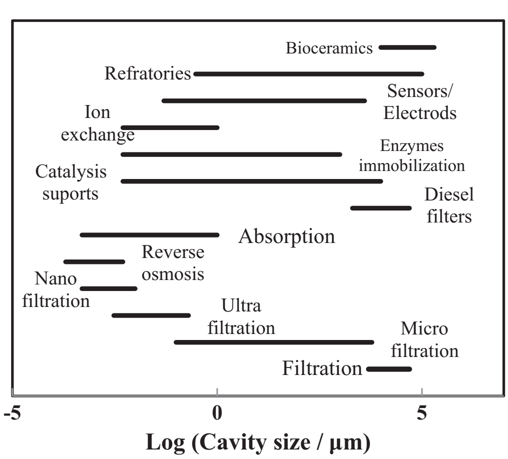

Fig. 1. Average pore size range for a set of representative applications. Adapted from Han et al., 2003a; Han et al., 2003b; Vitorino et al., 2013; Sanches et al., 2014.

2.6. Mathematical description of extrusion process

The extrusion of ceramic pastes can be mathematically described using Benbow model which takes in to account parameters such as flow properties of the material, extrusion rate and physical/geometrical details of the extruder (Benbow et al., 1989; Blackburn and Lawson, 1992). Thus, the extrusion of ceramic pastes through dies with circular cross section and having a square entry can be described by Eq. (1) (Wildman and Blackburn, 1998; Ribeiro et al., 2006; Raupp-Pereira et al., 2007).

$$P = 2(\sigma_0 + \alpha V^m)\ \ln\left(\frac{D_0}{D}\right) + (\tau_0 + \beta V^n)\ \frac{4L}{D} \tag{1}$$

where P is the extrusion pressure, α is a velocity-dependent factor for the convergent flow, β is the velocity-dependent factor for parallel flow, n and m are exponents, σ_0 is the paste bulk yield value, τ_0 is the characteristic initial wall shear stress of the paste, D_0 and D are the diameters of the barrel and of the die, respectively, L is the die-land length and V is the extrudate velocity.

The initial model was subsequently adapted to dies with complex geometries (Benbow et al., 1991a,b; Ribeiro et al., 2006), Eqs. (2) and (3), which take in to account the contributions of several pressure drop along the die (Fig. 1).

$$P = p_0 + \ldots + p_7 \tag{2}$$

$$\begin{aligned} P = {} & \left[2(\sigma_0 + \alpha V^m + \tau_0 \cot\theta)\ \ln\left(\frac{D_0}{D_1}\right) + \beta V^n \cot\theta\right] \\ & + \left[2\left(\sigma_0 + \alpha\left(\frac{4Q}{\pi Dh^2 N}\right)^m\right)\ \ln\left(\frac{D_1}{Dh\sqrt{N}}\right)\right] \\ & + \left[4\left(\tau_0 + \beta\left(\frac{4Q}{\pi Dh^2 N}\right)^n\right)\left(\frac{Lh}{Dh}\right)\right] + \left[(\tau_0 + \beta V^n)\left(\frac{L_2 M_2}{A_2}\right)\right] \\ & + \left[\ln\left(\frac{A_2}{A_3}\right)(\sigma_0 + \alpha V^m)\right] + \left[(\tau_0 + \beta V^n)\left(\frac{4L_3}{D_3 - d_i}\right)\right] \\ & + \left[\ln\left(\frac{A_3}{A_4}\right)(\sigma_0 + \alpha V^m)\right] + \left[(\tau_0 + \beta V^n)\left(\frac{4L_4}{d_0 - d_i}\right)\right] \end{aligned} \tag{3}$$

D_i is the diameter in each specific position (Fig. 1), N is the number of internal holes having diameter Dh, Q is the volumetric flow rate, A_x is the area at location x, L_x is the die-land length at location x, and θ is the angle of die-entry region.

Note that Eq. (3) is dependent on known geometrical parameters of the die-land (A_i, D_i, L_i and θ), of processing parameters (V), and also of unknown physical parameters (σ_0, α, β, τ_0) and parameters that are simply mathematically fitted (n and m). As reported in previous works (Ribeiro et al., 2005; Andrade et al., 2011; Vitorino et al., 2014)