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Gelcasting of alumina–chitosan beads

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Abstract

Several papers have reported the advantageous combination of chitosan and ceramic particles for such applications as biomimetic scaffolds, membranes, pollution remediation and gelcasting complex shapes. This work presents a novel gelcasting consolidation mechanism, based on the effects of pH changes on chitosan solubility and zeta potential of alumina particles. Unlike other chitosan-based gelcasting methods, it employs a small content of organic material (lower than 3 wt%) and does not require crosslinking agents (such as glutaraldehyde). With this new method alumina beads with 0.5–1 mm diameter could be produced, whose porosity and specific surface area could be tuned for various applications.

Keywords: Gelcasting; Alumina; Chitosan; Beads

1. Introduction

Chitosan is a natural polymer obtained from the alkaline deacetylation of chitin, a polysaccharide extracted from crabs and shrimps. There have been several reports on the advantageous combination of chitosan and ceramic particles for applications in biomimetic scaffolds [1–3], membranes for pollution remediation [4–6] and gelcasting complex shapes [7–9] For the latter application, chitosan behaves as a binding agent that, besides promoting suitable mechanical strength, also presents biocompatibility and low toxicity for handling and during the burnout and sintering steps.

In aqueous media, chitosan behaves as a cationic polyelectrolyte and becomes soluble in acidic pH because of the conversion of glucosamine groups (R–NH_2) into R–NH_3^+ units [10]. For chitosan to be used in gelcasting processes, two requirements must be fulfilled: (i) the dispersion of the ceramic particles must be carried out in acidic pH (~2–5), at temperatures in the range of 20–70 °C to allow for chitosan to remain dissolved and (ii) the ceramic particles must have positive surface charges. Otherwise, upon increasing the pH or in an anionic medium, chitosan precipitates in a gel form. These are the reasons for the successful combination with alumina and zirconia [8], SiC [9] and hydroxyapatite [2] systems, which are usually dispersed in acidic pH.

In gelcasting processes to obtain pieces with complex shapes and large volumes, the consolidation of chitosan–ceramic particles suspensions occurs in two steps [7–9]. First, cross-linking reactions amongst chitosan molecules in solution are triggered by glutaraldehyde, glycerol or epycloridrine, causing a primary hindering in the mobility of the ceramic particles. Next, the drying step forces lead the gelled chitosan molecules to precipitate, increasing even further the mechanical strength of the system. The first step is required in order to prevent the volumetric shrinkage that follows binder-free suspensions after drying [11]. Other consolidation strategies include tapecasting thin films, for example, in which drying is used as the single hardening mechanism.

In this study, a novel gelcasting consolidation mechanism is presented in which the pH-sensitive chitosan is blended with surface charged particles to obtain spherical beads of alumina (0.5–1 mm). This novel methodology uses very low content of chitosan (~2.6 wt%), no toxic crosslinking agents and allows for tuning the porosity and specific surface area of the beads, so that tailored applications can be envisaged.

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Table 1
Properties of the raw materials employed in the tests.

		Alumina[a]	
Chemical analysis (%; typical values)		Na_2O: 0.08; Fe_2O_3: 0.02; SiO_2: 0.03; CaO: 0.02; MgO: 0.07	
Specific surface area (BET; $m^2\ g^{-1}$)		Typical: 7.5; measured: 7.2 ± 1.0	
Particle size (μm; D_{50}/D_{90})		Typical: 0.5/2.0; measured: 0.61/0.95	
Density (Helium picnometry; $g\ cm^{-3}$)		3.96 ± 0.05 (before firing)	
Isoelectric point (pH; dispersant-free)		8.53 (Fig. 2)	
Loss of ignition (%, 800 °C)		0.80 (Fig. 3c)	
			Chitosan[b]
Molecular weight ($g\ mol^{-1}$)			54.350
Desacetilation degree (%)			96
Solubility in water (pH range, at 25 °C)			≤6 (Fig. 2)
Loss of ignition (%, 800 °C)			97.85 (above 200 °C, Fig. 3b)
	Alumina + chitosan mixture (wt%)		
Alumina suspension	Alumina	74	50
	Acetic acid solution (0.1 M)	26	
Chitosan solution	Chitosan	2	50
	Acetic acid solution (0.1 M)	98	

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2. Materials and methods

Details of the raw materials employed and of the compositions tested are presented in Table 1. The role of pH on aqueous chitosan solutions was evaluated through turbidity tests using a UV–Vis spectrophotometer (Carry 50, Varian) with the methodology described elsewhere [10]. The alumina powder was characterized by obtaining (a) particle size distribution (ASTM C1070-01) and (b) zeta potential *versus* pH (using 2 vol% suspension) (Zetasizer NanoZS, Malvern), (c) specific surface area (BET method, Gemini 2370, Micromerictis, ASTM C1069-09) and (d) density (Helium picnometry, Ultrapicnometer, DP Union) measurements.

The chitosan solution (2 wt% of chitosan in 0.1 M acetic acid solution, pH = 4) was stirred at 40 °C, during 24 h. The alumina suspension (75 wt%/40 vol% alumina in 0.1 M acetic acid solution, pH = 4) was processed in a paddle mixer (IKA, Germany). After 5 min stirring at 1000 rpm, the suspension was deaerated for 1 h. Then, the chitosan solution and the alumina suspension were mixed at 100 rpm during 5 min (Fig. 1a). The

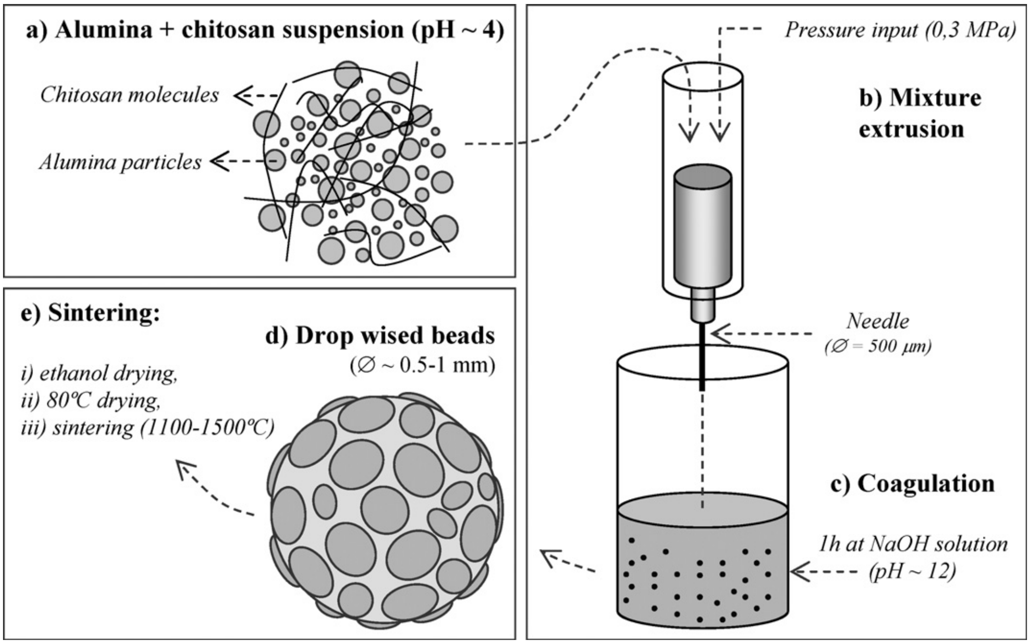

Fig. 1. Schematic representation of the processing method developed.

water–chitosan–alumina ratio required for a suitable spinning and mechanical strength were previously determined to produce an easily extrudable suspension, with suitable mechanical strength for handling. The chitosan–alumina suspension was poured in to a 50 ml syringe with a 500 μm × 10 mm needle. The syringe was connected to an air compressor operating at constant pressure of 30 kN m^{-2} (Fig. 1b), with which the suspension was dropper in a stirring 2 M NaOH solution (pH = 12), generating individual beads (Fig. 1c). The beads remained in the NaOH solution during 1 h and then were washed until neutral pH. Next, they were kept in absolute ethanol during 24 h to remove the water, and dried at 80 °C, during 24 h (Fig. 1d). The dried samples were sintered at 1100–1500 °C (1 °C min^{-1} up to 600 °C, 5 °C min^{-1} up to maximum temperature, during 5 h and 5 °C min^{-1} cooling rate) (Fig. 1e).

Thermogravimetry (TGA-Q50, TA Instruments, 10 °C min^{-1}, 25–800 °C, synthetic air atmosphere) testes were carried out in the as-received chitosan and alumina and in the dried green beads. The specific surface area (SSA) and apparent porosity (ASTM C373; ethanol was used as immersion fluid) of the dried green and sintered beads were measured. Their microstructure was investigated using scanning electron microscopy (SEM, Philips XL30 FEG).

3. Results and discussion

3.1. Chitosan as a binder for gelcasting ceramic particles

The alumina employed in this work presented a typical zeta potential curve, indicating highly positive charged particles surfaces in pH's lower than 7 (Fig. 2). Similar results for equivalent alumina grades can be found in literature [11], confirming the favorable condition for its dispersion in water without the using other dispersants (except the acetic acid). In acidic pH below 6, chitosan solution had a high transmittance, indicating that the polymer is dissolved and behave as cationic polyelectrolyte. Therefore, both chitosan and alumina were positively charged at pH 4, thus allowing a stable suspension to be obtained.

The consolidating step of a gelcasting method, on the other hand, requires the opposite condition: the polymeric molecules must restrain the solid particles mobility. Here, the consolidation mechanism is based on the pH change imposed to the beads when in contact with NaOH solution (pH ~ 12), producing two simultaneous binding effects: (a) in pH > 8, alumina particles become negatively charged (Fig. 2), behaving as adsorption sites for the positively charged chitosan dissolved molecules and (b) as a result of the contact with alkaline solutions and anionic medium, chitosan precipitates as a gel due to the deprotonation of the $(R–NH_3)^+$ groups [10], restraining even more alumina particles mobility. Therefore, upon drop-wising the suspension in the coagulation alkaline solution, this mechanism preserves the drops' initial shape and spherical beads were produced. Fig. 3 presents the aspect of the beads obtained (a) and the non-consolidation behavior of the chitosan-free reference sample (b).

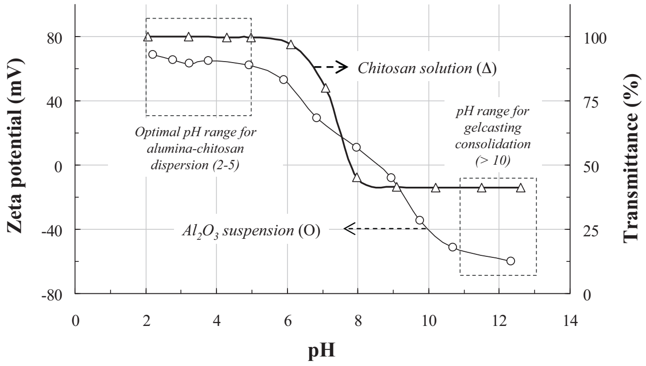

Fig. 2. Variation of zeta potential and UV–visible transmittance with the pH for alumina suspension and chitosan solution, respectively.

3.2. Characterization of the beads produced

In comparison to other gelcasting methods, the one employed in this work has an interesting processing advantage: it requires a very small amount of polymer for consolidation (chitosan content in the dried system is 2.6 wt%), as can be seen in Table 1 and in the thermogravimetry results (Fig. 4a). The loss of ignition of chitosan bonded alumina beads is smaller than 4 wt% and a significant part of these volatiles (~60 wt%) is comprised by water vapor (free-water remained from the drying process, Fig. 4b, and from the decomposition of residual aluminum hydroxide from calcined alumina, Fig. 4c). This result indicates that the first heating before sintering can be carried out without concerning significant toxic volatiles generation during the polymer burnout. The intense binding effect of chitosan is attributed to the fact that chitosan is a strong, long chain polymer and to the significant contribution of chitosan adsorption on the alumina particles before its gelation.

With regard to porosity and specific surface area, Fig. 5 indicates that the beads can be grouped in three different categories, considering the different stages of the process.

(1) The non-dried elements were attained in the first step, after the end of the coagulation and neutralization but before drying in ethanol (Fig. 5a). They had the highest porosity values (above 80%) reflecting the presence of a large amount of water in the structure. During the drying in ethanol, part of these pores collapse owing to capillarity forces (as it can be seen following for the dried green ones). However, if they were kept wet, these beads can be used in water remediation and as scaffolds for biologic tissues.

(2) The dried green ones, obtained after drying with ethanol and at 80 °C but before sintering. They had porosity close to 70% according to Fig. 5b. The fracture surface in Fig. 3c indicates that the pores in their structure were generated with a combination of non-optimized particles packing and voids originally occupied by water that were partially preserved during the chitosan gelation. The SSA measurements point a surface area of 3 m^2 g^{-1} and pore sizes bellow 1 μm, which are interesting characteristics when applications such as ion exchange or drug delivery are envisaged.

(3) The sintered ones had decreasing porosity and SSA levels with increasing firing temperatures, as shown in Fig. 5c. Despite high sintering temperatures and grain growth, at least 15% of pore fraction remained in the structure. This effect can be explained considering the large initial fraction of pores in the green samples and the weak compacting forces in the extrusion process. Depending on the sintering temperature (and therefore on their porosity and SSA), compacted beads could be used in thermal insulation (those fired up to 1300 °C) or in filtering and fluidized bed reactors (the up to 1300 °C fired ones).

It is important to highlight that the size of the elements prepared with this novel approach is limited to ~5–6 mm. This limitation occurs because the setting mechanism of this gelcasting method requires contact of the chitosan molecules

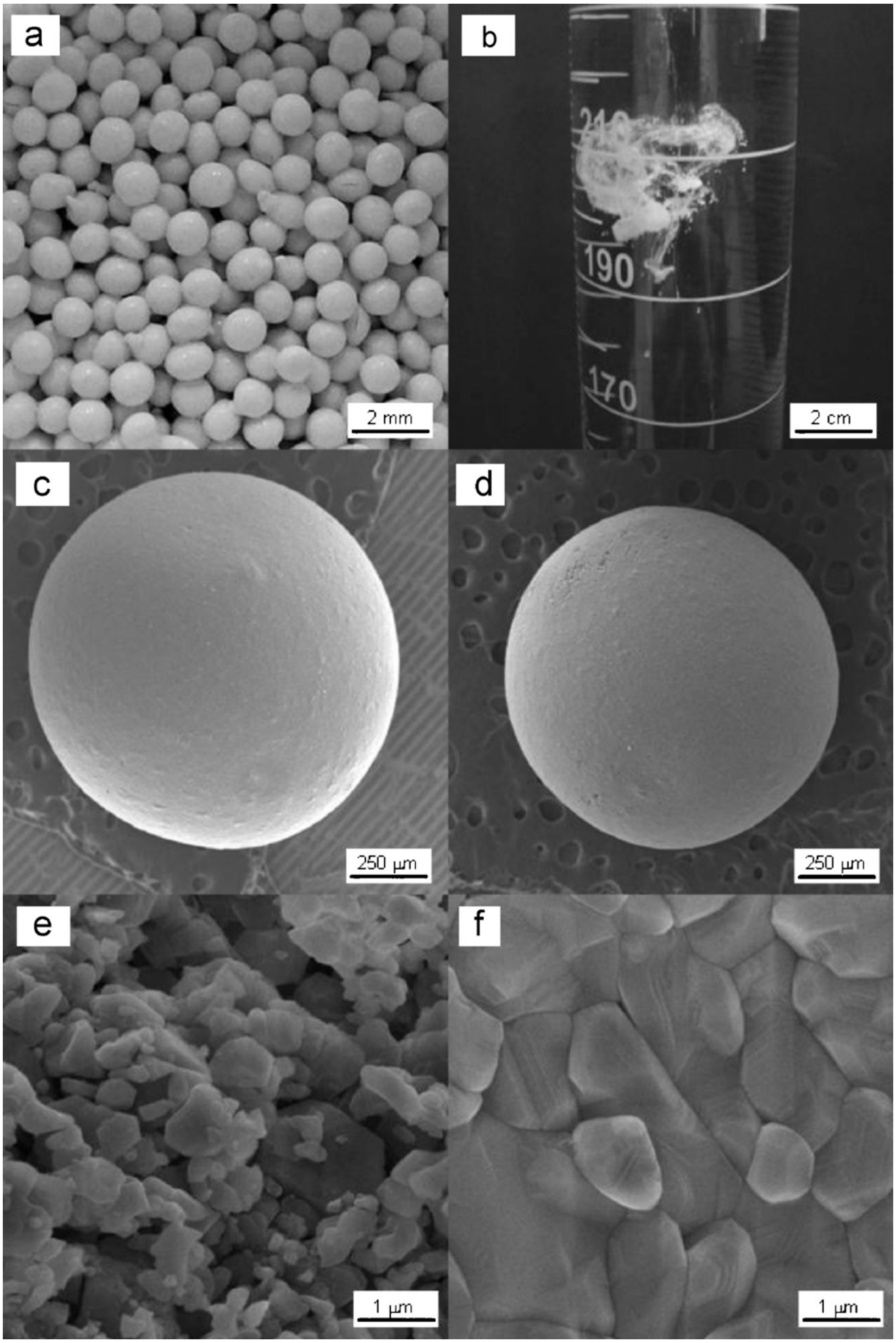

Fig. 3. (a) Beads after neutralization, (b) chitosan-free suspension drop-wised in the alkaline solution, SEM of beads after (c) drying and (d) sintering at 1500 °C and SEM of fracture surface of (d) dried-green and (e) 1500 °C samples.

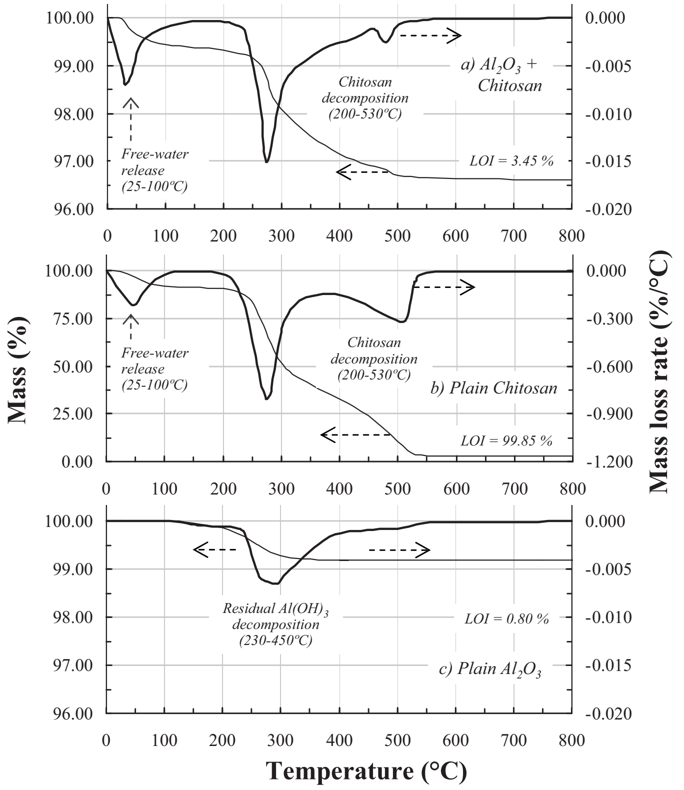

Fig. 4. Mass loss and mass loss rate for (a) alumina–chitosan dried beads and as-received, (b) chitosan and (c) alumina.

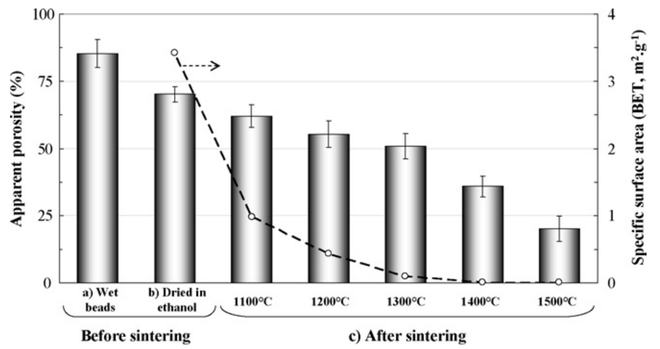

Fig. 5. Apparent porosity and specific surface area (SSA) of the microelements cast before and after sintering.

with a coagulating solution. Therefore, larger parts do not present a homogenous coagulation and microstructure. Presently, efforts have been carried out in authors' research group in order to produce chitosan–alumina gelcast continuous fibers, whose thin cross-section allows its consolidation by this mechanism.

4. Remarks

This work presented a novel gelcasting method for alumina that uses chitosan as binding agent. An important innovation is the small content of polymer employed in the consolidation before sintering (<3 wt%). By means of pH adjustment (~4), an optimal condition for dispersing alumina particles was achieved with chitosan dissolved molecules. The consolidation mechanism used was based on the precipitation of the chitosan in a highly alkaline anionic electrolyte (2 M NaOH solution). Beads were obtained with uniform shape and size (0.5–1 mm diameter). Upon varying the processing conditions (drying and sintering temperatures), one may tune the porosity and surface area of the beads for specific applications.

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