



A PCE-based rheology modifier allows machining of solid cast green bodies of alumina

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Abstract

The performance of a poly(carboxylate ether) (PCE)-based superplasticizer to enable the machining of green bodies that are solid cast from suspensions of alumina was investigated. An alumina loading of 35 vol% in the presence of 1.25 wt% superplasticizer was established to be suitable for lathing and removal of significant amount of material through drilling. A reduction of 77% in the diameter of green bodies that corresponds to a 59% reduction in volume was achieved. The lathed green bodies exhibited smooth terraces without visible cracks. All of the green bodies were sintered without a polymer burnout step.

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1. Introduction

Solid casting is the method of choice for the production of several ceramic objects from laboratory crucibles to turbine blades since it is scalable, simple, and necessitates only low cost capital investment [1,2]. In general, for further shaping of solid cast and then sintered bodies, only limited post-sintered machining, such as grinding, can be used due to high hardness and low toughness of these objects [3]. On the other hand, machining of the green body can (i) allow additional machining processes, such as milling, drilling, and lathing to be implemented [4], (ii) increase production speed due to faster material removing rates [5], and (iii) eliminate early tool wear and possible crack formations [6]. Therefore, for cost-effective and simple fabrication of ceramics, there is a need for developing systems that can produce green bodies with enough strength to withstand machining.

In solid casting, high particle loadings and well-packing is necessary to produce high strength green bodies; however, at higher loadings the viscosity increases and homogeneity of the

slurry decreases significantly [7]. Here, through the use of a PCE-based superplasticizer, we show the machinability of well-packed and high strength green bodies that are solid cast from 35 vol% aqueous alumina suspensions with 200 nm particle size. We drilled the solid-cast cylindrical bodies without visible cracks and obtained terraced structures with smooth surfaces. To the best of our knowledge, this study is the first of its kind to provide thin walls that are produced by drilling of a solid-cast green body of alumina. In addition, this system does not necessitate binders to sustain its strength and therefore, the binder burnout step is eliminated from the process.

2. Experimental

An alumina nanopowder (AKP-50, Sumitomo Chemicals, Japan) with average particle size of 200 nm, purity of > 99.99%, and BET surface area of 10.9 m²/g was used to prepare suspensions. Dynamic light scattering (Malvern Instruments, Ltd.) measurements revealed a single population peak that corresponds to 220 nm particle size (data not shown). Scanning electron microscopy (Leo Supra 35VP) indicated the particles have round shape with no irregular morphology (data not shown).

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The comb-type PCE-based superplasticizer, hereafter referred to as superplasticizer, is composed of acrylic acid (AA), 2-acrylamido-2-methylpropane sulfonic acid (AMPS), and maleic anhydride (MA) modified poly(ethylene glycol) (PEGMA) with molecular weight of 1000 g/mol. The superplasticizer was synthesized through a method that is described by Salami and Plank [8]. The ratio of the monomers was 25/25/1 (AA/AMPS/PEGMA) and the reaction was carried out at pH 8. These conditions were chosen based on the superplasticizing ability of this copolymer that was reported in our previous work [9].

Suspensions with 30–40 vol% alumina particles and different amounts of copolymer were prepared using an ultrasound probe (Vibra Cell 75041, Bioblock Scientific) in pulse mode (2 s on, 2 s off) for 4 minutes to break soft agglomerations. The suspensions were stirred for 24 h in a capped container to prevent evaporation.

The rotational rheology was conducted in Anton-Paar MCR 302 rheometer with cone-plate geometry of 50 mm/2° and a gap size of 0.208 mm. After loading of each sample, a thin layer of low-viscosity paraffin oil was employed around the outer edge of the plates to protect the sample from evaporation. Temperature was set to 25 °C and the shear rate was changed from 0.1 to 1000 s⁻¹.

Zeta potential of the suspensions was monitored by using Zetasizer nanoseries (Malvern Instruments, Ltd.). After addition of 0.001 wt% alumina particles to superplasticizer solutions and 1 h of stirring, pH of the mixture was adjusted in between 2–12 through the use of aqueous solutions of sodium hydroxide and hydrogen chloride. Subsequently, six measurements with at least 20 cycles were performed at 25 °C and the average value was reported.

Compression tests on green bodies were performed with Zwick/Roell Z100 universal testing machine according to ASTM 773 standard. All suspensions were cast in homemade gypsum molds (3/4 vol/vol gypsum to water ratio) with an inner diameter of 11 mm and a height of 15 mm. All samples were de-molded after 24 h and then dried at 70 °C for 24 h. Each experiment was repeated 5 times.

AccupycII-1340 gas pycnometer was used to measure percentage of theoretical density of alumina green bodies. Before measurement, each sample was covered with silicone oil to prevent penetration of helium through open pores.

For machining, the green bodies were drilled 5 mm deep with 1.1–8.2 mm drill bits using conventional mounting heads. Machining speeds were 700–1200 rpm for lathing and 500–900 rpm for drilling. Drilling deeper than 4–5 mm without getting rid of excess swarf initiated internal cracks. Machined samples were sintered at 1500 °C for 2 h with a heating rate of 5 °C/min with no binder burnout step. Shrinkage rates were reported based on measurements from 25 samples.

3. Results and discussion

3.1. Electrokinetic study and rheological characterization

We tracked the electrokinetic behavior of alumina particles at their native state and in the presence of the superplasticizer. This superplasticizer has both carboxylic acid and sulfonate groups that gradually promote more negative charge as the

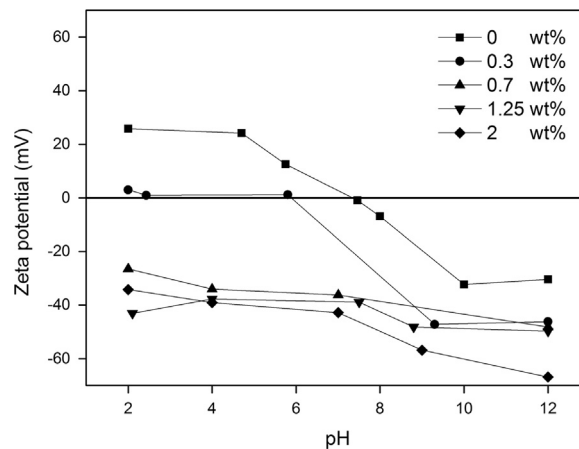


Fig. 1. Effect of pH on zeta potential of the alumina suspensions in the presence of different amounts of superplasticizer.

slurry gets more basic. Cesarano and Aksay suggested that the electrostatic repulsion on the backbone of the copolymer facilitates the expanded random coil configuration leading to an increased stability [10]. The surface of alumina particles were shown to hold Al–OH bonds and positively charged sites of Al–OH₂⁺ between pH 7 and 8 [11]. Here, the isoelectric point (IEP) of alumina particles was measured to be at pH ~7.6 in consistent with previous reports [12,13]. Above 0.3 wt% addition of superplasticizer, the zeta potential of alumina particles was determined to be below –25 mV over a wide pH range (2–12) (Fig. 1). Therefore, we concluded to utilize this superplasticizer in native pH levels without the adjustment of pH throughout the experiments.

In general, viscosities in the range of 0.3–10 Pa s were found to meet the flowability requirements of solid casting and shear rates of 1–100 s⁻¹ are frequently encountered in the process [14–17]. Lower viscosities result in well-packed green bodies that is necessary to produce high strength structures [18]. We monitored the shear viscosity of 35 wt% alumina suspensions in the presence of 1–4 wt% superplasticizer at the shear rate of 1 s⁻¹ (Fig. 2a). The viscosity exhibited a sharp drop at 1.25 wt% addition of the superplasticizer. This kind of dip in the viscosity of PCE-based copolymers was shown to arise from steric contribution of PEG side chains [19] and ionic charge in the backbone of the copolymers [20]. Also, at 35 vol% alumina loading, the system with 1.25 wt% superplasticizer displayed lowest shear thinning behavior manifested by the lowest slope in viscosity versus shear rate graph [21,22] indicating better dispersion of alumina particles (Fig. 2b) [23].

Fig. 3 shows the effect of alumina content on the rheological behavior of the suspensions. As expected, shear thinning behavior increased with alumina content since the coagulation of particles became more probable at higher levels of loading [24].

Krieger–Dougherty model is used to determine maximum particle loading in suspensions: [25]

$$\mu = \mu_0 \left(1 - \frac{\phi}{\phi_{\max}} \right)^{-\left(\frac{\mu}{\phi_{\max}} \right)} \quad (1)$$

where μ is the viscosity of the suspension (Pa s), μ_0 is the

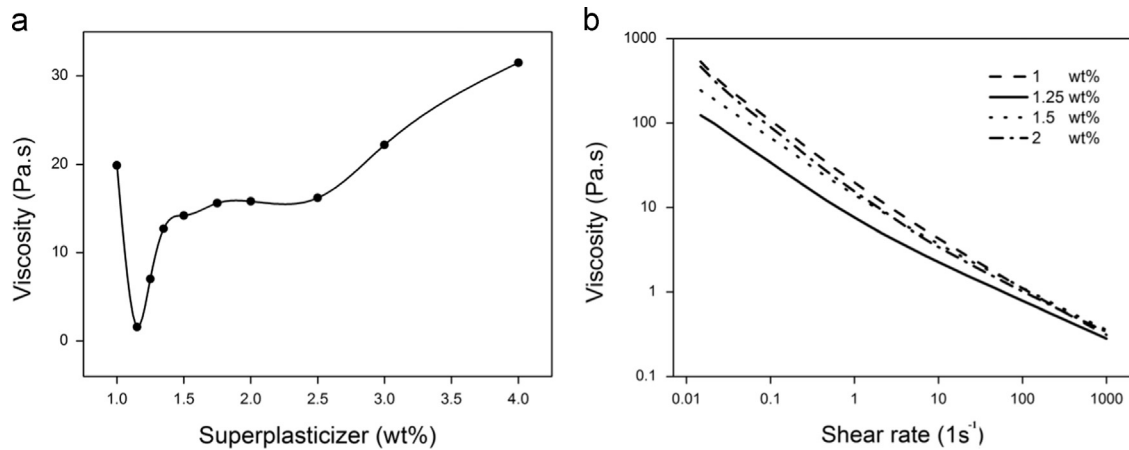


Fig. 2. (a) Viscosity of 35 vol% alumina suspensions in the presence of 1–4 wt% superplasticizer at shear rate of 1 s^{-1} , (b) dependence of viscosity to shear rate at 35 vol% alumina suspensions with different amounts of superplasticizer.

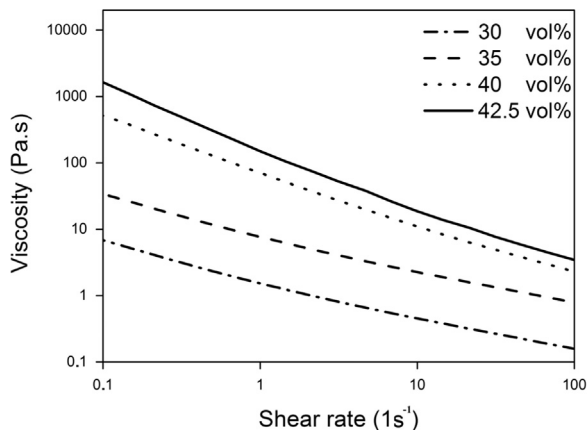


Fig. 3. Viscosity of alumina suspensions as a function of shear rate in the presence of 1.25 wt% superplasticizer.

viscosity of the media (Pa s), ϕ_{max} is the maximum particle loading (vol%) achievable for a system. Feeding particle loadings and viscosities to Krieger and Dougherty model at 1 s^{-1} shear rate provided a ϕ_{max} value of 45.7 vol%. This amount of maximum loading is consistent with empirical data where the flowability of the suspensions halted at 45 vol% (data not shown).

3.2. Mechanical characterization and machinability of green bodies

Traditionally, binders such as poly(vinyl alcohol), poly(ethylene imine), poly(vinyl pyrrolidone), and high molecular weight poly(ethylene glycol) were used to increase the mechanical strength of the green bodies that are slip cast from suspensions [26–28]. These binders are usually employed at least more than 4 wt% and although adding more binder contributes to the mechanical properties, it hinders the flowability of the slurry during casting [29]. Rheology modifiers such as poly(acrylic acid), poly(maleic acid), and Na-Carboxymethyl cellulose were utilized in the presence of binders to homogenize the slurries and impose better packing

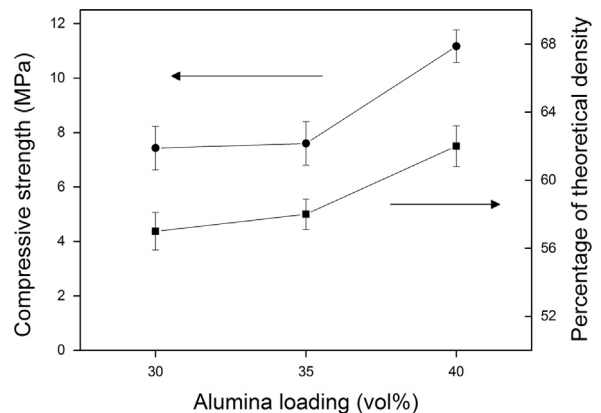


Fig. 4. Compressive strength and percentage of theoretical density of green bodies with different vol% alumina loadings at 1.25 wt% superplasticizer addition.

of particles. In these systems, total amount of additive can reach to 4–10 wt% [30–32]. Even at these concentrations of the polymers, machinable green bodies were not reported. On the other hand, in gel casting process, a common method to produce machinable green bodies, crosslinkable polymers (e.g., poly(acrylamide) and poly(ethylene glycol) dimethacrylate) are used to form a network to host ceramic particles [33]. In these systems, the polymer content is 10–15 wt%. In all of these methods, there is a need for careful binder burnout procedure, which can be as slow as $1 \text{ }^\circ\text{C}/\text{min}$, to prevent structural defects that may appear due to the presence of the polymers at aforementioned amounts [34,35].

Here, the compression tests were performed on 30–40 vol% alumina loaded samples with 1.25 wt% superplasticizer without any binders. The packing of the green bodies were tracked with helium pycnometry to find their percentage theoretical density. As expected, the compressive strength and percentage theoretical density of green bodies increased with alumina loading (Fig. 4). The percentage of theoretical density at 30 vol% loading was larger than 55 vol% loaded gel cast samples that were previously reported [36,37].



Fig. 5. Photograph of (a) sintered alumina samples that were drilled with (from left to right) 1.1, 2, 4, 6, and 8.2 mm drill bits before sintering, (b) a green body after lathing.

Although, it is desirable to have high strength green bodies, fifteen samples with 40 vol% alumina content could not withstand machining and failed during the process. Therefore, a concentration of 35 vol% alumina (with 1.25 wt% superplasticizer) was chosen for testing reliability of green body machining. We consistently get smooth surfaces without visible cracks (over 60 samples) as exemplified by the inset in Fig. 5a and b. The largest inner diameter of 8.2 mm was attained with a wall thickness of ~ 1.25 mm indicating that the green body can go through 59 % volume reduction (inset in Fig. 5a) without any crack formation. Sintered solid cast bodies shrunk $16.2 \pm 1.8\%$ at the outer diameter and $17.5 \pm 0.9\%$ at the inner diameter independent of the initial diameter of the drill bit. Fig. 5b exemplifies a lathed green body before sintering; this terraced body had a smooth surface and did not experience any cracking during the process. Machined green bodies fabricated by solid casting were similar to those which were produced via gel casting, starch consolidation, and protein coagulation casting in terms of green body strength and reproducibility [38–41].

4. Conclusions

Here, by the use of a single additive, a PCE-based superplasticizer, we demonstrated the machinability of solid cast green bodies. This superplasticizer provided sufficient mechanical strength such that green bodies could withstand machining operations with no formation of visible cracks and flaws. Exclusion of binders from the green body eliminated the time-consuming binder burnout step. We believe that the use of this superplasticizer can also be extended to other types of solid cast ceramics.

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