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Journal of the European Ceramic Society 34 (2014) 453–463
www.elsevier.com/locate/jeurceramsoc

Room-temperature injection molding of aqueous alumina-polyvinylpyrrolidone suspensions

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Received 11 May 2013; received in revised form 8 August 2013; accepted 15 August 2013
Available online 6 September 2013

Abstract

Room-temperature injection molding, a novel, environmentally benign ceramic processing method, produced dense, near-net shape alumina rings by utilizing unique flow properties of aqueous, highly loaded (>50 vol.%) ceramic suspensions with ≤5 vol.% polyvinylpyrrolidone (PVP) dispersed using Darvan 821A. The rheological behavior of suspensions along with microstructural and mechanical properties of resulting specimens were evaluated by varying PVP content to determine the optimal composition for forming. Parallel-plate rheometry revealed that suspensions containing ≤5 vol.% PVP were yield pseudoplastic at room temperature, which facilitated processing without heating or complex chemical reactions. Alumina rings with high green densities (>60% true density (TD)) were machined before binder removal, and increasing PVP content was observed to enhance green machinability. After binder burnout and sintering, bulk densities were ~98%TD with <16% linear shrinkage. Scanning electron microscopy revealed minimal pore formation within specimens. Ultimate strength of samples was determined using ASTM C1323-10, and a maximum C-strength of 261 ± 57.6 MPa was obtained.

Keywords: Injection molding; Alumina; Colloidal processing; Ceramic processing; Near-net shape forming

1. Introduction

Ceramic injection molding is a powerful processing alternative that allows for the rapid production of ceramic components with complex geometries without the need for costly machining.[1–3] The process has garnered a great deal of attention over the past 50 years, and it has found success in industry when compared with other conventional fabrication techniques.[3] The method borrows from plastic injection molding in that a feedstock consisting of a ceramic powder and polymer is prepared and heated into a flowable state, transferred into a mold, formed into a desired shape and then solidified by removing the applied heat and cooling.[4–6] In ceramic injection molding, the polymer must be removed from the formed part, and then the ceramic can be sintered to near full density.[7]

The type and amount of organic components are critical in the preparation of a ceramic suspension, and, thus, the formation of a robust ceramic component by injection molding. Literature reflects that most feedstocks used in injection molding are based on thermoplastic polymers, commonly polypropylene or low-density polyethylene, and then combined with some type or blend of wax and a dispersant, like stearic acid.[2,3,8,9] Organic content in a feedstock is commonly 20 wt.% or higher depending on the material system,[8] and prior to sintering the binder component must be removed, whether by pyrolysis or solvent debinding,[10,11] without negatively affecting the structural integrity of the part.[12] The inclusion of a polymer binder often imparts strength to formed green bodies,[13] although the amount of binder employed can lead to a great deal of porosity within a specimen after it is removed, causing significant shrinkage or warping and/or preventing full densification of the final part.[10]

Initial study and development of ceramic injection molding relied more heavily on organic solvents.[3] Because aqueous feedstocks pose significant advantages over the incorporation of more toxic materials and solvents into feedstocks due to their low impact on the environment and on human health,[14] significant advancement has been made in the development of aqueous injection molding processes. Binders based on

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0955-2219/$ – see front matter
http://dx.doi.org/10.1016/j.jeurceramsoc.2013.08.017

Table 1
Compositions of alumina-PVP suspensions with corresponding curve-fit parameters using the Herschel–Bulkley equation for yield-pseudoplastic fluids, average green and sintered densities and C-ring strength values for sintered samples prepared by room-temperature injection molding of suspensions with varying content of PVP with molecular weight of 55,000 g/mol.

Al_2O_3 powder content in vol.% (wt.%)	Polymer content in vol.% (wt.%)	Dispersant content in vol.% (wt.%)	σ_y(Pa)	k (Pa s^n)	n	Average green density in g/cm^3(%TD)	Average sintered bulk density in g/cm^3 (%TD)	Average grain size (μm)	Average C-ring strength (MPa)
57.9 (84)	0 (0.0)	4.4 (1.9)	4.57	3.94	0.408	2.56 ± 0.02 (64)	3.92 ± 0.02 (98)	–	–
56.7 (84)	1 (0.5)	4.3 (1.9)	25.1	7.47	0.391	2.52 ± 0.01 (63)	3.88 ± 0.02 (98)	3.20 ± 2.5	206 ± 36.5
54.9 (82)	2.5 (1.2)	4.2 (1.8)	30.7	26.1	0.279	2.50 ± 0.02 (63)	3.89 ± 0.01 (98)	3.66 ± 2.5	261 ± 57.6
53.0 (81)	4 (1.9)	4.0 (1.8)	35.3	17.1	0.326	2.43 ± 0.02 (61)	3.88 ± 0.02 (98)	3.18 ± 2.0	210 ± 31.8
51.7 (80)	5 (2.5)	3.9 (1.8)	59.4	12.8	0.398	2.38 ± 0.06 (60)	3.84 ± 0.06 (97)	3.40 ± 2.2	192 ± 27.2

methylcellulose[15] or polysaccharides like agar,[16] which gel at temperatures at or below 37 °C, have been incorporated into water-based feedstocks for injection molding. Feedstocks based on binders that require temperature-induced gelation must be heated to uniformly mix. Additionally, the injection molding operation itself requires heating of the feedstock to decrease viscosity to enter a mold cavity as well as cooling to solidify the part after forming. The binder must give ideal flow properties to a feedstock such that when heated or cooled allow for production of near-net shape parts without defects.[17] Consequently, binder selection as well as the careful control of feedstock temperatures during mixing and injection molding is critical to develop a novel suspension suitable for ceramic injection molding.[18]

The optimal rheology of a feedstock for injection molding is typically pseudoplastic, also referred to as shear thinning, or of a Bingham-type behavior, such that the feedstock does not flow at low shear stresses.[19,20] However, by taking advantage of the unique *yield*-pseudoplastic flow properties (i.e. being both shear thinning and having a yield stress[20]) of aqueous, highly loaded (>50 vol.%) ceramic suspensions with a minimal amount (<5 vol.%) of non-toxic, water-soluble polyvinylpyrrolidone (PVP), the aim of the present work was to develop an alternative aqueous, room-temperature processing method with lower environmental burden based on traditional injection molding to produce dense, near-net shape alumina components. Through control of the yield point and inherent shear-thinning rheological response of yield-pseudoplastic alumina suspensions by varying PVP content, this method eliminates the need for heating and cooling feedstocks to process as is required in conventional injection molding. Furthermore, high solid loadings often result in higher green and sintered densities.[21] Additionally, this method does not require complex in situ chemical reactions or temperature control as in other unconventional molding and casting methods.[15,22,23] This paper presents an alternative processing method that effectively produces near-net shape alumina parts without use of any harsh crosslinking or curing agents or further chemical processes. By utilizing the yield-pseudoplastic behavior of aqueous alumina-PVP suspensions dispersed with Darvan 821A, dense alumina specimens were prepared by injection molding at room temperature. PVP content in suspensions was varied to ascertain the optimal formulation that resulted in flow properties amenable to the fabrication of alumina specimens with suitable microstructural and mechanical properties by room-temperature injection molding.

2. Experimental procedure

2.1. Alumina-PVP suspension preparation

Alumina suspensions used in this study consisted of deionized (DI) water and A-16 SG alumina (Almatis, New Milford, CT) with BET surface area of 7.8 ± 0.22 m^2/g, determined using a TriStar 3000 gas adsorption analyzer (Micromeritics Instrument Corporation, Norcross, GA), and an average particle size of 0.48 ± 0.13 μm, found using a Beckman Coulter LS 230 particle size analyzer (Brea, CA). Darvan 821A (R.T. Vanderbilt Company, Inc., Norwalk, CT) was used as a dispersant. Darvan 821A is a low-toxic aqueous solution of 40% ammonium polyacrylate with a molecular weight of 3500 g/mol that is highly soluble in aqueous systems.[14,23,24] The polymer binder used was polyvinylpyrrolidone (PVP, 1-ethenyl-2-pyrrolidinone homopolymer, Sigma–Aldrich, St. Louis, MO) to modify the rheological properties of the suspension.

An aqueous slurry was prepared using DI water, dispersant and alumina powder by ball milling in Nalgene bottles with alumina milling media (U.S. Stoneware, East Palestine, OH) for 24 h. Alumina powder was incrementally added to a dispersant and DI water solution to obtain highly loaded, dispersed alumina slurries. A typical slurry contained 225 g of alumina powder in 37 mL of DI water and 5 mL dispersant. A polymer solution of PVP and DI water was mixed separately by magnetic stirring for 4–8 h. After both the slurry and polymer solution were dispersed, the PVP-water mixture was added to the alumina slurry and ball milled over a 12-h period. The amounts of PVP with molecular weight of 55,000 g/mol in suspensions evaluated were 1, 2.5, 4 and 5 vol.% to determine the optimal binder content that resulted in favorable forming and final sintered and mechanical properties. The compositions studied are highlighted in Table 1. Suspensions with 2.5 vol.% PVP with molecular weights of 10,000 g/mol, 360,000 g/mol and 1,300,000 g/mol (compositions listed in Table 2) were also prepared to evaluate the effect of molecular weight on the final properties of the samples.