



Room-temperature injection molding of aqueous alumina-polyvinylpyrrolidone suspensions

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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 $\sim 98\%$ 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.

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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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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 ₂ O ₃ powder content in vol.% (wt.%)	Polymer content in vol.% (wt.%)	Dispersant content in vol.% (wt.%)	σ_y (Pa)	k (Pa s ^{<i>n</i>})	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

methylcellulose¹⁵ 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 stress²⁰) 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 m²/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.

Table 2

Alumina suspension compositions with corresponding Herschel–Bulkley curve-fit parameters, average green and sintered densities and C-ring strength values for sintered samples prepared by room-temperature injection molding of suspensions with 2.5 vol.% PVP of varying molecular weights.

PVP molecular weight in g/mol	Al ₂ O ₃ powder content in vol.% (wt.%)	Polymer content in vol.% (wt.%)	Dispersant content in vol.% (wt.%)	σ_y (Pa)	k (Pa s ^{<i>n</i>})	n	Average green density in g/cm ³ (%TD)	Average sintered bulk density in g/cm ³ (%TD)	Average C-ring strength (MPa)
10,000	55.1 (83)	2.5 (1.2)	4.2 (1.8)	12.6	12.0	0.320	2.48 ± 0.04 (62)	3.88 ± 0.03 (98)	233 ± 73.8
55,000	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)	261 ± 57.6
360,000	53.9 (82)	2.5 (1.2)	4.1 (1.8)	52.7	8.48	0.510	2.41 ± 0.02 (60)	3.86 ± 0.04 (97)	246 ± 59.8
1,300,000	52.4 (81)	2.5 (1.2)	4.0 (1.8)	56.8	4.92	0.621	2.36 ± 0.03 (59)	3.78 ± 0.05 (95)	–

2.2. Room-temperature injection molding procedure, binder burnout and pressureless sintering

Because commercially available ceramic injection molding machines traditionally use heating and cooling processes throughout the forming procedure, a novel room-temperature injection molding apparatus was constructed. The mold cavity was specifically designed to produce a part that would be amenable to characterization, matching ASTM C1323-10 for the determination of the ultimate strength of compressively loaded ceramic C-ring specimens.²⁵ By fabricating a ceramic ring rather than a simpler, more common geometry, like a bar, the process was developed to overcome complications that were inherent to the production of ring-shaped parts, such as convergent flow effects during filling that resulted in potential pore or defect formation in addition to the development of hoop stresses during solidification and drying that caused cracks in specimens.⁵ A mold was made to fabricate a ceramic ring-shaped green body with a 2.54-cm outer diameter, 1.5875-cm inner diameter and a width of 6.35 mm (refer to Fig. 1), and three ports out of which

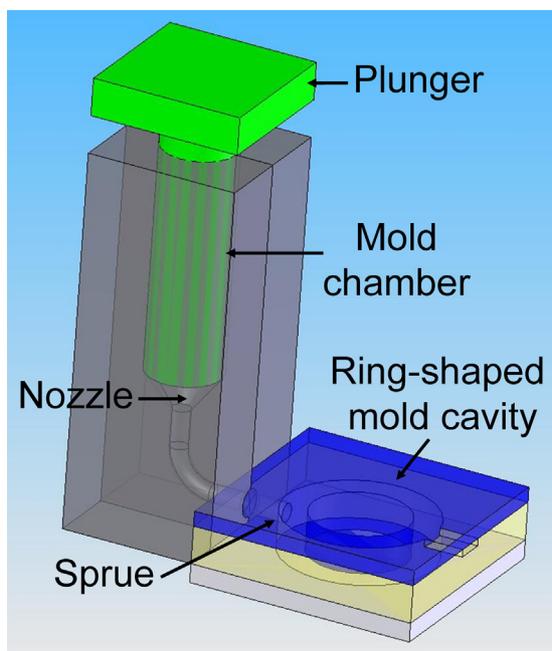


Fig. 1. Schematic of room-temperature injection mold device.

extra material could flow during filling (shown in Fig. 2a). The bottom plate and outer ring support with injection port were machined from steel. A cylindrical rod with a diameter and height of a 6.35 mm was inserted in the center of the bottom plate, and a 6.35-mm section of EPDM (ethylene propylene diene monomer) closed-cell foam rubber tube with a firmness of ~5–9 psi and outer diameter of 1.5875 cm and inner diameter of 6.35 mm (McMaster-Carr, Elmhurst, IL) was placed on the rod. The top plate was machined from transparent Plexiglas. A low-friction Teflon tape (McMaster-Carr, Elmhurst, IL) and Grade 40 ashless filter paper (Whatman, UK) were adhered to the top and bottom steel plates of the ring-shaped die that came in contact with the ceramic-PVP suspension during filling to facilitate more rapid demolding and cleaning of molds. The top and bottom plates were then fitted above and below the outer ring support, respectively, using screws to secure the plates together to create the mold cavity. The mold cavity was then attached to the suspension chamber with a 3.175-mm-diameter rubber O-ring fixed between the two to ensure a tight seal, resulting in a 3.175-mm-diameter sprue, through which the suspension entered the mold cavity from the suspension chamber.

Liquid Wrench L312 Teflon spray (Indian Trail, NC) was used to lubricate the inner surfaces of the mold cavity and chamber prior to suspension loading to facilitate the removal of a formed part from the mold. The injection mold chamber was loaded with 5 mL of the alumina-PVP suspension using a 6-mL luer-slip syringe (VWR, Radnor, PA). The cylindrical 1.27-cm diameter steel pushrod was inserted into the cylindrical chamber with diameter of 1.27 cm, and the entire mold apparatus was placed between compression platens in an electromechanical test frame (MTS Insight 100 load frame, MTS Systems Corporation, Eden Prairie, MN), as shown in Fig. 2b.

A compression force at a crosshead speed of 100 mm/min was transferred to a 1.27-cm diameter ball bearing sitting atop the pushrod to ensure that the load was uniformly applied to the pushrod. This force, applied at a constant rate on the pushrod, exerted the pressure needed to overcome the yield point of a yield-pseudoplastic suspension, causing it to flow and fill the ring-shaped mold cavity. As a result, an alumina ring was produced. A VM-25 miniature air piston vibrator (Cleveland Vibrator Co., Cleveland, OH) was attached to the mold using cable ties. The pneumatic vibrator had a frequency of 16,000 vibrations per minute at 80 psi and was initiated immediately prior to filling for the duration of the injection molding process.

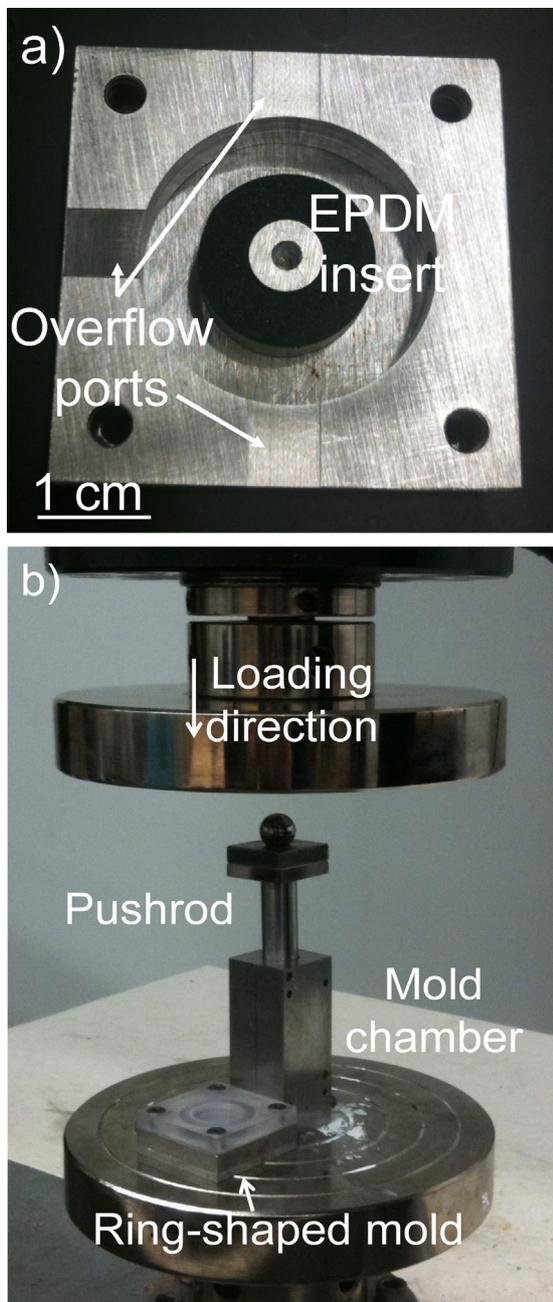


Fig. 2. (a) Ring-shaped mold with EPDM foam centerpiece and three escape ports across and to the left and right of the injection site. (b) The injection mold setup between two compression platens of the load frame prior to the injection molding operation. A pneumatic vibrator with dimensions of 5.5 cm × 1.6 cm × 2.3 cm was fixed on top of the ring-shaped mold using cable ties (not pictured) during forming.

When activated the vibration appeared to assist in the filling of the mold by preventing closed pore formation due to air bubbles. The injection mold setup is highlighted in Fig. 2b. After forming, a part was allowed to dry at ambient conditions for 1 h prior to removal from the mold.

The binder burnout cycle for formed alumina-PVP samples was determined by thermogravimetric differential thermal analysis (SDT 2960 Simultaneous TG-DTA instrument, TA Instruments, New Castle, DE) of PVP, which indicated

significant weight loss beginning at 325 °C and ending at 480 °C. Removal of the binder from the formed samples was accomplished using a Sola Basic Lindberg/Blue Tube Furnace (Ashville, NC) at a heating rate of 2 °C/min to 700 °C with an isothermal hold of 1 h followed by cooling to room temperature. The sample was then transferred to a Thermo Scientific Lindberg/Blue M 1700 °C Box Furnace (Ashville, NC) for pressureless sintering, heating at a rate of 5 °C/min to 1620 °C with a 1.5-h hold to densify the alumina ring.

2.3. Characterization

A TA Instruments ARG2 rheometer (New Castle, DE) with a 40-mm parallel-plate geometry and a gap of 500 μm was used to characterize the rheological responses of suspensions with varying PVP contents at 25 °C. A moisture trap was also employed during testing to avoid temperature differences and premature drying of the suspension while testing. By considering the sprue diameter of 3.175 mm and the applied compression rate of 100 mm/min used for room-temperature injection molding, the shear rate applied to alumina-PVP suspensions during forming was determined to be 4.20 s⁻¹. The calculated shear rate is significantly lower than that of traditional injection molding, which can be on the order of 100–1000 s⁻¹.³ Consequently, flow curves up to a maximum shear rate of 100 s⁻¹ were obtained to quantify the low-shear rheological behavior of the alumina-PVP suspensions utilized in this study. Flow curves were fitted to the Herschel–Bulkley model for yield-pseudoplastic fluids,²⁰ which was defined as:

$$\sigma = \sigma_y + k\dot{\gamma}^n \quad (1)$$

where σ was stress, σ_y represented the shear yield stress, $\dot{\gamma}$ was the shear rate applied to the material, the consistency or apparent viscosity was k and flow index of the material was n , which varied from 0 to 1. Flow behavior was considered yield pseudoplastic when a suspension demonstrated a yield stress and $n < 1$.²⁰ The yield stress of each suspension evaluated was found by extrapolating its curve fit to the axis limits, and the correlation factor, R , of fitting the curve parameters to Eq. (1) was always ~0.99. The pH of each suspension was determined using an Oakton PH5 meter (Vernon Hills, IL).

After a ring-shaped alumina part was formed via injection molding, it was then machined before binder removal to chamfer the outer edges and ensure sample surfaces were sufficiently parallel in accordance with the ASTM C1323-10 C-ring test²⁵ using a polishing wheel with 320, 400 and 600 grit silicon carbide grinding cloth (LECO 810-265/269-PRM). To qualitatively assess the green machinability of parts formed prior to binder burnout, a custom steel polishing mount with micrometer was machined to the exact dimensions of the alumina ring-shaped part such that every specimen polished experienced identical machining conditions. Each sample was inserted into the mount and polished using silicon carbide polishing papers of 320, 400 and 600 grit for 30 s on each paper in increasing order at ~200 rotations per minute (RPM). The effect of machining in the state prior to binder removal was qualitatively observed by examining

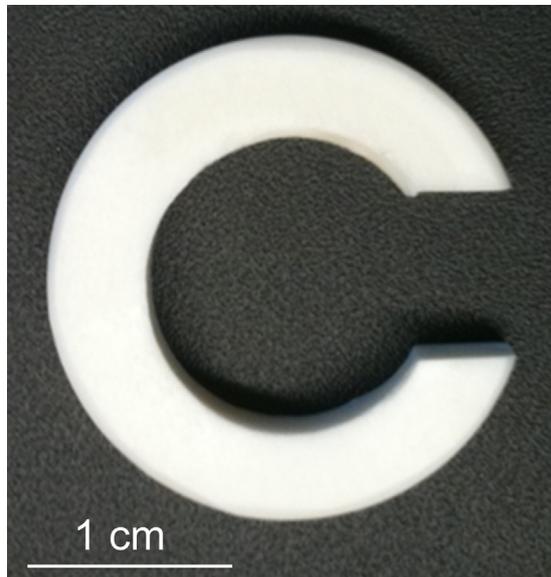


Fig. 3. Final sintered alumina specimen after machining.

the final surface finish of each sample for fracture, cracking or chipping after polishing.

Density of the alumina parts before and after sintering was measured using the Archimedes technique. Microstructural analysis was performed using an FEI Philips XL-40 scanning electron microscope (SEM) to examine sintered, polished and thermally etched (1400 °C, 1-h hold) samples. The average grain size was determined by evaluating five SEM micrographs for a particular sample composition and measuring the length of 50 arbitrary grains in each image using ImageJ image processing and analysis software. A total of 250 line segments representing 250 different grain lengths were averaged to obtain a mean grain size for each composition. A slow-speed saw with a diamond blade (Leco Corporation, St. Joseph, MI) was used to cut a notch in the densified specimens resulting in the desired C-shape for mechanical testing (refer to Fig. 3). If the heat treatments resulted in warping of the ring-shaped sample, it was placed on a mandrel with adjustable diameter and then machined using a diamond-tipped blade (McMaster-Carr, Elmhurst, IL) on a rotating lathe to ensure outer surfaces were parallel for mechanical testing. Each C-ring specimen was positioned between two MTS platens of an electromechanical test frame as highlighted in Fig. 4 and compressively loaded until fracture in accordance with ASTM C1323-10²⁵ to determine ultimate strength of the specimens. The maximum engineering tangential (hoop) stress, $\sigma_{\theta max}$, which occurred on the outer edge of the specimen as indicated in Fig. 4, was calculated by utilizing the maximum compressive load, P , applied by platens of the electromechanical test frame initiating fracture. At least six samples were tested to obtain an average C-ring strength for a given suspension composition. The ASTM C1323-10 mechanical characterization method is particularly sensitive to external surface flaws as it causes maximum tension at the outer surface of the specimen.²⁵ After mechanical testing fractographic analysis was performed following the procedure outlined in ASTM C1322-05b²⁶ to

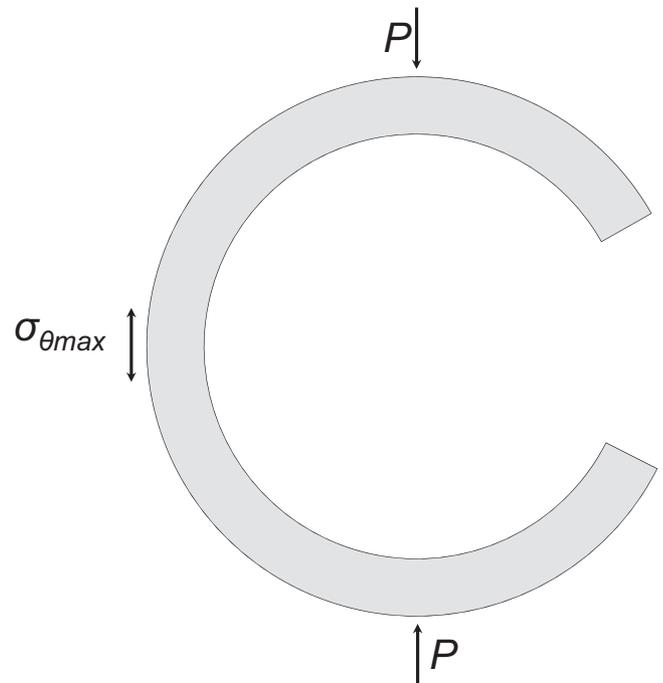


Fig. 4. Schematic of C-ring specimen during loading for the determination of ultimate strength using ASTM C1323-10 (modified from standard²⁵). P represents the maximum compressive load applied by platens of an electromechanical test frame during testing, and $\sigma_{\theta max}$ is the engineering tangential (hoop) stress.

evaluate the angle and origin of fracture for each specimen using an Olympus SZX7 Zoom Stereo Microscope.

A two-tailed t -test²⁷ was applied to compare the means of the densities, grain sizes and mechanical strengths for varying PVP content to determine if data sets were statistically different. To infer whether a Student's t -test for samples with equal variance (homoscedastic) or a Cochran's t -test for samples with unequal variance (heteroscedastic) should be applied, an F -test was used to calculate the ratio, F_0 , of the two variances. Two data sets were considered homoscedastic when the value of F_0 fell between the upper- and lower-tail percentage points, $F_{0.05, u, v}$ and $F_{0.95, u, v}$, respectively, with u and v being the degrees of freedom, and heteroscedastic when $F_0 > F_{0.05, u, v}$ or $F_0 < F_{0.95, u, v}$.²⁷ The p -values calculated from either the Student's or Cochran's t -tests using the Excel function, $TTEST$, were considered to be statistically different when $p < 0.05$.²⁷

3. Results and discussion

3.1. Rheological behavior and processability of alumina suspensions with varying PVP content

Flow curves of alumina-PVP suspensions prepared with ~4 vol.% Darvan 821A for polymer contents of 0, 1, 2.5, 4 and 5 vol.% PVP (MW = 55,000 g/mol) with powder loadings of 57.9, 56.7, 54.9, 53.0 and 51.7 vol.% alumina, respectively, suggested that suspensions behave as yield-pseudoplastic fluids regardless of PVP or powder content with curve fit parameters to the Herschel–Bulkley model listed in Table 1. An increase in yield strength, which often indicates flocculation within a

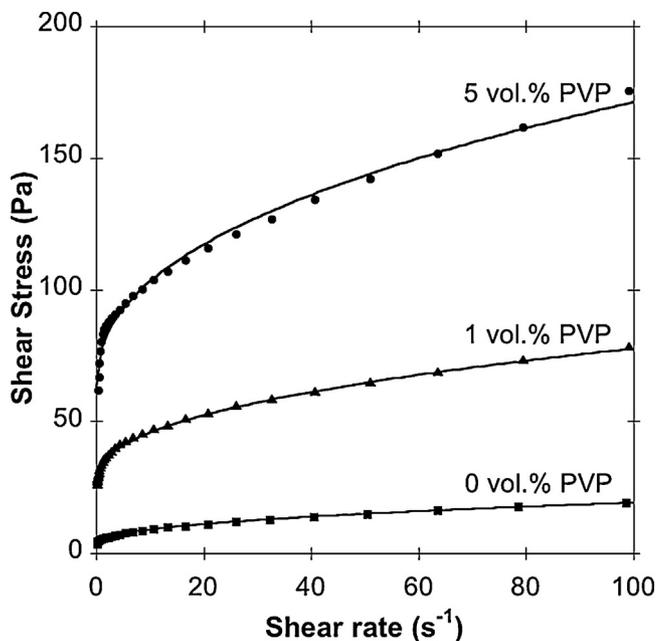


Fig. 5. Flow curves of alumina suspensions with 0, 1 and 5 vol.% PVP (MW = 55,000 g/mol). Curve fits to the Herschel–Bulkley fluid model are shown as black continuous lines with $R > 0.99$.

suspension, would be expected with an increase in overall solids content.^{27,28} Because both PVP and powder contents were varied simultaneously in this study, the marked difference in flow properties could not be simply attributed to the amount of PVP or powder incorporated into a suspension. The 0 vol.% PVP suspension, which had the highest solids loading, had a yield point of 4.57 Pa, and laboratory observations indicated it flowed due to gravitational forces. Fig. 5 shows the flow curves for 0, 1 and 5 vol.% PVP compositions with corresponding curve fits to the Herschel–Bulkley model (correlation factor, $R > 0.99$). With increasing PVP and decreasing powder contents, an increase in yield shear stress, σ_y , was observed. The suspension without polymer had the lowest yield point observed in this study, suggesting that PVP, even in small amounts, greatly affected the rheology of the suspensions examined for room-temperature injection molding.

During forming the yield point of suspensions without PVP was observed to be too low, as suspensions flowed into the mold before pressure was applied to the suspension via the load frame. This suggested that the rate at which the suspensions entered the mold could not be adequately controlled, resulting in unpredictable flow patterns that could cause defects in formed specimens, thus, making suspensions without PVP undesirable for room-temperature injection molding. With the introduction of a small amount of polymer, all suspensions containing PVP exhibited a yield shear stress high enough that suspensions did not flow prematurely into the mold cavity until after pressure was initiated using the load frame. Additionally, after the suspension completely filled the mold and pressure was removed, the suspension did not flow allowing the suspension to retain its shape during drying, confirming that PVP was necessary to control the flow properties of alumina suspensions for room-temperature injection molding.

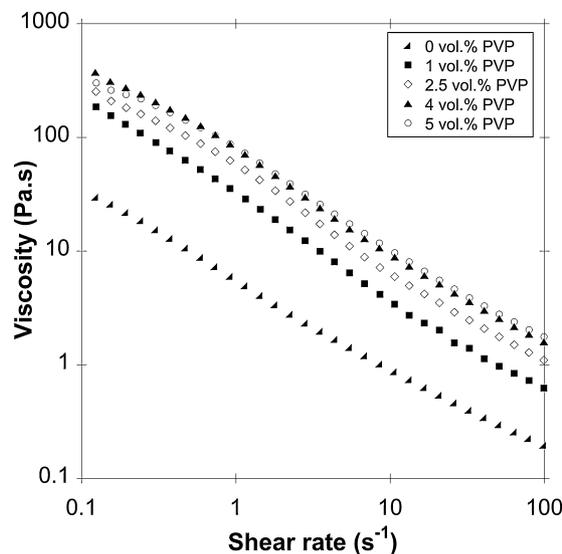


Fig. 6. Log viscosity against log shear rate plots of alumina suspensions prepared with varying contents of PVP with molecular weight of 55,000 g/mol. Increasing PVP content resulted in higher apparent viscosities of suspensions.

Although yield point increased with PVP content, the change in consistency, k , and flow index, n , exhibited a more complex relationship with PVP content. Consistency increased until a peak value of 26.1 Pa s^n was attained at a PVP concentration of 2.5 vol.% and then began to decrease with increasing PVP content. All flow indices indicated that suspensions were highly shear thinning regardless of PVP content. A maximum flow index of 0.408 was observed for suspensions containing no polymer, and n decreased until a minimum value of 0.279 was observed for 2.5 vol.%, suggesting that this composition was the most shear thinning. The flow index then began to increase once again at PVP contents > 2.5 vol.%. A highly shear-thinning response was most desirable as a relatively low viscosity aided in the complete filling of the mold and minimized pore formation by allowing entrained air bubbles to be ejected from the suspension more readily during injection molding with the pneumatic vibrator, thus enhancing processability. Fig. 6 shows a comparison of the apparent viscosity at different shear rates of all suspensions examined in this study. It was observed that viscosity also increased with increasing polymer content, while decreasing at higher shear rates for all formulations examined due to the pseudoplastic nature of the suspensions evaluated.

The pH of suspensions with varying PVP content changed negligibly and was 9.6 ± 0.05 , which was above the isoelectric point (IEP) of alumina in water. It has been observed that the surface charge of PVP is effectively neutral such that it does not alter the IEP of alumina-water suspensions.²⁹ The rheological results matched the findings of a previous study,³⁰ which examined alumina-PVP suspensions with a Dolapix CE64 dispersant. This past study³⁰ surmised that neutral PVP introduced a small amount of flocculation, because yield stress was indicative of flocculation within a suspension.³¹ By increasing polymer content or molecular weight, this weak flocculation could be enhanced, manifesting itself as an increase in yield stress. This manipulability allows for the careful control and engineering

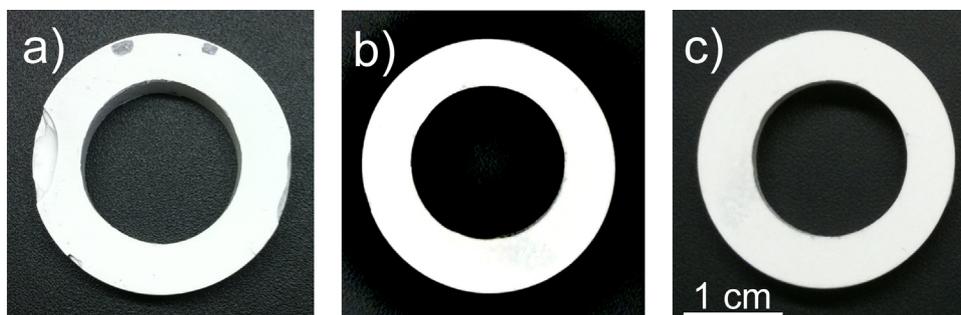


Fig. 7. Images of alumina parts with (a) 1, (b) 2.5 and (c) 5 vol.% PVP content after machining in the green state using a polishing mount. Samples with less than 2.5 vol.% PVP chipped during machining suggesting a lower green strength when compared with samples with higher binder content.

of the flow properties of suspensions with minimal amounts of polymer to tailor suspensions to a variety forming applications. To determine the ideal properties of suspensions for room-temperature injection molding, a variety of characterization methods were utilized to find the optimal compositions that yielded dense, strong alumina parts.

3.2. Green machinability and density of alumina components

Ring-shaped specimens were successfully prepared by room-temperature injection molding, suggesting that hoop stresses that developed during drying were minimized, making this a near-net shape drying process. Although sections of the specimen remained in contact with the mold during drying, no cracking due to drying gradients was observed, suggesting that capillary forces during drying did not cause defects. Prior to binder removal alumina green bodies produced by room-temperature injection molding of ceramic-PVP suspensions with varying polymer amount were deemed machinable such that the samples did not crack or shatter during the polishing procedure. It was observed that increasing binder content enhanced the machinability of the green bodies. As highlighted in Fig. 7, green bodies formed using suspensions with ≥ 2.5 vol.% PVP exhibited little chipping or cracking compared to samples made with suspensions consisting of 1 vol.% PVP. Samples prepared with 0 vol.% PVP often did not have enough structural integrity to be removed from the mold after forming and broke either during mold removal or polishing. It was concluded that samples without PVP were too fragile to be machined in the green state using the polishing wheel and mount. Suspensions with PVP contents of 2.5, 4 and 5 vol.% were less brittle and thus less likely to chip or crack during machining using the polishing mount, suggesting that parts made using these compositions could be polished in an automated process. Note that while the 1 vol.% PVP suspensions could not be polished using the polishing mount without introducing defects, it could be polished by hand. This method was used to prepare 1 vol.% PVP suspensions for mechanical testing.

Table 1 highlights the green density values of specimens prepared with suspensions containing varying PVP contents after binder removal. Alumina samples made by room-temperature injection molding exhibited green densities $>60\%$ of the true

density ($TD = 3.98 \text{ g/cm}^3$) of alumina regardless of initial PVP content. Specimens prepared with 0 vol.% PVP exhibited the highest green density of 2.56 g/cm^3 (64%TD). Of the specimens prepared with polymer-containing suspensions, those consisting of 1 and 2.5 vol.% PVP were statistically the same ($p = 0.26$) with $2.52 \pm 0.01 \text{ g/cm}^3$ (63%TD) and $2.50 \pm 0.02 \text{ g/cm}^3$ (63%TD), respectively, and exhibited statistically higher green densities than 4 and 5 vol.% PVP. The green density p -values for specimens prepared with 1 vol.% PVP when compared with 4 and 5 vol.% PVP suspensions were $p_{1 \text{ vol.}\%, 4 \text{ vol.}\%} = 7.3 \times 10^{-3}$ and $p_{1 \text{ vol.}\%, 5 \text{ vol.}\%} = 0.0041$, respectively, and for specimens initially containing 2.5 vol.% PVP compared with 4 and 5 vol.% PVP suspensions were $p_{2.5 \text{ vol.}\%, 4 \text{ vol.}\%} = 0.00042$ and $p_{2.5 \text{ vol.}\%, 5 \text{ vol.}\%} = 0.005$, respectively. These p -values were less than 0.05 suggesting that the green density data sets were statistically different, whereas specimens prepared with 4 and 5 vol.% PVP suspensions were statistically similar ($p_{4 \text{ vol.}\%, 5 \text{ vol.}\%} = 0.10$). Overall, parts formed by room-temperature injection molding using suspensions with PVP were successfully machined and sintered into the desired C-shaped part in accordance with the ASTM standard as highlighted in Fig. 3.

3.3. Sintered density and microstructure

Archimedes density analysis confirmed that samples reached $\sim 98\%$ TD regardless of initial PVP content after binder burnout and pressureless sintering. Specimens prepared without PVP exhibited statistically higher sintered density values. Although the density of samples prepared with suspensions using 5 vol.% PVP appeared to decrease, the density values were determined to be statistically similar to samples using other compositions with lower PVP contents. This suggested that polymer content did not dramatically influence the final density and internal porosity of the ceramic part. Density results are highlighted in Table 1. Linear shrinkage for all samples after sintering was $<16\%$.

Analysis of the internal structure using SEM revealed an overall dense microstructure with some porosity between and within grains (micrographs of samples prepared with 1, 2.5, 4 and 5 vol.% PVP are shown in Fig. 8). By applying a t -test,²⁷ the mean grain size of specimens prepared with 2.5 vol.% PVP was determined to be statistically larger than those containing 1 and 4 vol.% PVP as $p < 0.05$ ($p_{1 \text{ vol.}\%, 2.5 \text{ vol.}\%} = 0.043$ and

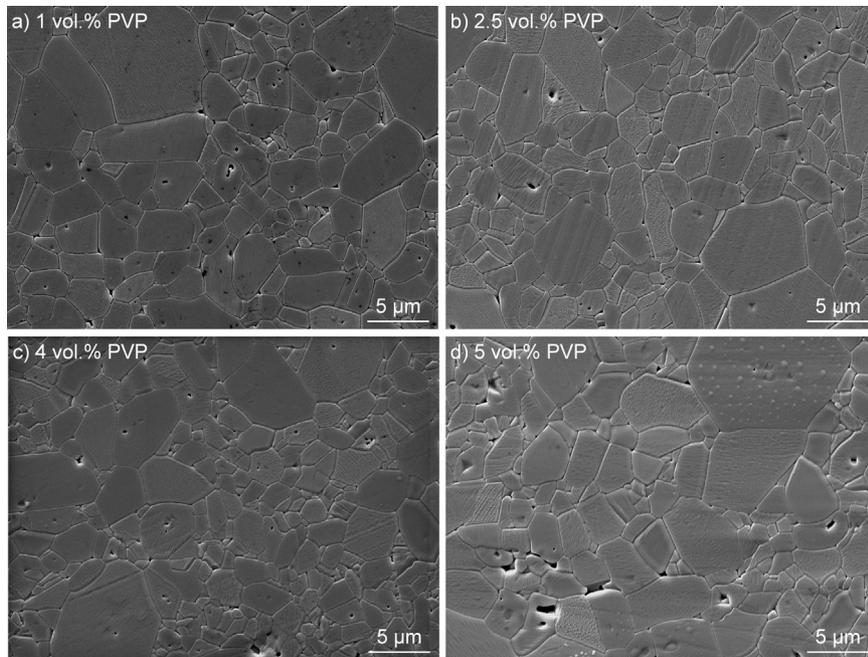


Fig. 8. SEM micrographs of polished and thermally etched surfaces of alumina samples prepared with suspensions containing (a) 1 vol.% PVP, (b) 2.5 vol.% PVP, (c) 4 vol.% PVP and (d) 5 vol.% PVP. All samples were sintered at 1620 °C.

$p_{2.5 \text{ vol.}\%, 4 \text{ vol.}\%} = 0.019$) yet similar to specimens using 5 vol.% PVP ($p_{1 \text{ vol.}\%, 5 \text{ vol.}\%} = 0.22$), which was similar to all compositions evaluated. Mean grain sizes of specimens manufactured using suspensions with different PVP contents are highlighted in Table 1. The slight discrepancies in values suggested that there was no apparent trend with PVP content that resulted in a particular grain size, although 2.5 vol.% yielded slightly higher grain sizes than 1 and 4 vol.% PVP suspensions.

3.4. Mechanical properties

Average C-ring strength values that were determined using the ASTM C1323-10 test²⁵ for samples fabricated using alumina suspensions with 1, 2.5, 4 and 5 vol.% PVP are shown in Table 1 and plotted in Fig. 9. Despite the fact that specimens of 2.5 vol.% PVP had a mean grain size that was statistically similar to those with 5 vol.% PVP and higher than specimens of 1 and 4 vol.%, there was a statistically significant peak of 261 ± 57.6 MPa in strength for 2.5 vol.% PVP content ($p_{1 \text{ vol.}\%, 2.5 \text{ vol.}\%} = 0.04$, $p_{2.5 \text{ vol.}\%, 4 \text{ vol.}\%} = 0.036$ and $p_{2.5 \text{ vol.}\%, 5 \text{ vol.}\%} = 0.024$). Samples with 5 vol.% PVP exhibited a significant drop in average C-ring strength, though the values were found to be statistically similar to the strengths of samples prepared with 1 and 4 vol.% PVP suspensions. When comparing the values from this study to those in literature, an average C-strength value was found to be 230 MPa for commercially available surface-finished 99.8% pure alumina tubular specimens³² and 275.3 ± 16.6 MPa for tubular gun barrel specimens prepared using 95% pure alumina AD995 by CoorsTek.³³ The method of preparation for these tubular specimens is unknown due to proprietary information, but the density and C-strength values obtained by room-temperature injection molding of alumina-polymer suspensions is comparable.

The ASTM C1323-10 test is prone to causing fracture at defects located at the outer surface of specimens.²⁵ The increase in strength for specimens prepared using 2.5 vol.% PVP suggested that the distribution and size of pores within these samples, not the size of grains, minimized their influence on failure resulting in higher C-strength values. Fractographic analysis revealed that the majority of fractures originated at pores on or near the outer surface of C-rings regardless of PVP content, intimating that the amount of PVP in a suspension affected the overall arrangement and/or size of strength-limiting pores that

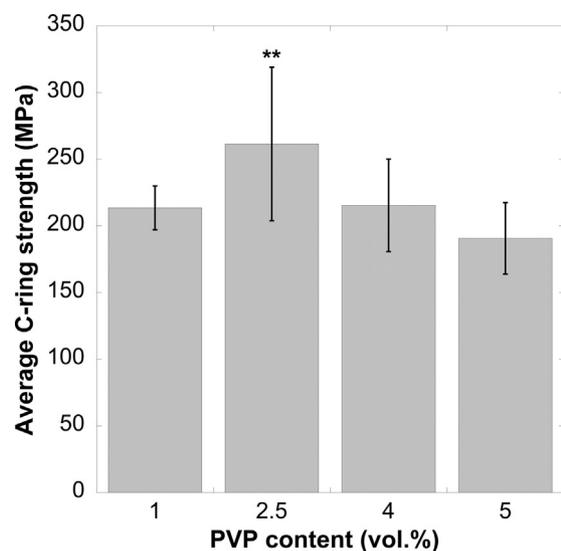


Fig. 9. Plot of average C-ring strength data for sintered specimens prepared with suspensions containing 1, 2.5, 4 and 5 vol.% PVP (MW = 55,000 g/mol). Specimens of 2.5 vol.% PVP exhibited the highest average C-strength. ***p*-Values for specimens prepared with 2.5 vol.% PVP were less than 0.05 indicating a statistically significant peak in strength for these specimens.

resulted in fracture at lower loads for samples prepared with 1, 4 and 5 vol.% PVP suspensions. The favorable mechanical and microstructural properties of specimens prepared with 2.5 vol.% PVP implied that the flow behavior of such suspensions, including the relatively low viscosity and flow index, which allowed the suspension to fill the mold and minimize strength-limiting defect development, was ideal for processing by room-temperature injection molding. In spite of this conclusion, the large standard deviation in all samples, particularly samples prepared with 2.5 vol.% PVP, suggest that further processing improvements are needed to tighten this distribution and improve the reproducibility of dense, high-strength alumina parts with uniform microstructures.

3.5. Varying molecular weight at optimal PVP concentration

The desirable flow properties and apparent peak in strength along with relatively high green and sintered densities suggested that 2.5 vol.% PVP was the optimal concentration of polymer to use in the alumina suspensions for room-temperature injection molding. Three additional suspensions using PVP with molecular weights of 10,000, 360,000 and 1,300,000 g/mol with alumina contents of 55.1 vol.%, 53.9 vol.% and 52.4 vol.%, respectively, were evaluated to determine the effect of molecular weight on the rheological behavior of the suspensions as well as on microstructural and mechanical properties of samples fabricated by room-temperature injection molding.

The formulations of the alumina-PVP suspensions prepared using 2.5 vol.% PVP with molecular weights of 10,000, 55,000, 360,000 and 1,300,000 g/mol are given in Table 2. Each composition exhibited yield-pseudoplastic behavior (refer to Table 2 for the Herschel–Bulkley model curve fit parameters) similar to that of suspensions prepared with varying contents of 55,000 g/mol PVP. It was observed that the yield points in suspensions increased with increasing molecular weight and decreasing powder content, while consistency values and flow indices varied with increasing molecular weight. Suspensions with 10,000 g/mol PVP exhibited the lowest yield stress of suspensions containing polymer, whereas the yield stress of formulations having PVP molecular weights $\geq 360,000$ g/mol jumped significantly to >50 Pa, only surpassed in magnitude by suspensions with 5 vol.% PVP of 55,000 g/mol, which had $\sigma_y = 59.4$ Pa. Although consistency increased from 12.0 Pa s^n at 10,000 g/mol to 26.1 Pa s^n for 55,000 g/mol, it then decreased in value from 8.48 Pa s^n to 4.92 Pa s^n for 360,000 g/mol and 1,300,000 g/mol, respectively. Shear-thinning behavior was reflected by all flow indices, and n decreased in value from 0.320 for 10,000 g/mol until reaching a minimum value of 0.279 at a molecular weight of 55,000 g/mol. Above 55,000 g/mol n increased significantly, and the maximum value was observed in suspensions containing 1,300,000 g/mol. Most notably, compositions including PVP with a molecular weight of 1,300,000 g/mol exhibited the lowest consistency value and the highest flow index of 0.621, which implied that they were the least shear thinning of all PVP-containing suspensions studied. Furthermore, the suspensions with 2.5 vol.% PVP

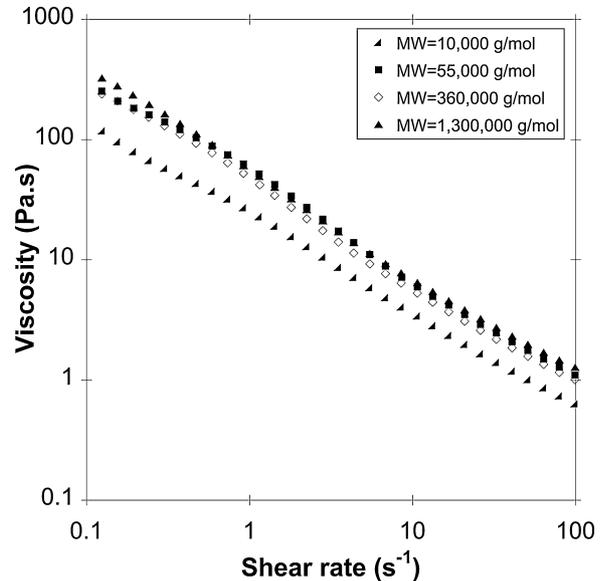


Fig. 10. Plots of log viscosity vs. log shear rate of alumina suspensions prepared with 2.5 vol.% PVP of varying molecular weights.

of 55,000 g/mol had the highest consistency and lowest flow index, making it the most shear thinning of the suspensions.

Fig. 10 shows a comparison of the apparent viscosity at different shear rates of all suspensions containing 2.5 vol.% PVP with varying molecular weights examined in this study. Although suspensions with 10,000 g/mol PVP exhibited the lowest apparent viscosity, the overall apparent viscosities for suspensions with PVP of 55,000 g/mol, 360,000 g/mol and 1,300,000 g/mol were comparable, as highlighted in Fig. 10. Due to the order of magnitude increase in molecular weight, suspensions with 1,300,000 g/mol were expected to have a significantly higher viscosity, but they were observed to have only a slightly higher viscosity than suspensions prepared with 55,000 g/mol and 360,000 g/mol over the shear rates evaluated. This slight increase in viscosity could potentially be attributed to the decrease in alumina content in suspensions prepared with PVP of higher molecular weights, but further analysis of suspensions at constant powder loadings would be needed to isolate the main factor.

The low yield point and apparent viscosity made suspensions containing 10,000 g/mol PVP more difficult to control during injection molding, though samples were successfully fabricated for testing. On the other hand, the slightly higher viscosity of suspensions with 1,300,000 g/mol PVP impacted processability by preventing fabrication of alumina samples without large macroscopic defects. These defects likely resulted from air bubbles developing and becoming trapped within suspensions during forming due to the lower degree of pseudoplasticity and the slightly higher apparent viscosity of suspensions with 1,300,000 g/mol PVP. Consequently, parts for mechanical characterization could not be prepared with this high of a molecular weight. Additionally, the specimens exhibited low green and sintered densities when compared with specimens prepared using PVP with lower molecular weights. The inferior microstructural properties that plagued specimens prepared with 1,300,000 g/mol PVP were likely the result of the improper flow

characteristics of these suspensions, suggesting that this molecular weight was not suitable for room-temperature processing.

Alumina parts prepared using 10,000 g/mol and 360,000 g/mol PVPs were machinable prior to binder removal. These samples exhibited green densities comparable to those made using 55,000 g/mol PVP, even though the lower molecular weight yielded the highest green densities (refer to Table 2). Green bodies with 10,000 g/mol and 55,000 g/mol had green densities that were statistically similar ($p=0.26$) and statistically higher than samples with 360,000 g/mol and 1,300,000 g/mol ($p<0.05$). After binder removal and pressureless sintering, densities of $\sim 98\%$ TD were attained for specimens prepared with 10,000 g/mol, 55,000 g/mol and 360,000 g/mol (density values highlighted in Table 2). Specimens using 1,300,000 g/mol had a statistically lower density of 3.78 g/cm^3 (95%TD).

There appeared to be a notable difference in C-ring strengths of samples with 10,000 g/mol having lower values than those produced with 360,000 g/mol (values shown in Table 2), but statistical analysis revealed that mechanical properties were comparable (all $p>0.05$). The C-strength values were statistically similar to all samples prepared with varying amounts of 55,000 g/mol PVP. Despite the similar mechanical properties, the highly shear-thinning flow behavior needed for room-temperature processing as well as high green and sintered densities distinguished suspensions containing 2.5 vol.% PVP with a molecular weight of 55,000 g/mol from all other suspensions examined in this study as the optimal PVP molecular weight and concentration to be incorporated into alumina suspensions for room-temperature injection molding.

4. Summary and conclusions

A novel, environmentally benign room-temperature injection molding method has been developed and successfully applied to an alumina system. Through careful control of high ceramic powder loadings and a minimal amount of polymer additives, the viscosity of an alumina-PVP suspension was optimized to afford room-temperature injection molding of dense, near-net shaped alumina ring-shaped parts. Analysis of the flow properties suggested that the suspensions exhibited yield pseudoplasticity, which was ideal for room-temperature injection molding. Consistent with a previous investigation,³⁰ PVP was a neutral species at the pHs of suspensions studied here, and it likely induced a controlled degree of weak flocculation with varying PVP content, making these suspensions tailorable to the room-temperature processing method examined in this study. Because powder content was varied simultaneously with PVP content and molecular weight, further study of the rheological behavior of suspensions with constant powder loadings is needed to fully ascertain whether the amount and/or molecular weight of PVP is the main factor in obtaining specimens with desirable properties as well as suspensions with suitable rheology for room-temperature injection molding.

After preparing an alumina part by room-temperature injection molding, specimens were dried for roughly an hour in air and then removed from the mold. In traditional ceramic injection

molding, parts are typically ejected from a mold within the first minute of forming.² To reduce drying times of specimens prepared by room-temperature injection molding, modifying the current process, for example by utilizing a more porous mold material to facilitate evaporation, will be required to promote more rapid demolding times. The polymer binder in dried specimens, which were machinable in the green state, was effectively removed by thermal pyrolysis, resulting in parts with high green densities ($>60\%$ TD). High sintered densities (98%TD) were achieved by pressureless sintering, and SEM micrographs confirmed that sintered samples had an overall dense microstructure. Minimal shrinkage ($<16\%$ linear) of samples was observed. Alumina specimens with mechanical properties comparable to literature were successfully fabricated by this unique room-temperature processing method.

Suspensions containing 2.5 vol.% PVP (MW = 55,000 g/mol) resulted in the most favorable combination of properties in formed alumina specimens. The suspensions exhibited a yield shear stress such that suspensions did not flow under gravitational stresses, thus preventing premature filling of the mold and providing for a higher degree of control of the flow during forming. Additionally, suspensions with 2.5 vol.% PVP (MW = 55,000 g/mol) had the lowest flow index observed in this study, suggesting that the rheology was most suitable for the production of alumina samples with relatively high green and sintered densities along with high C-strengths via room-temperature injection molding. As a result, 2.5 vol.% PVP with molecular weight of 55,000 g/mol was considered the optimal concentration and type of polymer in the suspensions prepared and processed in this study. Further development of injection molding alumina-PVP suspensions at room temperature will ultimately allow for faster and less expensive fabrication of near-net shape ceramic parts with complex geometries through this unique green injection molding process.

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