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Effect of Rheological Properties of Zircon-Alumina Suspensions on Density of Green Casts

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Rheological properties of aqueous suspensions (48 vol%) of zircon-alumina mixtures containing different amounts of polyelectrolyte as dispersant were studied. Slip casting in a plaster mold and pressure filtration at 8 MPa experiments were performed to correlate the rheological properties of the suspensions with the relative density of green casts. Flow curves fitted satisfactorily to the Casson model. The Casson viscosity values remained nearly constant whereas Casson yield stress parameter decreased to a minimum and then increased with increasing the amount of dispersant added. The influence of particle size distribution (PSD) of the powder mixtures on Casson yield stress parameter and on the minimum viscosity was also examined. Green densities increased as yield stress Casson parameter decreased. The mixture of alumina and zircon as fine and coarse powders produced bimodal PSD which maximized the green density of the compacts. Some weakly flocculated suspensions having low apparent viscosity and small yield stress produced casts with relatively high densification. This is attributed to a slight higher viscosity at low shear rates of these suspensions in which settling of particles and /or segregation of components can not occur.

Keywords: *zircon, alumina, rheology, slip casting, pressure filtration*

1. Introduction

Reaction sintering of alumina and zircon is a common route to obtain a mullite-zirconia composite. Several studies showed that materials composed of mullite and zirconia may be obtained using alumina and zircon powders by the traditional method that consisted in: premix milling, dry-pressing operations to produce the compacts and sintering. However, as the mean diameter of these powders was large, the achieved density was relatively low[1]. To improve sinterability very fine powders must be chosen as densification must occur before mullitization[2].

A high solid concentration of fine and colloidal particles are needed for slip casting and pressure filtration processes, but currently these slips are difficult to cast.

Rheological behavior of concentrated suspensions is mainly dominated by hydrodynamic effects, Brownian motion, electrostatic and steric repulsion and van der Waal's attraction. With large particles (or hard-sphere systems) the colloidal interparticle forces may be ignored and the contribution of hydrodynamic effects to rheology depend on their volume concentration, shape, size, relative orientation and position[3-5]. The particle size distribution (PSD) is an important parameter for these concentrated suspensions, acting mainly on the maximum solid volume fraction. To enhance particle packing, small particles must fit the interstices between large ones. Theoretical models were developed to design an optimum PSD mainly based on Furnas', and Andreasen' s works which were described and further modified by Dinger and Funk[6]. Experimental results have confirmed that bimodal[7-9] or a continuous broad particle size distribution[10-12] can be used to achieve a high particle packing efficiency and to minimize the viscosity.

As the particle size decreases to the colloidal range, flow behavior is strongly influenced by interparticle colloidal interactions such as repulsion and van der Waal's attraction, which control spatial arrangement (network structure) and dynamics of the suspended particles. Thus, an extra increase in viscosity and a complex rheological behavior are observed as a result of the formation of flocs due to relatively high van der Waal's attraction as compared with the repulsion force. Certainly, flocculation has a considerable effect on size and shape of the flocs. By enclosing and thus immobilizing some liquid the flocs have the effect of increasing the effective solid volume and thus, the viscosity of the suspension increase[3-5]. Particle flocculation in the suspension leads to a low packing density because the flocs can not be close packed. On the other hand, well-dispersed particles in the suspension optimize the rheological properties and the packing density of the cast.

In this work, a polyacrylate based dispersant was used to control the degree of dispersion (to improve the rheology) of concentrated aqueous suspensions of alumina-zir-

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con mixtures. The effects of the amount of dispersant added and the PSD of the different powder compositions on the rheological properties and on the green density of compacts, which were obtained by slip casting and pressure filtration at 8 MPa, were examined.

2. Materials and Methods

Starting powders used in this study were commercially available α-Al_2O_3 and $ZrSiO_4$. Cumulative fraction finer than diameter CFFT vs. particle diameter D curves of alumina and zircon were determined using a Sedigraph 5000D. Figure 1 shows that the mean particle sizes were 0.4 and 2 μm, respectively. The specific surface area (BET) was 9.5 m^2/g for α-Al_2O_3 and 4.1 m^2/g for zircon.

Powder compositions of different alumina/ zircon (wt%) ratios in the mixtures (45.5/54.5, 51.7/48.3 and 35.1/64.9) were studied. These proportions correspond to: a) stoichiometric, b) with a 6 wt% excess of alumina and c) with a 10 wt% of zircon excess, respectively. The stoichiometric alumina to zircon weight ratio (45.5/54.5 wt%) corresponds to the stoichiometric α-Al_2O_3/$ZrSiO_4$ mole ratio that forms mullite and zirconia after complete conversion at high temperature.

Aqueous 48 vol% suspensions were prepared by adding the powder to aqueous solutions with different polyacrylate content (Dolapix CE64, Zschimmers and Schwartz) at pH 9.1-9.2. After mixing, the suspensions were dispersed by ultrasonic process for 30 min.

Flow curves of the suspensions were obtained using a concentric cylinder viscometer Haake vt550 with NV sensor system at 25 °C.

The consolidation of suspensions by slip casting was carried out in a plaster mould to produce samples in a form of bars (12 x 12 x 60 mm^3).

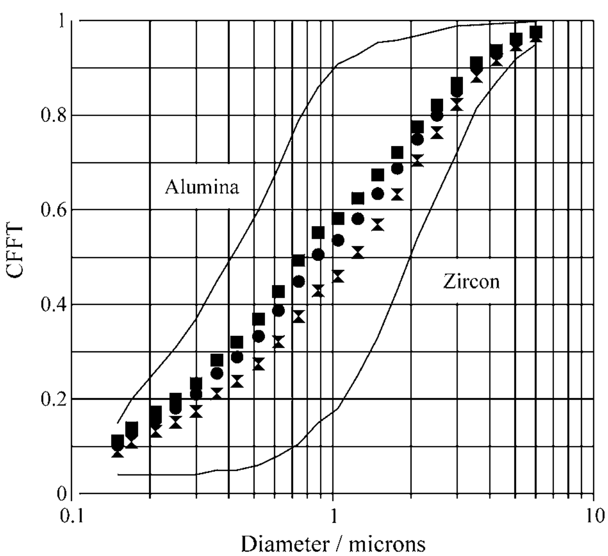

Figure 1. Cumulative fraction finer than diameter CFFT *vs.* particle diameter D curves of alumina and zircon mixtures: ● stoichiometric, ■ with a 6 wt% excess of alumina and ⧗ with a 10 wt% excess of zircon.

For pressure filtration a metallic sintered porous filter with a wet filter paper was employed. Uniaxial pressure (8 MPa) was applied from the top and the liquid moved through the porous filter. Pressure was maintained constant for 30 min. Cylindrical cast samples (25 mm diameter and 10-15 mm thick) were obtained.

Bars and cylindrical compacts were dried 24 h at room temperature and then at 110 °C up to a constant weight. Relative density (% of the theoretical) was measured by Hg immersion.

3. Results and Discussion

3.1. Effect of the amount of dispersant on the rheological properties of the 48 vol% suspensions

The isoelectric point (iep) of alumina used has been determined to be at pH near 9. Previous works on the casting behavior of a commercial zircon powder[13,14] showed the electrophoretic mobility measurements as a function of the pH . They reported that the iep was at pH 5 and the zeta potential became strongly negative with further increase in pH. According to these results, the zircon particles had a high negative zeta potential in the basic pH range. Thus, at pH close to 9, an electrostatic attraction between the neutral alumina particle and the high negatively charged zircon particle can occur.

Figure 2 shows the flow curves of the aqueous 48 vol% suspensions of: stoichiometric composition, with a 6 wt% excess of alumina, and with a 10 wt% excess of zircon powder mixtures for different amounts of polyacrylate added.

Both shear stress and apparent viscosity, which is the shear stress to shear rate ratio at any shear rate, decreased to a minimum and then gradually increased with increasing the amount of dispersant added. For these suspensions, the maximum degree of dispersion of the particles is achieved when the suspension contained a 0.22-0.24 wt/wt % of dispersant that produced a minimum of viscosity. All the suspensions having a minimum viscosity showed a nearly Newtonian behavior (well stabilized suspensions).

At pH 9 alumina and zircon exhibited opposite charges because of the differences in pH_{iep} Adsorption of polyacrylate on alumina was favored by electrostatic and specific mechanisms. Previous studies have shown that polyelectrolytes on alumina can give electrostatic and steric stabilization. However, weak adsorption of polyacrylate on zircon particles was expected , in the basic pH range, due to an electrostatic repulsion between the polyacrylate anion in solution and the highly negative surface. Then, polyacrylate adsorption mainly on alumina surface generated high negative zeta potentials and therefore, electrostatic interaction between zircon and alumina particles changed to repulsive at pH 9. Then, a minimum in viscosity was obtained as both powders had highly negative surfaces at low electrolyte concentration (high zeta potential).

High apparent viscosities and non Newtonian flow behavior were obtained at polyacrylate concentrations lower than 0.22-0.24 wt%. The flow behavior changed to shear

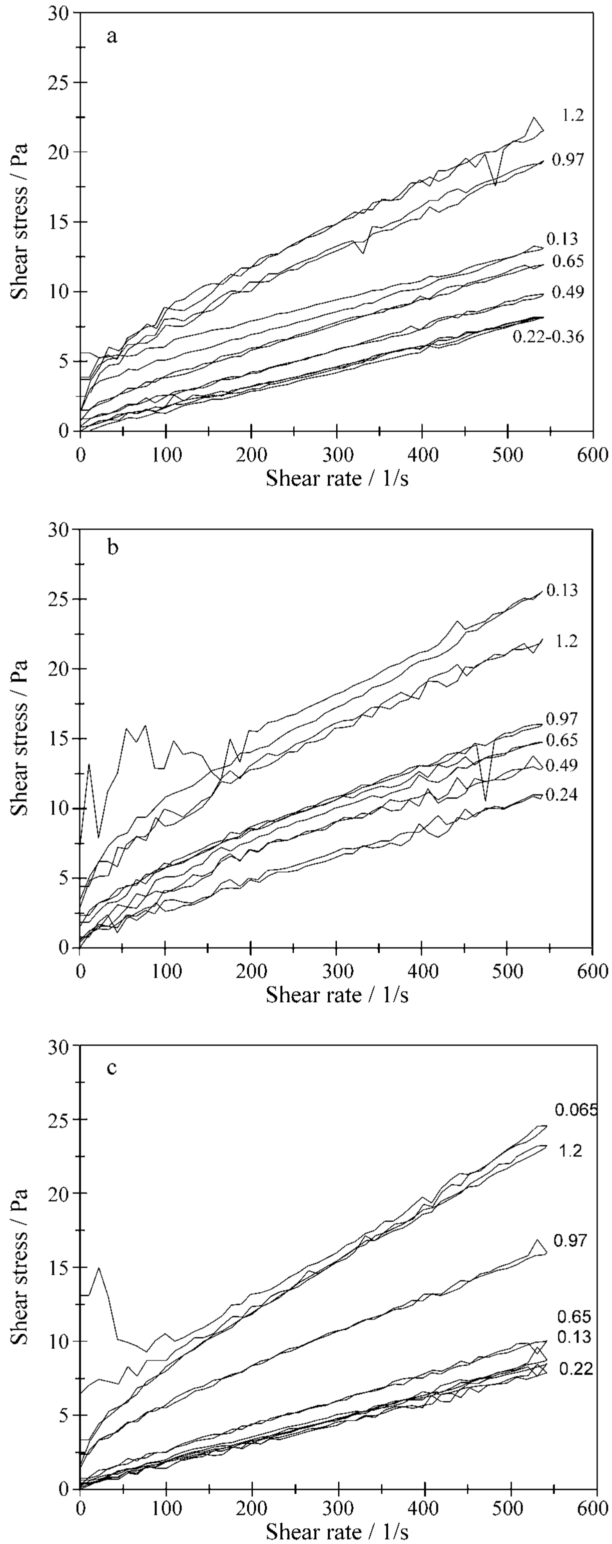

Figure 2. Shear stress vs. shear rate curves for alumina-zircon suspensions (48 vol%) with different content (wt/wt %) of dispersant. **a**: stoichiometric, **b**: with a 6 wt% excess of alumina, c: with a 10 wt% excess of zircon powder mixtures.

thinning or plastic depending on the powder composition. Flow curves exhibited a slight hysteresis loop indicating that the suspension was not fully deflocculated. This may be explained by an insufficient adsorption of polyacrylate anion (mainly on the alumina surface) due to low amount of available dispersant. Incomplete adsorption reduced the net negative charge of the mixed powders and consequently repulsion was low. Moreover, heterocoagulation between the uncoated alumina and zircon particles produced a significant increase in viscosity. With increasing shear rates, the breakdown of the flocs released some immobilized liquid that increased the volume of free liquid; therefore suspension viscosity decreased (shear thinning behavior).

For polyacrylate additions higher than 0.65 wt%, the apparent viscosity and the shear thinning behavior gradually increased probably due to the presence of an excess of polyelectrolyte in solution. High amounts of non adsorbed polyelectrolyte in solution can promote flocculation by double layer compression (high ionic strength) and depletion mechanisms[15].

The differences between the three compositions studied were examined. Suspensions of the three alumina-zircon mixtures at pH 9.1-9.2 containing 0.22-0.24 wt% of polyacrylate showed a minimum viscosity. The composition with the zircon excess in the mixture had the lowest minimum viscosity . The viscosity of the suspension decreased close to the minimum by addition of 0.13 wt% of dispersant due to low specific surface area of this mixture. The dispersant concentration required to obtain minimum viscosity was lower than that for the other compositions.

At low polyelectrolyte concentration, the suspension of the mixture that contained the highest amount of alumina showed higher viscosity values than the ones of the other compositions as fine alumina particles gave high specific surface area. Also, the higher is the content of alumina in the mixture, the lower is the zeta potential of the powders. As suspension pH was near pH_{iep} of alumina, negative surface charge of the uncoated alumina powder was lower than the one of the zircon. Therefore, electrostatic repulsion decreased.

For polyacrylate concentrations higher than 0.65 wt%, the viscosity of all the alumina/zircon ratio mixtures increased to similar values.

Flow curves of Figs. 2 a, b, c were fitted with the Casson model:

$$\tau^{1/2} = \tau_c^{1/2} + (\eta_c D)^{1/2}$$

where τ is the shear stress [Pa], D is the shear rate [s^{-1}] and τ_c and η_c are the Casson yield stress and viscosity parameters, respectively. Except for the suspensions with 0.13 wt% of dispersant that showed a time dependency, the Casson model showed a good fit of the experimental data.

Figure 3 shows the viscosity and yield stress Casson model parameters as a function of the dispersant content. Casson viscosity remained unchanged whereas yield stress Casson parameter decreased to a minimum and then increased with increasing the amount of dispersant added. Guo *et al.*[15] related the τ_c parameter with the magnitude of the attractive interparticle interactions. Thus high τ_c parameter is indicative of the formation of flocs due to relatively high van der Waals attraction as compared with the repulsion force.

The large variation in the yield stress Casson parameter τ_c (Fig. 3b) with increasing amounts of polyacrylate added may be explained by significant differences in the strength of the network structure of the suspensions. Well dispersed suspensions gave a very low τ_c parameter. Low amount of dispersant adsorbed as well as high amounts of non adsorbed polyelectrolyte in solution caused flocculation, which increased the strength of the network resulting in a high τ_c.

At constant dispersant concentration, the magnitude of τ_c is affected also by the PSD of the mixtures as is showed in Fig. 3 b. Suspension with an excess of alumina exhibited high τ_c values because of the small particle size and a high content of fine sized particles. Based on the fine size fraction, this powder mixture had high number concentration of particles, which determined more particle-particle bonds in a network structure. τ_c values decreased with increasing the content of zircon in the mixture because of high amount of coarse particles. Previous results showed that extrapolated and measured yield stress vary inversely with particle size and , at constant solid concentration and particle size, yield stress decreases with increasing zeta potential.

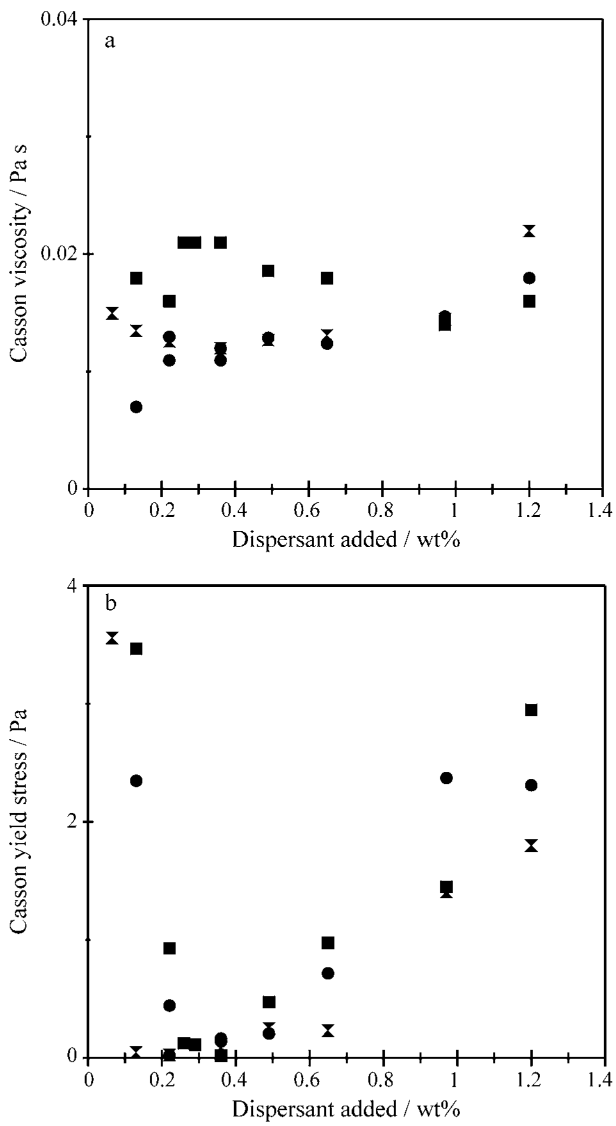

Figure 3. a: viscosity, **b**: yield stress Casson model parameters (best fit of flow curves of Fig. 1 a, b, and c as a function of the dispersant content for alumina-zircon suspensions of: ● stoichiometric, ■ with a 6 wt% excess of alumina and ⧗ with a 10 wt% excess of zircon powder mixtures.

3.2. Effect of PSD on the minimum viscosity of 48 vol% suspensions

Figure 4 shows the frequency vs. particle diameter curves for alumina and zircon, which were obtained from cumulative curves given in Fig. 1. Alumina and zircon powders showed narrow distributions with a maximum in frequency at diameters of 0.6 and 1.8 μm, respectively. Contribution of the <0.15 μm fraction was important in the PSD of alumina. Figure 5 shows the corresponding curves for the mixtures, which were calculated by considering the individual distribution of alumina and zircon and the volume fraction of each component. These curves exhibited broader distributions than those of Fig. 4. The presence of two maximum of frequency centered at 0.6 and 1.8 μm indicated that the distributions were bimodal.

Suspensions containing the optimum amount of dispersant showed a nearly Newtonian behavior, but the apparent viscosity slightly decreased with increasing shear rate reaching a plateau at high shear rates. The degree of shear thinning increased as the content of fine alumina in the mixture. Values of the Newtonian viscosity in the high shear rate region were 16, 14.5 and 19.7 mPas for

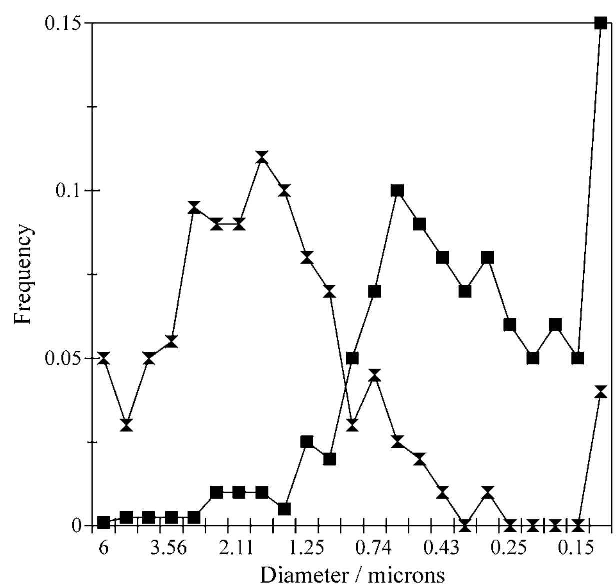

Figure 4. Frequency *vs.* Particle diameter curves for: ● alumina and ⧗ zircon powders.

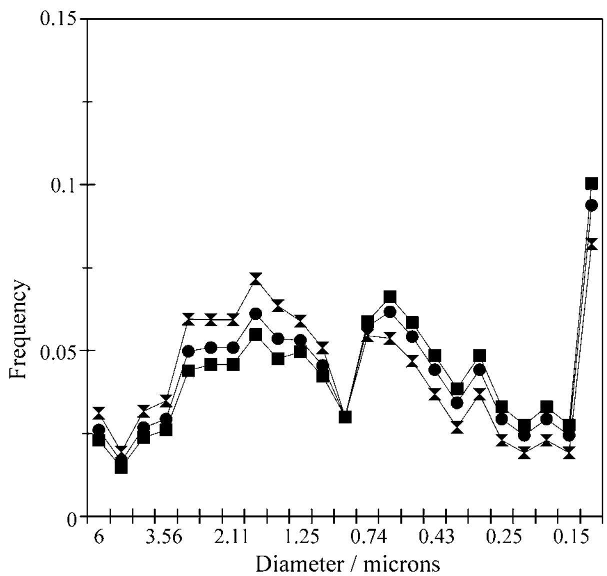

Figure 5. Frequency vs. Particle diameter curves calculated from data of Fig. 4 and volume fraction of each component for: ● stoichiometric, ■ with a 6 wt% excess of alumina and ⧗ with a 10 wt% excess of zircon powder mixtures.

stoichiometric, with an excess of zircon and with more alumina mixtures, respectively. The mixture with an excess of zircon exhibited the lowest viscosity. The volume fraction of each component in this mixture (0.383 for alumina and 0.616 for zircon as fine and coarse powders) was close to the optimum proportions for binary powder mixtures. As initially described by Furnas [6], particle packing of powders having bimodal distributions with an appropriate size ratio of components is optimized (apparent volume of the pack reaches a minimum) with a 0.29 volume fraction of fines. In this conditions apparent volume of fines just equals the pore volume between coarse particles. For the mixture with more alumina, the volume fraction of fines increased to 0.555 and consequently had an excess of fines with respect to the optimum proportion which produced high viscosity suspensions due to high specific surface area.

3.3. Effect of the rheological parameters on the density of green casts

Figures 3 a and b show that Casson yield stress parameter exhibited a dependence on the amount of dispersant added (*i.e.* on the interparticle colloidal forces) and on the PSD (particle size) stronger than that of the Casson viscosity. Therefore, τ_c can be used to study the influence of rheological properties on green density of casts.

Figures 6 and 7 show the relative density of green compacts obtained from 48 vol% suspensions of the three compositions studied by slip casting and pressure filtration, respectively as a function of the yield stress Casson parameter.

Density was nearly constant up to a certain τ_c value and then decreased with increasing τ_c. Compacts resulting from well dispersed Newtonian suspensions or with low τ_c parameter in which repulsion between particles was comparatively large (at a constant Casson viscosity) gave compacts with the highest green density. Low density compacts could be prepared from suspensions characterized by a high τ_c parameter indicating strongly attractive interparticle interactions which were related to low electrostatic repulsion due to insufficient adsorption of polyacrylate. This result agreed with that of previous studies on alumina[16], which showed that the network structure resulting from a strongly attractive interactions resisted consolidation and, although

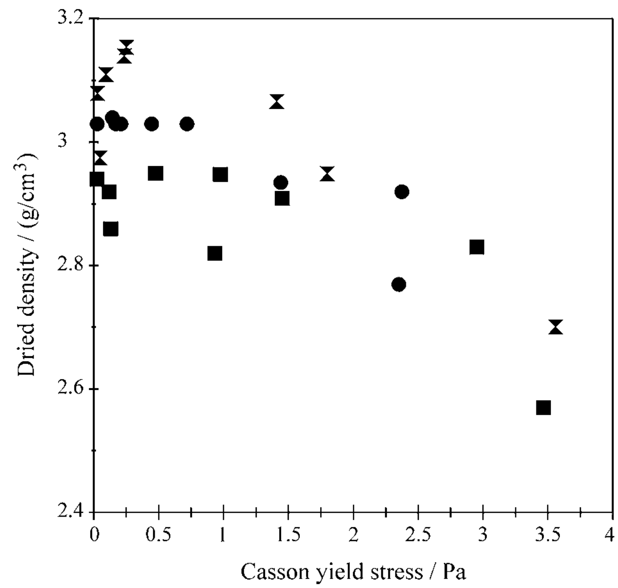

Figure 6. Relative density of green compacts prepared from 48 vol% suspensions of: ● stoichiometric, ■ with a 6 wt% excess of alumina and ⧗ with a 10 wt% excess of zircon powder mixtures by slip casting.

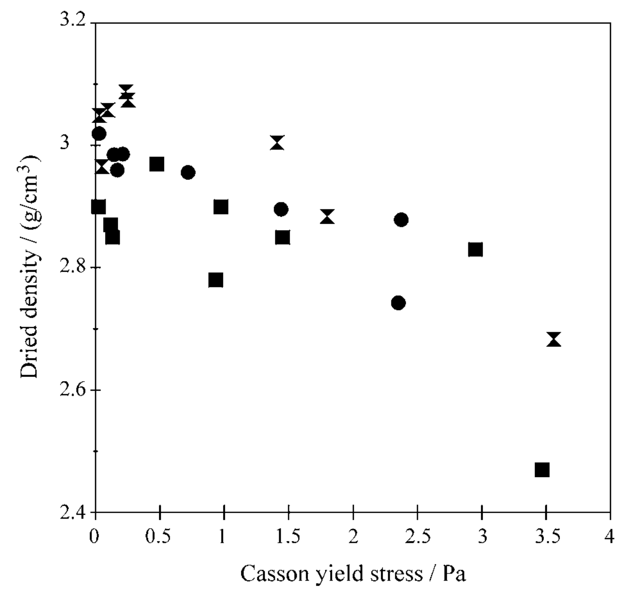

Figure 7. Relative density of green compacts prepared from 48 vol% suspensions of: ● stoichiometric, ■ with a 6 wt% excess of alumina and ⧗ with a 10 wt% excess of zircon powder mixtures by pressure filtration.

it was compressible, a poor packing density was obtained. For suspensions with large excess of dispersant in solution, intermediate τ_c values were obtained. The influence of van der Waal's attraction became dominant due to reduced electrostatic repulsion between particles but density values were close to those from well dispersed suspensions. Density only decreased 3% from the maximum value for suspensions containing 1.2 wt% of dispersant. These suspensions may be considered as weakly flocculated because they exhibited higher viscosity than the minimum but smaller τ_c and lower shear thinning character than those resulting from high attractive forces. Weakly flocculated suspensions showed a different packing behavior[16]. As the strength of these network structures are lower than that formed by highly attractive interactions a comparative higher density can be obtained[16].

Relative density values of 70.4, 70.7, 71.2 and 69.9, 70.3, 70.2 % TD were found for green compacts prepared from the minimum viscosity suspensions (very low τ_c) by slip casting and pressure filtration for mixtures with more alumina, stoichiometric, with an excess of zircon, respectively. However, Figs. 3 and 4 show that compacts prepared from the zircon excess composition achieved maximum density (72 and 71%TD) at a τ_c value somewhat higher than that corresponding to the other compositions. Since this powder contained a high proportion of coarse and dense zircon particles, weak flocculation may be favorable. Slightly higher viscosity at low shear rates prevents settling of zircon particles and reduces segregation of components.

An estimation of packing density of binary mixtures can be obtained using the idealized Furnas' equation which assumes a dense random packing of the matrix and inclusion (spherical) particles[17]. Values of 76, 78 and 82% should be obtained for mixtures with more alumina, stoichiometric, with an excess of zircon, respectively. However, a further modification of this model was developed, which consider the combined effects of inclusion surfaces and inclusion contacts[17]. This model is expected to be valid to predict the packing density when the volume fraction of inclusions is less than 0.74 and when the inclusion particle size is larger than that of the matrix[17]. Although the predicted values for binary mixtures with more alumina, stoichiometric, with an excess of zircon reduced to 74, 75 and 78%, respectively they were somewhat higher than that of the experimental density values. As the colloidal size fraction of the mixtures was high (nearly 50% of the total weight was finer than 1 μm), the strong influence of the colloidal interparticle forces at small interparticle separations (high fine size content and high solid volume concentration) on the degree of dispersion can not be avoided.

4. Conclusions

Rheological properties of aqueous suspensions (48 vol%) of zircon-alumina mixtures were determined to study the effects of the amount of polyacrylate added and of the particle size distribution of the different powder compositions. Rheological properties were correlated with green density of compacts obtained by slip casting and pressure filtration at 8 MPa.

Flow curves fitted satisfactorily to the Casson model. The Casson viscosity values remained nearly constant whereas the Casson yield stress parameter showed a strong dependence on the amount of dispersant employed (*i.e.* on the interparticle colloidal forces) and on the PSD (particle size). Therefore, Casson yield stress parameter was used to correlate rheology with the green density of compacts.

Suspensions characterized by low yield stress Casson parameter (at a constant Casson viscosity) in which repulsion between particles was comparatively large gave compacts with the highest green density. Maximum relative density values of green compacts were 70.4, 70.7, 72.0 and 69.9, 70.3, 71.0 % for well deflocculated suspensions of mixtures with more alumina, stoichiometric and with an excess of zircon, by slip casting and pressure filtration, respectively. These values were obtained using 0.22 to 0.49 wt% of polyacrylate as dispersant at pH 9.1-9.2.

The lowest minimum viscosity for suspension of zircon excess composition may be attributed to a mixture with bimodal PSD and fine volume fraction near to 0.3 which maximized packing density of particles. Low yield stress Casson parameter was favorable for processing suspensions that contained high proportion of zircon particles. Probably, high viscosity at low shear rates prevented settling and reduced segregation of components.

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