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RHEOLOGICAL ANALYSIS OF CERAMICS SUSPENSIONS WITH HIGH SOLIDS LOADING

Luiz Fernando Grespan Setz[1,a], Laís Koshimizu[1,b],
Sonia Regina Homem de Mello-Castanho[2,c], Márcio Raymundo Morelli[1,d]

[1]Departament of Materials Engineering, Federal University of São Carlos,
Rodovia Washington Luís, km 235, S. Carlos, SP 13565-905 - Brazil

[2] Materials Science and Technology Center, Nuclear and Energy Research Institute,
Av. Lineu Prestes, 2242, Cidade Universitária, S. Paulo, SP 05508-900 - Brazil

[a]lfsetz@yahoo.com.br, [b]laiskoshimizu@yahoo.com.br, [c]srmello@ipen.br, [d]morelli@ufscar.br

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Abstract. The pure oxides (yttria, zirconia, titania, alumina, etc.) pastes ceramics production by concentrate suspensions is interesting because differently than plastic ceramics (clays), where these behaviours are often empirical available, the rheological suspensions behaviour are extensively studied. Thus, controlling the concentrate slips rheological parameters, is possible extend these analysis for better understand and control the plastic pastes production, providing subsidies to obtain after shaping process, such as extrusion and calendering, suitable products for the desired application. Thus, alumina suspensions rheological behaviour, with high solids loading (> 50 vol.%) adequately stabilized, slip cast shaped are available in this work. High solids loading suspensions, up to 60 vol.%, presents adequate flow for thickeners/plasticizers elements adds to produce ceramic plastic pastes.

Introduction

Ceramic plastic shaping are very extensive employed in traditional ceramics, where clays predominate. In these materials, plasticity is achieved with small water amounts added [1] while in "pure" oxide systems organic compounds (plasticizers and binders) must be added with a solvent to promote adequate plasticity [2].

The extrudable ceramic paste plastic behaviour is controlled by several factors [3]: (i) volume fraction, shape and particle size distribution, (ii) dominant interparticles forces, (iii) surface chemistry, (iv) packing density and (v) liquid phase rheological behaviour.

The ceramic plasticity measurement and control are very important to achieved good production conditions (reduced processing times and correct shapes) however, due a variety parameters involved and the lack of sensitive methods for quantification and evaluation the complex relationship between flow characteristics and properties of components such as extruded, this behaviour are empirical [4]. Thus, the ceramics masses plasticity are predicted by stress-strain compression curves [5, 6].

How the suspension rheology are extensive studied, their knowledge can be extrapolate to ceramic pastes behaviour to produce adequate products [7-9]. Thus, in this work, the alumina suspensions rheological behaviour with high solid loading, but fluid enough to be added later, thickeners/plasticizers additives, that promote plastic masses to be shaped by calendering, were studied.

Experimental Procedure

A high purity α-A_2O_3 powder (Almatis, A1000, USA) was used, with a specific surface area of 8.2 $m^2\ g^{-1}$ (BET - Monosorb, Quantachrome, USA) and average particle size of 0.67 μm (SediGraph 5000ET, Micromeritics, USA). The particles morphology was observed in Scanning Electronic Microscopic (SEM - Quanta 600FEG, FEI Company, USA).

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The stability of the α-Al_2O_3 powders was studied as a function of pH through zeta potential measurements, which were performed using Phase Analysis Light Scattering (ZetaPALS, Brookhaven Instruments Corporation, USA). The samples were prepared to a solid content of 0.01 vol.% in deionized water produced by a Milli-Q Plus pure water generating system from Millipore (USA). The ionic strength was fixed at 10^{-3} M using KNO_3 (Aldrich-Chemie, Germany) as indifferent electrolytes. The pH adjustments were made by adding appropriate amounts of HNO_3 and KOH. Prior to measurements, all suspensions were homogenized with an ultrasounds probe for 1 min.

Suspensions of α-Al_2O_3 powder were prepared in deionized water to a solids concentration of 42-60 wt.%. Dispersion was achieved by adding 0.2 wt.% of citric acid referred to the dry solids, in accordance with existent works [10, 11]. To reduce powder agglomerates, the slurries were ball milled for milling times up to 24 hours, using alumina balls.

The rheological behaviour of all prepared slurries was performed with a rheometer (Haake RS600, Thermo, Germany) capable to operate at either controlled shear rate (CR) or controlled shear stress (CS) modes. The sensor system consisted on a double-cone rotor and a stationary plate, this system being surrounded by a cylindrical wall. The chamber is protected with a solvent trap to reduce evaporation phenomena. For characterizing the slurry stability the flow curves were determined in controlled rate mode (CR). Measurements were performed by increasing the shear rate from 0 to 1000 s^{-1} in 5 min, maintaining at 1000 s^{-1} for 2 min and returning to 0 in 5 min. Temperature was maintained constant at 25°C during these experiments. Rheological parameters were analysed by Haake software RheoWin 3.61.0004 for all suspensions produced from CR flow curves.

Small ceramic discs with 1.5 cm in diameter were obtained by slip casting suspensions prepared at different conditions on plaster of Paris moulds [12]. The green density of the disc-shaped specimens was measured by mercury immersion (Poresizer 9320, Micromeritics, USA) after drying for 48 h at room conditions. Shaped discs were sinterized at 1600°C/1 h in a vertical furnace (LindbergBlue, USA). The density values were determined by using the Archimedes' principle method. All density values were reported as percentage of theoretical density (T_d) of alumina (3.99 g cm^{-3}).

Results and Discussion

Figure 1 presents the α-Al_2O powders scanning electronic microscopy (SEM) micrograph, where can be observed lamellar particles with some particle size distribution variation. Morphology is important because directly influence the concentrated suspensions behaviour [13].

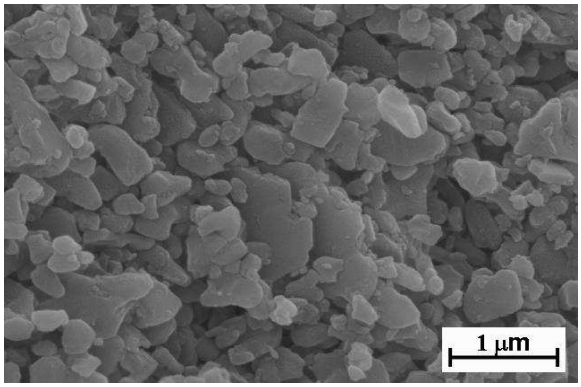

Fig.1. α-Al_2O_3 powders SEM micrograph

The alumina Zeta potential curve is showed in Figure 2. How expected, the isoelectric point occur at ~pH 9.0 [13], and the stability values ($|>20mV|$) are observed below pH 7 and above pH 11. The citric acid amount (0.2 wt.%) used as dispersant, in concentrate suspensions, promotes a ~pH 5, and according to the results presented in Fig. 1, shows Zeta potential value sufficient to obtain stable suspensions.

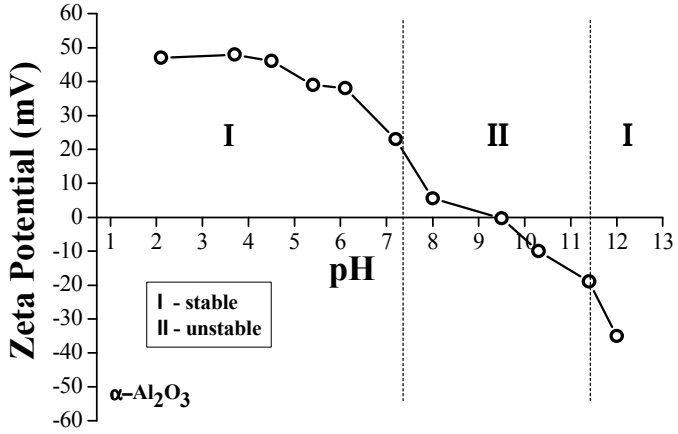

Fig. 2. α- Al_2O_3 Zeta potential curve

The alumina suspensions flow curves, with different solid contents, are shown in Figure 3. Can be observe an expected increase in flow resistance and a behaviour change, from shear thinning to shear thickening (dilatancy), due to solids loading increase.

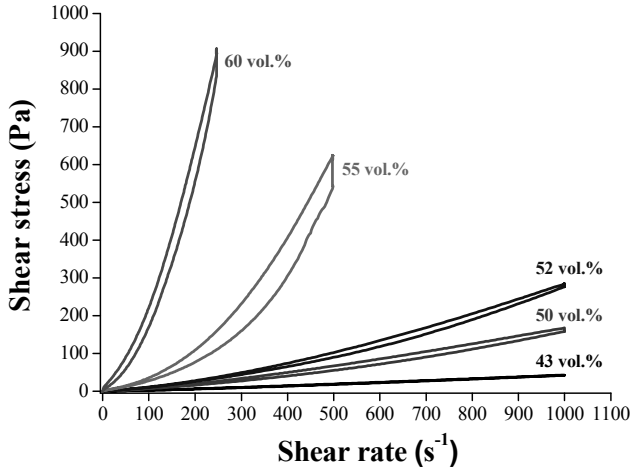

Fig. 3. Flow curves for suspensions with different solids loading, obtained in CR mode

The transition shear thinning to shear thickening, with solid content increase, are displaced to lower shear rates (Fig. 4), starting at shear rate of 50 s^{-1} in suspensions with 43 vol.%. This behaviour change is similar to that happens with kaolin concentrate suspensions [14]. The viscosity increase from 400 s^{-1} in kaolin suspensions, is attributed to "house of cards" structure formed by the difference electrostatic charge between the edges and faces of kaolin particles (kaolinite) which have platelet shape. In the alumina suspensions this behaviour is attributed to lamellar morphology of the alumina particles and also the particle size (0.67 μm) [13], associated with high solids concentration.

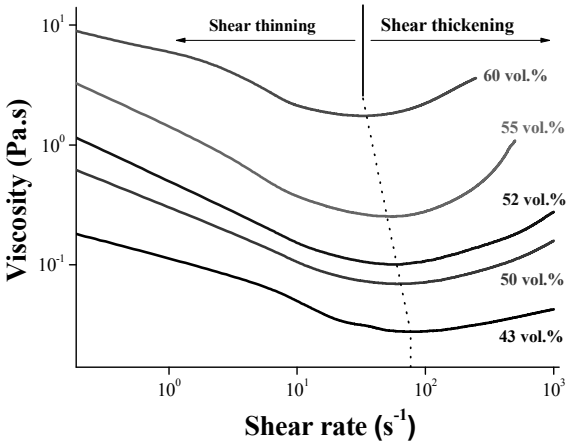

Fig. 4. Viscosity curves versus shear rate highlighting the transition shear thinning to shear thickening, for alumina suspensions with different solids loading

The Cross model was used in this study because it can adequately predict the general form of flow curves by introducing values of the limit viscosity extrapolated to zero shear rate (η_0) and infinite shear rate (η_∞) providing important and accurate information on the behaviour conditions of high and very low shear rates, near the resting conditions [13].

Figure 5 shows the variation of relative viscosity with the volume fraction of solids (η_r–φ curves) of the milled suspensions calculated in the high shear rate region by fitting the experimental η_∞ data (symbols) to the Krieger–Dougherty model (continuous line) [15], where φ_{max} values up to 0.62 were found, very near the maximum solids loading used in this work.

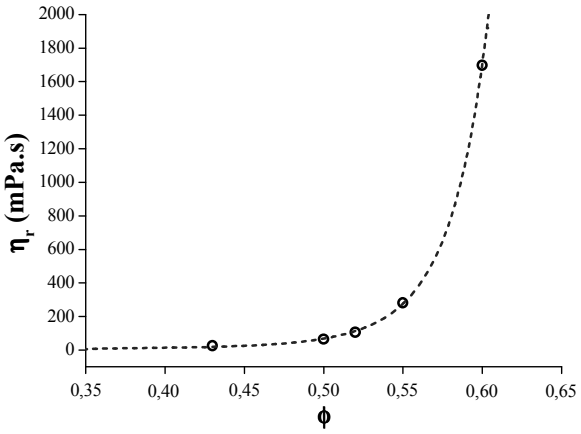

Fig. 5. Variation of viscosity of alumina suspensions with volume fraction of solids

Rheological analyses for all suspensions studied are presented in Table 1. All parameters are increased with solid content, as expected. Thixotropy negative values, determined by rheometer software, are due shear thickening behaviour from the shear rate of 50 s^{-1}. Although not observed large areas in flow curves between the up and down curves, the difference is due to the rheometer software considers the full extent of measurement. The values of dynamic viscosity at 10 s^{-1} are considered because of that, generally, this is the value achieved by casting in plaster Paris moulds (slip casting).

Suspensions with maximum solids concentration used (60 vol.%), are suitable for production of plastic ceramic bodies by adding thickeners/plasticizers additives, such as hydroxypropyl methylcellulose (HPMC) [16], for example. Concentrate suspensions showed viscosities values of the order of 2000 mPa.s at 10 s^{-1}, in other words, sufficiently fluid for slip casting shaping [2, 6].

The relative density of all the green pieces shaped presented values of ~70 T_d%. Independent of the fraction of solids it was possible to obtain similar products. The difference in solids content directly influences the speed of shaping and drying processes, then, is always seeking a middle ground, forming a quick but sufficient to allow an adequate dimensional control of the product.

Density values after sintering (1600°C/1 h), as expected, due to good values achieved in the green densities were high, resulting in suitable products, dense and homogeneous. All density values are presented in Table 1.

Table 1. Alumina suspensions rheological properties and relative green and sintered at 1600°C/1 h densities

Solid content [vol.%]	Solid content [wt.%]	Cross model parameters		Thixotropy [Pa s^{-1}]	Viscosity at 10 s^{-1} [mPa.s]	Green density [T_d%]	Sintered density [T_d%]
		Viscosity at 0 s^{-1} [mPa.s]	Limite viscosity [mPa.s]				
43	75	54,8	26,3	-889,5	48,5	70,0 ± 0,6	98,9 ± 0,1
50	80	17010,0	65,7	-8761,0	103,4	70,1 ± 4,2	99,0 ± 0,1
52	81	28550,0	106,5	-8742,0	150,1	70,4 ± 0,7	99,2 ± 0,2
55	83	49570,0	280,6	-20460,0	383,9	70,4 ± 1,8	98,8 ± 0,2
60	85	4841,0	1698,0	-24320,0	2183,0	70,4 ± 3,8	98,7 ± 0,2

Conclusions

The alumina suspensions with high solid loading exhibit a transition from shear-thinning to shear-thickener in shear rate close to 50 s^{-1}, attributed to the lamellar morphology of the α-Al_2O_3 particles and also the particle size (0.67 μm). The viscosity achieved in aqueous suspensions with concentrations of 85 wt.% is suitable for adding thickeners/plasticizers elements for the production of plastic ceramic pastes.

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References

[1] P. Souza Santos: *Ciência e Tecnologia de Argilas*, Vol. 1, Edgard Blücher Ltda, São Paulo (1989).
[2] J.S. Reed: Principles of Ceramics Processing, John Wiley & Sons, Inc., New York (1995).
[3] J.J. Benbow, E.W. Oxley and J. Bridgwater: Chem. Eng. Sci. Vol. 42 (1987), p. 2151.
[4] M.J. Ribeiro, J.M. Ferreira and J.A. Labrincha: Ceram. Int. Vol. 31 (2005), p. 515.
[5] T.A. Ring: *Fundamentals of Ceramic Powder Processing and Synthesis*, Academic Press, Inc., San Diego (1996).
[6] D.W. Richerson: *Modern Ceramic Engineering*: Properties, Processing, and Use in Design**,** Marcel Dekker (1992).
[7] F.F. Lange: J. Am. Ceram. Soc. Vol. 72 (1989), p. 3.
[8] J.A. Lewis: J. Am. Ceram. Soc. Vol. 83 (2000), p. 2341.
[9] M.G. Rasteiro and I. Salgueiros: Particul. Sci. Technol. Vol. 23 (2005), p. 145.
[10] P.C. Hidber, T.J. Graule and L.J. Gauckler: J. Am. Ceram. Soc. Vol. 79 (1996), p. 1857.
[11] I.R. Oliveira, A.R. Studart, R.G. Pileggi and V.C. Pandolfelli: Dispersão e Empacotamento de Partículas - Princípios e Aplicações em Processamento Cerâmico. Fazendo Arte Editorial, São Paulo (2000).
[12] A. Carvajal and R. Moreno: Bol. Soc. Esp. Ceram. V. Vol. 27 (1988), p. 11.
[13] R. Moreno: *Reología de Suspensiones Cerámicas*, Consejo Superior de Investigaciones Científicas, Madrid (2005).

[14] B. Ferrari, R. Moreno and F.F. Lange: Bol. Soc. Esp. Ceram. V. Vol. 39 (2000), p. 229.
[15] L.F.G. Setz, I. Santacruz, M.T. Colomer, S.R.H. Mello-Castanho and R. Moreno: J. Eur. Ceram. Soc. Vol. 30 (2010), p. 2897.
[16] A.R.F. Pardo, M.R. Morelli: Processamento Viscoplástico e Conformação Cerâmica por Rolos a Frio a Partir de Suspensões Concentradas de Alumina. Doutorado (Tese). São Carlos (2005).Universidade Federal de São Carlos (UFSCar). (SP)

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Rheological Analysis of Ceramics Suspensions with High Solids Loading
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