Journal of the European Ceramic Society 20 (2000) 259–266

Effects of polysaccharides on the rheology of alumina slurries

Jong Cheol Kim [a,*], Keun Ho Auh [a], Christopher H. Schilling [b]

[a] *Hanyang University, Ceramic Materials Research Institute, Seoul 133-791, South Korea*
[b] *Ames Laboratory [1] and Department of Materials Science and Engineering, Iowa State University, Ames, USA*

Received 28 January 1999; received in revised form 12 May 1999; accepted 25 May 1999

Abstract

The rheological behaviors of alumina slurries with polysaccharides having different concentrations and molecular weights were analyzed. The polysaccharide molecule absorbs to the surface of alumina powder in an aqueous slurry to give sorbate-mediated steric hindrance. Rheological measurements were used to compare the strength of alumina particulate networks. The network strength of alumina slurry increased at first and decreased later with the increase of molecular weight of polysaccharides. The network strength of alumina slurry became weaker with the addition of polysaccharides of low molecular weight and stronger with the addition of polysaccharides of higher molecular weight. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Polysaccharides; Rheology; Suspensions

1. Introduction

Advanced alumina ceramics are typically produced by a process of mixing colloidal alumina powder with an organic additive to form a slurry into a mold, slow heat treatment to pyrolyze the organic additives, and sintering at high temperature. Large concentrations of the organic additive up to 40–70 vol% are typically needed to maintain plasticity during molding in order to prevent brittle behavior, which occurs at lower concentrations of organic additive.[1,2] The evaporization of hydrocarbon additives and the gases produced by them during pyrolysis cause unwanted cracks and shape distortion. Long thermal treatments are necessary to complete pyrolysis because rapid heating could produce internal stresses that can cause unwanted cracks and deformation.[3] Evaporation and gaseous diffusion leave some decomposed residue behind.

Aqueous medium is necessary in order to eliminate these organic additives in an efficient way and evaporate without causing cracks, deformation, and microstructure contamination in sintered parts. Simple addition of water to alumina powder results in a dramatic reduction of slurry plasticity if the water concentration is beneath a critical value. Forming becomes impossible under this critical concentration because insufficient water tends to produce a stiff slurry. This critical water concentration is usually much smaller for aqueous clay slurries as opposed to aqueous alumina slurry. Clay-based ceramics are much easier to mold at smaller concentrations of water, which also makes them less susceptible to cracks during drying.

Plasticity of an aqueous slurry is related to the interparticle potentials between particles and stresses in the particular network. A particular network shows brittleness when a fracture stress is lower than a yield stress. It is necessary to decrease the strength of this brittle network to make particles yield. High packing densities can be obtained by consolidating weak networks. The big difference in rheology between advanced alumina ceramics and clay-based ceramics can be attributed, to a large extent, to inherent differences in particle morphology and the nature of the surface charge.[4–6] The unique morphology of clays, along with a superposition of attractive van der Waals and electrostatic repulsive forces, contributes to the high degree of plasticity of clays.

The major step in improving the plasticity of concentrated slurries of alumina powders is to develop a weakly-flocculated state by coating powders with a substance producing a superposition of long-range attraction and short-range repulsive forces. Two general methods are reported: one is using the hydration-layer approach and the other is using the steric-hindrance

---

* Corresponding author.

[1] Ames Laboratory is operated by Iowa State University under the contract number W-7405-eng-82 with the US Department of Energy.

PII: S0955-2219(99)00168-5

approach. The hydration-layer approach[7–15] is adding a short-range, repulsive interparticle force, which was produced by the surface adsorption of indifferent electrolytes in a dispersed aqueous slurry. The added salt decreases the long-range potential and induces a short-range potential. The interparticle strength of attractive networks attained by adding salt to dispersed slurry is much lower than the attractive networks produced without salt. Ducker et al.[15] first proved the existence of this short-range repulsive potential caused by the indifferent electrolyte. Ducker et al.[15] showed that the addition of the electrolyte increased the viscosity until a maximum is reached after which further additions of electrolyte have little effect to the viscosity.

Steric-hindrance is possible with the generation of a steric adlayer that inhibits complete mutual approach of individual particles. Yin et al.[16] first introduced the method of weak-flocculation by adsorbate-mediated steric-hindrance and reported the formation of high-density, low-viscosity slurries with polymethacrylates adsorbed on alumina powders suspended in heptane or paraffin oil. After that, Schilling[17] and Bergström et al.[18] reported significant improvements in the packing densities of centrifuged slurries in which short-range repulsive forces were established by the adsorption of fatty acids to alumina powders suspended in decalin. Kramer and Lange[2] also produced short-range repulsive force by absorbing small molecules to the surface of Al_2O_3 powders to give steric hindrance effects. Kramer and Lange[2] suggested that short-range force only persists during particle packing when the molecules were chemically reacted with surface ions but physically adsorbed molecules were displaced either by particle pushing during particle compaction or by water adsorbed by the organic additives.

Recent research focused on developing aqueous slurry by the method of weak-flocculation by adsorbate-mediated steric-hindrance effects, analogues producing highly-concentrated and plastic slurries of alumina powders without the concerns of the organic residues after heat treatment. Luther et al.[19] suggested that the citrate ion adsorbs to the surface of alumina particle and reported significant reductions in the viscosities of aqueous alumina slurries by the use of ammonium citrate additives. Chan and Lin[20] reported significant reductions in viscosity by the adsorption of steric acid onto alumina powder surfaces in paraffin/polypropylene slurries. Schilling and co-workers[21,22] reported significant improvements in the rheology of aqueous dense slurries of alumina powder, weakly-flocculated slurries with maltodextrin. Schilling and co-workers[22,23] reported significant improvements in the packing densities of aqueous slurries of alumina powder with maltodextrin additives. These slurries showed a high degree of plasticity based on viscosity measurements. Schilling et al.[23] also performed surface chemical analysis to study the mechanism of enhanced plasticity caused by polysaccharide. Schilling et al.[23] also reported that this mechanism primarily entails the reduction of interparticle attraction by adsorbate mediated steric hindrance and maltodextrin acts as an additive to help slip-casting by strengthening alumina bodies during drying.[24]

Schilling et al.[23] used a commercially available maltodextrin having an average molecular weight of 3600 Daltons. In this research, we studied the rheological properties of alumina slurry with polysaccharides of different molecular weights and concentrations. These studies will help establish an understanding of the advantages of polysaccharides in molding dense slurry for the advanced alumina processing.

2. Experimental procedure

Commercially available, α-Al_2O_3 powder having an equiaxed particle shape, an average particle size of 0.4 μm, and a specific surface area of 8.5 m^2/g (A-16 SG, from Alcoa Corporation, Bauxite, AR, USA) was used. Commercially-available maltodextrins (Grain Processing Corporation, Muscatine, IA, USA), dextrans (Sigma, St. Louis, MO, USA), pullulan (Sigma, St. Louis, MO, USA) and soluble starch(Difco Corporation, Detroit, Michigan, USA) were used.

The average molecular weight of these polysaccharides is listed in Table 1 and is based on chromatography measurements reported by each manufacturer. Slurries were prepared with deionized water 160 ml at room temperature by adding polysaccharides to an aqueous solution of 0.01 M NaCl. The amounts of polysaccharides were changed into three levels in weight base: 2.376 g(low), 3.168 g(middle), and 4.752 g(high). Then alumina powder 156 g was added to achieve the volume fraction of 20% in every slurry. Schilling et al.[23] reported that about 0.02 g of maltodextrin 040 per g of alumina absorbs to alumina in the same alumina volume concentration. This amount is very close to 3.168 g of maltodextrin in the slurries used in this research, which is useful to study the effects of polysaccharide concentrations on the rheological properties of alumina slurries.

Each slurry was then sonicated for 2 min using a sonifier (CV17 Vibracell, sonics and Materials Inc., Danbury, CT, USA). The sonicator was operated at 60–80% of the maximum power output of 600 W. After sonication, the slurries were equilibrated in a shaker for 24 h to reach the equilibrium. We did not add acids or bases to the slurry in order to avoid the possible interactions between polysaccharides and acids or bases. PHs of slurries with polysaccharides and without acids or bases are found to be around 8.9, where alumina particles have little electrostatic repulsive force.

Aqueous alumina slurry was loaded into a stainless-steel container that was encased in a temperature controlled bath which was maintained at 25°C. The total volume of the slurry for rheological measurement is 65.4 ml. A long cylindrical spindle was connected to a rheometer(-Rheostress RS75, Gebrueder Haake GmbH, Germany). The specifications of the container and the spindle, and the spaces between them were same with DIN Standard 5100 No. 40. Shear rate increased from 0.13 to 400 s^{-1}. Data, including shear stress and shear rate were collected five times after getting stable data and averaged in a dedicated computer.

3. Results and discussions

Fig. 1 shows the shear stresses of alumina slurries with different concentration of maltodextrin M200 at different shear rates, where shear stresses increased with increasing shear rate. Schilling et al.[24] reported that aqueous slurries of 20 vol% alumina exhibit a transition from strongly-flocculated, pseudoplastic behavior to a Newtonian-like state upon the addition of maltodextrin 040. Fig. 1 also shows similar significant effects of maltodextrin M200 addition on the shear stresses, which implies that maltodextrin M200 is important in the steric hindrance effects of alumina particles in a slurry. Fig. 2 shows the shear stresses of alumina slurries with different concentration of maltodextrin M100 at different shear rates. Shear stresses also increased with increasing shear rate as shown in Fig. 2. Figs. 1 and 2 show very similar concentration effects of maltodextrin on the shear stresses. Fig. 3 shows the shear stresses of alumina slurries with different concentration of maltodextrin M040 at different shear rates. Shear stresses increased with increasing shear rate as shown in Figs. 1 and 2. Figs. 1–3 show high shear stresses in alumina slurries with low concentration of maltodextrin and lower shear stresses with mid and high concentrations of maltodextrin.

Fig. 4 shows shear stresses as a function of shear rate and dextran 9500 concentration in alumina slurries. Shear stresses increased with increasing shear rate as shown in Figs. 1–3. Fig. 4 shows high shear stresses in alumina slurries with low and mid concentrations and lower shear stresses with high concentration. Fig. 5 shows similar shear stresses as a function of shear rate and dextran 69,000 concentrations in alumina slurries. Shear stresses increased with increasing shear rate as shown in Figs. 1–4. Fig. 5 shows similar shear stresses in alumina slurries with (different dextran 9500) concentrations. Fig. 6 shows shear stresses as a function of shear

Table 1
Average molecular weight of polysaccharides

Specimen	Average molecular weight, Dalton
Maltodextrin M200	900
Maltodextrin M100	1800
Maltodextrin M040	3600
Dextran 9,500	9500
Dextran 69,000	69,000
Pullulan	72,500
Dextran 2,000,000	2,000,000
Soluble starch	–

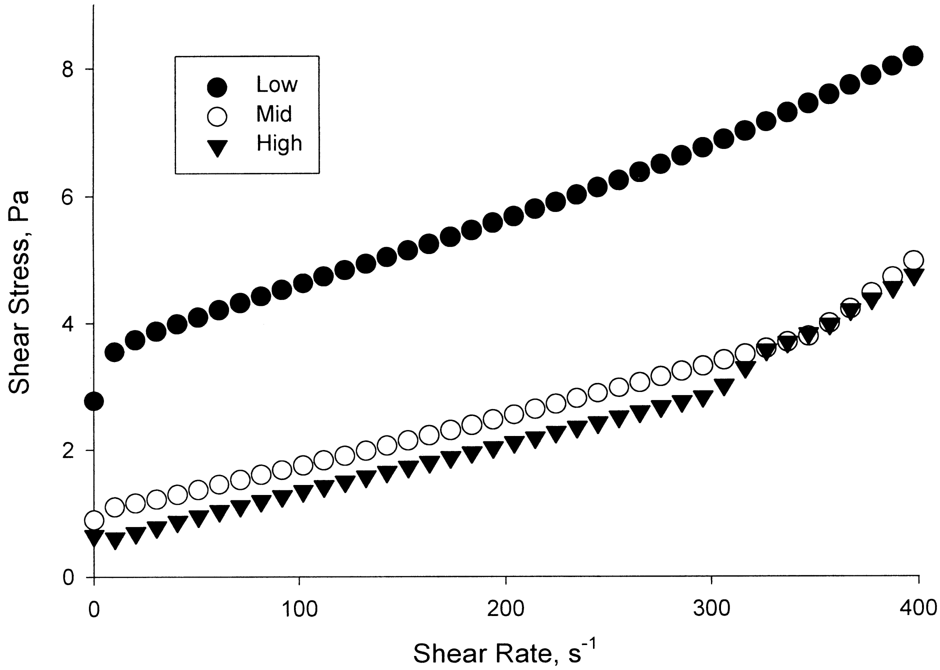

Fig. 1. Shear stress as a function of shear rate and maltodextrin M200 concentration in alumina slurries. All slurries contained an alumina fraction of $\phi = 0.2$ and 0.01 M NaCl.

rate and dextran 2,000,000 concentrations in alumina slurries. Shear stresses increased with increasing shear rate as shown in Figs. 4 and 5. Fig. 6 shows low shear stresses in alumina slurries with low and mid concentrations and higher shear stresses with high concentration. Concentration effects were reversed with increasing molecular weight (dextran 9500–2,000,000) in Fig 6. This conversion in the concentration effects of dextran seems to be related to the molecular configuration of polysaccharide in aqueous alumina slurries.

Fig. 7 shows shear stresses as a function of shear rate and pullulan concentration in alumina slurries. Shear

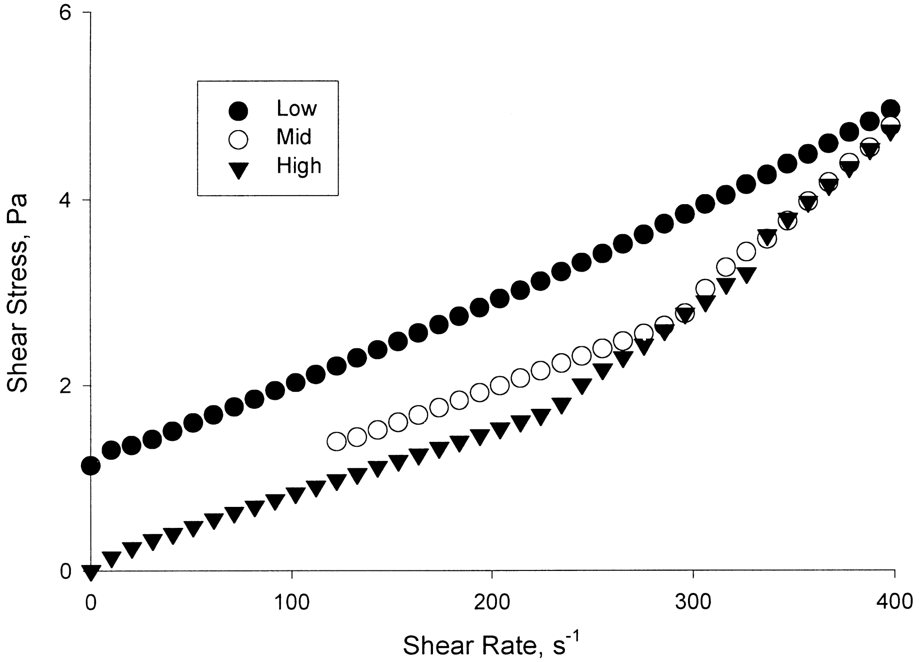

Fig. 2. Shear stress as a function of shear rate and maltodextrin M100 concentration in alumina slurries. All slurries contained an alumina fraction of $\phi = 0.2$ and 0.01 M NaCl.

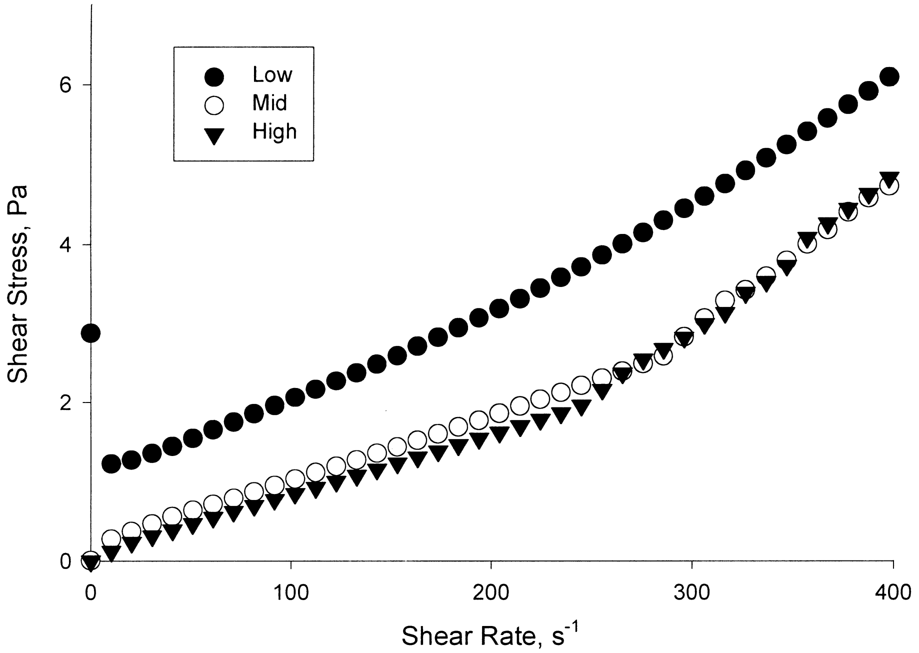

Fig. 3. Shear stress as a function of shear rate and maltodextrin M040 concentration in alumina slurries. All slurries contained an alumina fraction of $\phi = 0.2$ and 0.01 M NaCl.

stresses increased with increasing shear rate as well. Fig. 7 shows similar shear stresses with alumina slurries with dextran 69,000 in Fig. 5 and dextran 2,000,000 in Fig. 6. Concentration effects were reversed a little bit like Fig. 6, where alumina slurries with pulluran showed similar shear stresses with alumina slurries with dextran 69,000. Pullulan and dextran 69,000 have similar average molecular weights and these molecular weights seem to be related to the rheological behavior in aqueous alumina slurries with polysaccharides. Shear stress increases

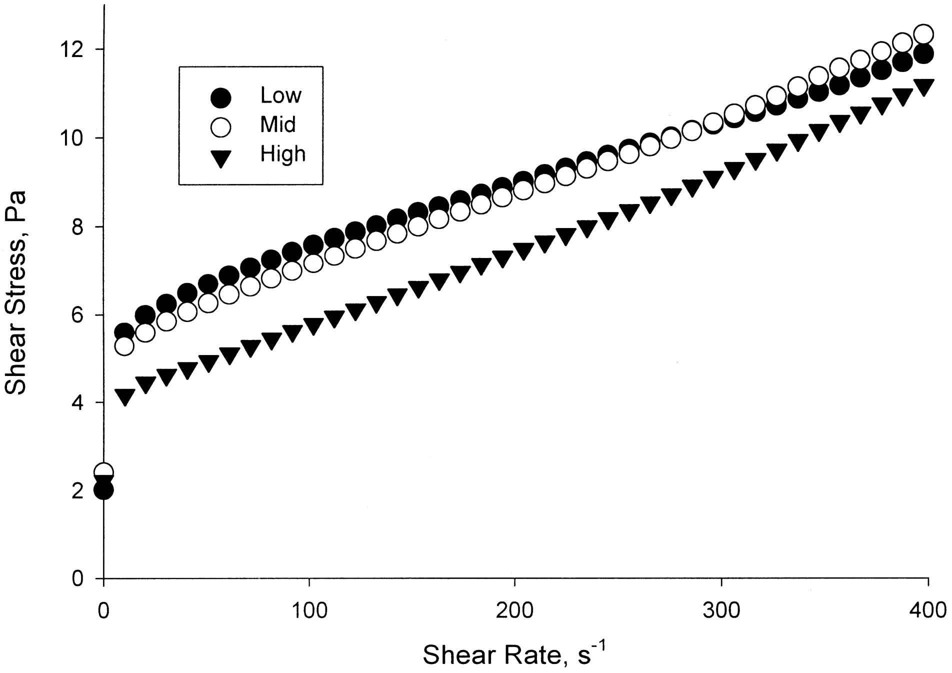

Fig. 4. Shear stress as a function of shear rate and dextran 9500 concentration in alumina slurries. All slurries contained an alumina fraction of $\phi = 0.2$ and 0.01 M NaCl.

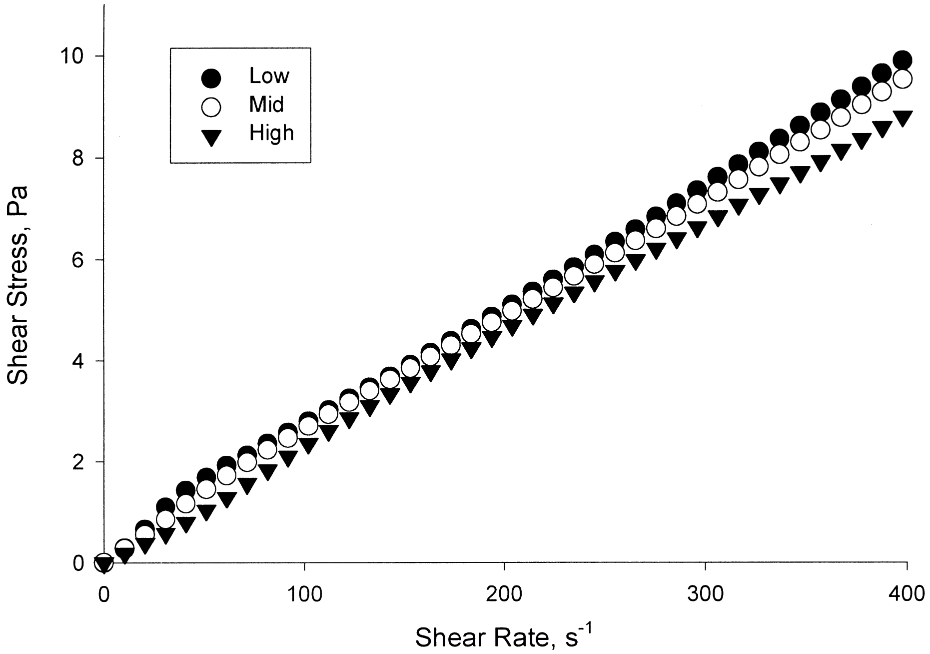

Fig. 5. Shear stress as a function of shear rate and dextran 69,000 concentration in alumina slurries. All slurries contained an alumina fraction of $\phi = 0.2$ and 0.01 M NaCl.

with increasing polysaccharide concentration may be related to possible polysaccharide to polysaccharide interaction in an aqueous alumina suspension.

Fig. 8 shows shear stresses as a function of shear rate and soluble starch concentration in alumina slurries. Shear stresses increased with increasing shear rate as well. Fig. 8 shows similar shear stresses with alumina slurries with maltodextrin 100 in Fig. 2. Concentration effects in Figs. 2 and 8 were similar to each other and alumina slurries with soluble starch showed similar shear stresses with alumina slurries with maltodextrin. Shear stress decrease with the increase of polysaccharide concentration is related to typical steric hindrance effects.

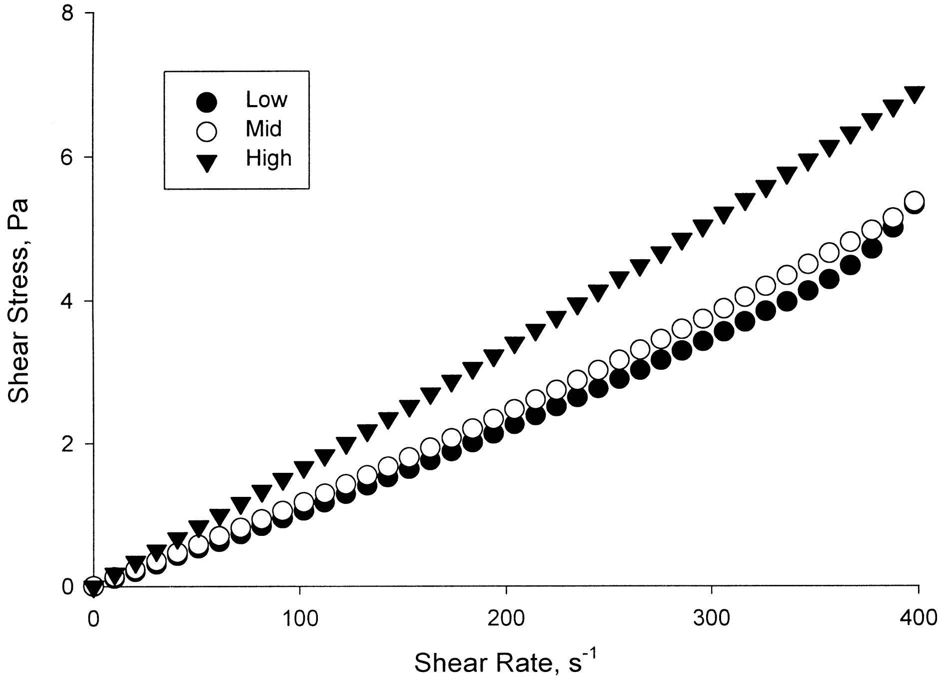

Fig. 6. Shear stress as a function of shear rate and dextran 2,000,000 concentration in alumina slurries. All slurries contained an alumina fraction of $\phi = 0.2$ and 0.01 M NaCl.

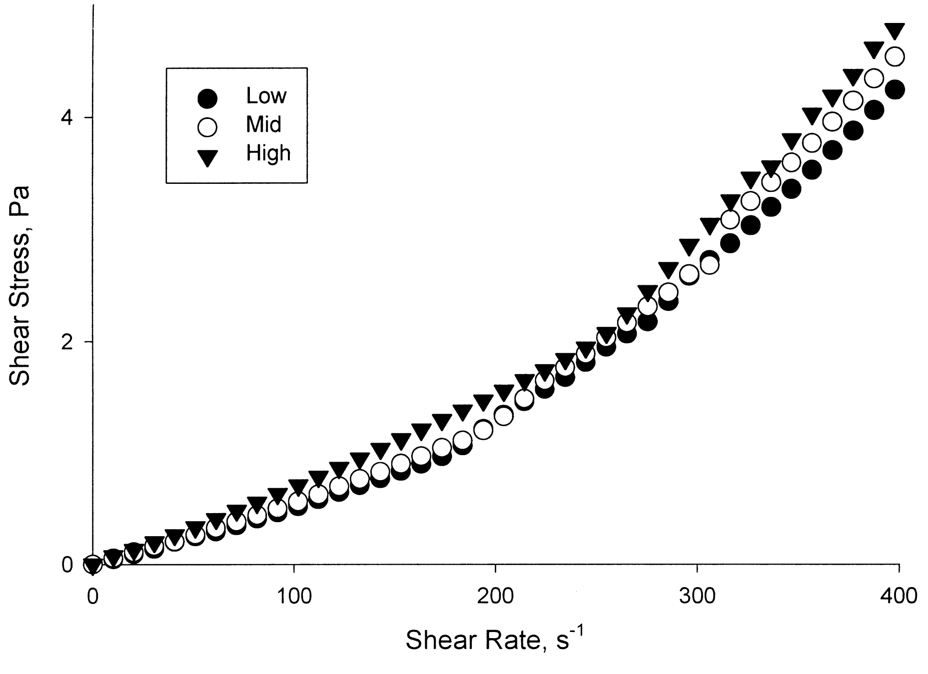

Fig. 7. Shear stress as a function of shear rate and pullulan concentration in alumina slurries. All slurries contained an alumina fraction of $\phi = 0.2$ and 0.01 M NaCl.

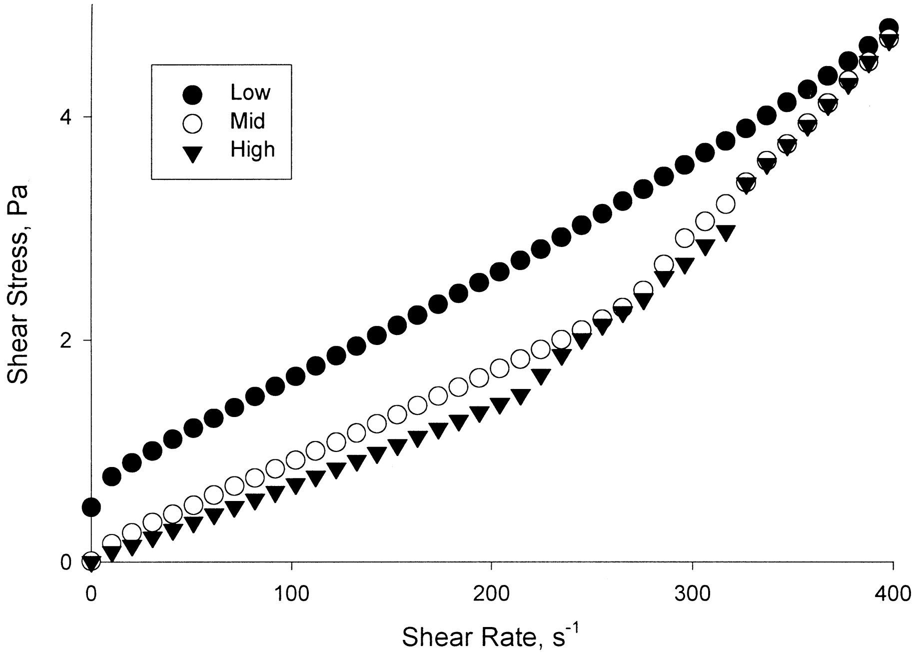

Fig. 8. Shear stress as a function of shear rate and soluble starch concentration in alumina slurries. All slurries contained an alumina fraction $\phi = 0.2$ and 0.01 M NaCl.

4. Conclusions

Shear stresses at different strain rates decreased greatly showing Newtonian-like behavior for most of the alumina slurries with polysaccharides. Shear stresses increased with the increase of shear rate for all slurries. Shear stress decreased with the increase of polysaccharide concentration but increased with increasing the polysaccharide concentration in an aqueous slurry with dextran 2,000,000 and pullulan. These effects seem to be related to the possible polysaccharide to polysaccharide interaction in aqueous alumina suspension.

Even though effects of molecular weight of polysaccharide show some fluctuations, shear stresses increased with the increase of polysaccharide molecular weight at first but decreased later, in general. Shear stresses at different strain rates are related to the polysaccharide content and their molecular weights.

Acknowledgements

The authors wish to thank the Office of Basic Energy Sciences at the U.S. Department of Energy for supporting this research.

References

1. Pujari, V. K., Effect of powder characteristics on compounding and green microstructure in the injection molding process. *J. Am. Ceram. Soc.*, 1989, **72**(10), 1981–1984.
2. Kramer, T. and Lange, F. F., Rheology and particle packing of chem- and phys-adsorbed alkylated silicon nitride powders. *J. Am. Ceram. Soc.*, 1994, **77**(4), 922–928.
3. Stangle, G. C. and Aksay, I. A., Simultaneous momentum, heat and mass transfer with chemical reaction in a disordered porous medium: application to binder removal from a ceramic green body. *Chem. Engr. Sci.*, 1990, **45**(7), 1719–1731.
4. van Olphen, H., *An Introduction to Clay Colloid Chemistry*, 2nd edn. John Wiley and Sons, New York, 1977.
5. Pashley, R. M. and Israelachvili, J. N., DLVO and hydration forces between mica surfaces in Mg^{+2}, Ca^{+2}, Sr^{+2}, and Ba^{+2} chloride solutions. *J. Colloid Interface Sci.*, 1984, **97**, 446–455.
6. Lawrence, W. G., The structure of water and its role in the clay–water system. In *Ceramic Processing Before Firing*, ed. G. Y. Onoda Jr. and L. L. Hench. John Wiley and Sons, New York, 1978, pp. 193–210.
7. Velamakanni, B. V., Chang, J. C., Lange, F. F. and Pearson, D. S., New method for efficient colloidal particle packing via modulation of repulsive lubricating hydrating forces. *Langmuir*, 1990, **6**, 1323–1325.
8. Chang, J. C., Velamakanni, B., Lange, F. and Pearson, D., Centrifugal consolidation of Al_2O_3 and Al_2O_3/ZrO_2 composite slurries vs interparticle potentials: particle packing and mass segregation. *J. Am. Ceram. Soc.*, 1991, **74**(9), 2201–2204.
9. Velamakanni, B. V., Lange, F. F., Zok, F. W. and Pearson, D. S., Influence of interparticle forces on the rheological behavior of pressure-consolidated alumina particle slurries. *J. Am. Ceram. Soc.*, 1994, **77**(1), 216–220.
10. Chang, J. C., Lange, F. F. and Pearson, D. S., Viscosity and yield stress of alumina slurries containing large concentrations of electrolyte. *J. Am. Ceram. Soc.*, 1994, **77**(1), 19–26.
11. Chang, J. C., Lange, F. F., Pearson, D. S. and Pollinger, J. P., Pressure sensitivity for particle packing of aqueous alumina slurries vs: interparticle potential. *J. Am. Ceram. Soc.*, 1994, **77**(5), 1357–1360.
12. Luther, E. P., Kramer, T. M., Lange, F. F. and Pearson, D. S., Development of short-range repulsive potentials in aqueous, silicon nitride slurries. *J. Am. Ceram. Soc.*, 1994, **77**(4), 1047–1051.

13. Franks, G. V., Velamakanni, B. V. and Lange, F. F., Vibraforming and in-situ flocculation of consolidated, coagulated, alumina slurries. *J. Am. Ceram. Soc*., 1995, **78**(5), 1324–1328.
14. Franks, G. C. and Lange, F. F., Plastic-to brittle transition of saturated, alumina powder compacts. *J. Am. Ceram. Soc*., 1996, **79**(12), 3161–3168.
15. Ducker, W. A., Xu, Z., Israelachvilli, J. N. and Clake, D. R., Forces between alumina surfaces in salt solutions: non-DLVO forces and their effect on colloidal processing. *J. Am. Ceram. Soc*., 1994, **77**(11), 437–443.
16. Yin, T. K., Aksay, I. A. and Eichinger, B. E., Lubricating polymers for powder compaction. In *Ceramic Transactions Volume 1, Ceramic Powder Science II*, ed. G. L. Messing, E. R. Fuller Jr. and H. Hausner. American Ceramic Society, Westerville, Ohio, 1988, pp. 654–662.
17. Schilling, C. H., Plastic shaping of colloidal ceramics, Ph.D. thesis, University of Washington, Seattle, Washington, 1992.
18. Bergström, L., Schilling, C. H. and Aksay, I., Consolidation behavior of flocculated alumina suspensions. *J. Am. Ceram. Soc*., 1992, **75**(12), 3305–3314.
19. Luther, E. P., Yanez, J. A., Franks, G. V., Lange, F. F. and Pearson, D. S., Effect of ammonium citrate on the rheology and particle packing of alumina slurries. *J. Am. Ceram. Soc*., 1995, **78**(6), 1495–5000.
20. Chan, T.-Y. and Lin, S.-T., Effects of stearic acid on the injection molding of alumina. *J. Am. Ceram. Soc*., 1995, **78**(10), 2746–2752.
21. Schilling, C. H., Biner, S. B., Goel, H. and Jane, J. L., Plastic shaping of aqueous alumina suspensions with sucrose and maltodextrin additives. *J. Environmental Polymer Degradation*, 1995, **3**(3), 153–160.
22. Goel, H., Schilling, C. H., Biner, S. B., Moore, J. A. and Lograsso, B. K., Plastic shaping of aqueous alumina suspensions with saccharides and dicarboxylic acids. In *Science, Technology, and Commercialization of Powder Synthesis and Shape Forming Processes*, ed. J. J. Kingsley, C. H. Schilling and J. H. Adair. American Ceramic Society, Westerville, Ohio, 1996, pp. 241–252.
23. Schilling, C. H., Bellman, R. H., Smith, R. M. & Goel, H. Plasticizing aqueous suspensions of concentrated alumina with maltodextrin sugar, accepted in *J. Am. Ceram. Soc*.
24. Schilling, C. H., Garcia, V. J., Smith, R. M. and Roberts, R. A., Ultrasonic- and mechanical behavior of green- and partially-sintered alumina: effects of slurry consolidation chemistry, accepted in *J. Am. Ceram. Soc*.