

# Effects of Monosaccharides and Disaccharides on the Rheological Behavior of Dense Alumina Slurries

## II. Oscillation Testing Method

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Complex viscosities of dense alumina slurries over 45% volume density measured with the oscillating method were correlated well with Casson model. Among several monosaccharides and disaccharides studied here, fructose and sucrose showed good rheological properties in making dense alumina slurry plastic compared to other monosaccharides and disaccharides like glucose, galactose, arabinose, xylose and maltose. Sucrose content or additional water content in dense alumina slurry with sucrose contributed to the plasticity of the slurries

**Key words :** Monosaccharide, Disaccharide, Rheology, Alumina, Slurry, Oscillation

## I. Introduction

Rheology is the science of deformation and flow.<sup>1)</sup> Rheological properties in ceramic processing is important for shape forming. A better understanding on the rheological property is needed to improve the reliability of the processing and also to advance to new methods of forming.<sup>2-4)</sup> The rheological properties of alumina slurries based on stress-relaxation measurements have been studied a lot with an equibiaxial extensional rheometer. The rheological behavior of alumina suspensions deviate from Newtonian behavior due to many variables like inter-particle interactions and polymer to particle interaction.

Slurries can form agglomerates depending on the nature of the particle interactions. Agglomerated particles form networks and the networks are affected by time-dependent physical, chemical reactions and mechanical stirring. These networks show shear thinning behavior because the initially continuous network breaks into smaller flow units. This time dependent process is usually faster at higher temperature and agitation. Complex interactions occur during the flow of suspensions with mixed particle sizes. Hindered rotation and mutual particle interference cause dilatant behavior. Particle size and its distribution are important to the rheological properties of the alumina suspension.

Schilling et al.<sup>5-7)</sup> studied alumina slurries with polysaccharides. They found that saturated aqueous solutions of monosaccharides and disaccharides form very thick but pourable pastes with a very strong shear thickening. This pourability was found even in dense alumina slurry with monosaccharides and disaccharides.

The rheological properties of saturated monosaccharide

and disaccharide solutions in dense alumina slurry were studied in order to increase the solid volume content without sacrificing plasticity. Forced oscillation testing method was performed and this method is a non-destructive method to determine the viscous and elastic components of a viscoelastic substance.

## II. Experimental Procedure

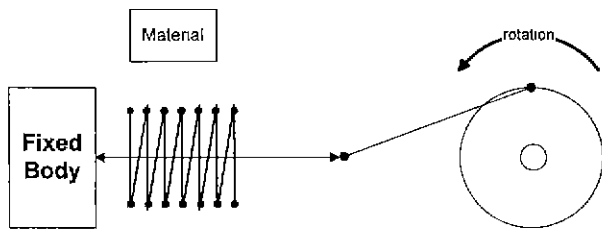
All slurries were prepared with deionized water and calcined  $\alpha$ - $\text{Al}_2\text{O}_3$  powder having an equiaxed particle shape, an average particle size of 0.4  $\mu\text{m}$  and a specific surface area of 8.5  $\text{m}^2$  per gram (Type A-16 SG, Alcoa Corporation, Bauxite, AR, U.S.A). Glucose, galactose, fructose, arabinose, xylose, maltose, and sucrose were used in the as-received condition (Sigma, St. Louis, MO, U.S.A). Their chemical structures were summarized in Part I of this paper.<sup>8)</sup> At the same time, sample preparation and testing conditions were reported in Part I of this paper.<sup>8)</sup>

Fig. 1(a) shows the schematic representation of the oscillating test method and Fig. 1(b) shows the phases of the applied torsion, the elastic response and the viscous response. Data, including storage modulus  $G'$  and the loss modulus  $G''$  were collected three times after getting stable data and averaged in a dedicated computer.

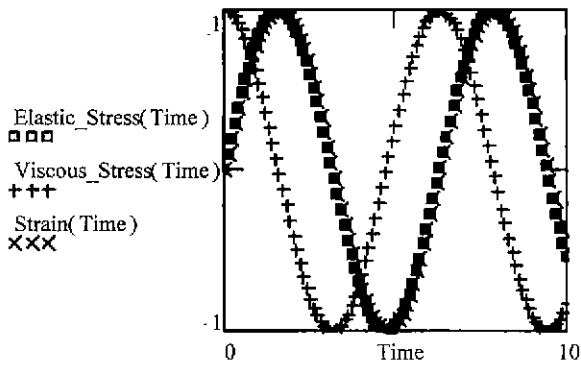
## III. Results and Discussion

### 1. Effect of different monosaccharides and disaccharides

Fig. 2 shows the results obtained from the oscillating testing in different frequency (unit, rad in sec). Elastic



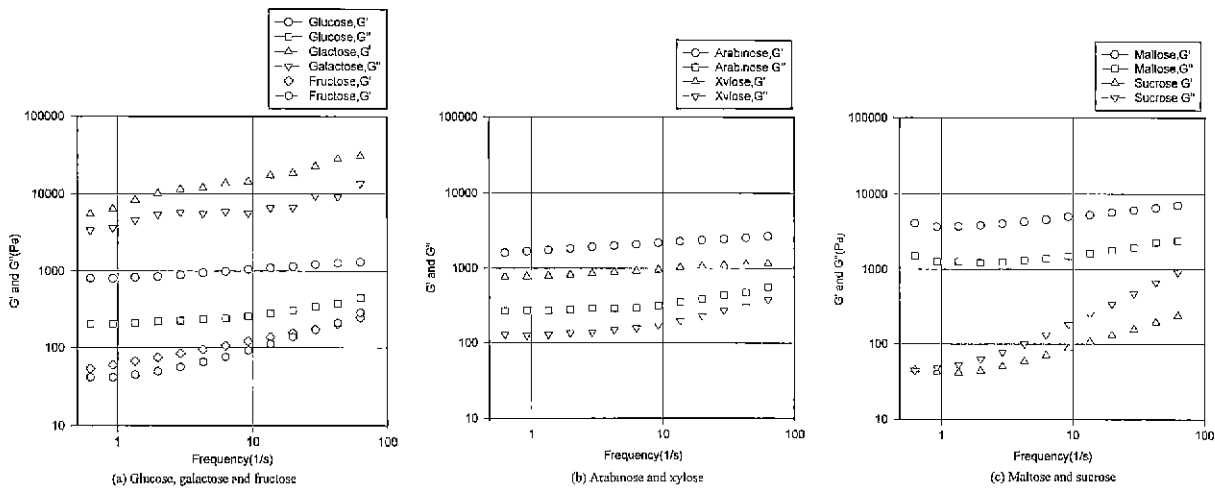
a) oscillating method



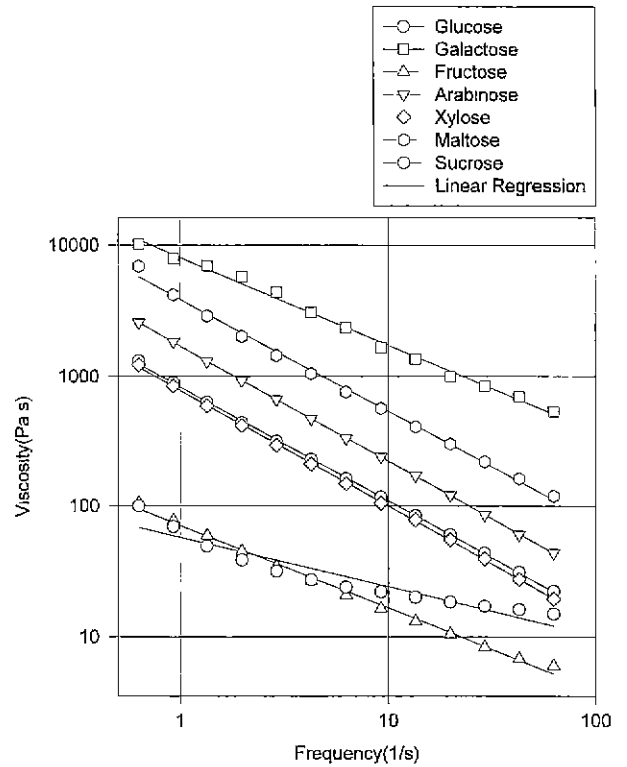
b) phase difference in oscillating mode

**Fig. 1.** Schematic representation of the oscillating method and the phase differences in oscillating mode.

components  $G'$  (storage modulus) are far greater than the viscous components  $G''$  (loss modulus) in the slurries containing glucose, galactose, arabinose and xylose over all frequency range whereas  $G'$  is almost same with or less than  $G''$  in the slurries containing fructose and sucrose. At the same time, general levels for both moduli were low for these two slurries containing fructose and sucrose. This means that other slurries containing glucose, galactose, arabinose and xylose are far more elastic and stiff than the slurries containing fructose and sucrose. Slurries containing glucose, galactose, arabinose and xylose showed that the changes of  $G'$  and  $G''$  with frequency are similar to the curves generally observed in



**Fig. 2.**  $G'$  and  $G''$  in different frequency at fixed stress 4 Pa.



**Fig. 3.** Complex viscosities with linear regressions.

the curves of viscoelastic solid compared to the slurries containing fructose and sucrose which are similar to those of viscoelastic liquid.<sup>91</sup> Fig. 3 shows the change of complex viscosities with frequency and their linear regressions obtained from oscillation testing. We found that these data were well fitted both in linear regressions and in Casson model which follows.

$$\eta = ((\tau_0/\gamma)^{0.5} + \eta_p^{0.5})^2$$

where  $\eta$  is the viscosity,  $\tau_0$  the yield stress,  $\gamma$  the shear rate and  $\eta_p$  the viscosity limit.

**Table 1.** Constants in Casson Model

Name	Sugars	$\tau_0$	$\eta_p$
A-GL	Glucose	752	2.6
A-GA	Galactose	4127	550.8
A-FR	Fructose	46	3.3
A-RA	Arabinose	1439	10.4
A-XY	Xylose	707	2.2
A-MA	Maltose	4160	0.02
A-SU	Sucrose	30	7.4

In Fig. 3, slurries containing fructose and sucrose showed quite lower viscosities over all frequency range compared to other slurries. Especially, slurry containing sucrose showed some deviation in a linear dependency of viscosity on the frequency whereas all other samples showed linear dependence on frequency with similar slopes in Fig. 3.

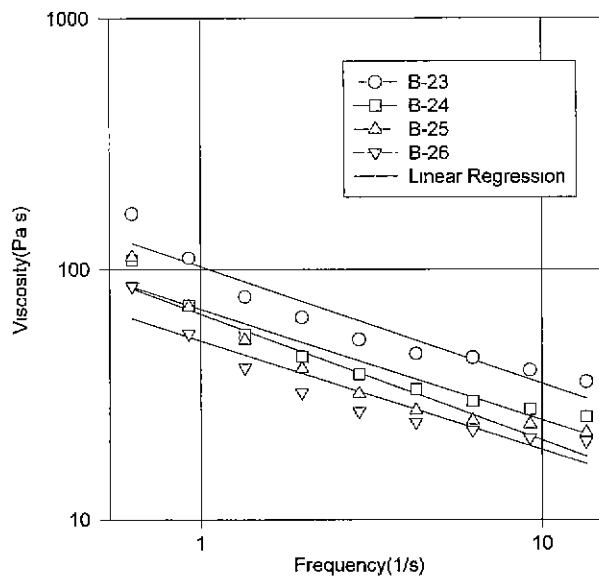
The yield stress,  $\tau_0$  and the viscosity limit,  $\eta_p$  were obtained through regression analysis. Alumina slurries containing sucrose and fructose show very low  $\tau_0$  (30 and 45, respectively) but alumina slurries containing galactose and maltose show much higher  $\tau_0$  (4127 and 4160, respectively) than slurries containing sucrose and fructose as shown in Table 1. This shows that fructose and sucrose are most effective in improving rheological properties of dense alumina slurries.

**2. Effect of sucrose content**

Among monosaccharides and disaccharides studied here sucrose and fructose were effective in plasticizing dense alumina slurries. We selected sucrose as a representative additive in order to check whether the concentration of saturated solution affects the plasticity of dense alumina slurry (series-B). Sucrose was added as saturated sucrose solution and its content increased from 23 ml to 26 ml as shown in Table 2. Fig. 4 shows storage moduli  $G'$  and loss moduli  $G''$  in series-B. Even

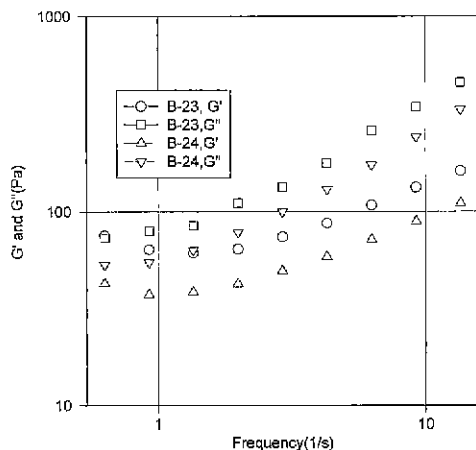
**Table 2.** Constants in Casson Model with Different Sucrose Contents in Series B

Name	Sat. Sol. Vol., ml	$\tau_0$	$\eta_p$
B-23	23	43	15.9
B-24	24	26	12.4
B-25	25	32	8.1
B-26	26	20	9.4

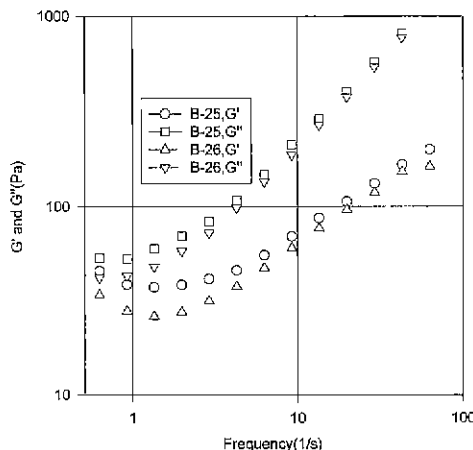


**Fig. 5.** Complex viscosities with linear regressions.

though all curves showed minor difference, the ratio  $G''/G'$  increased with sucrose addition. Fig. 5 shows complex viscosities at different sucrose content in alumina slurries with linear regressions where viscosities decreased with the increase of sucrose content. Linear regressions do not fit well with complex viscosities but complex viscosities were correlated well with Casson model corresponding to the results in Fig. 3. This is mainly because Casson model can correlate both linear and nonlinear changes of



(a) B-23 and B-24



(b) B-25 and B-26

**Fig. 4.**  $G'$  and  $G''$  in different frequency.

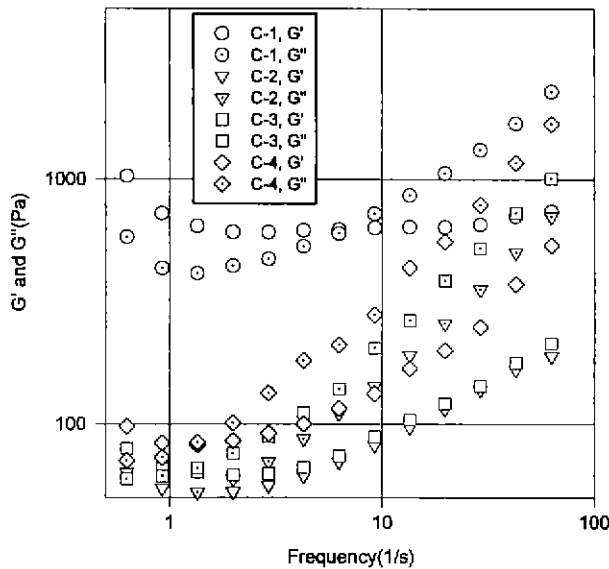


Fig. 6.  $G'$  and  $G''$  in different frequency.

viscosities. Table 2 shows  $\tau_0$  and  $\eta_p$  values in Casson equation where  $\tau_0$  and  $\eta_p$  decreased a little with increasing the amount of saturated sucrose solution. This means alumina slurries become more plastic with the addition of the saturated sucrose solution even though  $\tau_0$  and  $\eta_p$  showed minor changes compared with series-A. Alumina slurries become a little more fluid with the addition of saturated sucrose solution.

### 3. Effect of additional water content

Effects of additional water content in the alumina slurry with sucrose were checked. Fig. 6 shows the changes in storage modulus  $G'$  and loss modulus  $G''$  with different water content added as an extra in alumina slurries with

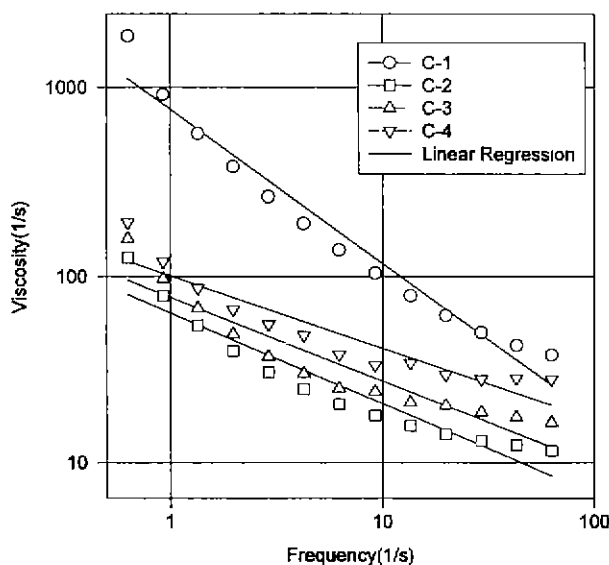


Fig. 7. Viscosities with linear regressions.

Table 3. Constants in Casson Model with Different Sucrose Contents

Name	Suppl. Water, ml	$\tau_0$	$\eta_p$
C-1	1	1107	0.23
C-2	2	53	2.5
C-3	3	64	3.7
C-4	4	62	10.4

sucrose. Fig. 7 shows complex viscosities with different additional water contents in alumina slurry with sucrose. Water addition in the alumina slurry with saturated sucrose solution caused a slight increase in  $G''/G'$ . Fig. 7 showed viscosity drop a lot at first and increase a little later with more water addition. Table 3 shows the constants in Casson model where  $\eta_p$  showed a gradual increase and  $\tau_0$  showed a relatively big decrease at first. These trends in Table 3 are different from the results in Table 2 where both  $\tau_0$  and  $\eta_p$  decreased in series-B. Generally speaking, effect of water addition seems to be different from the effect of sucrose addition. Even though it is somewhat hard to understand all, general trends showed the contribution of water to the plasticity of the alumina slurry.

## IV. Conclusions

Complex viscosities of dense alumina slurry measured with the oscillating test correlated well with Casson model. Fructose and sucrose were effective in the plasticity of alumina slurries. Main reason to this effect seems to be molecular configuration rather than molecular weight. Fructose has strong charges around both ends of the fructose molecule helpful to the steric hindrance effect. Main reason to the plasticity improvement with sucrose addition seems to be related to its decomposition into fructose and glucose upon hydrolysis. In the case of dense alumina slurry with sucrose, change in sucrose content or additional water content contributed to the viscosities of the slurries.

## References

1. J. S. Reed, "Ch. 15 Rheological Behavior of Slurries and Pastes," in *Introduction of Ceramic Processing*, pp. 227-252, John Wiley & Sons, Inc., New York, 1988.
2. L. Bergstrom, et al., "Rheology and Processing of  $Al_2O_3$ -SiC Whisker Composite Suspensions," pp. 391-395, *Ceramic Processing Science and Technology*, Edited by Hans Hausner, Gary L. Messing and Shin-ichi Hirano, Ceram. Trans. vol. 51, American Ceramic Society, Westerville, OH, 1995.
3. E. P. Luther, J. A. Yanez, G. V. Franks, F. F. Lange and D. S. Pearson, "Effect of Ammonium Citrate on the Rheology and Particle Packing of Alumina Slurries," *J. Am. Ceram. Soc.*, **78**(6), 1495-1500 (1995).
4. V. Ramakrishnan and Pradip, "Yield Stress of Alumina-

- Zirconia Suspensions," *J. Am. Ceram. Soc.*, **79**(10) 2567-76 (1996).
5. C. H. Schilling, S. B. Biner, H. Goel and J.-L. Jane, "Plastic Shaping of Aqueous Alumina Suspensions with Sucrose and Maltodextrin Additives," *J. Environmental Polymer Degradation*, **3**(3), 153-60(1995).
  6. C. H. Schilling, S. P. Huss and J. N. Gray, "Regulating Density Gradients in Slip Consolidation: A New Methodology"; pp. 117-131 in *Science of Whitewares*, Edited by V. E. Henkes, G. Y. Onoda and W. M. Carty, American Ceramic Society, Westerville, Ohio, 1996.
  7. C. H. Schilling, R. Bellman, R. M. Smith, H. Goel and H. Giesche, "Plasticizing Aqueous Suspensions of Concentrated Alumina with Maltodextrin," Submitted to *J. Am. Ceram. Soc.* Jan. 1997.
  8. J. C. Kim, K. H. Auh and C. H. Schilling, "Effects of Monosaccharides and Disaccharides on the Rheological Behavior of Dense Alumina Slurries: I. Creep Testing Method," Submitted to *Korean Ceramic Society*, Jan. 1999.
  9. G. Schramm, *A Practical Approach to Rheology and Rheometry*, Haake, New Jersey. 1994