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Effects of Monosaccharides and Disaccharides on the Rheological Behavior of Dense Alumina Slurries
I. Creep Testing Method

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Rheological properties of dense alumina slurries over 45 volume % with different monosaccharides and disaccharides were checked in order to increase the solid content of dense slurries without sacrificing plasticity using creep testing method. Strain in creep test showed good correlations with Burger model which is expressed as an exponential function of time. Among several monosaccharides and disaccharides studied here, fructose and sucrose were most effective in making dense alumina slurry plastic than other monosaccharides and disaccharides like glucose, galactose, arabinose, xylose and maltose. In the case of dense alumina slurry with sucrose, sucrose content or additional water content enhanced to the plasticity of the slurries.

Key words : Monosaccharide, Disaccharide, Rheology, Alumina Slurry, Burger

I. Introduction

Non-clay based ceramics have received much attention due to their excellent properties in recent several decades. Even though there has been significant advance in controlling particle size, shape, and surface chemistry, there are still many problems in the application of traditional shape-forming techniques which were mainly designed for aqueous, and clay-based slurries. Many researchers have worked to improve the plasticity of non-clay ceramics with high content of organic binder in order to use plastic-forming techniques.[1-3] Decomposition of hydrocarbon binders causes environmental hazards and many problems during sintering like unwanted cracks and shape distortion due to gas generation during pyrolysis, and degradation in sintering properties due to residual carbon.[2] This is why aqueous slurry is necessary to produce ceramics without residual hydrocarbon, unwanted cracks, and shape distortions in sintered parts. In order to improve the plasticity of ceramics the rheological properties of ceramics were studied, compared, and analyzed.[4-17]

Major difference is mainly attributed to the nature of surface charges and the adsorption behaviors on ceramic surfaces. Non-clay ceramic powders do not have particle shapes and surface properties which are necessary for particle rearrangement during forming process. Generally speaking, two different approaches have been tried to improve the plasticity of concentrated slurries of non-clay ceramic powders. The one is the hydration-layer approach[5-12] and the other is adsorbate-mediated steric hindrance.[4,13-17] The hydration-layer approach used short-range, interparticle forces which were produced by the surface adsorption of indifferent electrolytes in dispersed, and aqueous slurries of non-clay ceramic powder. Adsorbate-mediated steric hindrance creates steric adlayer inhibiting complete mutual approach of individual particles.

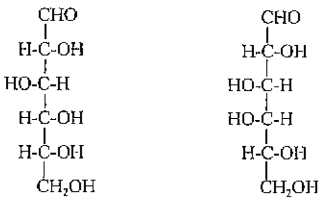
Recently, Schilling and co-workers have studied dense alumina slurries with polysaccharides.[4,14,15] It was observed that saturated aqueous solutions of monosaccharides and disaccharides form very thick but pourable pastes with a very strong shear thickening.[18] It was necessary to add saturated monosaccharide and disaccharide solution in certain proportions into alumina powder in order to observe this effect. This effect depends on time because monosaccharide and disaccharide molecules absorb water gradually and dense alumina slurry dries. This effect of pourability was found even in dense alumina slurry with monosaccharides and disaccharides.

In this study, the rheological properties of dense alumina slurries made with saturated monosaccharide and disaccharide solutions were studied in order to decrease drying shrinkage and increase solid volume content without sacrificing plasticity. Creep rheology testing methods were performed. Creep method[19] is a non-destructive method to determine the viscous and elastic components of a viscoelastic substance. Especially in creep testing, zero-shear viscosity of fluids at extremely low shear rates can be determined which will represent the rheological properties like sedimentation, sagging, and slumping.

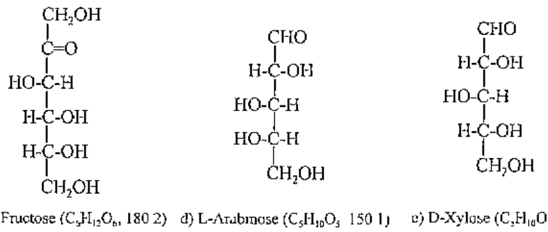
II. Experimental Procedure

All slurries were prepared with deionized water. Alumina slurries were prepared with calcined 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 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). Fig. 1 and 2 show the chemical structures of monosaccharides and disaccharides used in this research[20]: monosaccharides which are not hydrolyzable into smaller units in Fig. 1 and disaccharides which are hydrolyzable in Fig. 2. All monosaccharides and disaccharides were used in the state of saturated solution. Saturated monosaccharide and disaccharide solutions were made by adding monosaccharide and disaccharide into water until it saturated. This saturated solution was added using buret into the alumina powder (100 g). All the blends were hand mixed in a plastic bottle with a spatula thoroughly after each addition of 0.1 ml monosaccharide and disaccharide solution. This process was repeated until all blend became one wet big ball where 0.1 to 0.2 ml addition of saturated solution to this big ball made a pourable dense slurry.[18] Slurries made in this way were kept in the shaker during experiment.

Three series (series-A, B and C) have been designed as experimental conditions. Series-A was designed to check which monosaccharides and disaccharides are most effective in increasing plasticity of slurries. Table 1 shows the monosaccharides and disaccharides used in this research and their contents in the form of supersaturated solution with the alumina powder 100 g necessary in order to make a pourable dense slurry. Solid volume percentages in Table 1 vary from 51 to 57%. We selected sucrose for the following experiments (series-B and -C) because sucrose showed good effects in plasticizing dense alumina slurry after reviewing the results in series-A. We checked the effect of sucrose content by changing the relative content of sucrose with the alumina powder 100 g as shown in Table 2. (series-B) Saturated solution of sucrose content varied from 23 to 26 ml with different solid volume content. Another experiment (Series-C) was designed to check the effect of additional water content to dense alumina slurry made of 100 g alumina and 21 ml saturated sucrose solution. Water content increased from 1 to 4 ml and solid volume percentages were lowered as a result as shown in Table 3.

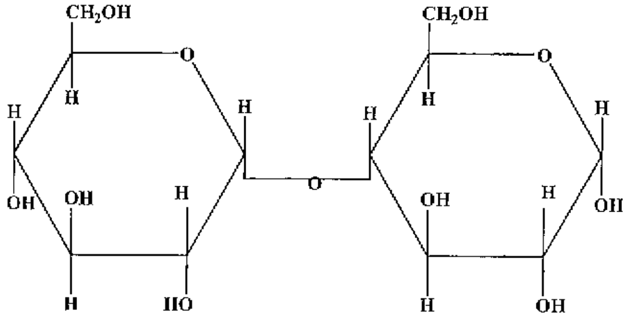


a) D-Glucose ($C_6H_{12}O_6$, 180 2) b) D-Galactose ($C_6H_{12}O_6$, 180 2)

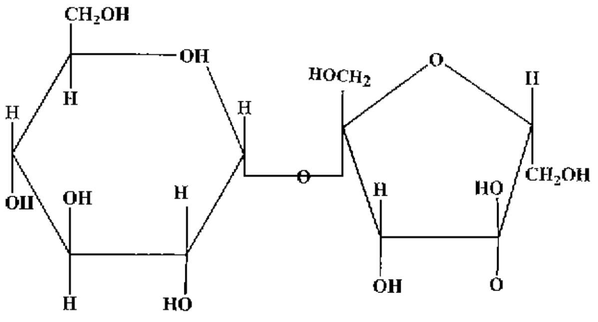


c) D-Fructose ($C_6H_{12}O_6$, 180 2) d) L-Arabinose ($C_5H_{10}O_5$ 150 1) e) D-Xylose ($C_5H_{10}O_5$, 150 1)

Fig. 1. Chemical Structure of Monosaccharides.



a) Maltose($C_{12}H_{22}O_{11}$, 342 3)



b) Sucrose($C_{12}H_{22}O_{11}$, 342 3)

Fig. 2. Chemical Structure of Disaccharides.

There are many measuring configurations in the rheo-

Table 1. Different Monosaccharides and Disaccharides

Name	Sugars	Sat. Sol. Vol., ml	Solid Vol.(%)	Sat. Sol. (Sugar(g)/Water(ml))
A-GL	Glucose	24	51.3	1.0
A-GA	Galactose	24	51.3	2.0
A-FR	Fructose	20	55.8	2.5
A-RA	Arabinose	19	57.1	1.0
A-XY	Xylose	19	57.1	1.25
A-MA	Maltose	20	55.8	2.5
A-SU	Sucrose	22	53.4	2.5

Table 2. Different Sucrose Content

Name	Sat. Sol. Vol., ml	Solid Vol.(%)	Sat. Sol. (Sugar(g)/Water(ml))
B-23	23	52.3	2.5
B-24	24	51.3	2.5
B-25	25	50.3	2.5
B-26	26	49.3	2.5

Table 3. Different Water Content with Fixed Content of Sucrose

Name	Sat. Sol. Vol., ml	Suppl. Water, ml	Solid Vol.(%)	Sat. Sol. (Sugar(g)/Water(ml))
C-1	21	1	53.4	2.5
C-2	21	2	52.3	2.5
C-3	21	3	51.3	2.5
C-4	21	4	50.3	2.5

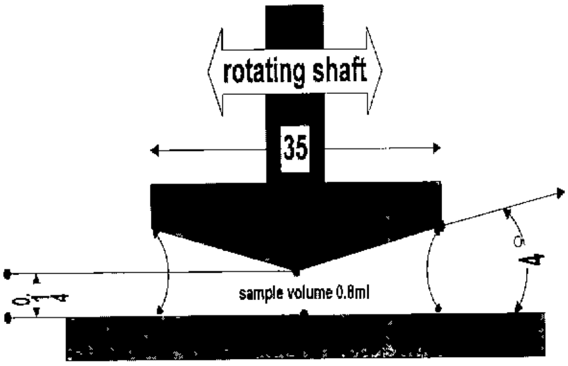


Fig. 3. Cone and plate configuration used in the rheological testing.

logical testing of slurries.[19] We selected cone and plate configuration which is very useful for viscous and dense ceramic slurries. The total volume of the slurry for rheological measurement is 0.8 ml in this cone and plate configuration. The slurry was loaded into a stainless-steel cone and plate as shown in Fig. 3. Cone spindle was connected to a rheometer (Rheostress RS75, Gebrueder Haake GmbH, Germany). The specifications of cone and plate, and spaces between them were same with the Haake configuration "C35/4°".[19]

Creep tests were done at a constant stress 4 Pa for 300 seconds in order to determine the viscoelastic properties of alumina slurry. Fig. 4 shows the stress applied in the creep testing with time. There are two basic building blocks (spring and dash pot) as shown in Fig. 5. Most simple models explaining the rheological behaviors of viscoelastic material are Kelvin-Voight model and Maxwell model. Kelvin-Voight model is a parallel connection of a spring and a dashpot block but Maxwell model is a serial connection of a spring and a dashpot block. Both blocks receive same strains in Kelvin-Voight model and same stresses in Maxwell model in simulating viscoelastic liquid. Both Kelvin-Voight model and Maxwell model are not enough to simulate the viscoelastic behavior of dense slurries. In fact, most viscoelastic materials show rheological behaviors of Burgers model which was constructed by serial connection of Kelvin-Voight model and Maxwell model as shown in Fig. 6.

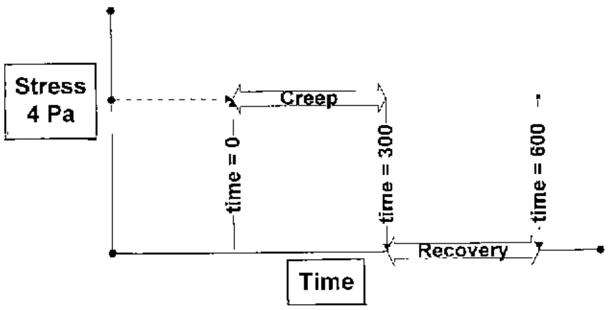


Fig. 4. Stress applied in creep test.

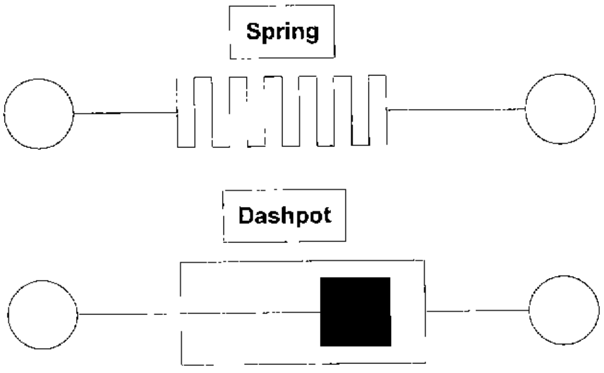


Fig. 5. Spring and dashpot model

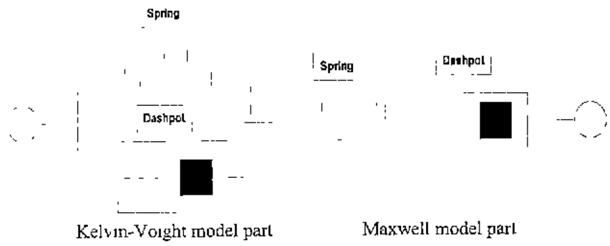


Fig. 6. Schematic diagram of Burger model.

III. Results and Discussions

1. Effect of different monosaccharides and disaccharides

Fig. 7 shows the creep and recovery behaviors of alumina slurries which agree with the typical creep behavior of viscoelastic materials represented by Burger model. Slurries containing fructose and sucrose showed much more deformation at a constant pressure 4 Pa compared to other slurries. Creep deformations were correlated with Burger model as follows.

$$\gamma = \alpha - \beta \exp(-\theta/\lambda)$$

where $\alpha = \tau/G' + \tau/G''$, $\beta = \tau/G''$, and γ is the strain, θ the retention time, τ the constant shear stress, G' the storage modulus, G'' the loss modulus, and λ the retardation time.

Values of constant α and β were obtained from Fig. 7 through mathematical manupulations and these are related to G' and G'' by the relation of $G''/G' = \beta/(\alpha-\beta)$. Alu-

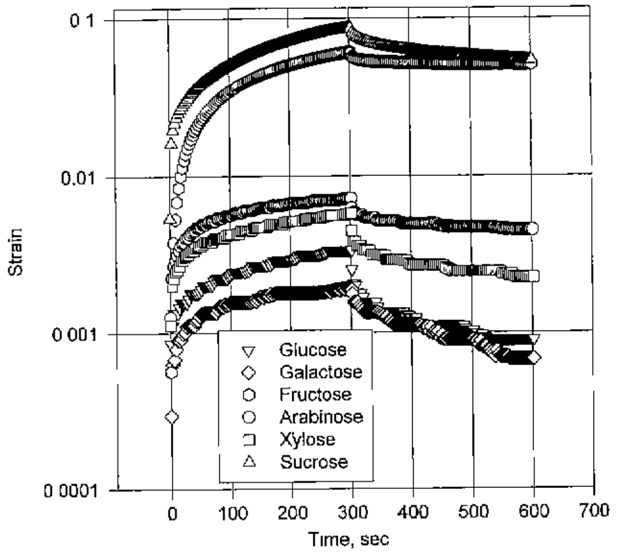


Fig. 7. Creep behavior of alumina slurries with different mono- and di-saccharides.

Table 4. Constants in Burger Model

Name	α	β	λ	G''/G'
A-GL	0.0156	0.0107	0.0056	2.2
A-GA	0.0075	0.0051	0.0132	2.1
A-FR	0.2832	0.2722	0.0062	24.7
A-RA	0.0284	0.0187	0.0124	1.9
A-XY	0.0238	0.0149	0.0079	1.7
A-SU	0.4655	0.3931	0.0040	5.4

mina slurries with fructose and sucrose have high G''/G' term which means these slurry are far more viscous than elastic compared to other slurries. At the same time, their α and β values are far bigger than other slurries which means that G' and G'' are quite lower than other slurries by the followings equations as summarized in Table 4, which contains α, β, and λ values in Burger model.

$$G' = \tau_i/(\alpha-\beta)$$
$$G'' = \tau_i/\beta$$

Steric hindrance depends on the thickness of adsorbed layer, the chemical nature of adsorbed molecules and the concentration of added polymers. There are many interesting points in above results. First of all, it is very difficult to make dense slurry with water at this level of alumina powder content. This was possible with the addition of monosaccharides and disaccharides. Second, there is little difference in the rheological properties whether there is a monosaccharide or a disaccharide. This implied that molecular weight is not important in this experiment. Third, these differences in the rheological properties between fructose and sucrose, and the other monosaccharides and disaccharides seem to be the molecular properties of these molecules. Fructose have stronger charges at the ends of molecule[20] which may prevent particle agglomeration by providing steric hindrance effect. Then, what is the common point between fructose and sucrose which showed better rheological properties? This seems to be due to the fact that in the process of hydrolysis, the sucrose solution becomes an equimolar mixture of glucose and fructose. This fructose with stronger charges at the ends of molecule[20] seems to contribute to the plasticity of dense slurry as mentioned above.

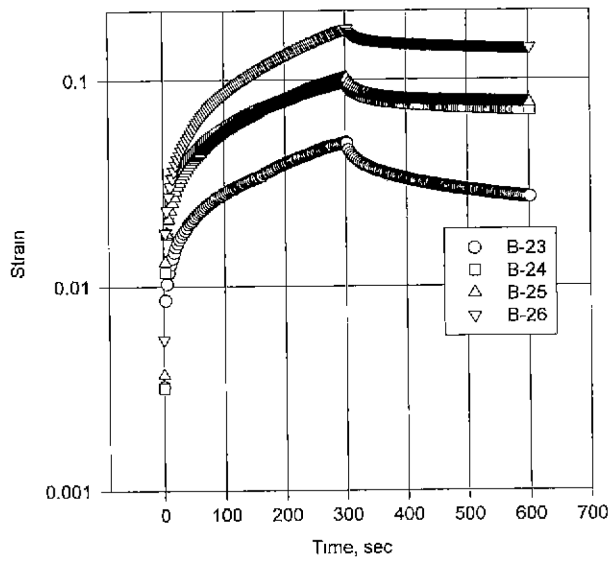


Fig. 8. Creep behavior of alumina slurries with different sucrose content.

2. *Effect of sucrose content*

Among several monosaccharides and disaccharides sucrose showed good effects in plasticizing dense alumina slurries. Sucrose was selected as a representative additive in order to check whether the concentration of saturated sucrose solution affects the plasticity of dense alumina slurry. (series-B) Sucrose contents in this research were as shown in Table 2 where saturated sucrose solution content increased from 23 ml to 26 ml. Creep deformations in Fig. 8 showed that alumina suspensions become more plastic with the addition of the saturated sucrose solution even though they showed minor changes compared with series-A. Creep deformations in Fig. 8 correlated well with Burger model. Saturated solution's general increase caused increase in G''/G' value calculated from α and β values as shown in Table 5. This means that alumina suspensions become more fluid with the addition of saturated sucrose solution even though the amount of change is minor in the range covered in this report.

3. *Effect of additional water content*

Fig. 9 shows the creep behaviors of alumina slurries with sucrose and additional water in the creep test of the series-C slurries. These strains correlated well with

Table 5. Constants in Burger Model with Different Sucrose Contents

Name	α	β	λ	G''/G'
B-23	0.298	0.254	0.0030	5.8
B-24	0.469	0.391	0.0050	5.0
B-25	0.584	0.509	0.0040	6.8
B-26	1.395	1.300	0.0020	13.7

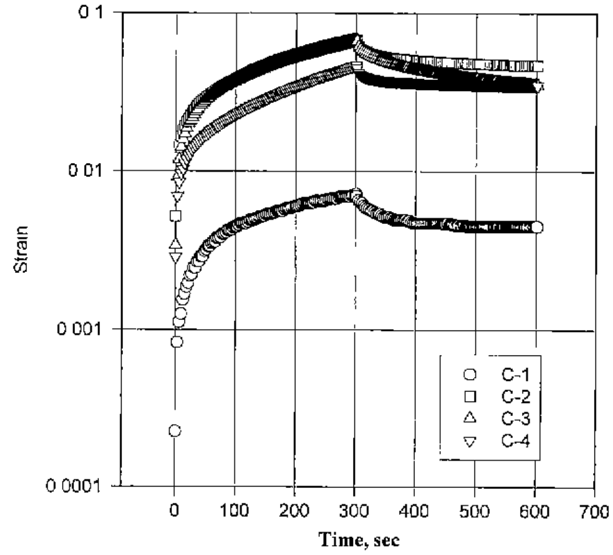


Fig. 9. Creep behavior of alumina slurries with sucrose and different water content.

Table 6. Constants in Burger Model with Different Sucrose Contents

Name	α	β	λ	G''/G'
C-1	0.0312	0.0272	0.007	6.8
C-2	0.3739	0.3139	0.003	5.2
C-3	0.3603	0.3108	0.004	6.3
C-4	0.5397	0.5040	0.001	13.1

Burger model and Table 6 shows the rheological constants α, β, and λ in Burger model. Constant α and β increased with water addition but constant λ decreased with water addition. Consequently, the effect of water addition is different from the effect of sucrose addition and general trends showed water increase made more deformation.

IV. Conclusion

Strain in creep test showed good correlations with Burger model which is an exponential function of time. Fructose and sucrose are the best in plasticizing dense alumina slurry among the monosaccharides and disaccharides. Main reason to this effect seems to be molecular configuration rather than molecular weight. Fructose has strong charges around both ends of fructose molecule which are very helpful to the steric hindrance effect. Sucrose seems to decompose upon hydrolysis into fructose and glucose. Main reason to the increase of plasticity with sucrose related to its decomposition into fructose and glucose upon hydrolysis. In the case of dense alumina slurry with sucrose, sucrose content or additional water content contributed to the plasticity of the slurries even though these two variables showed somewhat different contributions in different rheological properties.

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