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Determining critical ceramic powder volume concentration from viscosity measurements

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Abstract

This paper presents a method to determine the critical powder volume concentration (CPVC) of ceramic slurry from viscosity measurements. It was found that the CPVC determined in this manner could be successfully applied as a criterion of low bound to the extrusion process. Our experience indicated that only slurry with solid contents higher than CPVC could be successfully extruded. The slurries consist of dispersed alumina and kaolin particles in deionized water with additives such as sodium salt of polyacrylic acid (PAA), carboxymethyl cellulose (CMC), stearic acid and glycerol. The viscosity data from Brookfield rheometer were satisfactorily fitted with an empirical equation modified from Brodnyan equation: $\eta = \eta_0 \exp\left\{\frac{2.5\phi + 0.399\phi^{0.001}(p-1)^{1.48}}{1-(b\dot{\gamma})k\phi}\right\}$. The CPVC was then calculated from the best-fit k value as $1/k$ = CPVC, which is equivalent to the maximum particle packing fraction. Reasonable correlation was also found between best-fit p and k values. Effects of formulation and shear rate on CPVC were also discussed.

Keywords: A. Extrusion; Viscosity; CPVC; Brodnyan equation

1. Introduction

Extrusion is an important forming technique in the ceramics industry owing to its ability to provide complex shapes and forms with dimensional accuracy, and to its adaptability for mass production. Most of the research work on extrusion relate efforts to find the appropriate formulations which offer a balance between rheological performance during plastic forming and a minimum amount of binders in the mix [1–5]. Satisfactory extrusion results can be obtained only when a proper formulation is used. To find such a formulation, however, usually involves an intensive trial-and-error procedure and a lot of experimental work. It would then be desirable to save time and money if some kind of preliminary work can help to identify the proper range of formulations before extrusion experiments.

The concept of critical powder volume concentration (CPVC) has been around for quite some time [6]. It represents the maximum volume loading of powder in the fluid that yields a coherent stiff paste and does not break or separate. Markhoff et al. [7] used a torque rheometer to determine the CPVC. They added oil at a constant rate to the ceramic mix and recorded its torque value. The volume at which the maximum torque occurred was interpreted as being the CPVC point [7]. In other cases, researchers tried to obtain maximum packing data through various means and used it as the CPVC. For example, Pierce and Holsworth [6] used the dry paint films density to determine the critical pigment volume concentration. They also showed that other indirect methods such as measurements of tensile strength, elongation at break, or water vapor permeability of paint films could also produce the same results on CPVC. Tekahashi et al. [1] used the compaction density of dry powders under a high pressure as an approximation to CPVC. On the other hand, Chou and Lin [8] had proposed to use the sedimentation test to obtain an estimation of the maximum packing fraction of solid particles in an aqueous system. Pujari [9] estimated the CPVC from either mechanical exotherm or green density, but found some discrepancy between these two methods. In theory, the CPVC is influenced by factors such as the particle size and shape distribution of

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ceramic powder, its state of dispersion, the type and quantity of various additives. The relationship between CPVC and these factors is complicated. Bierwagen [10] had proposed a model to predict CPVC for paints. Basically, he assumed spherical particles with a known size distribution and uniform adsorption of oil and polymers on the surface. The densest random packing of these particles was then calculated and taken as its CPVC.

The objective of this work is to develop a method for predicting CPVC of concentrated ceramic slurries from viscosity measurements. An empirical equation for relative viscosity as a function of solid content and shear rate will first be established. From that equation, the CPVC can be calculated using a best-fit parameter and it is then used as a low bound criterion for obtaining successful extrusion results.

2. Experimental

2.1. Viscosity measurement

The ceramic powders used herein were mixtures of kaolin (Unimin, Canada; density = 2.813 g/cm^3) and α-alumina (Showa, Japan). Its volumetric ratio of kaolin/alumina was fixed at 6:1 (corresponding weight ratio = 4.22) throughout this work. This ratio was determined from our previous work on preparing porous ceramic plates [11]. Particle size distribution of both kaolin and alumina were measured by either light scattering or natural sedimentation technique (LPA 3100, Photal, Japan).

A number of additives (reagent grade) were also included for the purpose of good extrusion. The sodium salt of polyacrylic acid (PAA) (MW = 6000, Polysciences, USA) works as a dispersant; sodium salt of carboxymethyl cellulose (CMC) (viscosity ≈400–500 cP at 2%, 20°C, Showa, Japan) as both a binder and a pore former; glycerol as a plasticizer and sodium stearate as a lubricant. Deionized water was chosen as the vehicle. Table 1 lists the formulation of each slurry used in this work. The mixtures were vigorously stirred at 30°C for 1 h to achieve good dispersion before viscosity measurement. The apparent viscosity of slurry was measured using the Brookfield DV III series rheometer and following the standard testing procedure ASTM D2196-81 [12]. The viscometer speed (shear rate) was increased from 20 rpm (shear rate = 4.2 s^{-1}) until 200 rpm (shear rate = 42 s^{-1}) at a step change of 20 rpm. Viscosity data were read at each speed after 30 s. For comparison, viscosity of the fluid without any ceramic powder was also measured. The relative viscosity would be fitted by a new empirical equation modified from Brodnyan equation. A critical powder volume concentration can then be determined from the best-fit parameter of this empirical equation for each formulation. The mathematical fitting work was performed using SigmaPlot software (version 2.01, Jandel, USA).

Table 1
Compositions of tested slurries

Sample	Composition
B0	(α-Al_2O_3 + kaolin) + (1.2 mg Na-PAA/g solid + DI Water)
B1	(α-Al_2O_3 + kaolin) + (DI Water)
B2	(α-Al_2O_3 + kaolin) + (0.3 wt% CMC + DI Water)
B3	(α-Al_2O_3 + kaolin) + (0.3 wt% CMC + 0.3 wt% glycerol + DI Water)
B4	(α-Al_2O_3 + kaolin) + (0.3 wt% CMC + 0.3 wt% glycerol + 0.3 wt% sodium salt of stearic acid + DI Water)

2.2. Extrusion

To test the ideas that the CPVC values determined as above can be used as a low bound criterion for extrusion, we therefore, carried out a number of extrusion experiments with formulations shown in Table 1 and at solid contents both below and above the CPVC values. Sufficient quantities of kaolin and α-Al_2O_3 powders were first poured into a Z-blade mixer and mixed for 10 min. Next, the aqueous solution with proper additives was added for an additional 60 min of mixing. The paste was then aged in a sealed plastic bag for three days before extrusion. Finally, a horizontal single screw extruder (Jai-Chang, Taiwan) was used for extrusion tests to obtain 1 cm diameter ceramic rods. An extrusion will be claimed to be successful if the extrudate can hold its shape after at least 5 cm off the die without any support. Otherwise the extrudate will bend due to insufficient strength.

3. Results and discussion

The particle size distributions of both kaolin and alumina are presented in Fig. 1. Their mean sizes are 0.5 and 2.0 μm respectively. Since kaolin is the major component in this mixture, we can therefore expect that the rheological behavior be dominated by characteristics of kaolin.

Next shown in Figs. 2–4 are the representative viscosity data versus solid volume fraction for samples B0, B2 and B4 respectively. Data for samples B1 and B3 exhibited basically the same behavior and will not shown here. All the slurries showed a shear-thinning characteristic as their viscosity decreased with shear rate. The viscosity increased steeply as the solid content approached the state of maximum packing. From Figs. 2–4, one can also notice that the relative viscosity was of the order of 10^4 for B0 sample, but was of the order of

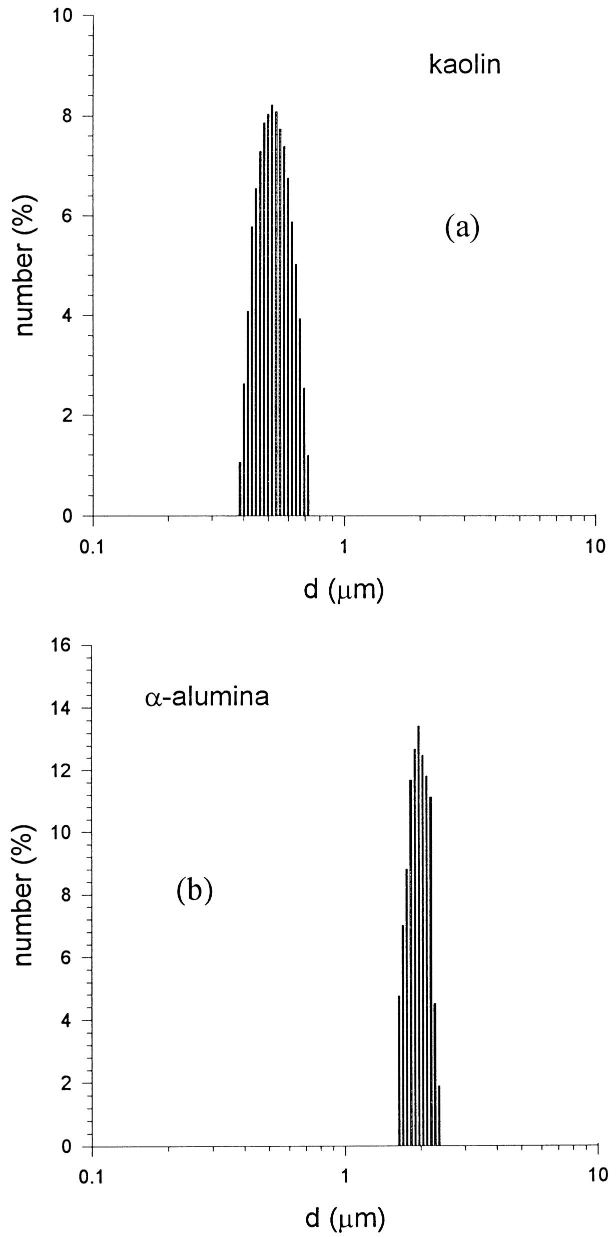

Fig. 1. Particle size distributions of (a) kaolin and (b) alumina used in this work.

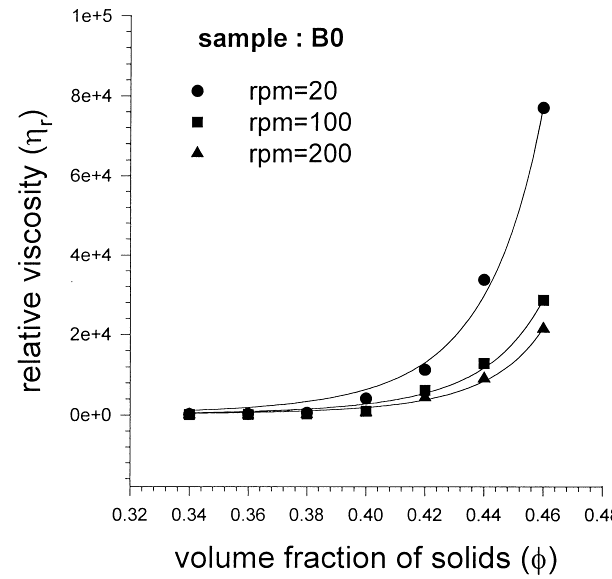

Fig. 2. Relative viscosity versus solid volume fraction at different shear rates for sample B0, where the solid curves are drawn from our best fitted empirical equation.

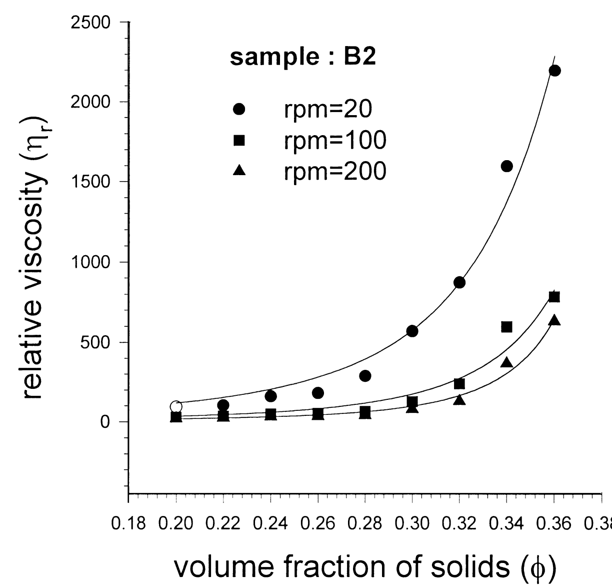

Fig. 3. Relative viscosity versus solid volume fraction at different shear rates for sample B2, where the solid curves are drawn from our best fitted empirical equation.

10^3 for samples B2 and B4. This difference was mainly due to the presence of CMC, which increases the fluid viscosity to a great extent. Nonetheless, the relative viscosity reported in this work was still much higher than those reported for the ceramic-polymer systems [13,14]. These large values of relative viscosity would affect our choice of appropriate equations for expressing the functional dependency of viscosity upon solid concentration.

4. CPVC from rheological measurements

It has always been of great interest for researchers to find an appropriate equation for describing the functional dependency of relative viscosity upon solid concentration. Rutgers [15] had compiled a list of over 100 such equations, of which the Mooney equation is a popular one. The viscosity of slurry η is expressed in

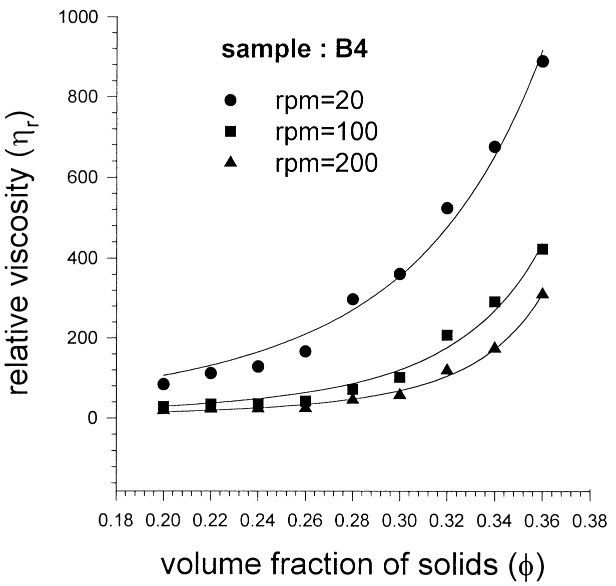

Fig. 4. Relative viscosity versus solid volume fraction at different shear rates for sample B4, where the solid curves are drawn from our best fitted empirical equation.

terms of fluid viscosity η_0, particle volume fraction ϕ and parameter k as follows:

$$\eta = \eta_o \exp\left(\frac{2.5\phi}{1 - k\phi}\right) \quad (1)$$

where k, the self-crowding factor, can also be expressed as $1/\phi_m$ with ϕ_m being the maximum packing fraction of solid particles. ϕ_m will be taken as the critical powder volume concentration in this work. Brodnyan [16] later modified the Mooney equation for the prolate ellipsoids to give his equation as follows:

$$\eta = \eta_0 \exp\left\{\frac{2.5\phi + 0.399(p-1)^{1.48}\phi}{1 - k\phi}\right\} \quad (2)$$

An additional factor, p, was introduced to include the effects of particle shape factor on viscosity. p was defined as the axial ratio of the ellipsoids considered by Brodnyan. An increase in p, meaning more ellipsoidal, corresponds to an increase in k or a decrease in the packing fraction of ϕ_m. The Brodnyan equation would reduce to Mooney equation for $p = 1$, i.e. spherical particles as a limiting case. When this equation was applied to our viscosity data, unreasonable results, such as negative or very small k values (i.e. leading to $\phi_m < 0$ or > 1), were obtained.

After extensive trial-and-error procedure, we then developed the following empirical correlation modified from the Brodnyan equation as the most appropriate one for the viscosity data obtained in this work. Meaningful parameters of p and k can be obtained from the best-fitted results. The agreement between experimental and fitted data is very satisfactory as exhibited in Figs. 2–4.

$$\eta = \eta_0 \exp\left\{\frac{2.5\phi + 0.399\phi^{0.001}(p-1)^{1.48}}{1 - (b\dot{\gamma})k\phi}\right\} \quad (3)$$

Table 2
Best fitted parameters from the modified Brodnyan's equation

Sample		rpm = 20 (Shear rate = 4.2 s^{-1})	rpm = 60 (Shear rate = 12.6 s^{-1})	rpm = 100 (Shear rate = 21 s^{-1})	rpm = 160 (Shear rate = 33.6 s^{-1})	rpm = 200 (Shear rate = 42 s^{-1})
B0	p	4.768	4.410	4.405	4.283	4.126
	k	2.060	2.035	2.025	2.010	2.000
	b	0.162	0.056	0.033	0.021	0.017
	cpvc	0.485	0.491	0.494	0.497	0.500
B1	p	7.001	6.752	6.690	6.600	6.453
	k	2.121	2.080	2.060	2.030	2.020
	b	0.114	0.037	0.022	0.014	0.011
	cpvc	0.472	0.481	0.485	0.493	0.495
B2	p	4.851	4.181	3.871	3.539	3.251
	k	2.250	2.190	2.180	2.140	2.130
	b	0.148	0.056	0.035	0.024	0.020
	cpvc	0.444	0.457	0.459	0.467	0.470
B3	p	5.253	4.556	4.178	3.624	3.373
	k	2.225	2.160	2.150	2.110	2.100
	b	0.135	0.051	0.033	0.024	0.020
	cpvc	0.449	0.463	0.465	0.474	0.476
B4	p	4.997	4.220	3.834	3.416	3.221
	k	2.200	2.140	2.130	2.090	2.080
	b	0.124	0.052	0.034	0.024	0.020
	cpvc	0.455	0.467	0.470	0.479	0.481

Here, the $\phi^{0.001}$ term was retained to make sure that at $\phi = 0$, the relative viscosity equals to unity as required. Another modification we made to the Brodnyan equation was to include shear rate into the k term. The reason is that in our slurry, the particles were still agglomerated to some extent and could be broken up by the applied shear force. As a result, the maximum achievable particle packing would be influenced accordingly. The CPVC value is defined as $1/k$. Our best fitted parameters of p, k and b are listed in Table 2, whereas p is also plotted against $1/k$ (i.e. CPVC) in Fig. 5. Here we can clearly see the simple inverse linear relation between these two parameters. In other words, as p (a kind of shape factor) increases, the CPVC (or $1/k$) decreases. Also noted is that when the shear rate was increased, the shape factor p decreased and the CPVC increased accordingly. Presumably it is caused by the breakup of agglomerated particles. Also noted in Fig. 5 are the different p values for different slurries. Probably due to the platelet nature of kaolin particles, the p values of sample B1 were much higher than unity. However, the particle morphology would change to exhibit smaller p when an additive such as PAA or CMC was included.

Next plotted in Fig. 6 are the CPVC values versus compositions under different shearing conditions. When a dispersant was added to the ceramic system (B0), a larger CPVC or higher maximum particle packing than the original one (B1) would be obtained. However, when a certain amount of polymeric binder CMC was added to the system (i.e. B2), the CPVC values decreased. The presence of polymeric binder would either adsorb onto particle surface or simply fill in the spaces between particles, hence decreased the maximum achievable solid fraction of the system. This situation was improved somewhat if a plasticizer (glycerol, B3) and lubricant (sodium stearate, B4) was added to the system. These additives should help to produce a better distribution of CMC within ceramic particles and therefore higher packing fractions as indicated in Fig. 6.

Finally, we prepared various mixes having solid contents either slightly higher or lower than the CPVC values

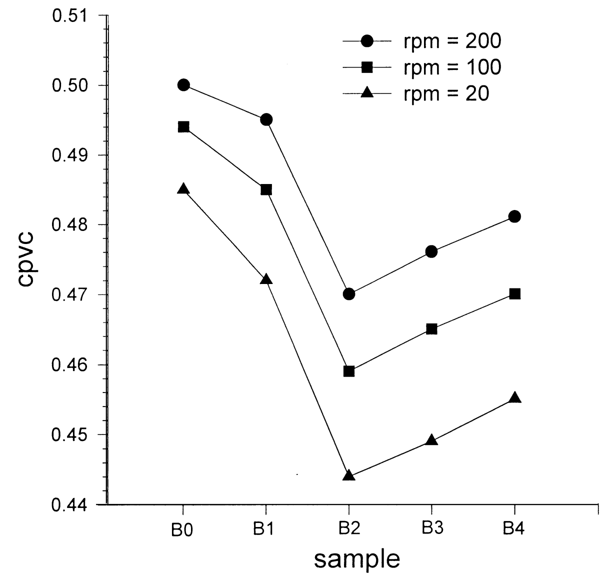

Fig. 6. CPVC values versus compositions under various shearing rates.

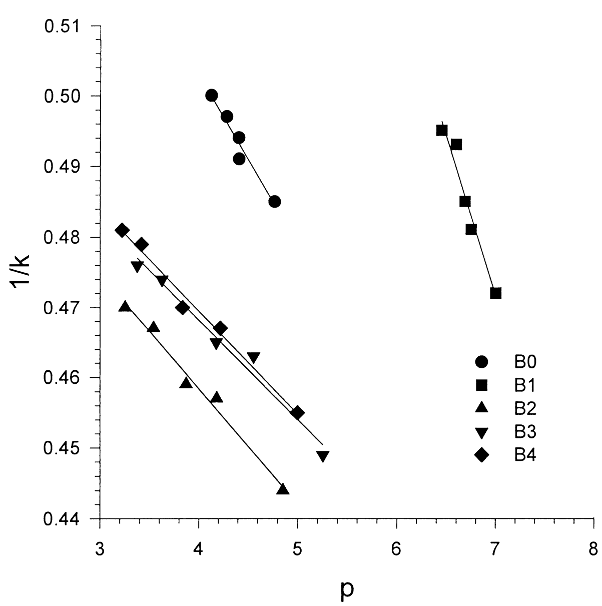

Fig. 5. Correlation between best-fit p and $1/k$ values for various conditions.

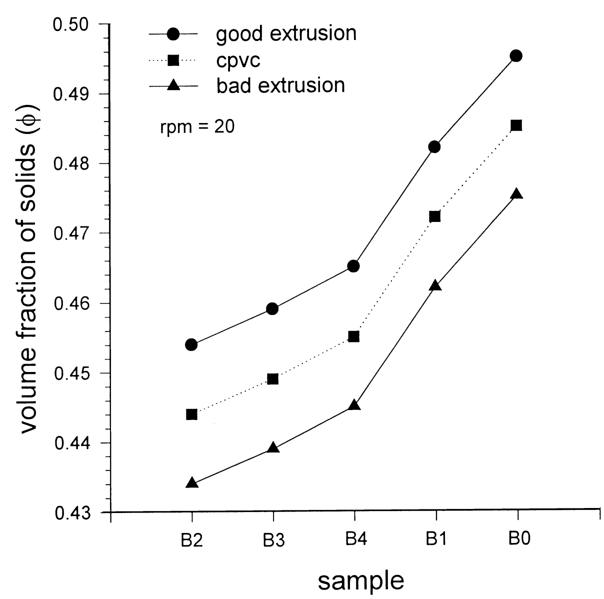

Fig. 7. Relation between extrusion results and CPVC for various compositions.

as reported earlier and carried out extrusion experiments. The results are now shown in Fig. 7. Successful extrusion was obtained for these mixes having solid contents higher than the CPVC, while those with solids less than CPVC were too soft to produce satisfactory extrudate. The CPVC determined from rheological measurement can be used as a criterion for low bound of solid concentration. As for the upper bound, it is likely limited by the erosion problem and power of extruder.

5. Conclusions

Based on the results shown above, we can conclude that the modified Brodnyan's equation can adequately fits the η_r versus ϕ data over the entire tested range of shear rates. The best fitted parameters of k and p are reasonable in terms of their respective physical meaning. The CPVC is then calculated by $CPVC = 1/k$. In general, as the shear rate increases, the shape factor of particle decreases and CPVC or maximum particle packing increase. After the addition of polymeric binder (CMC), the CPVC decreases to some extent due to the presence of CMC within the spaces of ceramic particles. However, further addition of additives such plasticizer and lubricant can help the distribution of CMC in the system and hence to produce higher CPVC values. Extrusion experiments verified that the CPVC thus determined could be used as a reasonable criterion for low bound of solid content in obtaining successful extrusion operations.

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