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Modeling paste properties with minimum experimentation

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The bulk shear stress of a paste that results in a 350 grade maraging steel after a reduction heat treatment was successfully modeled. The maximum solids content was measured using the oil drop test and the reciprocal bulk shear stress test. These techniques were found to be in good agreement. Capillary rheometer experiments on solid-free (fluid phase) and solid-containing pastes allow the calculation of a relative bulk shear stress under most circumstances. The Dougherty-Krieger equation was then used to calculate the intrinsic viscosity [η] and solve for the bulk shear stress of the unknown paste sample.

Key words: Extrusion, paste, modeling, Fe_2O_3.

Introduction

A variety of models have been developed to describe the effect of solids content on suspension viscosity [1-3]. Recently, some of these models, including the Mooney, Eq. (1); Chong, Eq. (2); and Dougherty and Krieger, Eq. (3) equations have been applied to paste formulations [4].

$$\eta_r = \exp\left(\frac{[\eta]\cdot\phi}{1-\dfrac{\phi}{\phi_{max}}}\right) \tag{1}$$

$$\eta_r = \left[1+\frac{[\eta]\cdot\phi_{max}}{2}\left(\frac{\dfrac{\phi}{\phi_{max}}}{1-\dfrac{\phi}{\phi_{max}}}\right)\right]^2 \tag{2}$$

$$\eta_r = \left(1-\frac{\phi}{\phi_{max}}\right)^{-[\eta]\cdot\phi_{max}} \tag{3}$$

Equations that model high solids content suspensions typically consider the solids content, ϕ, the maximum possible solids content, ϕ_{max}, and the intrinsic viscosity [η] to calculate a relative property value. The relative paste bulk shear stress, σ_r, is defined as the ratio of bulk shear stress of the paste to the bulk shear stress of the fluid component of the paste. Several methods can be used to arrive at a value for ϕ_{max}. While physically meaningful, [η] is empirical and cannot be directly measured.

Pastes can be considered as being composed of two phases: a solid phase carried by a fluid phase composed of solvent, binder, and additives. As fluid phase is introduced to a powder, inter-particle spaces are gradually filled [5]. Particles with wet surfaces agglomerate into pellet-like aggregates. When the fluid content approaches the pore volume, incremental fluid additions cause the aggregates to agglomerate into a single, non-tacky, cohesive body. This state typically persists when pore saturation is between 90 and 100%. The bulk shear stress remains undefined until a critical fluid fraction is reached at 100% saturation. Increasing fluid content beyond full pore saturation causes particles to arrange in a less closely packed configuration and results in a tacky cohesive body that moderately resists shearing. Further fluid additions cause discontinuities in the paste structure and prevent it from supporting itself.

Pastes differ from suspensions in that they are capable of deforming plastically. Plasticity is defined as the ability of a material to continuously and permanently change shape without changing volume. Practically, plasticity must consider this deformation without the formation of structural discontinuity or rupture [6]. Depending on the characteristics of the powder raw material, plasticity may result wholly or partially from the rheology of the fluid phase. Pastes may behave plastically when the bulk shear stress exceeds the liquid limit, approximately 10 kPa [7].

The purpose of this paper is twofold: to propose a method by which, paste properties can be modeled rapidly and with minimum experimentation and to review paste characterization methods. This paper outlines and compares the techniques available for the determination of ϕ_{max} and subsequently, [η] and uses this information to arrive at a value for the paste bulk shear stress. A complex paste system that has been extensively characterized is presented as a benchmark.

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Paste Preparation

Material

A4M Methocel from Dow Chemical was used as a binder and Pegosperse 100S from Lonza was used in small concentrations as a lubricant. These additives are observed to burn out cleanly through chemical reaction or reduction during heat treating. Distilled, deionized water was used as a solvent in all experiments.

The composition was chosen for extrusion forming into a honeycomb geometry. A subsequent reduction heat treatment results in dense, lightweight metal articles of 350 grade maraging steel composition [8]. Identically prepared pastes were formulated with a batch composition as described in Table 1. Raw materials were characterized via Scanning Electron Microscopy (SEM) imaging, particle size analysis, and BET surface area and pore volume analyses. Particle size was found to be approximately 1 to 12 μm with an average size near 6 μm. Particle surface area ranged from 0.4 to 4.0 m^2/g. Desorption hysteresis indicated the internal porosity of the batch to be 3.1%. A characterization summary for each raw material can also be found in Table 1.

Method

Pastes were made by weighing individual constituents into the appropriate fractions to result in 1500 g batches. Solid raw materials were dry blended for 15 minutes in a commercial blender fitted with an open mixing paddle. The lubricant, previously dissolved in water, was subsequently added to the dry blend. Mixing continued for 2 minutes following the liquid addition. The granulated powder was pugged in a Buss kneader for approximately 5 minutes.

Capillary Rheometry

Benbow and Bridgewater [9, 10] developed an analysis technique using flow through a die of circular cross section to measure the rheological properties of pastes. The model given by Eq. (4) assumes a linear relationship between the extrusion pressure, P and extrudate velocity, V, and has the form:

$$P = 2(\sigma_o + \alpha V)\ln\left(\frac{D_o}{D}\right) + \frac{4L(\tau_o + \beta V)}{D}. \tag{4}$$

In this equation, D_o is the diameter of the barrel, D is the diameter of the die land, and L is the length of the die land. Variables σ_o and α are associated with flow into the die land, τ_o and β with flow through the die land. Here, σ_o is the bulk shear stress, α is a parameter characterizing the effects of velocity on σ_o, τ_o is the die wall shear stress, and β is a parameter characterizing the effects of velocity on τ_o.

Extrusion testing was conducted using a custom, stainless steel piston extruder fitted to a Satec universal testing machine. Seay [11] established that wall stresses between the paste and the barrel were negligible for this test set-up. The extrusion pressures at several speeds were measured with a single barrel of paste and no corrections were applied to the measured load values.

The barrel was charged with paste to a depth of 100 mm and tamped to remove large air pockets. The piston was driven downward by the testing machine at each of six constant extrudate velocities: 68.5, 27.4, 13.7, 6.9, 2.7, and 1.4 mm/s. Testing proceeded from fastest to slowest, followed by a return to the fastest velocity. Repeat measurements at the fastest velocity did not deviate from each other by more than 10%. Three interchangeable dies of circular cross section, 3.2 mm diameter, and with L/D ratios of 1, 8, and 16 were fitted to the rheometer.

Statistical analysis of error in property measurements was not undertaken because of the length of time required to prepare and characterize each sample. The data obtained for each paste are the ram force at each velocity for each die. Extrapolating the plot of the L/D

Table 1. Characterization and batch composition of 350 grade Maraging steel pastes

Raw Material	Source	Particle size (μm) at CWPF than			BET Surface (m^2/g)	Pore Volume (%)	Amount in Batch (%)
		10%	50%	90%			
Fe_2O_3	Pea Ridge Iron Ore	0.8	4.5	10.0	1.51	2.4	66.7
NiO	Ceramic Color	3.3	6.3	11.8	0.48	1.8	16.7
Co_3O_4	Ceramic Color	3.0	3.7	4.5	4.04	8.7	11.9
Mo	Atlantic Equipment	2.7	7.0	15.6	0.54	2.8	3.5
TiH_2	Reading Alloys	2.0	6.8	15.4	0.48	1.0	1.1
Fluid Material	Source						Amount in Fluid (%)
A4M Methocel	Dow Chemical Co.						19.6
100S Pegosperse	Lonza						2.0
H_2O							balance

ratio against P to zero enables the calculation of bulk shear stress using Eq. (5),

$$P=2(\sigma_o+\alpha V)\ln\left(\frac{D_o}{D}\right). \tag{5}$$

Six pastes of 350 grade maraging steel composition and varying solids fractions were prepared with a constant water-to-binder weight ratio of 4:1 and a constant lubricant concentration of 0.5% of the powder weight. The solids contents tested were 0, 30, 40, 50, 55, and 60 vol.%. The test at 0 vol.% solids (the fluid phase) permits calculation of relative properties.

Maximum Solids Content

The Oil Drop Test

The oil drop test is a modification of the ASTM standard Gardner-Coleman (D 1483-95) and spatula rub-out (D 281-95) tests and is used to rapidly estimate ϕ_{max}. In the oil drop test, approximately 40 g of dry mixed powder raw material was mixed with corn oil by hand in a small plastic bag. Use of oil reduces evaporation and provides good wetting of the powder. The liquid fraction is increased dropwise until a cohesive, workable paste having smooth texture and shape-retaining character is formed. Maximum solids content is then calculated from the weight of oil needed for pore saturation, the powder weight, and respective densities. This method provides a means to measure the fluid content needed to fill interparticle voids under mildly sheared conditions.

The oil drop test tends to underestimate ϕ_{max} because hand mixing is a low shear operation and can be ineffective in breaking up agglomerates. The amount of liquid present at ϕ_{max} has been assumed to be 90% of the oil drop test value because of the excess liquid required under low shear [10].

Zero Reciprocal Bulk Shear Stress Test

The resistance of a paste to a deforming stress is highly dependent on the thickness and rheology of the fluid layer that surrounds the particles. The thickness of this layer is directly proportional to the excess of liquid phase above that required to fill particle interstices. For a given solid composition, a change in extrusion properties with fluid phase content can be used to estimate the maximum solids content. The extrapolation of the reciprocal of extrusion pressure to 0 MPa^{-1} represents the critical value where the liquid phase exactly fills the interparticle voids. Compositions to the left of this critical value cannot be extruded because particles interlock and there is no mechanism to facilitate fluid flow. Any composition to the right of the intercept contains excess fluid and is theoretically extrudable.

Intrinsic Viscosity

Einstein calculated the relative viscosity $[\eta]$=2.5 for an infinitely dilute suspension of spheres by describing the flow around a single particle [12-13]. Deviations from this value may arise as a result of departure from the ideal condition considered by Einstein. Smith [14] summarized the causes for these deviations as [15-17]: high concentration suspensions, excessive amount of immobilized liquid on particle surfaces, the presence of stable agglomerates, and the swelling or penetration of the particle by the liquid medium.

The intrinsic viscosity can be changed in concert with ϕ_{max} to arrive at multiple solutions having approximately the same error. Beyond testing a wide variety of samples and fitting a curve, there is no way to directly measure $[\eta]$. The two point projection technique requires only two rheometric tests and the use of a low solids content suspension model.

The test is easy to perform and requires minimum experimentation. The fluid phase of the paste in question is characterized using capillary rheometry. The oil drop test is used to estimate ϕ_{max} and suggest an appropriate choice for the paste to be tested. The bulk shear stress of the fluid phase and paste samples are converted to relative values. This fixes the fluid phase sample at σ_r = 1. Rheometry of a single paste having $\phi < \phi_{max}$ allows a suspension model to be fit to the two points. Two points are sufficient to fit each model and solve for $[\eta]$. It is necessary to consider previous work with suspensions, pastes, and particle packing theory to arrive at the model and solution that represents the most legitimate interpretation of the data.

Experimental

Capillary Rheometry of Pastes

The dependence of relative paste bulk shear stress on solids content is shown in Figure 1. Through non-linear optimization of the data and interpretation of the resulting values of ϕ_{max} and $[\eta]$, the Dougherty-Krieger equation was shown to best model this paste system. The error in fitting the Dougherty-Krieger equation was minimized at $[\eta]$ = 2.3 and ϕ_{max} = 67 vol.%. Small changes in $[\eta]$ and ϕ_{max} resulted in the smallest increases in error of any model studied in this investigation. It is therefore expected to provide the best estimates for $[\eta]$.

Maximum Solids Content

The direct result of the oil drop test without correction is that ϕ_{max}=59.6 vol.%. By applying the 90% criterion to the test results, ϕ_{max} of the paste composition was estimated to be 62.1 vol.%.

A plot of the inverse of bulk shear stress and die wall shear stress against the ratio of fluid to solid volume for the five pastes is shown in Figure 2. The data point

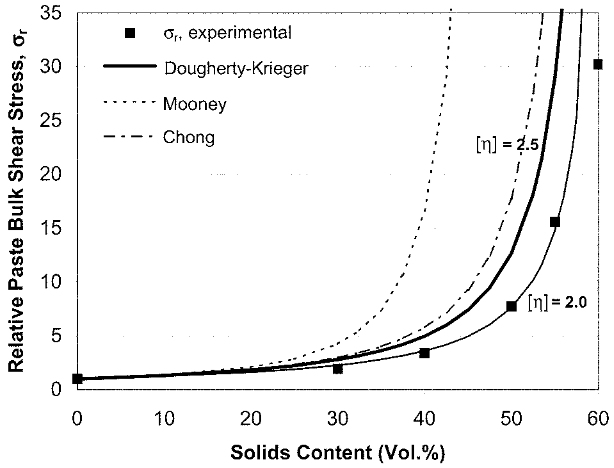

Fig. 1. Relative bulk shear stress of the 350 maraging steel pastes compared to plots of the Mooney and Chong equations at ϕ_{max} = 62.1% and $[\eta]$ = 2.5 and the Dougherty-Krieger equation at ϕ_{max} = 62.1% and $[\eta]$ = 2.0 and 2.5.

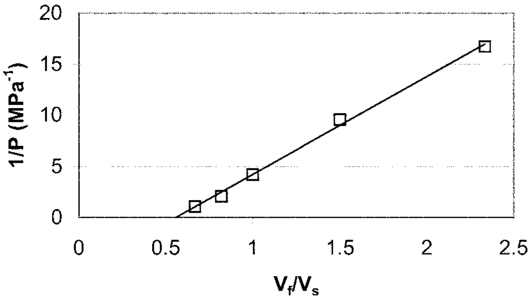

Fig. 2. Determination of ϕ_{max} from measurements of paste bulk shear stress.

at ϕ=0 cannot be plotted. The scale of the V_f/V_s axis is coarse, so it is important to test pastes with high enough bulk shear stress to permit a valid extrapolation of the data to the V_f/V_s intercept. A good linear fit is observed for σ_o, and the solids content at ϕ_{max} was measured to be 64.2 vol.%.

The two point projection was originally thought to be a valid method of predicting ϕ_{max} from an assumed $[\eta]$. This idea fails because it requires either *a priori* knowledge of or a reliable method to estimate $[\eta]$. Table 2 shows the results of the two point model projection to estimate ϕ_{max}, solving the Dougherty-Krieger, Mooney, and Chong equations at Einstein's calculated $[\eta]$=2.5. The Dougherty-Krieger equation is also solved with $[\eta]$=2.0.

The Mooney equation predicts values for ϕ_{max} in excess of 100% for any combination of data points. The Chong equation also predicts elevated values for ϕ_{max} at the assumed values for $[\eta]$. The Dougherty-Krieger equation solved with $[\eta]$=2.0 results in values for ϕ_{max} closest to those measured using the oil drop test. Beneficial use of this value would not be recognized until thorough testing was completed.

Table 3 shows the results of the two point model projection for $[\eta]$, solving the Mooney, Chong, and Dougherty-Krieger equations at the oil drop test value, ϕ_{max}=62.1%.

Table 2. Two point model projection results for the prediction of ϕ_{max} (vol.%)

Data Points (Vol.%)	Mooney	Chong	Dougherty-Krieger $[\eta]$=2.0	Dougherty-Krieger $[\eta]$=2.5
0-30	>100	86.9	>100	>100
0-40	>100	75.5	66.3	>100
0-50	>100	71.0	61.8	75.5
0-55	>100	69.0	61.7	69.1
0-60	>100	70.1	64.7	70.0

Table 3. Two point model projection results for the prediction of $[\eta]$

Data Points (Vol.%)	Mooney	Chong	Dougherty-Krieger
0-30	1.15	1.36	1.63
0-40	1.09	1.50	1.91
0-50	0.80	1.38	2.01
0-55	0.57	1.22	2.04
0-60	0.19	0.50	1.62

The exponential and power law models used to describe suspension and paste behavior tend to encounter difficulty as the relative property approaches infinity. This is because the simplification that the paste exhibits Bingham plastic behavior becomes less valid. For this reason, the paste ϕ tested with rheometry must be close enough to ϕ_{max} to fix the model equation at both ends of the curve yet low enough to show behavior that is consistent with the model used to determine the property. A plot of extrusion pressure against extrudate velocity is shown in Figure 3 and relates paste response to a variety of shear rates.

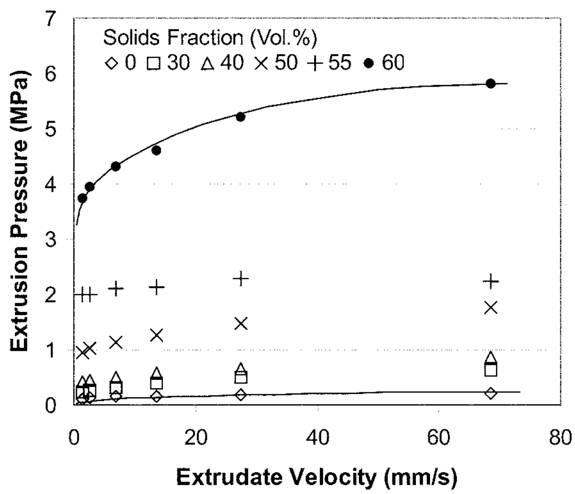

Fig. 3. Crossplot of extrudate velocity against extrusion pressure for each paste composition.

The point at 60 vol.% is inappropriate for curve fitting because of the substantial deviation from Bingham plastic behavior observed. The best agreement between values of $[\eta]$ calculated using the two point projection was obtained by measuring pastes having ϕ between 65 and 90% of ϕ_{max}.

Conclusions

Paste bulk shear stress may be rapidly modeled using the following procedure:

- Measurement of the maximum solids content, ϕ_{max}, using the oil drop test.
- Capillary rheometry of 1) the fluid phase composition and 2) a paste with identical fluid phase composition and ϕ between 65 and 90% of ϕ_{max}.
- Calculation of the relative bulk shear stress from rheometer test values.
- Application of the Dougherty-Krieger equation to these two points to calculate the intrinsic viscosity, $[\eta]$.
- Application of the Dougherty-Krieger equation to solve for σ_r of the unknown paste sample.

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