

Particle packing and rheological property of highly-concentrated ceramic suspensions: ϕ_m determination and viscosity prediction

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A model is proposed which is able to predict the maximum particle packing density (ϕ_m) over a wide variety of ceramic suspensions with very large difference in particle size/shape, particle surface chemistry, and solvent chemistry. This model provides a simple method to obtain ϕ_m directly through the use of a few viscosity-concentration data for a given colloidal suspension, rather than a best-fitting approach. The model is also capable of predicting the viscosity of a variety of ceramic suspensions under different conditions of shear. A comparison with some existing viscosity model is also presented. © 2000 Kluwer Academic Publishers

1. Introduction

The use of colloidal processing to produce ceramic parts has attracted great attention for years primarily because this technique offers a simpler and cheaper way to fabricate ceramic parts with more reliable properties [1, 2] than those fabricated from other conventional powder consolidation methods. For green-shape processing through a colloidal suspension, a suspension with high solids loading and desirable rheological properties is essentially needed. The former requirement may ensure considerable degree of microstructure homogeneity and higher particle packing density [3–5]. The latter provides critical information on the feasibility of the suspensions for specific green-shaping applications such as slip casting, injection molding, etc.

In the study of rheological behavior of suspensions, the relation between solid loading (ϕ) and viscosity (η) has long received much attention. In short, increase in solid loading (ϕ) increases suspension viscosity (η). This ϕ - η relationship has been a focus of many theoretical and experimental considerations for years. Almost all of the theoretical work begins with the assumption of spherical, non-interacting rigid particles in a dilute solution. After the first equation proposed by Einstein [6] in describing ϕ - η behavior, i.e.,

$$\eta_r = (1 + 2.5\phi) \quad (1)$$

where η_r is the relative viscosity defined as a ratio of suspension viscosity (η_s) to the viscosity of suspending medium (η_o), a number of equations with an extended form of Equation 1 were vigorously proposed [7–9] for moderate concentration. However, for suspensions with highly-concentrated solid fraction as commonly used

in ceramic processing, the prediction of ϕ - η relation from the viscosity models aforementioned is much less accurate.

However, the predictive capability has much improved for concentrated suspensions by taking the particle size distribution and most critically, the maximum packing density (ϕ_m) into account, for instance, in an earlier study by Chong *et al.* [10]

$$\eta_r = \left[1 + \frac{0.75(\phi/\phi_m)}{1 - (\phi/\phi_m)} \right]^2 \quad (2)$$

where ϕ_m is the maximum particle packing density of a given powder. As indicated in Equation 2, suspension viscosity tends to be infinite when the solid concentration in the suspension is close to ϕ_m . Studies clearly confirm that the value of ϕ_m can be enhanced or reduced by altering the particle size distribution [11–13]. Furthermore, with the advancement and understanding of colloidal processing, interparticle interactions (attractive and repulsive potential) were found to play a crucial role in dominating rheological properties, e.g., viscosity, yield stress, and moduli of a suspension at a given particle size distribution [1, 14–17]. In a previous study [18], the author presented a change in ϕ_m due to the formation of particle agglomeration originating essentially from a change in interparticle potential and found ϕ_m can be reduced once the particles are agglomerated.

In view of the literature, the value, ϕ_m , is by far one of the most important parameters in describing the rheological properties of colloidal suspensions [10, 17, 19–23] as well as in the determination of interparticle distance [24, 25]. This is particularly critical in some

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one-parameter equations (i.e., the solid concentration, ϕ), for instance, as proposed by Chong *et al.* [10] and Kitano *et al.* [20]. However, the value of ϕ_m can be further complicated by irregular particles, e.g., high-aspect-ratio particles, and this makes a theoretical prediction more difficult for a real suspension system. So far, the most frequently-used method in determining ϕ_m is by means of a best-fit procedure to the rheological data for a give suspension. The lack of a formulation for ϕ_m may have drawbacks on a deeper understanding on the effect of material parameters on rheological properties for a further improvement of the suspensions for specific green-shaping process as well as for other applications, e.g., in the field of chemical engineering. This is thus the primary goal of the present study. In this paper, we propose an empirical equation primarily for ϕ_m determination and verify it by comparing the calculated ϕ_m with the reported ϕ_m available in the literature for a number of suspensions. Calculation will be conducted in detail as a demonstration of the predictive ability of the proposed model on highly-concentrated ceramic suspensions principally for injection molding applications. Furthermore, an experiment is performed by preparing a set of highly-concentrated zirconia-wax mixtures with different solid concentrations for a close comparison of ϕ_m between the experimentally-determined value and the calculated one.

2. Model

A variety of equations have been suggested for description of $\phi - \eta$ behavior of suspensions. Among them, one of the very simple forms for spherical particles is derived theoretically by Maron and Piere [26],

$$\eta_r = \left(\frac{1 - \phi}{\phi_m} \right)^{-2} \quad (3)$$

Latter, a remarkable empirical expression was carefully evaluated by Kitano *et al.* [20] by modifying Equation 3 with a parameter A which is related to the packing configuration of a given filler of arbitrary geometry,

$$\eta_r = \left(\frac{1 - \phi}{A} \right)^{-2} \quad (4)$$

Equation 4 is known to be applicable to a large variety of suspensions having low to high solids loading, and most importantly, is also valid for high-aspect-ratio fillers. However, Equation 4 is only useful for suspensions at a shear stress greater than 10^3 Pa. This is then improved by Dabak *et al.* [23] who proposed a model which is applicable over both low and high shear regions, having a general form of

$$\eta_r = \left[1 + \frac{[\eta]\phi_m \phi}{n(\phi_m - \phi)} \right]^n \quad (5)$$

where n is a suspension-dependent parameter and $[\eta]$ is the intrinsic viscosity which has a value of 2.5 for non-interacting, rigid spherical particles. At sufficiently

high shear rate, the value $n = 2$ and at low shear rate, the n must be determined separately.

However, all the equations given above need a known and precise value of ϕ_m or A and then a further prediction of suspension viscosity can proceed. Unfortunately, so far, the determination of ϕ_m both by analytical prediction [27] and by experiment, e.g., sedimentation technique [23], has its limitation on providing reliable information. Therefore, the prediction of ϕ_m is critically important and it should be best determined directly from rheological data measured experimentally in realistic systems.

Inspection of the relationship on viscosity - concentration equations, we found that they have a very basic form of

$$1 - \eta_r^{-1/n} = f(\phi) \quad (6)$$

here n is equal to 2 for most high-shear applications as described in Equations 3–5. Further, an extensive analysis reveals that a linear relationship between $1 - \eta_r^{-1/2}$ and ϕ is frequently observed for a large variety of suspensions with sufficient solid concentrations. (In fact, such linearity can also be extracted from a number of existing models, e.g., Equations 3–5. Therefore, Equation 6 can be expressed in an analytical form of,

$$1 - \eta_r^{-1/2} = a\phi + b \quad (7)$$

The constants a (slope of the straight line) and b (intercept value) have to be determined experimentally. From Equation 7, it is clear that when ϕ is close to ϕ_m the relative viscosity (η_r) of suspensions becomes infinite, i.e., $\eta_r^{-1/2} = 0$, and Equation 7 is expressed as,

$$1 = a\phi_m + b \quad (8)$$

Therefore, the maximum particle packing density ϕ_m can be calculated from Equation 8 by,

$$\phi_m = \frac{1 - b}{a} \quad (9)$$

Once the constants a and b are determined via $1 - \eta_r^{-1/2} - \phi$ relation, a model which is basically used to describe the viscosity behavior of suspensions is established. This model can be expressed by rearrangement of Equation 7, which yields

$$\eta_r = (1 - a\phi - b)^{-2} \quad (10)$$

For highly-concentrated suspensions, Equation 10 can be approximated as a form similar to that of Equation 4.

By incorporating Equation 9 into Equation 10, a new viscosity model is then proposed, having an expression of,

$$\eta_r = [a(\phi_m - \phi)]^{-2} \quad (11)$$

The term $(\phi_m - \phi)$ is clearly defined as the effective space available for the particles to move in the matrix media. When $\phi \Rightarrow \phi_m$, the effective space will reduce

and the viscosity of suspensions becomes thicker and finally turns to be infinite at the point of ϕ_m . Equation 11 is essentially a two-parameter equation and the parameters a and ϕ_m can be determined easily via a single $1 - \eta_r^{-1/2} - \phi$ plot through the use of a few viscosity-concentration data.

Since Equation 11 is proposed originally for highly-concentrated suspensions under sufficient shear conditions, it may be used to characterize the suspensions over a wide variety of materials as well as shearing conditions. For this purpose, we further propose that Equation 11 can have a more general form of,

$$\eta_r = [a(\phi_m - \phi)]^{-n} \quad (12)$$

where n is a flow-dependent parameter and is also suspension-specific. However, in the investigation, we find a fairly good predictive ability of the newly-proposed viscosity model with the use of $n = 2$, i.e., Equation 11, for many ceramic powder suspensions to be presented in following section.

3. Applications to ceramic suspensions

To examine the validity of Equations 7–9 for ϕ_m determination, rheological data available from the experimental work performed by Song and Evans [28] for primarily ceramic injection molding applications are first used for demonstration. The solid concentration are relatively high, e.g., up to 70 vol% and the average particle size employed is from 0.7 μm to 1.5 μm . These powders are essentially different in geometry as well as in the level of agglomeration.

By inserting the rheological data and corresponding solid concentration into Equation 7, Fig. 1 shows the resulting $1 - \eta_r^{-1/2} - \phi$ curves for four different ZrO₂ powders. As expected, the correlation is linear and by extrapolation of the value $1 - \eta_r^{-1/2}$ to 1, a corresponding value ϕ_m is obtained for each powder. A comparison of the maximum packing density between the calculated values (ca. ϕ_m) and the reported values (ϕ_m) is

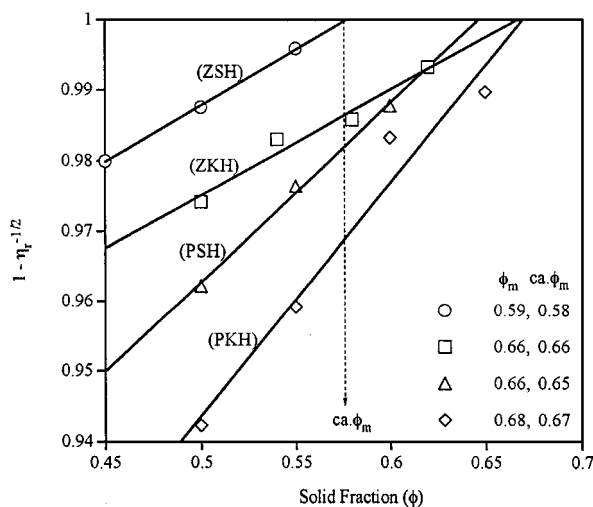


Figure 1 The $1 - \eta_r^{-1/2}$ versus concentration (ϕ) curves, showing a well-fitted linear correlation, for highly-concentrated suspensions prepared by Song *et al.* [28] for ceramic injection molding application.

TABLE I A list of the comparison between reported ϕ_m [23] and calculated ϕ_m from Equations 7–9 for different ceramic powder suspensions. The range of solid fraction for the calculation of ϕ_m for each suspension is also tabulated in parentheses

| Suspension (solid fraction) | ϕ_m (Reported) | ϕ_m (Calculated) |
|--|---------------------|-----------------------|
| Alumina-xylene (0.42–0.45) | 0.468 | 0.466 |
| Alumina-Glycerin (0.48–0.50) | 0.550 | 0.542 |
| Silica-Ethanol (0.500–0.598) | 0.652 | 0.655 |
| Silica-Glycerol (0.574–0.600) | 0.640 | 0.639 |
| Talc-Polyethylene (0.15–0.30) | 0.44 | 0.41 |
| CaCO ₃ -Polyethylene (0.22–0.34) | 0.52 | 0.55 |

also given in the legend of Fig. 1. The agreement is excellent.

Using the same methodology, the maximum packing density of a variety of ceramic suspensions which are selected simply because each has a reported ϕ_m value is computed and is given in Table I. It is obvious that the calculated ϕ_m has a value identical or close to the reported ϕ_m for each suspension. Since all the available data used for the determination of the maximum packing density in this study cover a wide spectrum of material parameters such as particle size, shape, distribution, and particle chemistry as well as the corresponding matrix fluids, it may further confirm the feasibility of the proposed equations, i.e., (7)–(9), for the determination of the maximum packing density for given colloidal suspensions.

4. Experimental verification

However, the rheological data on ϕ_m from the literature are mostly obtained through the use of best-fitting procedure. It may need to have a close and direct examination. For this purpose, ZrO₂-wax suspensions with different solids loading, i.e., 55–64 vol% (the preparation procedure was detailed elsewhere [19, 29]) with an incremental volume fraction of 1–2% were prepared. The use of small fractional interval of the solid particles in the suspensions may ensure a better approach with accuracy to the value of ϕ_m directly observed in comparison with the one calculated. The viscosity of the suspensions was measured at 85°C using a capillary rheometer (Shimadzu, CFT-500D, Japan). Accordingly, if the suspensions can not be sheared under a given shear stress (25 MPa) until the solid loading is increased up to some critical value and the critical value can then be considered as the solid loading that should be the fraction closest to the maximum packing density (ϕ_m). In order to justify the test, a corresponding concentration-viscosity curve was established and we find the extrapolated ϕ_m (to infinite viscosity) from the curve is rather close to the one observed from the shear-deformed method.

The resulting flow behavior of the suspensions at an increasing solid loading and the calculated ϕ_m shows

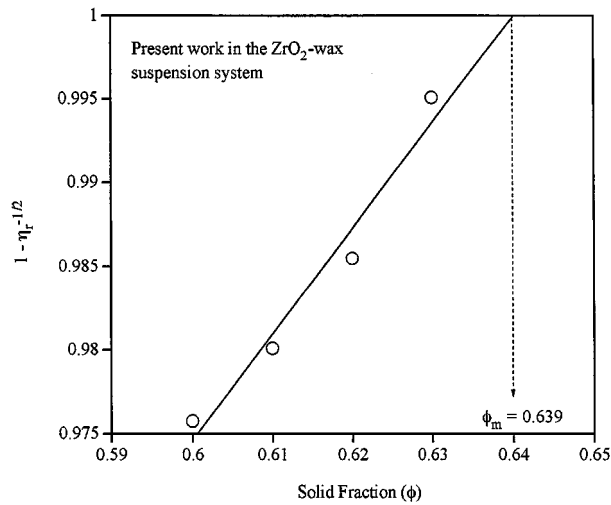


Figure 2 A comparison between the calculated ϕ_m via $1 - \eta_r^{-1/2} - \phi$ relation and the value obtained by a close examination on a series of highly-concentrated zirconia-wax suspensions with small increment of solid fraction prepared currently.

that the suspensions are virtually flowable until a solid loading of 0.64 is reached where no visible sign of flow can be detected under the maximum shear force. The suspension with the fraction of 0.64 behaves essentially like a rigid solid under the condition of shear. This indicates the maximum packing density should probably be in the range of 0.63–0.64. By inserting the obtained rheological data (some are abandoned due to the limitation of the instrument) into the equations and Fig. 2 shows, albeit not perfectly fitted, a linear relation with correlation coefficient as good as 0.98, together with an extrapolated value of $\phi_m = 0.639$. The extrapolated $\phi_m = \sim 0.64$ (estimated) was obtained from the concentration-viscosity curve. Both show good agreement. Therefore, it is reasonable to show that the calculated ϕ_m has a value just lying between the critical solids loading experimentally observed. The agreement on the maximum packing density between the experimental examination and the calculation is good. This further provides a direct and strong evidence on supporting Equations 7–9 for a given real suspension.

5. Viscosity prediction

With the achievement of ϕ_m via an extrapolation of Equations 7–9, it should be possible to use the viscosity model described in Equation 11 to predict the viscosity of suspensions. Since the parameters a and ϕ_m are determined experimentally for a given suspension, Equation 11 is a suspension-specific model which allows the viscosity of a given suspension to be predicted precisely once the parameters are accurately determined. To better illustrate this, the data of relative viscosities (η_r) from all the suspensions mentioned above are used and plotted against the relative viscosity calculated from Equation 11. Fig. 3 shows the resulting correlation (the plot in the inset is the data at lower viscosity values). As expected, the correlation is fairly good with a correlation coefficient $R^2 > 0.99$. This finding strongly indicates that the proposed viscosity model does offer a simple and reliable method for viscosity prediction of

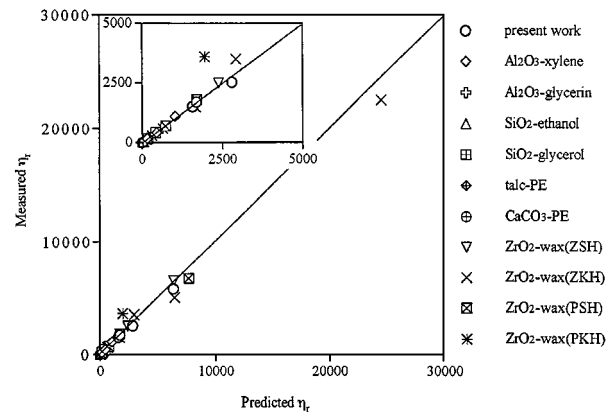


Figure 3 A comparison of the predicted viscosity using the newly-proposed viscosity model (Equation 11) with the measured viscosity for a wide variety of suspensions.

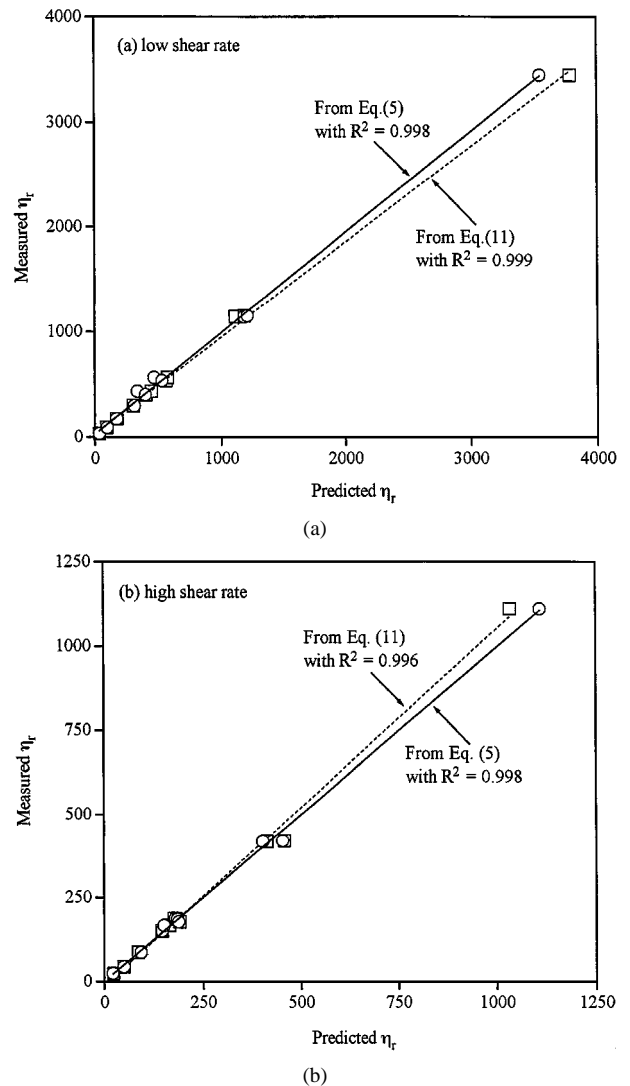


Figure 4 A comparison of the predictive capability of the viscosity model between the Dabak-Yucel model (Equation 5) and the model currently proposed (Equation 11) over (a) low shear rate and (b) high shear rate regions.

colloidal suspensions with a wide range of solid concentrations.

In comparison with existing viscosity models, the Dabak-Yucel model, i.e., Equation 5, is selected which has readily been confirmed to predict well the viscosity for a large variety of ceramic suspensions over a

wide range of shear conditions. The relative viscosities of the ceramic suspensions quoted from an article by Dabak *et al.* [23] determined at low and high shear rates are plotted against the relative viscosity predicted by Equations 5 and 11 and are shown in Fig. 4a and b, respectively. Obviously, both models illustrate roughly the same predictive capability of the suspension viscosity in a relatively accurate manner (their correlation coefficients are relatively high and nearly identical in both shear rate regions). According to Dabak *et al.* [23], the low and high shear rate regions can be used to represent non-Newtonian and Newtonian behaviors, respectively, and this seems to indicate that the viscosity model currently proposed is capable of predicting the viscosity behavior for both non-Newtonian (e.g., in cases of suspensions prepared currently and those reported by Song *et al.* [28]) as well as Newtonian fluids. Unlike the Dabak-Yucel model which is essentially a three-parameter model, the parameters used to characterize the equation have to be determined in a separate manner, Equation 11 does offer a very simple methodology for characterizing a given suspension with sufficient solid concentration.

6. Conclusions

A new model is proposed for the determination of the maximum packing density (ϕ_m) for essentially concentrated colloidal suspensions, which has, to our knowledge, rarely been reported. This model is essentially suspension-specific and provides a direct and simple methodology to calculate the ϕ_m in a relatively accurate manner. After the parameters a and ϕ_m , which are used to construct the newly-proposed equations, i.e., (7)–(9), are determined via experimentation, a corresponding viscosity equation, i.e., Equations 11 or 12, is established. This two-parameter viscosity equation was found to predict the viscosity of a variety of ceramic powder suspensions very well.

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