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Effect of surfactant adsorption on aggregate structure and yield strength of zirconia-wax suspensions

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The suspension structure and strength of the particle network in a flocculated zirconia-wax system have been investigated through capillary extrusion at a temperature above the melting temperature of the wax. Submicrometer zirconia particles were first coated with various amounts of stearic acid for providing steric stabilization of differing degrees before being blended with the wax of a fixed solids fraction (50 vol%). When the acid coverage was ∼20% of the nominal particle surface, an apparent particle network in a form of connected "dimples" together with isolated wax ligaments was found after shearing. As the acid coverage was raised further, a collection of discrete flocs rather than the particulate network was seen after deformation. The agglomerate flocs reduced their size as the acid adsorption was increased. Yield stress of the suspension, which is a macroscopic property, exhibited a linear dependence with the surface coating. A reduction over 90% in the yield value was found as the surface adsorption increased from 20 to 100% at the working temperature employed.

1. Introduction

The dispersion of particles in organic media has been an important subject in powder injection moulding (PIM) [1–4]. The structure of concentrated powder suspensions can be engineered via manipulation of the interparticle forces in given carrier fluids. Suspensions with appropriate flow properties are desired for complete mould filling while a uniformly packed structure with a certain yield stress is required for precise shape retention during dewaxing of the moulded compacts. The addition of powders to an organic matrix would inevitably alter the flow characteristic of suspension systems. The viscosity and yield stress of suspensions often follow a power-law dependence on particle concentration [1, 5–7]. Theoretically, the yield stress (τ_y) of suspensions can be expressed as a function of solids fraction, such that [5]

$$\tau_y = \frac{N\alpha}{8\pi d^3}\left(1 - \frac{\phi}{\phi_m}\right)^{-4} + \frac{3N\varepsilon\varepsilon_0 k\Psi_0^2}{4\pi \mathrm{d}} \qquad (1)$$

where N is the coordination number of particles, α the Hamaker constant, d the particle size, ϕ the solids fraction, ϕ_m the maximum solids fraction at which the viscosity approaches infinity, ε the dielectric constant of the carrier fluid, ε_0 the permittivity of air, Ψ_0 the surface potential of particles, and k the reciprocal Debye thickness of the electrostatic interaction layer. The first term on the right hand side of Equation 1 involves the van der Waals-London attraction between particles and the second term is merely a result of the electrostatic interparticle potential. Experimental evidence has verified the equation in a qualitative manner. The magnitude of the suspension yield stress increases with solids concentration [7, 8], decreasing particle size [9] and increasing surface potential of the particles [9, 10].

In wax-based ceramic systems, according to Song and Evans [11], several repulsive forces that would counter the London attraction may be negligible. These include the electrostatic stabilization mostly encountered in the aqueous fluids, the elastic stabilization, kinetic stabilization, and all the possible interactions between forces mentioned above. This argument is based on the fact that wax liquids are mostly of low molecular weight and dielectric constant. For improving the stability of powders in wax liquids, minor addition of organic surfactants such as fatty acids to the suspension system has been shown to effectively reduce the viscosity of suspension systems [1–4, 11] and has thus become a usual practice in PIM.

Johnson *et al.* [12] have nonetheless reported that these adsorbed acids of small molecules do not present sufficient chain length to provide a "true" steric stabilization when the adsorbed layers overlap as particles approach one another. Liu [4] recently demonstrated that the adsorbed layer serves merely to increase the interparticle spacing so that the attractive potential between particles is reduced. In an earlier report [13], we have shown that a suppressed flowability has been resulted when the powders possess a lesser degree of surface modification (by the stearic acid) in the concentrated zirconia-wax system. It was then postulated that a formation of powder agglomerates due mostly to the partial surface coverage (by the acid) is the main cause for the phenomena obtained since the van der Waals-London attraction was the dominant force for the interparticle potential in the given system. The interparticle attraction was anticipated to result in a geometrical interlocking of the particles and inhibit the powders from sliding over neighboring ones freely in the carrier fluid when subjected to external stresses. This hence hampers the suspension flow adversely. In this regard, we intend to provide further experimental evidence on the interparticle structure when different levels of stearic acid were introduced into the zirconia-wax suspension system. Different degrees of the acid adsorption on particle surface were expected to give rise to powder agglomeration of varying levels even when the powder mixtures were prepared under identical mixing operation. Microstructural observation of the fractured extrudates after the capillary rheometry has been compared in parallel with the rheological behaviours of the suspensions to elucidate the influence of suspension structure to the flow properties attained.

2. Experimental procedure

Yttria-stabilized zirconia powder (ICI-3Y, Australia) with an average particle size of 0.24 μm and a specific surface area of 15 m^2/g was used as the starting material. The as-received powder presents a roughly spherical shape and is heavily agglomerated (Fig. 1). The powder was first mixed with stearic acid (Lancaster, USA, average molecular weight of 284.5 g/mol and melting point of 67 °C) of differing amounts by a ball miller using high-purity zirconia balls as a grinding medium in reagent-grade toluene for 24 h. The ratio of powder loading versus the toluene solvent was kept constant at a volumetric ratio of 1 : 5, which ensured the slurries with a relatively low viscosity to aid powder dispersion for adsorption purposes during mixing. The concentration of the added stearic acid in toluene varied from 1 to 10 mg/ml to give the zirconia powders with varying degrees of the acid adsorption. The mixed slurries were filtered through membrane filters after the mixing operation and the filtered cakes were washed repeatedly in toluene so that the acid-adsorbed powders were separated from the liquid solvent. Except those adhere strongly on the particle surface, all free acids were assumed to be removed from the surface after the treatment. The powders were then annealed at 150 °C for 24 h in air to ensure a chemical adsorption has been obtained on the powder surface, as claimed by Novak and co-workers [3]. Thermogravimetric analyzer (Netzsch Model 309A) with a precision of 0.01 mg was used in determining the actual adsorption amount of the acid. An adsorption isotherm which reveals the minimum amount for achieving the complete surface coverage by the stearic acid in the given powder-toluene mixture was determined, as illustrated elsewhere [14]. The zirconia powder with a desired surface-modification level was hence made possible. The relative surface coverage in a range of 20 to 100% of the surface area available from the zirconia powder was chosen in this study for comparing the acid-modification effect on the rheological and structural properties of the suspensions.

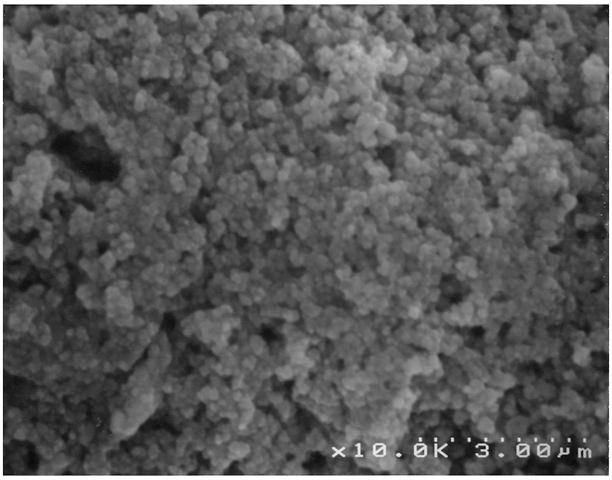


Figure 1 Particle morphology of the starting zirconia powder.

The surface-modified powders were then blended with paraffin wax (Echo Chemicals, Taiwan, average molecular weight of ~500 g/mol and melting temperature of 51 °C) in a pre-determined solids loading of 50 vol% by ball mixing in toluene again similar to the previous mixing operation. Notice that the solids loading was determined in terms of the "bare" powder volume used, i.e., the adsorbed acid layers were excluded from the loading calculation. The powder slurries presented a low viscosity characteristic with an aim to better disperse the particles in the given wax-toluene liquid. The chemisorbed acid layers were assumed to adhere strongly on the particle surface; therefore, the free acid molecule that might be separated from the particle surface by the impact collision of the milling balls during mixing was considered negligible. The slurries after 12 h mixing were then intensively agitated to evaporate the toluene solvent by use of a planetary mixer operated at a constant rotational speed of ~1000 rpm and at a moderate temperature ~40 °C. The dried granules were of mm in size typically and were about spherical in shape.

The powder granules were uniaxially pressed into cylinders of 10 mm in diameter and 10 mm in height, and were then extruded through a capillary rheometer (CFT-500D, Shimadzu Co., Japan) with a cylindrical orifice 1 mm in diameter and 10 mm long at a constant testing temperature of 58.5 °C. The apparent shear stress (τ) exerted upon the mixture was calculated from

$$\tau = \frac{PD}{4L} \tag{2}$$

where P is the applied pressure, D the orifice diameter of the die (1 mm), and L the length of the die orifice (10 mm). Typical shear rate investigated was in a range of 100–15000 s^{-1}. Bagley and Rabinowitch corrections with a L/D ratio of 10 equipped within the microprocessor-controlled rheometer were used to modify the viscosity results experimentally obtained. The extrudates after rheometry were fractured and the fractured surfaces were examined by scanning electron microscopy (Hitachi S-2700, Japan).

3. Results and discussion

The zirconia-wax suspension with the varying surface modifications exhibited a pseudoplastic behaviour over the shear-rate range investigated [13]. The shear viscosity (η) decreased pronouncedly as the surface coverage on the particle surface (by the acid) was increased. Reduction in the suspension viscosity was found particularly pronounced when the shear rate applied was at the lower rate regime and when the surface coverage on the particle surface approached toward the lower adsorption level (Fig. 2).

The yield stress of the suspensions was determined by a model proposed by Casson [15], who related the shear stress (τ) to shear rate (γ) by

$$\tau^{1/2} = \tau_y^{1/2} + (\eta \times \gamma)^{1/2} \tag{3}$$

Fig. 3 illustrates the linear dependence of $\tau^{1/2} - \gamma^{1/2}$. The yield stress ($\tau_y$) is estimated from the intercept by extrapolating the linear $\tau^{1/2} - \gamma^{1/2}$ dependence to $\gamma^{1/2} = 0$ and is shown in Fig. 4 for the suspensions with the varying adsorption levels. A linear dependence of the suspension τ_y to the surface coverage was found in the given suspension system. The yield values reduce pronouncedly in magnitude by as much as 93% when the surface modification was increased from 20 to 100%.

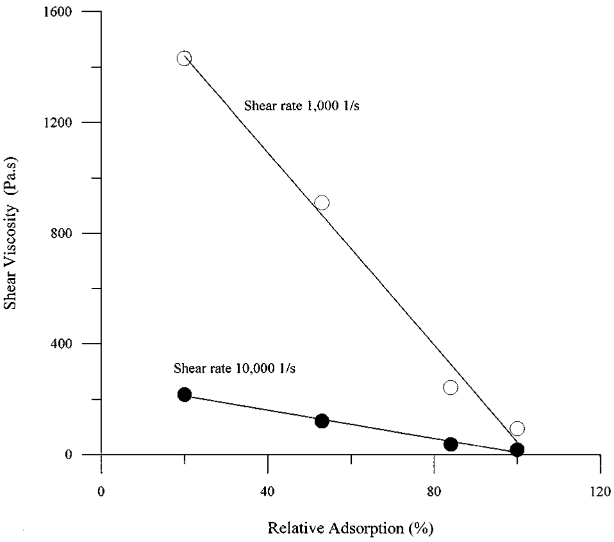


Figure 2 Shear viscosity of zirconia-wax suspensions (50 vol%) under various shear rates and acid coverages. Testing temperature was held constant at 58.5°C.

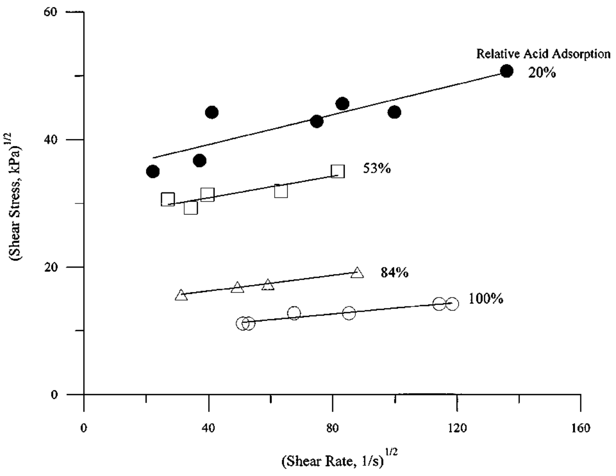


Figure 3 The linear dependence of (shear stress)$^{1/2}$ – (shear rate)$^{1/2}$ of suspensions at varying adsorption levels.

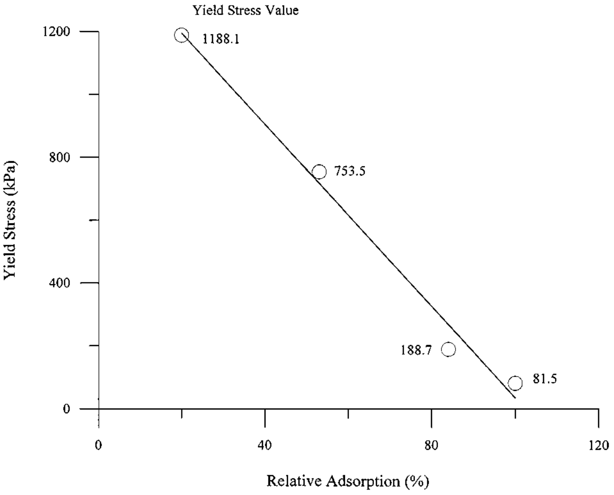
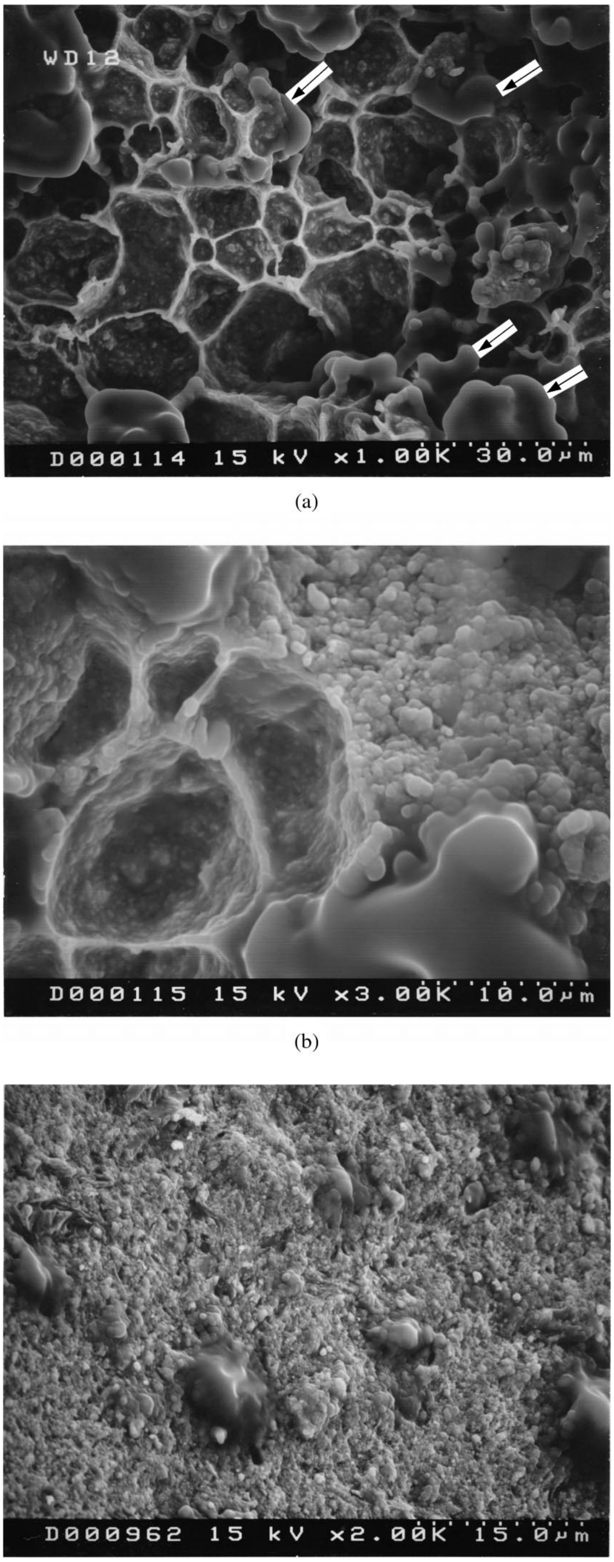


Figure 4 Yield stress of suspension at various acid adsorptions.

Microstructural examination of the fractured extrudates with the varying surface modifications reveals the "internal" particle structure after shearing. Fig. 5a shows the apparent particle network in a form of connected "dimples" together with isolated wax ligaments after shearing for the 20% surface-modification case. An enlarged micrograph (Fig. 5b) shows the dimples are in fact powder agglomerates and apparently present a continuous 3D structure after shearing. The floc size ranges from ~5 to 30 μm with either spherical or polygonal shape. The deformation of suspension appears to have occurred at the inter-floc interface, which suggests that the strength of the agglomerate may be substantially higher than the "bulk" shear stress applied ($\tau = 4903$ kPa) by an undetermined extent. Increasing the applied stress to a substantially higher level ($\tau = 15.20$ MPa) leads to a disappearance of the particle flocs (Fig. 5c). This suggests the breakup of agglomerates into smaller flow units may have occurred as the stress level was increased. One might suspect that the powder agglomerate found in Fig. 5a actually comes from the agglomerate in the as-received powder that have not been effectively broken down when dispersed in the liquid medium during mixing. For those agglomerates that have persistently existed in the mixture after the granulation operation, application of the shear stress involved in the rhemetry testing would have in fact introduced an additional "mixing" effect to the originally



(a)

(b)

(c)

Figure 5 (a) Particle network structure of suspension with 20% surface coverage by stearic acid underwent deformation at an applied stress of 4,903 kPa. Arrows indicate some wax ligaments. (b) An enlarged micrograph of 5(a). (c) Zirconia-wax suspension with the identical 20% surface coverage tested at an applied stress of 15.20 MPa.

undispersed mixtures. This hypothesis may be partially vindicated from Fig. 5a and c, from which, the increase of shear stress in rheometry has led to the powder agglomerate with a reduced size and occurrence.

The isolated wax ligament, as indicated by arrows in Fig. 5a, was found randomly scattered in the powder matrix without preferred orientation and shape morphology apparently. The wax liquid is hence probably not penetrated into the interstices of the powder agglomerates during mixing completely. Notice that the powder-wax mixtures were in toluene solvent with a considerable volume for providing a relatively low viscosity to aid particle dispersion. Even under such a condition, the agglomerate still exists and the cause for this is most likely from the insufficient acid coverage on the particle surface. The undispersed agglomerates may be of solid-bridge in character; in addition, the possibility of particles that were initially dispersed in the carrier fluid to re-combine toward one another in forming agglomerates might have also occurred as the applied shear stress involved during mixing was terminated. In the flocculated powder-wax system, Song and Evans [16] have proclaimed that for particles that were initially broken apart by the stresses involved during mixing/shaping, particles may still quickly re-flocculate toward each other by the London attractive force as the powder compact was subjected to an annealing process after forming. Similar flocculation of initially broken flocs to recombine themselves in the liquid wax at the end of mixing is expected to occur in our present system. This phenomenon would at least in part contribute to the powder agglomeration found in Fig. 5. The relative rate for the particles to re-join toward each other is expected to be faster than the rate of floc breakup as the acid coverage of particles was at a lower level. As evidenced in our model system, the occurrence of the powder agglomeration becomes critically apparent as the surface coverage of the acid was at the 20% level.

When the acid adsorption was raised further above the 20% coverage, a collection of discrete flocs rather than the particle network was seen after deformation, as shown in Fig. 6a and b for the surface coverage of 53% and 100%, respectively. Notice that the stress level used in Fig. 6a and b, in terms of the difference in stress magnitude between the applied and the yield stress of the suspensions observed, was held comparable to that of the 20% case (Fig. 5a). Fig. 6c shows a typical agglomerate in the 53% case. The outer surface of the agglomerate was surrounded by the wax, forming an outer “shell” around the floc. The floc seems to have reduced its size as the acid adsorption increased toward the full acid coverage (Fig. 6a and b). As shown in Fig. 6b, the floc presents a size similar to the average particle size of the as-received powder when compared to Fig. 1, and is better dispersed than all the other suspensions which were only partially coated by the acid.

As one realized, a powder network would impose a restriction to particle flow when an external stress was applied [13]. This constrained structure would lead to an increase in the yield strength and the viscosity as well for the powder suspension. Particles within the suspension can thus be conceptualized such that no relative motion between the particles is allowed to occur when the applied stress is below the critical yield value. Therefore, only when an external stress exceeds that of the suspension yield stress does the particle network collapse (to a certain extent) and the suspension begins to flow in compliance with the stress applied. In the

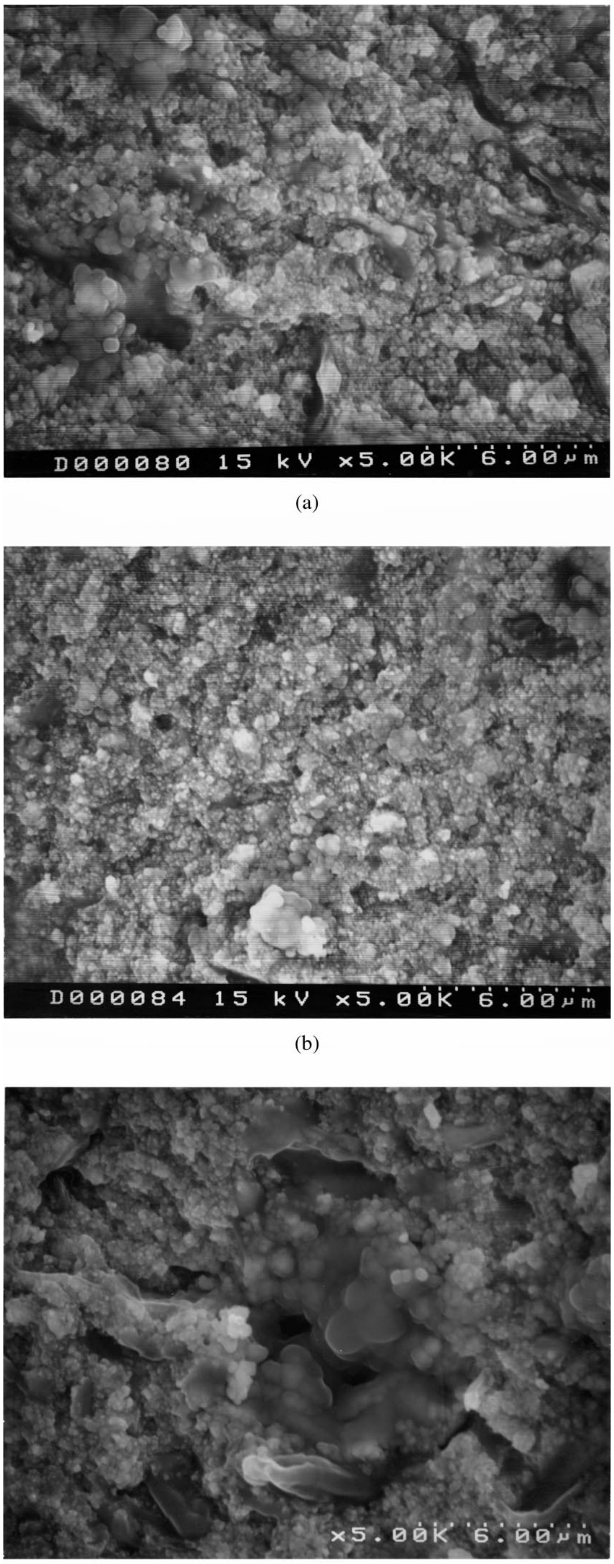


Figure 6 (a) Particle network structure of suspension with 53% surface coverage by stearic acid underwent deformation at an applied stress of 3,923 kPa. (b) Particle network structure of suspension with 100% surface coverage by stearic acid underwent deformation at an applied stress of 802 kPa. (c) An enlarged micrograph of 6(a) highlighting a large particle floc.

case that a carrier fluid presents a high intrinsic viscosity, the hydrodynamic resistive force exerted by the carrier medium is expected to contribute to the suspension rheology along with that from the interparticle forces. For the low molecular weight wax used in the study, the yield stress of the liquid wax alone was only ~75 Pa at the working temperature employed [16]. This value is relatively insignificant as compared to the suspension yield stresses illustrated in Fig. 4; therefore, the interparticle force should have played a major role in the determination of suspension yield stress in the given system.

The suspension yield strength may be expressed as a sum of the attractive force (τ_a) and the repulsive force (τ_r) from the interaction of solids phase, and the yield value of the matrix fluid alone $(\tau_y)_m$,

$$\tau_y = \tau_a + \tau_r + (\tau_y)_m \tag{4}$$

Since the wax presents a low resistance to flow in the given suspension, the above expression of the suspension yield may be solely represented from the interparticle effect. If this were true, we would anticipate that a significant drop of the yield stress of the suspensions to occur as the surface coverage of the acid increased over 20%, as evidenced in the prominent change of the deformation mechanism when the acid coverage was increased over this critical level. However, a linear dependence of the yield value to the acid coverage resulted (Fig. 4). The Casson's equation used to predict the suspension yield stress extrapolates a linear $\tau^{1/2} - \gamma^{1/2}$ dependency over a range of shear rates to $\gamma^{1/2} = 0$. As shown in Fig. 3, the linear $\tau^{1/2} - \gamma^{1/2}$ dependence of the 20% case is the one which presents the poorest linearity among all the adsorption levels investigated. It also seems that the linearity improves as the acid adsorption increases toward the full surface coverage in particular. This observation suggests that the extent of powder agglomeration in the concentrated suspension system may present a possibility of introducing potential "bias" in determination of the yield stress. For the determination of yield stress in a flocculated suspension system, obtaining more data points at a lower shear-rate regime may hence be of critical importance in order for accurate prediction of the yield value as the Casson's equation is applied.

4. Conclusion

This study provides a direct evidence of agglomerate breakdown as well as its deformation structure in a zirconia-wax system when the suspension was stressed under varying stress levels. The model zirconia powder was first modified with stearic acid of different degrees. This led to the suspension with powder agglomeration of different levels. The agglomerate was found to exist persistently in the mixture after mixing in a relatively low viscosity fluid and this became critically severe as the particle surface was insufficiently covered by the stearic acid. For the case of 20% acid coverage, a particle network was resulted when a lower stress level was applied, while the network was collapsed into smaller flow unit when the external stress was increased to a substantially higher magnitude. A notable reduction in the floc size has been observed as the surface modification approaches toward the full acid coverage. The suspension yield value exhibits a linear dependence with the degree of surface coverage.

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