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Suspension characteristics and rheological properties of mullite/zirconia powder in methyl isobutyl ketone

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Particle size and its distribution, sedimentation bulk density and rheology of mullite, zirconia, and mullite/zirconia mixed suspensions have been studied in terms of oxide loading (20, 30 vol%), and types of additives (dispersant, dispersant/plasticizer, dispersant/plasticizer/binder). Polyester/polyamine, dibutyl phthalate, poly(vinyl butyral), and methyl isobutyl ketone have been used as the dispersant, plasticizer, binder, and liquid medium, respectively. Sedimentation density significantly increased upon adding dispersant; the effect was more pronounced with zirconia suspension most likely due to the fine and hence high specific surface area of zirconia. With further addition of plasticizer and plasticizer/binder, the sedimentation density decreased. The suspension viscosity generally behaved in an opposite manner to the sedimentation density, i.e., low sedimentation density gave high low-shear viscosity, indicative of high order structure formation in the suspended particles. High shear rate rheology showed a shear thinning and its onset began at lower shear rate with higher solid loading. Mullite/zirconia mixed suspension gave intermediate sedimentation and rheological behavior, implying the two types of particles are non-interacting.

1. Introduction

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is a useful ceramic material for advanced structural applications because it has high strength and high creep resistance at both low and high temperatures, a low thermal expansion coefficient, low thermal conductivity, and good chemical and thermal stability. However, mullite may yet develop even wider applications if its low fracture toughness ($\sim$2 $\text{MPa} \cdot \text{m}^{1/2}$) can be improved. A well-known processing route to improve the fracture toughness of mullite is to disperse or precipitate tetragonal zirconia (t-ZrO_2) particles in a mullite matrix, this resulting in transformed monoclinic (m-ZrO_2) under an applied stress [1–4]. The stress-induced phase transformation accompanied by volume expansion and shear deformation may cause beneficial toughening mechanisms [5] to become operative. Several processing routes for preparing mullite/ZrO_2 composites have been reported in the literature:

i. reaction sintering of Al_2O_3 and $ZrSiO_4$ [6–8],
ii. sintering of conventional mixtures of mullite and ZrO_2 powders [1, 9, 10],
iii. reaction sintering of mixtures of ZrO_2 and mullite precursors [11–14], and
iv. alternatively reaction sintering of ZrO_2, Al_2O_3 and SiO_2 [8, 15–17].

Tape casting is a low-cost process which can be used for producing thin, flat sheets of laminated composites [18–20]. The colloidal processing of tape casting slurries is essential, since it enables ceramic particles to form dense, uniformly packed green tapes, these developing into fully dense, homogeneous microstructures during sintering [21]. Usually, tape casting slurries need the addition of several different processing additives, such as dispersant, for particle deflocculation, and binder and plasticizer for optimum strength and flexibility [18, 19]. Nonaqueous solvents have been more commonly used for tape casting because of the enhanced powder dispersion and drying in a short time, with less heating. In recent years aqueous tape casting [22, 23] has received more interest due to consideration of environmental and health legislation.

The rheological behavior of a suspension is sensitive to the state of particle suspension, and this is substantially affected by selected solvents and processing additives. Methodical studies on the stability of tape casting slurries are difficult because of the chemical multiplicity of suspension systems. In suspension processing, ceramic particle surfaces may be combined with solvents [24, 25] and also organic additives (dispersant, binder, plasticizer, and sometimes surfactant), which are often interactive [26]. It has been reported that the suspension stability may be affected by a wide variety of solvents and processing additives, but different results can be obtained with any given suspension systems [27, 28]. In the suspension system consisting of various processing additives, such as tape casting slurries, a competitive adsorption of these several components takes place onto the particle surface, which affects dispersion stability and rheological properties. In this study, we report the effects of incorporating multiple processing additives on grinding, suspension stability and rheological behavior of nonaqueous mullite/zirconia suspensions. Relatively few papers describing such relationships in ceramic suspension systems have been reported.

2. Experimental procedure

2.1. Materials

Mullite (Baikalox-SASM, Baikowski Chimie, France) and 3 mol% Y_2O_3-doped ZrO_2 (HWA-ZY3, Hanwha Advanced Ceramics, Australia) were used in this investigation. The particle size distribution (measured by laser scattering in distilled water) and SEM photographs of starting mullite and zirconia powders are shown in Figs 1 and 2, respectively. The mullite consists of agglomerated particles with a mean size 0.99 μm and a BET surface area of 13.3 m^2/g. It contains 3 wt% free SiO_2. Zirconia shows a relatively strong tendency to agglomeration, with a mean particle size of 0.59 μm and a BET surface area of 13.3 m^2/g. The powder includes 4.89 wt% Y_2O_3 and minute amounts of impurities (<20 ppm) of Al_2O_3, Fe_2O_3, and TiO_2. An extra pure grade of methyl isobutyl ketone (MIBK, Aldrich Chemical Co., USA), as received, was used as a solvent to prepare the suspensions. Polyester/polyamine condensation polymer ('Hypermer' KD-1, ICI Chemical Co., Spain) and a chemical grade of dibutyl phthalate (Aldrich Chemical Co., USA) served as the dispersant and plasticizer, respectively. Poly(vinyl butyral) (PVB, Aldrich Chemical Co., USA) was used as a binder.

2.2. Preparation of suspensions

Three types of mullite, zirconia and mullite/zirconia (50/50, vol%) suspensions were prepared by adding 20 and/or 30 vol% powders into MIBK, with only dispersant ('d') present, with dispersant/plasticizer ('dp'),

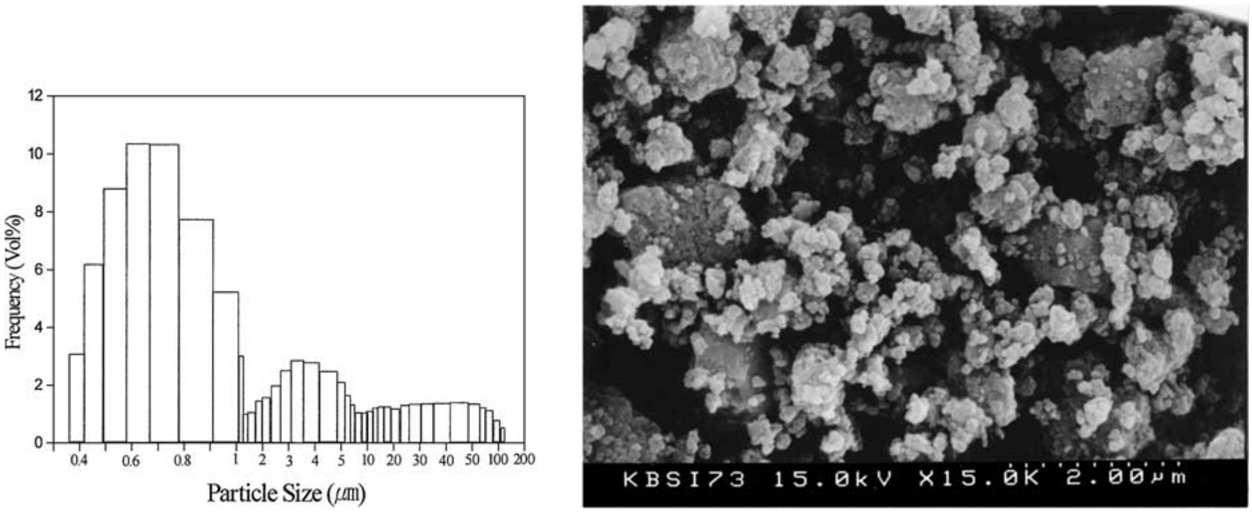

Figure 1 Particle size distribution and SEM micrograph of as-received mullite powder.

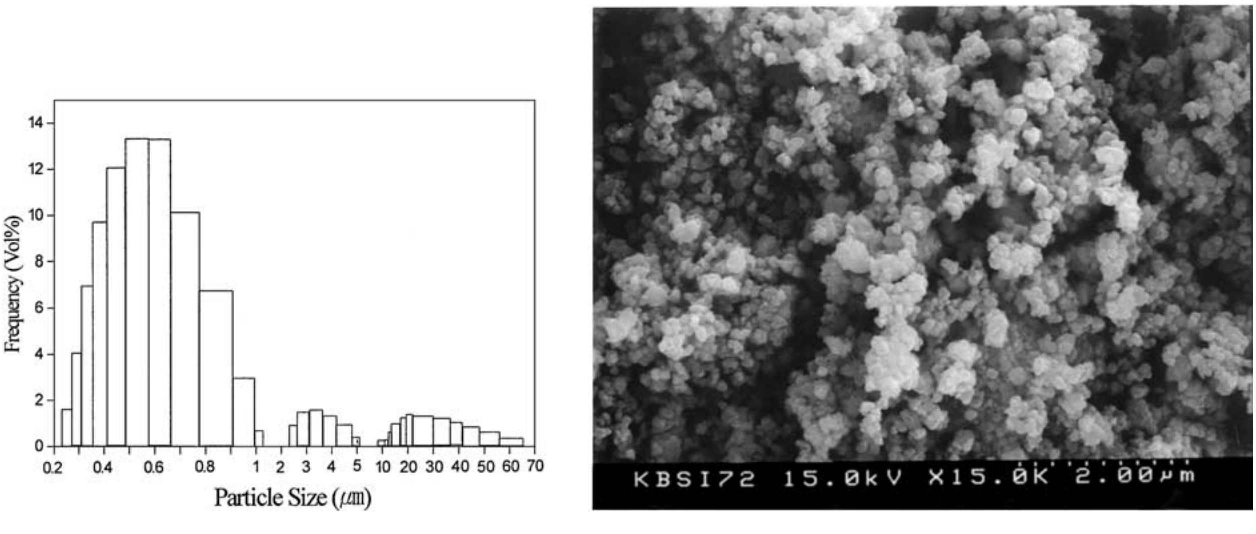

Figure 2 Particle size distribution and SEM micrograph of as-received zirconia powder.

and with dispersant/plasticizer/binder ('dpb'), respectively. The amounts of dispersant, plasticizer and binder added were 3, 5 and 6 wt%, respectively, based on the weight of oxide powder. Formulated suspensions were then ball-milled for 24 h using a high density zirconia lining and ball media.

2.3. Characterizations

To investigate the effect of processing additives on dispersibility of oxide particles in MIBK, sedimentation tests were carried out with 10 vol% suspensions. Each suspension of known weight was poured into 20 mL graduated cylindrical glass tube, and tightly capped to prevent solvent evaporation. The tubes were shaken several times, and treated ultrasonically in water bath to break down any soft agglomerated particles. The suspension particles were then allowed to settle until the sediment height no longer changed with time. Sedimentation bulk density was determined by dividing the weight of oxide powder by sedimentation bulk volume, measured directly from the height of the sediment.

Particle size distribution after milling was determined by a laser scattering technique (Microplus, Mastersizer, Malvern Instruments Ltd., England). The rheological properties of suspensions were measured using a controlled stress rheometer (CSL500, Carri-MED Ltd., England). Measurements were performed with a cone and plate fixture, with a cone diameter of 4 cm and angle of 2°.

3. Results and discussion

3.1. Sedimentation bulk density

Sedimentation bulk densities of mullite, zirconia, mullite/zirconia suspensions with 10 vol% solid loading are shown in Fig. 3. The processing additives greatly increased sedimentation bulk density, but the increase was somewhat different with individual suspension constituents. Zirconia with relatively small particle size and narrow size distribution (Fig. 2) showed a high packing density compared with mullite and mullite/zirconia. When added alone, the dispersant gave improved suspensions, however, introduction of additional components of plasticizer or plasticizer/binder decreased the degree of dispersion. A minor decrease in sedimentation bulk density with plasticizer (dibutyl phthalate) addition, compared with only dispersant, is probably due to the formation of organic bridges between particles. However, not all of the plasticizers decrease dispersibility, i.e., plasticizers such as benzyl butyl phthalate have been reported to deflocculate rather than coagulate the particles [29]. When the multiple processing additives are simultaneously added, the dispersibility of suspensions appears to depend on the competitive adsorption of additives onto the particle surface [30, 31].

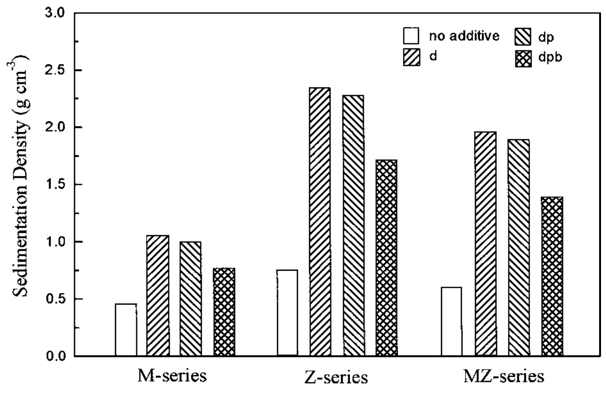

Figure 3 Sedimentation bulk density of 10 vol% mullite (M-series), zirconia (Z-) and mullite/zirconia (MZ-) suspensions with processing additives.

Decrease in sedimentation bulk density with binder addition is possibly due to the following:

i. the polar unreacted –OH side groups (typically 10–20%) of a binder (PVB) provide particle surface with adsorption force,

ii. dipole attraction of this side group also induces polymer–polymer network formation among the particles, resulting in agglomerated structure,

iii. such action of a binder considerably offsets repulsive potential energy between particles, created by electrical double layer and steric hindrance, and

iv. the large molecular weight of binder and its mechanically soft nature ties up particles, which directly contributes to the agglomeration and sedimentation.

3.2. Particle size distribution and rheological properties

The particle size distribution after milling is shown in Fig. 4 for 30 vol% mullite and zirconia suspensions. The milling process has broken up the coarser agglomerates of the starting powders, resulting in bimodal particle size distribution of <1 μm and 2–7.7 μm for mullite suspensions, and a unimodal one of relatively narrow range 0.36–1.06 μm for the zirconia suspensions. The effect of added plasticizer or plasticizer/binder on particle size distribution seems insignificant after ball milling of suspensions.

The effect of processing additives on the dispersion rheology has been investigated for the particular loadings of 20 and/or 30 vol% mullite and zirconia suspensions; the viscosity-shear rate relationships are shown

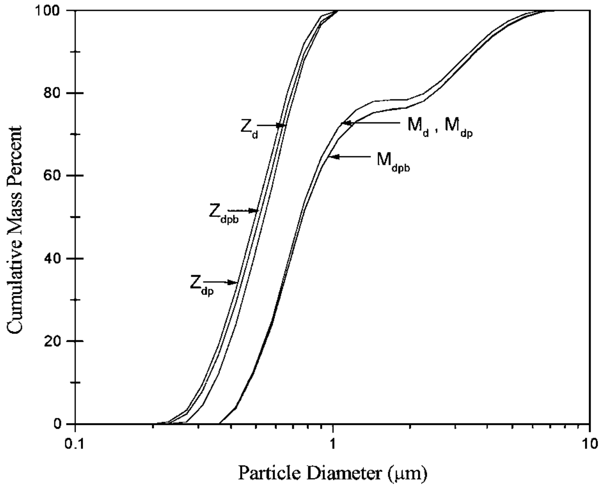

Figure 4 Particle size distribution of ball-milled 30 vol% mullite (M-series) and zirconia (Z-) with processing additives.

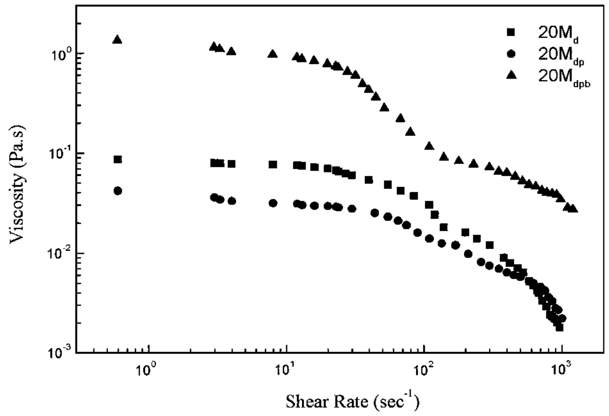

Figure 5 Log-log plot of apparent viscosity of 20 vol% mullite (M-series) suspensions with processing with processing additives as a function of shear rate.

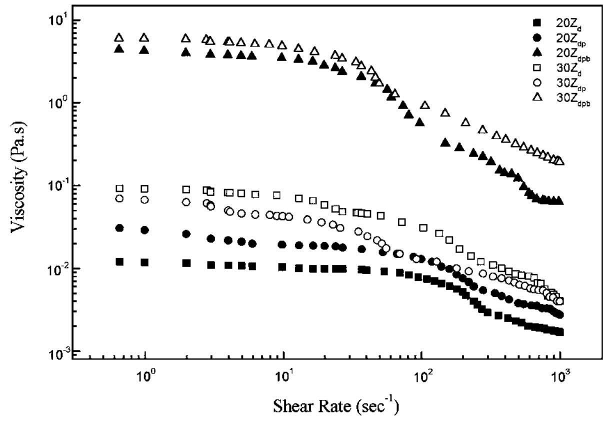

Figure 6 Log-log plot of apparent viscosity of 20 and 30 vol% zirconia (Z-series) suspensions with processing additives as a function of shear rate.

in Figs 5 and 6, respectively. Regardless of the oxide content and additive type, viscosity functions generally show a Newtonian plateau at low rate of shear, followed by a shear thinning region showing a rapid decrease of viscosity with increasing rate of shear, and in some case such as 20 vol% zirconia system with the addition of dispersant/plasticizer/binder (20Z$_{\text{dpb}}$), a second plateau region where the viscosity is virtually independent of the shear rate. In the literature, the two plateau viscosities are often referred to as η_o and η_∞, respectively. The shear thinning viscosity is described by a power law [32]:

$$\eta = m\dot{\gamma}n^{-1} \tag{1}$$

in which m (with units of $\text{N} \cdot \text{S}^n/\text{m}^2$) and the dimensionless quantity n are constant characteristic of the fluid. Clearly when $n = 1$ and $m = \mu$, one obtains the Newtonian fluid. If $n < 1$, the fluid is said to be pseudoplastic, and if $n > 1$ the fluid is described as dilatant. The majority of engineering fluids are shear thinning with the value of n ranging from 0.15 to 0.6.

At low rate of shear, particles are in equilibrium with the surroundings, i.e., the experimental time allowed is longer than the relaxation time of the dispersion. In such a situation, the resistance to flow i.e., the viscosity is governed by the particle-particle interactions in addition to the volume occupied by the solid particles described below [33]:

$$\eta_{\text{rel}} = 1 + k_1\phi + k_2\phi^2 + \cdots \tag{2}$$

In this equation η_{rel} is the relative viscosity ($\eta_{\text{suspension}}/\eta_{\text{solvent}}$), ϕ the volume fraction of particles, k_1 Einstein constant (2.5), k_i ($i > 1$) the interparticle interaction parameters. At low ϕ (<0.02), the higher order terms are neglected and Equation 2 becomes the Einstein equation, showing linear increase of viscosity with ϕ. In our experiments, the solid content is over 20 vol% and hence interactions between the particles should play an important role in determining the suspension viscosity.

When the suspensions contain additives other than the solid particles, the effective volume of the particle should increase due to the presence of an adsorbed layer, and this relation can be expressed as follow [34]:

$$D_{\text{p}}(\text{effective}) = D_{\text{p}} + 2\delta \tag{3}$$

$$\phi(\text{effective}) = f\phi \tag{4}$$

$$f = ((D_{\text{p}} + 2\delta)/D_{\text{p}})^3 \tag{5}$$

where D_{p} is particle diameter, δ the thickness of adsorbed layer, and f the effective volume fraction to work with the Equation 2. With the above in mind our rheology data will be discussed below.

The η_o for 20M$_{\text{d}}$ (20 vol% mullite with only dispersant) was approximately 10^{-1} ($\text{Pa} \cdot \text{s}^{-1}$). η_o decreased slightly with plasticizer (20M$_{\text{dp}}$) but increased by over an order of magnitude with the addition of binder (20M$_{\text{dpb}}$). The large increase in viscosity with addition of binder is consistent with the large decrease of sedimentation density with binder (Fig. 3). The PVB used as a binder in our experiments is a high molecular weight flexible polymer, tying up many particles in a bundle, which eventually results in a cohesive casting on drying. However, tying up many particles in suspension directly contributes to the particle interactions and hence increases low shear viscosity.

The onset of viscosity drop, viz. the start of power law behavior, is a sign of equilibrium structure break up and of orientation along the flow direction. Suspensions with a certain level of 3-dimensional structure could become oriented along the flow direction, and this would give lower viscosity, possibly by interlayer slip. Regardless of the additive type, the onset of viscosity drop starts at about 30 (s^{-1}). However, the power-law region ends at a much lower rate with binder (20M$_{\text{dpb}}$) as compared with the other two. This implies that the suspension structure built up by the primary binding of the particles by polymer chains is fairy uniform [35].

As shown in Fig. 6, with 20 vol% zirconia loading (20Z), η_o increases in the order of 20Z$_{\text{d}}$ < 20Z$_{\text{dp}}$ < 20Z$_{\text{dpb}}$, an order consistent with the reverse of values for sedimentation density. When the suspension forms higher order structures, the viscosity increases and sedimentation density decreases. In comparison with mullite suspensions, suspensions without binder show lower η_o for zirconia suspensions (20Z$_{\text{d}}$, 20Z$_{\text{dp}}$). However with binder present, the zirconia suspension

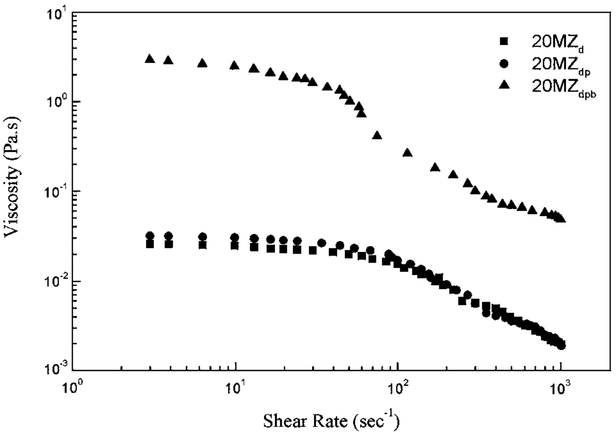

Figure 7 Log-log plot of apparent viscosity of 20 vol% mullite/zirconia (MZ-series) suspensions with processing additives as a function of shear rate.

($20Z_{dpb}$) gives much greater η_o value compared with mullite suspension ($20M_{dpb}$). This implies that PVB can tie up more of the zirconia particles than mullite particles, possibly due to the smaller average particle size of zirconia, as shown from the particle size distribution. The onset of shear thinning starts at a higher shear rate for zirconia suspensions, especially for $20Z_d$ and $20Z_{dp}$ as compared with mullite counterparts. This implies that break-up of zirconia suspensions needs more energy. As the solid content increases from 20 to 30 vol%, η_o increases by over one order of magnitude ($20Z_d$ vs. $30Z_d$). However, the increase of η_o with plasticizer and binder is smaller than for dispersant alone. This is in part due to the fact that not all of the additives are adsorbed on the particle surfaces, leading to the effective particle volume, described in Equations 3–5. Any additives not adsorbed on particle surfaces should affect suspension viscosity, notably, the onset of shear thinning behavior starts at much lower rate of shear at high particle loading. This indicates that the relaxation time distribution becomes broader with high order structures of the suspension, a concept which becomes more plausible with high solid loadings [36].

The effect of mixed oxides on suspension rheology has been studied for 20 vol% of mullite/zirconia mixture, and their viscosity–shear rate relationships are given in Fig. 7. The η_o value for mixed suspensions generally falls between the mullite and zirconia suspensions. This implies that mullite and zirconia particles are basically non-interactive and they behave intermediately in dispersion. It should also be noted that the η_o value for mixed dispersions is in the increasing order of $20MZ_d < 20MZ_{dp} < 20MZ_{dpb}$.

4. Conclusions

The effect of additive types and oxide loading on the sedimentation bulk density and suspension rheology have been carried out for mullite, zirconia, and mullite/zirconia suspended in an MIBK liquid medium. Addition of plasticizer and binder lowered the sedimentation density, with the effect more pronounced for the binder addition. This is in agreement with the increase in low-shear viscosity of the suspensions. Earlier onset of shear thinning behavior when binder was present was generally observed. It is suggested that the forces interacting with the particles with soft polymer chains appear most effective in relation to shear stress, leading to break up of the 3-dimensional structure of agglomerates. Mullite and zirconia particles appear to be non-interactive based on sedimentation bulk density and rheology measurements. This may imply both types of particles are effectively surrounded by the various additives.

Acknowledgements

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