EXAMINATION OF PARTICLE/PARTICLE INTERACTIONS AND THEIR IMPACT
ON RHEOLOGY AND MIXEDNESS OF AN ALUMINA/TITANIA SYSTEM

by

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ABSTRACT OF THE DISSERTATION

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In the manufacturing of ceramic particulate composites, improved manufacturing efficiency means two things, ease of production and increased performance. The effect of mixedness on the rheology of alumina-titania blends has been evaluated. Alumina and titania starting powders that have been examined ranged in particle size from nanoscale (50-200 nm) to micron scale (1-5 µm). Nano and micro-alumina powders have been combined individually with macro and micro-titania powders to determine how the nano/micro structure affects rheological properties and the mixedness of the final blended compositions. The effects of varying the mixing and processing techniques used to create the compositions; such as ball milling, wet mixing, high shear mixing, and varied mixing time, has been analyzed. The effect of varying surfactant additions (sodium stearate) on the mixedness and rheology of the alumina-titania blends has also been evaluated. The range of surfactant concentrations covers the measured adsorption limits of the particles in the blend, allowing sodium stearate to act not only as surfactant, but also as bulk lubricant.
Rheological evaluation of these blends included torque, dynamic stress, and capillary rheometry. Dynamic stress rheometry measures and compares the viscous modulus and the shear modulus of a blend, allowing determination of its dynamic yield stress. Capillary rheometry was used to evaluate the extrusion pressures of the alumina-titania batches, for analysis with a Benbow-Bridgewater model, yielding information on extrusion wall stresses and extrudate bulk strength. The mixedness was evaluated by SEM-EDS method, which created a compositional map of a cross-sectional area of extrudate for distributional evaluation by nearest neighbor and standard deviation calculations.

It was found that the use of nano-alumina and macro-titania increased processing requirements such as mixing energy and extrusion pressure, but produced extrudates with minimal flaws. Powder blends with macro-alumina and nano-titania were found to have desirable processing requirements with lower extrusion pressures and mixing energies, but produced extrudates with large flaws. Powder processing was found to have minimal impact on extrudate rheology but large impact on extrudate flaws. Powder blends with shorter processing times were found to have fewer flaws than those with longer mixing times or multiple extrusions.
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Introduction

The art of engineering ceramics has been around for thousands of years. In modern times, ancient ceramic art is joined with technical uses and requirements. Ceramics are used in a vast array of industries, from computer chip substrates and catalytic converters to fiber optic cable and piezoelectric materials. This increased range of use and need for precision creates many opportunities for examining and refining the processes by which ceramic parts are manufactured. All efforts to optimize manufacturing procedures must be welcome as improved methods lead to cost reduction and improved quality.

Alumina is a mineral commonly used in ceramic manufacturing. Its hardness allows it to be used as an abrasive while its low thermal expansion makes it a good choice for certain refractory applications[1, 2]. Titanium dioxide is often used as a pigment due to its whiteness[3]. It is also used for its photocatalytic properties which allow its use as a solar cell component[4]. Alumina and titania are often combined to create a commonly used wear resistance coating[5]. Many NOx catalysts also use an alumina titania compound. These catalysts convert harmful NOx gas into nitrogen and oxygen. NOx gas is a product of both diesel and gasoline engines making NOx catalysts largely in demand by the automotive industry[6].

Alumina titania NOx catalysts are manufactured by combining alumina and titania powders with a liquid phase and organic components to facilitate processing prior to extrusion and firing. The initial combining (mixing) and forming processes dictate how the alumina and titania will be distributed in the catalyst. It has long been known
that the distribution of components in a multi-component material can affect the material’s properties[7]. It was found that the stability and performance of a NOx catalyst is partially dictated by the preparation of the inorganic components[8].

One means of classifying distribution is to quantify the mixedness of the material. Mixedness refers to the arrangement of individual components within the material. There are almost as many methods of quantifying mixedness as there are studies about mixedness. Standard deviation, average, and variance are all means by which mixedness has been defined[9]. These values can apply to data from real samples as well as predictive models. One means of quantifying distribution is to look at the ratio of a quantity from an experimental sample as compared to the same quantity from a modeled ideal sample (one with a perfect distribution, homogeneity on the smallest length scale)[10].

The mixedness of a material can be varied by changing the processing of the initial components. Just how processing affects mixedness must be understood to ensure the optimal final properties will be attained. In the production of NOx catalysts; milling, mixing, batching, and forming can all affect the mixedness of the green body. In this thesis, the effect of processing on the mixedness of an alumina-titania green body will be evaluated. Nano and micron-sized aluminas and titanias will be combined stoichiometrically, processed with wet and dry procedures and extruded. The extrudate will be evaluated rheologically to determine the effects of processing on paste rheology. Compositional maps of the batch extrudate will be created and evaluated to determine the effect of processing variations on the mixedness of the green batch. Lastly, the bulk flaws in the extrudate will be quantified for batch to batch comparison.
2

Literature Review

2.1 Particle Interactions

2.1.1 Definitions

A particulate system can refer to any system with distinctly identifiable components. This can include; solid particles in a liquid, dry particles in air, or a mixture of two immiscible liquids. The nomenclature for particles and particulate groups varies greatly in the literature. The following definitions will provide consistent reference for this body of work.

Primary Particle

A primary particle can be defined as the smallest identifiable subdivision in a particulate system. An aggregate is a cohesive mass consisting of primary particles[11].

Aggregate

An aggregate is a cohesive mass of particulate subunits. The term aggregate is a generalized term which can apply to many systems[11].

Agglomerate

An agglomerate is a specific aggregate which occurs in a suspension and is held together by physical or electrostatic forces[11].
**Floc**

A floc is an aggregate which forms in a suspension by the addition of a polymer[11].

**Dispersion**

A dispersion is a two-phase system in which one phase is composed of discrete elements distributed in a continuous phase. For this thesis, a dispersion will refer to discrete solid particles dispersed in a liquid medium[11].

**Deagglomeration**

Deagglomeration is the dispersion of aggregates in a suspension[11].

**Deflocculation**

Deflocculation is a form of deagglomeration which occurs when a polymer is added to the suspension[11].

**Surfactant**

A surfactant is a surface active agent with two distinct components, one polar and one non-polar. These are also known as amphiphilic compounds[12].
Micelle

A micelle is an accumulation of surfactant molecules in a suspension which aggregate together. This process occurs when a specific concentration of surfactant in the system is reached, this is known as the critical micellular concentration and can be identified by the variations in the equilibrium and transport properties of the solution[12].

2.1.2 Low Solids Dispersions and Pastes

Low solids dispersions consist of a large volume of liquid phase with a small volume of solid phase. These solids are in a low enough concentration to flow easily within the liquid system which results in minimal particle interactions. Analyzing the rheological properties of low solids dispersions yields information about the interactions between free flowing aggregates.

The fundamentals of particle interactions start with the particle surfaces. Solid particles start with some inherent surface charge. Sometimes this is the result of defects in the crystal structure; sometimes it is caused by surface groups such as –COOH or H₃. Most metal oxides in suspension have a surface charge which is amphoteric and can become either positive or negatively charged based on the pH of the suspending medium. The pH is determined by the balance of H⁺ and OH⁻ ions in the solution. Depending on the inherent particle surface charge, there will be preferential adsorption of positive or negative ions from the solution. This imbalance creates a net charge known as the electrostatic potential on the particle surface. The surface charge on the particle will attract ions of the opposite charge for a short distance from the particle surface. This
arrangement of charges is known as the diffuse electrical double layer around the particle[12].

A suspension of like particles will all carry the same surface charge. The repulsion between particles of these charges is known as electrostatic repulsion. Apart from this repulsive force, an attractive force exists between particles of the same material in a suspension. This attractive force is the long-range van der Waals’ force. It is a force based on the accumulative attraction between atoms in the particles and tends to extend a distance approximate to the particle size. The theory of these competing forces was developed concurrently by two separate teams of scientists; Deryaguin and Landau, and Verwey and Overbeek; thus the naming of the theory as DLVO. Figure 2.1 illustrates graphically the competitive nature of the repulsive and attractive forces[12].

![Net interaction potential between particles](image)

**Figure 2.1** Net interaction potential between particles: A, force of attraction, R, force of repulsion, B, resultant force (Allen [13])
2.1.3 High Solids Dispersions and Pastes

High solids dispersions consist of a large volume of solid aggregates with a low volume of liquid phase. The high concentration of solids causes frequent particle collisions. Analyzing the behaviors of high solids dispersions or pastes yields information about particles with frequent interactions.

Concentrated systems, such as pastes, are dominated by different inter-particulate forces than dilute systems. The relationship of the liquid to the particle surface can be defined by a contact angle. This quantifies the tensions required for the spreading of the liquid on the surface and is determined by the interfacial tensions which exist between the air, liquid, and solid phases. Liquid placed on a solid will spread if equation 2.1 is true. Figure 2.2 shows a diagram of a liquid on a surface, and the resultant contact angle[13].

\[ \gamma_{SA} > \gamma_{SL} + \gamma_{LA} \cos(\theta) \]  

Liquid in a concentrated suspension can act as a liquid bridge between particles causing a capillary force to exist between the solid particles. The liquid bond between particles is called a pendular bond. The shape of this pendular bond is determined by the surface energies of the liquid-solid-air interfaces and the contact angle that those define. This contact angle will determine whether the pendular bond acts as an attractive or repulsive force. Figure 2.3 shows two contact angle scenarios, Figure 2.3 (a) shows a pendular bond in tension. This bond would act as an attractive force between the particles. Figure 2.3 (b) shows a pendular bond in compression. This bond would act as a repulsive force between the particles[14].

The motion of particles in the system can also affect the pendular bond. If external forces act on two particles to separate them, the pendular bond will rupture. The
bond will first exhibit a contact angle signifying tension, as in Figure 2.3 (a), it will then rupture which will reverse the surface curvature of the liquid on each particle surface. Figure 2.4 shows the particle-liquid interfaces of a ruptured bond[14].

Figure 2.2 Illustration of interfacial tensions; $\gamma_{LA}$ liquid-air, $\gamma_{SA}$ surface-air, $\gamma_{SL}$ surface-liquid, and the contact angle, $\theta$ (Allen [13])
Figure 2.3 Illustrations of forces due to (a) a low contact angle liquid between particles and (b) a high contact angle liquid between particles (German [14])
2.1.4 Role of Organics

Sometimes to assist the dispersion and processing of inorganics in a system, organic additives such as surfactants are used. A surfactant can alter the charge balance on the surface of a particle thereby encouraging or discouraging flocculation and the formation of agglomerates. Surfactants belong to a class of compounds known as amphiphiles. When added to a dilute suspension of particles in water, the polar end of the molecule will seek out a polar surface, while the non-polar end will prefer a non-polar surface. This results in the molecule being attracted to interfaces between polar and non-polar substances, such as a particle surface, where the non-polar end can be next to the non-polar particle surface while the polar end extends into the polar water. As particle surfaces become completely covered in surfactant, the interfacial charge at the surface will change. The surfactant will also act to physically increase the inter-particulate

Figure 2.4 Illustration of a ruptured pendular bond with contact angle $\theta$ and inter-particulate spacing $d$ (German [14])
distance, thereby exceeding the distance for van der Waals’ attraction and causing agglomerates to break down[12].

A limit exists for the addition of surfactant to a suspension at which all the particle surfaces have surfactant adsorbed to them. This is known as the adsorption limit and varies based on the size of surfactant molecule and the area of particle surface available. In the case of very small (nano) particles, there may not be room between particles in an agglomerate for the surfactant to reach some area of particle surface. These agglomerates of nanoparticles effectively behave as single particles of larger size though they are comprised of primary particles. Excess surfactant in a suspension which has exceeded the adsorption limit may form micelles. Micelles are groups of surfactant which form due to the lower surface energy of their non-polar ends clustering together while the polar ends extend into the water[12, 13].

Surfactants added to high concentration systems exhibit some similar purpose to those added to dilute suspensions. The surfactant still functions by adhering to particle surfaces and assisting with the breakdown of large agglomerates of particles. Adsorption limits exist in these systems, though the larger quantity of surface area greatly increases them. When an excess of surfactant is present, it can sometimes act as a bulk lubricant. These accumulations of surfactant flow with the liquid system in between larger agglomerates allowing them to move by each other more easily. This organic behavior has been known to aid in rheological processing methods such as extrusion[15].
2.2 Rheology

2.2.1 Stress and Strain

In 1929, E.C. Bingham coined the term “rheology” and defined it as the study of the deformation and flow of matter. Modern rephrasing has added that rheology is the study of deformation under applied stress. Stress can be applied as tension, compression, a shearing process, or some combination of the three. When under tension or compression, most liquids and solids respond in an idealized way, however, the application of a shear stress can cause a variety of unusual deformation patterns. Figure 2.5 shows the deformation of a cube due to stress for each stress type. The top of the figure shows an undeformed cube. This is followed by arrows which indicate the directions of stress on the cube based on the stress type being illustrated. The bottom images are of the cube as it would be deformed by the applied stress [12, 16].
Figure 2.5 Deformation of a cube by (a) compression (b) tension and (c) shear stress (adapted from Macosko [17])
Directions of stress can be clarified with three dimensional vector notation. The location where three mutually perpendicular planes intersect, such as the corner of a cube, creates a three vector intersection. Figure 2.6 labels the directions of a given intersection vectors as $x_1$, $x_2$, and $x_3$. Each vector is assigned the subscript of its perpendicular plane. When describing a stress on an object, the stress vector will have a two digit subscript, the first indicating the plane on which the stress is acting, the second indicating the direction of that stress. Figure 2.7 shows how this label system can be used to define directional stresses on a cube. A matrix of the stress tensors includes notation for stresses applied to any of the three perpendicular planes in any of the three directions[17].

\[
\begin{pmatrix}
\sigma_{11} & \sigma_{12} & \sigma_{13} \\
\sigma_{21} & \sigma_{22} & \sigma_{23} \\
\sigma_{31} & \sigma_{32} & \sigma_{33}
\end{pmatrix}
\]

The effect of stress on an ideal solid is measured in deformation, or strain. When applying a force, $F$, to a material, the resultant stress, $\sigma$, is defined by $F/A$ or force per unit area. For a tensile stress, $\sigma_T$, this causes a strain, $\gamma_T$, and the relationship is defined by Hooke’s Law (equation 2.2)

\[\sigma_T = Y\gamma_T\]  \hspace{1cm}  \text{(2.2)}

The constant, $Y$, is a material property known as Young’s modulus. As strain is the relative length of deformation, it is a unit-less quantity which means Young’s modulus has the units of stress, force per unit area. For a shear stress applied to a material, the constant is no longer described by Young’s modulus, but by $G$, the shear modulus[12].

\[\sigma = G\gamma\]  \hspace{1cm}  \text{(2.3)}
Figure 2.6 Three dimensional direction notation (Dealy [18])

Figure 2.7 Example of coordinate notation for stress vectors (Dealy [18])
Simple shear is when material planes slide over each other in the $x_1$ direction, thus leaving $x_2$ and $x_3$ unchanged. Figure 2.8 shows a $\sigma_{21}$ applied to a body and the resultant displacement. The ratio of this displacement to the height of the body is the shear strain, $\gamma$;

$$\gamma = \frac{\delta X_1}{\delta x_2} \quad 2.4$$

where $\delta x_2$ is the height of the square and $\delta X_1$ is the distance of the displacement. Figure 2.9 shows simple shear of constant velocity acting on a body. The velocity at any point, $v_1$, is then related as

$$v_1 = \frac{x_2}{h} V_w \quad 2.5$$

where $V_w$ is the constant velocity of the shearing force. A local shear rate, $\dot{\gamma}$, can then be defined as

$$\dot{\gamma} = \frac{dy}{dt} = \frac{dv_1}{dx_2} \quad 2.6$$

The shear rate is also known as the deformation rate or strain rate and is measured in units of reciprocal time, s$^{-1}$[18].
Figure 2.8 Deformation of a square due to simple shear (Dealy [18])

Figure 2.9 Deformation of a square under simple shear strain (Dealy [18])
2.2.2 Flow Behaviors

Most solids will follow Hooke’s Law for small applied stress and will recover their previous form once that stress is removed. This occurs until they reach some limit, \( \sigma_L \). If stress is applied which exceeds \( \sigma_L \), then permanent deformation will occur. This deformation is known as flow or creep. A viscous material is one which will not recover from the deformation once the stress has been removed. An elastic material is one which will reverse the strain and recover its pre-sheared configuration once the stress has been removed. This is also known as plastic flow[12, 17].

Newtonian flow behavior describes that of an ideal liquid. For this flow behavior the relationship between shear stress and shear rate is directly proportional. The constant by which the two quantities are related is a material property, \( \eta \), viscosity, as described in equation 2.7. For a Newtonian fluid, viscosity is independent of shear rate and dependent on temperature and pressure. A typical unit of viscosity is the Pascal second, Pa·s. The units of poise and centipoise, cp, are also used. 1 Pa·s = 10 poise = 1000 cp. One centipoise is approximately the viscosity of water at room temperature. Other fluids which exhibit Newtonian behavior include wine, sugar syrup, and pure paraffin oil[12, 17, 19].

\[
\sigma = \eta \dot{\gamma}
\]

Non-Newtonian fluid behaviors include those which are shear thinning, also known as pseudoplastic or power law, and those which are shear thickening, also known as dilatant. Shear thinning occurs when an increase in shear rate causes a decrease in viscosity. Shear thickening occurs when an increase in shear rate leads to an increase in viscosity. Examples of liquids which exhibit shear thinning include blood, yogurt, and
mayonnaise. An example of a shear thickening fluid is cornstarch and water[17, 20]. Figure 2.10 exhibits a typical curve shape for shear thinning, Newtonian, and shear thickening behaviors.

Some materials exhibit a resistance to flow unless a certain stress is overcome. This is known as a yield stress. There are two types of time independent fluids with a yield stress. A Bingham plastic is a material which exhibits Newtonian-like behavior (shear stress independent of shear rate) after overcoming a yield stress, the Bingham yield value, σ_B. The relationship is defined by equation 2.8 in which η_{pl} is the plastic viscosity.

\[
\sigma = \sigma_B + \eta_{pl} \dot{\gamma} \tag{2.8}
\]

An example of a Bingham plastic is a concentrated dispersion of coal in water[12].

A Herschel-Bulkley fluid will exhibit a shear thinning behavior after overcoming its yield stress. These fluids will have shear stress/shear rate curves which do not intersect the origin. The stress/strain relationship is defined by equation 2.9.

\[
\sigma = \sigma_0 + K \dot{\gamma}^n \tag{2.9}
\]

The quantity \(\sigma_0\) is called the primary yield value. In a plot of log (\(\sigma - \sigma_0\)) vs. log \(\dot{\gamma}\), n is the slope of the curve. Figure 2.11 illustrates typical curve behavior for a Bingham plastic and a Herschel-Bulkley fluid[12, 20].

Often with materials which exhibit yield stresses, the rheological behavior of interest is that which occurs after the applied stress has exceeded the yield stress, \(\sigma > \sigma_{ys}\). In these cases direct measurement of the viscosity as the ratio of shear stress to shear rate (as in equation 2.8) might not be preferable. A differential viscosity can be obtained by measuring the slope of the viscosity curve rather than its magnitude. In cases of fluids
with yield stresses, this quantity gives a greater depth of understanding of the material’s rheological behavior than simple viscosity analysis. Differential viscosity is also sometimes referred to as apparent viscosity\[12\].

\[\eta = \frac{\sigma}{\dot{\gamma}}\]  \hspace{1cm} 2.10

\[\text{slope} = \frac{d\sigma}{d\dot{\gamma}}\]  \hspace{1cm} 2.11

Time dependent fluids are ones in which the viscosity of the fluid depends not only on the shear rate but also on the amount of time during which the shear has been applied. When a material is being sheared at a constant rate it achieves equilibrium. When the shear is removed (shear rate = 0) a new equilibrium must be obtained. The time it takes the material to reorder itself into the new equilibrium is the relaxation time, \(t_{\text{relax}}\). The materials discussed up to this point exhibit very short relaxation times (ex. \(t_{\text{relax}} < 10^{-3} \text{ sec}\)). This means that the viscosity curves constructed for these materials will most likely not show evidence of this transition. On the other hand, some materials exhibit much longer relaxation times (ex. \(t_{\text{relax}} \geq 10 \text{ sec}\)). These are then classified as time dependent fluids\[12\].

Thixotropy is the time dependent rheological behavior which occurs when the differential viscosity at a particular shear rate decreases with time. Thixotropy can be observed in the viscosity curve for a material when stress is measured as shear rate is steadily increased to a maximum and then decreased at the same rate. A time independent material will show very little difference between the two curves but a thixotropic material will have a down curve with viscosity values below that of the up
curve. A material is said to exhibit negative thixotropy when the up curve lies above that of the down curve. Both of these behaviors create a hysteresis loop, as seen in Figure 2.12, the area of which is dependent on the degree of time dependence of the material. Negative thixotropy is not to be confused with rheopexy, which occurs when a material recovers some of its pre-sheared viscosity more quickly when a gentle shear stress is applied than when it is under no stress. Thixotropic behavior can be found in materials like bentonite and crude oils. Rheopexy, though rare, has been observed in suspensions of ammonium oleate[12, 16].
Figure 2.10 Curve behavior of (a) Newtonian, (b) shear thinning, and (c) shear thickening liquids (Hunter [12]).

Figure 2.11 Curve behavior of non-Newtonian fluids exhibiting a yield stress (a) Bingham plastic and (b) Herschel-Bulkley (adapted from Hunter [12]).
Figure 2.12 Hysteresis loops exhibiting (a) thixotropic behavior and (b) negative thixotropic behavior (adapted from Hunter [12])
2.2.3 Linear Viscoelasticity

A viscoelastic material is one which exhibits an instant deformation on the application of stress (much like an elastic solid) but then continues to deform according to some time dependent factor. Upon removal of the stress, most materials recover from some of the strain immediately and continue recovering at a more gradual rate as time approaches infinity. Sometimes, all of the deformation will be reversed, but in some cases there will be permanent deformation of the material. Viscoelastic fluids exhibit different behavior than viscoelastic solids. Figure 2.13 shows the stress vs. time relationship for a viscoelastic solid and viscoelastic fluid. The liquid approaches a stress of zero as time approaches infinity. The solid approaches some stress, $\sigma_\infty$, as time approaches infinity[17]. In Figure 2.13, $\lambda$ is the relaxation time. The labeling of a material as a viscoelastic solid or viscoelastic fluid is somewhat subjective and dependent on the relationship between relaxation time, $\lambda$, and observation time. For example, glass at room temperature is a super-cooled liquid, but unless an extremely large observation time (on the order of centuries) is considered, it is most practically regarded as a solid[16].

Viscoelastic fluids tend to behave very differently from viscous fluids. One phenomenon which has been observed in viscoelastic fluids is die swell. Die swell occurs when a viscoelastic fluid leaving a vertical pipe increases in width. This is opposite to the behavior of a viscous fluid which narrows as it leaves a confined diameter. Another interesting behavior of viscoelastic fluids, which was first observed by Weissenberg[21], is the effect of a stirring rod in a fluid. When a stirring rod is rotated in a viscous fluid it creates a vortex, meaning the liquid rises against the walls of the
container and lowers by the rod. If a stirring rod were rotated in a viscoelastic fluid, the fluid would surround and climb the rod. The height of the stirred fluid around the rod would be greater than the height of the fluid at rest while the height of the fluid at the edges of the container would be lower than the fluid at rest. Another difference between viscous and viscoelastic fluids occurs when a siphon is in use. A viscous fluid will cease to flow up a siphon once the siphon opening is lifted above the fluid level. A viscoelastic fluid will rise above the fluid level with the end of the siphon and continue to function until some height limit is exceeded. An example of a typical viscoelastic fluid is shampoo[12, 17].

A convenient way to visualize the stress-strain behavior of a material is to use spring-dashpot notation. Spring-dashpot notation uses two icons to model elastic and viscous behaviors. The spring is mechanical representation of ideal elastic behavior. This means it follows the stress-strain ratio found in equation 2.3 and the shear modulus is G. The dashpot is a representation of an ideal viscous element. This means it extends at a rate proportional to the applied force and can be determined using equation 2.10 solved for $\dot{\gamma}$. Figure 2.14 shows spring-dashpot depictions of the two ideal rheological conditions and how they can be combined to represent a fluid and a solid with real viscoelastic behavior[16].
Figure 2.13 Time dependent behavior as time approaches $\infty$ for (a) a viscoelastic solid, stress approaches $\sigma_e$ (b) and a viscoelastic fluid, stress approaches 0 (adapted from Tanner [16])
Figure 2.14 Spring-dashpot models of (a) elastic body, (b) viscous body, (c) Maxwell fluid, and (d) Kelvin-Meyer solid (Tanner [16])
2.2.4 Nonlinear Viscoelasticity

Many rheological behaviors vary greatly from the viscous, elastic, and linear viscoelastic regimes. Figure 2.15 exhibits a graphical representation of the range of possible rheological behaviors based on the strain amplitude graphed opposite the Deborah number. The Deborah number, $De$, is generally defined as the ratio of a materials characteristic relaxation time, $\lambda$, to the characteristic time, $t$.

$$De = \frac{\lambda}{t}$$  \hspace{1cm} 2.12

The Deborah number can also be described by assuming characteristic flow time, $t$, is inverse to the strain rate, $\dot{\gamma}$, equation 2.13. For oscillation flow, characteristic time is taken to be the oscillatory strain times the frequency, $(\gamma_0 \omega)^{-1}$, equation 2.14[17].

$$De = \frac{\lambda}{\dot{\gamma}}$$  \hspace{1cm} 2.13

$$De = \gamma_0 \lambda \omega$$  \hspace{1cm} 2.14

Some nonlinear rheological phenomena include; the existence of nonzero first and second normal stress differences in shearing, shear thinning, extensional thickening. Normal stress differences occur when a viscoelastic material is sheared between two parallel surfaces at some rate, $\dot{\gamma}$ . Using stress tensor notation the relationship between normal stresses, $N_x$, and shear stresses, $T_{xy}$, can be defined by the equalities, $N_1 \equiv T_{11} - T_{22}$ and $N_2 \equiv T_{22} - T_{33}$. The convention is defined as 1 being the direction of flow, 2 being the direction perpendicular to the parallel surfaces which are shearing the fluid, and 3 being the neutral direction. At sufficiently low shear rates, $T_{12}$ becomes linear and $N_1$ and $N_2$ approach $\dot{\gamma}^2$. Normal stress coefficients, $\psi_1$ and $\psi_2$, can then be defined and produce constant values for low $\dot{\gamma}$ [17].
Some polymer melts and high concentration polymer solutions exhibit a shear thinning behavior. At low shear rates, viscosity and shear coefficients behave in a linear viscoelastic manner, independent of shear rate. As shear rate increases, these properties begin to decrease dramatically, faster than the linear model predicts. This shear thinning behavior can also be observed in some time-dependent measurements. The time-dependent viscosity $\eta^+(t, \dot{\gamma})$ can be defined by equation 2.17.

$$\eta^+(t, \dot{\gamma}) = \frac{T_{12}(t, \dot{\gamma})}{\dot{\gamma}}$$  \hspace{1cm} 2.17

Again, at very low shear rates, the material will act as a linear viscoelastic material. Linear viscoelastic behavior also occurs when the material is at a low time, $t$, even if the shear rate is high. For this material to act in a nonlinear viscoelastic way, both the shear rate and time must be sufficiently high[17].

A linear viscoelastic material in under extensional stress will thin, as in Figure 2.5 (b). Some nonlinear materials exhibit the opposite behavior, extensional thickening. In terms of a fluid, this can be marked by the behavior of the viscosity. For some polymeric fluids, shear flow will cause a decrease in viscosity with increase in shear rate. For uniaxial extensional flow however, increasing extension rate, $\dot{\epsilon}$, will be met with an increase in viscosity, $\eta_{un}^+$, a thickening of the fluid. The dependence of viscosity on uniaxial extension rate and time is defined by equation 2.18.
Experimentally, a plateau of the extensional thickening may be observed, but some studies have shown that this plateau is temporary and serves as a maximum before a decrease in viscosity occurs. Since this seems to require a very high $\dot{\varepsilon}$, it is likely that other experimental variables will complicate the collection of this datum[17, 22].

$$\eta_e(t, \dot{\varepsilon}) = \frac{T_{11}(t, \dot{\varepsilon}) - T_{22}(t, \dot{\varepsilon})}{\dot{\varepsilon}}$$

2.18

Figure 2.15 Schematic diagram of rheological behaviors (Macosko [17])
2.2.5 Small Strain Experiments

There are a number of small strain experiments used to evaluate the rheology of viscoelastic materials. Stress relaxation involves the application of a small strain and observation of the resultant stress over some time, t. Creep experiments apply a constant stress, which is then removed. The strain is then plotted with time to see the behavior of the material both while under stress and after the stress is removed. Sinusoidal oscillation experiments involve the application of a sinusoidal strain wave. The result on the material is generally that a sinusoidal stress wave is produced which is offset from the strain wave by some phase angle, \( \delta \)[17].

Stress Relaxation

Stress for a linear viscoelastic material is time dependent and strain independent. The relationship can be described by equation 2.19 in which strain, \( \gamma \), is a constant while stress, \( \sigma \), and modulus, \( G \), vary with time. This equation can be rewritten as equation 2.20 which defines \( G(t) \) which is referred to as the relaxation modulus[21].

\[
\sigma(t) = G(t)\gamma \\
G(t) = \frac{\sigma(t)}{\gamma}
\]

One approach to modeling linear viscoelastic behavior during stress relaxation involves the use of a series of relaxation times to define a relaxation modulus-time curve. The model begins by suggesting that small changes in stress equal small changes in strain times the modulus, equation 2.21, which can be rewritten as equation 2.22.

\[
d\sigma = Gd\gamma
\]
\[
d\sigma = G \frac{d\gamma}{dt} dt = G \dot{\gamma} dt
\]

Integrating equation 2.22 yields,

\[
\sigma = \int_{-\infty}^{t} G(t - t') \dot{\gamma}(t') dt'
\]

The quantity \( t' \) is the past time variable which represents \(-\infty \) to present time, \( t \). This means the relaxation function completely relies on \( t - t' \) which is defined as \( s \). Equation 2.23 can be rewritten as

\[
\sigma = \int_{0}^{\infty} G(s) \dot{\gamma}(t - s) ds
\]

Thus the stress is defined as an integral of the relaxation modulus times the strain rate. This form of the relationship is frequently used because \( G(t) \) can be measured directly\[17\].

Assuming the relaxation modulus follows an exponential decay, equation 2.25, as has been observed experimentally, equation 2.23 can be rewritten as the Maxwell model where \( \lambda \) is the relaxation time, equation 2.26.

\[
G(t) = G_0 e^{-t/\lambda}
\]

\[
\sigma = \int_{-\infty}^{t} G_0 e^{-|t-t'|} \dot{\gamma}(t') dt'
\]

Experimentally, this model has shown good agreement with data, but only for a short time. An improvement to this model is to rewrite it such that it includes a series of relaxation times, \( \lambda_k \), multiplied by weighted constants, \( G_k \). Relaxation modulus can then be defined as equation 2.27 and substituted into equation 2.23 to produce equation 2.28, also known as the general linear viscoelastic model.
This model has been shown to provide curves which better approximate experimental data. Greater values of $N$ yield greater accuracy in the approximation. One drawback to this modeling methodology is that for each value of $\lambda_k$, a constant $G_k$ must be calculated from the experimental data using a non-linear regression method [17].

**Creep**

Given a one step shear history, $\sigma(t) = \sigma_0$, the strain of an elastic solid will be $\gamma(t) = \gamma_0$. For a viscous fluid, the application of continuous shear stress will cause continuous deformation. This is deformation is sometimes called creep and is dependent on the amount of time shear is applied, $t$, and the viscosity of the material, $\eta$. The relationship is defined in equation 2.29.

$$\gamma(t) = \sigma_0 \frac{t}{\eta} \tag{2.29}$$

The idealized relationships of equation 2.20 where $\sigma(t)$ and $G(t)$ are directly proportional and 2.29 where $\gamma(t)$ and $t$ are directly proportional are not typically observed experimentally. Most often, the strain increases rapidly at first and then continues to increase gradually. If the strain appears to approach a limiting value, then the material is said to be a viscoelastic solid. If the strain does not approach a limiting value, but continues to infinity, then the material is said to be a viscoelastic fluid. In some cases, it

\[
G(t) = \sum_{k=1}^{N} G_k e^{-t/\lambda_k} \tag{2.27}
\]

\[
\sigma = \int \sum_{k=1}^{N} G_k e^{-t'/\lambda_k} \gamma(t') dt' \tag{2.28}
\]
is impossible to determine whether strain is approaching a limiting value without very long observation times [16].

**Sinusoidal Oscillation**

When a sinusoidal strain is imposed on a material it will induce a sinusoidal stress wave. While these two waves will match in frequency, the stress wave will be displaced from the strain wave by some phase angle, \( \delta \). This can be expressed mathematically as follows in equations 2.30 and 2.31.

\[
\gamma = \gamma_0 \sin \omega t \quad 2.30 \\
\sigma = \sigma_0 \sin(\omega t + \delta) \\
\]

For these purposes \( \omega \) is the rotational velocity with units of angle over time. The stress wave can be decomposed into two waves, one in phase with the strain wave and one 90° out of phase with this wave.

\[
\sigma = \sigma' + \sigma'' = \sigma_0' \sin \omega t + \sigma_0'' \cos \omega t \\
\]

Trigonometry can be used to show that for this system equation 2.33 is true.

\[
\tan \delta = \frac{\sigma_0''}{\sigma_0'} \\
\]

This decomposition suggests two moduli, equations 2.34 and 2.35.

\[
G' = \frac{\sigma_0'}{\gamma_0} \\
G'' = \frac{\sigma_0''}{\gamma_0} \\
\]

The relationship can also be described by equation 2.36.
\[ \tan \delta = \frac{G''}{G'} \quad 2.36 \]

Using the relationships in equations 2.34 and 2.35, equation 2.32 can be rewritten as

\[ \sigma = G' \gamma_0 \sin \omega t + G'' \gamma_0 \cos \omega t \quad 2.37 \]

Equation 2.37 yields two distinct regimes for the description of stress. \( G' \) is the elastic modulus and \( G'' \) is the viscous modulus. If a sinusoidal strain is applied to an ideal elastic solid, the \( G'' \) term becomes 0 and the \( G' \) term defines the stress. Conversely, if a sinusoidal strain is applied to an ideal viscous fluid then the \( G' \) term becomes 0 and the \( G'' \) term defines the stress[17].

### 2.2.6 Rheological Evaluation

The quantitative definition of a yield stress varies depending on what measurement is being used to examine the material. A single material can have multiple yield stresses from various evaluations which may not correlate. Therefore it is important to discuss the different rheological evaluations for plastics and Bingham bodies.

One of the difficulties in rheological evaluation is the requirement of applying stress. Most evaluations require the material to be strained a certain amount or have a certain stress applied to them. This means that the evaluation itself may require the reordering of the material structure before data is being collected. Another issue with stress application is distribution of stress. Most quantitative evaluations assume stress is evenly distributed throughout the sample. This is not always easily accomplished and error due to non-uniform distribution must be taken into account. Due to these factors, most evaluations will yield an apparent yield stress rather than a theoretical yield stress. The apparent yield stress can still be very useful in predicting material behavior[23].
Rheometers can be classified in numerous ways. One way to categorize them is by the type of stress they apply, extensional or shear. Another distinguishing characteristic is whether large strains can be applied. Some rheometer geometries do not require a sample’s edges to be confined, this limits the evaluation to small strain values. Table 2.1 lists some rheological evaluation techniques and the categories they fall into. Another distinguishing characteristic is whether the application of stress is homogeneous. Homogeneous flow is when the stress is applied evenly to a sample surface. Non-homogeneous flow occurs when the sample material is not being uniformly stressed[17].

<table>
<thead>
<tr>
<th>Rheometer</th>
<th>Stress Applied</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bubble collapse</td>
<td>Extensional</td>
<td>Small strain</td>
</tr>
<tr>
<td>Rotating clamps, inflation methods</td>
<td>Extensional</td>
<td>Small strain</td>
</tr>
<tr>
<td>Simple extension, lubricated compression</td>
<td>Extensional</td>
<td>Small strain</td>
</tr>
<tr>
<td>Sliding plates</td>
<td>Shear</td>
<td>Small strain</td>
</tr>
<tr>
<td>Concentric cylinders</td>
<td>Shear</td>
<td>Small strain</td>
</tr>
<tr>
<td>Cone and plate</td>
<td>Shear</td>
<td>Small strain</td>
</tr>
<tr>
<td>Eccentric rotating disks</td>
<td>Shear</td>
<td>Small strain</td>
</tr>
<tr>
<td>Shear surface (wide gap)</td>
<td>Shear</td>
<td>Small strain</td>
</tr>
<tr>
<td>Parallel disks</td>
<td>Shear</td>
<td>Small strain</td>
</tr>
<tr>
<td>Capillary</td>
<td>Shear</td>
<td>Large strain</td>
</tr>
<tr>
<td>Slit</td>
<td>Shear</td>
<td>Large strain</td>
</tr>
<tr>
<td>Annulus</td>
<td>Shear</td>
<td>Large strain</td>
</tr>
</tbody>
</table>

Table 2.1 Rheometer evaluation techniques and requirements, adapted from Macosko[17]

Extensional methods include geometries like tension, lubricated compression, fiber spinning and bubble collapse. Many extensional methods require very simple sample prep and evaluation execution. Some issues with extensional methods include difficulty eliminating shear due to confining walls, as well as difficulty determining the role of strain in non-homogeneous flows. Extensional methods still make an attractive solution for the testing of things like high viscosity polymer melts. For these materials
the ease of creating a high viscosity sample lends them to simple extension, or tensile, testing[17].

Shear rheometers can be divided into two categories, those which use a drag flow and those which use a pressure driven flow to apply stress. Rotational rheometers fall into the first category. Rotational rheometers can operate either by controlled stress or controlled strain. Geometry of these rheometers also varies greatly and includes configurations such as cone and plate, vane, concentric cylinder, and parallel plate. Figure 2.16 shows these geometries and some of their physical parameters. The various geometries lend themselves to different measurements. The cone and plate geometry is reliable for measuring normal stress and has been used on films and coatings including cell-surface interactions of biomaterials. Parallel plate (or parallel disk) geometry is useful for measuring high viscosity materials and soft solids and has been used to determine yield stresses in thermotropic polymers. Vane geometry is useful for the analysis of medium to low viscosity fluids and avoids the issue of slippage while exhibiting high tolerance for large particles and air bubbles in a test material. The concentric cylinder shows great utility for the analysis of low viscosity fluids and has been used to study slip phenomena in food products[17, 24-27].
Another controlled strain rheometer is the torque rheometer. An instrumented batch mixer, the torque rheometer consists of a chamber or mixing bowl and two counter-rotating blades. One of the rotating blade shafts has a transducer which records the torque as the batch approaches a steady state. There are many blade configurations available, four of which are pictured in Figure 2.17. Torque rheometers are commonly
used to simulate large batch mixers or extruders and to produce compounded samples[17].

The analysis of torque rheometry curves varies based on the needs of the study. A typical torque rheometry curve for a ceramic paste can be seen in Figure 2.18. Ananthakumar used a stabilized torque value to analyze an alumina-boehmite system at various shear rates[25], while Kalyon used torque values in equation 2.38 to calculate system energy as a function of time[26], and Pileggi used torque values at the turning point (peak torque) to examine the rheology of refractory castables[27].

\[
E_s = \frac{\int \tau \Omega dt}{M_t}
\]  
2.38

**Figure 2.17 Torque rheometer blade geometries (www.cwbrabender.com[24])**
Pressure driven shear rheometers include capillary rheometers, slit rheometers, annular flow rheometers, and squeezing flow rheometers. These are most useful for high viscosity materials as high shear rates can be applied during the testing. Capillary geometry was one of the first to be used in rheometry for measuring viscosity. Figure 2.19 shows a schematic for a typical capillary rheometer. The rheometer geometry is cylindrical as is the die. Test material is packed into the barrel and pressure is exerted from the plunger. The material is then forced through the die land at some velocity, V. Assuming the material is incompressible; the velocity of the extrusion is determined by the ram velocity and the ratio of barrel diameter to die diameter[17, 28].

Figure 2.18 Example of torque rheometry data graphed with quantities of interest labeled
Assuming all forces in the plane perpendicular to the ram pressure are zero, the work done to increase the length of the paste of cross-sectional area $A$ and length $l$ by $dl$ is $\sigma Adl$. Assume an incompressible material,

$$A_{i,0} = Al$$
where $A_0$ is the initial cross-sectional area and $l_0$ is the initial length. This can be differentiated to yield equation 2.40.

$$\frac{dA}{A} + \frac{dl}{l} = 0 \quad 2.40$$

which can be converted to

$$\frac{dA}{A} + \frac{Adl}{A_0l_0} = 0 \quad 2.41$$

The work done can then be described by the integral

$$\int_{A_0}^{A} - \alpha A_0 l_0 \frac{dA}{A} = \left[ - \alpha A_0 l_0 \ln A \right]_{A_0}^{A} = \alpha A_0 l_0 \ln \left( A_0 / A \right) \quad 2.42$$

The work done by the extrusion pressure, $P_1$, can now be described as $P_1 A_0 l_0$.

Substituting the value from equation 2.42, the pressure can be written as,

$$P_1 = \sigma \ln \left( A_0 / A \right) \quad 2.43$$

For a cylindrical barrel and die land, this is equivalent to,

$$P_1 = 2\sigma \ln \left( D_0 / D \right) \quad 2.44$$

For high viscosity materials, the stress can be related to the rate of strain such that,

$$\sigma = \sigma_0 + \alpha V \quad 2.45$$

where $V$ is the paste velocity in the die land, $\sigma_0$ is the yield stress at zero velocity and $\alpha$ is a factor characterizing the effect of velocity on the stress. This can be inserted into equation 2.44 to produce an equation for the extrusion pressure.

$$P_1 = 2(\sigma_0 + \alpha V) \ln \left( D_0 / D \right) \quad 2.46$$
The quantity $\alpha V$ is analogous to the product of viscosity and shear rate in liquid shear, $\eta'$. Since the rate of extension is proportional to $V$, the quantity $\sigma$ in equation 2.45 can now be said to represent a bulk yield stress corrected for shear rate[28].

If motion in the die land is now to be considered, the pressure drop in the die land $P_2$ generates a net force on the paste $P_2\pi D^2/4$. This pressure is opposed by the wall shear force which is the product of the wall stress $\tau$ and the die perimeter $\pi DL$. These two concepts can be combined to restate the pressure drop in the die land.

$$P_2 = 4\tau \left( \frac{L}{D} \right)$$

A Newtonian approach would allow the viscous effects of the shear at the die wall to be proportional to $V$. In such a case, $P_2$ can be redefined as equation 2.48.

$$P_2 = 4(\tau_0 + \beta V) \left( \frac{L}{D} \right)$$

The parameters $\tau_0$ and $\beta$ characterize the paste where $\tau_0$ is the wall shear stress extrapolated to zero velocity and $\beta$ is a factor which accounts for the velocity dependence of the wall shear stress. $\tau_0$ is termed the initial wall stress and $\beta$ is termed the wall velocity factor[28].

An overall pressure drop can now be defined as the addition of the pressure drop in the barrel, $P_1$ and the pressure drop in the die land, $P_2$.

$$P = P_1 + P_2 = 2(\sigma_0 + \alpha V) \ln \left( \frac{D_0}{D} \right) + 4(\tau_0 + \beta V) \left( \frac{L}{D} \right)$$

Experimentally the parameters of overall pressure, velocity, length, and diameters can be measured or calculated. The factors $\sigma_0$, $\alpha$, $\tau_0$, and $\beta$ must be determined through a series of calculations from collections of experimental data. The data necessary to calculate these parameters must exhibit the relationship between extrusion pressure and extrusion velocity[28].
Data exhibiting the relationship between extrusion pressure and velocity can be collected by measuring the extrusion pressure of a single material at multiple speeds for values of L/D. The die length over die diameter can be varied by using multiple dies of the same diameter and varied length. A graph can then be created which plots L/D against measured extrusion pressure. Figure 2.20 is a sample graph for this type of analysis. Linear regression lines can be fit to the pressures of multiple die lengths for each velocity. For data collected at two velocities, \( V_1 \) and \( V_2 \), notation in the figure defines A as the pressure at zero L/d for \( V_1 \) and B for the pressure at zero L/d for the \( V_2 \). O is the label assigned to the origin, zero L/d and zero pressure. C and D are the pressures at some L/d, J, for \( V_1 \) and \( V_2 \) respectively. Benbow et al. determined equations to solve for the 4 factors in equation 2.49 utilizing the quantities in Figure 2.20. For these equations; the quantities OA, OB, CJ and DJ are pressure differences while the quantity OJ is a difference of L/d values[28].

\[
\sigma_0 = \frac{(OA)V_2 - (OB)V_1}{2(V_2 - V_1)\ln(D_o/D)} \\
\alpha = \frac{(OB) - (OA)}{2(V_2 - V_1)\ln(D_o/D)} \\
\tau_0 = \frac{V_2[(CJ)-(OA)] - V_1[(DJ)-(OB)]}{4(OJ)(V_2 - V_1)} \\
\beta = \frac{[(DJ)-(OB)] - [(CJ)-(OA)]}{4(OJ)(V_2 - V_1)}
\]
Figure 2.20 Example of data graphed to calculate extrusion factors (adapted from Benbow [28])
2.2.7 Extrusion Flaws

Experimental techniques which utilize extrusion pressures are subject the same defects as materials manufactured by extrusion. This can make them a useful tool for the observation of flow defects in a paste which may be more conveniently analyzed in a lab test than in a full production setting. Extrusion defects can occur in the bulk of the material as well as the surface.

Surface defects include ‘feathering’, tearing, and swelling[28]. Feathering is a succession of concentric cracks on the extrudate perpendicular to the extrusion direction[29]. Tearing is an extreme form of feathering and can be identified by the material curling back away from the concentric tears. These defects may be caused by a variety of factors including; flow instabilities in the die land and die region, extrusion velocity, and die parameters such as size and shape. Swelling is observed when the diameter of the extrudate increases as it leaves the die land. It is often a result of the extreme material deformation upon entering the die causing the product to regain the deformation on die exit, exhibiting elastic recovery. This can be minimized by utilizing a tapered section from the barrel into the die land[30].

Extrusion bulk defects include phase migration, where liquid phase becomes non-uniform within the extrudate. This can lead to regions which are liquid rich and regions which are dry resulting in non-uniform extrudate. Phase migration is caused when the phases move at significantly different rates under pressure. Causes include a large permeability in the particle phase as well as a low viscosity of the liquid phase. Experimentally, phase migration will cause the extrusion pressure to increase with time as liquid phase is diminished in the batch[28].
2.3 Mixing

The objective of mixing is to produce a mixture with a compositional arrangement which is appropriate for intended use of the mixture and conducive to further processing. The method of mixing must take into account the state of batch; wet, dry, or paste; as well as the amount of shear to be applied by the mixer. Wet mixing of powders is conducted by creating suspensions of particles in a fluid medium prior to mixing. Adjustment of the pH of the suspension can take advantage of electrostatic forces to produce flocced or dispersed suspensions. Suspensions of distinct particles can be combined to create multiple component suspensions. Further mixing of these suspensions may improve the quality of the mixture by breaking down particulate flocs. Some mixing methods apply shear to break down these flocs[31]. If a specific particle size distribution is desired, care must be taken that shear forces are not strong enough to break down the particles themselves. The possibility of contamination from the mixer assembly must also be considered as any abrasion of the mixer components from the batch will then be incorporated by the mixing process.[32]

2.3.1 Nomenclature and Definitions

Mixture nomenclature tends to vary throughout the literature, therefore definitions of common terms are being included to clarify the discussions and explanations in this thesis.
Mixing

Mixing, with respect to solid particles, can be defined as the action by which discreet particles of at least 2 components are induced to change from a state of segregation by an outside force.

Regular Mixture

A regular mixture of two components is one that has one component evenly distributed throughout the second. This configuration is not likely to be seen in experimental mixtures, Figure 2.21 (a).

Perfect Random Mixture

The definition of a perfectly random mixture is one in which the probability of finding a constituent within the mixture is the same for all points in the mixture.[9] In Lacey’s explanation, this mixture was labeled an ideal mixture.[14]

Cluster

For the sake of this thesis, a cluster is defined as a grouping of particles of the same composition in a matrix of particles of a different composition. A regular mixture will contain, by definition, no clusters, whereas a random mixture will contain some clusters. A mixture is completely clustered when all particles of one component are arranged in groups within a matrix of the other component. This is statistically less probable than a random mixture.
Mixedness

Mixedness is the degree to which a composition has altered from a segregated state. An example of poor mixedness would be the pre-mixed state in Figure 2.22 (a). An example of good mixedness would be the Random Mixture in Figure 2.21 (b).

Mixing Index

A mixing index is some means of quantitatively defining the mixedness of a composition. Usually denoted by M, there are numerous mixing indices to be found in the literature many of which have been catalogued by Weidenbaum in 1958 and again by Fan in 1970.[9, 33]

Length Scale

The length scale of a sample is the radius of a sphere which has the same volume as the sample.[34]

Critical Length Scale

The critical length scale of a sample is the smallest volume necessary to guarantee a specific property with a predetermined certainty, e.g., the smallest volume which will have a 99% chance of containing 2% batch additive.[34]
Figure 2.21 Mixture types. Two-dimensional mixtures of 100 components, 50 dark/50 light. a) A regular mixture and b) an example of a random mixture (adapted from Lacey[7])
Figure 2.22 Mixing mechanisms; two-dimensional mixtures of 128 components, 50 dark/50 light. (a) convective mixing, (b) shear mixing and (c) diffusive mixing. (adapted from Lacey [7])
2.3.2 Mechanisms of Mixing

A definitive paper by P.M.C. Lacey defined three mechanisms by which mixing of solid particles occurs. Lacey postulated that mixing can occur by convection, diffusion, or shear forces. The domination of one of these mechanisms over the others often occurs and will vary based on the type of mixer being utilized.[35]

Convective mixing involves the movement particles from one location in the mixer to another by means of exchange with another group of particles. This can be caused by a mixing blade physically moving a group of particles to another location within the mixing vessel. Shear mixing occurs when regions of different components are drawn out and made thinner which increases the interface between them. This occurs by the setting up of slipping planes between components in the mass. Diffusive mixing occurs when the particles of a component are induced to exchange with particles of a second component with an adjacent surface.[32]

Segregation, or demixing, occurs as a competing process within the mixing procedure. The mixing quality in a mixer depends directly on this equilibrium[36]. Moritz proposed two demixing classifications. The first classification is for demixing by separation of the components. This can be induced by differences in particle size, density, or morphology. The second classification is for demixing by the agglomeration of particles in the mixer, either by electrostatic forces or humidity interference[37].

Segregation by density variation was proven to occur for systems which have similar particle size and morphology. A study which used a V-type mixer to blend glass, steel, silicagel, and alumina spheres showed that lighter particles tended to separate out toward the outer regions of the mixer, whereas heavier particles tended to concentrate in
the stagnant areas[38]. Despite this occurrence, particle size is a more important factor for segregation than density[36].

Segregation of a mixture has been shown to be reversible in certain systems. A study performed with a range of particle sizes on a vibratory bed showed that the frequency of vibration had a strong effect on the segregation pattern of the particles. By varying the vibration the segregation pattern was shown to change from a layered segregation to a radial segregation. In the case of a continuous vibration, segregation by particle size was shown to be reversible and a more homogeneous mixture could be obtained[39].

It must also be noted that for some materials, an environment can be created whereby the surface charges will create an affinity for clustering (segregation). For coarse particles, these attractive forces are much smaller than the mechanical forces applied by mixing, and therefore will have little effect on the resultant mixedness of the batch. For small or nano-particles, however, these forces may cause the particles to form clusters which the mechanical forces of mixing will not be able to overcome. These same forces may also cause repulsion between particles. This is another factor that could cause a mixture to deviate from a perfectly random distribution, though this could cause the mixture to “err” on the side of homogeneity[40].

Because of the time dependent nature of the segregation-mixedness competition, mixing time becomes important to the final quality of mixture obtained. Sensitivity to time dependent segregation is affected by the mixture being evaluated as well as the type of mixer being used. It was found that longer mixing times caused segregation based on particle size in a rotating drum type mixer. When a rocking motion was added to the
mixing process, homogenous mixtures could be achieved at short mixing times, but segregation was still occurring at longer mixing times[41].

Recent work to determine methods of preventing segregation showed that varying the mixer orientation during mixing, specifically, in a “zig zag” pattern, reduced the segregation occurrence. A more practical solution explored was to put a baffle, or artificial obstruction, in a rotational mixture. This served to reorient the mixture during rotation so that the direction of segregation changed with each revolution, thus preventing full segregation from occurring[42].

2.3.3 Sampling

Two sampling methodologies exist for the evaluation of a property of interest for a given body. Direct sampling involves complete analysis of a portion(s) of a body for the property of interest. Indirect sampling allows for the evaluation of a parameter of the body which is affected by the property of interest. Considerations for both methodologies will be explored[32].

Indirect sampling is used when direct sampling would prove invasive, destructive, or inconvenient. Evaluation of total inorganic carbonate content in illites was evaluated indirectly by FTIR analysis of photoacoustic absorption of infrared light by carbon dioxide. Direct evaluation techniques to determine total inorganic carbonate content had exhibited low sensitivity and poor reproducibility[43]. Indirect sampling of a mixture requires the evaluation of some property affected by the degree of mixedness. Tensile stress or electrical resistivity could be parameters used to indirectly determine mixture quality of a ceramic[32].
Direct sampling allows for an exact evaluation of a portion of a mixture. This presents an accurate portrait of the whole only so far as the sample is representative of the whole. For this reason, multiple samples are often taken at random to ensure the collective results will be representative of the whole sample[32]. Electrothermal atomic absorption was used to evaluate direct samples of petroleum for metal content. Direct sampling was utilized because it required no sample pre-treatment which could introduce contamination and reduce instrument detection capabilities[44].

Sampling a constituent powder for characteristics such as particle size distribution or surface area has different sampling requirements than sampling a mixture for those same quantities. As long as the sampling areas for the powder give an accurate result, any inhomogeneities in the distribution of particle size within the powder may be disregarded as they will be corrected when the powder is mixed into a composition. Inconsistencies in a mixture, however, must be noted as they can be evidence of insufficient mixing times or dead zones within the mixer itself[13].

Various methods exist for the sampling of powders. These methods include cone and quartering, scoop sampling, table sampling, chute splitting, and spin riffling. Cone and quartering method involves making a heap of the mixture, flattening the heap, and using a cross shaped cutter to divide the flattened heap into four samples. Scoop sampling consists of taking a scoop, thrusting it into the mixture, and removing scoop with some material. This is prone to error as it only examines the surface of the mixture, not the bulk[45]. An improvement on scoop sampling is the sample thief. This device uses nested cylinders which contain circular cutouts to allow controlled collection of particulate. The inner cylinder can be rotated from the end of the thief handle thus
enabling it to assume a “closed” position during thief insertion and again after the sample collection has occurred. In this way, the thief can collect a sample from the bulk of a mixture without incurring contamination during the removal[46]. Table sampling involves feeding the mixture onto an inclined plane. The plane has holes which some of the sample will fall through and prism obstructions to fracture the flow stream. Mixture that does not fall through the holes becomes the sample. Accuracy for this sampling method is reliant on a uniform distribution of initial feed. This method has low accuracy, but is cheap and easy to implement. Chute splitting involves feeding the sample into a V shaped trough. The trough leads to chutes alternately facing either side of the trough. Half of the mixture is then used an feed for consecutive separations until the desired sample size is achieved[45].

A rotary sample divider, or spinning riffler, involves a controlled powder feed through a hopper onto a delivery chute which leads to a segmented collection tray on a rotating stage. In this manner, the entirety of a powder mixture can be divided into equal samples based on the number of segments in the tray. Greatest uniformity of sampling is achieved when the rotary stage speed is greater than the powder feed rate. This ensures that each segment is filled with particles from multiple parts of the powder. One limitation of the spinning riffler is that the powder to be analyzed cannot have a larger volume than the collective volume of the tray segments[46].

Of these described sampling methods, a spinning riffler is the best option for acquiring a uniform sample from a powder batch. This is ideal for testing of parameters like particle size distribution or surface area. When analyzing a mixture of powders, this method would greatly interfere with the mixture’s composition, which would interfere
with any attempt to assess the quality of the mixture. The structure of a mixture can be solidified by the injection of epoxy into the composition after mixing. This will trap the configuration and allow it to be analyzed[41].

The sampling of a slurry can be done with some of the same techniques as powder sampling. Thieves and scoops can be used to remove slurry samples for evaluation. Since the stability of many slurries is time-dependent, most suspensions should be agitated immediately prior to sampling[47]. If slurry sample is to be taken from a mixer, homogeneity within the mixer must be ensured. Some mixers can have dead zones. These zones are regions which may be out of the reach of the mixing blades and therefore consist of unmixed or poorly mixed slurry. In these cases, macro-scale sampling can be used. This is when the mixer is divided into regions based on its architecture. Samples are then taken at random from each region allowing the statistics of random sampling to be used to compare regions[48]. Small samples can be taken from an agitated slurry of fine particles with a syringe or pipette. Slurries with coarser particles can be accurately sampled by a suspension sampler. This uses gas pressure to propel the slurry into a predetermined number of sample containers[45].

To evaluate the structure of a slurry, a method was developed by which a slurry sample was obtained directly from the mixing process by scoop. The scoop was immediately immersed in liquid nitrogen. This froze the sample structure in its configuration allowing it to be analyzed with a scanning electron microscope. This method is only viable for slurries which maintain their structure for longer time than it takes to freeze[40]. Self supporting mixtures such as those for extrusion, injection molding, and jiggering can have samples cut out of them with minimal disruption to the
microstructure. For this reason almost any method of extracting a sample from the body will sufficiently preserve microstructure for observation[48].

Macro-scale sampling methods for mixture analysis are too disruptive to be used for micro-scale sampling of powders or slurries. These structures must be stabilized to preserve the particle configurations prior to sampling[41]. Lacey and Mirza proposed a method of stabilizing a particle mixture by impregnating with gelatin. Their technique allowed the analysis of the structure of the mixture at various points in the mixing process[49]. Micro-scale sampling can be restricted to green bodies. Macro-scale sampling techniques can be scaled down for micro-scale analysis of self supporting mixtures. This case merely requires that the green bodies be randomly chosen for evaluation. No preparation must be made for the mixture prior to sampling[40].

2.3.4 Mixing Probes

Characterization of a sample can be done either by direct or indirect analysis techniques or probes. Direct probes consist of the analysis of some physical or chemical property of the sample. Indirect probes are those which measure any post-processing property which can be correlated to mixture quality. Any technique chosen must be able to resolve variations in the mixture on a length scale less than or equal to the critical length scale of the mixture[48].

Indirect characterization of a mixture can be conducted by evaluating any number of material properties. Evaluation of a mixture based on indirect characterization has been conducted in a variety of studies which include examining the sintered density of silicon carbide[50], the solid-state reaction of lead magnesium niobate[51], the dielectric
constant of barium titanate[52], and the fracture density of an alumina-zirconia ceramic[53]. Indirect characterization is often convenient as it can utilize testing already being performed on post-processed mixtures for quality control. However, it cannot be used if mixture quality is not the only factor affecting the material properties. In cases where no material property varies solely based on mixture quality, direct characterization must be employed.

Direct characterization of a mixture can be conducted on either chemical or physical techniques. Physical probes require that the components of the mixture have distinctly different physical characteristics, such as morphology, particle size or color. A comparison of single screw mixers for immiscible polymer processing used imaged morphology to determine the mixture quality of the polymers. The same study also used chromatic variation to determine mixture quality in compositions where greater contrast was required[54]. Particle size measurement has also been used as a way of determining whether or not segregation has occurred in a single component powder[13].

Characterization with a chemical probe is frequently used to evaluate mixtures with components which are chemically distinct. Many techniques can be used to quantify the chemical ratios in a mixture. X-ray diffraction has been used to quantify the chemical composition of powder mixtures[55]. Many spectroscopic techniques can function as chemical probes for mixture evaluation. Atomic absorption spectroscopy, AAS, can be employed to determine the ratios of any sample which can be dissolved in solution. Inductively coupled plasma spectroscopy, ICP, can also determine elemental ratios and with greater sensitivity than AAS[56]. Ultraviolet (UV), visible (vis), and infrared (IR)
spectroscopy have all also been used to determine concentrations of chemicals in a mixture[57, 58].

Other chemical probes include use of an electron probe micro analyzer or a scanning electron microscope. Sample evaluation by either of these instruments can take advantage of the emission of characteristic x-rays, either by x-ray fluorescence or inelastic scattering of excited electrons. Characteristic x-rays are produced when an outer shell electron is transferred to an inner shell thus emitting an x-ray with energy specific to the difference of energies of the involved shells. Since these energy differences are unique to each element, analysis of the characteristic x-rays can be conducted to determine the chemical makeup of the analyzed sample. This analysis is often done by energy dispersive x-ray spectroscopy or wavelength dispersive spectroscopy both of which involve detectors mounted on the SEM or EPMA units and can give quantitative chemical makeup of an analyzed sample as well as chemical maps of an image area[59].

UV, vis, and IR spectroscopy techniques are possible options for looking at concentrations of organics in suspensions[57]. Evaluation of these same organics by SEM or EPMA methods is extremely difficult as many organic materials are compromised by radiation damage from the incident beam in these instruments. Even if the sample can be stabilized, attaining qualitative data is difficult as the EDS and WDS detectors have very limited sensitivity to the lighter elements which form the basis of organic materials. Direct chemical evaluation of organics is more easily done by nuclear magnetic resonance[60] or wet chemical analysis[61].
2.3.5 Quantification of Mixture Quality

2.3.5.1 Mixing Indices

Once evaluation of a mixture has been conducted, some method by which to quantify the mixture quality must be applied. The complexity of quantifying the degree of mixedness in a system is evidenced by the abundance of mixing indices found in the literature. There are a mounting number of reviews which attempt to catalogue the numerous indices. These emerged shortly after Lacey’s initial quantitative evaluation of mixing began in 1943[7].

Weidenbaum first catalogued attempts in the literature at defining a mixing index, M, while establishing criteria for his own mixing index in his 1958 study[33]. This collection was expanded upon by Fan, et al, in 1970. Fan’s work included a listing of significant mixing indices found in the literature. The listing included about three dozen distinct indices and spanned three decades of research[9]. Schofield compiled a list of mixing indices from the literature and emphasized the assumptions each made about whether M would increase with greater or lesser mixture quality[62]. Poux, et al., also conducted a review of mixing indices in 1991 which included over 40 equations for the definition of quality of a mixture. Poux organized these indices into four categories; indices for binary compositions based on variance, indices for binary compositions not based on variance, indices for multicomponent systems, and lastly, indices based on experimental work[36]. Some inconsistencies exist within the nomenclature for the indices. For example, while most of the indices define M as equal to zero when variance, \( \sigma \), is equal to variance prior to mixing, \( \sigma_0 \), some indices define M at \( \sigma = \sigma_0 \) as equal to 1[63].
Some common terms utilized in the mixing indices are arithmetic mean, variance, variance for a segregated system, and variance for a perfectly random system. These terms are defined in Table 2.2 where \( n \) is the number of spot samples, \( x_i \) is the \( i \)th value of \( x \), \( P \) is the concentration of one component in the mixture, and \( N \) is the number of particles in the mixture.

<table>
<thead>
<tr>
<th>Sample Arithmetic Mean</th>
<th>( \bar{x} = \frac{1}{n} \sum_{i=1}^{n} x_i )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample Variance</td>
<td>( \sigma^2 = \frac{1}{n} \sum_{i=1}^{n} (x_i - \bar{x})^2 )</td>
</tr>
<tr>
<td>Variance for a completely segregated system</td>
<td>( \sigma_0^2 = P(1 - P) )</td>
</tr>
<tr>
<td>Variance for a perfectly random system</td>
<td>( \sigma_r^2 = \frac{P(1 - P)}{N} )</td>
</tr>
</tbody>
</table>

Table 2.2 Common parameters used to define mixing indices [9]

Rose and Robinson[64] defined a mixing index, \( M \), such that

\[
M = 1 - \frac{\sigma}{\sigma_0}
\]

2.54

This equation was later used by Fuerstenau and Fouladi in their assessment of mixedness in a binary system. By using various ratios of glass beads or two distinct particle sizes, they found that the bulk density of the system could be correlated with the mixing index, \( M \), though unlike Rose and Robinson, they did not find the relationship to be linear[65].

Other mixing indices for binary systems which are based on variance include contributions from Lacey[35], Valentin[66], and Rumpf and Sommer[67]; equations 2.55-2.57, respectively.
The indices from Lacey and Valentin both assume that \( M = 0 \) for \( \sigma = \sigma_0 \) and \( M = 1 \) for \( \sigma = \sigma_R \). Rumpf and Sommer instead make the assumption that \( M = 0 \) for \( \sigma = \sigma_R \) and \( M = \sqrt{N} \sigma_0 \) for \( \sigma = \sigma_0 \). Many variations in assumptions among mixing indices are found in the literature and therefore a thorough investigation of the origins of the index must be made before even a qualitative comparison is considered.

Many binary mixing indices in the literature do not limit their calculation of \( M \) to be exclusively a factor of variance, \( \sigma^2 \). Manning’s examination of particle size, equation 2.58, which pre-dates Lacey’s definitions of mixtures, uses concentration of interest, \( X \), weight of interest, \( w \), and total sample weight, \( W \), to define variance for a random distribution[68]. In Hersey’s determination[10], equation 2.59, mixing index, \( M \), is equal to the standard deviation, \( \sigma_q \), of a sample divided by the theoretical standard deviation of sample concentration allowed by the mixture specification assuming 95% confidence limits and a normal distribution [36]. Hersey also introduced a new criterion, the mixing margin, \( (\sigma_q - \sigma_R) \), where \( \sigma_R \) is the standard deviation of a fully randomized sample[10]. Buslik’s defined mixture quality, \( M \), as the negative log of the weight of sample required for a standard deviation of 1%, equation 2.60 [69]. Stange also developed a mixing index for a binary system, equation 2.61, which defined standard deviation as a function of

\[
M = \frac{\sigma^2_0 - \sigma^2}{\sigma^2_0 - \sigma^2_R}
\]

2.55

\[
M = \frac{\log \sigma_0 - \log \sigma}{\log \sigma_0 - \log \sigma_R}
\]

2.56

\[
M = \sqrt{\frac{N(\sigma^2 - \sigma^2_R)}{N - 1}}
\]

2.57
concentrations, \( p \) and \( q \), and average sample weights, \( \bar{w} \), for two distinct components[70].

\[
\sigma_k^2 = \frac{X(1-X)w}{W}
\]

\[
M = \frac{\sigma}{\sigma_q}
\]

\[
M = -\log W_1
\]

\[
\sigma_k^2 = \frac{pq}{W} \left[ qw \left( 1 + \frac{\sigma^2}{w^2} \right)_p \right] + \frac{pq}{W} \left[ pw \left( 1 + \frac{\sigma^2}{w^2} \right)_q \right]
\]

A few indices for determining mixture quality of multicomponent mixtures have been developed. These are developed as extensions of binary mixing indices. Stange’s equation for standard deviation of a completely random sample, 2.62, was developed from his previous equation (2.60) for a binary composition.

\[
\sigma_k^2 = \frac{p^2}{W} \left[ \frac{(1-p)^2}{p^2} - p \sum (f w)_p + q \sum (f w)_q + r \sum (f w)_r + ... \right]
\]

In this equation, \( p \) is the concentration of the element that the standard deviation is being calculated for while \( q \), \( r \), etc... are proportions of other elements in the mixture.

Furthermore, \( W \) represents the sample weight, \( f \) is the weight fraction of a sample within a size class, and \( w \) is the weight of one size particle[71].

Equations for mixing indices developed by experimentation as extremely varied. Inouya developed his mixing index, equation 2.63, by measuring the concentration of particles detected by his probe where \( x_i(t) \) is the concentration of specified particles detected by the \( i \)th probe at time \( t \) and \( x_\infty \) is the expected concentration of specified particles in the homogeneous mixture[72]. Equations 2.64 and 2.65 were both developed
by results obtained with an optical probe. Oyama, equation 2.64, used an optic probe to determine a value for mixture quality, \( M \), where \( i \) is the light intensity corresponding to a maximum concentration difference and \( i_o \) is the light intensity corresponding to initial maximum concentration difference[73]. Gray, equation 2.65, also used results from an optic probe to determine his equation for variance, \( \sigma^2 \). In his equation, \( I \) is the reading directly from the probe and \( \bar{I} \) is the average of all the probe readings[74].

\[
M(t) = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n} \left[ \frac{x_i(t)}{x_m} - 1 \right]^2} \tag{2.63}
\]

\[
M = \left(1 - \frac{i}{i_o}\right) \tag{2.64}
\]

\[
\sigma^2 = \frac{1}{N - 1} \sum (I - \bar{I})^2 \tag{2.65}
\]

2.3.5.2 ANOVA Evaluation

Certain limitations have been identified with the use of mixing indices. The major limitation seems to be their inability to handle the effect of sampling variability[75]. Analysis of variance (ANOVA) can be used to quantify mixedness and avoid the variability issues of traditional mixing indices.

Mixing indices make the assumption that the measured variance, \( \sigma^2_{\text{measured}} \), is equal to the mixture variance, \( \sigma^2_{\text{mixture}} \). This is accurate as the measured variance is subject to any error in the sampling variance, \( \sigma^2_{\text{sampling}} \), as well as error in the probe used to evaluate the mixture, \( \sigma^2_{\text{probe}} \). Therefore instead of the assumed relationship in equation 2.66, a more accurate equation is 2.67[76].

\[
\sigma^2_{\text{measured}} = \sigma^2_{\text{mixture}} \tag{2.66}
\]
It is probable that the variance for a probe can be determined analytically, but there are no widely accepted methods for assessing sampling variance. Yip and Hersey acknowledged in their assessment of mixture quality of coarse sucrose particles with salicylic acid or crystal violet that the variance of sampling could not be determined, but was probably a considerable contribution to the measured variance[77].

Rollins et al. performed a theoretical assessment of various mixing indices and determined that they would not provide an accurate result when analyzing a mixture where some segregation was not present. Rollins also concluded that a large sampling error would obscure calculations for true variance of the mixture[75].

Instead, Rollins et al. proposed an alternate method for mixture evaluation which eschews mixing indices in favor or analysis of variance, ANOVA, testing. The one-way ANOVA expected value for the test statistic, $\zeta$, is defined as the explained variance divided by the unexplained variance (equation 2.68). In a case where $x$ samples are taken from $y$ populations, this also equates to a ratio which defines the numerator as the variance of the population means and the denominator as the mean of all the population variances (equation 2.69).[78].

Rollins defined explained variance as the measured variance and unexplained variance as the variance of sampling plus the variance of probe (equation 2.70). The study then defined a variance of error, $\sigma^2_{\text{error}}$, as a combination of sampling and probe variance. $\zeta$ can then be rewritten as a function of the variance of the mixture, $\sigma^2_{\text{mixture}}$ (equations 2.70-2.72). In this manner a test statistic has been defined as a function of the mixture variance[75].
Actual implementation of the ANOVA technique requires the consultation of probability (F test) tables which return a value for F based on the number of samples, the number of regions samples were taken from, and a predetermined confidence. If the value of F calculated from equation 2.69 is less than the F from the table, then the system is considered well mixed, within the predetermined confidence. If the calculated value of F is greater than the value of F from the table then the mixture must be considered segregated[48].

There are some concerns with using the ANOVA determination to describe mixture quality. The ANOVA calculations and use of probability tables assume that the error distributions of the variances in the calculations are Gaussian. Another issue is with the acquiring of samples. If the ANOVA test is to give a confidence of mixing quality for a given length scale, it must be possible to take multiple samples from a region of that length scale. Therefore, to give a confidence for 1 mm, it must be possible to take multiple samples from a 1 mm region. For mixtures which require homogeneity on a
very small length scale, it might be too difficult to acquire samples of sufficiently small size to utilize an ANOVA analysis\[48\].

2.3.5.3 Image Collection and Analysis

Image Collection

Some of the data on mixtures is acquired in the form of a sample image, such as chemical maps obtained with a Scanning Electron Microscope (SEM) or Electron Probe Microanalyzer (EPMA) and the addition of an Electron or Wavelength Dispersive Spectroscopy (EDS or WDS) system. To understand the limitations of this technique, the construction of a scanning electron microscope will be explored.

Figure 2.23 shows a schematic of an SEM electron column, deflection system, and electron detectors. The top of the column has an electron gun, the purpose of which is to provide a large stable current in a small electron beam. While standard SEMs might contain a Tungsten or Lanthanum Hexaboride cathode source which would then be heated to thermionic emission, a field emission SEM utilizes an applied electric field to excite electrons from the cathode source. Field emission SEMs typically use a Tungsten source as it contains the strength necessary to withstand the mechanical stress from the electron field. The advantage of a field emission source over a thermionic source is increased beam brightness, reduced thermal drift of the beam, and reduced evaporation of the cathode material\[59\].
The electron beam produced by the gun is too broad to produce a sharp image at high magnifications. A series of electron lenses are then used to reduce the diameter of the source beam. The spot size of the beam on the specimen can typically be reduced to 10 nm diameter. The penetration of the beam into the specimen is usually about a 1 µm depth[59].
Magnification is controlled by the scan coils which use electromagnetic deflection to direct the beam in such a way that a raster of a specified area is produced. Reducing the magnitude of deflection causes the beam to scan a smaller area of the specimen, thus producing an image of greater magnification. The magnification is defined as the ratio of the CRT (cathode ray tube) screen size to the raster size on the specimen[59].

The interaction of the beam with the specimen produces a variety of signals. Secondary electron and backscattered electrons are detected by an Everhart-Thornley (E-T) detector. This detector converts the electron inputs to a light signal which travels down a photomultiplier tube (PMT) and is amplified before being displayed on the CRT screen. This produces a topographical image of the specimen surface[59].

Along with secondary and backscattered electrons, the incident beam can also excite characteristic x-rays. These are produced when an electron from the incident beam interacts with a tightly bound inner shell electron in the specimen. This electron is ejected, thus leaving an inner shell vacancy. The vacancy is filled by an outer shell electron dropping down into the inner shell. An x-ray photon is then emitted with energy equal to that of the energy difference between the two shells. Since the energy levels of atomic shells are distinct for all periodic elements, this x-ray photon is characteristic of its particular element. Energy dispersive spectroscopy systems utilize a Si(Li) detector to determine the spectral analysis of a specimen based on the characteristic x-rays collected[59].

X-rays are collected for a given time (collection time) at each raster location to accurately represent the ratios of elements at the location. Collection time can be varied by the operator with longer times more likely to give accurate quantitative results.
Limitations of longer collection times include possible charging of the sample which would skew the collected data or possible drifting of the electron beam, which might be insignificant at shorter collection times, but apparent when times are extended[59].

Greater characteristic x-ray counts in a given time can be achieved by using a larger final aperture. This allows greater electron beam strength resulting in more x-ray counts, though too large an aperture will eliminate topographical contrast in the secondary electron image. Another way to increase x-ray counts is to use greater beam energy (example, increasing accelerating voltage from 5kV to 10kV). This will increase the number of counts/time being collected, the drawback being that resolution capabilities decrease with increased beam energy[59].

The incident beam spot size can be reduced to 10 nm on the specimen surface. This is not necessarily indicative of x-ray resolution as the beam interaction continues into the sample forming a penetration teardrop. While the excitation of signals continues throughout that depth, not all signals can escape to be detected. Figure 2.24 shows a diagram of a typical teardrop with the escape depths for secondary electrons, backscattered electrons, and x-rays. The size of the teardrop varies with beam intensity and sample density and defines the achievable spatial resolution for each emission type. The spatial resolution for characteristic x-rays also depends on the atomic weight of the interaction element. Equation 2.73 defines the spatial resolution, R, for characteristic x-ray detection based on accelerating voltage $E_a$, critical excitation voltage $E_c$, and mean specimen density $\rho$[79].

$$R = \frac{0.064(E_a^{1.68} - E_c^{1.68})}{\rho}$$  \hspace{1cm} 2.73
Common EDS detection errors unique to multicomponent systems are known as matrix effects. These are due to differences in the propagation of x-rays through the specimen to reach the detector as well as differences in elastic and inelastic scattering processes. These matrix effects can be divided into three quantities based on their causes; atomic number, $Z$; x-ray absorption, $A$; and x-ray fluorescence, $F$.

The atomic number error, $Z$, occurs because the production of characteristic x-rays only can occur when the energy of the incident electron, $E$, is above that of the critical excitation energy, $E_c$, of the characteristic x-ray of interest. Because $E_c$ varies between elements, Monte Carlo simulations have shown that x-ray generation volume decreases with increasing atomic number.

The x-ray absorption effect occurs when characteristic x-rays are generated deeper in the specimen. Photoelectric absorption will lessen the intensity of a characteristic x-ray as it moves through the specimen. If the x-ray is completely absorbed, it will not be detected. If the characteristic x-ray is not completely absorbed, it will exit the specimen with its original energy unchanged.
The x-ray fluorescence error occurs when photoelectric absorption results in the ionization of an inner atomic shell. This may cause the emission of a characteristic x-ray. If the specimen has a component with a critical excitation energy less than that of the emitted characteristic x-ray, it could cause fluorescence. In this case, the intensity detected for the second component will include not only its characteristic x-rays but those which occurred due to fluorescence from the other components characteristic x-rays[59].

There are several methods for correcting atomic number, absorption, and x-ray fluorescence errors. The most common is the ZAF method which combines the three errors into one variable and calculates the result experimentally. Equation 2.74 illustrates an equation which uses experimental values for a standard, \(i\), and the specimen of interest, \((i)\), to calculate the ZAF error and furthermore, the k-factor, \(k_i\), for the element. In this equation \(C_i\) is the weight fraction of the element in the standard, \(C_{(i)}\) is the weight fraction of the element in the specimen, \([ZAF]_i\) is the correction term for the element, \(I_i\) is the intensity measured from the standard, and \(I_{(i)}\) is the intensity measured from the sample. This equation must be applied separately to each element in the specimen for accurate calculation of the ZAF values[59].

\[
\frac{C_i}{C_{(i)}} = [ZAF] \frac{I_i}{I_{(i)}} = [ZAF] k_i
\]

An EDS system can be used to collect spectral information from each point in a raster by recording the characteristic x-rays emitted by the specimen. To facilitate the analyses of these spectra, elements of interest can be designated. The EDS software can then be used to display the collection results for the specific element in the raster, thus creating a map representing the locations of that element within the raster[59].
Differences in the quantity of an element present throughout the raster area may vary from point to point. This is represented in the compositional map by a variation in pixel intensity. Each pixel in the map has some intensity ranging from 0 counts of the element (typically represented by black) to the maximum count of the element (white or other color).

**Image Analysis**

Once an image has been collected, an image analysis must take place to quantify the quality of mixture of the components. Most image analysis techniques begin by isolating a component and converting the image into a binary representation in which one color represents the presence of the component to be measured and another color represents any location which does not contain the component. In an image where pixel intensity indicates the location of a component, thresholding can be used to convert the image into binary. Thresholding is a method by which a pixel intensity value is designated as the cutoff for presence of a component. Any pixel with that intensity or higher is then converted to black and any pixel with a lower intensity is converted to white. It is left to the operator to decide whether black or white will designate the presence of the component of interest as it can be found both ways in the literature[81, 82].

A binary composition can immediately be analyzed for area fraction of component of interest. Area fraction vs. length scale has been used in multiple studies as a method for quantification of mixture quality. The Multi-Scalar Analysis of Area Fractions technique, MSAAF, developed by Spowart et al, involves the division of a
binary image into aliquot squares of equal area, referred to as quilts. Assuming that
particles are placed entirely at random within an area, \( L^2 \), the number of particles within
the quilt squares should follow a Poisson distribution. A study of non-overlapping
particles of area fraction \( A_f \) for an area \( L^2 \) was conducted. For mono-sized particles, of
diameter, \( d_p \), a relationship between standard deviation of area fraction between
quilts, \( \sigma_{A_f} \), and the length of a quilt side, \( Q \), was predicted:

\[
\frac{\sigma_{A_f}}{A_f} = \left( \frac{\pi}{4A_f} \right)^{0.5} \left( \frac{Q}{d_p} \right)^{-1}
\]

where \( A_f \) is the total area fraction of the particles. As \( A_f \) and \( d_d \) are both constants for a
given image, the relationship between \( \sigma_f \) and \( Q \) for a fully random distribution is
inversely linear. When plotted against real data, this relationship can be seen to hold true
for large values of \( Q \). At smaller values of \( Q \), the \( \sigma_{A_f} \) begins to have smaller values than
the Poisson estimate. This indicates a greater degree of homogeneity which can be
attributed to the random placement of the particles being affected by their inability to
overlap one another[83].

Another method of evaluating mixture image data begins by creating planar point
fields. Planar point fields are created by applying a location identity for each particle of
interest in a mixture image. Image analysis software can be used to determine the central
location for each particle. Once these points have been identified, they can be used to
define variables, such as intensity, \( \lambda \), the mean number of points per area and \( r \), the inter-
point distance[81].

The K-function, \( K(r) \), is another means by which to analyze a planar point field.
If \((x_i, y_i)\) is a point in the data image, \( K^i(r) \) is the total number of points contained in a
circle whose center is \((x_i, y_i)\). \(K(r)\) can then be obtained by averaging \(K^i(r)\) for all locations \((x_i, y_i)\) in the data image. For a totally random process, the locations of \((x_i, y_i)\) will be chosen unsystematically, which is called a spatial randomness of points. The expression \(\lambda \pi r^2\) then describes the points on average, which can be divided by the intensity to yield the K-function:

\[
K(r) = \pi r^2
\]

(2.76)

When data yields a value higher than this function, clustering can be said to occur. When the data yields a value lower than the K-function, repulsion is occurring[84].

The pair correlation function, \(g(r)\), is the derivative of the K-function.

\[
g(r) = \frac{1}{2\pi r} \frac{dK(r)}{dr}
\]

(2.77)

Using this function, a totally random mixture would yield a \(g(r)\) equal to 1. This remains true for all values of \(r\). As in the K-function, experimental values of \(g(r)\) which fall above 1 indicate that clustering is occurring, while values below one indicate repulsion between particles. Possible error in this function can occur when the distance between particles becomes so small that the randomness of particle placement is hindered by their inability to overlap.[85].

Nearest-neighbor distance (nnd) is another tool for the analysis of planar point fields. NND has the ability to describe not only short range relationships, but also intermediate and long-range relationships by using higher order nearest-neighbors. A common method for using nearest-neighbor distribution is to compare the experimental mean and variance to that of a random Poisson distribution[86].

Defining \(R\) as some distance from a point within which no other points are encountered and \(R+dR\) as a distance in which 1 point is encountered, and \(P(R)\) is the
density function than the average nearest-neighbor distance, \( \langle R \rangle \), is described by equation 2.78.

\[
\langle R \rangle = \int_0^\infty R P(R) dR
\]

For a random distribution,

\[
\langle R \rangle = \frac{1}{2 \sqrt{N_A}}
\]

where \( N_A \) is the number of points per unit area. This same approach can be used to determine second, third, nth nearest-neighbor distributions[87].

To make nearest-neighbor distance statistics a more quantifiable tool, Anson et al. define two variables, \( Q \) and \( V \), which compare observed nearest-neighbor means and variances with means and variances expected from a Poisson (completely randomized) distribution.

\[
Q = \frac{\mu_o}{\mu_e}
\]

\[
V = \frac{\text{var}_o}{\text{var}_e}
\]

Equations 2.80 and 2.81 define \( Q \) and \( V \) such that \( \mu_o \) is the observed mean of nearest-neighbor distances, \( \mu_e \) is the expected mean of nearest-neighbor distances, \( \text{var}_o \) is the observed variance of nearest-neighbor distances, and \( \text{var}_e \) is the expected variance of nearest-neighbor distances. We can use these ratios to define 4 possible spatial point configurations which are described quantitatively in Table 2.3[88]. Figure 2.25 shows the graphical location of \( Q \) and \( V \) and labels the regions according to the spatial
configurations found for those values of Q and V. Figure 2.26 shows examples of distributions which might occur for each of the Q/V regions.

<table>
<thead>
<tr>
<th>Description of Configuration</th>
<th>Value of Q</th>
<th>Value of V</th>
</tr>
</thead>
<tbody>
<tr>
<td>Random distribution</td>
<td>Q ≈ 1</td>
<td>V ≈ 1</td>
</tr>
<tr>
<td>Regular distribution</td>
<td>Q &gt; 1</td>
<td>V &lt; 1</td>
</tr>
<tr>
<td>Clustered distribution</td>
<td>Q &lt; 1</td>
<td>V &lt; 1</td>
</tr>
<tr>
<td>Random distribution with clusters</td>
<td>Q &lt; 1</td>
<td>V &gt; 1</td>
</tr>
</tbody>
</table>

Table 2.3Explanation of numerical Q and V values[88]

Many software packages will calculate expected mean and variance values from an image. These include the Image Processing Tool Kit 5.0 add on for Adobe Photoshop.

The equations to calculate those values are:

\[
\mu_e = \frac{1}{2} \sqrt{\frac{A}{n}} + \left(0.0514 + \frac{0.041}{\sqrt{n}}\right) \frac{L}{n} \tag{2.82}
\]

\[
\text{var}_e = 0.0703 \frac{A}{n} + 0.037 \sqrt{\frac{A}{n^3}} L \tag{2.83}
\]

where L is the length of the boundary of the area, A, which contains n points of interest[88].

Figure 2.25 Map of ratio of means to ratio of variances with regions labeled by typical spatial arrangements (Anson [88])
Figure 2.26 Example of feature distributions for Q/V quadrants (Anson [88])
Tessellation techniques go one step further than determining of centroids and creation of a planar point field by using the point locations as “seeds” for the creation of a lattice of polygonal tiles. A tiles area is composed of all the points for which a specific seed is closest. This makes tile boundaries the locations which are equidistant from two seeds. The tile corners are locations which are equidistant from 3 seeds. This is known as the Voronoi (or Dirichlet) tessellation[89].

Voronoi cell tessellations have been used in conjunction with a variety of statistical analyses to assess material properties including volume fractions, morphology, particle size, orientations, and second-phase counts. Ghosh et al., used computer generated distributions to assess the ability of Voronoi cells in conjunction with finite-element methods to distinguish between various mixture configurations. They determined that the utility of the Voronoi tessellation was partially dependent on the distribution analysis method. It was found that the cumulative distributions and probability density functions for local area fractions were able to distinguish between patterns when the nearest-neighbor distance could not. This could be due to area fraction having a superior sensitivity to component size and orientation to nearest-neighbor distance[90].

Dirichlet tessellation of Voronoi cells is not the only method of creating tile boundaries. Johnson and Mehl defined their tessellation method by defining seed areas (features) rather than locations. In this manner, the boundary of a tile exists at the location which is equidistant between the edges of two particles rather than their centroids. One limitation of Voronoi cells is that the possibility exists for a tile’s boundaries to be either partially or entirely within a feature which can lead to misleading
statistical analysis. The Johnson-Mehl method of defining tile boundaries eliminates this issue[91]. Figure 2.27 shows Voronoi and Johnson-Mehl tessellations applied to the same set of features. The Voronoi tessellation shows that tile boundaries frequently fall within the feature areas.

Many of these methods can be adapted for the analysis of 3-dimensional data. Schwarz et al., determined that 3-dimensional locations could be determined by using stereographic pairs of transmission electron microscopy images. Once this datum was collected, nearest-neighbor analysis was found to accurately quantify the distribution of the points of interest[92]. Tessellation methods have also been applied to analysis of 3-dimensional data. Instead of polygons, the 3-dimensional cells are polyhedrons. The volume of the polyhedron is composed of all locations which are closest to the polyhedron seed[93].
Figure 2.27 a) Voronoi tessellation b) Johnson-Mehl tessellation (Gulliver [48])
Method of Attack

In ceramic pastes, mixture quality is an important factor which can dictate rheological properties and final properties of the ceramic. The ability to quantify the mixture quality of a multi-component paste becomes an important tool for quality control. Alumina and titania are sometimes used to form NO\textsubscript{x} catalysts. The functionality of these catalysts would be greatly reduced if the titania phase were not distributed within the alumina phase\cite{8}. The ease of processing a paste can also be related to the mixture quality. A paste which is very poorly mixed might require higher extrusion pressures than a paste which has a more uniform distribution. Due to increased inter-particulate spacing, a mixture with very little agglomeration might also be more difficult to extrude than one which includes agglomerates of a certain size. The greater number of individual particles would require a greater volume of liquid phase than a batch with some agglomeration. The goal of this work is to assess the effect of mixing technique and surfactant addition on the mixture quality of an alumina/titania paste and to relate this mixture quality to the rheology of the extruded binary paste. To achieve this goal, the following objectives will be met.

3.1 Objective One: To characterize the inorganic powder surfaces

The objective of the first part of this thesis will be to characterize the inorganic powders to be utilized. This will be achieved by measurement of particle size distribution and the zeta potential to determine isoelectric points of the powders. Surface behavior will also be assessed by introducing a surfactant to the powder systems and
analyzing changes in the powder properties. Properties analyzed will include particle size distribution and zeta potential analysis. Adsorption isotherms will also be created using thermal gravimetric analyses to examine the amount of surfactant which will adsorb to the powder surface. A rheological analysis will also be performed on the inorganic powders by means of dynamic stress rheometry. Slurries will be created from individual powders with varying concentrations of surfactant to assess the effect of surfactant on powder suspension flow.

3.2 Objective Two: To create a series of samples with varied formulations utilizing disparate mixing techniques

The objective for the second part of this thesis is to create a series of batches with various compositions using various processing techniques. The ratio of alumina to titania will remain the same for all batches. Variation to composition will occur by the substitution of a nano-alumina for the micron-sized alumina, substitution of nano-titania for micron-sized titania, incremental inclusion of a sodium stearate surfactant, and variation made in the concentration of liquid phase in the batch.

Variations in the mixing technique will be utilized to ensure a range of mixture qualities is present within the batch formulations. The control technique will include dry mixing, compounding, and extrusion. Variations to the control will include decreasing the compounding time, wet mixing the batch components, and extruding the batch multiple times.
3.3 Objective Three: To assess the rheological properties of the samples at various stages of processing

The third objective of this thesis is to determine the rheological properties of the batches at various stages of processing. This will be done by utilizing rheological tests at three stages of processing. Torque rheometry will be used to evaluate the compounding behavior of the batches. Capillary rheometry will be used to analyze necessary extrusion pressures and to determine certain batch properties such as yield and bulk stresses. Evaluation of the batch extrudate rheology will be conducted with dynamic stress rheometry via parallel plate method. In this way the rheology of the extruded pastes can be evaluated.

3.4 Objective Four: To determine mixture quality of the samples without degrading the extrudate structure

The objective of the fourth part of this thesis will be to evaluate the mixture quality of the batches. This will be conducted by using a scanning electron microscope energy dispersive spectroscopy system to collect a chemical map of extrudate sections and statistically evaluating the phase distribution for clustering. The distribution of the titania phase in an alumina matrix will be evaluated. The preservation of the sample structure after sectioning will be achieved by infiltrating the sample with a low viscosity epoxy, then polishing the sample surface for analysis. Extrusion flaws present in the SEM images will also be considered in the evaluation of mixture quality.
Experimental Procedures

4.1 System of Study

4.1.1 Inorganics

This investigation was conducted on two alumina powders and two titania powders. One coarse alumina and one nano-alumina were required. The coarse, micron sized alumina used was Almatis (Neville, PA) A-16 superground alumina. This is a high purity calcined alumina with less than 0.2% secondary oxides. A coarser, micron sized titania used was a Millennium (Hunt Valley, MD) Tiona AT-1 titania. This is a dry milled titania containing 98% anatase and less than 1.5% impurities.

The remaining alumina and titania components were pre-dispersed nanopowders. The alumina used was an Evonik Degussa (Essen, Germany) Aerodisp W 630 nano-alumina. This is a high solid content (40% by weight) dispersion with nano-sized primary particles. The titania used was an Evonik Degussa VP Disp W 740X nano-titania. This is a high solid content (40% by weight) dispersion of high purity fumed titania with nano-sized primary particles.

4.1.2 Organics

This study used two organic additives in extruded batches. A hydroxypropyl methyl cellulose binder was used in all extrusion batches. Hydroxypropyl methyl
cellulose is a nonionic water soluble polymer obtained by reacting methylene chloride and propylene chloride in the presence of caustic soda or sodium hydroxide[94].

The second organic used was sodium stearate. This is a single carbon chain fatty acid with 18 carbons which functions as a surfactant and lubricant. Sodium stearate can be created from stearic acid by the addition of the acid to a heated solution of sodium hydroxide in methanol. Rapid cooling of the solution will precipitate sodium stearate[95].

### 4.2 Powder Characterization

#### 4.2.1 Particle Size Determination

Particle size determinations of the as received inorganics with and without varied additions of sodium stearate were performed. Evaluations of the Evonik nano-dispersions were done with a Malvern (Worcester, UK) Zetasizer Nano ZS. The Zetasizer utilizes a non-invasive back scatter technology which can assess particle sizes ranging from 6 µm to 0.6 nm. Evaluations of the A16 alumina and AT1 titania were done with a Malvern Mastersizer 2000. The Mastersizer technology functions by passing particles through a focused laser beam. The deflection angle of the laser is inversely proportional to the particle size and measured by photosensitive detectors optimized to achieve maximum resolution across a broad range of particle sizes. The Mie particle scattering model is applied by the Mastersizer 2000 software to produce accurate sizing. Sub-micron resolution is improved by a dual-wavelength detection system. The Mastersizer’s single lens detection is accurate for particles ranging from 0.02 – 2000 µm.
Samples consisted of a 1% suspension of an inorganic in distilled deionized water. Samples were ultrasonicated 2 minutes prior to evaluation to minimize agglomerates. Particle size analysis results have been expressed in both differential volume and differential number. Differential volume refers to the volume of particles in a specific particle size range (window). Differential number refers to the number of particles in a specific particle size range (window).

Particle size analysis was performed on each as received inorganic, A-16 alumina, Aerodisp W 630 alumina, AT titania, and VP Disp W 740X titania, as well as on samples prepared with sodium stearate additions further described in section 4.2.2. Sodium stearate concentrations reflect the amount added over 100%, which refers to the water + inorganic system. Percent concentrations of sodium stearate analyzed were 0, 0.001, 0.005, 0.01, 0.05, 0.1, 0.5, 0.8, 1.0, 1.2, 1.5, 1.8, and 2.0 percent.

4.2.2 Adsorption Isotherm Creation

The amount of sodium stearate capable of adsorbing to the surface of each inorganic was assessed by the creation of adsorption isotherms. Series of samples were created for each inorganic; A-16 alumina, AT1 titania, Aerodisp 630 nano-alumina, and VP Disp W 740X nano-titania. Each sample consisted of an aqueous suspension of 10% by volume inorganic combined with a specific concentration of sodium stearate. The concentrations of sodium stearate ranged from 0-2% by weight and are the same used for particle size analysis in section 4.2.1. The prepared suspensions were mixed ultrasonically to facilitate dispersion. The suspensions were then centrifuged and the supernatant removed. The remaining solids were then dried at 100°C and subjected to
thermal gravimetric analysis (TGA) which measured the weight of surfactant which had remained adsorbed to the powder surface after centrifugation. The thermal analysis was conducted on a Perkin-Elmer (Waltham, MA) TGA7 instrument controlled by Pyris software version 3.52. Adsorption isotherms have been created by plotting the initial concentration of sodium stearate added to a suspension of inorganic and water vs. the amount of stearate adsorbed onto one gram of inorganic particles.

4.2.3 Zeta Potential Measurement

Zeta potential measurements have been performed with a Brookhaven ZetaPals instrument controlled by ZetaPals software. Unless at their zero point of charge, particles dispersed in a liquid have a charged surface. When an electric field is applied to the particle dispersion, the particles will move either toward the positive or toward the negative pole, thus revealing the sign of their surface charge. The speed at which they move toward the pole is proportional to the magnitude of their surface charge. The Brookhaven ZetaPals uses a laser beam to monitor the behavior of particles under the application of an electric field. The frequency of light scattered into the detector is Doppler shifted by an amount proportional to the velocity of the particles.

The samples analyzed were suspensions of powders in KCL 10^{-3}M solution. Each suspension was ultrasonicated to minimize agglomerates. Zeta potential was measured for each suspension over pH values ranging from 3 - 11. In this way, the isoelectric point (point of zero charge when zeta potential = 0) was determined. The inorganics analyzed for isoelectric point determination were A-16 alumina, AT1 titania, Aerodisp 630 nano-alumina, and VP W 740X nano-titania. The pH of the suspension was raised by
additions of a KOH $10^{-3}$M solution and lowered by additions of an HCl $10^{-3}$ solution.

Zeta potential was also measured for each of the powders with various surfactant additions as described in section 4.2.2. Zeta potential for samples with sodium stearate was measured at the suspensions’ real unadjusted pH value. Zeta potential was measured for samples of each inorganic with the following sodium stearate additions; 0, 0.001, 0.005, 0.01, 0.05, 0.08, 0.1, 0.5, 0.8, 1.0, 1.2, 1.5, 1.8, and 2.0%.

### 4.3 Batch Compositions

The analysis of batch properties was conducted by creating batches with variation in composition as well as variation in processing techniques. Batches created for rheological and mixedness testing each contained a solid phase and a liquid phase. The solid phase was comprised of two inorganic materials, an alumina and a titania. The weight ratio of alumina to titania was consistent for all batches and based on a 1:1 molar ratio. The liquid phase of the batches contained DDI water and hydroxypropyl methyl cellulose binder. The concentration of water varied between sets of batches to accommodate the practical rheology for extrusion of the batch. Batches of A16 alumina and AT1 titania were created at 16 and 20 percent water to examine the effect of solids loading variation on rheology and mixedness. The batches containing nano materials could not be created with less than 19% water or they became too stiff for the analysis methods. The concentration of hydroxypropyl methyl cellulose binder was maintained at 3% for all batches. A sodium stearate surfactant was also frequently included in concentrations of 1% but was also included in some batches at 0.5 and 0.1%. Some batches contained no sodium stearate additive.
The variations in processing included dry and wet mixing techniques, short versus long compounding time, and multiple extrusions. These techniques will be further explained by their procedures. Table 4.1 gives concentrations of each solid as well as the concentrations of each liquid for the batches containing A-16 alumina and AT1 titania. Table 4.2 gives concentrations of each inorganic and concentrations of each liquid for the batches containing A-16 alumina and nano-titania. Table 4.3 gives concentrations of each solid and concentrations of each liquid for the batches containing nano-alumina and AT1 titania. The concentrations total 100% not including any additions of sodium stearate which were added in surplus of 100%. Batch processing techniques are also listed to explain the variation between batches with identical chemistry.
Table 4.1 Batch formulations for batches containing A-16 alumina and AT1 titania

<table>
<thead>
<tr>
<th>#</th>
<th>Alumina %</th>
<th>Titania %</th>
<th>Water %</th>
<th>HPMC %</th>
<th>Stearate %</th>
<th>Processing Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>45.4</td>
<td>35.6</td>
<td>16</td>
<td>3</td>
<td>1</td>
<td>Dry mixed, compounded 30 minutes, extruded once</td>
</tr>
<tr>
<td>2</td>
<td>45.4</td>
<td>35.6</td>
<td>16</td>
<td>3</td>
<td>1</td>
<td>Dry mixed, compounded 7 minutes, extruded once</td>
</tr>
<tr>
<td>3</td>
<td>45.4</td>
<td>35.6</td>
<td>16</td>
<td>3</td>
<td>1</td>
<td>Dry mixed, compounded 30 minutes, extruded five times</td>
</tr>
<tr>
<td>4</td>
<td>45.4</td>
<td>35.6</td>
<td>16</td>
<td>3</td>
<td>1</td>
<td>Wet mixed, compounded 30 minutes, extruded once</td>
</tr>
<tr>
<td>5</td>
<td>43.2</td>
<td>33.8</td>
<td>20</td>
<td>3</td>
<td>1</td>
<td>Dry mixed, compounded 30 minutes, extruded once</td>
</tr>
<tr>
<td>6</td>
<td>43.2</td>
<td>33.8</td>
<td>20</td>
<td>3</td>
<td>0.5</td>
<td>Dry mixed, compounded 30 minutes, extruded once</td>
</tr>
<tr>
<td>7</td>
<td>43.2</td>
<td>33.8</td>
<td>20</td>
<td>3</td>
<td>0.1</td>
<td>Dry mixed, compounded 30 minutes, extruded once</td>
</tr>
<tr>
<td>8</td>
<td>43.2</td>
<td>33.8</td>
<td>20</td>
<td>3</td>
<td>0</td>
<td>Dry mixed, compounded 30 minutes, extruded once</td>
</tr>
<tr>
<td>9</td>
<td>43.2</td>
<td>33.8</td>
<td>20</td>
<td>3</td>
<td>1</td>
<td>Dry mixed, compounded 7 minutes, extruded once</td>
</tr>
<tr>
<td>10</td>
<td>43.2</td>
<td>33.8</td>
<td>20</td>
<td>3</td>
<td>1</td>
<td>Dry mixed, compounded 30 minutes, extruded five times</td>
</tr>
<tr>
<td>11</td>
<td>43.2</td>
<td>33.8</td>
<td>20</td>
<td>3</td>
<td>1</td>
<td>Wet mixed, compounded 30 minutes, extruded once</td>
</tr>
</tbody>
</table>

Table 4.2 Batch formulations for batches containing A-16 alumina and nano-titania

<table>
<thead>
<tr>
<th>#</th>
<th>Alumina %</th>
<th>Titania %</th>
<th>Water %</th>
<th>HPMC %</th>
<th>Stearate %</th>
<th>Processing Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>43.7</td>
<td>34.3</td>
<td>20</td>
<td>3</td>
<td>1</td>
<td>Wet mixed, compounded 30 minutes, extruded once</td>
</tr>
<tr>
<td>13</td>
<td>43.7</td>
<td>34.3</td>
<td>20</td>
<td>3</td>
<td>1</td>
<td>Wet mixed, compounded 7 minutes, extruded once</td>
</tr>
<tr>
<td>14</td>
<td>43.7</td>
<td>34.3</td>
<td>20</td>
<td>3</td>
<td>1</td>
<td>Wet mixed, compounded 30 minutes, extruded five times</td>
</tr>
</tbody>
</table>

Table 4.3 Batch formulations for batches containing nano-alumina and AT1 titania

<table>
<thead>
<tr>
<th>#</th>
<th>Alumina %</th>
<th>Titania %</th>
<th>Water %</th>
<th>HPMC %</th>
<th>Stearate %</th>
<th>Processing Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>15</td>
<td>43.7</td>
<td>34.3</td>
<td>20</td>
<td>3</td>
<td>1</td>
<td>Wet mixed, compounded 30 minutes, extruded once</td>
</tr>
<tr>
<td>16</td>
<td>43.7</td>
<td>34.3</td>
<td>20</td>
<td>3</td>
<td>1</td>
<td>Wet mixed, compounded 7 minutes, extruded once</td>
</tr>
<tr>
<td>17</td>
<td>43.7</td>
<td>34.3</td>
<td>20</td>
<td>3</td>
<td>1</td>
<td>Wet mixed, compounded 30 minutes, extruded five times</td>
</tr>
</tbody>
</table>
4.4 Processing Methods

The components in each batch were combined by either dry mixing or wet mixing. The dry mixing was achieved by milling inorganics together prior to combination with the organics. The wet mixing was achieved by creating slurries of each inorganic, combining the slurries, filter pressing the resultant slurry and then adding the organics during the compounding process. Dry mixing and wet mixing techniques were used on A16 alumina / AT1 titania batches but only wet mixing was utilized on the batches containing nano-alumina or nano-titania as these materials were acquired pre-dispersed to discourage the formation of large agglomerates.

4.4.1 Dry Mixing

Dry mixing of the batch components was conducted as follows. Each inorganic batch component was weighed out in accordance to the proportions described in Table 4.1. The alumina and titania were added to a 1 liter ball mill along with 120 cm$^3$ (1/8 mill volume) of 1 cm diameter cylindrical alumina milling media. Milling media was added to promote the mixing of the two powders and discourage adherence to the mill walls, not to alter the particle size distributions. The materials were then milled for 5 minutes at 50 rpm.

The liquid components of the batch were mixed together with the binder and sodium stearate (if present) added to distilled deionized (DDI) water in the proportions described in Table 4.1. The solution was mildly agitated to promote the dissolving of the organics. After milling of the inorganics and mixing of the organics, the two phases were combined in a low impact convection mixer for 1 minute. The purpose of this
combination was to prepare the batch for addition to the compounder which would plasticize the batch. Dry mixing was performed as the first step of processing for batches numbered 1-3 and 5-10 in Table 4.1.

4.4.2 Wet Mixing

Wet mixing of batches was achieved by the creation of slurries of the inorganic powders. The slurries were created with 40% solids loading. The nano-alumina and nano-titania were dispersed into 40% solids loading dispersions by the manufacturer and thus required no modification. The slurries of alumina and titania were created such that the proportion of inorganics would reflect the concentrations in Tables 4.1-4.3. The alumina and titania slurries were then combined and stirred by hand for 1 minute.

Once the alumina-titania slurry was created, it was then filter pressed. A Baroid (Halliburton, Houston, TX) filter press with 6 pressure chambers was used. The filter chamber was assembled with a medium flow rate filter paper. The slurry was then added to the chamber and fastened onto the press. Compressed air was used to provide 40 psi pressure to the filter press. Graduated beakers were used to collect the water pressed out of the slurries. Filter pressing was concluded when the volume of water extracted from the slurries indicated that the filter cakes were at the desired water percent. Organics were added at a later point in the batching process. They were not included in the slurries prior to filter pressing as their presence greatly inhibited the filter pressing process. Wet mixing was conducted on batches 4 and 11 from Table 4.1 as well as batches 12-14 from Table 4.2 and batches 15-17 from Table 4.3.
4.4.3 Compounding

The compounding of the batches was done with a Brabender Intelli-Torque Plasti-Corder (South Hackensack, NJ). Dual roller blades were used in a 350ml volume Prep Mixer mixing head. For the dry mixed batches, the mixer was started at 50 rpm and the batch was funneled into the chamber. For the wet mixed batches, the filter cakes were broken up into ~1.5 cm diameter portions. These were then added into the mixer along with the organic materials, binder, and sodium stearate if used. Batches were compounded at 50 rpm. The majority of the batches were compounded for 30 minutes. Batches 2, 9, 13, and 16 were compounded for a shortened time, 7 minutes.

4.4.4 Extrusion

Extrusion of the batches was performed in two stages. The first stage consisted of extrusion by a Loomis Piston Extruder (Levittown, PA). A solid disc was placed in the die head and the die head attached to the extruder. Material acquired from compounding was fed into the extrusion chamber. Pressure was then applied with the extrusion rod and maintained at 10,000 psi for 10 seconds to compress the batch and eliminate air pockets. Pressure was then released and the die head removed. A 15 mm diameter circular die was then placed in the die head and attached to the extruder. The batch was then extruded at a rate of 250 mm/minute. The extruded rod was collected and some set aside for dynamic stress evaluation.

Extrudate not set aside for dynamic stress evaluation was then utilized for capillary rheometry and mixedness evaluation. This material was extruded once more on
a Malvern (Worcester, UK) RH2000 capillary rheometer through a 1 mm diameter die at a rate of 10 mm/minute. This extrudate was then prepared for SEM analysis and evaluated for mixture quality.

4.5 Rheological Evaluation

The third objective of this thesis is to evaluate the effects of varying the batch composition and processing techniques on the rheology of the batch. Batch rheology was evaluated at three different processing points. Torque rheometry was used to evaluate the batch rheology during mixing, dynamic stress rheometry was used to evaluate the rheology of a batch after the bulk extrusion, and capillary rheometry was used to evaluate batch rheology during the fine extrusion process. Each of these evaluations gives information about the batch as it goes from disparate powders to a fine extrudate.

Rheological evaluation of the two coarse inorganics, A-16 alumina and AT1 titania, was also conducted. Each inorganic was mixed with water to form slurries of various solids loadings. A single solids loading was then chosen for an evaluation of sodium stearate additions. This set of evaluations was also conducted for a slurry of 1:1 molar ratio A16 and AT1. These data were collected to examine the effects of sodium stearate on the rheology of the individual components as well as the binary slurry. The nano-alumina and nano-titania were not examined this way as they were acquired in a pre-dispersed slurry which would have required drying out to yield significant dynamic stress rheometry data. The drying would have destabilized the dispersion thus rendering any evaluations obsolete.
4.5.1 Torque Rheometry

Torque rheometry was conducted on a Brabender Intelli-Torque Plasti-Corder (South Hackensack, NJ). Dual sigma blades were used in a 120ml volume 2-piece mixer head. For the dry mixed batches, the mixer was started at 50 rpm and the batch was funneled into the chamber. For the wet mixed batches, the filter cakes were broken up into approximately 1.5 cm diameter portions. These were then added into the mixer along with the organic materials, binder, and sodium stearate if used. Batches were evaluated 50 rpm for 16 minutes. Torque rheometry was performed on batches with varied compositions but not varied post-mix processing as this would be been redundant. Torque rheometry was done on batches 1, 4, 5, 6, 7, 8, and 11 from Table 4.1, batch 12 from Table 4.2, and batch 15 from Table 4.3.

4.5.2 Capillary Rheometry

Capillary rheometry was conducted on a Malvern (Worcester, UK) RH2000 capillary rheometer. Extrusion pressure was measured at multiple extrusion rates and for multiple dies. The extrusion rates evaluated were 1 mm/minute and 10 mm/minute. The dies used in the evaluation were both 1 mm diameter dies. The length of the dies varied such that one die had an L/d (length divided by diameter) of 16 and the other of 32. The results of this testing were that 4 peak extrusion pressures were obtained, one for each die at each speed. These values were then used to calculate batch parameters of bulk stress and yield stress. All batches listed in Tables 4.1, 4.2, and 4.3 were evaluated by capillary rheometry.
4.5.3 Dynamic Stress Rheometry

Dynamic stress rheometry was performed on a TA Instruments (New Castle, DE), AR-1000-N Rheometer. Slurries of A16 alumina, AT1 titania, and a 1:1 molar binary composition of the two were analyzed with a cup and vane geometry with increasing oscillatory stresses over the range of 0.1 – 100 Pascals. Solids loading samples evaluated were A16 alumina at 30, 35, and 40 weight percent, AT1 titania at 25, 35, 40, 45, 50, and 55 weight percent, and the binary composition at 30, 35, 36, 37, 38, and 39 weight percent. From these evaluations ideal solids loading for each inorganic was determined and used in a sodium stearate addition evaluation. The ideal solids loading was 30% for A16 alumina, 40% for AT1 titania, and 35% for the binary composition. Each slurry composition was evaluated with 1, 0.5, 0.1, 0.05, 0.01, 0.005, 0.001, and 0 percent sodium stearate.

For dynamic stress evaluation of the extruded batches, a parallel plate geometry was used on the TA Instruments AT-1000-N Rheometer. This geometry consisted of a striated base plate on which the sample was centered. The geometry, another striated plate parallel to the base, was then lowered to a set gap. This gap was chosen so that the geometry applied enough pressure to the sample to ensure consistent contact while having minimal destructive effect on the sample. Samples were obtained from the Loomis extruder. After extrusion from the Loomis Piston extruder, some extrudate was sectioned into 5mm discs. These discs were then evaluated on the rheometer with the parallel plate geometry and oscillatory stresses ranging from 100 – 50000 Pascals. Evaluations were conducted repetitively on at least 5 cylinders from each batch to ensure
isolated extrusion flaws would not skew data. All batches listed in Tables 4.1, 4.2, and 4.3 were evaluated by parallel plate dynamic stress rheometry.

4.6 Mixedness Evaluation

An evaluation of batch mixedness was conducted on all the batches listed in Tables 4.1, 4.2, and 4.3. The method of evaluation was to use an energy dispersive spectrometer in a scanning electron microscope to collect a chemical map of the batch extrudate surface and to evaluate that map statistically for distribution of phases.

4.6.1 Data Collection

Many steps had to be taken to prepare the sample for evaluation in an SEM. The starting sample was extrudate from the Malvern RH 2000 capillary rheometer.

4.6.1.1 Sample Preparation

Extrudate from the Loomis extruder was used as feedstock for a final extrusion with a vertical ram extruder (similar to the Malvern capillary rheometer) through a 1.25 mm diameter die. This die provided the samples for the batches containing A16 alumina and AT1 titania and the batches with A16 alumina and nano-titania. Damage to the 1.27mm die required that the samples of nano-alumina and AT1 titania evaluated were taken directly from extrusion through the Malvern rheometer and had a 1 mm diameter.

Extrudate from the Malvern rheometer was dried and sectioned into 5-6 mm segments. Seven segments (Figure 4.1 a) were then stood upright on an exposed piece of carbon tape in a hexagonal array as in Figure 4.1 b. Fine grit sandpaper was used to file
the tops of the segments to as even a length as possible. The carbon tape and segments were then transferred to the bottom of a hexagonal polystyrene weighing dish.

![Figure 4.1](image)

(a) Upright hexagonal array (b) Set in epoxy (c) Coated in carbon tape (d) Embedding

**Figure 4.1 Batch extrudate preparation for SEM evaluation; segments (a) upright hexagonal array (b) set in epoxy (c) coated in carbon tape (d)**

**Embedding**

The sample and hexagonal weighing dish were placed in a vacuum desiccator. A Ted Pella low viscosity embedding kit was used to mix a low viscosity epoxy. This epoxy was suspended in an upright beaker above the sample segments. A vacuum was pulled for 30 minutes. The beaker of epoxy was then upturned over the sample and the weighing dish was filled just until the ends of the sample segments were covered in
epoxy. The epoxy beaker was manipulated from outside the vacuum chamber so as not to lose vacuum during infiltration. The sample in epoxy was left in the vacuum for another 30 minutes to ensure infiltration. After this time, the sample was moved to a drying oven at 75°C and allowed 24 hours for the epoxy mixture to cure.

**Cutting and Grinding**

After the epoxy cured, a Dremel (Racine, WI) rotary tool with cut-off wheel was used to cut the excess epoxy away from the sample sides, leaving approximately a 1cm x 1cm x height sample.

60 grit silicon carbide grinding paper rotating at 100 rpms was used to grind the bottom of the sample to remove the remaining polystyrene. Any additional grinding of the sides was also performed with the 60 grit paper at 100 rpms. 120 grit silicon carbide grinding paper rotating at 80 rpms was used to grind the top of the sample down just to the point where all the sample segments were exposed. The sample was then ultrasonicated in DDI water for 30 seconds to loosen and remove any grit or clinging particulate.

**Polishing**

Polishing of the sample was done with a series of progressively finer polishing cloths. The procedure followed was to polish for 3 minutes on a 45 µm disc, 4 minutes on a 15 µm disc, 4 minutes on a 6 µm disc, and 4 minutes on a 1 µm disc. Samples were ultrasonicated in DDI water for 30 seconds after each polishing step to remove any loose particles or polishing remnants. Figure 4.1c is a polished epoxy set sample.
Coating

Coating was done by a Gatan (Warrendale, PA) Model 681 High Resolution Ion Beam Coater. A 5 nm layer of carbon was applied to the exposed segment surface of the sample. After carbon coating the sample sides and non-segment exposed top were covered with carbon tape to minimize the possibility of charging in the SEM. The final SEM ready sample is pictured in Figure 4.1 d.

4.6.1.2 Scanning Electron Microscopy

Secondary Electron Imaging

A Zeiss Gemini 982 (Jena, Germany) field emission scanning electron microscope was used to obtain all microscopy images. Secondary electron imaging was performed at a working distance of 15 mm, an aperture of 3, and a beam current of 5 kV. Images of each sample in tables 4.1-4.3 were obtained at magnifications of 10000, 5000, 3000, 2000, 1000, 500, and 100. Images contained 512x512 pixels.

Energy Dispersive Spectroscopy

A Princeton Gamma-Tech (Princeton, NJ) energy dispersive x-ray system was used in conjunction with the Gemini to collect elemental maps of extruded batch surfaces. Upon insertion of the EDS detector, the aperture was opened to 4 to allow greater numbers of characteristic waves to reach the detector. The beam current was raised to 10 kV and the focus was readjusted. A Sun Microsystem (Santa Clara, CA) IMIX software system was used to control the collection of compositional data. Once the
Gemini was focused on the sample area of interest, a spectrum was collected. Specific elemental windows were targeted based on knowledge of the sample composition. Each spectrum was collected for 5 minutes. Once the spectrum was collected, a digital compositional scan was taken. Compositional maps focused on aluminum, titanium, and oxygen and were taken at 1000X magnification and 100X magnification. The scan at 1000X magnification was taken with a resolution of 256x256 pixels for 20 minutes. A 1000X magnification scan covers an area of 115x115 µm. This is a small portion of the sample surface and all images were taken at locations approximately equidistant from the sample center and edge. The scan at 100X magnification was taken with a resolution of 128x128 pixels for 5 minutes. The 100X scan covers an area 1150x1150 µm. These images cover a significant portion of the sample surface and were taken of the center of the sample to minimize the inclusion of sample edges in the final image. Figures 4.2 and 4.3 are compositional maps of an A-16 alumina / AT1 titania batch (Al:Ti 1:1 molar ratio, 20% water, 3% HPMC binder, 1% sodium stearate) compounded for 30 minutes and extruded once. Figure 4.2 was taken at 1000x (256x256 resolution, 20 minute scan) and Figure 4.3 was taken at 100X (128x128 resolution, 5 minute scan). By setting both scans to operate at about 54.6 pixels per second, the scan qualities should be comparable.

The EDS resolution varies by element based on characteristic excitation energy. The characteristic excitation energy, $E_C$, for aluminum is 1.487 KeV and for titanium is 4.97 KeV[96]. These values, along with experimental density values, $\rho$, were entered into equation 2.73 to determine the EDS resolution, $R$, for aluminum and titanium at $E_0$ 10 KeV for each sample. Table 4.4 lists the compositions, densities, and resolutions for each batch.
Density was determined through Archimedes method. Samples of 2 cm length and 1 cm diameter were cut from batches extruded through the Loomis extruder, and their dry weight recorded. The samples were then boiled in distilled water for 15 minutes, cooled in a beaker with cold distilled water, then weighed on a suspension scale in a separate beaker of distilled water. The sample was then removed from the beaker, wiped of excess water, and reweighed to record a saturated mass. Density was calculated as mass of the sample in air, $M_s$, divided by the difference between the mass of the sample in air and the mass of the sample suspended in water, $M_w$.

$$ \rho = \frac{M_s}{(M_s - M_w)} \quad 4.1 $$

The significance of composition density is that a denser material allows a greater number of electron beam interactions to occur in a smaller volume. Therefore a material with a lower density leads to a larger minimum resolution, while a material with a greater density leads to a lower (and more desirable) minimum resolution.
<table>
<thead>
<tr>
<th>Batch</th>
<th>Density (g/cm²)</th>
<th>Al E&lt;sub&gt;C&lt;/sub&gt; (keV)</th>
<th>Ti E&lt;sub&gt;C&lt;/sub&gt; (keV)</th>
<th>Al Resolution</th>
<th>Ti Resolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>A16 Alumina-AT1 Titania, Wet Mix, 30 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>2.284</td>
<td>1.487</td>
<td>4.97</td>
<td>1.287</td>
<td>0.927</td>
</tr>
<tr>
<td>A16 Alumina-nano Titania, Wet Mix, 30 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>2.246</td>
<td>1.487</td>
<td>4.97</td>
<td>1.308</td>
<td>0.943</td>
</tr>
<tr>
<td>nano Alumina-AT1 Titania, Wet Mix, 30 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>2.221</td>
<td>1.487</td>
<td>4.97</td>
<td>1.323</td>
<td>0.953</td>
</tr>
</tbody>
</table>

Table 4.4 Aluminum and titanium resolution limits and batch densities
Figure 4.2 Compositional map of an alumina/titania batch taken at 1000x magnification for 20 minutes with a 256x256 resolution

Figure 4.3 Compositional map of an alumina/titania batch taken at 100x magnification for 5 minutes with a 128x128 resolution
4.6.2 Image Analysis

4.6.2.1 Compositional Maps

Compositional maps obtained with the EDS detector on the SEM were analyzed with Adobe (San Jose, CA) Photoshop add on Image Processing Toolkit 5.0 from Reindeer Graphics (Asheville, NC). The obtained image (Figure 4.2) was cropped to isolate a single elemental map (Figure 4.4).

![Compositional map of titanium from a 1000x image of an alumina/titania batch](image)

Figure 4.4 Compositional map of titanium from a 1000x image of an alumina/titania batch

Collected maps are comprised of a single pigment with varied intensities. To analyze the distribution of the element, an intensity cut-off value must be determined such that all pixels with equal or greater intensity are labeled as containing the element and all pixels with lesser intensities are labeled as not containing the element. This is known as thresholding. Thresholding was performed by ImageJ (Figure 4.5), a JAVA software program created by the National Institute of Health (Bethesda, MD). The thresholding function of ImageJ has been shown to yield consistently accurate results and removes operator variation from the procedure[97].
After thresholding, the cluster analysis feature in the Image Processing Toolkit add on was used to identify expected and observed values of mean nearest neighbor distances and variance in nearest neighbor differences. Using the ratios of observed to expected values, the quantities of $Q$ and $V$ were determined and plotted. Compositional maps of titanium and aluminum in the batches in Tables 4.1, 4.2, and 4.3 were collected. These maps clearly showed that the titanium, from titania in the batch, was distributed within a matrix of aluminum, from alumina in the batch. Therefore, the $Q/V$ values collected were from the titanium elemental maps.

Error bars were constructed for the $Q/V$ charts by taking four SEM/EDS maps from the 20% water, 1% sodium stearate, A16 alumina, AT1 titania, dry mixed, 30 minute, single extrusion batch. These titanium maps were collected from different samples of the same batch. The maps were then processed and their $Q/V$ values determined. The error bars represent the standard deviation of the $Q$ and $V$ values for these graphs.
**4.6.2.2 Extrusion Flaw Analysis**

Secondary electron images were collected at magnification of 100X. These images showed large extrusion flaws in the form of large pores or channels (Figure 4.6a). The contrast in intensity between these flaws and the segment surface allowed thresholding (Figure 4.6b), filtering (Figure 4.6c) and statistical analysis to be conducted. The secondary images were cropped, thresholded with the ImageJ software, then filters were applied to remove edge features and noise. The resultant binary image was then analyzed with the global function of the ImageJ software to yield information on the area fraction inhabited by the pores/channels and the average size of the pore channels. This datum was collected from 7 images for each batch. Average pore size and average area fraction were then graphed for inter-batch comparisons.
Figure 4.6 100X SEM image from alumina/titania batch (a) after thresholding (b) and after applied filters (c)

EDS maps of aluminum at 100X magnification were also collected (Figure 4.7a). Large pockets of alumina could be observed in the maps from some of the batches. ImageJ software was used to threshold these maps to identify the alumina-rich regions and analyze them statistically for each batch (Figure 4.7b). Two filters were used to refine the threshold results. The first was despeckle, which labeled features less than
11.54 µm as noise and removed them. The second filter used was a close holes feature which filled in ‘off’ pixels if they were surrounded by ‘on’ pixels (Figure 4.7c). These maps resulted in area fraction, average feature size, and maximum feature size data.

Figure 4.7 Aluminum compositional map at 100X from an alumina/titania batch (a) after thresholding (b) and after applied filters (c)
5

Research and Discussion

5.1 Powder Characterization

5.1.1 Particle Size Distribution

The particle size distributions of A16 alumina and AT1 titania, expressed in volume and number, are presented in Figure 5.1. The particle size distributions of Aerodisp W 630 nano-alumina and VP W 740X nano-titania are displayed in Figure 5.2. The volumetric particle size distribution of A16 alumina is bimodal, showing aggregates of 50.8 µm and 0.85 µm. Only submicron aggregates with a median of 0.34 µm are shown in the numeric particle size distribution, indicating that there are very few large aggregates as compared to the number of small aggregates. Volumetric particle size distribution of AT1 titania is also bimodal, consisting of aggregates of 24.6 µm and 0.59 µm. Again the larger aggregates are greatly outnumbered by the smaller. For this reason, the numeric particle size distribution is monomodal with the median at 0.33 µm. The particle size distribution for Aerodisp W 630 nano-alumina is monomodal for both volumetric and numerical assessments and results in medians of 99 nm and 88 nm, respectively. The VP W 740X nano-titania also results in a monomodal particle size distribution in both volume (median aggregates of 91 nm) and number (median aggregates of 68 nm). The nano-alumina and nano-titania were acquired as suspensions in which particles are kept dispersed and were used as received to prevent agglomeration during drying. It should be noted that the coarse alumina has a larger particle size than
the coarse titania. This will result in agglomerates of varying sizes and of varying strength. Evidence of this will be shown in the dynamic stress rheometry results in section 5.2.3.

Figure 5.1 Differential volume and differential number data for (a) A16 alumina and (b) AT1 titania
Figure 5.2 differential volume and differential number data for (a) Aerodisp W 630 nano-alumina and (b) VP W 740X nano-titania

Figures 5.3 and 5.4 show the effect of surfactant additions on the particle size distribution for the coarse A16 alumina. The agglomerate structure, as reflected by the volumetric distribution in Figure 5.3, does not change significantly as sodium stearate is increased from 0% to 1%. The same bimodal distribution is observed for the A16 alumina over this range. As the stearate additions are increased from 1% to 2%, the large aggregates dominate the volumetric distribution. The numeric particle size distribution for A16 with sodium stearate additions, Figure 5.4, shows a slight but steady increase in the aggregate size as stearate additions increase to 2%. This increase in particle size could indicate layers of adsorbed sodium stearate changing the effective particle size of the alumina particles.
Figure 5.3 Particle size distribution, differential volume of A16 alumina with sodium stearate
Figure 5.4 Particle size distribution, differential number of A16 alumina with sodium stearate
Figures 5.5 and 5.6 show the effect of surfactant addition on AT1 titania particle size distribution. The volumetric particle size distribution, Figure 5.5, is bimodal and shows that additions of sodium stearate reduce the size of large aggregates (median 24.6 µm). This could be attributed to the surfactant breaking down large, and apparently soft, agglomerates. The numeric particle size distribution, Figure 5.6, shows a slight increase in particle size at lower additions of sodium stearate. This is followed, mostly, by a decrease of the particle size as the stearate concentrations increase. This indicates that the stearate additions to coarse AT1 titania are breaking the large soft agglomerates while adsorbing on the surface.
Figure 5.5 Particle size distribution, differential volume of AT1 titania with sodium stearate
Figure 5.6 Particle size distribution, differential number, of AT1 titania with sodium stearate
Figures 5.7 and 5.8 show the effect of surfactant additions on the particle size of Aerodisp W 630 nano-alumina. The volumetric particle size distribution, Figure 5.7, indicates an increase in particle size with increased surfactant additions, similar to the trend observed in the coarse alumina. The numeric particle size, Figure 5.8, shows a slight increase with additions of up to 0.08% stearate. The particle size then decreases at higher surfactant concentrations, but values remain close (~80-100nm) regardless of surfactant additions.
Figure 5.7 Particle size distribution, differential volume of Aerodisp W 630 nano-alumina with sodium stearate
Figure 5.8 Particle size distribution, differential number of Aerodisp W 630 nano-alumina with sodium stearate
Figures 5.9 and 5.10 show the particle size distributions for increasing additions of surfactant to VP W 740X nano-titania. The volumetric particle size distributions, Figure 5.9, are very similar to those of the nano-alumina. Increased surfactant additions caused a gradual increase in the particle size, from \(~90\) nm to \(~126\) nm. This is due to adsorption of the surfactant on the particle surfaces resulting in a greater effective particle size. Unlike the nano-alumina, the numeric particle size distribution, Figure 5.10, results show that the surfactant additions lead to increased particle size.

Particle size distribution was not performed on batch blends. This was due to the size limitations of the Zetasizer and Mastersizer utilized in this evaluation. The range of particle sizes in the particle blend would be too large for either individual piece of equipment to assess accurately.
Figure 5.9 Particle size distribution, differential volume of VP W 740X nano-titania with sodium stearate
Figure 5.10 Particle size distribution, differential number of VP W 740X nanotitania with sodium stearate
5.1.2 Adsorption Isotherms

Figure 5.11 shows the adsorption isotherms for the four inorganics; A16 alumina, AT1 titania, Aerodisp W 630 nano-alumina, and VP W 740X nano-titania. The adsorption isotherms are plotted with adsorbed stearate per gram of inorganic vs. initial concentration of stearate added. The highest adsorption occurred with the nano-titania, while the adsorption isotherm of the coarse AT1 titania showed the lowest stearate adsorption, 0.1%. The maximum adsorption limit for the nano-titania was reached at an addition of ~1.5% sodium stearate. Maximum adsorption of stearate to A16 alumina was also observed at ~1.5% sodium stearate, though the adsorption limit was lower than that of the nano-titania. This is attributed to the variation in surface characteristics of the two inorganics.

The nano-alumina exhibited constant stearate adsorption for initial concentrations below 1% initial stearate concentration. At 1%, the adsorption level increases with increased initial stearate concentration, reaching a maximum adsorption level at 1.8% initial stearate addition.

The similarity in adsorption behavior between the A16 alumina and Aerodisp W 630 nano-alumina could be attributed to possible similarities between their surface electrokinetic properties, which will be discussed in greater detail in the next section. The great discrepancy in the AT1 titania and VP W 740X titania could be attributed to the differences in surface electrokinetics as well as the difference in surface area available for stearate adsorption.
5.1.3 Zeta Potential

Figure 5.12 shows the effect of sodium stearate additions on the zeta potential of suspensions of each of the inorganic powders; A16 alumina, AT1 titania, nano-alumina, and nano-titania. For each of the inorganics, the addition of sodium stearate generally lowered the zeta potential. The zeta potential for the titania materials was shown to drop at low stearate additions followed by a leveling off. The effect of stearate additions on the zeta potential of the nano-alumina followed the same trend as the zeta potential analysis of nano-titania. The zeta potential values for the A16 alumina decreased consistently with higher additions of sodium stearate.
Figures 5.13-5.16 show the zeta potential vs. pH for each of the individual inorganics; A16 alumina, AT1 titania, nano-alumina, and nano-titania. Figure 5.13 shows the zeta potential vs. pH for A16 alumina. The zeta potential values are initially positive at lower pH and become negative at higher pH, with an isoelectric point at 8.2. The isoelectric point is the pH value at which the zeta potential is zero, assuming the oxides are pure and insoluble. This is the point of minimum stability for the suspension when there is a maximum chance of coagulation due to lack of electrostatic repulsion.
Figure 5.14 shows the zeta potential vs. pH for AT1 titania. Zeta potential values were negative in the pH range investigated. Although the zeta potential values did not experimentally become positive in this pH range, there is a strong indication that the isoelectric point would occur with further reduction in pH. Interpolation would indicate a possible isoelectric point of 3.2 for AT1 titania.

Figure 5.15 shows the zeta potential vs. pH for Aerodisp W 630 nano-alumina. The zeta potential values are positive for low pH and become negative at higher pH values. The zeta potential is zero at a pH of 8.73, which defines the isoelectric point for the nano-alumina.

Figure 5.16 displays the zeta potential vs. pH for VP W 740X nano-titania. The zeta potential values recorded for the nano-titania remained negative for the pH range in the analysis. The zeta potential consistently decreased as the pH was increased. This allows for the possibility that the zeta potential would have equaled zero at some pH value lower than those evaluated.

Using the surface charge information in Figures 5.12-5.16, the adsorption isotherms in Figure 5.11 can be further evaluated. The data presented in Figure 5.14 indicates the surface of nano-titania is highly negative. This appears to favor high electrostatic adsorption of sodium stearate, as seen in Figure 5.11. The AT1 titania, also exhibited a negative charge, though weaker, which produces a favorable environment for electrostatic adsorption of stearate, though the amount adsorbed was much lower than the stearate adsorbed to the nano-titania. A16 alumina and nano-alumina displayed very close isoelectric points and exhibited similar electrokinetic surface properties, as seen in Figures 5.13 and 5.15. According to Figure 5.11, stearate adsorption reached a maximum
adsorption at, approximately, the same initial stearate addition for both alumina powders, however, the shape of the adsorption isotherms differed for the two alumina powders. In the central region of initial stearate additions (0.5-1.5 g stearate), the coarser, A16 alumina, illustrated a higher adsorption than the nano-alumina. This could be due to the breaking down of larger A16 aggregates into smaller components as greater quantities of sodium stearate were added. This would have created more surface area leading to higher adsorption values, up until the point where the maximum adsorption on A16 alumina was reached.

Figure 5.13 Zeta Potential vs. pH for A16 Alumina
Figure 5.14 Zeta Potential vs. pH for AT1 Titania

Figure 5.15 Zeta Potential vs. pH for Aerodisp W 630 nano-Alumina
5.1.4 Dynamic Stress Rheometry

Another component of characterization of the coarse inorganic powders was to evaluate their rheological properties in concentrated dispersions by using dynamic stress rheometry. The nano-powders were not evaluated with this method as that would have required altering the acquired dispersions which would invalidate the applicability of any results.

Figures 5.17-5.19 show the dynamic stress rheometry $G'$ curves for A16 alumina, AT1 titania, and a binary 1:1 molar composition of the A16 and AT1 respectively. Table 5.1 lists the stress at which each $G'$ curve yielded. In Figure 5.17, $G'$ curves for 30%,
35%, and 40% by weight solids loading are shown. These curves exhibited yield stresses at 0.63, 5.02, and 25.12 Pa, respectively. An increase in yield stress with solids loading is due to the increased interactions between particles creating networks which require greater stress to break down and allow for flow behavior. The purpose in evaluating multiple solids loadings is to determine the optimal initial curve for surfactant evaluation tests. As the addition of surfactant is hypothesized to increase the yield stress and $G'$ curve, the best solids loading is that which produces the lowest $G'$ curve with a distinctive yield stress. For the A16 alumina, the optimal curve shape occurs at 30% solids loading, which yielded at 0.63 Pa. Figure 5.18 shows the $G'$ curves for 40%, 45%, 50%, and 55% solids loading by weight of AT1 titania. Predictably, the yield point for each composition, as listed in Table 5.1, increases as the solids loading increases. The greater concentration of particles leads to a greater number of particle interactions which results in a higher resisting stress during the elastic region and a higher oscillatory stress required for transition to viscous flow (higher yield stress). For the AT1 titania, the optimal curve shape occurs at 40% solids loading, which yielded at 0.32 Pa. Figure 5.19 shows the $G'$ curve for a 1:1 molar ratio of A16 alumina and AT1 titania. This is the same proportion which will be used in the batch evaluations of rheology and mixedness. Figure 5.19 shows the $G'$ curves for 30%, 35%, 36%, 37%, 38%, and 39% solids loading by weight of the binary composition. From these curves, it was determined that a solids loading of 35% by weight, yielding at a stress of 5.01 Pa, would be used to evaluate the effect of sodium stearate additions on the yield point for the A16 alumina and AT1 titania binary composition.
Figure 5.17 $G'$ curves for A16 alumina at 30, 35, and 40% solids loading

Figure 5.18 $G'$ curves for AT1 titania at 40, 45, 50, and 55% solids loading
Figure 5.19 G' curves for the binary composition of A16 alumina and AT1 titania at 30%, 35%, 36%, 37%, 38%, and 39% solids loading

<table>
<thead>
<tr>
<th>Inorganic</th>
<th>Solids Loading (% Solids)</th>
<th>Yield Point (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A16 Alumina</td>
<td>30</td>
<td>0.63</td>
</tr>
<tr>
<td>A16 Alumina</td>
<td>35</td>
<td>5.01</td>
</tr>
<tr>
<td>A16 Alumina</td>
<td>40</td>
<td>25.12</td>
</tr>
<tr>
<td>AT1 Titania</td>
<td>40</td>
<td>0.32</td>
</tr>
<tr>
<td>AT1 Titania</td>
<td>45</td>
<td>0.63</td>
</tr>
<tr>
<td>AT1 Titania</td>
<td>50</td>
<td>2.00</td>
</tr>
<tr>
<td>AT1 Titania</td>
<td>55</td>
<td>6.31</td>
</tr>
<tr>
<td>A16 Alumina/AT1 Titania</td>
<td>30</td>
<td>5.01</td>
</tr>
<tr>
<td>A16 Alumina/AT1 Titania</td>
<td>35</td>
<td>10.00</td>
</tr>
<tr>
<td>A16 Alumina/AT1 Titania</td>
<td>36</td>
<td>10.00</td>
</tr>
<tr>
<td>A16 Alumina/AT1 Titania</td>
<td>37</td>
<td>15.85</td>
</tr>
<tr>
<td>A16 Alumina/AT1 Titania</td>
<td>38</td>
<td>63.10</td>
</tr>
<tr>
<td>A16 Alumina/AT1 Titania</td>
<td>39</td>
<td>63.10</td>
</tr>
</tbody>
</table>

Table 5.1 Yield point values for dynamic stress rheometry of A16 alumina, AT1 titania, and A16/AT1 binary slurries evaluated in Figures 5.17-5.19
Figures 5.20-5.22 are the $G'$ curves for A16 alumina, AT1 titania, and a binary mixture A16 and AT1. Each figure shows batches with the same inorganic composition but with varied concentrations of sodium stearate ranging from 0 to 1%. Table 5.2 lists these batches along with their stearate concentration and the yield point for each batch.

Figure 5.20 shows the $G'$ curves for a 30% solids loading by weight suspension of A16 alumina with varied concentrations of sodium stearate. The $G'$ curve exhibits very little change in yield behavior for suspensions with less than 0.05% sodium stearate. The range of yield stresses for suspensions with 0%, 0.001%, 0.005%, and 0.01% is about 2.00 - 3.16 Pa. As the concentration of sodium stearate is increased about 0.01%, the yield stress of the suspension also increases. The 0.05% batch exhibits a yield stress of 6.31 Pa, the 0.1% batch exhibits a yield stress of 10.00 Pa, the 0.5% batch exhibits a yield stress of 79.43 Pa, and the 1% batch exhibits a yield stress of 100.00 Pa.

Figure 5.21 shows the $G'$ curves for a 40% solids loading by weight suspension of AT1 titania with varied concentrations of sodium stearate. The yield stress in the $G'$ curves increases with increased additions of sodium stearate. This is a trend that applies to all the concentrations of sodium stearate added to AT1 titania. The yield stresses are 0.16 Pa, 0.20 Pa, 0.25 Pa, 0.40 Pa, 0.50 Pa, 0.63 Pa, 1.56 Pa, and 2.51 Pa for concentrations 0%, 0.001%, 0.005%, 0.01%, 0.05%, 0.1%, 0.5%, and 1% respectively.

Figure 5.22 shows the $G'$ curves for the binary composition of 35% solids loading suspension of a 1:1 molar ratio combination of A16 alumina and AT1 titania. The $G'$ curves for this suspension exhibit varied yield stresses as the concentration of sodium stearate is increased. The lowest yield stress, 1.59 Pa, does occur at 0% sodium stearate, but the subsequent yield stresses do not follow a predictable trend. The yield stresses for
0.001\%, 0.005\%, 0.01\%, and 0.05\% are 3.16 Pa, 3.98 Pa, 3.16 Pa, and 2.51 Pa respectively. The yield stress for 0.1\%, 0.5\%, and 1\% are 10.00 Pa, 19.95 Pa, and 3.98 Pas respectively.

Increase in the yield stress of a G’ curve with increased sodium stearate could be attributed to the effect the stearate has on agglomerates and agglomerate formation. Sodium stearate added to a suspension will adsorb onto particle surfaces and prevent particles from agglomerating. This keeps large agglomerates from forming in the suspension. The reason this increases the yield stress is that large agglomerates act effectively as larger particles. Larger particles mean less volume of liquid phase is necessary for viscous flow. As sodium stearate is added and the proportion of agglomerates is reduced, more liquid phase is needed to maintain a viscous flow. Since these are closed systems with a set volume of liquid phase, the flow behavior is such that a greater applied stress is required to cause the suspension to transition from elastic flow to viscous flow. This trend is clearly seen in the A16 alumina suspensions and AT1 titania suspensions.

The binary composition of A16 alumina and AT1 titania has more complex particle interactions than either of the singular suspensions. Due to the alumina and titania having opposing surface charges at most pH values, these particles are attracted to each other in the suspension. Small additions of sodium stearate (0\%, 0.001\%, 0.005\%, and 0.01\%) do not seem to be sufficient to prevent these agglomerates from occurring with any consistency. Larger additions of sodium stearate (above 0.05\%) begin to follow more predictable trends. This would explain the increased yield stresses for the 0.1\% and 0.5\% additions of sodium stearate. The 1\% addition once again reduces the yield stress.
This rheological behavior of the binary system can be further explained by utilizing the absorption and zeta potential data in Figures 5.11 and 5.12. At 0% sodium stearate, the alumina surface has a positive charge, while the titania surface has a negative charge. This leads to some agglomerate formation which reduces the effective number of particles allowing for a low yield point, as noted in Table 5.2. As sodium stearate is introduced to the system, Figure 5.12 shows us that the surface charge of the titania remains relatively constant while the charge on the alumina surface is reduced. This change in charge behavior creates less of an electrostatic attraction between the alumina and titania. Less agglomeration between the two inorganics means more effective particles, leading to higher yield points. Looking at the adsorptive data, it is seen that greater additions of sodium stearate lead to greater surfactant adsorbed to the alumina. The titania adsorption is fairly constant from even the smallest additions of surfactant. While increased adsorption leads to fewer agglomerates and higher yield points, increased concentrations of surfactant also lead to increased surfactant in the liquid phase. This surfactant acts as a bulk lubricant and facilitates the flow of inorganics, thus lowering the yield point. These opposing trends explain why the yield points for the binary system in Table 5.2 increase with surfactant additions up to 0.5% then subsequently decrease.
Figure 5.20 G’ curves for a 30% solids loading suspension of A16 alumina with varying concentrations of sodium stearate.

Figure 5.21 G’ curves for a 40% solids loading suspension of AT1 titania with varying concentrations of sodium stearate.
Figure 5.22 G’ curves for a 35% solids loading suspension of A16 alumina and AT1 titania with varying concentrations of sodium stearate.
<table>
<thead>
<tr>
<th>Inorganic</th>
<th>Sodium Stearate Concentration (% Stearate)</th>
<th>Yield Point (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A16 Alumina</td>
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<td>1.59</td>
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<td>A16 Alumina</td>
<td>0.001</td>
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<td>0.500</td>
<td>79.43</td>
</tr>
<tr>
<td>A16 Alumina</td>
<td>1.000</td>
<td>100.00</td>
</tr>
<tr>
<td>AT1 Titania</td>
<td>0.000</td>
<td>0.16</td>
</tr>
<tr>
<td>AT1 Titania</td>
<td>0.001</td>
<td>0.25</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
<td>AT1 Titania</td>
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<td>0.63</td>
</tr>
<tr>
<td>AT1 Titania</td>
<td>0.500</td>
<td>1.59</td>
</tr>
<tr>
<td>AT1 Titania</td>
<td>1.000</td>
<td>2.51</td>
</tr>
<tr>
<td>A16 Alumina/AT1 Titania</td>
<td>0.000</td>
<td>2.00</td>
</tr>
<tr>
<td>A16 Alumina/AT1 Titania</td>
<td>0.001</td>
<td>3.16</td>
</tr>
<tr>
<td>A16 Alumina/AT1 Titania</td>
<td>0.005</td>
<td>3.98</td>
</tr>
<tr>
<td>A16 Alumina/AT1 Titania</td>
<td>0.010</td>
<td>3.98</td>
</tr>
<tr>
<td>A16 Alumina/AT1 Titania</td>
<td>0.050</td>
<td>3.16</td>
</tr>
<tr>
<td>A16 Alumina/AT1 Titania</td>
<td>0.100</td>
<td>12.59</td>
</tr>
<tr>
<td>A16 Alumina/AT1 Titania</td>
<td>0.500</td>
<td>25.12</td>
</tr>
<tr>
<td>A16 Alumina/AT1 Titania</td>
<td>1.000</td>
<td>3.98</td>
</tr>
</tbody>
</table>

Table 5.2 Dynamic stress rheometry yield stresses for slurries with varying inorganics and sodium stearate concentrations
5.2 Effect of Composition and Processing on Paste Rheology

5.2.1 Torque Rheometry

Figure 5.23 shows the torque rheometry curves for the wet and dry mixed batches with A16 Alumina, AT1 Titania, 1% sodium stearate at 16% and 20% water. Two key points of interest in a torque rheometry curve are peak torque, the maximum amount of torque required to mix the batch, and homogenization time, the time from an initial torque value to a steady state torque value, here defined as that which has a tangential slope of less than 0.1 Nm/minute. Table 5.3 shows these values for the batches evaluated in Figure 5.23.

The peak torque values for both dry mixed batches are greater than the equivalent compositions which had been wet mixed. It is possible that the wet mixed batches are already compounded from their processing prior to the torque mixing and that they require less torque to plasticize inside the torque rheometer. Figure 5.23 also makes it apparent that the batches with higher water percent (20%) require less torque to mix than the batches with lower water percent (16%) whether the initial batching technique is wet or dry. This is due to the liquid phase allowing particles and agglomerates to flow more readily in the mixture. The homogenization times tend to be greater for peaks which require a higher amount of torque to plasticize. The exception to this among these batches is the wet mixed 20% water batch. This batch requires a longer time to homogenize than its higher peak torque dry mixed counterpart.

Figure 5.24 shows the torque rheometry curves for batches containing A16 alumina, AT1 titania, binder, 20% water, and varied concentrations of sodium stearate;
1%, 0.5%, 0.1%, and 0%. The peak torque and homogenization times for these batches can be found in Table 5.4. These batches show very similar curve shapes but there is a trend that indicates peak torque decreases as the sodium stearate concentration increases. The highest peak torque value is 4.3 Nm for the 0% stearate addition batch. The peak torque for the 1% sodium stearate batch is 3.56 Nm. The two intermediate batches fall in between with the 0.5% at a slightly higher peak torque, 3.92 Nm than the 0.1% batch, 3.72 Nm. The homogenization times for these batches are very close together. They range from 5 minutes to 5.13 minutes, a difference of less than 8 seconds. It can then be assumed that the addition of sodium stearate can decrease the amount of torque necessary to mix a batch but will not decrease the amount of time required for mixing.

Figure 5.25 shows the torque values for three wet mixed batches. Each batch was created from a different combination of the inorganics along with binder, 20% water, and 1% sodium stearate. Table 5.5 lists the composition, the peak torque, and homogeneity times for the curves in Figure 5.25. The batch containing the coarser alumina and titania had a peak torque of 2.94 and a homogeneity time of 4.9 minutes. The batch with nano-titania had a lower peak torque, 1.79 and shorter homogeneity time, 3.2 minutes. The assumption would have been that the addition of nano-materials would require greater liquid phase for additional flow and that not being present, would have increased peak torque and homogeneity time, as in the batch containing nano-alumina and AT1 titania. The nano-alumina and AT1 titania batch had a very large peak torque, 13.93 Nm, and the longest homogeneity time for any of the batches at 14.2 minutes.
Figure 5.23 Torque rheometry comparison of dry and wet mixing at 16% and 20% water

Figure 5.24 Torque rheometry evaluations of batches with varied sodium stearate additions
Table 5.3 Peak torque and homogenization times for curves in figure 5.19

<table>
<thead>
<tr>
<th>#</th>
<th>Batch</th>
<th>Peak Torque (Nm)</th>
<th>Homogenization Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>A16-AT1, 20% water, dry mixed, 1% stearate</td>
<td>3.56</td>
<td>5.10</td>
</tr>
<tr>
<td>6</td>
<td>A16-AT1, 20% water, dry mixed, 0.5% stearate</td>
<td>3.92</td>
<td>5.00</td>
</tr>
<tr>
<td>7</td>
<td>A16-AT1, 20% water, dry mixed, 0.1% stearate</td>
<td>3.72</td>
<td>5.13</td>
</tr>
<tr>
<td>8</td>
<td>A16-AT1, 20% water, dry mixed, 0% stearate</td>
<td>4.30</td>
<td>5.00</td>
</tr>
</tbody>
</table>

Table 5.4 Peak torque and homogenization times for curves in figure 5.20

<table>
<thead>
<tr>
<th>#</th>
<th>Batch</th>
<th>Peak Torque (Nm)</th>
<th>Homogenization Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11</td>
<td>A16-AT1, 20% water, wet mixed, 1% stearate</td>
<td>2.94</td>
<td>4.90</td>
</tr>
<tr>
<td>12</td>
<td>A16-nanoTi, 20% water, wet mixed, 1% stearate</td>
<td>1.73</td>
<td>3.20</td>
</tr>
<tr>
<td>15</td>
<td>nanoAl-AT1, 20% water, wet mixed, 1% stearate</td>
<td>13.93</td>
<td>14.20</td>
</tr>
</tbody>
</table>

Table 5.5 Peak torque and homogenization times for curves in figure 5.21
5.2.2 Capillary Rheometry

Figures 5.26 – 5.31 show bulk yield stress, also called bulk stress, and wall shear stress values extrapolated to a zero velocity as obtained from a Benbow analysis of capillary rheometry pressures. Tables 5.6-5.9 list the batch compositions evaluated and the wall shear and bulk yield stresses of those batches. Figure 5.26 is a comparison of the wall shear stresses for A16 alumina – AT1 titania batches with 1% sodium stearate and varied processing at 16% and 20% water. The wall shear stress values for these batches can be found in Table 5.6. The wall shear stresses for the 16% water batches are consistently higher than those of the 20% water batches. The greater availability of liquid phase in the higher water percent batch makes it easier for the material to transition to a viscous flow. The processing variations do not create much variation in the wall shear stress of the batches. The lower water concentration composition does exhibit a lower wall shear stress for the wet mixed batch, but the other processing techniques never cause wall shear stress to vary more than 0.01 MPa.

Figure 5.27 is a comparison of the bulk stresses for A16 alumina – AT1 titania batches with 1% sodium stearate and varied processing at 16% and 20% water. The bulk stresses exhibit more varied behavior as a result of processing technique than the wall shear stresses in the previous figure. The bulk yield stress values for these batches can be found in Table 5.6. In the case of both batch compositions (high and low water %) the wet mixing technique exhibited higher bulk stress than the dry mixing technique for the batch composition. Higher bulk stress is generally a desirable property as it relates to the ability of the extruded batch to hold its shape post-extrusion. The batches which are mixed for the short mixing time have almost identical bulk stresses. For the 20% water
batch this is an increase in the bulk stress, but for the 16% water batch, this marks a decrease in bulk stress from that of the longer mixed batch. Putting the batch through multiple extrusions increases its bulk stress for both the 16% and 20% water batches, though the change in stress from the single extruded batch is more drastic for the 20% water batch.

Figure 5.26 Wall shear stresses for A16 alumina – AT1 titanias batches with varied processing techniques at 16% and 20% water
Figure 5.27 Bulk stresses for A16 alumina – AT1 titania batches with varied processing techniques at 16% and 20% water

<table>
<thead>
<tr>
<th>#</th>
<th>Batch</th>
<th>Wall Shear Stress (MPa)</th>
<th>Bulk Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A16 Alumina-AT1 Titania, Dry Mix, 30 min mix time, single extrusion, 16% water, 1% stearate</td>
<td>0.05462</td>
<td>0.16638</td>
</tr>
<tr>
<td>2</td>
<td>A16 Alumina-AT1 Titania, Dry Mix, 7 min mix time, single extrusion, 16% water, 1% stearate</td>
<td>0.05349</td>
<td>0.06852</td>
</tr>
<tr>
<td>3</td>
<td>A16 Alumina-AT1 Titania, Dry Mix, 30 min mix time, 5x extrusion, 16% water, 1% stearate</td>
<td>0.06177</td>
<td>0.38650</td>
</tr>
<tr>
<td>4</td>
<td>A16 Alumina-AT1 Titania, Wet Mix, 30 min mix time, single extrusion, 16% water, 1% stearate</td>
<td>0.03937</td>
<td>0.40702</td>
</tr>
<tr>
<td>5</td>
<td>A16 Alumina-AT1 Titania, Dry Mix, 30 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>0.02525</td>
<td>0.00946</td>
</tr>
<tr>
<td>9</td>
<td>A16 Alumina-AT1 Titania, Dry Mix, 7 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>0.03070</td>
<td>0.06950</td>
</tr>
<tr>
<td>10</td>
<td>A16 Alumina-AT1 Titania, Dry Mix, 30 min mix time, 5x extrusion, 20% water, 1% stearate</td>
<td>0.02762</td>
<td>0.47818</td>
</tr>
<tr>
<td>11</td>
<td>A16 Alumina-AT1 Titania, Wet Mix, 30 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>0.03213</td>
<td>0.29937</td>
</tr>
</tbody>
</table>

Table 5.6 Bulk and wall shear stresses for batches containing A16 alumina – AT1 titania and 1% sodium stearate with varied water concentration and processing
Figure 5.28 shows the wall shear stress variations for the batches containing A16 alumina and nano-titania as well as those with nano-alumina and AT1 titania with varied processing techniques. The wall shear stresses for these batches can be found in Table 5.7. All of these batches were wet mixed and vary by length of mixing time and number of extrusions. For both compositions, the wall shear stress is lower for batches mixed for a shorter time as well as those extruded multiple times. For the batch containing A16 alumina and nano-titania, the greatest reduction in wall shear stress was observed in the batch extruded 5 times. The shortening of the mixing time did not greatly change the wall shear stress required to extrude the batch. For the batch containing nano-alumina and AT1 titania, the opposite is true. The shorter mixing time for this material showed a greater reduction in wall shear stress than the multiple extrusion of this material, which changed very little.

Figure 5.29 shows the bulk stress variations for the batches containing A16 alumina and nano-titania as well as those with nano-alumina and AT1 titania with varied processing techniques. The bulk yield stresses for these batches can be found in Table 5.7. The batches containing nano-alumina and AT1 titania show lower bulk stresses than the batches containing A16 alumina and nano-titania. Processing does not have a great impact on the bulk stress of the nano-alumina AT1 titania batch as the bulk stress for all 3 processing techniques ranges from 0.064 – 0.164 MPa. The bulk stress values for the batches containing A16 alumina and nano-titania do vary with processing. The bulk stress is greater for the batches with shorter mixing time and multiple extrusions.
Figure 5.28 Wall shear stresses for batches with nano-powders with varied processing techniques

Figure 5.29 Bulk stresses for batches with nano-powders with varied processing techniques
<table>
<thead>
<tr>
<th>#</th>
<th>Batch</th>
<th>Wall Shear Stress (MPa)</th>
<th>Bulk Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>A16 Alumina-nano Titania, Wet Mix, 30 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>0.03055</td>
<td>0.47010</td>
</tr>
<tr>
<td>13</td>
<td>A16 Alumina-nano Titania, Wet Mix, 7 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>0.02722</td>
<td>1.42870</td>
</tr>
<tr>
<td>14</td>
<td>A16 Alumina-nano Titania, Wet Mix, 30 min mix time, 5x extrusion, 20% water, 1% stearate</td>
<td>0.01306</td>
<td>0.98847</td>
</tr>
<tr>
<td>15</td>
<td>nano Alumina-AT1 Titania, Wet Mix, 30 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>0.03159</td>
<td>0.06499</td>
</tr>
<tr>
<td>16</td>
<td>nano Alumina-AT1 Titania, Wet Mix, 7 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>0.01617</td>
<td>0.12619</td>
</tr>
<tr>
<td>17</td>
<td>nano Alumina-AT1 Titania, Wet Mix, 30 min mix time, 5x extrusion, 20% water, 1% stearate</td>
<td>0.02391</td>
<td>0.16328</td>
</tr>
</tbody>
</table>

Table 5.7 Bulk and wall shear stresses for batches containing nano powders with variations in processing

Figure 5.30 compares the bulk and wall shear stresses from batches of the same chemistry and processing techniques but varied inorganics. The batches are composed of 20% water with 1% sodium stearate, wet mixed, with a 30 minute mixing time and extruded once. The bulk yield and wall shear stress values for these batches can be found in Table 5.8. The batch with A16 alumina and AT1 titania is compared to the batch with A16 alumina and nano-titania and the batch with nano-alumina and AT1 titania. The wall shear stresses for all three batch compositions are very similar and vary less than 0.002 MPa. However, the bulk stresses for the batches are shown to vary with composition. The batch containing the A16 alumina and nano-titania shows the greatest bulk stress while the batch containing nano-alumina and AT1 titania shows the lowest bulk stress. In the batch, a 1:1 molar ratio of alumina to titania (which all batches are created with) creates a batch with a greater volume of alumina than titania. This means it is possible that the alumina used in the batch dominates the titania contribution in determining the bulk stress of the batch. While the nano-titania in the A16 alumina –
nano-titania batch does contribute to the raising of the bulk stress, the batch with nano-alumina and AT1 titania shows a drastic drop in bulk stress from the batch with A16 alumina and AT1 titania.

Figure 5.31 shows the bulk and wall shear stresses from a batch of A16 alumina and AT1 titania with 20% water, dry mixed with a 30 minute mixing time and extruded once. Each batch contains a different concentration of sodium stearate; 1%, 0.5%, 0.1%, or 0%. The bulk yield and wall shear stress values for these batches can be found in Table 5.9. Wall shear stress and bulk stress values both follow the same trend of decreasing with increasing sodium stearate additions. These trends are logical as the surfactant facilitates batch flow, but also reduces extrudate stiffness. Sodium stearate is typically added to a batch to reduce the wall shear stress of the batch, allowing it to require less force to extrude. Other components are then added to the batch to improve the bulk stress.
Figure 5.30 Wall shear and bulk stresses for batches with varied inorganics

Figure 5.31 Wall shear and bulk stresses for batches with varied stearate concentrations
Table 5.8 Bulk and wall shear stress values for wet mixed batches with varied inorganics

<table>
<thead>
<tr>
<th>#</th>
<th>Batch</th>
<th>Wall Shear Stress (MPa)</th>
<th>Bulk Stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>A16 Alumina-AT1 Titania, Dry Mix, 30 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>0.02525</td>
<td>0.00946</td>
</tr>
<tr>
<td>6</td>
<td>A16 Alumina-AT1 Titania, Dry Mix, 30 min mix time, single extrusion, 20% water, 0.5% stearate</td>
<td>0.04739</td>
<td>0.13262</td>
</tr>
<tr>
<td>7</td>
<td>A16 Alumina-AT1 Titania, Dry Mix, 30 min mix time, single extrusion, 20% water, 0.1% stearate</td>
<td>0.08200</td>
<td>0.43264</td>
</tr>
<tr>
<td>8</td>
<td>A16 Alumina-AT1 Titania, Dry Mix, 30 min mix time, single extrusion, 20% water, 0% stearate</td>
<td>0.19324</td>
<td>3.73195</td>
</tr>
</tbody>
</table>

Table 5.9 Bulk and wall shear stress values for wet mixed batches with varied stearate concentrations

5.2.3 Dynamic Stress Rheometry

Figures 5.32 – 5.38 show the G’ curves obtained by performing dynamic stress rheometry with a parallel plate geometry on extruded pastes. These paste samples were taken after compounding and extrusion of the batch through a 10 mm diameter circular die. Analyzing the G’ behavior of the batch at this point yields information about the agglomerate nature of the batch. The batch compositions and yield stresses of these curves can be found in Table 5.10. Figure 5.32 shows the G’ curves for batches containing A16 alumina, AT1 titania, binder, 16% water and 1% sodium stearate. The effect of processing on the G’ yield behavior can be analyzed by comparing these curves. The dry mix, 30 min, 1x batch has the lowest yield stress of the batches, yielding at 6310
The 7 minute mix batch has a slightly higher yield at 7943 Pa while the 5x extruded batch yields at 12590 Pa. The wet mix batch has the highest yield stress of 19950 Pa. Though the wet mixed batch has the highest yield stress, it also exhibits a much sharper slope during yield. This indicates that the transition between elastic flow and viscous flow is happening uniformly at the yield stress, unlike for the dry mixed batches which exhibit yield over a longer range of applied stresses, meaning a range of applied stresses is required for the transition to viscous flow. This may indicate that the wet mixing process has created different agglomerate structure than the dry mixing. When G’ yields over a large range of stresses, it indicates that the agglomerate breakdown necessary for viscous flow is occurring over a range of agglomerate sizes. The wet mixed batch would therefore have a uniform agglomerate structure which would yield after a specific stress was reached as opposed to over a range of stresses.

Figure 5.33 shows the G’ curves for an A16 alumina AT1 titania batch with 20% water and 1% sodium stearate for varying processing techniques. The G’ curves are very similar for these batches. The 5x extruded batch exhibits the lowest yield at 31620 Pa followed by the 30 min mix 1x extruded batch at 39810 Pa, the 7 min mix 1x extruded batch at 39810 Pa, and the wet mixed 30 min mix 1x extruded batch at 46683 Pa. The shape of the curves is also very similar. They exhibit a sharp transition from elastic to viscous flow indicating that the 20% water compositions have a greater uniformity of agglomerate size than the 16% compositions in Figure 5.32.
Figure 5.32 $G'$ curves of batches with A16 alumina and AT1 titania, binder, 1% sodium stearate and 16% water with varied processing.

Figure 5.33 $G'$ curves of batches with A16 alumina and AT1 titania, binder, 1% sodium stearate and 20% water with varied processing.
<table>
<thead>
<tr>
<th>#</th>
<th>Batch</th>
<th>Dynamic Stress Rheometry Yield Stress (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A16 Alumina-AT1 Titania, Dry Mix, 30 min mix time, single extrusion, 16% water, 1% stearate</td>
<td>6310</td>
</tr>
<tr>
<td>2</td>
<td>A16 Alumina-AT1 Titania, Dry Mix, 7 min mix time, single extrusion, 16% water, 1% stearate</td>
<td>7943</td>
</tr>
<tr>
<td>3</td>
<td>A16 Alumina-AT1 Titania, Dry Mix, 30 min mix time, 5x extrusion, 16% water, 1% stearate</td>
<td>12590</td>
</tr>
<tr>
<td>4</td>
<td>A16 Alumina-AT1 Titania, Wet Mix, 30 min mix time, single extrusion, 16% water, 1% stearate</td>
<td>19950</td>
</tr>
<tr>
<td>5</td>
<td>A16 Alumina-AT1 Titania, Dry Mix, 30 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>34354</td>
</tr>
<tr>
<td>9</td>
<td>A16 Alumina-AT1 Titania, Dry Mix, 7 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>39810</td>
</tr>
<tr>
<td>10</td>
<td>A16 Alumina-AT1 Titania, Dry Mix, 30 min mix time, 5x extrusion, 20% water, 1% stearate</td>
<td>31620</td>
</tr>
<tr>
<td>11</td>
<td>A16 Alumina-AT1 Titania, Wet Mix, 30 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>46683</td>
</tr>
</tbody>
</table>

Table 5.10 Dynamic stress rheometry yield stresses for A16 alumina and AT1 titania batches

Figure 5.34 shows batches with A16 alumina and VP W 740X nano-titania, binder, 20% water, and 1% sodium stearate. Table 5.11 lists the batch compositions and yield stresses for these batches. Much like the G’ curves of the batches in Figure 5.33, these batches exhibit very similar yield stresses and curve shape. The yield stresses for the 7 min 1x extrude mix, 30 min 5x extrude mix, and 30 min 1x extrude mix are 15850 Pa, 19950 Pa, and 23397 Pa, respectively. These curves exhibit a sharp yield slope indicating the same uniform agglomerate nature found in the A16 alumina AT1 titania at 20% water batches.

Figure 5.35 shows batches with Aerodisp W 630 nano-alumina and AT1 titania, binder, 20% water, and 1% sodium stearate with varied processing. These batches had much higher yield stresses than the previous A16/nanoTi batches. The 7 min mix 1x batch yielded at 25120 Pa, the 30 min mix 1x batch yielded at 39810 Pa, and the 30 min mix 5x extrude batch yielded above 100000 Pa, (thus exceeding the test parameter).
What this indicates is that the structure of the agglomerates/particles in the Aerodisp/AT1 titania batches requires much greater stresses to transition from elastic to viscous flow than either the A16/nano-titania or A16/AT1 batches.

Figure 5.34 G' curves of batches with A16 alumina and nano-titania, binder, 1% sodium stearate and 20% water with varied processing
**Figure 5.35** $G'$ curves of batches with nano-alumina and AT1 titania, binder, 1% sodium stearate and 20% water with varied processing

<table>
<thead>
<tr>
<th>#</th>
<th>Batch</th>
<th>Dynamic Stress Rheometry Yield Stress (Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>12</td>
<td>A16 Alumina-nano Titania, Wet Mix, 30 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>23397</td>
</tr>
<tr>
<td>13</td>
<td>A16 Alumina-nano Titania, Wet Mix, 7 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>15850</td>
</tr>
<tr>
<td>14</td>
<td>A16 Alumina-nano Titania, Wet Mix, 30 min mix time, 5x extrusion, 20% water, 1% stearate</td>
<td>19950</td>
</tr>
<tr>
<td>15</td>
<td>nano Alumina-AT1 Titania, Wet Mix, 30 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>39810</td>
</tr>
<tr>
<td>16</td>
<td>nano Alumina-AT1 Titania, Wet Mix, 7 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>25120</td>
</tr>
<tr>
<td>17</td>
<td>nano Alumina-AT1 Titania, Wet Mix, 30 min mix time, 5x extrusion, 20% water, 1% stearate</td>
<td><strong>&gt;100000</strong></td>
</tr>
</tbody>
</table>

Table 5.11 Dynamic stress rheometry yield stresses for batches containing nano powders
Figure 5.36 compares the $G'$ curves for wet mixed batches, which had been mixed for 30 minutes and extruded once, containing 20% water and 1% sodium stearate. The yield stress values for these curves are $39810 \text{ Pa}$ for the A16 alumina and AT1 titania, $23397 \text{ Pa}$ for the A16 alumina nano-titania, and $39810 \text{ Pa}$ for the nano-alumina and AT1 titania batch, as listed in Tables 5.10 and 5.11. The curve shapes for all the batches with nano powders indicate a sharp transition between elastic and viscous flow. The batch containing the coarse powders, A16 alumina and AT1 titania, exhibits some early yielding with a sharp yield point at $39810 \text{ Pa}$. An explanation for the high yield stress of the nano-alumina batch, and also for those in Figure 5.35 could be that the nano-alumina batches have increased particles and therefore particle interactions. Since all the batch compositions contain a greater volume of alumina than titania, the substitution of a nano-alumina for a coarse alumina greatly increases the number of particles in the system. It is logical that these particles would require greater stresses to produce a viscous flow.
Figure 5.36 G’ curves of wet mixed batches with 20% water, 1% sodium stearate, and varied inorganic components

Figure 5.37 shows the G’ curves for A16 alumina AT1 titania batches with 20% water and varied amounts of sodium stearate, 1%, 0.5%, 0.1%, and 0%. At higher sodium stearate concentrations the curve shape becomes very shallow and while the material does seem to be yielding, the shape of the curve is such that multiple locations could be considered the yield stress. Figure 5.38 shows the G’ curves from Figure 5.37 with two yield points identified for each curve. Table 5.1 lists the batch compositions and yield stress values as identified in Figures 5.37 and 5.38. The primary yield for the batches containing 0.1, 0.5, and 1% stearate occurs at 5012 Pa. The yield stress for the batch with 0% sodium stearate is much higher, 19950 Pa. This implies that even very small quantities of sodium stearate greatly weaken the agglomerates in the A16 alumina AT1 titania batch. The secondary yield points for these materials are also listed in Table 5.12. The 1% and 0.5% batches yield at 39810 Pa while the 0.1% batch yields at 25120 Pa. The 0% batch again has the highest yield point, 50120 Pa.

The shape of the curves is also of interest and can be seen to transition from a very shallow sloped yield in the 1% stearate batch to a very sharp yield in the 0% stearate batch. The behavior of these curves implies that even small additions of sodium stearate change the agglomerate structure of the A16 alumina AT1 titania batch. The appearance of two yield points implies that the structure consists of agglomerates of multiple strengths and that the increase of sodium stearate to the batch will change the impact of these agglomerate types on the yield stress. Increased sodium stearate may be reducing
the number of weaker agglomerates to the point where flow behavior is dictated by the stronger agglomerates broken down at the secondary yield point.

Figure 5.37 G’ curves of dry mixed A16 alumina and AT1 titania batches with 20% water and varied sodium stearate concentrations
Figure 5.38 G’ curves of A16 alumina and AT1 titania batches with varied sodium stearate and yield points identified

<table>
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<th>#</th>
<th>Batch</th>
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<td>A16 Alumina-AT1 Titania, Dry Mix, 30 min mix time, single extrusion, 20% water, 0% stearate</td>
<td>19950</td>
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</tbody>
</table>

Table 5.12 Dynamic stress rheometry yield stresses for batches with varied stearate concentrations

5.2.4 Rheological Discussion

It is important to discuss some properties of the blends for this evaluation. In a well dispersed system, a particle packing model can be applied to the distribution of particles in the paste. It must be noted that the systems evaluated in this thesis are not well dispersed systems. The acquired nano-powder suspensions are not comprised of suspended primary particles, but of agglomerates of nano-particles, similar to bunches of grapes. Combination of these agglomerates with coarse powders in high concentration pastes leads to further agglomeration. Some of the agglomerates present during the initial batch combination will be broken down during the mixing and extrusion processes, but some will not. Knowing the agglomerate size negates the need for a particle packing model.
5.3 Evaluation of Batch Mixedness

5.3.1 Compositional Maps

Figures 5.39-5.55 are the SEM/EDS results at 1000X magnification for all the batches evaluated along with the binary images which result from the thresholding and filtering of the titanium maps. The SEM/EDS maps figures consist of four quadrants. The upper left quadrant is a map of titanium locations, the upper right quadrant is a map of the aluminum locations, the lower left quadrant is a map of the Oxygen locations, and the lower right map indicates locations where x-rays of any element were collected. The “K” designation next to the element label under each map indicates that the counts collected were x-rays emitted from the K shell of the electron and exhibited the corresponding energy.

Q/V values were obtained from quantifying the thresholded and filtered titanium maps in Figures 5.39-5.55. Table 5.13 shows all of the Q/V values calculated for these maps and a description of their batch compositions. A description of the procedure for this quantification is found in section 4.6.2.1. Figures 5.56-5.63 compare these quantities graphically. Figure 5.56 shows the location of Q/V values for all the batches containing 20% water and 1% sodium stearate. Each quadrant of the Q/V chart has been labeled with the distribution description as designated by Anson[88]. In this figure, it can be seen that all of the Alumina-Titania batches with 20% water fall into the region with a
more regular distribution and less clustering than a perfectly random mixture. This
general similarity between batches is expected. Though there are processing variations
between some batches, all the batches still go through three stages of processing; mixing,
compounding, and extrusion, which decreases the likelihood that any batch will have
more clusters than a perfectly random distribution (1,1 coordinate on the Figure 5.56
chart). Figure 5.57 shows these same batches and their distribution within the
regular/less clustered quadrant. The batches containing Aerodisp W 630 nano-alumina
and AT1 titania generally contain more clusters than the other compositions. The batches
with A16 alumina and VP W 740X nano-titania contain the least clusters while the
batches containing A16 alumina and AT1 titania generally have the greatest regularity in
their distributions.

The clustering behavior of the inorganic compositions as observed in the Q/V
charts might be explained by looking at the rheological data. We see in the torque results
in Figure 5.25 and the dynamic stress rheometry of Figure 5.36, that the Aerodisp W 630
nano-alumina AT1 titania batch requires greater energy to mix and greater stress to
achieve viscous flow than the other batch compositions, yet the wall shear stress as seen
in Figure 5.30 is approximately the same for all compositions. This means that the nano-
alumina AT1 titania batch is likely not receiving enough energy from the mixing and
extrusion processes to break down as many of the titania agglomerates as the batches
with other inorganics. Another factor in the clustering behavior is the particle size
differential. The coarse inorganics, A16 alumina and AT1 titania, have approximately 1
µm diameters while the nano-alumina and nano-titania have about 100 nm diameters.
Considering the alumina makes up the majority of the composition, by mass and volume,
this means that the A16 alumina nano-Titania batch consists of large alumina particles and small agglomerates of nano-particles. The alumina particles act similarly to media in a ball mill, breaking down the titania clusters. This effect is reduced in the A16 alumina AT1 titania batch where the titania particle size is on par with the alumina particle size. In this batch, clusters of both alumina and titania may be breaking and reforming throughout the mixing and extruding processes with some equilibrium number of clusters being detected by this evaluation. In the nano-alumina AT1 titania batch, the alumina particles are much smaller than the titania. These particles do not have the mass necessary to break apart titania clusters during inter-particle collisions. This helps explain why more titania clusters were detected in the batches containing these inorganics.

Figure 5.58 compares the effect of processing on A16 alumina AT1 titania batches with 1% sodium stearate at 16% and 20% water. The batches with 20% water show a much greater agreement in both Q and V values than the batches with 16% water. The batches with 16% water show great disparity in V values ranging from 2.75 to 0.56. The batch mixed for only 7 minutes had the largest V value. This indicates that it had the most random distribution of titania. The 16% batch extruded 5 times also showed a greater randomness to the titania distribution than the batches mixed for 30 minutes and extruded once. These batches, both wet and dry, exhibited V values of about 0.56. While their V values were similar, the Q value of the wet mixed batch was somewhat higher (~0.2) than that of the dry mixed batch. This indicates that less clustering of titania present in the wet mixed batch.
Disparity in the batches containing 16% water implies that this is not enough liquid phase to allow consistent mixing within the batch. The torque rheometry results in Figure 5.24 show that the 16% water batch requires more energy to mix than the 20% water batch, for both wet and dry mixed batches. In this figure it can be seen that not only is the peak value for the 16% water batches higher, but the stabilized torque value is also significantly higher. This helps explain why the batch mixed for only 7 minutes has such a significantly higher V value than the batches mixed for 30 minutes. The higher stabilized torque indicates that more energy is going into the 16% batch than the mixing of the 20% batch. Consequently, the reduced mixing time has a greater impact on the mixture quality of the 16% water batch than the 20% with reduced mixing time.

The 5x extruded 16% water batch exhibited a higher V value than the single extrusion 16% water batch indicating a higher degree of randomness. Looking at Table 5.6, it can be seen that this 5x batch exhibited the highest wall shear stress of any of the batches containing 1% sodium stearate. This high shear stress would have created a shear profile across the cross-section of extrudate. It is possible that this shear disparity was compounded by the multiple extrusions, thereby creating more randomness in the 5x extruded batch with 16% water than the single extrusion batch with 16% water.

Figure 5.58 also shows a significant difference in the clustering in dry mixed batches containing 16% water and the wet mixed batch containing 16% water. Reduced liquid phase could equate with reduced particle mobility during processing. This would mean that the clustering behavior during the initial mixing takes on a greater significance as it is less likely to change during the resulting processing. It is possible that the wet
mixing process prevented large agglomerates of the titanium from forming thus creating a batch with less clustering than any of the dry mixed batches.

Figure 5.59 shows the Q/V chart for the batches containing A16 alumina, AT1 titania, 20% water and 1% sodium stearate. The V values of all of the batches fall within the range of error, therefore it can be assumed that processing did not significantly affect the degree of regularity in the titania distribution in these batches. The Q value however did show a significant shift towards clustering for the 5x extruded batch. There was also a shift away from clustering in the wet mixed batch. The slight increase in clustering in the 5x extruded batch is difficult to account for. It is possible that the extra processing in the form of multiple extrusions caused some desegregation to occur which was not observed in the other batches. This chart also indicates that the batch which was wet mixed exhibited less clustering than the other batches. Similar to the 16% water 1% sodium stearate batches, this indicates that wet mixing discourages the formation of large titania agglomerates.

Figure 5.60 shows batches with A16 alumina, AT1 titania, 20% water and varied concentrations of sodium stearate; 1%, 0.5%, 0.1%, and 0%. The V values do not vary significantly among these samples. That implies that the degree of randomness or regularity in these batches is independent of stearate concentration. The Q value is also similar for the 1%, 0.1% and 0% stearate batches, but shifts towards clustering for the 0.5% batch. The limited affect of stearate concentration on titania Q/V values could be attributed to the very low adsorption of stearate to AT1 titania observed in the adsorption isotherm in Figure 5.7. This low adsorption would mean that the stearate added to the batch is either adsorbing to the alumina surfaces or acting as a bulk lubricant. The
addition of 0.1% stearate does not significantly change the titania distribution from a batch with 0% sodium stearate. The addition of 0.5% stearate, however, may be a high enough concentration that it is breaking down the agglomerates of alumina. The particles of titania, which may not adsorb as much stearate, may find it easier to remain agglomerated during the initial mixing. This would leave larger effective units of titania which the smaller alumina particles would have difficulty breaking down during compounding and extrusion. The addition of 1% sodium stearate, which might saturate alumina and titania surfaces, would then be sufficient to break down agglomerates of both inorganics, thus reducing exhibiting the reduced clusters seen in the Q/V results for the 0 and 0.1% batches.

Figure 5.61 shows the Q/V values for batches with varied inorganics, 20% water, and 1% sodium stearate, wet mixed with a 30 minute mix time and extruded once. The A16 alumina AT1 titania batch exhibits the lowest V value, indicating the most regular distribution. Both of the batches containing nano-materials have a slightly more random distribution than the batch with the coarse materials. This could be due to their being a larger discrepancy in particle size distributions between the components of those batches. The particle size differences are accompanied by particle number differences, since mass is being held constant. This leads to changes in the mixing behavior of the inorganics which results in the batches with nano-powders having slightly more random distributions than the batch with two coarse inorganics.

Figure 5.61 also shows that the batch with nano-alumina and AT1 titania has the lowest Q value, which indicates the greatest amount of clustering. The A16 alumina and VP W 740X nano-titania exhibits the least amount of clustering. This could be due to its
high adsorption of sodium stearate as observed in the adsorption isotherm in Figure 5.11. The presence of the stearate could deter the nano-titania from forming clusters. The clustering of AT1 titania in the nano-alumina batch might be attributed to the titania moving more easily among the nano-alumina than it could when coarse alumina particles separated the titania particles combined with the reduced inter-particle collisions with agglomerates of comparable size as discussed in Figure 5.57.

Figure 5.62 shows the Q/V chart for the A16 alumina, VP W 740X nano-titania batch with 20% water and 1% sodium stearate with varied processing techniques. The batch with the short mixing time has the lowest V value, indicating a more regular distribution than the other batches. This is somewhat counter-intuitive, but the process of mixing and demixing is cyclic for many compositions and it is possible that this batch exhibits maximum mixing at a very short mixing time, after which some demixing occurs which would explain the increased V value in the 30 minute mixed batches. More intuitive is that the 5x extruded batch would show a more regular distribution than the 1x extruded batch. The batches exhibit very little shift in Q values, though the batch with the 7 minute mix time does seem to exhibit slightly more clustering than the batches with longer mixing times.

An important source of error regarding the batches containing VP W 740X nano-Titania is the resolution limit of the EDS detector. In Table 4.4, the resolution limits for titanium are calculated as ranging from 0.927-0.953 µm. These values are significantly larger than the 100 nm particles of nano-Titania included in the batch. Figure 2.1 illustrates the relationship of attractive and repulsive forces between particles. It can be seen that at very small distances, the attractive force dominates. This is a frequent
occurrence with nano-particles. The small size of the nano-particles allows van der Waals’ attraction to dominate which leads to nano-powder agglomerates with significant strength. In many situations these agglomerates act as effectively larger particles. It is likely these particles which are being detected with the EDS detector in the EDS maps of titanium for the batches containing the nano-titania. While this may lead to the non-detection of smaller nano-particles or agglomerates, the majority of agglomerated nano-titania will be detected and supply sufficient data for Q/V analysis.

Figure 5.63 shows the Q/V chart for the batch containing Aerodisp W 630 and AT1 titania with 20% water and 1% sodium stearate. The batch with the 7 minute mix time shows the highest V value and the lowest Q value. This indicates that the titania distribution in this batch is the most random and has the most clustering of titania. Discussion of previous charts pointed out the tendency of all Aerodisp W 630 AT1 Titania batches to have greater amounts of clustering. If the combination of nano-alumina and coarse titania does allow for the creation of more clusters, it can be seen that the 30 minute mix time is more effective at breaking these clusters down than the 7 minute mix time. The batch which has been extruded 5 times has the lowest V value and the highest Q value indicating that it has the most regular distribution of titania and the least amount of clusters. The repetitive extrusions of this batch seem to continue to break down titania clusters, though not as significantly as a longer mixing time. The Q/V results for this batch indicate that the distribution benefits from applied stresses. Longer mixing times and multiple extrusions contribute to a more regular batch with less clusters of titania.
The resolution limits, as listed in Table 4.4 range from 0.927 µm to 0.953 µm for titanium. This range is above the average particle size for the AT1 titania and the nanotitania. At first glance this may imply that this method is insufficient to evaluate titania in these batches. The justification for this method relies on the fact that these batches are not fully dispersed. The components in each batch consist not of primary particles, which are represented by the particle size data in section 5.1.1, but by agglomerates of these particles which are never broken down. The high concentration of these compositions guarantee that the inter-particle distances will be short enough to allow the dominance of attractive forces over repulsive forces between particles.

Even though particles exist in agglomerates within the batch, it is still probable that some of these agglomerate diameters may be smaller than the resolution capabilities. If a raster point encounters a location with agglomerates from multiple components, it will record characteristic x-rays from both components at that location. Both components will register at some intensity for that raster location, but that intensity will be less than a raster point which contained a single component. The lower intensity makes this location more likely to be on the “not containing component” side of the threshold, thereby leaving that agglomerate unrepresented in the final analysis. It is also possible that a small agglomerate may be near other similarly sized agglomerates. If these agglomerates are measured together at a raster location, they will appear as a single location on the thresholded component map. If this occurs frequently in a batch, the Q value for the batch may be calculated as higher than the reality due to these clustered agglomerates being measured as a single unclustered entity.
Figure 5.39 SEM EDS map with processed titanium map of A16 alumina, AT1 titania, 16% water, 1% sodium stearate batch dry processed, 30 min mix, 1x extrude at 1000X magnification
Figure 5.40 SEM EDS map with processed titanium map of A16 alumina, AT1 titania, 16% water, 1% sodium stearate batch dry processed, 7 min mix, 1x extrude at 1000X magnification
Figure 5.41 SEM EDS map with processed titanium map of A16 alumina, AT1 titania, 16% water, 1% sodium stearate batch dry processed, 30 min mix, 5x extrude at 1000X magnification
Figure 5.42 SEM EDS map with processed titanium map of A16 alumina, AT1 titania, 16% water, 1% sodium stearate batch wet processed, 30 min mix, 1x extrude at 1000X magnification
Figure 5.43 SEM EDS map with processed titanium map of A16 alumina, AT1 titania, 20% water, 1% sodium stearate batch dry processed, 30 min mix, 1x extrude at 1000X magnification
Figure 5.44 SEM EDS map with processed titanium map of A16 alumina, AT1 titania, 20% water, 0.5% sodium stearate batch dry processed, 30 min mix, 1x extrude at 1000X magnification
Figure 5.45 SEM EDS map with processed titanium map of A16 alumina, AT1 titania, 20% water, 0.1% sodium stearate batch dry processed, 30 min mix, 1x extrude at 1000X magnification
Figure 5.46 SEM EDS map with processed titanium map of A16 alumina, AT1 titania, 20% water, 0% sodium stearate batch dry processed, 30 min mix, 1x extrude at 1000X magnification
Figure 5.47 SEM EDS map with processed titanium map of A16 alumina, AT1 titania, 20% water, 1% sodium stearate batch dry processed, 7 min mix, 1x extrude at 1000X magnification
Figure 5.48 SEM EDS map with processed titanium map of A16 alumina, AT1 titania, 20% water, 1% sodium stearate batch dry processed, 30 min mix, 5x extrude at 1000X magnification
Figure 5.49 SEM EDS map with processed titanium map of A16 alumina, AT1 titania, 20% water, 1% sodium stearate batch wet processed, 30 min mix, 1x extrude at 1000X magnification
Figure 5.50 SEM EDS map with processed titanium map of A16 alumina, nanotitania, 20% water, 1% sodium stearate batch wet processed, 30 min mix, 1x extrude at 1000X magnification
Figure 5.51 SEM EDS map with processed titanium map of A16 alumina, nanotitania, 20% water, 1% sodium stearate batch wet processed, 7 min mix, 1x extrude at 1000X magnification
Figure 5.52 SEM EDS map with processed titanium map of A16 alumina, nanotitania, 20% water, 1% sodium stearate batch wet processed, 30 min mix, 5x extrude at 1000X magnification
Figure 5.53 SEM EDS map with processed titanium map of nano-alumina, AT1 titania, 20% water, 1% sodium stearate batch wet processed, 30 min mix, 1x extrude at 1000X magnification
Figure 5.54 SEM EDS map with processed titanium map of nano-alumina, AT1 titania, 20% water, 1% sodium stearate batch wet processed, 7 min mix, 1x extrude at 1000X magnification
Figure 5.55 SEM EDS map with processed titanium map of nano-alumina, AT1 titania, 20% water, 1% sodium stearate batch wet processed, 30 min mix, 5x extrude at 1000X magnification
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Table 5.13 Q and V values for A16 alumina/AT1 titania, A16 alumina/nano-titania, and nano-alumina/AT1 titania batches
Figure 5.56 Q/V chart with defined regions for all batches containing 20% water and 1% sodium stearate

Figure 5.57 Q/V chart for all batches containing 20% water and 1% sodium stearate
Figure 5.58 Q/V chart for batches containing A16 alumina and AT1 titania at 16% and 20% water and 1% sodium stearate

Figure 5.59 Q/V chart for batches containing A16 alumina and AT1 titania at 20% water and 1% sodium stearate
Figure 5.60 Q/V chart for batches containing A16 alumina and AT1 titania at 20% water with varied stearate concentrations

Figure 5.61 Q/V chart for wet mix batches with varied inorganics at 20% water and 1% sodium stearate
Figure 5.62 Q/V chart for batches containing A16 alumina and VP W 740X nanotitania at 20% water and 1% sodium stearate

Figure 5.63 Q/V chart for batches containing Aerodisp W 630 nano-alumina and AT1 titania at 20% water and 1% sodium stearate
5.3.2 Extrusion Flaws

5.3.2.1 Alumina-Rich Regions

Distribution maps for Q/V evaluation were created from titanium locations. The ratio of alumina to titania in the batches created batches with particles or agglomerates of titania in a matrix of alumina. Still, in some batches, large regions of alumina can be identified. Figure 5.64 shows a side by side comparison of a secondary electron image and an alumina map at 100X magnification. The dark regions in the SEM image can be seen to correspond to large regions of alumina detected in the SEM/EDS map. It is possible that the large regions of alumina polished unevenly with comparison to the rest of the sample, thereby leaving it either slightly raised or depressed and subject to the topographical imaging by secondary electrons.

Figures 5.65-5.81 show the SEM/EDS maps at 100X magnification. The upper right quadrant of these figures features a map of the aluminum (which equates to the alumina) locations in the sample. These maps were taken at 100X magnification and 10 kV for a period of 5 minutes. Figure 5.82 contains maps from all of the batches containing A16 alumina and AT1 titania and 1% sodium stearate. Table 5.13 lists the number of features, percent area fraction, average feature size, and maximum feature size for the alumina regions analyzed from the 100X magnification EDS maps. In Figure 5.82, it can be seen that the 16% water batches tend to have a greater number of alumina regions than their 20% water counterparts. This does not hold true for the 5x extruded batch with 16% water which shows almost no alumina regions. This is confirmed by the data in Table 5.13 which shows that the 16% water batches had much greater numbers of alumina regions. Though the 5x extruded 16% batch had only 2 alumina regions, the dry
mixed for 30 minutes, dry mixed for 7 minutes, and wet mixed batches had 38, 81, and 91 alumina regions respectively. It is possible that the reduced liquid phase in these batches increased the likelihood of the formation of small alumina regions. It could also be assumed that the extra processing of the 5x extruded batch was sufficient to break down these small regions, thereby explaining the lack of alumina regions in the 16% water 5x extruded batch.

Figure 5.86 shows the average alumina region size in each batch. When comparing the A16 alumina AT1 titania batches with 16 % water to those with 20% water, it must be recognized that while the 16% batches generally contain more alumina regions, the regions in the 20% batches are consistently larger. This is verified in Table 5.13 which shows that average feature size of the 16% batches ranges from 3.03 µm for the 5x extruded batch to 12.95 µm for the batch dry mixed for 30 minutes. The average feature size for the batches containing 20% water ranges from 7.17 µm for the wet mixed batch to 22.14 µm for the 5x extruded batch.

The alumina regions in the batches containing 20% water and 1% sodium stearate vary greatly depending on processing. The largest alumina regions, both in number and in size, are in the 5x extruded batch. This is counterintuitive as it seems that extra processing should contribute to the distribution of the alumina. Looking at the aluminum map from the SEM/EDS in Figure 5.82, the alumina in the 5x extruded batch with 20% water seems to be mostly because of a single large alumina region. The crack running through this region separates it into multiple sections, thereby skewing the statistics. The presence of such a large single region allows the possibility that this image may not be representative of the batch.
Figure 5.83 shows the batches containing A16 alumina, AT1 titania, and 20% water with varied concentrations of sodium stearate; 1%, 0.5%, 0.1%, and 0%. Looking at Figures 5.85 and 5.86, it can be seen that the batch containing 0% sodium stearate contains the greatest area fraction of alumina regions, 5.1%, as well as the largest diameter alumina regions, averaging 19.67 µm. The batches with additions of sodium stearate contain alumina regions of reduced size and number. The sizes of the alumina regions in the batches containing 0.1%, 0.5%, and 1.0% sodium stearate are over a relatively small range; 9.83 µm, 11.46 µm, and 14.05 µm, respectively. The area fractions of these batches are also within a small range; 2.1% for the 0.1% stearate batch, 1.3% for the 0.5% stearate batch, and 2.1% for the 1.0% stearate batch. The larger alumina regions in the 0% stearate batch can likely be attributed to the fact that one of the main functions of sodium stearate is to break down large agglomerates. The similarity in the data for batches with 0.1%, 0.5%, and 1.0% sodium stearate implies that not much sodium stearate is needed to inhibit the formation of large alumina regions.

Figure 5.84 shows the aluminum maps for batches containing nano-powders. The dry mixed for 7 minutes batch with A16 alumina and nano-titania shows a singular very large region of alumina. This single region has caused the area fraction, 7.3%, and average region diameter, 24.14 µm, to be larger than the A16 other batches with these inorganics but varied processing. The batch containing A16 alumina and nano-titania which was mixed for 30 minutes exhibited a number of larger alumina regions making up an area fraction of 1.7% and an average diameter of 18.07 µm. The batch which was extruded 5x contained only a single feature with a diameter of 5.42 µm. While it is likely that the large single feature in the 7 minutes mix time batch is not present throughout the
entire length of the extrudate, the reduced mixing time of this batch might increase the likelihood that larger alumina regions will remain. Increased processing could also explain the minimal alumina regions in the 5x extruded batch.

The batches containing nano-alumina and AT1 titania are unique in this portion of analysis. The fact that the starting inorganic is already at such a small particle size makes it extremely unlikely that very large regions of alumina will form. This is confirmed in the images in Figure 5.84 as well as the statistics in Table 5.13. Though not void of alumina regions, the area fractions of alumina are never more than 0.1% for any of the batches containing nano-alumina, and the average region diameter is around 5 µm for all the batches. Looking Figures 5.85 and 5.86 it can be seen that the batches containing nano-alumina and AT1 titania contain the least area fractions of alumina regions and the smallest average diameters for alumina regions.

Figure 5.64 SEM image and compositional map of A16 – AT1 batch exhibiting alumina deposits
Figure 5.65 SEM EDS map at 100X magnification of A16 alumina, AT1 titania, 16% water, 1% sodium stearate batch dry processed, 30 min mix, 1x extrude
Figure 5.66 SEM EDS map at 100X magnification of A16 alumina, AT1 titania, 16% water, 1% sodium stearate batch dry processed, 7 min mix, 1x extrude
Figure 5.67 SEM EDS map at 100X magnification of A16 alumina, AT1 titania, 16% water, 1% sodium stearate batch dry processed, 30 min mix, 5x extrude
Figure 5.68 SEM EDS map at 100X magnification of A16 alumina, AT1 titania, 16% water, 1% sodium stearate batch wet processed, 30 min mix, 1x extrude
Figure 5.69 SEM EDS map at 100X magnification of A16 alumina, AT1 titania, 20% water, 1% sodium stearate batch dry processed, 30 min mix, 1x extrude
Figure 5.70 SEM EDS map at 100X magnification of A16 alumina, AT1 titania, 20% water, 0.5% sodium stearate batch dry processed, 30 min mix, 1x extrude
Figure 5.71 SEM EDS map at 100X magnification of A16 alumina, AT1 titania, 20% water, 0.1% sodium stearate batch dry processed, 30 min mix, 1x extrude
Figure 5.72 SEM EDS map at 100X magnification of A16 alumina, AT1 titania, 20% water, 0% sodium stearate batch dry processed, 30 min mix, 1x extrude
Figure 5.73 SEM EDS map at 100X magnification of A16 alumina, AT1 titania, 20% water, 1% sodium stearate batch dry processed, 7 min mix, 1x extrude
Figure 5.74 SEM EDS map at 100X magnification of A16 alumina, AT1 titania, 20% water, 1% sodium stearate batch dry processed, 30 min mix, 5x extrude
Figure 5.75 SEM EDS map at 100X magnification of A16 alumina, AT1 titania, 20% water, 1% sodium stearate batch wet processed, 30 min mix, 1x extrude
Figure 5.76 SEM EDS map at 100X magnification of A16 alumina, nano-titania, 20% water, 1% sodium stearate batch wet processed, 30 min mix, 1x extrude
Figure 5.77 SEM EDS map at 100X magnification of A16 alumina, nano-titania, 20% water, 1% sodium stearate batch wet processed, 7 min mix, 1x extrude
Figure 5.78 SEM EDS map at 100X magnification of a16 Alumina, nano-titania, 20% water, 1% sodium stearate batch wet processed, 30 min mix, 5x extrude
Figure 5.79 SEM EDS map at 100X magnification of nano-alumina, AT1 titania, 20% water, 1% sodium stearate batch wet processed, 30 min mix, 1x extrude
Figure 5.80 SEM EDS map at 100X magnification of nano-alumina, AT1 titania, 20% water, 1% sodium stearate batch wet processed, 7 min mix, 1x extrude.
Figure 5.81 SEM EDS map at 100X magnification of nano-alumina, AT1 titania, 20% water, 1% sodium stearate batch wet processed, 30 min mix, 5x extrude
Figure 5.82 100X aluminum EDS maps for A16 alumina AT1 titania batches with 1% sodium stearate.
Figure 5.83 100X aluminum EDS maps for A16 alumina AT1 titania and varied concentrations of sodium stearate
Figure 5.84 100X aluminum EDS maps for batches containing nano-powders

A16 Alumina and VP W 740X nano-Titania, 20% water, 1% Sodium Stearate

Aerodisp W 630 nano-Alumina and AT1 Titania, 20% water, 1% Sodium Stearate
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<th>Maximum Feature Size (µm)</th>
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Table 5.14 Statistical analysis of alumina-rich regions in 100X EDS maps
Figure 5.85 Chart of area fractions of alumina regions from EDS map analysis

Figure 5.86 Chart of average alumina region diameter from EDS map analysis
5.3.2.2 Macro-Pore Evaluation

Figures 5.87-5.89 show the SEM images from wet mixed batches containing 20% water and 1% sodium stearate with different inorganics. Each figure contains 4 images taken of various samples from the same batch composition. These images are examples of those that were used to evaluate the presence of macro-pores within the extrudates. Macro-pores are those which are detected in the sample cross-section. Edge artifacts were not included in this evaluation. Any pore below 4 µm was also not included in these statistics. Since all images were taken at 100X magnification, the image size is 1150 x 1150 µm, but all particulate outside the sample diameter was edited out of the image before statistical analysis.

Figures 5.87-5.89 provide images for visual comparison of how macro-porosity can vary between batches. Figure 5.87 shows the wet mixed batch containing A16 alumina, AT1 titania, 20% water, and 1% sodium stearate. This batch exhibits some small porosity. The analysis of this batch revealed that, on average, a sample surface contained 40 macro-pores which took up 0.47% of the surface area. Figure 5.88 consists of images from a wet mixed batch containing A16 alumina, nano-titania, 20% water, and 1% sodium stearate. This batch has very obvious macro-pores which take up 5.46% of the surface area. Figure 5.89 shows the wet mixed batch with nano-alumina, AT1 titania, 20% water, and 1% sodium stearate. This batch has virtually no macro-porosity and averages an area fraction of 0.19% macro-pores. This lack of macro-porosity can be seen in the other nano-alumina AT1 titania batches as well, regardless of processing technique.

Table 5.15 contains the macro-pore statistics for all batches. These statistics include number of macro-pore features, area fraction of macro-pores, average macro-pore
diameter, and maximum macro-pore size. It should be noted that the area fraction is a percent of the cropped rectangular image. The batches containing nano-alumina were extruded with 1 µm die as opposed to the 1.25 µm die used for the other batches. The experimental area fraction values for those three batches have been normalized to facilitate comparison with the other batches.

Figures 5.90 and 5.91 show the average macro-pore area fraction and the average macro-pore diameter respectively for each batch in Table 5.15. Examining the batches containing A16 alumina and AT1 titania with 1% sodium stearate, it can be observed that the batches with 16% water have a greater area fraction (4.79% for the 7 minute mix batch to 7.33% for the 5x extrude batch) of macro-porosity than the batches with 20% water (ranging from 0.47% for the wet mixed batch to 6.44% for the 5x extrude batch). This distinction is not so noticeable when looking at the average pore sizes in Figure 5.91. The average macro-pore size for a 16% water batch ranges from 4.16 µm in the 5x extruded batch to 10.06 µm in the wet mixed batch. For the 20% water batches, the range of average pore size is smaller from 5.86 µm for the wet mixed batch to 8.19 µm for the 7 minute mixed batch. The 16% water batches having greater area fraction of macro-pores but the same average macro-pore size as the 20% water batch implies that the 16% water batches contain a greater number of macro-pores. This can be verified by the data presented in Table 5.15. The 16% water batches all contain a greater number of macro-pores than the 20% water batches with the same processing.

The A16 alumina AT1 titania batches with 16% water and 1% sodium stearate tend to have more macro-porosity than the batches with A16 alumina AT1 titania 20% water and 1% sodium stearate. Macro-porosity seems to be air pockets which enter the
batch during the transition from compounding to extruding but fail to escape during the compression stage of the extrusion process. The batch rheology plays a big role in whether the trapped air will manage to escape. In Figures 5.32 and 5.33, extrudate rheology is examined for these 16% water and 20% water batches. Figure 5.32 shows that though all the 16% water batches exhibit yield stresses, the shape of the curve implies that a greater stress would be required for a full transition from elastic to viscous flow. The 20% batches however, require a slightly higher stress to yield, but do some completely. This higher stress requirement for the yielding of the 16% water batches might explain how the macro-pores formed. Their might not have been sufficient pressure during the extrusion process for the air pockets to escape the bulk of the batch.

Batches 5-8 in Table 5.15 are composed of A16 alumina AT1 titania and 20% water with varied concentrations of sodium stearate including 0%, 0.1%, 0.5%, and 1.0%. The area fraction of macro-pores and average size of the micro-pores can be compared in Figures 5.90 and 5.91. The area fraction of macro-porosity, as described in Figure 5.90, shows that porosity decreases with a decrease in sodium stearate. Though the 1.0% and 0.5% sodium stearate batches both exhibit 4.2% macro-porosity, the 0.1% sodium stearate batch only exhibits 3.96% porosity and the 0% sodium stearate batch exhibits 1.49% porosity. This trend is somewhat reversed in Figure 5.91, which displays average pore size data. This data set shows that the largest pores are present in the 0% sodium stearate batch, averaging 9.15 µm. The 0.1% stearate batch has pores which average 7.85 µm diameters while the 0.5% sodium stearate batch contains pores which average 3.92 µm diameters. The 1.0% sodium stearate batch resists this trend with pores that average 7.73 µm in diameter. This reverse trend implies that a batch with 0% sodium stearate
will contain few larger pores. As the concentration of sodium stearate is increased, the macro-pores will become smaller, but more numerous. This behavior may be clarified by re-examining Figure 5.37, which shows the dynamic stress rheometry of an extruded paste with A16 alumina, AT1 titania, 20% water, and varied concentrations of sodium stearate. As discussed in Section 5.2.3, the rheological behavior exhibited by these batches cannot always be described by a single yield stress. The curve shapes for these batches exhibit what appear to be multiple yield stresses. As the concentration of sodium stearate is decreased, the curve becomes flatter, exhibiting increasingly monomodal yield structures. This agrees with the assumption that viscous flow of a batch during extrusion results in less macro-porosity. As the concentration of sodium stearate is increased in the batches, the stress required for viscous flow becomes a range of stresses and a definitive yield stress becomes harder to achieve. This helps to explain why the macro-porosity is reduced, but not eliminated as sodium stearate additions are increased.

Table 5.15 along with Figures 5.90 and 5.91 also describe the macro-porosity found in batches containing nano-powders. As seen in Figures 5.88 and 5.89, the macro-porosity in these batches greatly varies with inorganic composition. The batches containing A16 alumina and nano-titania exhibit greater area fractions of porosity than the other batch compositions. Not only do they exhibit some of the largest area fractions of macro-pores, but Table 5.15 shows that they also contain some of the largest individual macro-pores. The A16 alumina nano-titania batch mixed for 30 minutes with a single extrusion contained a macro-pore with a diameter of 111 µm while the batch with the same composition extruded 5x included a macro-pore with a diameter of 122 µm.
These batches contain the only macro-pores to exceed 100 µm in any of the batches analyzed in Table 5.15.

Figure 5.90 shows that the wet mixed batches containing nano-alumina, AT1 titania, 20% water, and 1% sodium stearate exhibit the least amount of porosity. The area fraction of macro-pores for the batch mixed for 30 minutes and extruded once is 0.19% while the area fraction for the 7 minute mixed batch and 5x extruded batch are 0.14% and 0.88% respectively. These small area fractions can be confirmed in the images in Figure 5.87. Along with small area fractions, Figure 5.91 also confirms that the batches containing nano-alumina and AT1 titania contain smaller diameter pores. The average pore diameter for the batch mixed for 30 minutes and extruded once is 4.51 µm, while the average macro-pore diameters for the batch mixed 7 minutes and the 5x extruded batch are 3.65 and 7.07, respectively.

While the batches containing A16 alumina and AT1 titania could have their macro-porosity related to their rheological behavior, the batches containing nano-powders do not follow that relationship. Looking at Figure 5.36, the dynamic stress yield point is lowest for the batch containing A16 alumina and nano-titania. This would have equated with low macro-porosity, which is not the case. Batches containing A16 alumina and nano-titania can also be seen in Figure 5.85 to exhibit large area fractions of alumina regions. It is possible that the substitution of nano-titania for a coarse titania destabilizes the agglomerate network. This would allow for the large regions of alumina found in Figure 5.85 as well as the macro-pores described in Table 5.15. The batch containing nano-alumina and AT1 titania contains almost no macro-porosity. This batch also exhibited the fewest alumina-rich regions in Figure 5.85. The nano-alumina, which is the
most massive component in this batch, helps it to form a tight agglomerate network. This network seems to have acted to prevent the formation of large macro-porosity.

Figures 5.90 and 5.91 also show some variation in macro-porosity based on processing technique. In Figure 5.90, it can be seen that for each batch composition, the largest frequency of macro-pores was found in the 5x extruded batch. This is true for the A16 alumina AT1 titania batches with 16% and 20% water as well as the batches containing nano-powders. A possible explanation for this is that the multiple extrusions give increased opportunity for introducing air pockets into the extrudate. It can also be seen in these figures that the batches with the least amount of macro-porosity are those which were formed with a reduced mixing time. Batches containing coarse and nano-powders both show the least area fraction of macro-porosity in the batches which were only compounded for 7 minutes. A possible explanation for this is that the shortened mixing time left some weak agglomerates present in the batch. During the extrusion process, the pressure would have broken down these agglomerates creating a batch with higher effective number of particles which could have filled the space which would have created macro-pores in a more highly processed batch.

The macro-pores evaluated in these samples appear to be predominantly spherical. If the macro-pores are being generated in the batch prior to extrusion, the resultant pores would likely be elongated channels throughout the extrudate. Evaluation of cross-sections of the extrudate parallel to the direction of extrusion could determine the true shape of these pores. It is possible that the macro-pores are being formed during the pressure-induced infiltration process as a result of the epoxy being forced into the
sample. If this is the case, a lower viscosity epoxy might reduce the frequency of macro pores in the samples.

Figure 5.87 100X SEM images of batches with A16 alumina, AT1 titania, 1% sodium stearate, wet mixed
Figure 5.88 100X SEM images of batches with A16 alumina, VP W 740X nanotitania, 1% sodium stearate, wet mixed
Figure 5.89 100X SEM images of batches with Aerodisp W 630 nano-alumina, AT1 titania, 1% sodium stearate, wet mixed
Figure 5.90 Average macro-pore diameter for each batch evaluated

Figure 5.91 Average area fraction of extrudate macro-pores for each batch evaluated
<table>
<thead>
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<th>#</th>
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<td>15</td>
<td>nano Alumina-AT1 Titania, Wet Mix, 30 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>29.00</td>
<td>0.19</td>
<td>4.51</td>
<td>13.87</td>
</tr>
<tr>
<td>16</td>
<td>nano Alumina-AT1 Titania, Wet Mix, 7 min mix time, single extrusion, 20% water, 1% stearate</td>
<td>20.71</td>
<td>0.14</td>
<td>3.65</td>
<td>9.47</td>
</tr>
<tr>
<td>17</td>
<td>nano Alumina-AT1 Titania, Wet Mix, 30 min mix time, 5x extrusion, 20% water, 1% stearate</td>
<td>37.43</td>
<td>0.88</td>
<td>7.07</td>
<td>31.28</td>
</tr>
</tbody>
</table>

Table 5.15 Statistical analysis of extrudate macro-pores in 100X SEM images
6

Conclusions

6.1 Powder Characterization

It was established that the adsorption of a surfactant to a particle surface is strongly dependent on both available surface area and surface charge. Alumina particles, which were shown to have weak surface charge in the presence of sodium stearate, did not exhibit much variation in adsorption behavior based on particle size. Both Titania inorganics exhibited a strong negative charge in the presence of the stearate, but the nano-Titania showed much greater adsorption (0.02-0.03 g adsorbed/1 g powder) than the larger particle size AT1 titania (~0.002 g adsorbed/1 g powder).

Surface charge also affected the way that sodium stearate additions changed particle size distributions. For the pre-dispersed nano-materials, stearate additions caused minor increases in apparent particle size. For the A16 alumina, the stearate additions seemed to produce agglomerateation of smaller particles, possibly due to reduced electrostatic repulsion triggered by an increase of the pH towards that of the A16 isoelectric point. Stearate additions lowered the effective particle size of the AT1 titania, indicating that even low adsorption to the surface was enough to break down some large agglomerates.

Surfactant additions increase the dynamic yield stress of A16 and AT1 slurries indicating the breakdown of agglomerates creating greater numbers of particles which require greater applied stress to achieve viscous flow. Behavior of slurries with stearate
additions in a binary, A16 alumina AT1 titania, system become unpredictable as particle interactions and possible preferential adsorption lead to varied agglomerate formation.

6.2 Effect of Composition and Processing on Paste Rheology

Increased Liquid Phase and Pre-Mixing Decrease Mixing Energy Requirements

Mixing energy required to plasticize a batch has been shown to increase with decreased liquid phase (3.56 Nm for 20% water batch as opposed to 8.46 Nm for 16% water batch) or with decreased sodium stearate additions (3.56 Nm for 1% stearate batch as opposed to 4.3 Nm for 0% stearate batch). Pre-mixing procedure was shown to affect mixing energy requirements as wet mixed batches, which have components combined as slurries prior to compounding, required less mixing energy to reach homogenization (4.57 minutes for wet mixed 16% water batch as opposed to 6.04 minutes for dry mixed 16% water batch).

Batch Composition Dictates Extrusion Shear Stress and Bulk Yield Behavior

Water content is shown to play a greater role in facilitating batch flow than processing variations. This is evident as the wall shear stresses for 16% water batches exceeded those of the 20% water batches for all processing variations (an average of 0.23 MPa less for 20% water batches). Processing variations were shown to have greater impact on bulk yield of A16 alumina AT1 titania batches, though processing seemed to play a lesser role in the extrusion properties of the batches containing nano-powders. Increased bulk yield stress could be found as a result of wet mixing of A16 alumina AT1
titania batches (0.30 MPa for wet mix as opposed to 0.01 MPa for dry mix) and also of extruding the material multiple times, 0.47 MPa for 5x extruded as opposed to 0.01 MPa for single extrusion of A16-AT1 batch. The effect on wall shear and bulk yield stresses of reducing mixing time was varied showing minor impact on the composition containing only coarse powders but greater impact on batches containing nano-powders. Both nano powder batches benefited from a shorter mix time as was evidenced by lower wall shear stresses and higher bulk yield stresses. The batch with nano-titania showed a decrease in wall shear stress from 0.031 MPa to 0.027 MPa and an increase in bulk yield stress from 0.47 MPa to 1.43 MPa with reduced mixing time. The batch with nano-alumina showed a decrease in wall shear stress from 0.032 MPa to 0.016 MPa and an increase in bulk yield stress from 0.065 MPa to 0.126 MPa with reduced mixing time. Increasing sodium stearate additions were shown to lower both wall shear (from 0.193 MPa to 0.025 MPa for a 1% stearate increase) and bulk yield stresses (from 3.732 MPa to 0.009 MPa for a 1% stearate increase) in the batch.

**Batch Composition Dictates Transition from Elastic to Viscous Flow**

Compositional variations were shown to have greater effect on post-extrusion batch rheology than processing variations. Batches containing nano-alumina exhibited greater dynamic yield stresses than those containing A16 alumina while batches containing nano-titania had reduced dynamic yield stresses than those with the AT1 titania. Variations in sodium stearate changed the curve shape of G’ curves indicating that increased additions of sodium stearate broaden the distribution of agglomerate sizes.
creating a wider range of stress over which the batch transitions from elastic to viscous flow.

6.3 Evaluation of Batch Mixedness

**Titania Distribution Dominated by Batch Composition**

Batch composition was shown to have a greater influence on titania distribution than batch processing variations. Variations in titania could be seen in batches with different inorganic components. Batches containing A16 alumina and nano-titania exhibited the least amount of titania clustering with Q values consistently over 1.4. The batches with nano-alumina and AT1 titania however, had slightly lower Q values (~0.2 less than A16 AT1 batches) and increased V values (~0.15 greater than A16 AT1 batches).

The exception to this was found in the large variations in V values for the A16, AT1, 16% water batches. The 30 minute mixed, single extruded batches had V values around 0.56 which increased to 1.285 and 2.747 for the multiple extrusion batches and short mixed batches, respectively, indicating that these batches showed a much greater randomness in their composition. Batches containing A16 and AT1 20% water had fairly consistent Q and V values with Q ranging from 1.337 to 1.295 and V ranging from 0.591 to 0.554. These values indicate that all those batches had fairly regular distributions with little clustering. Variations in stearate additions exhibited slightly more impact on Q and V values with Q values ranging from 1.209 – 1.310 and V values ranging from 0.54 – 0.593 for batches with sodium stearate additions ranging from 0 – 1%.
The influence of batch composition on titania distribution does not extend to the presence or absence of sodium stearate. Figure 5.60 shows that changing the concentration of sodium stearate in the batch has very little effect on the titanium distribution. This is confirmed by the data set in Table 5.13 which shows that the variations in stearate only lead to minor shifts in Q, from 1.209 for the 0.5% stearate batch to 1.310 in the 1.0% stearate batch. The shifts in V are over an even shorter range (0.54 for the 0% stearate batch to 0.53 in the 0.1% stearate batch). No trend can be observed regarding titania distribution and sodium stearate concentration.

**Presence of Alumina Regions Influenced by Batch Composition**

Though somewhat inconsistent, there is enough evidence in Figures 5.85 and 5.86 to suggest that the frequency and magnitude of large regions of alumina, as detected in 100X magnification SEM/EDS maps, can be altered by tailoring batch composition. The increase of water from 16% to 20% in the A16 alumina AT1 titania batches led to an increase in the area fraction of alumina regions for most processing conditions. The alumina regions detected in the nano-powder batches were distinctly influenced by batch composition. The nano-powder batches containing A16 alumina and nano-titania exhibited larger (1.7% area fraction for the A16 alumina nano-titania batch as opposed to 0.1% for the nano-alumina AT1 titania batch) and larger alumina regions (18.07 µm average diameter for the A16 alumina nano-titania batch verse 4.18 µm average diameter for the nano-alumina AT1 titania batch).

The weak effect of batch processing on alumina regions can be seen in Figure 5.85 where the area fraction of alumina regions in batches extruded 5x varies between
containing the greatest area fraction of alumina regions for all batches (8.5% area
fraction, greatest of all A16 alumina AT1 titania batches with 20% water) and the
smallest area fraction of alumina regions (0% area fraction for both A16 alumina AT1
titania with 16% water batch and the A16 alumina nano-titania batch). There is some
evidence that a shortened mixing time leads to increased alumina regions in the A16
alumina AT1 titania batches (both 16% and 20% water) and the A16 alumina nano-titania
batches.

**Macro-Porosity Dictated by Composition and Processing**

The data in Figures 5.90 and 5.91 has shown that the presence of macro-pores is
dictated, not only by batch composition, but also by the processing of the batch. It’s been
shown that a batch with reduced water content will produce a greater cross-sectional area
fraction of macro-pores. This is evident in the comparison between the A16 alumina
AT1 titania batches with 16% and 20% water. The 16% water batch, dry mixed with a
30 minute mix time and single extrusion exhibits 7.23% area fraction macro-pores
whereas the 20% water batch with similar processing only exhibits 4.2% macro-porosity.

Further evidence of the effect of batch composition on macro-porosity can be seen
in the comparison of the nano-powder batches. The wet mixed batch containing A16
alumina and nano-titania, mixed for 30 minutes and extruded once contains 5.46% area
fraction of macro-pores whereas the nano-alumina AT1 titania batch with the same
processing only exhibits 0.19% macro-pores. The A16 alumina nano-titania batches
show consistently greater area fractions of macro-pores than the nano-alumina AT1
titania batches regardless of processing.
The influence of sodium stearate concentration can be seen in the area fraction of macro-pores for batches containing varying stearate levels. The area fraction is seen to increase with increased concentrations of sodium stearate from 1.49% macro-pores in the 0% stearate batch to 4.2% macro-pores in the 1% stearate batch. This trend is mostly reversed for the average diameter of macro-pores in a batch with the 0% and 0.1% sodium stearate batches having the larger macro-pores than the 0.5% and 1% stearate batches (9.15 µm and 7.85 µm diameters as opposed to 3.92 µm and 7.73 µm diameters).

**Batch Processing Introduces Macro-Pores to Extrudate**

Within each batch composition, trends can be observed regarding the effect of processing on area fraction of macro-pores. For all compositions, the greatest concentrations of macro-pores are found in the batches which have been mixed for 30 minutes and extruded 5 times. Conversely, the batches with the least mixing history, those mixed for 7 minutes and extruded once, exhibit the least concentrations of macro-porosity. To use the A16 alumina AT1 titania batch with 20% water and 1% sodium stearate as an example; the batch with the least processing, 7 minute mix, has an macro-pore area fraction of 2.58%, the batch with the 30 minute mix time and single extrusion has a macro-pore area fraction of 4.2%, and the batch with the greatest processing, 30 minute mix time and 5 extrusions, has a macro-pore area fraction of 6.44%.

Further evaluation is required to determine conclusively whether macro-pore formation is a result of processing with insufficient pre-extrusion compaction or infiltration of an epoxy with insufficiently low viscosity. Macro-pores may be reduced vacuum extrusion, which utilizes a vacuum to reduce air pockets in an extrudate batch.
Utilizing a lower viscosity epoxy during infiltration also may inhibit the formation of macro-pores.

6.4 Overall Conclusions

Looking over all the characterization, rheological, and mixture analysis data, some conclusions about alumina titania batch compositions and processing can be drawn. Regarding the use of sodium stearate in the batch, while adsorption limits of stearate on inorganic surfaces could be reached at concentrations of stearate below 1%, the addition of 1% stearate was shown to lower the required mixing energy as well as the facilitate extrusion by lowering wall shear stress. Varying the concentration of stearate did not adversely affect titania distribution in a batch and was shown to reduce the area fraction of alumina-rich regions as well as reduce the size of macro-pores in the extrudate.

Comparing the effect of 16% and 20% water concentration in batches with A16 alumina and AT1 titania, it was shown that 20% water yields greater consistency of batch properties as well as greater ease of processing. The 20% water batch required lower mixing energies than the 16% water batch. With regards to extrusion properties, the 20% water batches resulted in easier extrusion and lower wall shear stresses, without sacrificing much in bulk yield stress. The titania distribution in the 16% water batches was erratic and often far from a regular distribution while the 20% water batches maintained fairly regular distributions with fewer clusters than the 16% water batches. The one area where 16% exhibits some superiority is that batches with 16% water generally contained fewer large alumina regions than the batches with 20% water.
However the 20% water batches contained smaller area fractions of macro-pores than the 16% water batches.

Variations in inorganic batch compositions led to batches with varying advantages. The nano-alumina AT1 titania batches generally had the least desirable processing qualities. These batches required the most mixing energy, exhibited the most resistance to viscous flow, extruded with high wall shear stresses and the lowest bulk stress, and also exhibited the greatest amount of titania clustering. The advantage of a batch containing these inorganics would be that the extrudate quality was consistently better than the batches with other organics and showed the fewest large regions of alumina and almost no macro-porosity.

The batch containing A16 alumina and nano-titania exhibited opposite characteristics to the nano-alumina AT1 titania batch by exhibiting favorable processing behavior such as low mixing energy requirements, smooth transition from elastic to viscous flow, and high extrudate bulk stress. These batches also exhibited the least amount of titania clustering. The greatest disadvantage of these batches was their increased extrudate flaws in the form of large regions of alumina and large area fractions of macro-porosity.

The batches containing A16 alumina and AT1 titania showed no advantage over the A16 alumina nano-titania batches. Most processing properties for the batches containing A16 alumina and AT1 titania were slightly less desirable than those of the batches containing A16 alumina and nano-titania. This was evidenced by increased mixing energy requirements, increased resistance to viscous flow and decreased extrudate bulk stress found in the batches with A16 alumina and AT1 titania. The titania
distribution for batches with A16 alumina and AT1 titania was similar to that of the batches with A16 alumina and nano-titania in regularity but with slightly more clustering. The extrudate flaws, such as alumina regions and macro-porosity, were similar for batches containing A16 alumina both with AT1 titania and nano-titania.

If a batch was being created with coarse inorganics, wet mixing generally produced a more consistent batch (fewer extrudate flaws) than a dry mixed batch, though it required greater mixing energy and extrusion pressures to form. Dry mixed batches tended to exhibit greater bulk stress after being subjected to multiple extrusions. Short mixing times and multiple extrusions were shown to have negligible effect on dynamic yield behavior and minimal effect on titania distribution, though the 5x extrusion of the nano-alumina AT1 titania batch did reduce the titania clustering.

The place where processing most greatly affected the batch quality was in extrusion flaws. Alumina regions were found to vary with processing, though they did not follow a specific trend. Some batches, such as those containing A16 alumina and AT1 titania with 16% water and those containing A16 alumina and nano-titania, exhibited fewer alumina regions with greater processing. The batches with A16 alumina and AT1 titania with 20% water didn’t follow this trend and maintained large alumina regions even in the 5x extruded batch. Macro-porosity showed consistent variation as a result of processing technique. Generally speaking, the less processing applied to the batch, the fewer flaws in the batch. This means that the batches with the fewest areas of macro-pores were those mixed for only 7 minutes while the batches mixed for 30 minutes and extruded 5 times exhibited the greatest areas of macro-porosity.
Future Work

This work has shown ways to manipulate batch rheology and extrudate distribution qualities by varying composition and processing techniques. A logical further step to this work would be to continue on a hypothetical batch production line to the analysis of fired properties of the batch. As this work was done with the formation of $\text{Al}_2\text{TiO}_5$ in mind, the effect of batch variations and firing cycles on the formation of this compound could be assessed.

This method of distributional analysis was most effective for coarse materials. This is due to resolution limitations in the techniques. Other imaging methods for nano-materials could be explored to allow the analysis of distribution of nano-powders in batches which do not contain micron components. Utilizing a backscatter detector, which respond to variations in atomic number, an elemental map with higher resolution could be obtained.

The addition of organic components to a batch is often necessary to facilitate extrusion. In a multicomponent composition the effectiveness of the organic can be affected by preferential adsorption and other electrostatic impulses of the batch components. Varying the organic used, the pH of the mixture, as well as the order of additions could greatly affect the adsorption behavior of the organic. Work which analyzed these factors and their importance on the resultant rheological and distributional behavior of a batch would allow greater precision in fine tuning manufacturing production. These are variables which will change depending on the chemistry of the inorganic components of the batch as well as their particle size distributions.
Lastly, the presence of macro-pores in the batch extrudates leads to questions on how the compositional changes and processing variations in the batch affect the mechanical properties of the extrudate. Research on the mechanical properties, such as density, hardness, and fracture toughness for green and fired extrudates could give valuable information on the importance or insignificance of macro-pores in the extrudate. As a corollary, a study on the ability of non-destructive evaluations such as ultrasound to determine the presence of 3 dimension porosity in an extrudate could be conducted.
References


Curriculum Vitae

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   • C.R. August, L.E. Reynolds, and R.A. Haber. Effect of aqueous based fatty acid
     chain length on the thermal decomposition and rheological properties of extruded thin
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