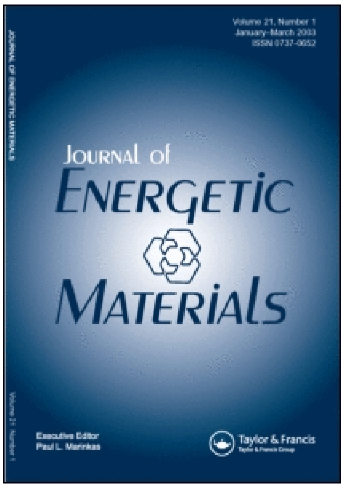

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An Overview of the Rheological Behavior and Characterization of Energetic Formulations: Ramifications on Safety and Product Quality

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The characterization of the flow and deformation behavior (rheology) of energetic materials is a significant challenge. This challenge stems first from the ubiquitous viscoplasticity and the concomitant wall slip of concentrated suspensions of energetic formulations, which involve either a gel phase (for example, solvated nitrocellulose) or high degrees of solid fill (most energetic formulations attempt to approach the maximum packing fraction of the solid phase). The rheological behavior of such suspensions is very sensitive to the microstructure of the suspension during processing, as well as myriad of factors including the migration of the binder and the particles, mixing history, and entrainment of air into the suspension. Although difficult, one needs to generate a detailed understanding of the flow and deformation behavior of various energetic formulations to eliminate or minimize the hazards associated with their processing using both batch and continuous technologies and in assuring an acceptable product quality. In the following, an overview of the various factors, which are important in the rheological characterization of energetic formulations, is provided along with their ramifications on the safety of the processing of the energetic formulation and various determinants of quality.

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Background: Rheological Behavior of Concentrated Suspensions

The rheological behavior and processability of dilute to concentrated suspensions have been the subject of numerous investigations. Information on the dependence of the shear viscosity material function on the filler content, particle size, particle size distribution, particle shape, and orientation in the flow field are summarized in various reviews [1–7]. Until the 1980's investigations of the flow and deformation behavior of concentrated suspensions have been restricted to solid concentrations, which are below sixty–four percent by volume. The majority of these studies have utilized the Couette flow [8–11]. However, such data may be problematic since the Couette flow can involve the migration of the solid particles and the resulting concentration gradients as well as wall slip effects [12,13].

Suspensions, which are filled at solid loading levels close to the maximum packing fraction of their solid phase and suspensions, which involve a ‘‘gel’’ based binder, present special challenges in the characterization of their rheological behavior. As shown by Kalyon and co–workers, the behavior of such materials are subject to a wall slip in both the rotational and capillary rheometers [14,15] and flow instabilities in die flows associated with the mat formation and filtration of the binder [16,17]. Such suspensions can exhibit rheological dilatancy with an intimate relationship to slip at the wall during the flow [18].

Since the concentration of solids approaches the maximum packing fraction, the rheological behavior and the processability of highly filled suspensions are very sensitive to the amount and distribution of air entrained during processing [19]. Air entrainment is related to the geometry and operating conditions employed during processing, especially on the degree of fill distribution in the continuous processor [20]. Furthermore, the entrainment of air also affects the wall slip behavior of the energetic suspension.

The simulations of the continuous processing behavior of highly filled suspensions require especially the incorporation of their wall slip behavior into the analysis. The wall slip behavior of such highly filled suspensions can be characterized employing viscometric flows [14,15]. Even for simpler materials like melts of homopolymers, the chemical composition and the roughness profile of the walls play a significant role in controlling the wall slip behavior [21,22]. The characterized wall slip behavior of a concentrated suspension can be employed in the simulation of its continuous processability using model flows like generalized plane Couette flow [23,24] or extrusion flows including the single screw extrusion flow, under both isothermal and non-isothermal conditions [25] and the twin screw extrusion flow [26].

In the following an overview of the various important factors affecting the rheological characterization of propellants and explosives is provided. These factors include their flow and deformation behavior involving wall slip, flow instabilities, migration of the ingredients of the energetic formulation during flow and deformation, air entrainment effects, mixing dynamics, and ramifications of all these major factors on safety and product quality.

Major Factors that Affect the Rheological Behavior of Energetic Formulations

Wall Slip

The characterization of the flow and deformation behavior of energetic formulations, including propellants and explosives, is first and foremost complicated by the occurrence of the wall slip. The wall slip behavior of a concentrated suspension consisting of sixty percent by volume of particles in a thermosetting binder is demonstrated in Fig. 1. The suspension sample undergoes steady torsional flow in between two parallel disks; the disk at the top is rotating and the disk at the bottom is stationary. Before the onset of deformation, a straight-line marker is placed at the free surface of the suspension and the edges of the two disks, as shown in Fig. 1. Upon the rotation of the top

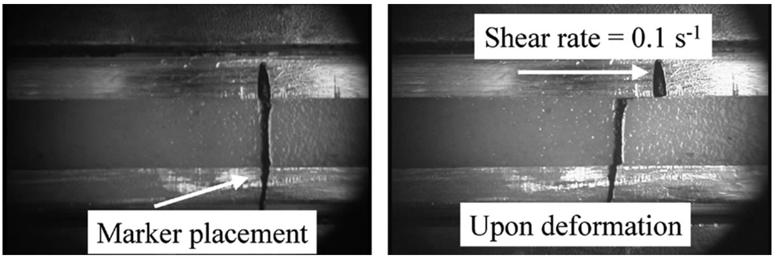


Figure 1. Typical wall slip behavior of energetic suspensions in steady torsional flow.

disk, discontinuities appear at both the top and the bottom suspension/wall interfaces, suggesting a wall slip.

The slip at the wall of the concentrated suspension occurs on the basis of the formation of a binder-rich region next to the wall, i.e., the slip layer thickness (Fig. 2). The occurrence

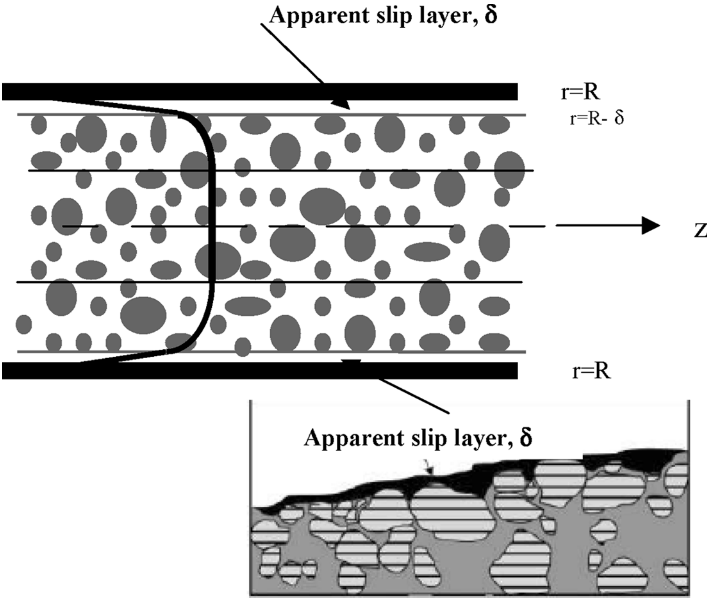


Figure 2. Formation of the apparent slip layer during the flow of energetic suspensions.

of the wall slip decreases the deformation rate imposed on the suspension in comparison to the no-slip condition under similar wall shear stress. To characterize the wall slip behavior and to correct the rheological characterization data collected for this wall slip, the traditional method has been to systematically change the surface to volume ratio of the rheometer and to determine the slip velocity from the slope of the apparent shear rate versus the reciprocal diameter or gap height data collected at constant wall shear stress [14,15,27]. In capillary flow this requires that the capillary diameter be changed while keeping the length/diameter ratio of the capillary a constant [14,27]. In a rectangular slit flow, this requires that the gap of the slit be systematically altered to allow the surface/volume ratio to change [28,29]. In steady torsional flow the change in surface to volume ratio is again tantamount to changing the gap of the rheometer. In squeeze flow inverse solution methodologies can be applied to allow the wall slip velocities to be determined as part of the characterization [30].

The traditional technique of systematically changing the surface to volume ratio of the suspension during rheological characterization to determine the slip velocity is only applicable to characterization under steady state condition, i.e., the slip velocity values are determined at the corresponding wall shear stress values under steady flow conditions. On the other hand, the flow visualization technique illustrated in Fig. 1 can be used for the characterization of the time-dependent behavior of the wall slip [31]. This technique allows the time-dependent determination of the slip velocity and the true deformation rate of the suspension (hence the true shear viscosity of the suspension) directly [15]. The deformation of the marker line is optically recorded as a function of time as the disk at the top rotates. Computerized image analysis of the recorded images generates the velocity of the suspension found adjacent to the wall, $\vec{V}_f$ as a function of time [31]. The slip velocity at the wall, $\vec{U}_s$, can then be determined from:

$$\vec{U}_s = \vec{V}_f - \vec{V}_w \tag{1}$$

where $\vec{V}_w$ is the wall velocity.

Upon initiation of flow, the deformation rate of the suspension decreases, while the shear stress and the wall slip velocity increase with increasing time [31]. Under typical steady torsional flow conditions a steady state behavior can be achieved at which the true deformation rate can be as small as 1/5th of the imposed apparent shear rate. The ramifications include the time-dependence of the start-up flows in continuous processing and the decreasing of the shear rates and total stains which can be introduced into the suspension during rheological characterization and processing.

The typical steady-state slip velocity at the wall versus wall shear stress behavior of energetic suspensions employing Newtonian binders follows the Navier's slip condition shown in Equation 2. The wall slip velocity, $\mathrm{U_s}$, versus wall shear stress, τ_{w}, data can be fitted by:

$$U_s = \beta\tau_{\mathrm{w}} \tag{2}$$

where β is the Navier's slip coefficient, which for various materials also depends on the nature of the walls of the rheometer [21,22]. For the simulant of the solid rocket fuel used in the Space Shuttle program (a suspension with 76.5 percent by volume solids) the value of the Navier's slip coefficient, β was determined to be $7.4 \times 10^{-4}\,\mathrm{mm/(Pa\text{-}s)}$ under typical processing conditions [14,15].

As shown recently [29], a power law relationship between the slip velocity, $\mathrm{U_s}$, and wall shear stress, τ_{w}, is expected if the binder of the energetic suspension is non-Newtonian.

$$U_s = \pm\frac{\delta}{m_b^{1/n_b}}(-\tau_{\mathrm{w}})^{1/n_b} = \pm\beta(-\tau_{\mathrm{w}})^{1/n_b} \tag{3}$$

The Navier's slip coefficient, β, is related to the thickness of the apparent slip layer, δ, (see Fig. 2) and the parameters of the shear viscosity of the binder, power law index, $\mathrm{n_b}$, and the consistency index, $\mathrm{m_b}$, represented using a Power-law relationship, $\tau_{yz} = -m_b|dV_z/dy|^{n_b-1}(dV_z/dy)$ for 1-D flow with a sole velocity component in the z-direction, V_z, changing only in one direction, y.

For various explosive and solid rocket fuel formulations the rheological characterization data indicate that the suspension can flow as a plug (lubricated at the wall with the apparent slip layer) above a wall shear stress value, whereas for some other energetic suspensions, the suspensions exhibit plug flow at wall shear stress values that are smaller than a critical shear stress value. The formation of a plug suggests the interlocking of the particles during flow and the development of an infinite shear viscosity, i.e., solid like behavior. Whether the plug flow is observed at wall shear stress values that are smaller than a critical shear stress or at wall shear stresses that are greater than a critical shear stress depends primarily on the breadth of the particle size distribution [15].

Ramifications of the Wall Slip

The major ramifications of wall slip include the following:

1. Since the wall slip effect is related to the changes in the surface to volume ratio of the rheometer or the processing geometry during flow and deformation, unless the wall slip effect is specifically probed, characterized, and the rheology data corrected for the wall slip, the rheological characterization data from one type of rheometer will not match with data collected with another rheometer.
2. Again due to the surface/volume ratio effects, experimental results collected with a processor with a specific size cannot be scaled up or down to other processors with different sizes. For example, processing data collected with a single screw extruder with a barrel diameter of 1″ cannot be scaled up to a geometrically similar extruder with a 2″ barrel diameter. This is because the surface to volume ratio of a 1″ extruder is twice that of the 2″ extruder and the wall slip would generate a more pronounced effect with the smaller extruder.
3. The formation of an apparent slip layer, consisting solely of the binder phase at the wall (Fig. 2) suggests

that instrumentation which aims to characterize the composition or properties of an energetic suspension within the confines of the manufacturing hardware (dies, mixer surfaces etc.) needs to penetrate beyond the apparent slip layer thickness to probe the behavior of the bulk of the suspension [29]. If the analytical methodology remains as a surface-limited method, only the binder rich apparent slip layer is characterized. This has important ramifications especially in the selection of on-line analysis instrumentation to be used during the processing of energetic formulations.

Constitutive Equation

As indicated energetic formulations are viscoplastic suspensions, which are subject to wall slip and yield stress formation. The wall slip behavior needs to be characterized as part of the process of the characterization of parameters of a viscoplastic constitutive equation [14,15,29]. The most commonly used viscoplastic fluid model for representing the shear viscosity of concentrated suspensions of energetic formulations is the Herschel-Bulkley fluid [32], which suggests solid like behavior at shear stress values which are smaller than the yield stress value of the fluid, τ_0, in one-dimensional flow.

$$\tau_{yz} = \pm\tau_0 - m\left|\frac{dV_z}{dy}\right|^{n-1}\left(\frac{dV_z}{dy}\right) \tag{4}$$

for $|\tau_{yz}| > \tau_0$ ($-$ sign is used for negative shear stress, τ_{yz}) and the shear rate $(dV_z/dy) = 0$ for $|\tau_{yz}| < \tau_0$. Again, here the flow is based on one velocity component, V_z, changing in only one direction, y, under steady state conditions.

The typical method used for the characterization of the yield stress involves the extrapolation of the shear stress versus the shear rate curve to zero shear rate. However, for concentrated suspensions like energetic suspensions such conventional techniques of the characterization of viscoplasticity generate misleading and incorrect results. Such extrapolated values of the yield stress depend on the geometries of the rheometers employed and the wall slip behavior of the suspension [14,18,29].

Ramifications of Proper Characterization of Parameters of Wall Slip Behavior and Shear Viscosity Material Function of Energetics

The proper characterization of the parameters of the shear viscosity of the energetic suspension is very important since only adequately-characterized parameters of wall slip and the shear viscosity of the energetic suspension will allow a realistic simulation of the processing behavior of the energetic formulation in the confines of both batch or continuous processors [26] and proper tool design and process optimization. If the simulation used for assessing the safety of the process is not realistic on the basis of weak rheological parameters, then the benefits of simulation are lost or worse the results become misleading, i.e., the apriori prediction and determination of the hot spot formation (temperature exceeds the decomposition/initiation temperature of the energetic formulation), or the presence/absence of dead zones (the energetic formulation stagnates in the processor), or pipeline (the energetic formulation is exposed to very little intermixing) flows are not possible [26].

Flow Instabilities during Pressure Driven Characterization of Energetic Suspensions: Migration of the Binder in the Flow Direction, Demixing Effect

Pressure driven flows of propellants and explosives can give rise to flow instabilities associated with the time-periodic formation of mats of solids in converging flows and the filtration of the binder through the mat of solids [16,17,33]. Such time-dependent demixing of the ingredients of the formulation of energetic suspensions does affect the quality of the degree of mixing of the suspension and hence its ultimate properties. It also renders the continuous processing operation unstable and poses a safety threat in continuous processing of energetic suspensions [16]. The extrudate emerging from the die can be resin-rich or poor in a cyclic fashion. At relatively high screw speeds the pressure before the die can rapidly be affected by dramatic demixing and pulverization of the energetic particles in the continuous processor [16]. This effect is the source of multiple incidents in the energetics manufacturing industries.

Capillary flow experiments can be used to provide a better understanding of the flow instabilities of energetic suspensions occurring in continuous processing operations [16,33]. Under unstable flow conditions, the average pressure necessary to extrude the suspension grows unbounded with time, with generally increasing amplitude of oscillations. The time periodic

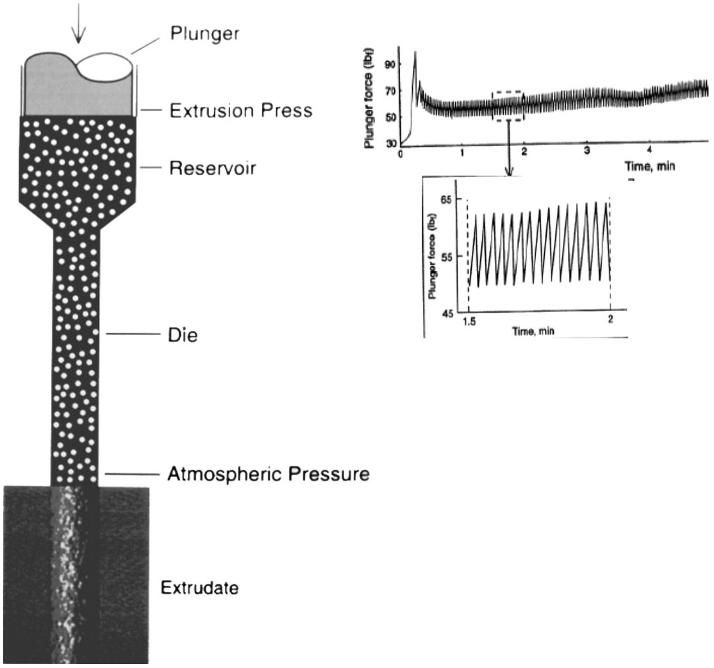


Figure 3. Pressure versus time during unstable flow in a ram extruder due to the time-dependent migration and filtration of the binder phase of the energetic suspension.

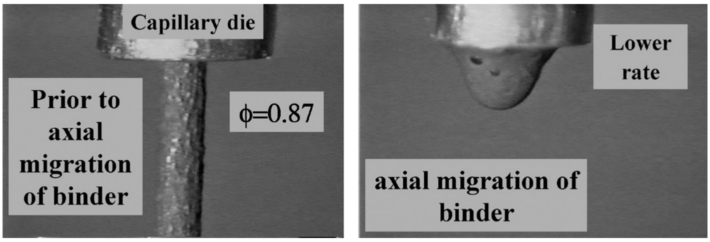


Figure 4. Steady extrusion of an aluminized solid rocket fuel formulation (a) and unstable flow of the same suspension due to the migration of the binder of the energetic formulation (b).

oscillations in extrusion pressure are related to the time periodic mechanism of formation of a mat of solids at the capillary or die and its break-up (Fig. 3). This occurs concomitant with the filtration of the binder. During the most severe conditions of filtration, the binder, containing visible air pockets, emerges from the capillary to form drops that momentarily cling to the bottom of the die (Fig. 4) [33].

The apparent shear rate range at which the flow of the highly filled suspension is stable can be broadened by increasing the viscosity of the matrix (lower temperature), increasing the shear stress at the wall, and through the use of dies with greater diameters. For the die flow of an energetic suspension where the suspension flows like a plug with a shear stress dependent slip velocity at the wall, U_s, the flow becomes unstable when the filtration velocity, V_m, becomes greater than the slip velocity of the plug [16,33]. The critical apparent shear rate value for each die at which the flow instabilities are on-set can be predicted on the basis of the comparison of filtration and wall slip rates [16].

Ramifications of Binder Migration during Flow and Deformation

Obviously in the processing of propellants and explosives the filtration of the matrix and thus the unstable region should be avoided. Otherwise, the additional loss of the binder, due to axial migration at solid loading levels that are very close to the maximum packing fraction, will render the energetic suspension unprocessable. The unstable region in converging flows can be avoided by the proper selection of the production rate and the geometry of the channel through which the suspension is flowing. For example the experimental data and the results of the theoretical approach for a rocket fuel simulant simulant (used in the Advanced Shuttle Rocket Motor, ASRM, program) suggested that the critical apparent shear rate, below which flow instabilities prevail, decreases with an increasing channel diameter [33].

Particle Migration Effects

Energetic materials like solid rocket fuels and gun propellants are suspensions consisting of a polymeric binder incorporated with rigid particles. The particles are generally symmetric with low aspect ratios and broad particle size distributions to allow achievement of relatively high solid packing ratios. The concentration of the rigid particles needs to be relatively high and in most cases approaches the maximum packing fraction of the solids (the characteristic concentration of the solid particles above which there is no fluidity). In the flow and processing of such highly filled suspensions a number of mechanisms act to generate gradients in the concentrations of particles in the transverse to flow direction, i.e., in the direction of the imposed deformation rate. When the Reynolds number is greater than 10^{-3} the inertial effects give rise to the radial migration of solid particles [34,35]. Furthermore, the migration of the particles, and the resulting development of particle concentration gradients in transverse to flow direction occur upon inhomogeneous flows in the absence of inertial effects. Thus, they even occur during creeping flows in which the prevailing Reynolds number approaches zero [12,13]. Since the shear viscosity of most energetic suspensions is very high the flow of energetic suspensions could be considered as creeping flow and is thus subject to the migration of particles even in the absence of inertial effects.

The migration of particles from high shear rate to low shear rate was further documented in wide-gap Couette flow (where shear rate is not uniform) by Abbott et al., 1991, using magnetic resonance imaging [13]. In pressure-driven channel flow (rectangular slit and capillary) a number of investigators observed the blunting of the velocity profile (Karnis et al., [37]). Such blunting can be considered to be a consequence of particle concentration gradients. Allende and Kalyon [38] showed that such particle migrations in pressure-driven flows could occur if the particle radius over the channel gap is relatively high. They further indicated that increasing wall slip velocities reduce the migration rate and also provided a simple experimental means to assess the importance of migration effects in die flows [38].

Phenomenological models of migration of neutrally-buoyant, unimodal, and spherical particles suspended in Newtonian fluids, across planes of shear during nonhomogeneous shear flows generally attribute the migration to irreversible interactions. By using scaling arguments, Leighton and Acrivos [12] were able to derive a general expression for the diffusive flux of particles in simple shear flow. Phillips et al. [1992] used Leighton and Acrivos [1987] flux expressions to develop a diffusion equation that describes the evolution of particle concentration distributions over time [39]. This diffusion equation assumes that there are two primary causes for particle migration, i.e., particle interactions and local variations of the concentration-dependent suspension viscosity. The Phillips et al. [1992] model was further modified by Allende and Kalyon [38] by using two different boundary conditions, i.e., the continuity of the flux at the axis of symmetry and the incorporation of apparent slip at the wall (wall slip is prevalent in the flow of concentrated suspensions including energetic suspensions).

Following Leighton and Acrivos [12] and Phillips et al. [39] consider a suspension of hard spheres with radius a in a Newtonian fluid with viscosity η_o. The number of collisions or interactions experienced by a particle is in the order of $\dot{\gamma}\phi$, where $\dot{\gamma}$ is the local shear rate and ϕ is the particle volume fraction. The gradient in the collision frequency over a characteristic distance of O(a) is given by $a\vec{\nabla}(\dot{\gamma}\phi)$. Therefore, the particle flux $\vec{N}_c$, occurring due to a gradient in collision frequency, is given by (Phillips et al. [39])

$$\vec{N}_c = -K_c a^2 \phi(\phi \vec{\nabla}\dot{\gamma} + \dot{\gamma}\vec{\nabla}\phi) \tag{5}$$

where K_c is a constant that is determined from the experimental data. The first term in Equation (5) implies that even in the absence of a gradient in the particle concentration, the migration of particles will result if gradients in shear rate, $\dot{\gamma}$, exist. The second term in Equation (5) states that a gradient in the particle concentration will cause a spatial variation in the frequency of collisions. If a non-homogeneous shear flow is started in a suspension with a uniform concentration distribution, ϕ, the first term in Equation (5) gives rises to a flux, which in turn generates a concentration gradient and hence induces a second flux proportional to $\vec{\nabla}\phi$. Thus, the two terms in Equation (5) are in general in opposite directions. Particles migrate from regions of high to low shear rate, and from regions of high to low concentration.

In addition to the flux caused by gradients in collision frequency, the interactions between particles are affected by a gradient in suspension viscosity caused by the presence of gradients in the particle concentration that gives rise to a displacement in the direction of lower viscosity [12]. The magnitude of this displacement during each irreversible interaction is scaled with the relative change in suspension viscosity, i.e., $(a/\eta_s)\vec{\nabla}\eta_s$ [12]. If each interaction causes a displacement over a characteristic distance of O(a) and the interaction frequency scales as $\dot{\gamma}\phi$, then the flux $\vec{N}_\eta$ due to a viscosity gradient, is given by (Phillips et al. [39])

$$\vec{N}_\eta = -K_\eta a^2 \frac{\dot{\gamma}\phi^2}{\eta_s} \vec{\nabla}\eta_s \tag{6}$$

where K_η is a diffusion constant that needs to be determined from experimental data, and $\eta_s = \eta_s(\phi)$ is the shear viscosity of the concentrated suspension. (Phillips et al. [39]) provide a conservation equation for solid particles, which can be written in a Lagrangian reference frame as:

$$\frac{\partial \phi}{\partial t} + \vec{v} \cdot \vec{\nabla} \phi = -\vec{\nabla} \cdot \left(\vec{N}_c + \vec{N}_\eta \right) \tag{7}$$

These results suggest for example that if a concentrated suspension of energetic particles and/or binder is placed into the gap between two cylinders one of which is rotating and the other is stationary (with a relatively large gap to allow shear rate gradients to exist) concentration gradients will be established with a high concentration of particles at the outer wall and a relatively low concentration of particles at the inner wall. The

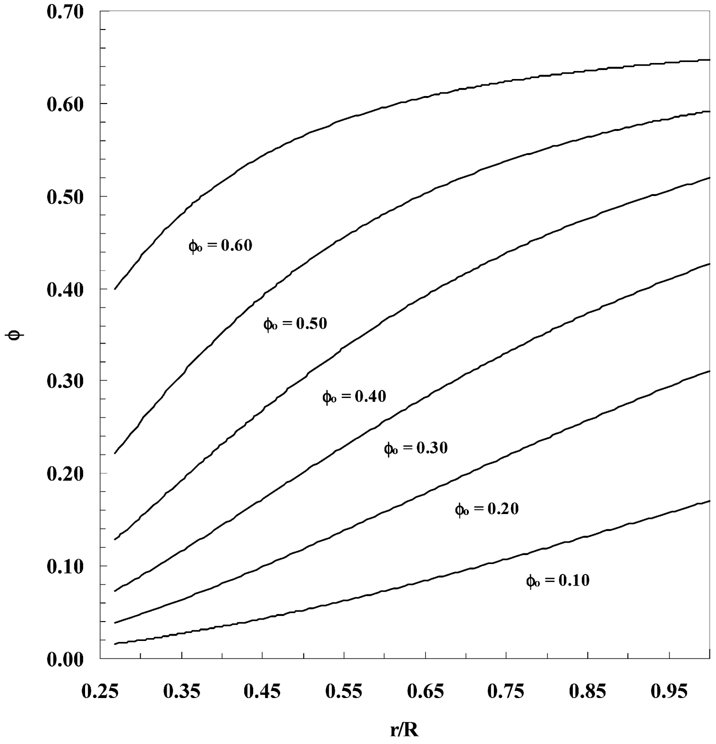


Figure 5. Development of concentration gradients in cylindrical dies upon the migration of particles due to shear rate gradients [40].

durations to reach these steady state concentration distributions will be a function of the particle radius over the gap ratio. Allende [40] calculated the development of the concentration distributions for a particle radius over the gap ratio of 0.02. The non-dimensional inner cylinder radius is $\kappa = 0.27$. Fig. 5 shows the theoretical distributions of particle concentration at various volume particle loading levels, ϕ, under steady state conditions [40]. The concentration of particles is significantly greater at the zone with the smaller shear rates (adjacent to the inner cylinder rotating, versus zones with greater prevailing shear rates, i.e., adjacent to the stationary outer cylinder).

Ramifications of Particle Migration: Burn Rates as Functions of Concentration and Size of Particles

Experimental work has shown that changes in the concentrations of the energetic particles will lead to changes in burn rates. For example, the experimental work of Homan et al. [41] using energetic thermoplastic binders incorporated with RDX type nitramine particles has clearly shown that the burn rate of the energetic suspension would be a function of the

Figure 6. Theoretical burn rate distributions due to shear-induced migration of particles of an energetic formulation.

concentration of particles. The results indicate that as the concentration of the RDX particles increases then the burn rate also increases across the entire range of particle sizes considered in the 2 to 32 micron size range, as shown in Fig. 6 [Fair et al. 42]. Thus, the conditions that will generate particle concentration distributions will also lead to distributions of the burn rates, directly affecting the quality of the energetic grains that are manufactured. It should be noted that such migration effects are likely to occur not only in extrusion flows but in every process where a shear rate gradient needs to be established, for example, to fill a shell, including bayonet feeding of larger structures.

Air Entrainment Effects

Since the formulations of propellants and explosives involve volume fractions of solids which approach the maximum packing fraction of the solid phase, the incorporation of even small concentrations of air, makes a significant difference in the rheological behavior and hence the processability of highly filled suspensions [43,44]. In general the suspension samples processed without vacuum can contain an additional few percent by volume air under ambient conditions. The shear viscosity of the suspension decreases and wall slip velocity values increase with the incorporation of air into the suspension. The air entrained into an energetic suspension sample can be studied using x-ray radioscopy and magnetic resonance imaging micrographs [19]. The amount of air entrained into the suspension increases at partially full regions in the batch or continuous processor in comparison to suspension samples collected from completely full sections of the processor [19,20]. For example, the density values of samples collected from the reversely configured screw sections of a twin screw extruder (which necessitate completely full mixing volume) are greater than those of the samples collected from the partially full sections of the same extruder i.e., at forwardly configured screw sections [20].

The air entrained into the suspension also affects the development and nature of the slip layer (binder rich region found adjacent to the wall) of the suspension during die flows. Under

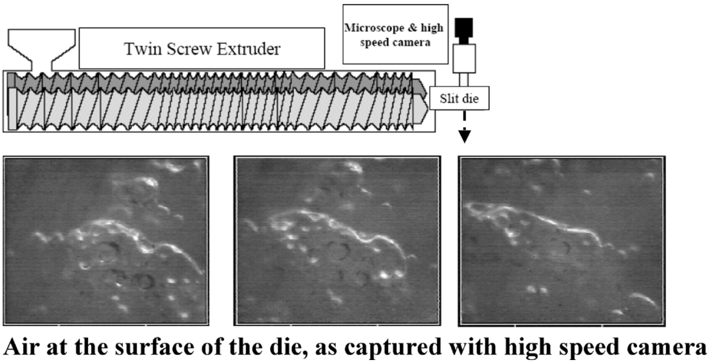


Figure 7. Entrainment of air: documentation in rectangular slit flow.

moderate die pressures, pockets of air cling to the wall momentarily and are spread out to be later dragged-on by the bulk of the suspension. The wall of the die appears to be covered partially with films of air during extrusion, with the air film continuously being removed and replenished (Fig. 7). The effect of air entrainment on the development of wall slip behavior is shown in Fig. 8. The wall slip velocities are significantly greater with increased air entrainment [43,44] to significantly affect the processing, especially the viscous energy dissipation behavior of the energetic suspensions [44].

Ramifications of Air Entrainment

The entrainment of air under different modes alters the rheological behavior of energetic suspensions. Rheological characterization under relevant air entrainment conditions allows the assessment of the air entrainment effect. Under certain conditions at which the suspension is very close to its maximum packing fraction the removal of air can introduce significant viscous energy dissipation effects and render the process unstable [44], including the development of hot spots which can be detrimental to the processing of the energetic material.

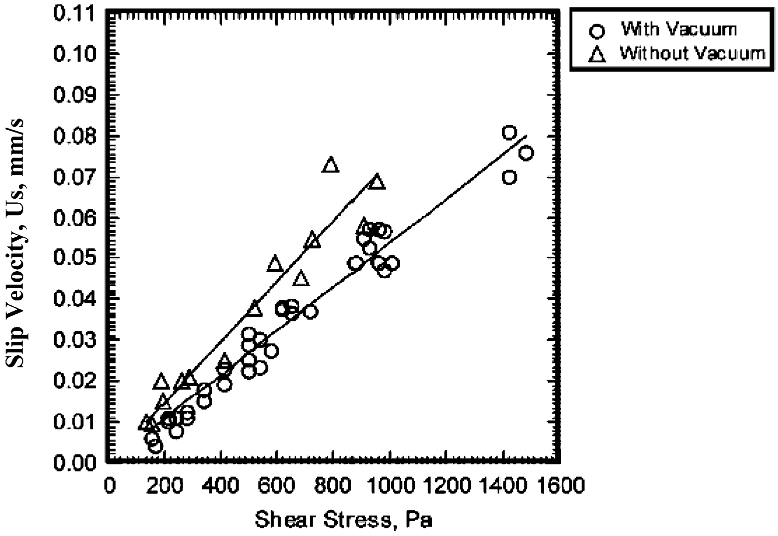


Figure 8. Slip velocity at the wall with and without air entrainment.

Time-dependent Flow Instabilities and Extrudate Distortions

For generating the net shape of energetic grains it is very important to generate grains that are distortion free. The development of the flow instabilities is intimately linked to the wall slip behavior of the material even for the pure polymer [45–46]. Figure 9 shows the development of flow instabilities for a pure binder as a function of flow conditions in a capillary die [46]. As the shear rate is increased the surfaces of the extrudates become distorted. The distortions become significantly severe as the apparent shear rate in the die increases.

Ramifications of Flow Instabilities and Extrudate Distortions

Upon the onset of flow instabilities the extrudate becomes distorted. The grains that are generated during manufacturing under such unstable conditions cannot generally be used and

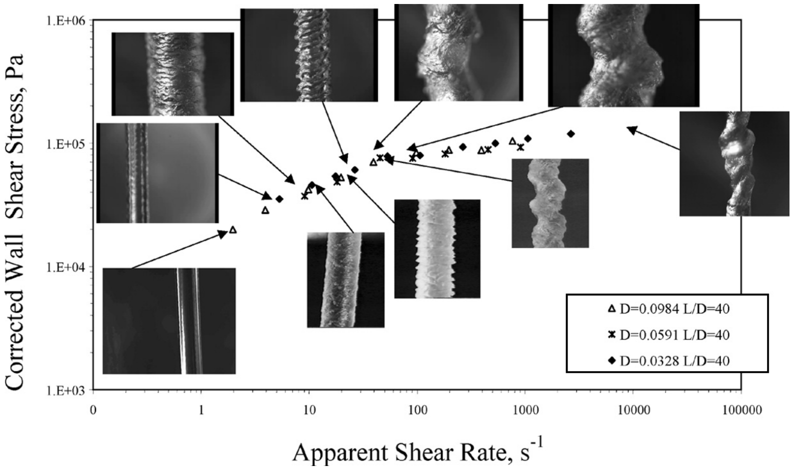


Figure 9. Development of flow instabilities and resulting extrudate surface/bulk irregularities.

need to be recycled or discarded. Furthermore, the onset of unstable conditions give rise to time-dependent boundary conditions as well as time-dependent pressure, velocity and temperature conditions in the processing geometry. Thus, it is important to eliminate conditions under which flow instabilities are likely to occur during the course of the manufacturing process. During rheological characterization capillary and rectangular slit flows can be used to determine the shear stress conditions under which extrudate distortions are to occur in ram extrusion and twin screw extrusion so that such conditions are eliminated during manufacturing flows [45].

Microstructural Distributions and Effects on Rheological Behavior

One of the most challenging aspects of any mixing operation, where two or more identifiable components are brought together, is the characterization and control of the state of the mixture, i.e., the degree of mixing or the ''goodness'' of mixing of the energetic suspension. In the non-diffusive mixing of a viscous polymeric binder with solid components, the complete description of the state of the mixture would require the specification of the sizes, shapes, orientations, and the positions of the ultimate particles of the components.

If the materials of interest are opaque or if transparent barrel sections cannot be built, the mechanisms of mixing can be studied through ‘‘post-mortem’’ analysis. In this technique, generally a distinguishable tracer is added into a mixer in a step or pulse fashion. Upon certain duration of mixing, the mixture is systematically removed from the mixer and sectioned to allow the investigation of distributive and dispersive mixing aspects. Kalyon and co-workers [47,48] have employed color-incorporated thermoplastic elastomers, followed by computerized image analysis, to investigate the distributive mixing of thermoplastic elastomers in the regular flighted and kneading disc elements of twin screw extruders.

On the other hand, the rapid advent of imaging and sensing technology has facilitated the introduction of various powerful techniques, including the magnetic resonance imaging and x-ray based techniques, to the analyses of opaque mixtures. Kalyon et al. [19] have employed magnetic resonance imaging, wide-angle x-ray diffractometry, and x-ray radioscopy. The mixing state progressively changes in the mixing volume of a batch or continuous mixer as a function of residence time. It is, however, possible for some portion of the material to be subject to very little mixing action. Thus, it is very important to be able to quantify the degree of mixing to allow linkages to the rheological behavior.

Wide-Angle X-Ray Diffraction Technique

The particular advantage of diffraction analysis is that it discloses the presence of a substance, as that substance actually exists in the sample, and not in terms of its constituent chemical elements. If the sample contains more than one compound/phase that constitute the same chemical elements, all these compounds are disclosed by diffraction analysis. Quantitative analysis is possible, because the intensity of the diffraction pattern of a particular phase in a mixture of phases depends on the concentration of that phase in the mixture. The relation between integrated intensity, I_x, and the volume fraction or concentration, c_x, of a phase in a composite can also be determined by WA-XRD. The ratio of intensities from two phases in a given mixture is independent of absorption effects (μ_m) and varies linearly with concentration:

$$I_1/I_2 = (K_1/K_2)c_1/c_2 \tag{8}$$

Such normalized measurements can be calibrated with control samples and the concentration ratios of multiple components in a composite can be determined quantitatively. The x-ray diffraction techniques can be applied to assess the degree of mixing of live propellants live explosives and their simulants [49–51]. If one makes N measurements of concentration c_i of one of the components, then the mean concentration is:

$$\bar{c} = \frac{1}{N}\sum_{i=1}^{N} c_i \tag{9}$$

The variance, s^2, arising from the differences in the individual concentration, c_i, measurements, provides an index to quantitatively assess the degree of mixing. The variance is given by:

$$s^2 = \frac{1}{(N-1)}\sum_{i=1}^{N}(c_i - \bar{c})^2 \tag{10}$$

A small variance value implies a homogeneous system. The maximum variance occurs if the components are completely segregated, and is given by:

$$s_o^2 = \bar{c}(1-\bar{c}) \tag{11}$$

If the standard deviation, s, is normalized to its maximum value, s_o, a quantitative measure of the degree of mixedness, mixing index, MI, can be defined.

$$\text{Mixing index} = 1 - \frac{s}{s_o} \tag{12}$$

The mixing index values range from zero, for completely segregated system, to one, for a homogeneous system. The results of the quantitative x-ray diffraction analysis of the relative volume fraction of the CAB binder, obtained by employing the relative integrated intensities of various ingredients are given in Fig. 10. The statistical analysis of the results is also presented. Such techniques can be used in the characterization of the microstructural distributions of energetic formulations prior to rheological characterization on the one hand and during processing on the other hand to provide linkages of the rheological behavior to the thermo-mechanical history occurring during processing.

Figure 11 shows the flow curves (wall shear stress versus the apparent shear rate), obtained with concentrated suspension samples subjected to differing specific energy inputs and hence suspensions with differing degree of mixedness [52,53]. The results indicate that with improved homogeneity of the distributions of the ingredients of the formulation the particles are

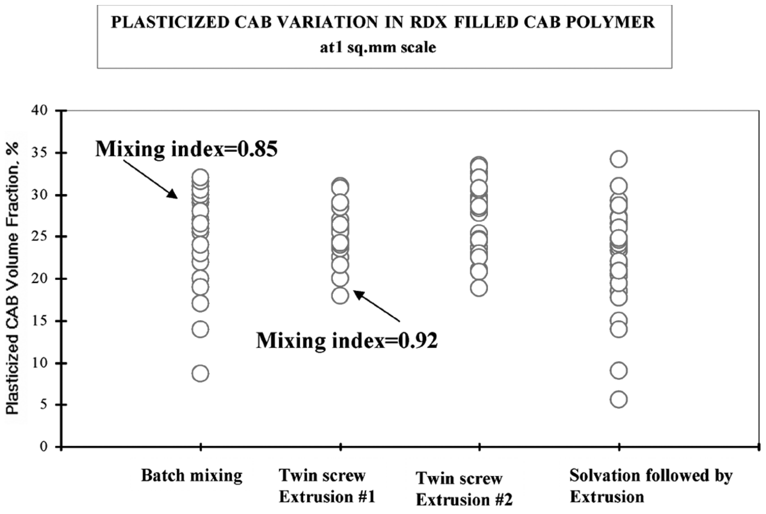


Figure 10. Degree of mix of a LOVA formulation upon processing under different processing methods and conditions.

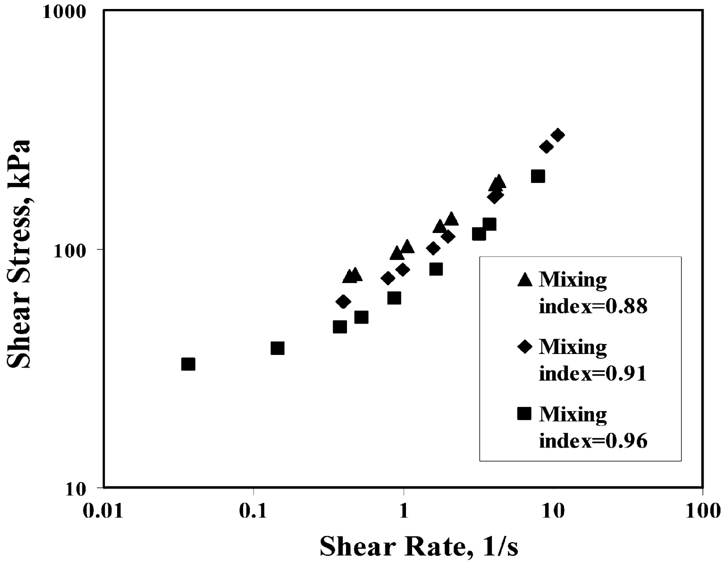


Figure 11. Flow curves of a processing simulant as affected by the specific energy input and resulting degree of mix upon processing [53].

better coated leading to decreased values of the shear viscosity of the suspension [52,53].

Ramifications

The dependence of the rheological behavior on the processing conditions suggests that unless the processing conditions are reproducible and controllable the rheological characterization data of energetic suspensions will be subject to significant variability. The ability to generate data from a pilot plant and then to relate the findings to actual manufacturing operations is also diminished since the thermo-mechanical histories experienced by the energetic formulation during processing in the pilot plant and the manufacturing operation will be different. It is suggested that the rheological behavior of the specimens from the actual manufacturing operation be characterized on an on-line basis to allow realistic understanding of the flow and deformation behavior of the energetic formulation.

Viscoelastic Material Functions

How important are the viscoelastic material functions for energetic suspensions? The viscoelasticity of the concentrated suspensions is a very complicated aspect [17,54]. This complication arises from the changes in structure which occur during rheological characterization employing rotational rheometers including the formation of strings of particles which can give rise to negative first normal stress difference values during simple shear [54]. The extrudate swell values of the concentrated suspensions of rigid particles are in the range for Newtonian fluids (swell ratios are around 1) as affected by the viscoplasticity of the suspension associated with the formation of a network of particles. Generally, the relaxation modulus values upon step strain exhibit a significant drop associated with the relaxation of the binder of the suspension followed by a very slow relaxation [17]. There is significant benefit to be had by the characterization of the dynamic properties of energetic suspensions since the storage and loss moduli versus strain and frequency behavior can fingerprint the suspension and time-scans can pinpoint if there are significant changes in structure with solvent loss, aging, curing etc. However, it should again be noted that the rotational rheometers, which are used for the characterization of the viscoelastic material functions, would be subject to significant wall slip that may render the data difficult to interpret for routine quality control or parameter estimation tasks.

Choice of Rheometers

The various factors listed, especially the wall slip effects, suggest that the choice of the rheometer is very important if realistic and usable rheology data are to be collected. Clearly, the torsional data will be subject to wall slip and data analysis and interpretation are difficult, unless sophisticated data analysis and collection methods are used [31]. The capillary flow data are usable if multiple dies with differing diameters at constant length over diameter ratio and different length over diameter ratios at constant diameter are used [14,15]. However, this generates a very lengthy procedure. Instead a rectangular slit die with pressure transducers installed flush with the wall of the die can be used provided that there is a gap-altering capability to the rheometer [55,56]. This type of adjustable-gap rheometer is very convenient and has proven very useful in the characterization of energetic suspensions. Figure 13 shows an adjustable gap rheometer manufactured by MPR Inc. of Hackensack, NJ [57] that is utilized at NSWC/IH for the characterization of energetic formulations. An off-line version of this rheometer is also available from MPR [Fig. 13a] in conjunction with a remote filling station to allow the tamping–free filling of the barrel of the rheometer using disposable cartridge elements, which allow filling under vacuum with remote control of the operation (Fig. 13b) [57].

Another suitable rheometer used in the characterization of energetic formulations is the squeeze flow rheometer [30]. An explosion proof version of this rheometer is shown in Fig. 13c

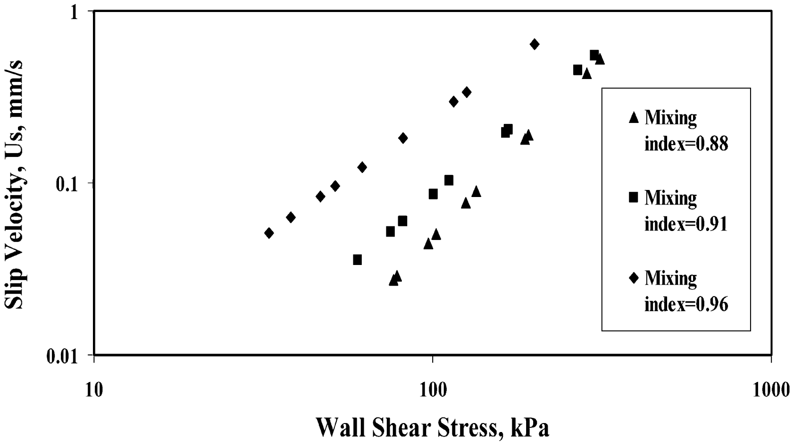
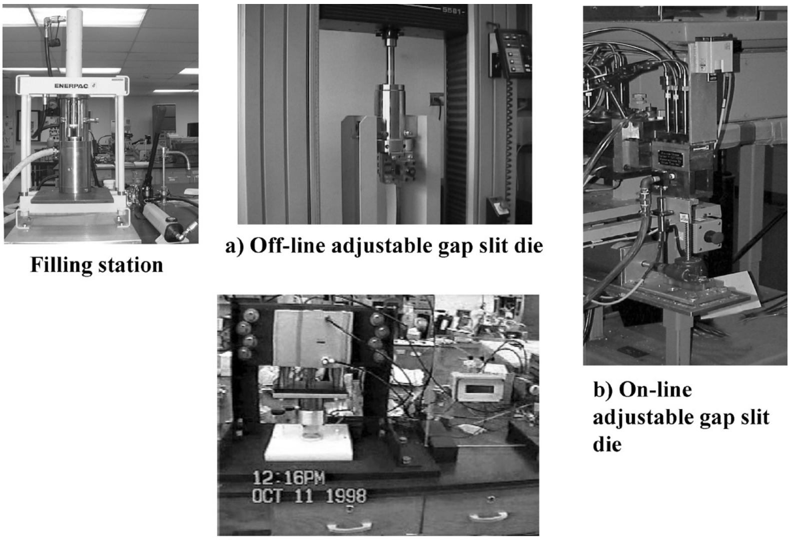


Figure 12. Wall slip behavior of a processing simulant as affected by the specific energy input and resulting degree of mix upon processing.



Filling station

a) Off-line adjustable gap slit die

b) On-line adjustable gap slit die

c) Squeeze flow rheometer-explosion proof

Figure 13. Specialized rheometers for rheological characterization of energetic formulations: a) Off-line slit rheometer with adjustable gap and filling station b) On-line slit rheometer with adjustable gap c) Squeeze flow rheometer- explosion proof version used in the energetics manufacturing industry.

and is in use at ATK Systems at Radford, for the characterization of gun propellants (this explosion-proof rheometer is again available from MPR Inc. of Hackensack, NJ) [57]. This type of rheometer is especially important in the characterization of the energetic materials as they are being processed and allows quantitative data to be generated.

Ramifications

The rheology data can only be generated if the rheometers are adequate for the characterization of energetic materials. Besides the obvious safety aspects that need to be considered (need to be explosion proof etc.), such rheometers also need to accommodate the wall slip, flow instability, and viscoplasticity of the energetic formulations to provide parameters of wall slip and viscoplasticity, which can be used in day-to-day quality control as well as providing parameters to allow simulation and design of tooling upon the solution of the conservation equations [58].

Conclusions

The characterization of the rheological behavior of energetic formulations present special challenges including wall slip, viscoplasticity, changing nature of the microstructure of the energetic suspension during preparation of the samples for rheological characterization and processing, air entrainment, the migration of particles, and the filtration of the binder to lead to demixing of the ingredients, the development of flow instabilities which render the flow time-dependent. The understanding and the characterization of such factors not only allow accurate rheology data to be generated but also provide the basic wherewithal necessary to enable the safety assurance, optimization, and quality control for the manufacturing operation for the energetic formulation.

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