Twin Screw Extrusion Processing of Energetic Materials

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ABSTRACT

The continuous processing of various energetic formulations is a challenge that requires the apriori characterization of the rheological behavior of the energetic formulation, mathematical modeling of the process, a good understanding of the structure development aspects and ways of verifying and characterization of microstructural distributions of energetic grains. These steps facilitate the generation of a detailed understanding of the flow and deformation behavior and the thermo-mechanical history that the energetic material will experience in the continuous processor. Such work, done prior to the actual continuous processing of the live materials, eliminates or minimizes the subsequent risk associated with the precarious trial and error procedures and experimental studies that are prevalent in other industries. However, the determination of the physical, rheological and processability characteristics of energetic formulations under various relevant sets of operating conditions of the extrusion process, the development, the fabrication and the installation of instrumentation for the characterization of specific material properties, the data analysis and the determination of material parameters, and the mathematical modeling of the thermo-mechanical history of the energetic formulations in the extruder and the die are not straightforward. The challenges include the slip at the wall of the viscoplastic suspensions, possible segregation of the binder and the migration of the particles in the transverse to flow direction, the important role played by air, the formation of flow instabilities and associated surface and bulk distortions of extrudates, the formation of hot spots, the important role played by the distributive and dispersive mixing of the ingredients as affected by the deformation history and the specific energy input in the extruder. The quantitative characterizations of the degree of mixedness of live propellants and explosives and the particle size and the defect density distributions of the crystalline particles of the energetic materials are also necessary to link the processing history in the extruder to the mechanical and burn rate properties of the processed energetic grains. In this paper some of these challenges are reviewed to contribute towards the improved safety of the twin screw extrusion process and better control of the quality of the energetic grains.

Key words: Extrusion, energetics, twin screw, continuous processing
I. INTRODUCTION:

Various Government organizations and defense contractors are engaged in the development of advanced energetic compositions for use in a wide variety of applications. Many of these formulations are intended to be processed via continuous processing techniques, most commonly the fully intermeshing co-rotating twin screw extrusion process. Continuous processing allows better control of the microstructure and hence the consistency of the energetic product in comparison to batch processes. The principal factor is the significantly greater surface to volume ratio of the continuous processor in comparison to the batch processor. However, the energetic materials involve very sensitive ingredients, the processability of which in a suspension is always precarious and require strict exposure limits in temperature, residence time and stress. Furthermore, the scale up of the processing operation is also not straightforward due to the rheological behavior of the compositions and the processability and the physical properties of the energetic formulations being principally affected by the very high degree of solid fill of the formulations, which by design needs to approach the maximum packing fraction of the solid phase. The mathematical modeling techniques for continuous processing need to take into consideration their extremely high degree of fill which imparts various solid-like characteristics to the energetic formulations including the development of viscoplasticity and wall slip over and above various phenomena specific to highly filled formulations, including the interlocking of the particles, migration of the binder in the direction of the pressure gradient, and the extensive roles played by the entrained air etc.

In the following a summary of what we have learned is reviewed and typical results are presented.

II. RHEOLOGICAL BEHAVIOR

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). The Couette flow involves the migration of the solid particles and the resulting concentration gradients (12, 13).

Suspensions which are filled at solid loading levels close to the maximum packing fraction of their solid phase, present special challenges in the characterization of their rheological behavior and mathematical analyses of their continuous processability. As shown by Kalyon and co-workers, the behavior of such materials are subject to wall slip in both rotational and capillary rheometers (14, 15) and flow instabilities in die flows associated with 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 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).

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 isothermal (25a) and non-isothermal conditions (25b) and the twin screw extrusion flow (26).

In the following various important factors affecting the continuous processing and manufacturability of propellants and explosives will be discussed. These factors include their flow and deformation behavior involving wall slip, flow instabilities, air entrainment effects, and continuous processing.

Wall Slip

The characterization of the flow and deformation behavior of propellant and explosives is first and foremost complicated by the occurrence of wall slip. The wall slip behavior of a concentrated suspension consisting of sixty percent by volume of particles in an acrylonitrile terminated polybutadiene, PBAN, matrix is demonstrated in Figure 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 Figure 1. Upon the rotation of the top disk, discontinuities appear at both the top and bottom suspension/wall interfaces, suggesting 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 (Figure 2). The occurrence of 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 wall slip, the traditional method has been to change systematically the surface to volume ratio of the suspension and to determine the slip velocity from the slope of the apparent shear rate versus reciprocal diameter or gap height data collected at constant wall shear stress. In capillary flow this requires that the capillary diameter be changed while keeping the length/diameter ratio of the capillary a constant (27, 28).
This traditional technique of systematically changing the surface to volume ratio of the suspension during rheological characterization to indirectly determine the slip velocity is very labor intensive. As an alternative technique for determination of wall slip velocities in parallel disk torsional flows, the flow visualization technique illustrated in Figure 1 can be used. This technique allows the determination of the slip velocity and the true deformation rate 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, \( \tilde{V}_f \) as a function of time. The slip velocity at the wall, \( \tilde{U}_s \), can then be determined from:

\[
\tilde{U}_s = \tilde{V}_f - \tilde{V}_w
\]  

where \( \tilde{V}_w \) is the wall velocity.

Wall slip behavior is generally time dependent (29). With increasing duration of deformation, the deformation rate of the suspension decreases, while the shear stress and the wall slip velocity increase. Under typical conditions the steady state behavior is achieved at which the true deformation rate can only be about 1/5th of the imposed apparent shear rate. The ramifications include the time-dependence of the start-up flow in extrusion, and the decreasing of the shear rates and total stains which can be introduced into the suspension in the extruder upon the onset of slip.

The typical steady-state slip velocity at the wall versus wall shear stress behavior of energetic suspensions follows the Navier’s slip condition shown in Equation 2. The wall slip velocity, \( U_s \), versus wall shear stress, \( \tau_R \), data can be fitted by:

\[
U_s = \beta \tau_R
\]

where \( \beta \) 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 ASRM solid rocket fuel simulant (a suspension with 76.5 solids) the values of the Navier’s slip coefficient, \( \beta \) was determined to be \( 7.4 \times 10^{-4} \) mm/(Pa-s) at typical processing conditions (14, 15).

The true shear viscosity behavior of concentrated suspensions can then be determined upon the corrections for wall slip. With increasing capillary diameter, at constant capillary length/diameter ratio, the shear stress increases. For example for some solid rocket fuels the data indicate that the suspension flows as a plug above a wall shear stress value, whereas for some other energetic suspensions, the suspensions exhibit plug flow at wall shear stress values which are smaller than a critical shear stress value. In summary, various novel rheological characterization techniques need to be used to characterize wall slip and then use the data as part of the mathematical simulation effort. Applications of these techniques allow data to be corrected to generate the true rheology and also provide the interface condition i.e., slip velocity versus stress in extrusion and die flows.
Constitutive Equation

The most commonly used viscoplastic fluid model for concentrated suspensions is the Herschel-Bulkley fluid (30), which exhibits solid like behavior at shear stress values which are smaller than the yield stress value of the fluid in one-dimensional flow. However, for concentrated suspensions like energetic suspensions the conventional techniques of the characterization of viscoplasticity may generate misleading and incorrect results. The yield stress value of a suspension is generally determined by the extrapolation of the shear stress versus shear rate curve to the zero shear rate value and, thus, by the best fit of the data. However, our data indicate that the extrapolated yield stress value would have depended on the geometries of the rheometers employed and the wall slip behavior of the suspension. The yield stress is affected by wettability of the solids by the binder and increases with decreasing wettability.

Flow Instabilities During Processing and Flow of propellants and explosives

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. Such time-dependent demixing of the ingredients of the formulation of highly filled 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 as affected by dramatic demixing and pulverization of the energetic filler in the continuous processor.

Capillary flow experiments can be used to provide a better understanding of the flow instabilities of concentrated suspensions occurring in continuous processing operations (16, 31). 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 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. 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.

The apparent shear rate range in 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 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, 31). 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).
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 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 used during the analysis of the propellant used in the Advanced Shuttle program (ASRM) suggested that the critical apparent shear rate, below which flow instabilities prevail, decreases with increasing channel diameter. The migration of the particles in the transverse to the flow direction needs to be assessed also (12, 13, 32).

**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 (19, 33). 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 continuous processor in comparison to suspension samples collected from completely full sections of the continuous processor (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 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 (Figure 3).

**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 are intimately linked to the wall slip behavior of the material even for the pure polymer (34-36).
MATHEMATICAL MODELING OF EXTRUSION AND DIE FLOWS

This is a challenging numerical problem since unwinding of the channel cannot capture the full three-dimensional character of the flow and the three-dimensional character of the geometry needs to be conserved (37-44). The approach requires the full three-dimensional calculations to be carried-out over the entire flow channel. The flow in the extruder is unsteady since the flow domain changes as the kneading discs rotate. The inertia effects can be ignored, because of the highly viscous nature of propellants and explosives and the creeping nature of the resulting flow.

The equations of conservation of momentum and mass are:

\[ \nabla p = \nabla^2 \eta \dot{u} \]
\[ \nabla \cdot \dot{u} = 0 \]
\[ \dot{u} = \dot{u}(x, y, z; t) \]  

(3)

where \( p \) is the pressure, \( \dot{u} \) is the velocity, and \( t \) is the time, which determines the location of the flow domain.

An inherent difficulty in the simulation of flow in twin screw extruders is related to the specification of boundary conditions at the entrance and exit planes of the kneading discs. One can resolve this problem by using as boundary conditions at the entrance and exit planes, the velocity distributions obtained from the solution of the pseudo-three dimensional flow equations, which assume that velocity gradients in the axial direction are negligible. These boundary conditions will only ensure consistency of the solution to the problem.

One can employ the Penalty/Galerkin Finite Element Method in the discretization. In this method, the continuity equation is considered as a constraint on the equations of conservation of momentum, and the pressure, \( p \), is approximated by using a large positive number, \( \beta_p \) (penalty parameter):

\[ p = -\beta_p \eta \left( \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \right) \]  

(4)

When Equation 4 is substituted into Equation 3, the equations of momentum become:

\[ -\frac{\partial}{\partial x} \left[ \beta_p \eta \left( \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \right) \right] - \frac{\partial}{\partial y} \left( 2\eta \frac{\partial u_x}{\partial x} \right) - \frac{\partial}{\partial z} \left[ \eta \left( \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} \right) \right] \]

\[ -\frac{\partial}{\partial z} \left[ \eta \left( \frac{\partial u_y}{\partial z} + \frac{\partial u_z}{\partial x} \right) \right] = 0 \]  

(5)
\[- \frac{\partial}{\partial y} \left[ \beta_p \eta \left( \frac{\partial u_x}{\partial x} + \frac{\partial u_y}{\partial y} + \frac{\partial u_z}{\partial z} \right) \right] - \frac{\partial}{\partial x} \left[ \eta \left( \frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} \right) \right] - \frac{\partial}{\partial y} \left( 2 \eta \frac{\partial u_y}{\partial y} \right) \]

\[- \frac{\partial}{\partial z} \left[ \eta \left( \frac{\partial u_y}{\partial z} + \frac{\partial u_z}{\partial y} \right) \right] = 0 \]

\[- \frac{\partial}{\partial z} \left[ \eta \left( \frac{\partial u_x}{\partial z} + \frac{\partial u_z}{\partial y} \right) \right] - \frac{\partial}{\partial x} \left[ \eta \left( \frac{\partial u_x}{\partial x} + \frac{\partial u_z}{\partial x} \right) \right] \]

\[- \frac{\partial}{\partial y} \left( 2 \eta \frac{\partial u_z}{\partial z} \right) = 0 \]  

The Finite Element Method can be employed to solve Equations 5-7. For complicated screw elements like the kneading discs, for each stagger angle the computational domain is described by the complete set of pairs of kneading discs with each pair divided into two sections of uniform thickness in the axial direction.

Applying the Galerkin's method to Equations 5-7 with the weighting function designated as \( N_e^j (x, y, z) \), the discretized equations take the matrix form:

\[ K \vec{x} = \vec{f} \]  

where \( K \) is the stiffness matrix and \( \vec{f} \) is a force vector formed by specific boundary conditions. The coordinates and the solutions in an element \( D_e \) are expressed through:

\[ \begin{pmatrix} x^e \\ y^e \\ z^e \end{pmatrix} = \sum_{j=1}^{Nod} \begin{pmatrix} x_j^e \\ y_j^e \\ z_j^e \end{pmatrix} N_e^j (m, q, s) \]  

\[ \begin{pmatrix} v_x^e \\ v_y^e \\ v_z^e \end{pmatrix} = \sum_{j=1}^{Nod} \begin{pmatrix} v_{xj}^e \\ v_{yj}^e \\ v_{zj}^e \end{pmatrix} N_e^j (m, q, s) \]

where \( m, q, \) and \( s \) are iso-parameters and \( Nod \) is the total number of nodes.

Typical results for the distributions in the z-velocity (velocity component in the direction of the main flow), the second invariant of the rate of deformation tensor, the magnitude of the stress tensor and the temperature distributions in the transverse to flow direction in a fully-intermeshing co-rotating twin screw extruder for a double base propellant are shown in Figures 4-7. Such
distributions need to be analyzed in detail to identify conditions of geometry and operating conditions that lead to precarious conditions for processing of the energetic material. Generally one searches for evidence for the formation of hot spots at which the temperature exceeds the decomposition temperature. Furthermore, one needs to determine residence times which exceed the typical decomposition times of the energetic material for a given temperature history using the particle tracking techniques which are described next.

**Tracking Technique**

Given the Eulerian velocity field, the trajectory \( \tilde{x} = \tilde{x}(\tilde{X}, t) \) of a fluid particle initially located at a point \( \tilde{X} \) is obtained from the solution of the ODE's:

\[
\begin{align*}
\frac{d\tilde{x}}{dt} &= \tilde{u}(\tilde{x}, t) \\
\tilde{x}(t = 0) &= \tilde{X}
\end{align*}
\]

This set of first order ODE's is solved using Euler's first order predictor-corrector method. The algorithm is:

\[
\begin{align*}
\tilde{x}_{n+1}^p &= \tilde{x}_n + \Delta t \tilde{u}(\tilde{x}_n, t_n) \\
\tilde{x}_{n+1}^c &= \tilde{x}_n + \frac{\Delta t}{2} \left[ \tilde{u}(\tilde{x}_{n+1}^p, t_{n+1}) + \tilde{u}(\tilde{x}_n, t_n) \right] \\
t_{n+1} &= t_n + \Delta t \\
\tilde{x}_0 &= \tilde{X} \\
t_0 &= 0
\end{align*}
\]

The residence time distribution function provides information on the distribution of the retention time of the material in the extruder and will be an important factor to determine the time-temperature history of the propellant and explosive in the extruder that will lead to a capability for pinpointing the conditions amenable to initiation. The residence time distributions in the extruder can be determined by integrating the Eulerian velocity field and obtaining the time it takes for individual melt particles to traverse the axial length of the extruder. The residence time so obtained can then be normalized by the mean residence time, which is the ratio of the total volume of the extruder available for flow to the volumetric flow rate. One observes that the deviation of the flow pattern from plug-like behavior and hence the breadth of the distribution increases as the stagger angle of the kneading discs used in the screw configuration decreases. Thus, the residence time distribution approaches the distribution of fully flighted regular screws as the stagger angle decreases. In general for all configurations, no particle seems to spend less than about 39 percent of the mean residence time in the extruder while the maximum retention time is less than 300 percent of the mean residence time. The lower the stagger angle, the longer are the tail portions of the distribution. The smaller stagger angles thus generate a broader distribution, which include both the relatively smaller residence times (channeling) and the longer
residence times (relative stagnation). This allows one to identify regions of stagnation, as well as potential 'pipe-line flow' regions where the material encounters the least resistance in its path through the extruder. The possibility of the existence of such 'pipe-line flows' appears to increase as the stagger angle decreases.

Such detailed mathematical modeling results provide the user detailed information on the thermo-mechanical history experienced by the propellant and explosive in the extruder. The stress distributions are used to determine the adequateness of dispersive mixing and investigate the possibility of particle attrition. Residence time distributions are used to identify pipeline flows and to investigate existence of stagnant regions and material degradation and premature curing (for thermosetting binders of the energetic formulation) in the extruder. Temperature and shear rate distributions of the propellant and explosive in the extruder are used to identify conditions that could lead into detonation (provided that the detonation characteristics of the propellant and explosive are known). Overall, the modeling of the extrusion process determines conditions, which are precarious, and the processing window in which acceptable propellant and explosive quality can be obtained.

MICROSTRUCTURAL ANALYSIS OF PROPELLANTS AND EXPLOSIVES

DEGREE OF MIXING

Background

One of the most challenging aspects of any mixing operation, where two or more identifiable components are brought together, is the characterization of the state of the mixture i.e., the degree of mixing or the "goodness" of mixing. 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.

Direct measurement techniques can provide detailed information on the process and the development of the microstructure of the composite. The simplest technique, which can be utilized to determine the mechanisms of mixing in a batch or continuous mixer, is the injection of a dye into a transparent fluid and then to follow the distribution and the interfacial area growth of the non-diffusive tracer.

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 (38) 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.

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, Iₓ, and the volume fraction or concentration, cₓ, 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 (µm) and varies linearly with concentration:

\[ \frac{I_1}{I_2} = \left( \frac{K_1}{K_2} \right) \frac{c_1}{c_2} \]  

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 (45-47). If one makes N measurements of concentration cᵢ of one of the components, then the mean concentration is:

\[ \bar{c} = \frac{1}{N} \sum_{i=1}^{N} c_i \]  

The variance, s², arising from the differences in the individual concentration, cᵢ, measurements, provides an index to quantitatively assess the degree of mixing. The variance is given by:

\[ s^2 = \frac{1}{(N-1)} \sum_{i=1}^{N} (c_i - \bar{c})^2 \]  

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

\[ s^2_0 = \bar{c}(1- \bar{c}) \]
If the variance is normalized to its maximum value the resulting parameter is called the intensity of segregation, $I_{seg}$.

$$I_{seg} = \frac{s^2}{s_0^2} = \frac{s^2}{s(1-s)}$$  \hspace{1cm} (17)

The intensity of segregation values range from unity, for completely segregated system, to zero, for a homogeneous system. A representative set of results of the quantitative x-ray diffraction analysis of relative volume fraction of the CAB binder, obtained by employing the relative integrated intensities of various ingredients are given in Figure 8. The statistical analysis of the results is also presented. The fours sets of specimens are associated with four different methods of processing of the same propellant. The results clearly indicate that the poorest degree of mixedness is achieved with the processing technique which uses a solvent and designated as “solv-ext” and the most homogeneous mixture is achieved with twin screw extrusion, designated as “TSE-1”. Such techniques can be used in the characterization of the microstructural distributions of energetic grains ensuing from the twin screw extrusion process and can be linked to the thermo-mechanical history in the twin screw extruder.

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**REFERENCES**


Demonstration of Apparent Wall Slip

60% vol. solids
Apparent wall slip in filled polymers

- Occurs on the basis of the formation of a particle-free apparent slip layer (Vand Layer)
- Alters apparent rheological behavior
- Needs to be incorporated into simulation as the wall boundary condition (Navier’s slip condition)
Air lubrication of the wall revealed
Figure 4
Figure 5
Figure 8

PLASTICIZED CAB VARIATION IN RDX FILLED CAB POLYMER
at 1 sq.mm scale

Plasticized CAB Volume Fraction, %

BATCH-1  TSE-1  TSE-2  SOLV-EXT

Figure 8