Processing of Nanoenergetics with a Fully-Functional Mini-Twin Screw Extruder*

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Abstract: A 7.5 mm twin screw extruder was developed specifically for the processing of energetic formulations involving nanoparticles. This novel twin screw extruder was demonstrated upon the processing of gamma and alpha alumina nanoparticles with a gel-based binder in the absence and presence of dispersing agents. Quantitative measures of degree of mixedness were obtained on samples processed with the twin screw extruder and with conventional processing methods using wide-angle x-ray and thermo gravimetric analysis and were corroborated with microscopy. Twin screw extrusion process generated more homogeneous mixtures of nanoparticles in comparison to those processed using conventional (intensive batch) mixing technologies and the use of surfactants further improved the homogeneity. With increasing homogeneity the suspension exhibited lower elasticity and shear viscosity. Overall, the results of this study emphasize the important roles played by the surface properties of rigid particles, the interfacial tension between the particles and the binder and the rheological behavior of the binder. In the absence of properly-selected binder and surfactant/s the processing of nanoparticles, without agglomeration, is difficult to achieve. This finding may be relevant to the evaluation of past efforts, which have aimed to improve the ultimate properties of energetic formulations by incorporating nanoparticles.

I. Introduction

The development of energetic formulations is a challenge and requires mixing and processing of ingredients at multiple scales. Typically at least three different mixing operations, i.e., hand mixing for the smallest scale followed by batch mixing using a pint size mixer and batch mixing in a gallon size mixer which are in turn followed by larger scales of mixing more relevant to manufacturing. Each scale of mixing and type of mixer generates a different degree of mixedness, and the associated structuring and burn rate/mechanical properties. Generally there is a mismatch in the properties of the energetic formulations going from one scale of mixing to another especially when nanoparticles are employed as part of formulation development/testing effort. The results could be misleading, generating time delays in development and cost overruns.

The incorporation of nanoparticles into formulations to produce nanocomposites and nanoenergetic materials is also a significant challenge. Some of the special challenges to produce energetic grains using nanometal powders (5-100nm range) by encapsulating them into various binders including energetic binders include:

- The need to conserve particle size of nanoparticles by preventing the formation of particle clusters.
- The need to select proper wetting agents and binders.
- The need to tailor the process to the rheological behavior of the dispersion.
- The need to work at a relatively very small processing rates (especially due to the very high cost of some of the newly-available nanoparticles).

- The need to generate very small specimens for further testing and validation for the development of new formulations without resorting to hand mixing or batch mixing at low volumes to generate very poorly mixed samples which cannot be scaled up.

Here a novel twin-screw extrusion processor was developed specifically to represent the smallest industrially relevant twin-screw extruder ever designed and constructed (1-3). This 7.5 mm co-rotating twin-screw extruder is equipped with various types of safety features, thus is differentiated from machinery available to civilian industries. It allows for the first time the development of energetic formulations by generating similar structures for different scales of development while retaining fully the ability to be scaled up to any continuous processing scale. A series of projects with inert materials were also carried out with the 7.5 mm twin screw extruder to test the safety features of this novel continuous processor, along with tests of its flexibility, limitations and ease of use. The processing of gel bases systems in conjunction with the novel 7.5 mm twin-screw extruder is presented along with the comparisons to the results of conventional intensive batch mixers for benchmarking of the results.

II. Experimental

II.1 Materials: The materials of the investigation were nanoparticles of α-Al_2O_3 and γ-Al_2O_3 incoporated into a hydrogel based binder. The hydrogel binder consists of carboxy methyl cellulose available from Hercules, incorporated with deionized water. The relevance of this binder stems from the understanding that most of the current energetic formulations involve nitrocellulose/NC solvent based systems which form a gel and act as the binder. Our previous work with solvated NC systems has revealed that the use of hydrogels would allow the

simulation of the rheology and processability behavior of such NC based energetic formulations. However, the dispersion of particles, especially nanoparticles, pose difficult to overcome challenges when gels are used as the binders. Here nanoparticles of alumina are mixed into a hydrogel binder. The rheological behavior of the resulting suspensions as well as the quantitative measures of the degree of mixedness were characterized and compared for the batch and twin screw extruded suspensions. Specifically, the degree of mixedness analysis carried out using wide-angle x-ray diffraction and thermo gravimetric analysis of the twin screw extruded samples were compared and contrasted with the batch mixed specimens of the CMC hydrogel- nano alumina system. The SEM and TEM micrographs and optical micrographs were also used to collaborate the findings of the WAXD and TGA analysis.

Nanoparticles: The nanoparticles of the suspensions processed in the twin screw extruder consisted of two types of alumina, i.e., α-Al_2O_3 and γ-Al_2O_3. The nanoparticles of γ-Al_2O_3 were received from Inframat Advanced Materials, LLC, CT., and USA and are reported to have a particle size of 40 nm. SEM analysis of the γ-Al_2O_3 indicated that the particle sizes of γ-Al_2O_3 are in the 10- 100 nm range. The gamma alumina nanoparticles appear to be of near-spherical in shape. The α-Al_2O_3 nanoparticles were also received from Inframat Avanced Materials, LLC, CT. The reported mean particle size is 150 nm. The particles exhibit relatively higher aspect ratios in comparison to γ-Al_2O_3 and the particles are flaky. The particle size distribution of the α-Al_2O_3 nanoparticles is broader than that of the γ-Al_2O_3.

The nanoparticles were also subjected to an x-ray analysis to determine their crystallite size using line broadening technique. This method determines the mean crystallite size of the particles using the Scherrer analysis. In this x-ray method the full width at half the maximum values of the

crystallite peaks associated with α-Al_2O_3 and γ-Al_2O_3 were measured and converted to crystallite sizes. The Sherrer analysis results from these diffraction patterns indicated that the crystallite sizes of α-Al_2O_3 and γ-Al_2O_3 were 13.6 nm and 44 nm, respectively.

Binder: The binder of the twin screw extrusion study was sodium carboxymethylcellulose mixed with deionized (DI) water. The typical linear viscoelastic properties of the hydrogel binder are shown in Figure 1. The hydrogel binder exhibits the typical behavior of a gel with frequency independent values of the storage, G', and loss moduli, G". The storage modulus, G', values much greater than the loss modulus G" values indicative of the relatively high elasticity of the gel network. As shown in Figure 1 the storage modulus G' values are in the 3.2x10^4 and 5.9x10^4 Pa range at 20 °C temperature which about one order of magnitude grater than the loss modulus, G" values. The higher storage modulus, G', values in comparison to the loss modulus, G", values are indicative of the solid-like nature of the hydrogel. The parallel nature of the storage and loss modulus values are indicative of the gel structure (see Figure 1).

Batch mixing: An intensive batch mixer/torque rheometer, manufactured by Haake Buchler Instruments, Inc., Saddle Brooke, NJ (EU-5V), with a mixing volume capacity of 60 ml, was used to mix the nanoparticles with the hydrogel binder at a temperature of 25 °C. Such intensive mixers are used partially full and a degree of fill of 60% was employed during the batch mixing. The torque, T, and hence the specific energy, E_s, input generated during the mixing process could be monitored during mixing as:

$$E_s = \frac{\Omega \int_0^{t_m} T dt}{M_t} \quad (1)$$

where Ω is the rotational speed of the blades of the mixer, t is time, M_t is the total weight of the mixture in the mixer and t_m is the duration of the batch mixing. In the batch mixing experiments the total duration of the mixing process, t_m, was varied systematically in order to assess the effects of the specific energy input, expanded during the mixing process. Since the adding order of ingredients affects the goodness of mixing, first Alumina particles were suspended in DI water and sonicated to stabilize the suspension. Later, CMC polymer was added to this suspension and premixed by hand to let the polymer interact with water and form a gel. This pre-mixed paste was fed into the mixer, while the blades continued to rotate at 25 rpm. The point that torque reaches a steady level is referred to as "time equal to zero". This premixed material was then subjected to an additional 5, 20 and 40 minutes of mixing at 25 rpm in the torque rheometer/batch mixer to generate the specimens which will be designated as "specimens batch mixed for additional 5, 25 and 45 minutes".

Twin screw extrusion:

Basic Design of the MPR 7.5 mm twin screw extruder

The MPR 7.5 mm twin screw extruder (1-3) shown in Figures 2 and 3 was used (overall view, the screws used and the barrel halved opened to reveal the twin screw in Figure 2 and the screws upon a dead stop during processing to reveal the degree of fill distribution in the mixer in Figure 3). Some of the critical dimensions of the extruder are: the bore diameters are 7.5mm and the

screws are 7.38mm in diameter, the clearance between the screw and the barrel is D/128 (+/- 60 microns), the centerline distance between screws is 6.27 mm, the screw root diameter of the screw is 5.04 mm and the tolerance on the screw diameter is +/- .5"/1000". The fully-intermeshing co-rotating twin screw extruder is designed with a slit die as an integral part of the assembly (Figure 2). The dimensions of the die are: width of 10mm, gap of 1 mm and length is 50.8mm including the converging flow section and 36.8mm long for the straight land section.

The assembly included two temperature control zones, one at the die, and the second for the extruder barrels. The machine is fitted with three thermocouples for controlling the metal temperature of the top and bottom barrel halves and the die assembly. The screw speed is controllable between zero RPM and 200 RPM. The barrels and screws are machined from a heat-treated alloy stainless steel and ferritic nitro carburized to reduce the potential of adhesive wear between the screws and the barrel bores. The drive is a ¼ HP motor, hydrostatic, 0-1100 RPM, 100% explosion proof. This is coupled through a parallel shaft speed reducer, 11.66 to 1 reduction ratio to give us a screw speed of 200 RPM when taking into account the speed increase, 2.166 to 1, through the ring and pinion gear set on the agitator shafts.

The screw configuration was designed through mathematical modeling of the mixer/extruder and die area. The screws are monolithic (Figure 2), that is, they are constructed from a solid piece of bar stock with no welds, joints, cracks or crevices for material to migrate into. The screw design consists of three sealed mixing and vacuum zones, as shown in Figure 2. The fully-flighted conveying/plasticization section (Section I) is sealed with a reverse fully-flighted element. As shown with mathematical modeling the screw elements need to be completely full to be able to generate the pressure necessary to force the binder of the suspension to go through

the reversely configured section, which follows the forwarding elements. As shown in Figure 3 this is indeed what was revealed when the extruder was brought to a dead stop and the distribution of the material in the extruder was investigated. The mixing of the nanoparticles into the hydrogel (Section II) is sealed with four pairs of 90 degree kneading discs. The screw is also expected to be completely full at the second kneading disc section and immediately preceding the set of kneading blocks (Figure 3) and at the fully-flighted section preceding the die. These were again the locations that experiments revealed to be completely full as expected, as shown in Figure 3. The imposition of vacuum and consequent devolatilization takes place in the section between the kneading disks and the die (Section III).

Data Acquisition and Control:

A PC based and field point capable data acquisition and process control system was used (Figure 4). The system is a state-of-the-art open architecture PC based system, and includes the instruments to monitor and control zone temperatures, product temperature, process pressure and screw speed. The software allows the remote running of the equipment. The field point technology also allows the data to be accessible remotely and the extruder to be run remotely (turn on, off, set the screw speed, set the temperatures of the oil circulating, using the remote Internet connections and also wireless.

There is one explosion proof pressure transducer and thermocouple combination at the converging section of the die inlet. There is one temperature control thermocouple in the die assembly. Two temperature control thermocouples are placed in the barrel, one in the upper, and one in the lower half. Temperature control is through the circulation of heat transfer

medium at desired temperature. An intrinsically safe tachometer pickup is located at the coupling to the parallel shaft reducer to monitor screw speed.

Feeding of the ingredients:

A number of options were tested for the feeding of the ingredients. The nanoparticles arrived in a water medium since they were completely oxidized. The CMC was initially in powder form. The loss in weight and volumetric feeders of K-Tron and Brabender (integrated to the MPR control system, Figure 4) were tested. Furthermore, a belt-driven system from Weigh-Ahead Inc. of Canada was also tested. The Brabender and the K-Tron units generated acceptable feed rate results. A miniaturized pump was used for the feeding of the nanoparticles in a water carrier (Figure 4).

Twin screw extrusion processing runs:

The pressure data were collected to determine the pressure drop at the die. The temperature of the material could be followed with the thermocouples as verified with the thermal imaging camera which was incorporated into the experimental set up. Such thermal images were collected at regular intervals to allow the following of the temperature history of the extrudate. The binder content of the extrudates were also determined to assure that the binder could be conserved in the extruder.

After each run, upon reaching a steady state, as revealed by the steady values of torque, pressure and temperature, a dead stop was made and the pictures of the distributions of the mixture in the extruder (the degree of fill distributions) were captured. Typical results are shown in Figure 3 and revealed that the locations at which completely full sections are expected on the basis of

mathematical modeling were indeed completely full (at and preceding the two kneading block/reverse screw sections and at the fully-flighed screw sections preceding the die).

Rheological Characterization:

Dynamic properties: The small-amplitude oscillatory shear flow was used for the characterization of the linear viscoelastic properties of the suspension samples as a function of time, strain and frequency. The Advanced Rheological Extended System (ARES) of Rheometric Scientific (currently TA Instruments) was used in conjunction with the 8 mm parallel disk fixtures for the small-amplitude oscillatory shear experiments. Considering that the gap between the plates was typically kept at 1 mm, the quantity of the suspension probed during the small-amplitude oscillatory shear experiments was around 70 mg.

Degree of Mixedness Analysis (measures of concentration distributions): The following analysis was used to characterize the statistics of the concentration distributions to provide a measure of the "degree of mixedness or mixing indices" of the graphite and the binder. If N measurements of the concentration, c_i, of one of the ingredients of the formulation are made, then the mean, $\bar{c}$, and the variance, s^2, of the concentration distribution of this ingredient are calculated from:

$$\bar{c} = \frac{1}{N}\sum_{i=1}^{N} c_i \qquad (2)$$

$$s^2 = \frac{1}{(N-1)} \sum_{i=1}^{N} \left(c_i - \bar{c}\right)^2 \qquad (3)$$

The difference between the mean concentration, $\bar{c}$ and the known overall concentration, ϕ, of an ingredient (minor or the major component) is indicative of the quality of the sampling technique (4-14). This difference between $\bar{c}$ and ϕ diminishes as the number N, of the characterized samples, increases. The measured concentration values of a component of the mixture depend also on the sample size (4-6, 14). These concentration values approach the overall concentration of the component in the mixture, ϕ, as the sample size or "the scale of the examination" is increased. On the other hand, as the scale of the examination is reduced the concentrations of the ingredients would deviate significantly from their mean values and in the limit the variance of the concentrations measured would reach the variance of a segregated sample (4- 14).

The variance s^2, arising from the distributions of the individual concentration values, i.e., c_i measurements, provides the most basic measure of the concentration homogeneity of a mixture (9). Thus, the determination of the statistics of the extent to which the concentration values at various regions of the volume of the mixture differ from the mean concentration can be used as an index to quantitatively assess the "degree of mixedness" (11).

A small variance value would suggest that the mixture approaches the behavior of a homogeneous system, where most of the samples yield concentration c_i values that are approaching the mean concentration, $\bar{c}$. On the other hand, if the components of a mixture are

completely segregated, the maximum variance occurs. The value of the maximum variance (or the square of the between-sample standard deviation) for a completely segregated system can be defined by assuming that the samples are taken from either one component or the other without crossing a boundary (10, 11):

$$s_0^2 = \bar{c}\left(1-\bar{c}\right) \tag{4}$$

On the other hand, the most ideal state of random mixing possible would be achieved when the variance of the concentrations of the targeted ingredient sampled from different locations in the mixture would reach the variance of the binomial distribution. The variance for the binomial distribution is given as (9, 10):

$$S_r^2 = \frac{\overline{C}(1-\overline{C})}{n} \tag{5}$$

where S_r^2 is the variance of a random mixture determined on the basis of the binomial distribution and n is the number of particles in the sample, with each particle belonging to either the minor or the major component. As the number of particles in a mixture, n, increases the variance of the binomial distribution would approach zero.

The variance of the distribution of the concentrations of a given ingredient can be normalized with its maximum value and the resulting parameter provides a measure of the degree of mixedness, i.e., one possible mixing index for that particular ingredient. This parameter, s^2/s_0^2

would be equal to one for completely segregated ingredients and would decrease towards zero as the homogeneity of the mixture improves. Other definitions of mixing indices can be derived from the concentration distributions, the mean composition, the sample weight and the particle size distributions of the components (10). Various factors might affect the calculated mixing indices. For example, the mixing indices show an increase with a decrease in the amount of the minor phase (10). Sample size (4, 10) and the number of samples analyzed also affect the values of the mixing indices.

For this study the following measure of the degree of mixedness, i.e., mixing index, which is based on the standard deviation of the distribution of the concentration of one of the ingredients of the formulation over the standard deviation of the completely segregated sample for the same ingredient, was used. This mixing index would exhibit a value of zero for a completely segregated sample and its value would approach one for a completely random distribution of the concentrations of its ingredients.

$$\text{Mixing Index} = 1 - \frac{s}{s_0} \qquad (6)$$

Wide-Angle X-Ray Diffraction (WXRD): Diffraction patterns can be analyzed quantitatively, because the intensity from a particular phase in a mixture of phases depends on the concentration of that phase in the mixture. However, the relation between the integrated intensity I_x and the volume fraction ϕ_x of a phase is nonlinear, because the diffracted intensity depends strongly on the absorption coefficient of the mixture, μ_m, which itself depends on the

concentration. For a two-phase material, (with absorption coefficients μ_1 and μ_2 for the individual phases) the absorption coefficient for the mixture becomes (4-8):

$$\mu_m = \phi_1 \mu_1 + \phi_2 \mu_2 \tag{7}$$

The integrated intensity from phase 1 is then given by:

$$I_1 = K_1 \phi_1 / \mu_m \tag{8}$$

where K_1 is a constant that depends on the material and the incident beam used, but not on the concentration. The ratio of intensities from phases 1 and 2, however, is independent of μ_m and varies linearly with concentration (4):

$$I_1 / I_2 = (K_1 / K_2) \phi_1 / \phi_2 \tag{9}$$

The intensity values associated with the amorphous phase and the nanoparticles were normalized with the total intensity values and the variance values of these ratios were obtained. These variance values are equivalent to the variances of the distributions of the concentrations of the amorphous binder phase and nanoparticles, respectively.

A Rotaflex (rotating anode) RTP300RC x-ray diffractometer by Rigaku was used for small beam size scans at a fixed voltage of 40 kV and current of 80 mA. Samples were run at a scanning speed of 0.5 degree per minute, using a sampling width of 0.02°, and within the Bragg angle, 2θ

range of 13-50°. The x-ray probe had 1.5mm diameter (1.18 mm2) at a Bragg angle, 2θ, of 90 degrees.

Typical x-ray diffraction pattern of the composite, i.e., the typical intensity versus the Bragg angle data is shown in Figure 5. The deconvolution of the diffraction pattern to separate the contributions of its ingredients was made possible upon the identifications of the peaks, which are associated with the pure ingredients, i.e., the alumina nanoparticles and the CMC hydrogel binder as shown in Figure 5. The mixing indices were calculated on the basis of the variance values of the ratio of the intensity of the γ-Al_2O_3 and the intensity of the amorphous over the total intensity, i.e., $I_{\gamma\text{-}Al2O3} / I_T$ or $I_{Amorph.}/ I_T$, respectively. Degree of mixedness was calculated by using same statistical and theoretical approach with the previous work (4, 7).

Thermo Gravimetric Analysis (TGA): A TA Instruments Thermo Gravimetric Analyzer, Q50, was used for the characterization of the decomposition of the individual components and the mixtures as a function of temperature. The Thermo Gravimetric Analyzer measures the rate of weight change of a specimen as a function of increasing temperature under a controlled inert gas environment. In TGA the sample size was around 2 mg.

Each specimen was scanned from ambient to 700 °C with a heating rate of 15 °C/min (Figure 6). Individual runs with just the CMC and the nanoparticles separately were also carried out. TGA and DSC analysis of pure CMC revealed that the CMC loses its moisture around 100 °C and it starts decomposing partially around 215 °C. Decomposition continues at decreasing rates until 700 °C. However, CMC does not completely decompose and leaves a residue of about 33-34%.

The CMC concentration for different mixture samples could be determined by using a calibration curve. To be able to generate the calibration curve; three different mixtures with CMC volume fractions of 0.25, 0.27 and 0.29 (as measured in dry samples, i.e., upon the removal

of the water from the mixture) were used. These samples with known concentrations were run under the same conditions in the temperature range between 25 °C to 700 °C. TGA and DSC analysis of pure nano γ-Al_2O_3 indicated that the nano γ-Al_2O_3 only loses its moisture around 100 °C and this amount, depending on the environments relative humidity, changes between 1 to 2%. Mixing indices were also calculated from the results of the thermo gravimetric analysis experiments by following Equations (2-6) and compared with the mixing indices obtained with wide-angle x-ray diffraction.

III. Results and Discussion

Rheology

The typical small-amplitude oscillatory shear behavior of the suspensions (with γ-Al_2O_3) is shown in Figures 7 and 8. The storage and loss modulus, and the magnitude of complex viscosity values of the suspension samples prepared with the twin screw extrusion process are significantly smaller than those processed with the conventional intensive batch processing method. Generally the reductions of the elasticity and the shear viscosity of a suspension occur when better distribution and dispersion of the phases are achieved (better concentration homogeneity and a reduction of the particle agglomerates) (12-14).

Degree of mixedness analysis

The distributions of the ratios of the intensities arising from the gamma alumina nanoparticles over the total intensity obtained with the wide angle x-ray diffraction method are shown in Figure 9. The broader the variation of the intensity ratios around the mean the poorer is the homogeneity of the concentrations of the gamma alumina nanoparticles versus the gel binder. According to these results, as also suggested by the dynamic properties, more homogeneous mixtures of γ-Al_2O_3 could be obtained with the twin screw extrusion process in comparison to the batch mixing process.

The concentration distributions for the batch and twin screw extruded samples as obtained with x-ray diffraction and using the TGA method indicate that the degree of mixedness, MI, values are indeed greater for the suspensions processed with twin screw extrusion versus those prepared with the conventional batch processing method suggesting that a better concentration homogeneity of the γ-Al_2O_3 nanoparticles could be achieved with the twin screw extrusion process in comparison to the batch process. The degree of mixing value for the twin screw extrusion product is 0.98 versus 0.93 obtained for the degree of mixing for the batch mixed product of γ-Al_2O_3 nanoparticles in the hydrogel binder employing x-ray diffraction. The degree of mixedness values of γ-Al_2O_3 nanoparticles were also determined with the TGA method to verify the findings from the x-ray method (Figure 9). The distributions of the concentration of alumina nanoparticles in the binder as obtained with the TGA method are shown in Figure 10. Overall, the TGA results also validate the findings of the x-ray method for γ-Al_2O_3. The variation of the concentrations of γ-Al_2O_3 is much broader indicating a poorer state of homogeneity of the γ-Al_2O_3 nanoparticles upon batch mixing in comparison to the twin screw extrusion based dispersion of the γ-Al_2O_3 nanoparticles. The degree of mixedness values for γ-Al_2O_3 are 0.9 for the batch mixed samples and 0.95 for the twin screw extruded samples (1 represents a perfectly homogeneous mixture and 0 represents a segregated sample with no intermixing of the ingredients) with the values corroborating the degree of mixedness data collected with the x-ray diffraction method.

Microscopy

Overall, the better distribution and smaller cluster sizes of the γ-Al_2O_3 suspensions processed with twin screw extrusion could be clearly seen under polarized microscopy as shown in Figure

10. The much better distribution of the phases is clearly indicated in the comparison shown in Figure 10.

The micrographs and the x-ray plus the TGA results indicate that in spite of the much better homogeneity achieved with the twin screw extrusion of the nanoparticles with the hydrogel binder the particles remain as clusters (at reduced domain sizes upon twin screw extrusion). This is shown further in the typical SEM micrograph in Figure 11. Both the alpha and gamma alumina nanoparticles appear as clusters not coated individually by the binder and clearly identified interfaces forming between the nanoparticles clusters and the CMC binder. The cluster formation aspect of the nanoparticles is shown further in Figures 12 and 13 where micrographs obtained with transmission electron microscopy are shown. The TEM micrographs clearly indicate that some of the nanoparticles form floccules, which have significantly reduced surface to volume ratios in comparison to those of the individual nanoparticles.

These results do explain the main challenge in being able to use nanoparticles in their formulations without generating clusters that cannot be broken down. In previous studies Greenberg et al. (15, 16) have investigated the coating of energetic particles with the binder, which was found to be critical in the development of important properties like sensitivity. Although twin screw extrusion does help in better distributing and dispersing of the nanoparticles clusters and reducing the size of the cluster domains the use of the proper binder and surfactants to allow the binder to wet properly the surfaces of the nanoparticles and separate them from each other appears to be critical.

IV. Conclusions:

This study has demonstrated some of the challenges associated with the dispersion of nanoparticles in energetic formulation. The conclusions are summarized as:

1. The incorporation of nanoparticles into gel-like binders commonly used in various energetic formulations has been explored using a novel twin screw extruder specifically designed and built to handle nanoparticles and energetic materials at relatively low flow rates.
2. The twin screw extrusion process is shown to have various inherent advantages including the small size of the processed material within the confines of the processor at any given time, ability to remove the air content during the process, the ability to shape the formulation as part of the process, the higher surface to volume ratio to give rise to better temperature control, and the better dispersion of the nanoparticles in the binder matrix.
3. However, the adequate dispersion of the nanoparticles in energetic formulations is not a simple task regardless of which process is used, if the formulation does not allow for the proper wetting of the nanoparticles by the binder. If the binder and the surfactants are not selected properly the nanoparticles will remain in cluster domains. The sizes of the cluster domains can be reduced but are not likely to be completely eliminated alone on the basis of the by the use of the twin screw extrusion technology.
4. The use of surfactants has been successfully demonstrated to enable better dispersion of the nanoparticles.
5. The availability of this novel mini twin screw extruder will for the first time allow the testing of binders and surfactants aiming to generate realistic mixtures that can be scaled up into manufacturing scale.

6. The task of development of formulations will be significantly improved since the mini extruder will eliminate the need to mix ingredients by hand or with a pint sized batch mixers and eliminate the formation of poor degrees of mixedness which are likely to terminate some promising programs and eliminate efforts the results of which cannot be scaled up to the manufacturing stage.

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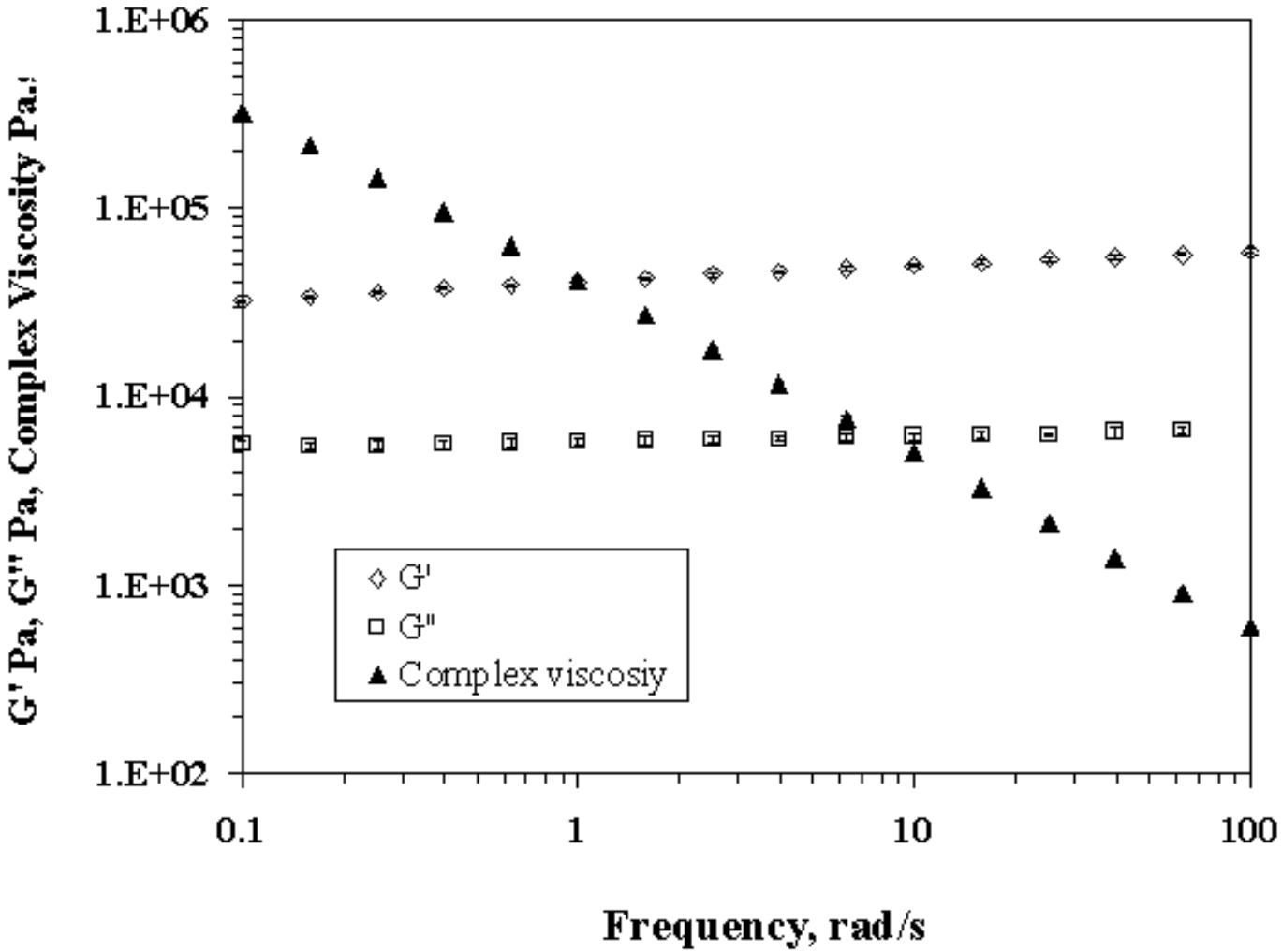
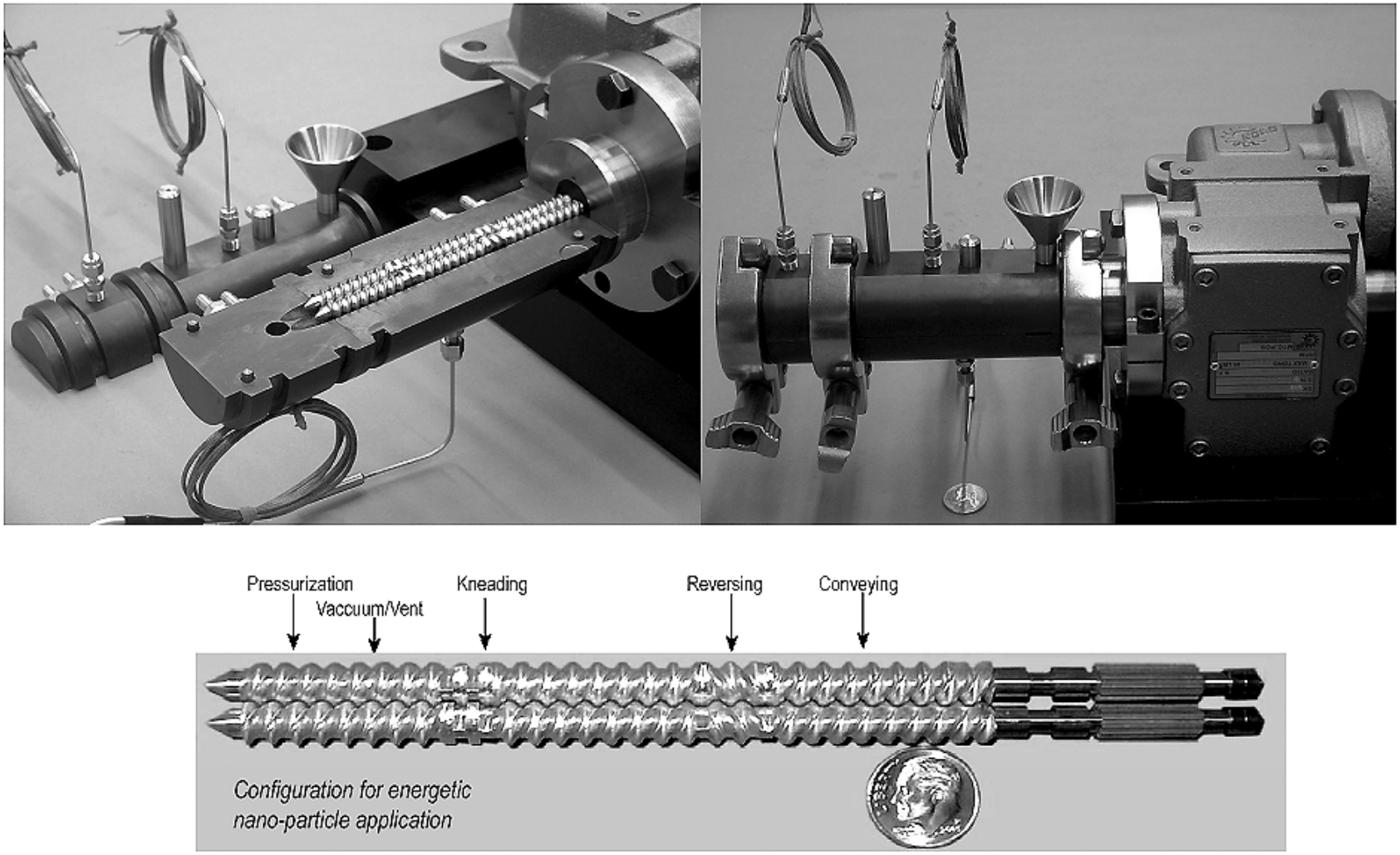
List of figures:



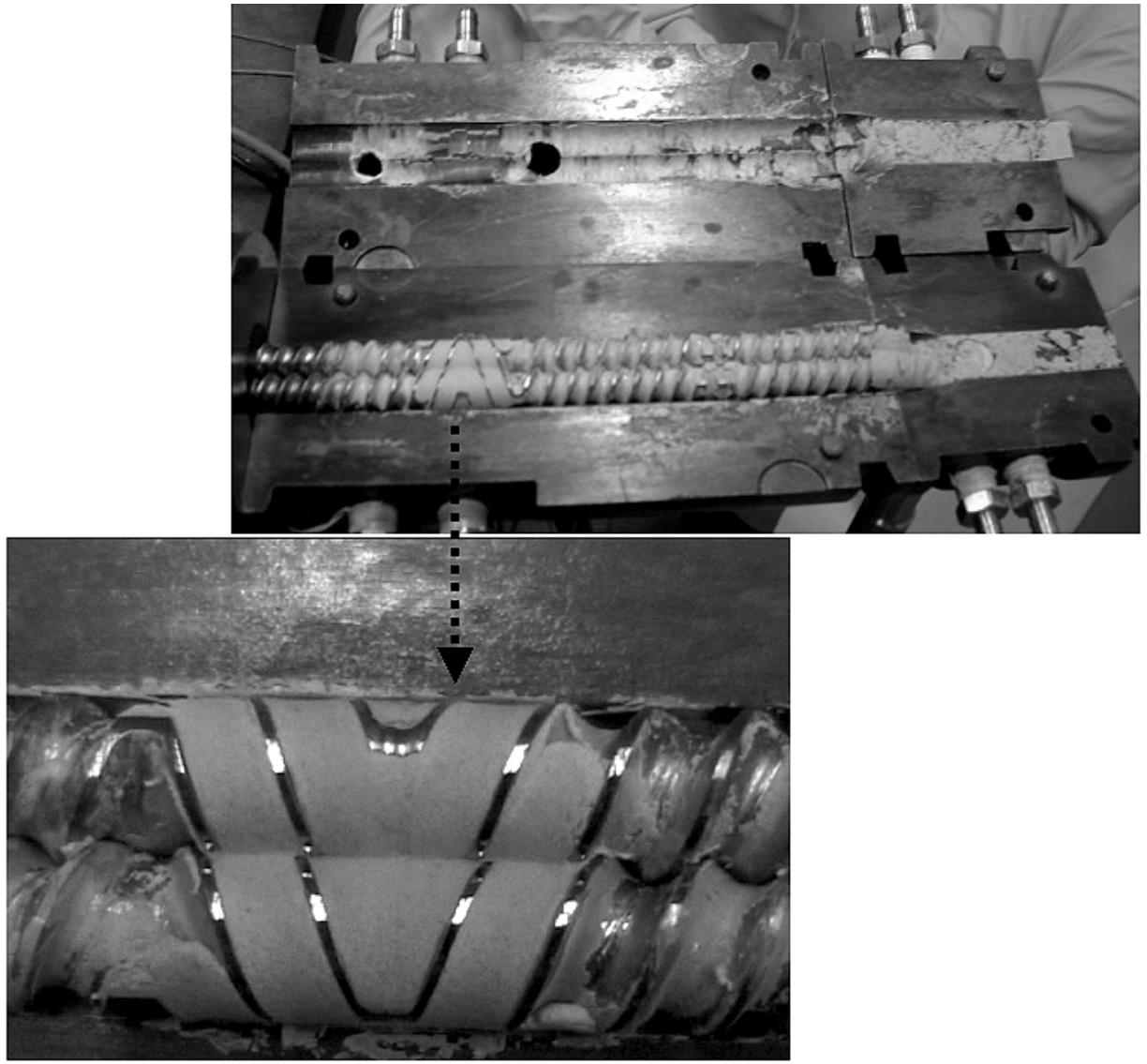
Typical dynamic properties of gel binder

Figure 1



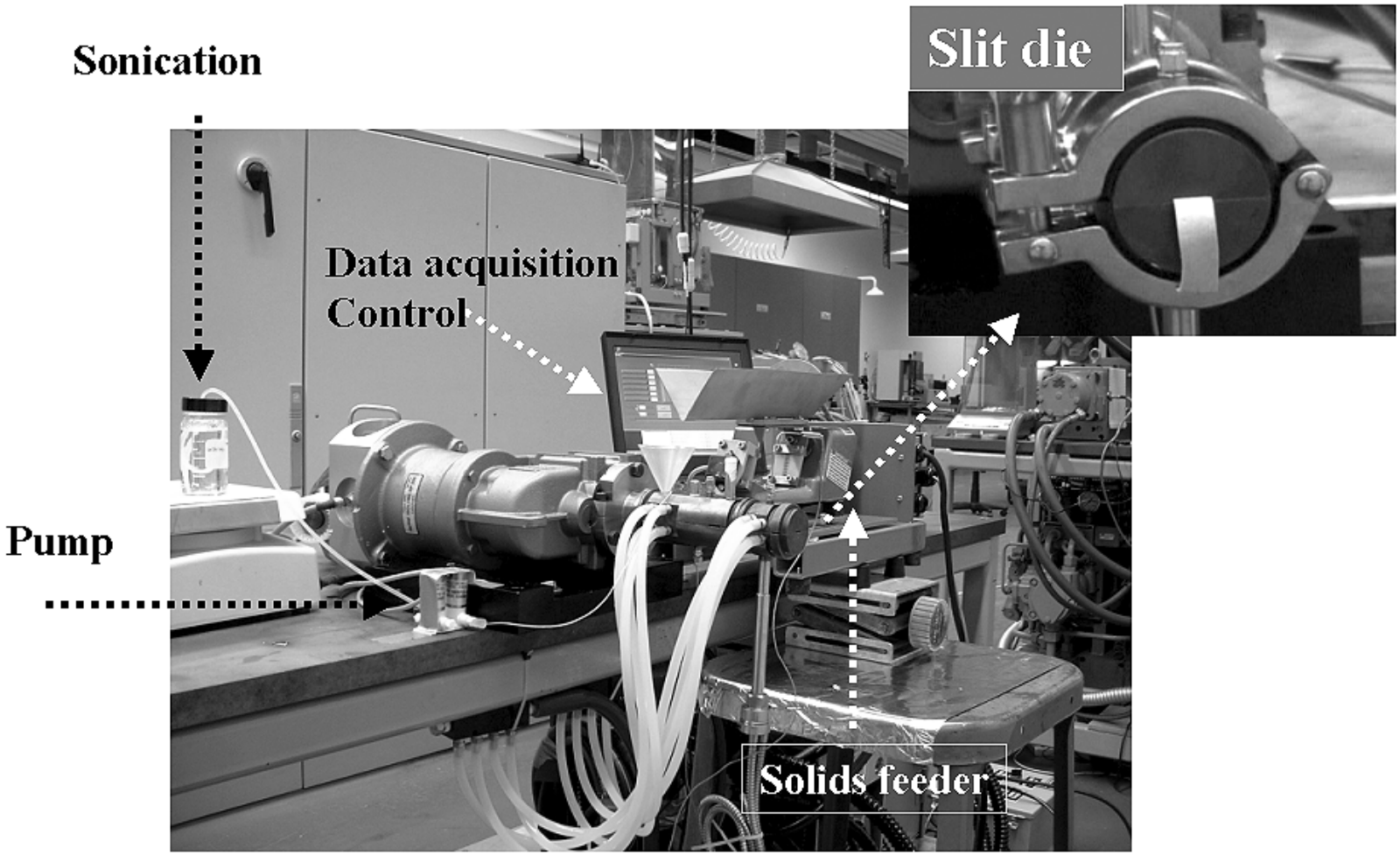
Twin screw extruder specifically designed and built for incorporating nanoparticles.

Figure 2



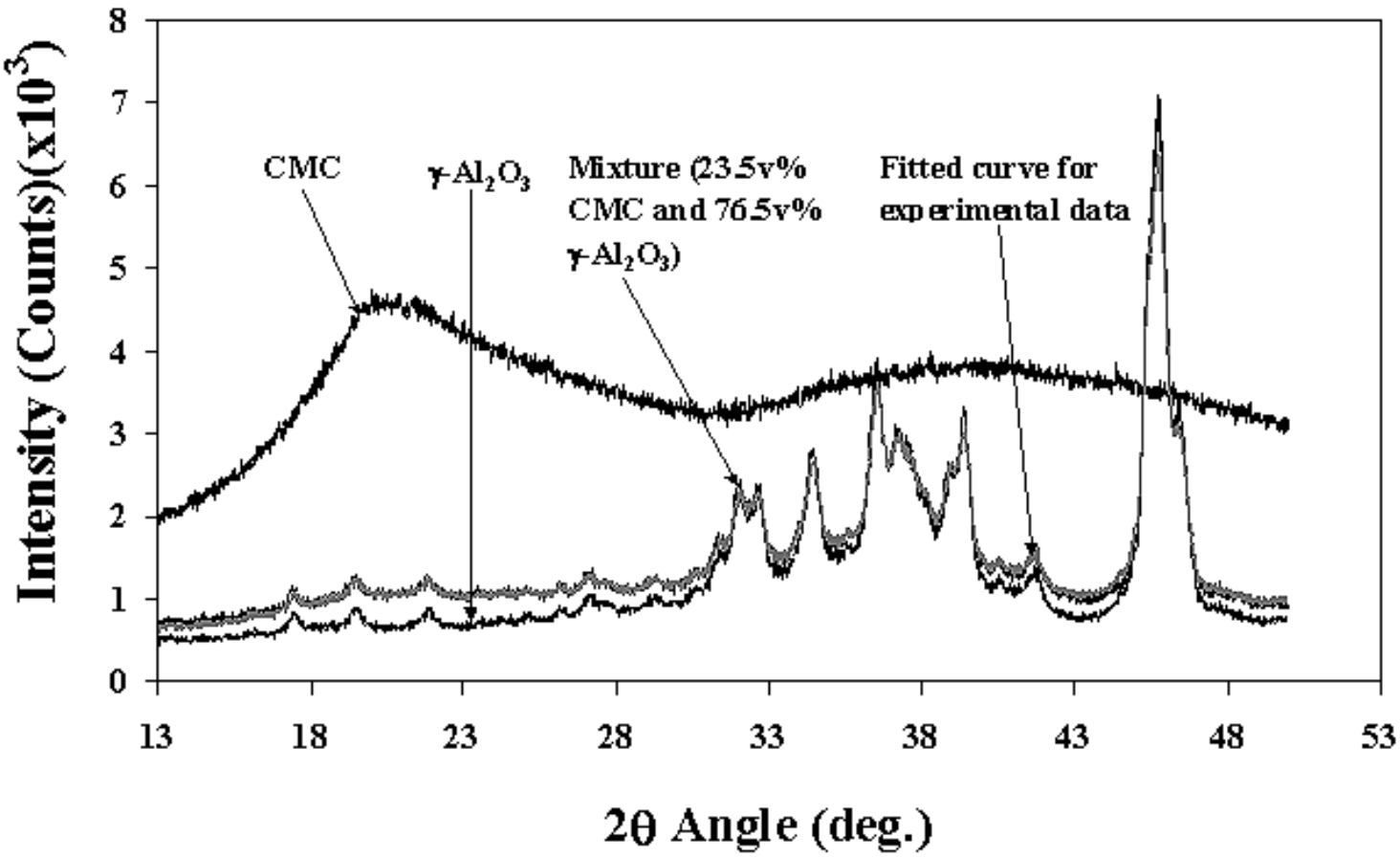
The typical degree of fill distributions in the twin screw extruder upon a dead stop.

Figure 3



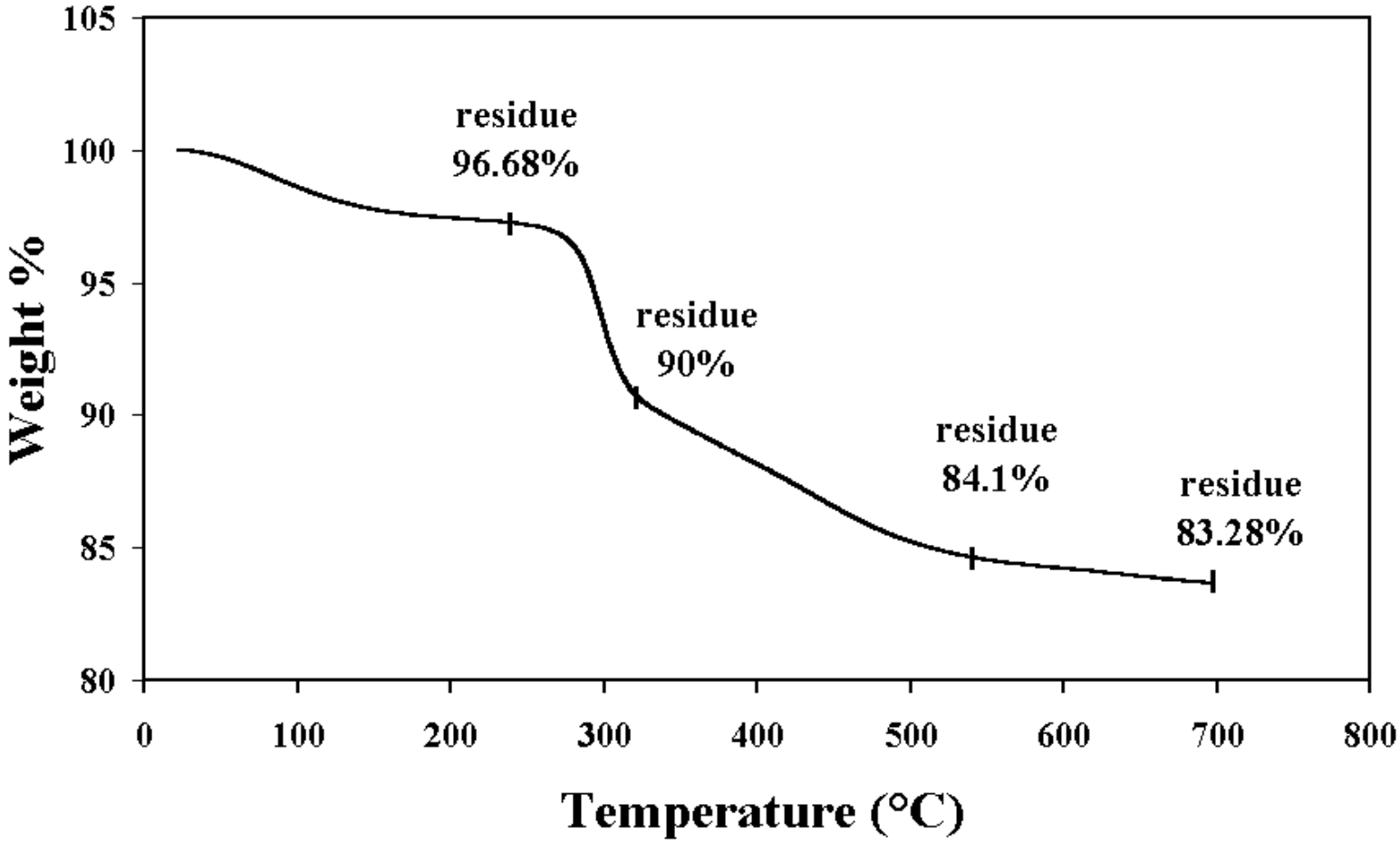
The auxiliaries of the twin screw extruder specifically designed and built for incorporating nanoparticles

Figure 4



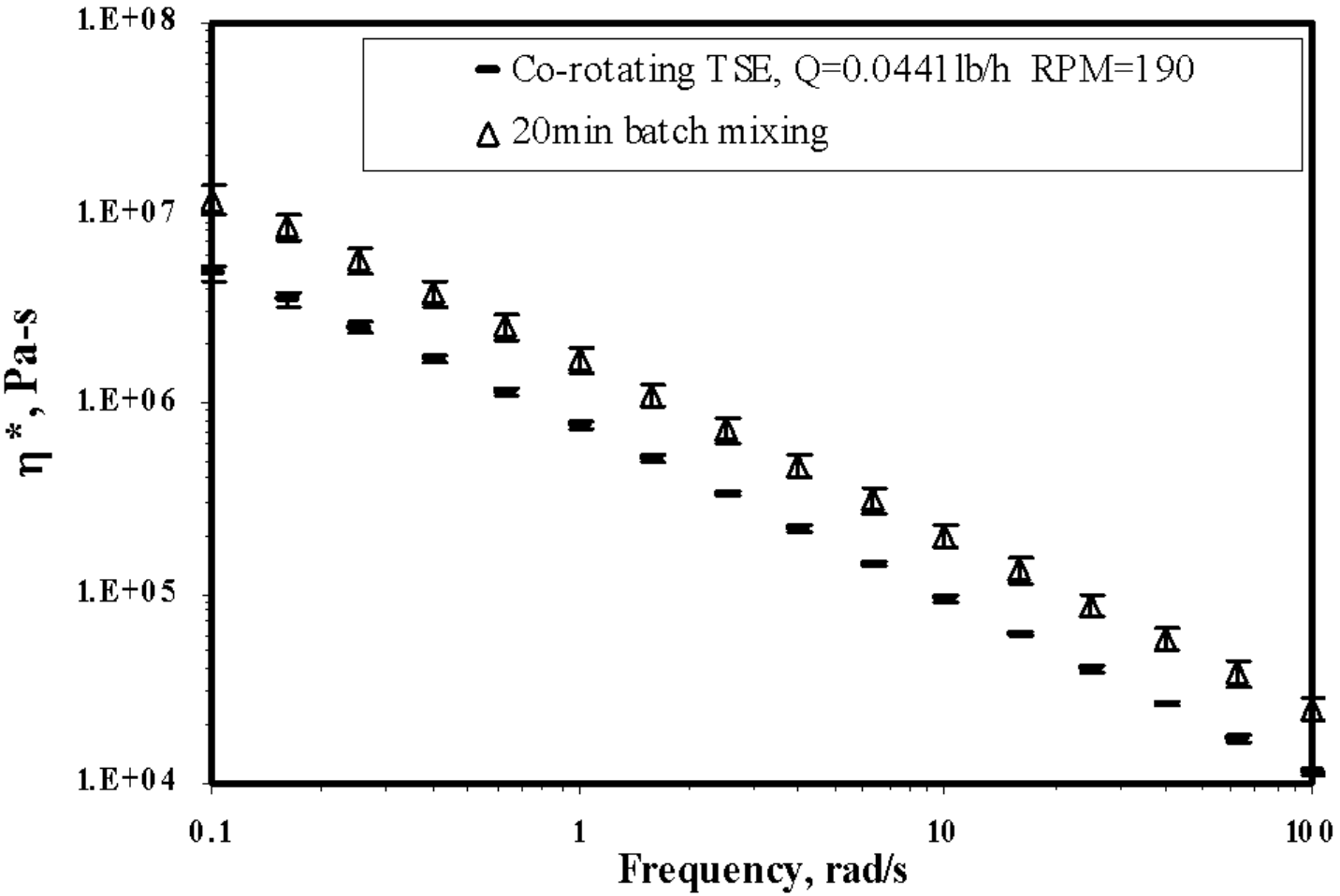
Typical x-ray diffraction patterns of the simulant formulation and its various ingredients.

Figure 5



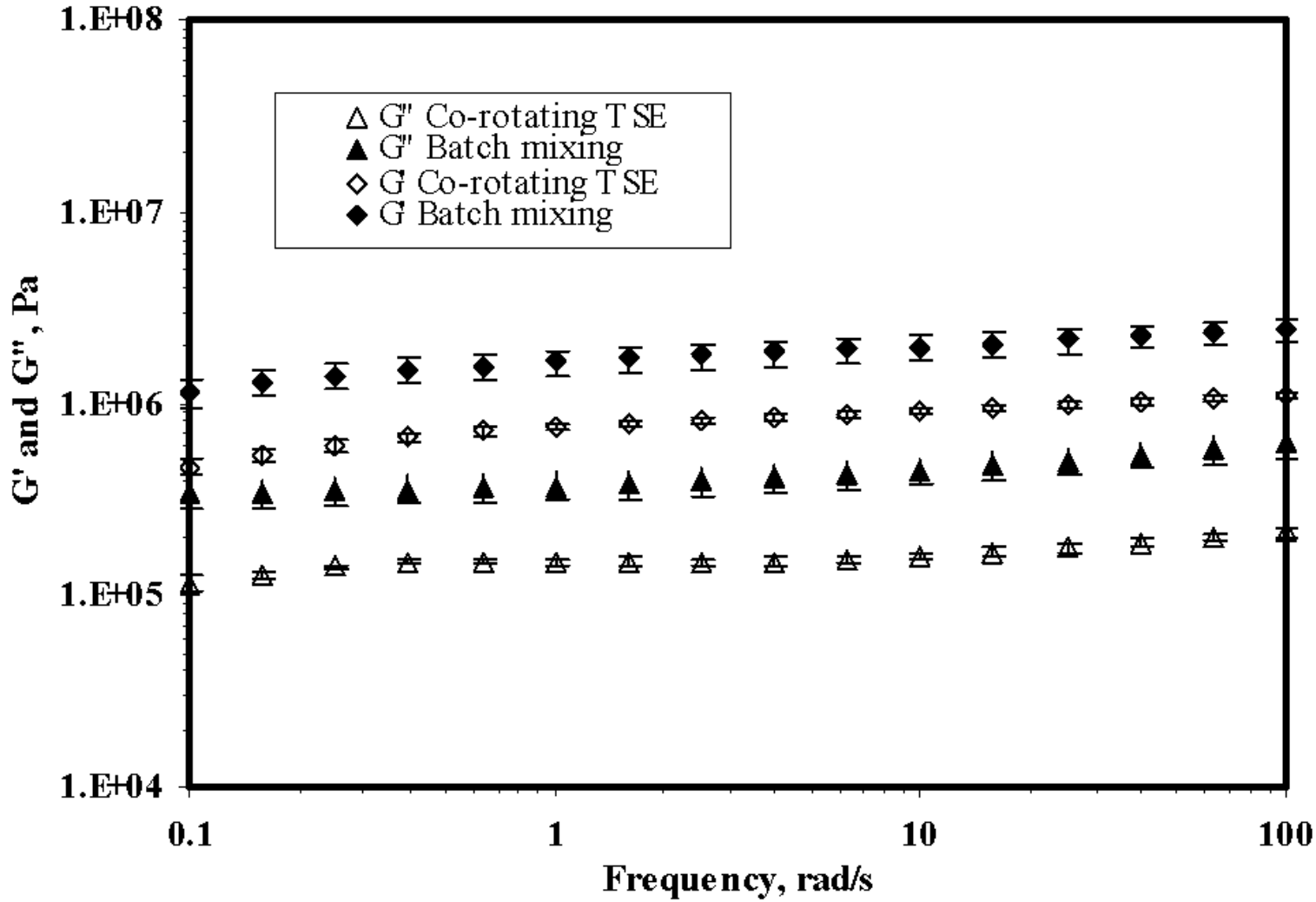
Typical thermo-gravimetric analysis results of the simulant formulation.

Figure 6



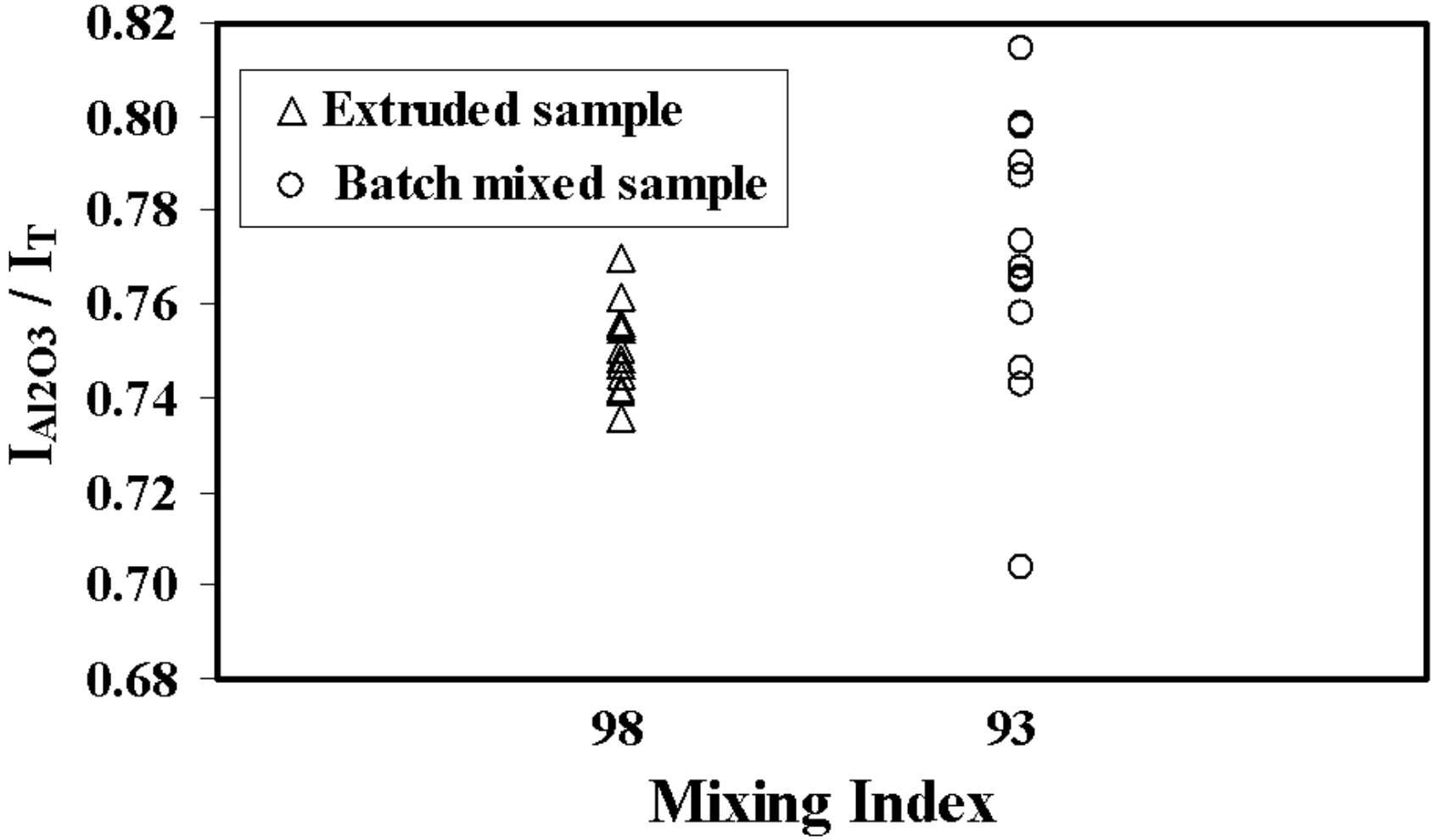
Confidence intervals of the magnitude of complex viscosity, η*, data for mixtures prepared with conventional and twin screw extrusion processes

Figure 7



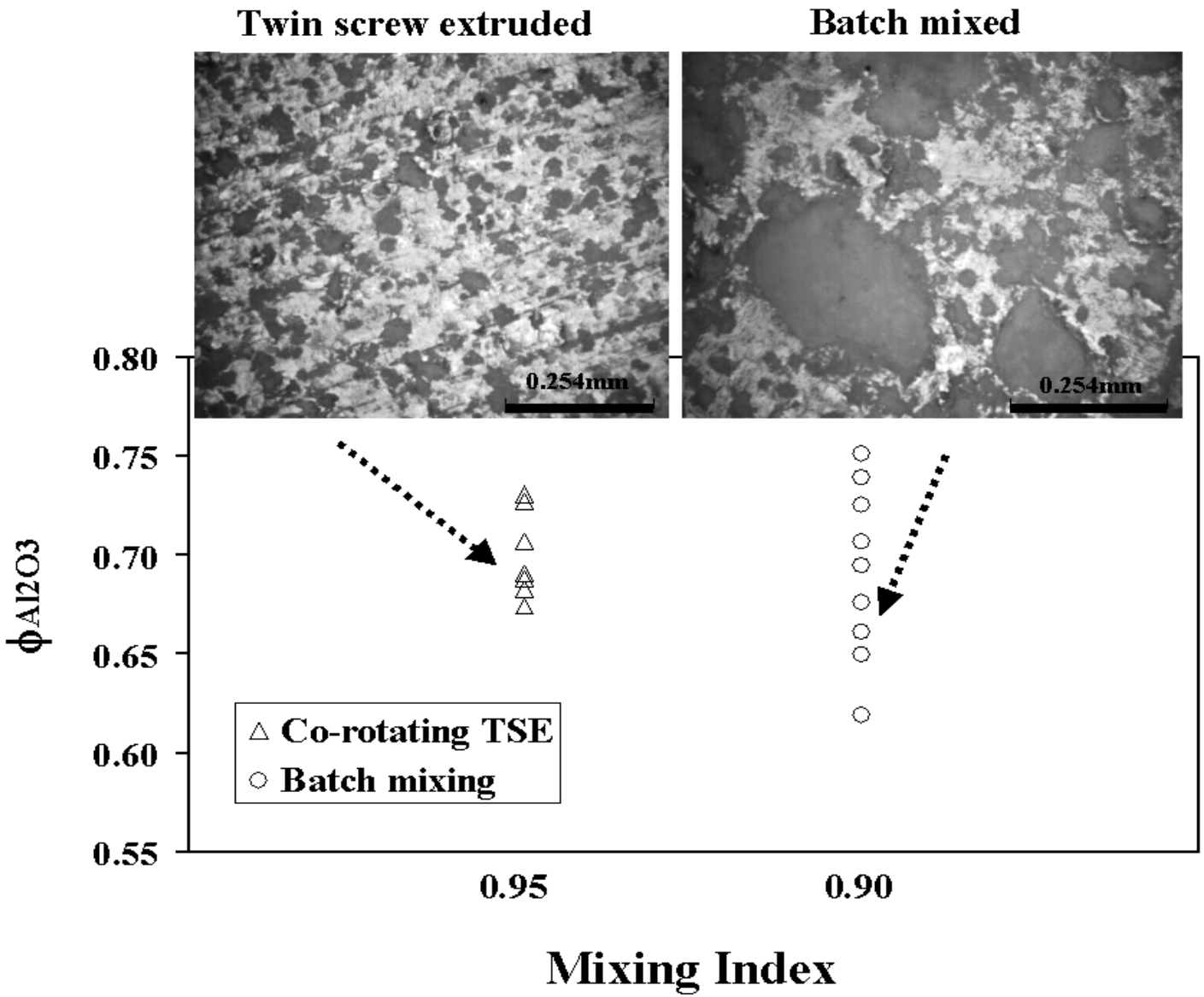
Confidence intervals of the storage modulus, G', and loss modulus, G", data for mixtures prepared with conventional and twin screw extrusion processes

Figure 8



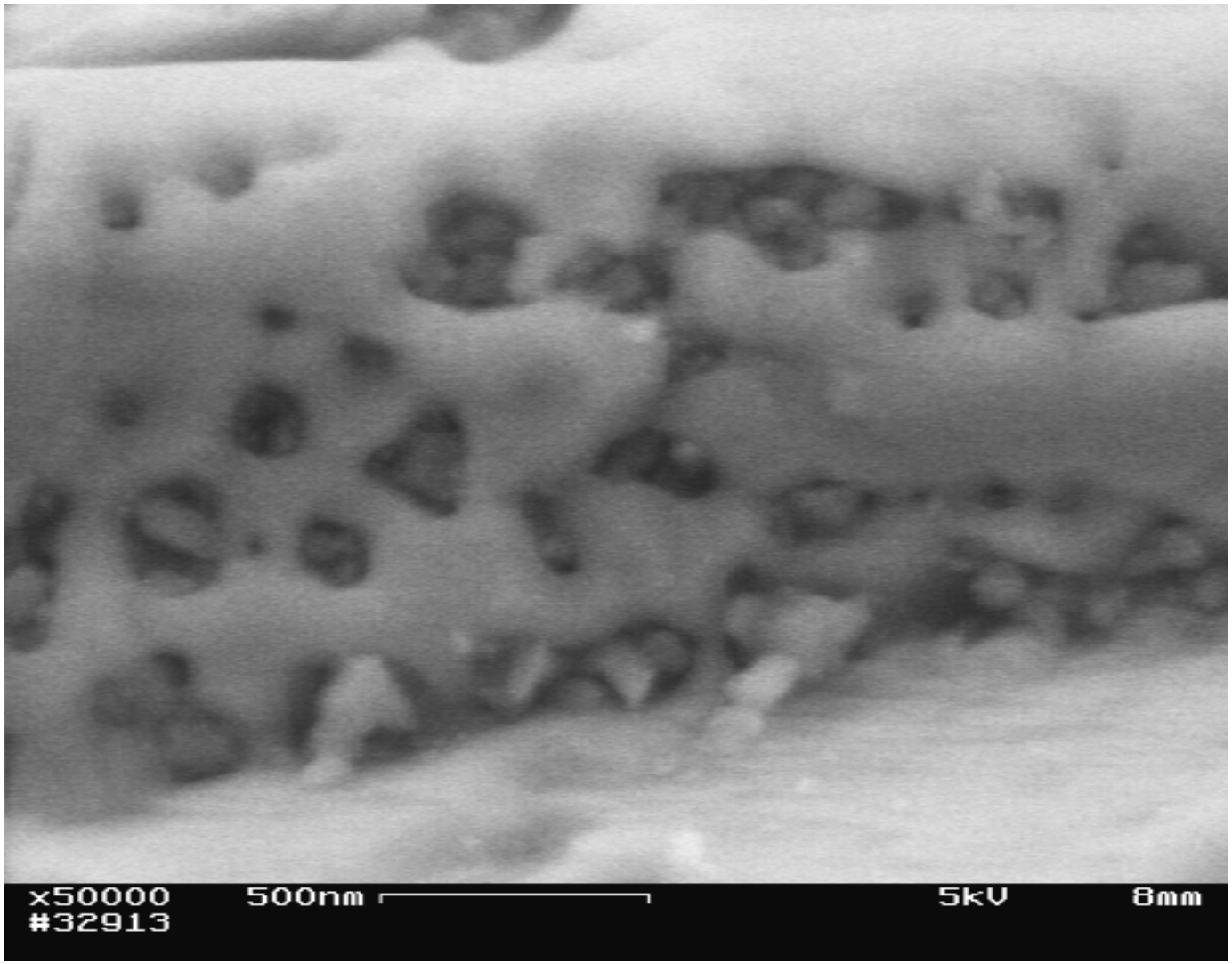
Scatter of the x-ray diffraction data for mixtures prepared with conventional and twin screw extrusion processes and their mixing indices

Figure 9



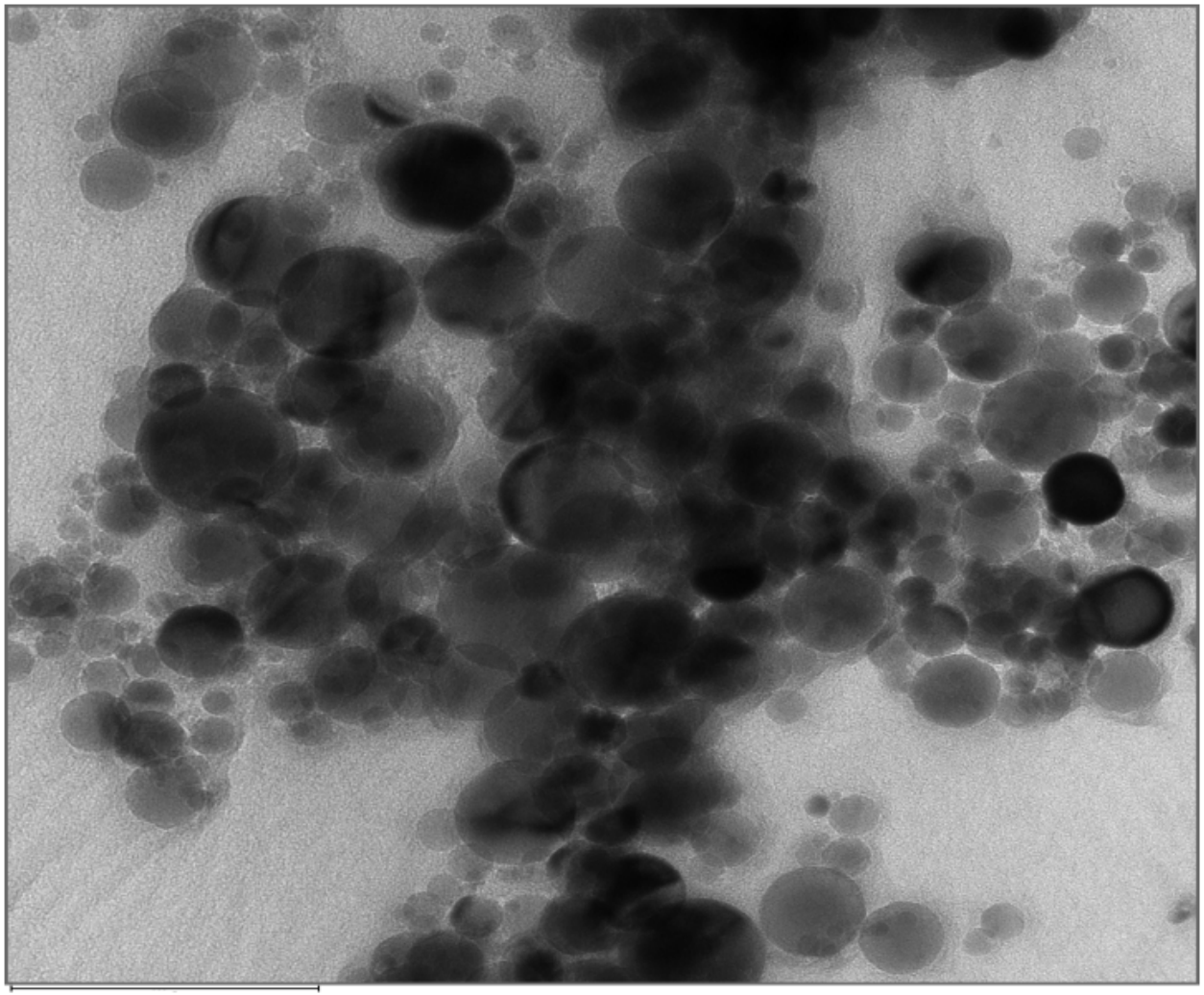
Scatter of the thermo-gravimetric analysis data for mixtures prepared with conventional and twin screw extrusion processes and their mixing indices

Figure 10



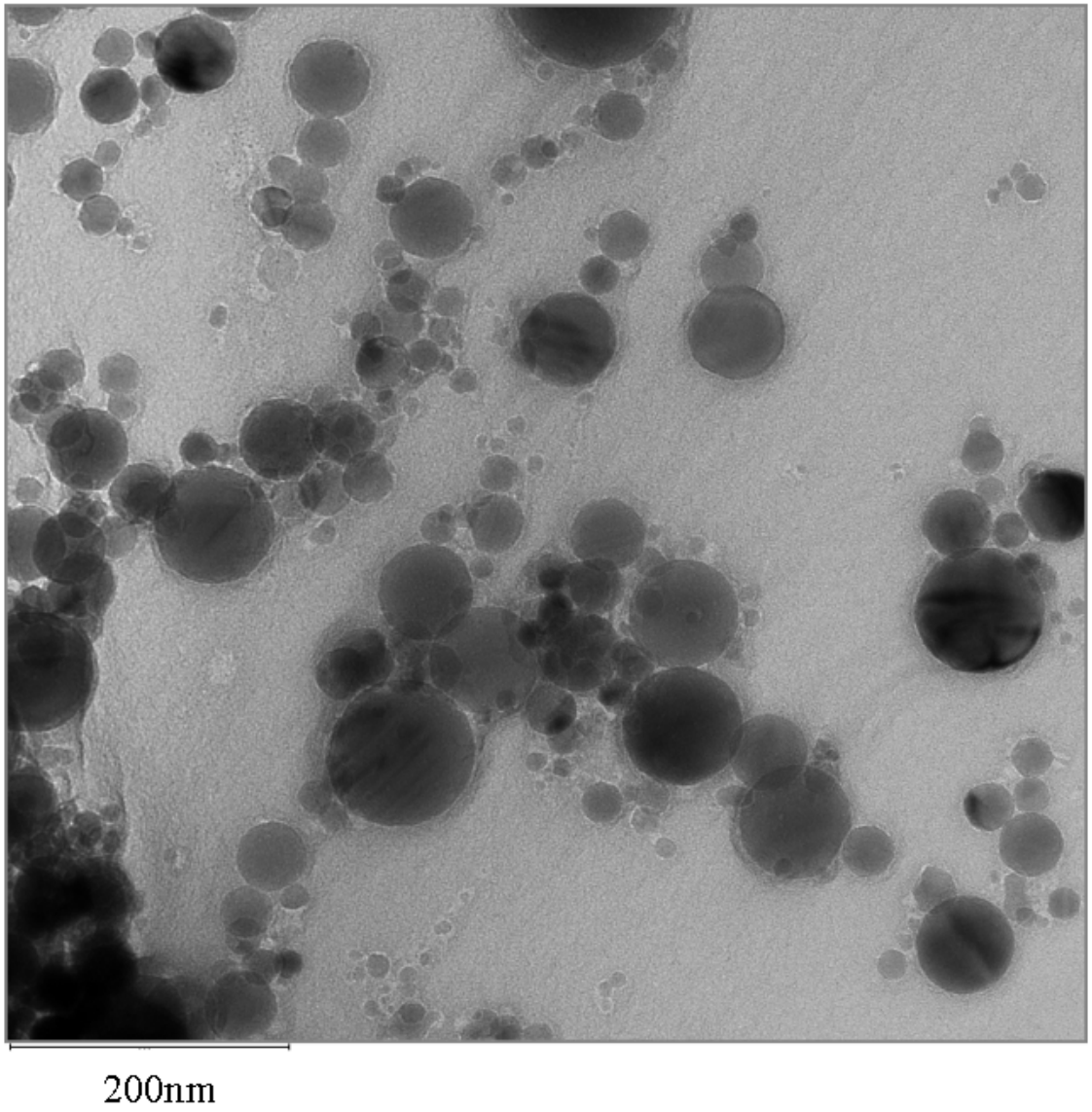
Typical scanning electron microscope, SEM, micrograph of batch mixed samples

Figure 11



Typical transmission electron microscope, TEM, micrograph showing nanoparticle clusters

Figure 12



Typical transmission electron microscope, TEM, micrograph showing better dispersion of nanoparticles

Figure 13