**"Twin Screw Extrusion Processing of a Nanoalumina Based Formulation in Conjunction with a Molding Powder Preparation Methodology"**

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**Abstract**

Various energetic formulations that rely on the mixing together of plasticized cellulosic polymers compounded together with various solvents and myriad energetic particles exhibit gel-like characteristics. Gelation during processing retards or prevents the distributive and dispersive mixing of the ingredients and the shaping of the formulation. Incorporation of various types of nanoparticles into such formulations is expected to accelerate the formation of such gels during processing and increase their moduli. Here it is demonstrated that the effective distributive and dispersive mixing of the ingredients of an energetic simulant based on a nanoaluminized cellulose acetate butyrate formulation, which cannot be achieved with conventional technologies including roll-milling, can be achieved upon the use of the twin screw extrusion technology starting from a molding powder, in conjunction with a judicious selection of operating conditions and extrusion geometries.

## Introduction

Rapid and reliable processing of energetic formulations is an important challenge that becomes more complicated upon the use of nanoparticles as part of the formulation. Under such conditions, the abilities to use scaleable and industrially relevant processing methods are valuable assets [1]. Other challenges associated with the manufacturing of energetic grains with nanometallic powders (5-200nm range) involve the control of the particle sizes of nanoparticles by preventing the formation of particle clusters, the selection of proper wetting agents and binders, the tailoring of the process to the rheological behavior of the dispersion, and the need to work at a relatively very small processing rates.

Twin screw extrusion process allows the melting and mixing together of multiple ingredients, the devolatilization of the air or other gases from the system as well as the shaping of the energetic grain [2-4]. Here, a novel twin-screw extrusion processor i.e., the smallest industrially relevant twin-screw extruder, ever designed and constructed [5, 6] is used for the compounding of a molding powder (energetic simulant) with nanoparticles of alumina in conjunction with an elastomeric binder, which is notorious in giving rise to strong gelation in the process. Two different methods were used for the preparation of a molding powder, followed by its compounding with nanoparticles of alumina in the extruder. The procedures used are discussed along with the rheological behavior of the resulting compounds. Some of the challenges associated with the rheological characterization of solvated systems are also elucidated.

## Experimental

### Materials

The goal of this project was to process an inert formulation that would be representative of a likely future formulation containing nanomaterials. The following inert formulation was chosen: 75 % Dechlorane Plus (inert simulant of HMX), 5% 100-200 nm nano-aluminum oxide (inert simulant of nano-aluminum), 8% cellulose acetate butyrate (CAB) and 12% acetyl triethyl citrate (ATEC). The final formulation was processed upon the compounding of an apriori prepared molding powder together with a nano-aluminum slurry using the twin screw extrusion technology.

Molding Powder Preparation.

The raw materials, ATEC, CAB, Dechlorane plus 515, and 50% ATEC-50% nano alumina paste, were received from Picatinny Arsenal. The details of all the formulations are given in Figure 1, including the final formulation, the molding powder, and Al-slurry formulation. The molding powder was prepared using a solvent concentration of 14% by weight. The mixing of the molding powder, which consisted of Dechlorane Plus, CAB (elastomer), and ATEC (plasticizer) was carried out using two separate procedures. In the first procedure, a Haake torque rheometer was utilized for 10 min. at room temperature.

The Haake Torque Rheometer is an intensive mixer with two counter-rotating and intermeshing roller type agitator blades. The rotational speed of the counter-rotating rollers was 32 rpm. The volume of the mixing head was 60 cc. Such intensive mixers are used partially full and a degree of fill of 70% was employed during the batch mixing. The roller blades were operated at 32 rpm speed and at ambient conditions. The ingredients of the molding powder were introduced as a premix to the mixing chamber. The solvent mixture (80% ethyl acetate and 20% ethanol) was added in steps up to the point at which the solvents constituted 14% by weight of the mixing powder. The molding powder was mixed for 10 minute after the last drop of solvent was added.

The torque, T, and hence the specific energy, $E_s$, input generated during the mixing process could be monitored during mixing as:

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

where $\Omega$ 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 second method of the preparation of the molding powder, the ingredients of the molding powder were mixed in a Baker Perkins batch mixer for 15 minutes. Here, the

ingredients were placed in the mixer with a solvent mixture (80% ethyl acetate and 20% ethanol) of 14% by weight of the total material. The material was mixed at 60 rpm at room temperature. Afterwards, the material was dried in an oven overnight at 70° C and then broken up into powder using an attritor ball mill. The ball mill used 2000 g of steel balls (3/16") to process 175 grams of molder powder mixed with 500 g of distilled water. The mill was run for 45 minutes at 400 rpm. Afterwards, the pulverized molding powder was collected. Upon the inspection of the powder, it became evident that there were chunks of relatively harder material that could be distinguished from the rest of the powder. These chunks were further broken down upon an additional 30 minutes of milling at 600 rpm.

Nano aluminum slurry

The Nano-Aluminum slurry was prepared by first manual mixing of 10 g of nano-Al, 10 g of ATEC, and 22 g of acetone. This mixture was then sonicated under heat to drive off the solvent. After 6 hours of sonication, the mixture was placed into a drying oven at 70° C for overnight drying.

**Twin screw extrusion set up:**

The MPR 7.5 mm twin screw extruder [5, 6] shown in Figure 2 was used. 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 10 mm, gap of 1 mm and length is 50.8 mm including the converging flow section and 36.8 mm 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 up to 200 rpm. The barrels and screws are machined from a heat-treated alloy of

stainless steel and a ferritic nitro carburized to reduce the potential of adhesive wear between the screws and the barrel bores. The drive is a ¼ HP motor, 100% explosion proof.

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. The mixing of the nanoparticles into the molding powder (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 and at the fully-flighted section preceding the die. 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 were used (Figure 2). 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.

**Twin Screw Extrusion runs:**

The wet molding powder was fed to the extruder using a Harvard apparatus infusion pump with an aluminum syringe with a diameter of 23 mm. The calibration of the infusion pump was performed to enable accurate control of the feeding rate of the molding powder (Figure 2). The n-Al-slurry (n-Al and solvents) was fed into the extruder using a Biochem micro-diaphragm pump. The micro-pump was calibrated using the time-dependent weight change of the vial holding the n-Al slurry at differing pulse rates, for example, at 20 pulses/min. At this pulse rate, the pump generated a 10.4 mg/pulse feed rate, which was equal to 9.650 μl per pulse.

The MPR 7.5 mm, L/D=15 co-rotating fully intermeshing twin-screw extruder was run at the targeted flow rate of 20 g/h at ambient temperature. The molding powder was fed from an infusion pump at a 16.24 g/h flow rate. The n-Al-slurry was fed from a liquid vial feeder by micro-diaphragm pump at a flow rate of 3.8 g/h. Thermal images were taken at every 20 s interval during extrusion. A twin-flighted set of complex screws containing reversely configured kneading discs and full-flighted elements with 7.5 mm diameter and screw lead length were used. At the targeted flow rate of 20 g/h, the actual flow rate was determined to be 18.8 g/h.

A dual pressure, temperature transducer was placed along the rectangular slit section at a distance of 32.8 mm away from discharge. The molding powder was introduced first into the extruder, followed by the n-Al-slurry down stream in the extruder. During the twin screw extrusion processing experiments, the rotational speed of the screws was 40 rpm. The minimum residence time in the twin screw extruder was about 15 min.

The system took an additional 10 minutes to reach steady-state upon the first exit of the extrudate from the die (25 minutes upon the initiation of the experiment). The samples were collected at 15 s intervals to validate the flow rate and the solvent concentration upon thermogravimetric analysis. The typical flow rate was determined to be 18.8 g/h and the

actual solvent content was determined from thermo-gravimetric analysis as 22.2%. During the twin screw extrusion process, the torque value was around 19% of the maximum available and the pressure drop through the die was negligible. The temperature was 19°C. After the achievement of the steady-state was assured upon the flow rate and solvent concentration measurements, the extruded samples were collected into a vial for subsequent characterization of their dynamic properties.

**Roll Mill runs**

The conventional roll milling process has been suggested as an alternative processing method for the compounding of the molding powder with the nano-Al and was investigated to provide a benchmark for the efficacy of the mixing in the twin screw extrusion process. The process of roll milling began with 20 g of molding powder being wet with 50 g of butyl carbitol. Into this slurry, 2.2 g of the ATEC-nano-Al paste was added. This mixture was premixed manually and placed into an Exakt 3 Roll Mill set. The roll speed was set to 70 rpm. After each pass, the material was collected and put back through the mill, starting a new pass. The simulant underwent six consecutive passes through the roll mill. During the first 3 passes, the material became visibly more viscous. This process was repeated 3 times to create three separate trials. The roll milled suspension was dried in an oven at $60^{o}$ C under a steady flow of air to remove the butyl carbitol.

**Dynamic properties:**

A number of rheological material functions can be characterized to follow the progress of the mixing and compounding processes [7-10]. Here the small-amplitude oscillatory shear was used to characterize the dynamic properties (linear viscoelastic material functions) the storage modulus, G", the loss modulus, G" and the magnitude of complex viscosity. Dynamic properties are very sensitive to the changes in the microstructure of the suspension, i.e., provide an accurate fingerprint indication of the distributive and dispersive mixing efficacies of the ingredients of the formulations and changes in their physical properties [9]. The ARES rotational rheometer was used to characterize the linear viscoelastic properties of the processed suspension samples. The experiments were conducted at room temperature without the impingement of air/$N_2$ stream on the fixtures holding the specimen to minimize the solvent loss during testing. Disks with diameters of 8

mm and 25 mm were used in the small-amplitude oscillatory shear experiments. The dynamic properties of the samples of the molding powder and the extruded complete simulant formulation were characterized.

**Results and Discussion**

The mixing that could be achieved with the conventional process of roll milling [11-12] was very poor in comparison to what could be achieved with the twin screw extrusion process. A number of quantitative methods are available for the quantitative characterization of the degree of mixedness at various scales of examination [13-19]. However, the product of the roll milling process exhibited gross segregations, an example of which is the occurrence of color inhomogeneities that were encountered with the conventional roll milling process, as shown in Figure 3. Such gross inhomogeneities were not evident in the product of the twin screw extrusion process. Furthermore, as will be indicated in the discussion of the dynamic properties, the confidence of the data emanating from the compounds obtained with the twin screw extrusion process were relatively narrow, indicative of the relatively higher degree of mixedness achieved with the twin screw extrusion process. The rest of the program was carried out using the twin screw extrusion process for the compounding of the nano-Al with the molding powder.

**a. Dynamic properties of the molding powder:**

A visual inspection of the molding powder prepared by the Baker Perkins Mixer indicated that the degree of mix of this material was not acceptable. Thus, an additional test involving the thermo gravimetric analysis of the second molding powder samples was carried out. The TGA results (results not shown here) indicated that there was indeed significant scatter in the degree of mixing of the ingredients when the second method of molding powder preparation was utilized. All of the results to be discussed next were obtained with the Haake intensive mixer (mini- Banbury mixer).

The first dynamic oscillatory shear experiment conducted on the molding powder prepared with the Haake intensive mixer was the strain sweep (at 5 rps frequency) to determine the typical linear viscoelastic range. The dynamic properties were sensitive to strain magnitude over a wide range of strains indicating that the molding powder suspension was highly non-

linear and susceptible to wall slip. Based on these findings the rest of the dynamic oscillatory experiments were conducted at the smallest possible strain (0.03%) below which the material properties were relatively insensitive to the strain magnitude. The solvent content of the sample was determined upon the completion of the strain sweep experiment to be 15 %.

Time sweep experiments were conducted under constant frequency and strain to follow up on the rapid solvent loss issue. The change in material properties were monitored and related to solvent concentrations, which were measured at the beginning and end of the experiments. These time sweep experiments were conducted at 0.03% strain amplitude and 5 rps frequency. The sample data are shown in Figure 4. The magnitude of complex viscosity values increased from approximately 100 kPa.s at the beginning of the test, to over 1 MPa.s within 5 minutes of testing and similarly significant increases were also observed in the time dependent values of the storage and loss moduli (Figure 3). These results clearly suggest the sensitivity of the material properties to the solvent concentration and the difficulties associated with the determination of the rheological properties of such solvent incorporated formulations [7-10]. All of the data was subsequently collected using time scans and the mean values of the solvent concentrations determined during the course of the small-amplitude oscillatory shear experiment. The results are reported as a function of the solvent concentrations.

**b. Dynamic properties of the twin screw extruded simulant formulation:**

Similar to the experiments carried out on the molding powder, the strain sweep experiment was first carried out on the extruded simulant sample at 5 rps frequency. As expected from the behavior of the molding powder, the dynamic properties of the extruded sample were also sensitive to strain magnitude over a wide range of strains, indicating that the simulant suspension is highly non-linear. Similar to the molding powder characterization experiments, the rest of the dynamic oscillatory experiments were conducted at the smallest possible strain (0.03%) below which the material properties were relatively insensitive to strain magnitude. The typical solvent concentration of the sample was determined to be 22 % upon the completion of the strain sweep test. The significant increases of the dynamic properties (Figure 5) were thus a result of the solvent loss mainly through the free surfaces of the suspension during small-amplitude oscillatory shear characterization. Time sweep

experiments were also performed at 0.03% strain and 5 rps frequency for the twin screw extruded sample. The changes in material properties were monitored and related to solvent concentrations, which were measured at the beginning and end of the experiments.

**c. The comparison of the dynamic properties of the molding powder and the n-aluminized simulant formulation:**

The dynamic properties of the molding powder and the extruded simulant samples are compared as shown in Figures 6 and 7. All the dynamic properties of the extruded final formulation are lower than those of the molding powder. The lower dynamic properties of the final formulation are expected primarily due to the higher solvent (22%) and the increased amount of plasticizer (ATEC) in the final extruded formulation. These two factors compensate for the presence of the nano particles. Thus, although the final formulation has n-Al particles, which would typically increase the viscosity of the paste, its binder phase is also significantly richer in the solvent and plasticizer, which gives rise to a reverse, i.e., competing effect. In the case of the final extruded formulation, the increase in the solvent and plasticizer content predominates over the addition of the nano particles.

The narrowness of the confidence intervals observed in the dynamic properties of the compounded nanosuspensions is indicative of the relative homogeneity of the compounded formulation (Figures 6 and 7). There are a number of methods that can be utilized to determine quantitatively the degree of mixedness of energetic formulations relying on wide-angle x-ray diffraction, energy dispersive x-ray, thermo gravimetric analysis and rheological characterization of various material functions [11-19]. If the degree of mix is relatively poor, one would observe a significant variation of the dynamic properties since they are accurate fingerprints of the structure and hence the degree of mix of the ingredients. Generally, a relatively poor degree of mix would generate a relatively higher yield stress and shear viscosity and elasticity that would be immediately evident in the spread of the dependence of the dynamic properties on frequency.

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## VI. References


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## *Final Formulation containing 22% Solvent Corresponding Binder Phase*

| | Volume% Binder | Wt % Binder |
|---|---|---|
| ATEC | 21.26% | 24.9% |
| CAB | 13.63% | 16.6% |
| Ethyl acetate 80% | 50.41% | 46.8% |
| Ethanol 20% | 14.69% | 11.7% |
| Total Solvent= | 65.1% | 58.5% |

## *Molding Powder Formulation containing 14% Solvent Corresponding Binder Phase*

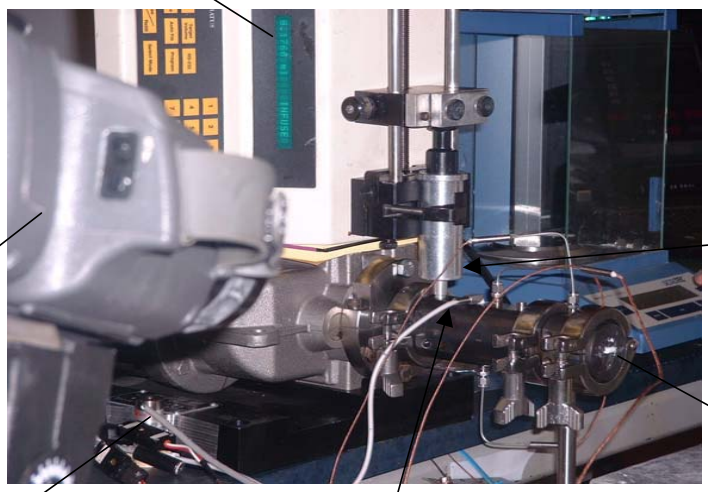
| | Wt % | Volume% |
|---|---|---|
| ATEC | 24.05% | 21% |
| CAB | 27.49% | 23% |
| Ethyl acetate 80% | 38.77% | 43% |
| Ethanol 20% | 9.69% | 13% |
| Total Solvent= | 48.46% | 55.56% |

Figure 1

# Experimental set-up

Harvard apparatus infusion pump

*Mini TSE set-up*

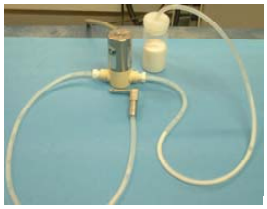


Molding powder feeder
*16.24 g/h*

Thermal imaging camera

Die

Diaphragm pump

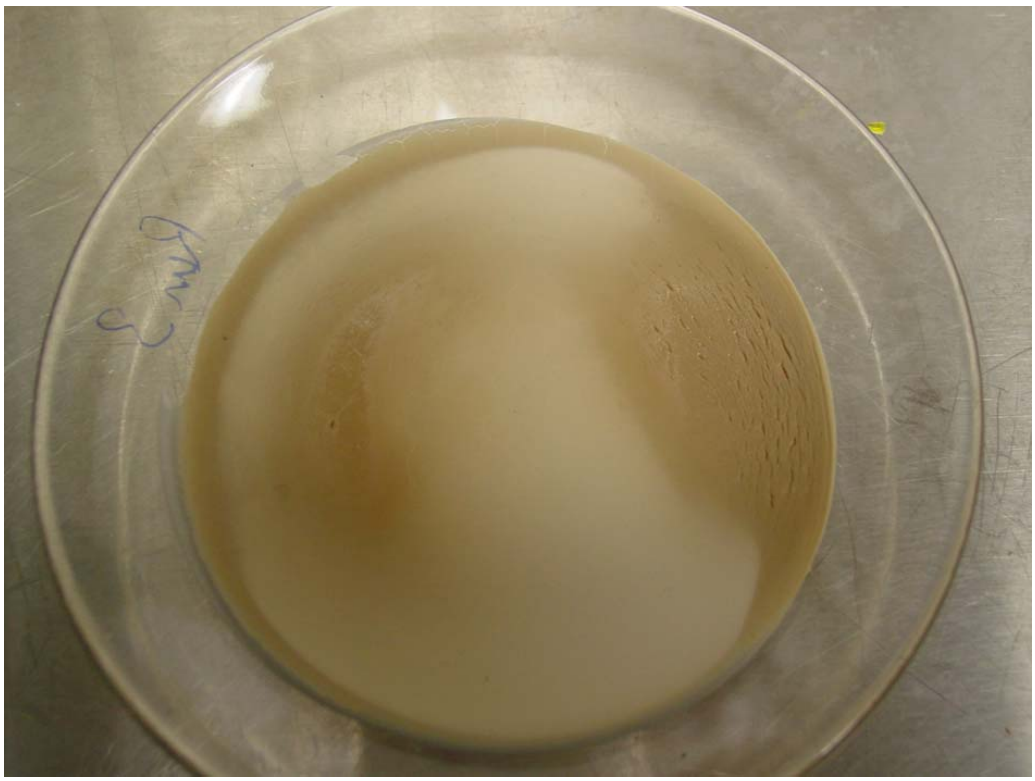


Al-slurry feeder
*3.8 g/h*

Extrusion screws

**Section III** **Section II** **Section I**

Figure 2



Typical color inhomogeneities of roll milled formulation

Figure 3

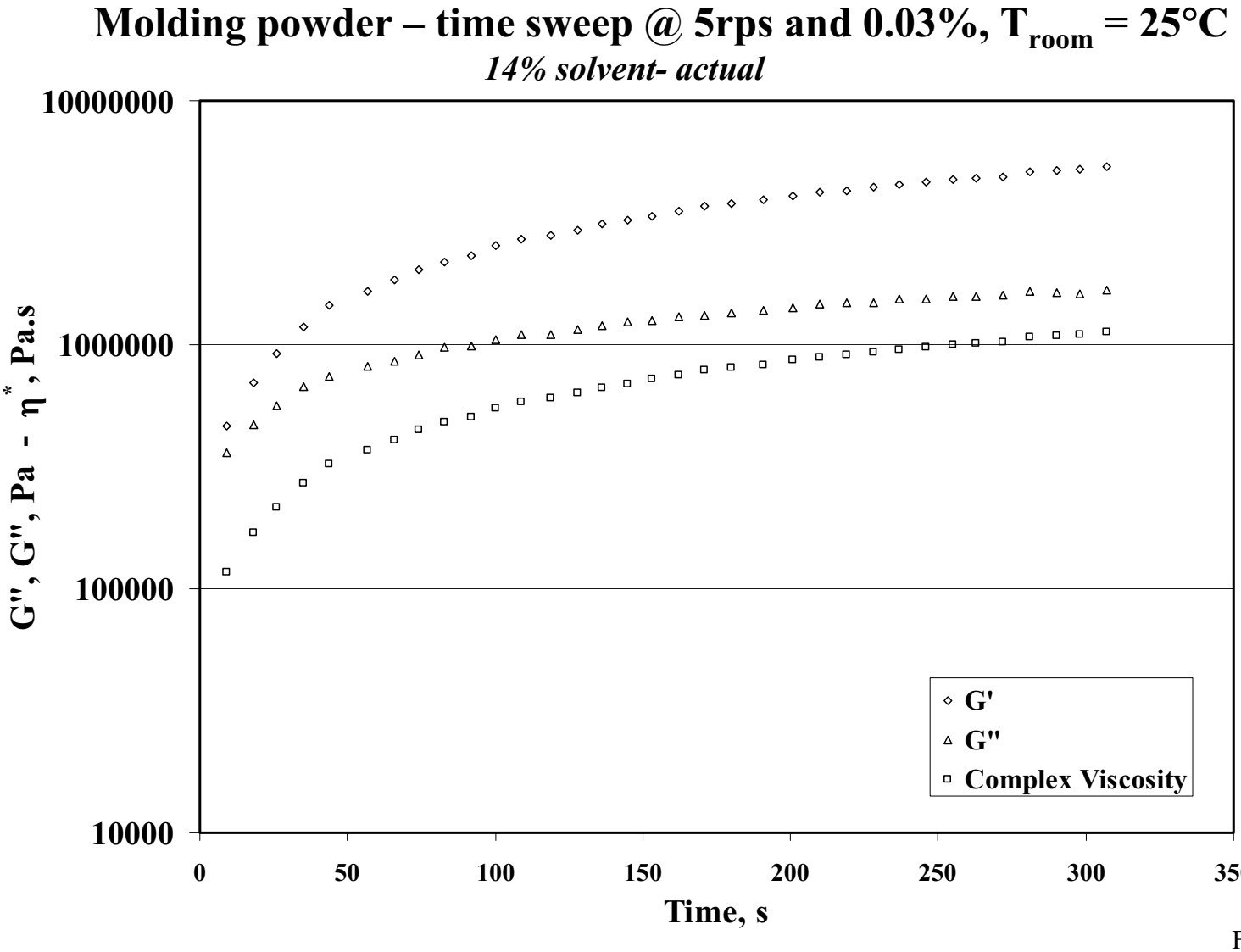

Molding powder – time sweep @ 5rps and 0.03%, T room = 25°C
14% solvent- actual
10000000
1000000
100000
10000
G'', G', Pa - η*, Pa.s
0
50
100
150
200
250
300
350
Time, s
G'
G''
Complex Viscosity

Figure 4

**Samples from Mini TSE – time sweep @ 5rps and 0.03%, $T_{room}$ = 25°C**

***22.2% solvent level-actual***

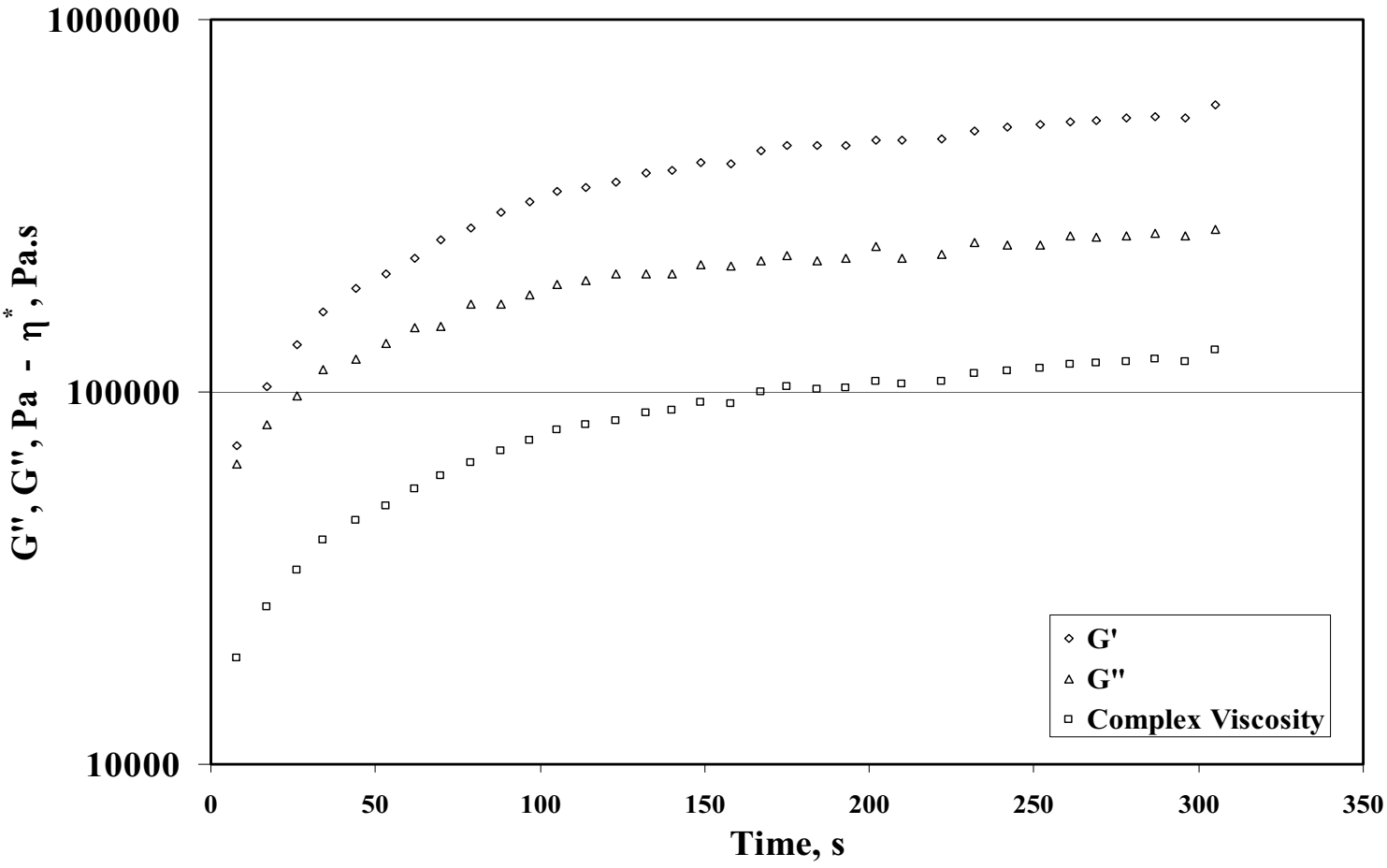
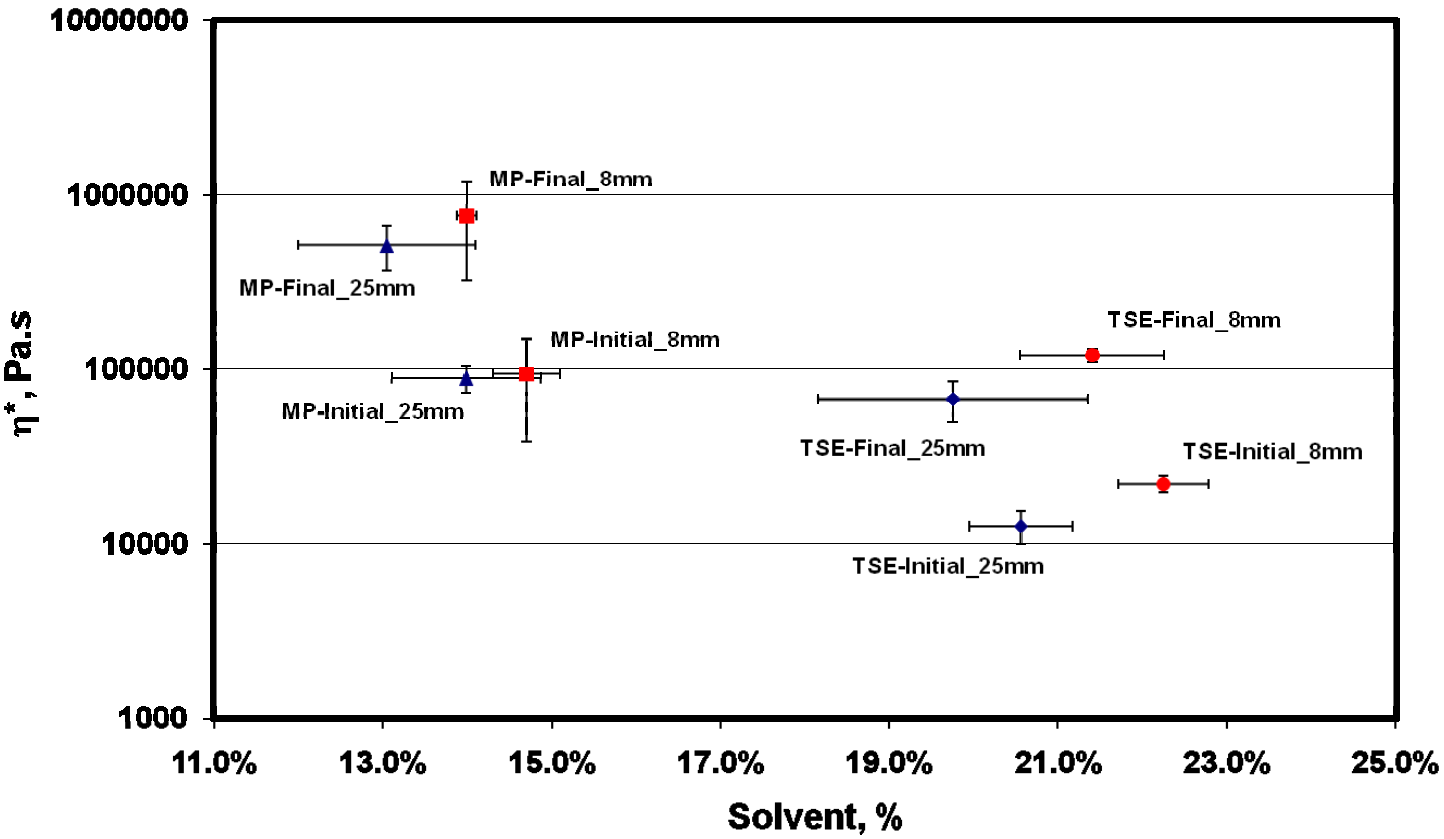
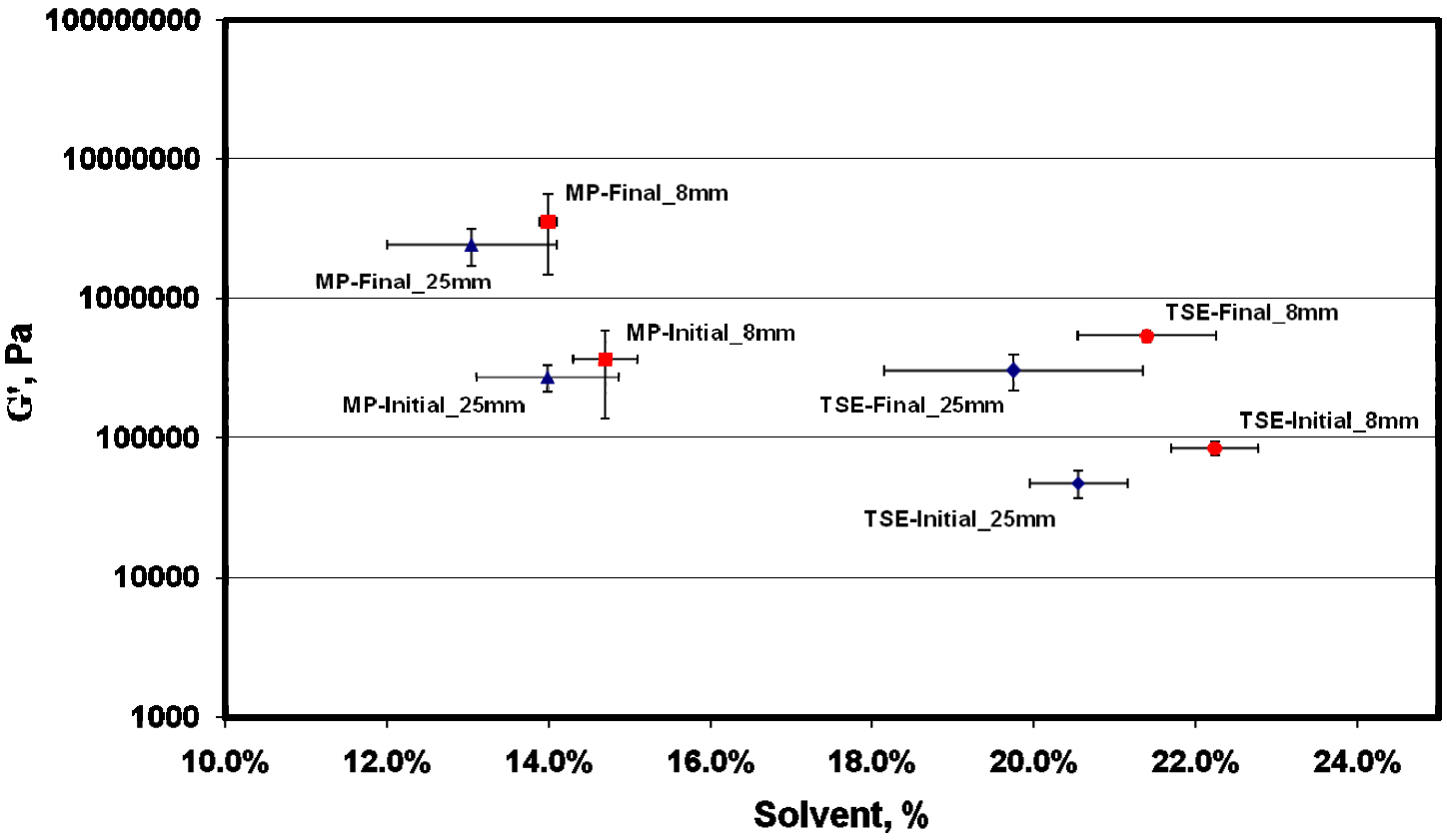



Figure 5




Comparison of Molding Powder and Final Extruded Formulation
Tested in the 8 and 25 mm Fixtures

Figure 6




Comparison of Molding Powder and Final Extruded Formulation
Tested in the 8 and 25 mm Fixtures

Figure 7