Rheological Characterization of NASA Propellants and Modeling/Simulation of the Mixing Process for Scale-Up to Production

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Introduction

A joint effort was conducted between the U.S. Army RDECOM-ARDEC, the Polymer Processing Institute at New Jersey Institute of Technology, and Alliant Techsystems (ATK) / Thiokol Propulsion, to investigate the fluid dynamics of the mixing process for NASA's Space Shuttle Booster Rocket Propellant using modeling and simulations through computer aided computational fluid dynamics supported by laboratory rheological data. Results of the effort will be used as a means to accurately predict scale-up of the mixing process to support production requirements.

ATK / Thiokol Propulsion provided drawings of the 8PI (5-gallon) vertical mixer, propellant ingredients and the mixing procedure used in a 1-gallon mixer to ARDEC. A mesh file was created from the mixer drawings using Fluent GAMBIT and the initial conditions from the mixing procedure. Five mixes using combinations of 20μm and 200μm sized particles of Ammonium Perchlorate (AP) were then prepared in the ARDEC Energetics Rheology Laboratory (ERL) using a Thermo Haake torque mixer. The following tests were performed on these mixes using a RDA III Dynamic Analyzer:

1. Dynamic Strain Sweep to determine optimal strain percentage at selected temperatures.

2. Dynamic Frequency Sweep to determine the Complex Viscosity, Storage modulus G', and Loss modulus G".

3. Dynamic Time Sweep conducted at different temperatures to verify thermal stability.

The mesh drawing of the mixing vessel and the rheological data were then inputted into POLYFLOW software (computational fluid dynamics) for development of a dynamic model to correlate with the actual laboratory data. The model presents the velocity profile and pressures within the mixing vessel and performs particle tracking so that the progress of the mixing and particle movement can be observed within the vessel.

The modeling software will ultimately be used to model the 600-gallon production vertical mixer for projecting the process boundary conditions. ATK / Thiokol Propulsion will verify the model by conducting mixing studies using the production-sized mixer.

Materials

ATK/Thiokol Propulsion, Brigham City, UT, supplied the ARDEC ERL with the required ingredients to facilitate the mixing of the TP-H1148 propellant. The ingredients for the propellant are outlined in Table 1 as follows:

Table 1. Ingredients for the TP-H1148 propellant.

Name	Density, g/cc
HB Polymer ($[C_4H_6]x[C_3H_3N]x[C_3HO_2]$)$_n$	1.16
Aluminum Powder	2.70
Iron Oxide (Fe_2O_3)	5.15
ECA, lube oil additive	1.00
200μm Ammonium Perchlorate (NH_4ClO_4)	1.95
20μm Ammonium Perchlorate (NH_4ClO_4)	1.95

All ingredients were received in individual, sealed containers and were found to be in good condition with the exception of the 20μm AP. Small crumbs were discovered among the otherwise free flowing material. These crumbs, however, were easily broken up by applying slight pressure.

Rheological Characterization Procedure

Mixing Protocol

The main objective of this work effort was to provide the model with the rheological properties of the propellant at different mixing stages as designated by the modeling team.

The mixing protocol in Procedure PTP-0586, obtained from Alliant Techsystems /Thiokol Propulsion, was broken into five different stages and subsequently five corresponding mixes as a function as AP concentration. Materials were collected from each of these mixing stages and rheological testing was performed immediately after.

Procedure PTP-0586, however, was designed for an open-batch mixer and therefore was unsuitable for the closed-rotational torque Thermo Haake mixer in the ARDEC ERL.

The Thermo Haake mixer with sigma blades, has a working chamber volume of 90cc. To achieve a good quality mix, Thermo Haake recommended a 70% fill criteria, which in this case is 63cc. The theoretical amount of material charged for each mix was calculated based on this criteria. Table 2 shows the material charged for each mix and their respective density.

All the pre-conditioning steps as outlined in Procedure PTP-0586 were followed for all five mixes described in Table 2. Two runs of each mix were performed to verify data reproducibility.

Mix I: The Thermo-Haake mixer was preheated to 110^{o}F and the 3 pre-weighed and preconditioned components, namely, Aluminum, Fe_2O_3 and HB Polymer, were introduced into the mixer in the same order as called for in Procedure PTP-0586 at an initial mixing speed of 5rpm. After all the materials were loaded into the mixer, the mixing speed was incrementally

Table 2. Materials charged in the Thermo Haake Mixer.

Material:	Descriptions:	Density[g/cc]
Mix I, MIX IA		
Solid #1	Al Powder	2.70
Solid #2	Fe_2O_3	5.15
Binder #1	HB Polymer	1.16
	Total	1.73*
Mix II		
Solid #1	Mix I	1.73
Solid #2A (50%)	200μm AP	1.95
	20μm AP	1.95
Binder #1	ECA	1.00
	Total	1.77*
Mix III		
Solid #1	Mix I	1.73
Solid #2A (100%)	200μm AP	1.95
	20μm AP	1.95
Binder #1	ECA	1.00
	Total	1.82*
Mix IV		
Solid #1	Mix I	1.73
Solid #2A (100%)	200μm AP	1.95
Solid #2B (50%)	20μm AP	1.95
Binder #1	ECA	1.00
	Total	1.84*
Mix V		
Solid #1	Mix I	1.73
Solid #2A (100%)	200μm AP	1.95
Solid #2B (100%)	20μm AP	1.95
Binder #1	ECA	1.00
	Total	1.85*
*Effective density		

increased by 5rpm, to 35rpm. The duration of this mix cycle was 30 minutes from beginning to end. Mix IA was the hand-mixed version of Mix I for reasons which will be explained later in the Result and Discussion section. The material from Mix I and IA were used as a base for the subsequent Mixes II to V.

Mixes II to V: The Thermo-Haake mixer was preheated to 145^{o}F and the required pre-weighed and preconditioned components as listed in Table 2 for each Mix, were introduced into the mixer in the same order as called for in Procedure PTP-0586 at an initial mixing speed of 5rpm. After all the materials were loaded into the mixer, the mixing speed was incrementally increased to the final speed of 20rpm. The duration of the four mix cycles was approximately 47 minutes.

To establish consistency and data reproducibility, a second set of runs (from Mix I to V) was repeated following the same procedures and parameters as the first set of runs.

Material from each of the mixing runs were collected and tested, immediately, in the subsequent Dynamic Mechanical Properties tests.

Dynamic Mechanical Properties

The following tests were performed in the RDA-III, using the parallel plate fixture for each of the material collected from the 5 mixing stages of the TP-H1148 propellant using the Thermo Haake mixer:

1. *Dynamic Strain Sweep* experiments were conducted at a frequency of 5 rad/s to determine optimal strain percentage (%) at the selected temperatures of 110°, 145° and 165°F to generate adequate torque.

2. *Dynamic Frequency Sweep* experiments were conducted with frequency ranging from 0.1 rad/s to 100 rad/s at 110°, 145° and 165°F at the optimal strain levels as determined from the Dynamic Strain Sweep experiments.

Modeling Procedure

Mesh Creation

To create the model of the mixing vessel a finite element drawing of the 8PI vertical mixer is needed. In generating the finite element drawing a 3 dimensional computer drawing was created in AutoCAD and then imported in to Fluent GAMBIT where the mesh is created.

In GAMBIT the wire mesh frame is created and the disconnectivities, areas where the wire mesh frame does not connect correctly, are cleaned up to create the solid finite element mesh. While in GAMBIT, boundary conditions are created and volumes are designated as solid (i.e, the wall and mixing blades) or fluid (i.e., mixture). These are very important steps in the building process of any model.

Model Data Input

To further define the model Polydata, a sub-program of Fluent POLYFLOW, is used to define motion of moving parts and the working fluid properties. In this portion of the modeling step, the data from the rheological experiments is used to further define the model. Polydata creates stress/strain curves and uses viscosity data that are needed in defining the fluid properties from the data obtained from the rheological experiments.

When the input of rheological data is complete the definition of any of the moving parts is necessary. In this case the definition of the motion of the mixing blades is required. The blades rotate in a planetary motion within this 8PI vertical mixer. The inner blade rotates in the counter-clockwise direction at 40rpm and the outer blades in the clockwise direction at 80rpm, while both blades rotate about the center of the mixer in the counter-clockwise direction. The blades' motion around the mixer is ignored due to the symmetry of the rotation about the center of the mixer.

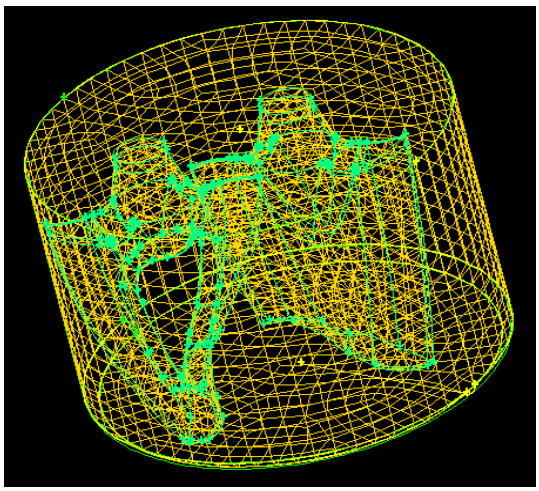

Figure 1. Mesh of 8PI Vertical Mixer

After the data input is complete, the computer runs time step sequences with a converging iterative solution at each time step. Each time step is based on the rotation of the mixer blades; in this case 0.05 seconds. Once the flow analysis is completed, the mixing analysis is then put through Polydata using the same conditions. When the iterations are completed, Polystat is used to observe the calculated model and data. Outputs include:

- Separation/Segregation Scale
- Particle Dispersion
- Time Average Efficiency of Mixing

This data is the main data used in the overall analysis.

With this information the dynamics of the vessel can be determined and observed. Along with determining the dynamics of the vessel, the model allows one to change inputs and conditions to observe with out experimentation of those conditions.

Results and Discussion

Propellant Mixing

As previously mentioned, the ARDEC ERL utilized a closed-rotational torque mixer that was different from Thiokol's open-vertical batch mixer. Due to this reason, procedure PTP-0586 was not strictly followed in terms of the speed and mixing time. The ARDEC ERL Torque mixer uses the more "gentle" sigma blades suitable for energetic material. Higher mixing speeds were used to achieve the equivalent mixing effect of the open-vertical batch mixer.

Mix I: The modified mixing protocol as described in the Experimental Procedures Section was followed. Material from this mixing run was very fluid in nature. A small amount of "leakage" from between the plates of the mixer was observed during the mixing process. Material was collected at the end of the mixing run. A powder-rich region was found toward the rear of the mixing chamber at the base of the right mixing blade. The collected mixture

was hand-mixed vigorously for 10 minutes to incorporate the “wet” and “dry” materials. The quantity of this material was only adequate to satisfy the requirement for the subsequent mixing runs for Mixes II and III only. Additional “Mix I” material was needed to perform Mixes IV and V. Therefore, a second “Mix I” or Mix IA material was performed to be used for Mixes IV and V.

Mix IA: Due to the “leakage” problem caused by the fluid nature of the material and the uneven mixing result for Mix I, Mix IA was made instead by vigorously hand-mixing the material from start to finish for 10 minutes.

Mixes II to V: The modified mixing protocol, as described in the Rheological Characterization Procedure Section, was followed. The required amount of materials, as shown in Table 2 for each Mix, was loaded into the mixer after the mixer was preheated to the required temperature. No “Leakage” was observed during the mixing process. Fluidity of Mixes decreased from a slurry consistency to a thick paste from Mixes II to V. Material was collected at the end of each mixing runs and was found to be uniformly mixed.

Figure 2 represents the Torque, Speed, Temperature and Specific Energy Input (SEI) vs. Time plot for Mix V. The SEI is a function of mixing time. The longer the mixing cycle, the higher the specific energy input. Table 3 summarizes the Average Specific Energy Input (SEI) measurements for all 5 Mixes, both runs 1 and 2. The measurements increase progressively from 1,500 to 29,250 J/Kg as the quantity of AP increases through the Mixes I to V. The Mix I value, however, is a single, discrete point since there was only one batch of Mix I material processed through the Thermo Haake mixer.

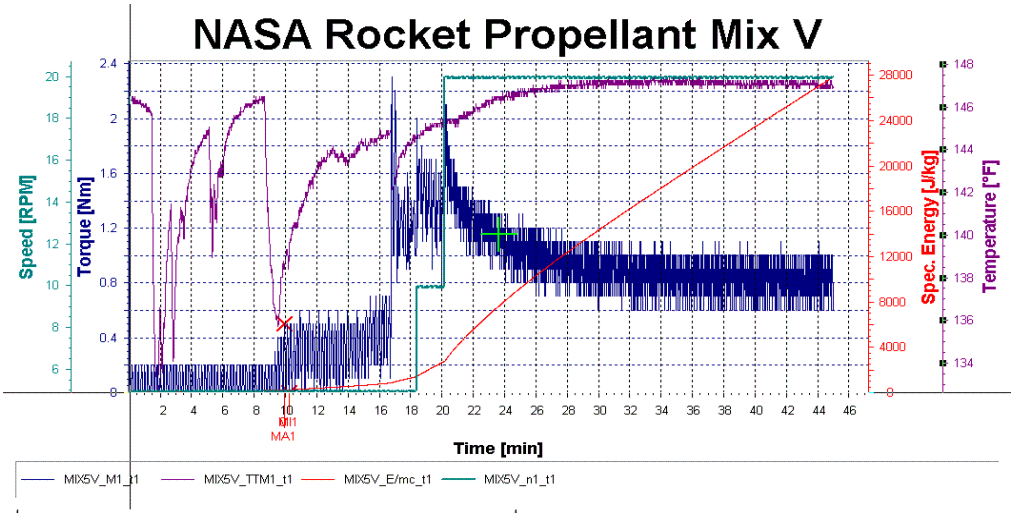

Figure 2. Thermo Haake Mixing plot for Mix V.

Table 3. Average Specific Energy Input (SEI) at the end of the mixing.

Mix	SEI, J/kg
I	1,500*
II	8,500
III	19,250
IV	24,250
V	29,250

*Single point

Dynamic Mechanical Properties

Figure 3 shows the Complex Viscosity of Mix V, Run 1 at the three test temperatures. This plot indicates that the Complex Viscosity decreased as the temperature increased which is what was anticipated. Similar results were found for other Mixes.

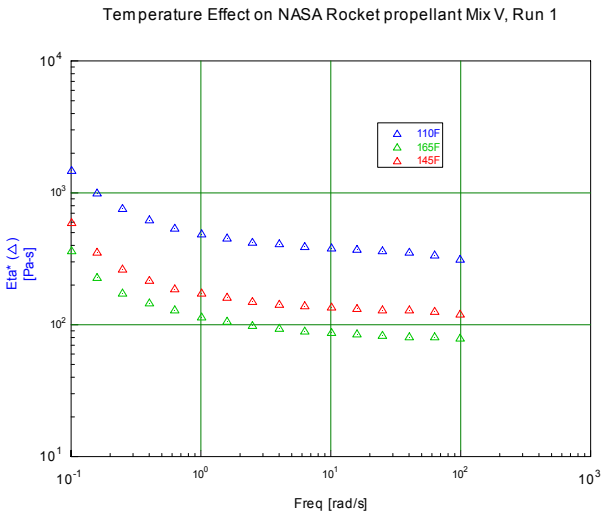

Figure 3. Complex Viscosity of Mix V at 110°F, 145°F and 165°F.

Figure 4 represents the Complex Viscosity plot for all five Mixes at 145°F. The plot shows that Mix I, II are near-Newtonian in nature, but exhibited a small slope for viscosity-frequency curve (a weak power-law); Mix III and Mix III A-2 are 100% power-law; while Mix IV and Mix V are typical suspension with higher sensitivity at lower shear range of 0.1 to 1.0 rad/s, and slight power-law from 1.0 to 100 rad/s.

The Complex Viscosity varies from 29% to 10% as the frequency increases from 0.1 to 100rps at 145°F. This could be attributed to the fact that Mix I was hand-mixed. For Mix II, runs 1 and 2, the Complex Viscosity varies from 14% to 15% as the frequency increases from 0.1 to 100rps. For Mix III, runs 1 and 2, the Complex Viscosity varies from 65% to 49% as the frequency increases from 0.1 to 100rps. For Mix IV, runs1 and 2, the Complex Viscosity varies from 27% to 18% as the frequency increases from 0.1 to 100rps. Mix V, runs 1 and 2, the Complex Viscosity varies from 4% to 13% as the frequency increases from 0.1 to 100rps. Similar variations were found for the data for 110°F and 165°F.

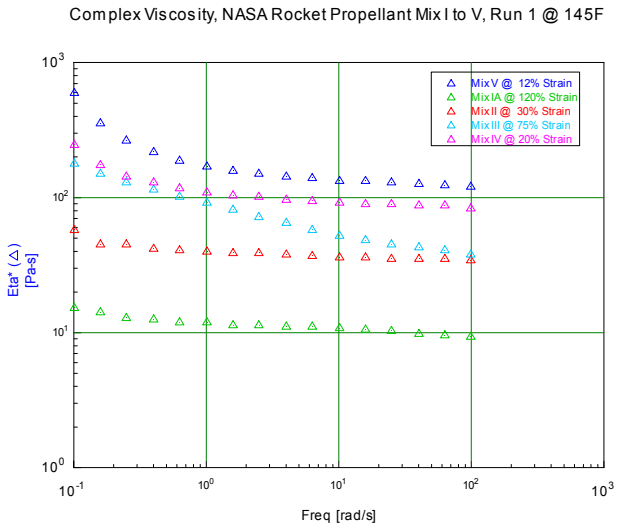

Figure 4. Complex Viscosity of all five Mixes, Run 1 at 145°F.

Table 4 summarizes the Complex Viscosity variation for all five mixes from the frequencies of 0.1 to 100rps for the 3 test temperatures.

Table 4. Complex Viscosity %Variation between Runs 1 & 2.

Mix	Test Temperature		
	110°F	145°F	165°F
I	27 - 7	29 – 10	28 - 12
II	7 - 10	14 – 15	16 - 14
III	78 - 55	65 – 49	51 - 42
IV	6 - 21	27 – 18	21 - 18
V	16 - 20	4 – 13	18 - 13

The plots for Complex Viscosity of all five Mixes (Run 1) at the three temperatures, 110°F, 145°F and 165°F show that the data for each of the mixes follow the same general trend. These plots also show that the Complex Viscosity increased as the AP concentration increased from Mix I to Mix V. Again, data for Run 2 show a similar result.

Model Results

With the model, the data can help to track different aspects of the mixer. In Figure 5 below, the mixer blades are being tracked through the torque. In this chart it is noticed that blade 2 is showing a negative torque, this is due to the fact that it is rotating in the opposite direction from blade 1. This chart also will give an approximation of what the output torque from the mixer motor should be.

To help determine the mixing of the 8PI vertical mixer the model also outputs among the data the segregation scale and time average efficiency of mixing. With the segregation scale, shown in Figure 6, the smaller the ratio of the segregation scale the better the mixing occurs. Upon inspection of the segregation data the mixing asymptotes to approximately 0.007 close to 2 minutes of mixing.

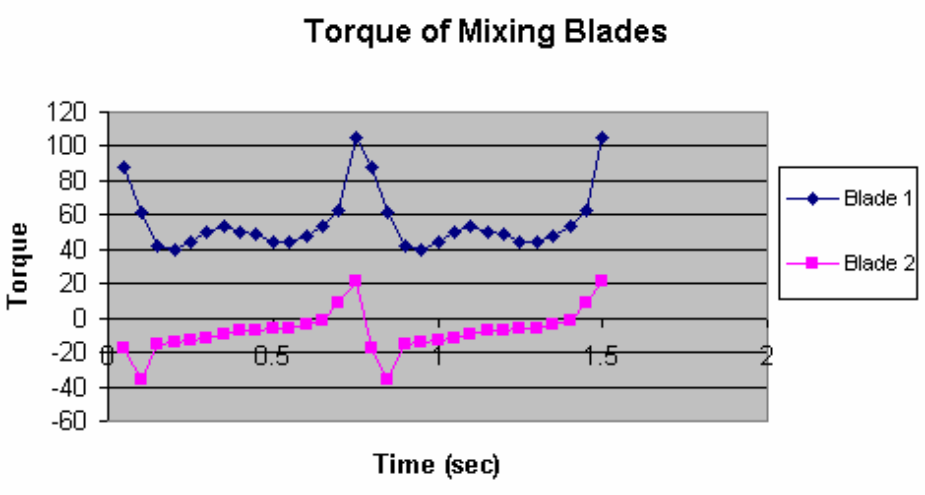

Figure 5. Torque of Mixing Blades

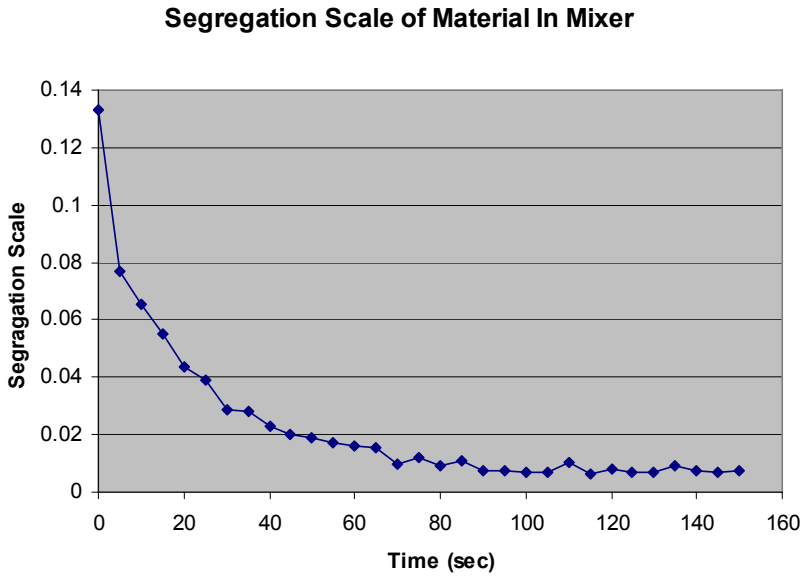

Figure 6. Segregation Scale

A closer look of the model shows the particle distribution of the physical distortion. Within 1 second of mixing (see Figure 7) the model says that the particles see a different physical distortion, stretching and shear. This is evident in the scale notation showing that there is no uniformity in the particles inside the mixing vessel in the figure below.

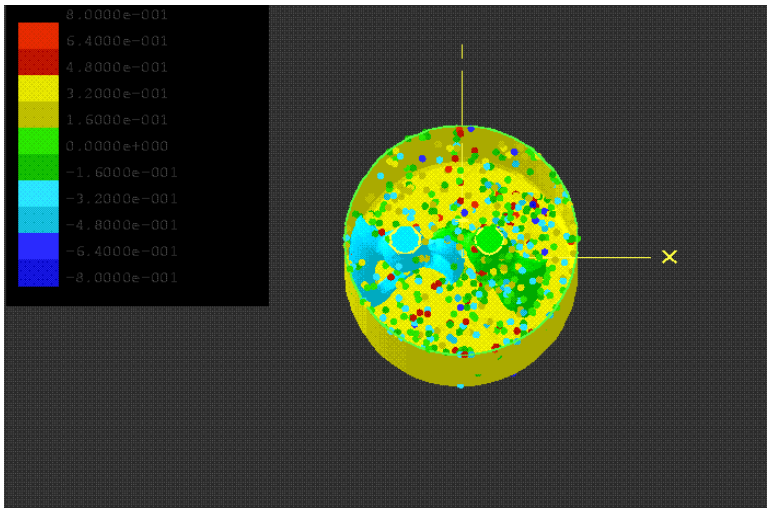

Figure 7. Time Average Efficiency of Mixing @ 1 second

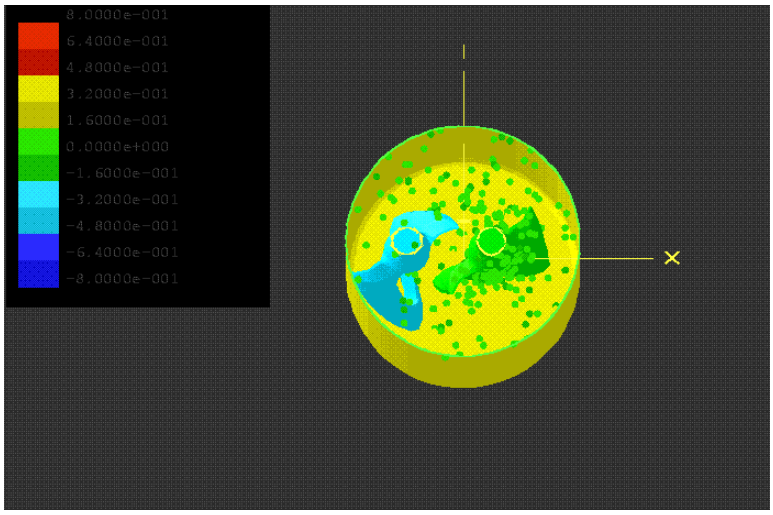

Figure 8. Time Average Efficiency of Mixing @ 150 second

At 100 seconds the particles start to become more uniform in the physical distortion. And at 150 seconds (see Figure 8) the stretching and shear that the particles see is almost completely uniform over the mixing vessel.

In comparison the particles inside a small area over time, shown in red in Figures 9 and 10, distribute over the total fluid volume over time. When the time reaches approximately 2.5 min the particles are well distributed in the mixing vessel.

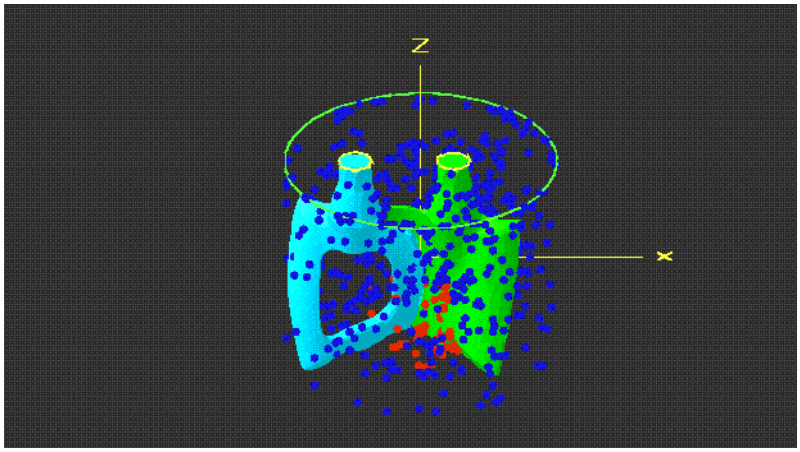

Figure 9. Particle Distribution @ 0 Seconds

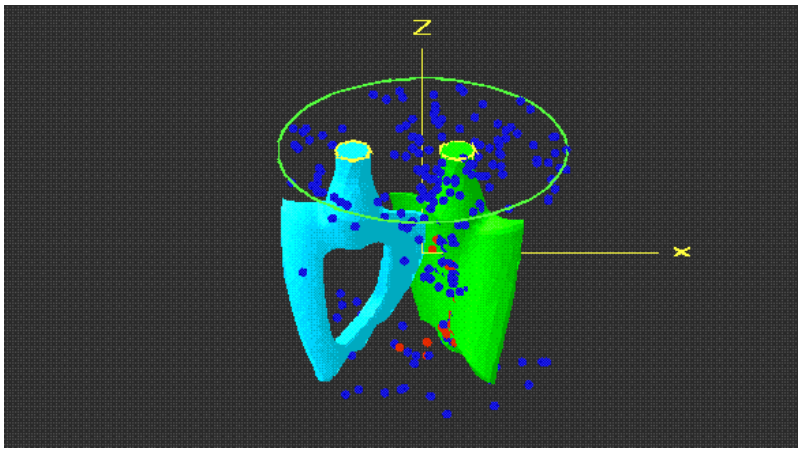

Figure 10. Particle Distribution @ 150 Seconds

Conclusions

Rheological Data

The following conclusions are drawn from the conducted experimental work:

1. The mix quality from the Thermo Haake experiments was generally good, yielding a uniform, homogeneous mix. The Specific Energy Input increased as the Ammonium Perchlorate (AP) concentration increased.

2. Overall, the Complex Viscosity data generated by the RDA III is generally reproducible with the exception of Mix III.

3. The Complex Viscosity increased as the AP concentration increased. Mixes I and II were found to be near-Newtonian in nature, but exhibited a small slope for viscosity-frequency curve (a weak power-law); Mix III was 100% power-law; while Mix IV and Mix V were typical suspension with higher sensitivity at the lower shear range of 0.1 to 1.0 rad/s, and slight power-law from 1.0 to 100 rad/s.

4. The Complex Viscosity of all five mixes decreased as the temperature increased.

Model and Simulation

1. With the help of the rheological data it can concluded that from the model, with all ingredients in the 8PI vertical mixer, that:

2. Mix V takes approximately 2.5 minutes for the material to be distributed throughout the mixer.

3. The Time Average Efficiency of Mixing at 150 second shows a uniform physical distortion of the particles.

4. The segregation scale of Mix V levels to approximately .007 at about 2 minutes