# Characterization of Gelling Systems for Development of Hypergolic Gels

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## Abstract

Hypergolic gels are being considered as an alternative to liquid and solid propellants. Hypergols are typically toxic making gel development challenging. In order to reduce the risks associated with the identification and characterization of suitable gelled propellants, water based simulants have been used for initial testing. Several gelling agents were investigated; xanthan gum, agar, hydroxypropyl cellulose, Cekol MW 2000 and Cekol MW 30000. The rheological properties of these inert gels were investigated at low shear rates through traditional techniques. Rheological behavior was also investigated at high shear rates (up to 10<sup>6</sup> 1/s) with a commercial capillary rheometer and a custom designed propellant grade capillary rheometer. Numerical simulations were compared to initial results from the propellant grade capillary rheometer for validation purposes. It was found that the simulation accuracy is very sensitive to viscosity at high shear rates, especially in predicting the capillary pressure drops. In addition to rheological characterization, impingement and atomization was investigated using a like doublet impinging jet apparatus. The effect of rheological properties on the formation of droplets following injection and impingement was considered. Out of the inert gels tested only water gelled with 1 wt.% agar exhibited acceptable properties for shear thinning rheological behavior and impingement and atomization.

## **1. Introduction**

A gelled propellant has been defined a number of different ways, but the most common property is a solid-like behavior when at rest [1]. Gelled propellants offer unique advantages over traditional liquid and solid propellant alternatives. The solid like behavior of a gelled propellant reduces spill risks associated with liquid rocket propellants. In addition, gelling agents have the ability to increase the energy density of the propellants through the addition of energetic gelling agents and additives. The shear thinning behavior at high shear rates required for suitable gelled propellants also allows typical liquid propellant throttling systems to be used. The risks due to leakage and exposure are elevated when dealing with toxic hypergolic propellants (hypergols) and thus the gelation of hypergols is the subject of an ongoing research effort.

Hypergols currently under consideration for gelation at Purdue University are monomethylhydrazine (MMH), red fuming nitric acid (RFNA) and various hydrocarbon fuels. The toxic and carcinogenic properties of MMH and the corrosive properties of RFNA make their use for preliminary studies challenging. In lieu of actual propellants, inert gel simulants such as deionized water are being investigated for initial rheological characterization. Detailed analysis of simulant properties were conducted including rheological characterization over a wide range of shear rates, numerical flow simulations and impinging jet spray atomization. The low risk and cost associated with experimentation on simulants allows a large knowledge base to be developed that can be applied to hypergols as well as other propellants in the future.

## **1.1 Desirable gelled propellant characteristics**

Stated requirements for gelled propellants are low freezing and high boiling points, low toxicity, high energy content, shear-thinning behavior, good chemical and thermal stability, and sufficient mechanical stability. The criteria established by the Purdue team for selecting gelling agents are: availability, combustibility, amount of gelling

agent needed for complete gelation, and ability to form a stable gel (should not flow under its own weight, i.e. have an appreciable yield stress) [1].

#### **1.2 Current research overview**

Current research efforts are focused on the development of methods for characterizing hypergolic gelled propellants. The first step towards this goal involves the development of gelled simulants. These simulants are evaluated for their adherence to the desirable characteristics described above. The characterization has been accomplished through rheological characterization at both low and high shear rates as well as impinging jet spray testing. The apparatuses used will be described in the following sections. Results and analysis will also be described in detail along with initial numerical simulation of shear rate behavior.

# 2. Experimental Setup

#### 2.1 Gel characterization at low and high shear rates

Rheological characterization was carried out using rotational and capillary rheometers. Since the relevant range of shear rate for propulsion systems varies from  $10^{-2}$  to  $10^{6}$  1/s, both instruments are necessary for the propellant characterization. For the detection of the rheological behavior of the simulants at low shear rates, a rotational AR-G2 Rheometer with Smart Swap<sup>TM</sup> Geometry (TA Instruments, Delaware, USA) was used. The rotational rheometer imposes a well-defined stress or strain to the sample and records the strain or stress response. Due to measurement limitations, only shear rates up to 1000 1/s can be achieved. A cone and plate geometry (60 mm) was used in this study because it allows a homogeneous strain distribution in the sample. All measurements were performed at a constant temperature of 25°C [2].

The viscosity data at higher shear rates was determined using a high shear capillary rheometer (RH2000, Bohlin Instruments). Different from the rotational rheometer, the sample is pushed through a capillary of constant cross section diameter and the flow rate and pressure drop are recorded when the flow is fully developed. High shear rates were achieved by using a die with a diameter of 0.5 mm. The values were recorded at shear rates varying from 1000 to 50000 1/s. All measurements were performed at a constant temperature of 25°C.

#### 2.2 Validation of propellant-grade capillary rheometer

The efforts to characterize liquid propellant gelling systems extend to high shear rate ranges as well. This high shear rate environment is typical in the feeding or injection system in a rocket application. Thus, it is necessary to identify and characterize gelling systems under high shear rate. This section introduces a development of a capillary rheometer that is uniquely designed to measure the behavior of these typically toxic propellants under high shear rates. Water and water/3 wt.% HPC gels are considered as sample working fluids in order to validate this capillary rheometer as an instrument for evaluating the high shear rate regime.

#### 2.2.1 Experimental Apparatus

The custom capillary rheometer design allows for the measurement of fluids whose rheology is affected by intensity and duration of applied shear stress at high rates around  $10^6$  1/s. Two capillaries are used in series, the first allows for pre-shearing of the gels. Data from the second capillary in the series provides critical information regarding the rheology of gels that have been extruded through an injector at high speed. Gels are driven through the capillary assembly by a piston with a high-speed electronic pressure regulator to obtain velocities necessary to achieve high shear rates. In Figure 1, a simplified schematic is shown next to a photograph of the capillary rheometer system with key components labeled.



Figure 1. Simplified schematic (left) and photograph (right) of the capillary rheometer system.

A critical element of the system design is the piston that forces the gels through the capillaries. Redundant dynamic spring loaded seals and o-ring face seals are incorporated to ensure no gel will leak past the piston even at speeds up to 4 cm/s. Any leaks would result in incorrect mass flow rate calculations and viscosity measurements and may allow the release of toxic propellant vapors. The piston must also reciprocate smoothly to avoid creating vortices in the gel flow. A cross sectional view of the piston is shown in Figure 2. The system is capable of operating at pressures up to 3000 psi pushing the piston.



Figure 2: Cross sectional drawing of the rheometer piston assembly.

## 2.2.2 Experimental Procedure

In order to perform an experimental measurement, gel is loaded into a piston/tube assembly that is completely removable from the system. This allows personnel to load hazardous gels in a fume hood and then transport the assembly to the rheometer in a sealed container. Low pressure nitrogen regulated up to 125 psi pushes the gel loading piston assembly, loading the gel into the rheometer piston assembly. High pressure nitrogen regulated up to 3000 psi using an ER3000 electronic controller, pushes the rheometer piston forcing gel to flow through the capillaries. High pressure pneumatic valves ensure the gel flows through the capillaries during testing and does not flow back into the

loading tube or rinse tank. In addition, the rheometer piston is vented in the event a hazardous gel should begin decomposition or off-gassing. After each test the system is flushed with deionized water several times to rinse away any excess gel remaining in the tubing, piston or capillaries. A National Instruments SCXI-1001 chassis and LabVIEW virtual insturments [3] are used for remote data acquisition. The recorded data includes all pressure transducers shown in Figure 1 and the linear encoder output showing the position of the rheometer piston.

#### 2.2.3 Computational Model Description

The simulations reported here are conducted with an in-house, unstructured grid code known as the General Equation and Mesh Solver (GEMS). [4, 5] The GEMS code solves the Navier-Stokes equations in conjunction with the continuity and energy equations. Laminar calculations were performed for all shear-thinning fluid cases as the turbulence models are not well developed for non-Newtonian fluids. For Newtonian fluids, Wilcox's k-omega 2006 [6] was used to approximate the turbulence behavior especially in sudden expansion sections right after the capillaries.

The rheological model is crucial to describe the realistic behavior of the shear-thinning fluids. A Generalized Newtonian Constitutive equation is widely used to define the non-linear relationship between the shear stress and deformation of the material. It preserves a form of viscosity for Newtonian fluids by defining the viscosity as not a constant but a function of the shear rate as:

$$\tau_{ij} = \eta(\dot{\gamma})\dot{\gamma}_{ij} \tag{1}$$

where  $\eta$  is a viscosity function,  $\dot{\gamma}_{ij}$  is the second-order strain rate tensor, and the shear rate,  $\dot{\gamma}$ , was obtained by the second invariant of the strain rate tensor. In the present simulation, the viscosity function was substituted by the Carreau-Yasuda model, Eq. (2), where the relevant parameters of the model are obtained by fitting the viscosity versus shear rate curve. The viscosity curve in simulations was measured by a rotational rheometer that has a practical operation limit of shear rates up to 1000 1/s. For this reason, the viscosity at the high shear rate Newtonian plateau was assumed as a base fluid viscosity,

$$\frac{\eta(\dot{\gamma}) - \eta_{\infty}}{\eta_0 - \eta_{\infty}} = \left[1 + \left(\dot{\gamma}\lambda\right)^a\right]^{\frac{n-1}{a}}$$
(2)

where  $\eta_0 = 720(Pa \cdot s)$ ,  $\eta_\infty = 0.001(Pa \cdot s)$ , a = 1.308,  $\lambda = 5.354$ , and n = 0.148 for water/3 wt.% HPC Gel. The value of  $\eta_\infty = 0.001(Pa \cdot s)$  assumes that the base liquid is water, however it will be demonstrated that the value changes when polymeric materials are used. Thus the value needs to be determined experimentally through high shear rate rheological characterization. Detailed numerical methods are introduced in Ref. [7, 8].

Capillary rheometer flows are simulated using a computational domain as shown in Figure 3 that was started from the instrument tube inlet and terminated at the tube exit. The inlet boundary is specified by a given flow rate, the exit boundary was imposed as a back pressure condition, the centerline was treated as an axis and wall surfaces are imposed as a no-slip condition. As indicated in Figure 3, the pressure histories are monitored in three wall locations labeled by  $P_1$ ,  $P_2$  and  $P_3$ , which corresponds to the location of the pressure transducers during experiments. In order to determine the efficient size of the computational mesh, the grid convergence study was conducted using four different candidate grids. The candidate grids are varied by the grid numbers in axial and radial directions. The convergence to the exact solution is checked by the pressure drop across the domain ( $P_1 - P_3$ ) and unsteadiness frequency detected by the mass flow rate through a tube. The test results are summarized in Table 1. Based on the results, Grid C was chosen for a parametric study for shear-thinning capillary flows as a practical level. In Grid C, the pressure drop and frequency nearly approach to Grid D, the finest grid, in spite of less grid number.



Figure 3: Computational Meshes of Capillary Rheometer.

Table 1: Summary of Grid Convergence Study							
Label	Total Grid # (*1000)	Axial Grid #	Radial _ Grid #	Newtonian Fluid (Water)		Shear-Thinning Fluid (3% HPC/Water Gel)	
				ΔP (bar)	Frequency (KHz)	ΔP (bar)	Frequency (KHz)
Grid A	52.8	660	80	41.9	38.0	33.1	26.0
Grid B	90.0	900	100	41.0	29.0	33.1	30.0
Grid C	126.0	900	140	40.6	28.0	32.9	23.5
Grid D	141.6	1180	120	40.2	26.0	32.7	22.5

Table	1:	Summary	of	Grid	Convergence	Study
					<u> </u>	

# 2.3 Gelled simulant atomization

This section closely follows the work done by Mallory and Sojka [9] and presents the spray behavior of the five different water-based gelled propellant simulants. Like doublet impinging jets were used for this study. Tests were performed using a unique experimental facility, shown in Figure 4, which allowed the flow to be examined under a variety of conditions.



Figure 4: Atomization study experimental apparatus

The experimental system is comprised of two positive displacement pistons driven by high pressure air, having an operating range from 0 to 6.9 MPa (0 to 1000 psi). The modular design, Figure 5, allows easy variation of impingement angle, 20, (via rotational stages), injector length-to-diameter ratio (by substituting tip elements), impingement jet length-to-diameter ratio (by using translation stages), and jet velocity profile (by varying upstream boundary conditions). The system is capable of run times of up to eight minutes, depending on flow rate. Data was acquired in the form of high speed (up to 10000 fps with 600x800 pixel resolution) digital images.



Figure 5: Modular injector design with optical diagnostics

## 3. Results

## 3.1 Gel characterization at low and high shear rates

#### 3.1.1 Shear rate rheological theory

In general, gels for propulsion applications demonstrate shear thinning behavior. This is the tendency of the fluid to decrease in effective viscosity as shear rate increases. One model commonly used to describe this behavior is the power-law. Previous researchers often used the power-law (Ostwald-de Waele) rheological model to describe a Non-Newtonian fluid [10]:

$$\eta = K \dot{\gamma}^{n-1} \tag{3}$$

Here *K* is the consistency index, *n* the power-law (flow behavior) index and  $\eta$ , the effective viscosity. In the case where n = 1, the power-law model describes a Newtonian fluid. Shear thinning behavior is described by 0 < n < 1 while shear thickening behavior occurs for n > 1 [10]. The advantages of this model are the ease with which calculations can be made and the success the model has in predicting flow-rate versus pressure-drop measurements.

Gels can be formed by the formation of cross linked networks, i.e. by either strong (irreversible) chemical bonds or weak (reversible) van der Waals interactions or hydrogen bonding from agglomerated particles or molecular monomers. They can be classified as either a "strong gel" or a "weak gel", but usually only "weak gels" are suitable for propulsion since they need to be atomized [1].

#### 3.1.2 Low and high shear rate rheology

The materials investigated in water were xanthan gum (XG), agar, hydroxypropyl cellulose (HPC), Cekol MW 2000, and Cekol MW 30000. Xanthan gum is a shear-thinning, high molecular weight polysaccharide which functions as a hydrophilic colloid commonly used to thicken/stabilize emulsions. Agar is derived from a polysaccharide that accumulates in the cell walls of agarophyte red algae and forms a porous, rigid, brittle gel. HPC is an ether of cellulose that forms an entangled network of polymers when dissolved in water. Cekol is a long chain polymer derived from cellulose by introducing carboxymethyl groups on the cellulose backbone, forming strong bonds when gelled [11].

The mixing process for gel formation is strongly dependent on the solvent and type of gelling agent. Typically, the inert gellant is mixed with distilled water using a standard kitchen mixer to obtain a homogenous solution with the desired rheological properties [12]. To ensure homogenous mixing, the gellant is added slowly and in small concentration increments to a vortex of well agitated distilled water. The rate of addition must be slow enough to permit particles to separate in the water. Addition of the powder should be completed, however, before any appreciable viscosity buildup is observed. Stirring continues until a homogenous solution is formed. The water-based simulants were prepared using the formulations in Table 2 and the samples are shown in Figure 6 [9].

Gelling Agent	Concentration (wt.%)	Mixing Temperature (°C)	
Xanthan gum	4	30	
Xanthan gum	20	30	
Agar	1	80	
HPC	3	30	
Cekol MW 2000	7	30	
Cekol MW 30000	5	30	

Table 2: Gelled Propellant Simulant Formulation.



Figure 6: (a) 3 wt.% HPC, (b) 7wt.% Cekol MW 2000, (c) 1 wt.% agar, (d) 4 wt.% xanthan gum, (e) 20 wt.% xanthan gum, and (f) 5 wt.% Cekol MW 30000

Viscosity measurements at varying shear rates are important to demonstrate the shear-thinning behavior, to describe gel atomization and to get data for pressure drop calculations in gelled propulsion systems. Typical effective viscosity versus strain rate data as a function of gellant concentration and type are presented in Figure 7, where shear thinning behavior is observed for all systems at intermediate shear rates. Note that the Newtonian behavior at low shear rates, otherwise known as the upper plateau, is absent in agar and xanthan gum over the low shear rate range tested.

Small concentrations of long chain polymers, such as carboxymethylcellulose (CMC), are capable of increasing the viscosity of pure water up to  $10^7$  [13] (at low shear rates). When high shear is applied, the viscosity of the systems is decreased by a factor of  $10^5$ , showing the high shear dependence. Even though different instruments using different approaches to characterize these gels were used, the data obtained show that the combination of both methodologies is adequate to measure the fluid properties in a very wide condition range.

Mixtures with HPC, Cekol MW 2000, and Cekol MW 30000 gel by forming an entangled polymer structure, resulting in strong bonds between molecules. As a result, all of the gelling agents have a higher effective viscosity than agar or particulate based gels, which do not form an entangled network. Mixtures with 4 wt.% xanthan gum form a very viscous liquids and can be atomized, so it is interesting to see that agar (a rigid, brittle gel) would have similar rheological behavior. This indicates that there may be a critical viscosity value to achieve atomization and/or viscosity is not solely responsible for the ability of a gel to atomize, but the formation of the gel may be a more important factor. Future work will investigate additional rigid, brittle gels to see if the same rheological trend is seen [9].



Figure 7: Effective Viscosity vs. Shear Rate

## 3.2 Propellant-grade capillary rheometer simulation and experimental results

#### 3.2.1 Error Analysis of a Capillary Rheometer under the high shear rate

The accuracy of the propellant grade capillary rheometer at a high shear rate is evaluated by experiments and simulations using pure water. The experiments were conducted by imposing different levels of pressure on the piston as illustrated in Figure 8 and simulations were computed by applying several inlet flow rates. The experimental and numerical results are summarized in terms of the flow rate as shown in Figure 9. The data points for experimental data in Figure 9 represent averaged values over the plateaus shown in

Figure 8 as well as an additional test series providing seven total plateaus. While collecting experimental data, the piston speed and rheometer dimensions were used to evaluate the propellant flow rate.



testing.



The pressures from experimental data seem to be 40% higher at maximum than those from simulation data. This discrepancy is believed to be caused by practical factors that can serve as a source of losses. The secondary flows in the expansion section, hydraulic instabilities, turbulence motion, etc. may be factors. The influence of such losses on the viscosity measurement at the high shear rate was also considered. The shear stress at the wall in the second capillary is calculated as:

$$\sigma_w = \frac{\Delta P_2 R_2}{2L_2} \tag{4}$$

where  $P_2$  is a pressure drop across the second capillary and  $R_2$  and  $L_2$  are a radius and length of the second capillary, respectively. The wall shear rate for Newtonian fluids can be expressed by the flow rate, Q, and a capillary radius,  $R_2$ , as

$$\dot{\gamma}_{w} = \frac{4Q}{\pi R_2^3} \tag{5}$$

and finally the viscosity is obtained as:

$$\eta_{w} = \frac{\sigma_{w}}{\dot{\gamma}_{w}} \tag{6}$$

According to this calculation procedure, based on pressure drop information in Figure 9, the viscosity-shear rate curve can be obtained as shown in Figure 10. Considering the viscosity of pure water is 0.001 Pa\*s, calculated viscosities resulted from experiments and simulations exhibit non-negligible errors because all pressure drop errors are converted into viscosity errors. In particular, errors in experiments seem to be slightly higher than in simulations. In the investigated shear range, the maximum error is 0.02 Pa\*s equivalent to 20 times of the viscosity in pure water. Note that this level of error can be significant in low viscosity fluids and be acceptable in high viscosity fluids.



Figure 10: Viscosity curve at high shear rate for pure water.

## 3.2.2 Characterization of water/3 wt.% HPC gel in the high shear rate range

Water/3 wt.% HPC gel is used as a sample working fluid in order to demonstrate the capability of the propellant grade capillary rheometer in characterizing shear-thinning gelled simulants at high shear rates. Data reduction was performed with the same procedure used for water tests. The experimental data using water/3 wt.% HPC gel are shown in Figure 11 and the pressure information in terms of a flow rate is summarized with simulation results in Figure 12. Note that the simulation indicated inFigure 12 used the C-Y model based on an assumption that the viscosity at ultimate high shear rate approaches to one of a base fluid. In this respect, the viscosity at the high shear rate plateau is assumed as 0.001 Pa•s, the viscosity of the pure water.



Figure 11: Capillary pressure history from water/3 wt.% HPC testing.



Figure 12: Capillary pressure in terms of flow rate for water/3 wt.% HPC tests and simulations.

The model significantly underestimates the pressure drop through both capillaries. This is theorized to be caused by a base fluid assumption in C-Y model. This assumption will be corrected by incorporation of a measured viscosity. Viscosity can be determined based on experimental data as described below. The shear stress at the wall remains same as Eq. (4). To determine the shear rate, the Rabinowitsch-Mooney equation [14] should be evaluated as:

$$\dot{\gamma}_{w} = \left(\frac{3Q}{\pi R^{3}}\right) + \sigma_{w} \left[\frac{d}{d\sigma_{w}} \left(\frac{Q}{\pi R^{3}}\right)\right]$$
(7)

The relationship between Q and  $Q/\pi R^3$  is correlated as a function the shear stress at the wall,  $\sigma_w$ , as:

$$\frac{Q}{\pi R^3} = a\sigma_w^{\ b} \tag{8}$$

Where, a and b are fitting coefficients. The first derivative of this fitted equation, Eq. (8), is

$$\frac{d}{d\sigma_{w}} \left(\frac{Q}{\pi R^{3}}\right) = ab\sigma_{w}^{b-1}$$
(9)

Equation (9) can be substituted into Eq. (7), and finally the shear rate at the wall is determined. The viscosity curve in terms of shear rate is shown in Figure 13. As expected, simulation results underestimate the viscosity about 10%

of experimental values. It is obvious that a base fluid viscosity assumption in C-Y model for water/3 wt.% HPC gel is shown to be inappropriate and the high shear rate viscosity should be used instead.

In Figure 13, the viscosity appears to reach an almost constant value corresponding to a Newtonian plateau in the C-Y model. The C-Y model is re-fitted based on experimental data both from rotational and commercial capillary rheometer as shown in Figure 14. The corrected C-Y coefficients are  $\eta_0=720$  (*Pa\*s*),  $\eta_{\infty}=0.174$  (*Pa\*s*), a = 1.309,  $\lambda=5.362$ , and n=0.148. Figure 13 shows that the viscosity from numerical simulations based on a base fluid viscosity at the high shear rate is underestimated by 10% compared to the viscosity from experiments. Whereas the simulation based on a measured high shear rate viscosity, Figure 14, shows an excellent agreement with experiments.

These simulation results are specific to water/3 wt.% HPC gel and are intended to confirm experimental data. Compared with experimental results, the simulation pressure drop was underestimated in a base fluid viscosity-based C-Y model and overestimated in a high-shear-rate viscosity corrected C-Y model. This capability would be enhanced by a rheological model based on more complete experimental data in a future study.



Figure 13: Viscosity curve at high shear rate for Water/3% HPC Gel.



In simulations, depending on the high shear rate viscosity assumption used, two different flow patterns were observed as shown in Figure 15: (a) a steady mode in a high shear rate viscosity corrected C-Y model and (b) an unsteady mode in a based-fluid viscosity C-Y model. These may be caused by the fact that the shear rate in the capillaries is in the high shear rate regime mostly above  $10^5$  1/s. In a steady mode, the flow seems to remain stable due to a strong viscous damping of instability factors, and in an unsteady mode, the vortex shedding due to an unstable vena contracta near the inlet lip of capillaries is observed. The detailed description of this unsteadiness is introduced in Ref. [7] and [8].



## 3.3 Impingement and Atomization

#### 3.3.1 Gelled propellant spray results

Previous atomization research utilizing HPC used the following spray parameters: 0.508 mm straight edge orifice, a free jet length to orifice diameter ratio, x/d, of 60, and an impingement angle of 100°. Despite high jet velocities and varying the L/d ratio, no drop formation was achieved with this entangled polymer, as demonstrated in Figure 16 [15]. This motivated the continued investigation of potential gelling agents of different molecular structures.



Figure 16: Sheet formation of 3 wt.% HPC showing no sheet breakup

Xanthan gum is known to form a viscous liquid at higher concentrations and also atomizes. Therefore, it was chosen as an alternative gelling agent in hopes that comparison of its properties to a stiff gel would provide insight. The spray parameters used were: 0.508 mm straight edge orifice, a free jet length to orifice diameter ratio, x/d, of 60, and an impingement angle of 100°. The internal length-to-diameter ratio, L/d, was varied between 4 and 50 to determine its influence on atomization. One can see that a high jet exit velocity is needed when using a small L/d in order to achieve significant breakup. However, if L/d is increased the jet exit velocity can be half as much and still achieve the same degree of breakup, as shown in

Figure 17. In all cases, with the exception of the low velocity and low L/d combination, impact waves can be seen emanating from the impingement point. Ligament formation is also evident with droplets forming at high velocities.



L/d = 50 $u_{gel} = 83.6 \text{ m/s}$ 

L/d = 50 $u_{gel} = 84.6 \text{ m/s}$ 

Figure 17: Sheet formation of 4 wt.% xanthan gum

Agar was the next gelling agent investigated. It formed a gel and was able to atomize, as shown in Figure 18. The spray parameters were: 0.686 mm and 0.838 mm straight edge orifices, free jet length to orifice diameter ratios, x/d, of 23, 60, and 74, and impingement angles of 80° and 140°. In this case only the internal length-to-diameter ratio, L/d, was held constant at 50. For all of the tested parameters impact waves can be seen emanating from the impingement point. As the impingement angle increased, the sheet size decreased and disappeared resulting in a fully developed spray. When the spray became fully developed, the impact waves were less pronounced.



 $2\theta = 80^{\circ}$ x/d = 74 $u_{gel} = 44.7 \text{ m/s}$ 



Dia. = 0.838 mm  $2\theta = 140^{\circ}$  x/d = 23 $u_{gel} = 54.9$  m/s



Dia. = 0.686 mm  $2\theta = 140^{\circ}$  x/d = 60 $u_{gel} = 43.3$  m/s

Figure 18: Sheet formation of 1 wt.% agar

The last two gelling agents, Cekol MW 2000 and Cekol MW 30000, did not form impingement waves, nor did they breakup at any of the tested spray parameters.

# 3.3.2 Analysis of gelled impingement results

Based on the observed results, having a high effective viscosity and shear thinning behavior does not necessarily mean a gel will atomize. Instead, a critical factor influencing the gel rheological behavior (and its atomization) is how the gelling agent interacts with the solvent at the molecular level. The cellulose/polymer gelling agents form bonds with water creating an entangled structure, whereas agar absorbs the water and forms a network around it rather than bonding to it. This reconfirms previous research that entangling polymers are not an optimal choice to achieve atomization [15].

Results combining rheological measurements and atomization trials indicate that gels that are suitable for good atomization should have a specific viscoelastic behavior as observed in some previous work concerning

water/hydroxyethyl cellulose (HEC) and JP-8/silica. Among the several viscoelastic techniques utilized to characterize gels, the stress relaxation test appears to identify a priori the behavior of the gel during atomization. A stress relaxation test is based on the application of an instant deformation to the sample to investigate how the sample molecules relax from a high energy state to a lower energy state while the strain is maintained. Different gels types exhibit different behaviors during relaxation tests. Particulate gels, such as silica gels, show little relaxation of the stress, in a way indicating that for these gels there is little relaxation or re-accommodation of their molecules under an imposed strain. In contrast polymeric gels exhibit significant stress relaxation which would indicate that the high energy imposed by the imposed deformation (strain) is relaxed by re-accommodation of the molecules resulting in a decreasing stress. This phenomenon, also known as a reptation of the polymeric molecules, is typical of many viscoelastic materials and provides an indication of the elastic nature of the fluid. In contrast particulate gels, such as silica/JP-8 gels, do not show this behavior and it appears that their molecules do not exhibit the reptation phenomenon observed on polymeric gels. Instead they seem to act as true solids as shown in Figure 19. Figure 19 also shows that silica gels relaxation behavior is dependent on the applied shear. A behavior that classifies them as plastic materials, i.e. materials that behave as solids when the stress applied is less than the yield stress and as liquid when the stress applied is larger than the yield stress. The nature of the relaxation test cannot show the transformation from a true solid to a true liquid behavior because a constant strain is imposed. What it shows is a fast, almost instantaneous, decay in the stress as true liquids until the yield stress is reached followed by stress plateau typical of solid materials at stresses lower than the yield stress of the material.



Figure 19: Typical relaxation test for particulate gels (silica) and polymeric gels (HEC).

In a way particulate gels exhibit a dual liquid/solid behavior but not simultaneously, i.e. depending on the applied stress, they can exhibit one of the behaviors, whereas viscoelastic materials exhibit a joint elastic/liquid behavior experimentally evidenced by the smooth relaxation of the stress (see HEC gels in Figure 19). The later materials are the ones that provide liquid flows with elastic characteristics that translates into a number of well known phenomena, such as die swell, rod climbing upon rotation and elastic recover to name a few, which appear to affect the formation of droplets producing sheets instead of droplets as the ones illustrated in

Figure 16. Our preliminary tests seem to indicate that the relaxation tests could be a rheological technique used to identify suitable gelling agents.

#### 4. Future Work

The combination of theoretical and experimental rheological characterization of gel systems under a large range of shear rates and a number of viscoelastic tests, along with primary and secondary atomization studies and computer models describing the flow of these complex fluids are necessary steps towards the definition of gels that are suitable for hypergolic systems. A custom capillary rheometer designed to characterize the rheological properties of true gel hypergols in addition to stimulants at shear rates on the order of  $10^6$  1/s is guiding future gel development. The effort to find an apparently predictive viscoelastic test opens new avenues to search new gelling agents that add plasticity rather than elasticity to the gels. Results with agar gels are providing progress toward that goal. New experiments using gelling materials like Dibenzylidene sorbitol (DBS), a gelling agent able to produce fragile "plastic gels" having significant thixotropic properties, are being currently investigated and new gelling agents are being sought. In addition to determining the right rheological properties to be able to form droplets in simulant gels, experiments will be conducted to assess the compatibility of the gelling agents with the fuel and oxidizer. A matrix with the relevant properties required by the gelling agents and assignment of the points is guiding the identification of optimal gelling agents. The most promising hypergolic gels will be tested using the custom propellant grade capillary rheometer.

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