

Qualitative Study of Thixotropy in Gelled Hydrocarbon Fuels

P.H.S. Santos, M.A. Carignano and O.H. Campanella

Abstract— Gelled fuels have arisen as a potential replacement for conventional solid and liquid propellants since they combine the attractive properties of liquid and solid materials. The time dependence on the rheological properties of gelled fuels can play an important role in the design of injection, atomization and combustion systems. The present paper presents the Non-Newtonian and thixotropic behavior of silica/hydrocarbon fuel gels. Viscosity measurements showed qualitatively evidence of thixotropy in the fluid. In addition, no recovery was observed when the sample was left to rest for long times.

Index Terms— fumed silica, gel, rheology, viscosity

I. INTRODUCTION

Rheological properties of gels have been of great importance in different areas due to their distinctive properties and potential applications. Gels can be formed by the addition of particles or polymers to a liquid phase forming a system with a macroscopic continuous structure[1]. The gellant particles, molecules or chains entrap the liquid forming a 3D network that changes the properties of the material from a flowing liquid to a solid. Recently, gels have been the focus of several studies in the rocket science area. Gelled propellants have arisen as a potential alternative to improve safety and performance for rocket applications becoming a promising alternative for next generation propulsion systems[2].

The great advantage of using gelled propellants is the fact that they combine the properties of liquid and solid materials[3]. In terms of application, gels can be used as mono or bipropellant, which in the last case both fuel and oxidizer are gelled. The safety is increased not only by separating the fuel and oxidizer in the bipropellant engine, but also due to the solid-like behavior of gels during storage, so they can be handled, transported and stored in safer way[4]. Storage stability is a further advantage of gelled propellants since some liquid systems have to be continuously vented to prevent overpressure in the tank[5].

Moreover, their viscoelastic properties and yield stress reduce the risk of leakage. Compared to solid propellants, gels allow a wide range thrust control by adjusting the mass flow into the combustion chamber[3-4]. Finally, high performance of gelled propellants can be achieved by the addition of metal particles to the gel with no sedimentation in the tank due to its rheological properties[6].

Organic cellulose based derivatives gellants, such as HPC (hydroxypropylcellulose) and HEC (hydroxyethylcellulose), and fumed silica are commonly used for gelled propellants applications[2]. The organic agents are typically used in combination with MMH (monomethylhydrazine) whereas fumed silica (SiO_2) is a common choice for gelling nitric acid and hydrocarbon fuel simulants. The use of fumed silica as gelling agent for rocket applications arises from the distinctive 3D network that those particles are able to form at relatively low concentrations.

A significant characteristic of fumed silica particles is their high surface area ($200 \text{ m}^2/\text{g}$)[7]. The surface of fumed silica plays an important role in the formation of aggregates and gels. Hydrophilic groups in the particle surface make fumed silica capable of building hydrogen bonds between themselves to create a gel structure. Due to its hydrophilic characteristics, in combination with hydrophobic solvents (non-hydrogen bonding) like mineral oils, terpenes, fluorocarbons, aliphatics and aromatic hydrocarbons, the interaction between silica particles and the solvent is too weak, resulting in a particle-particle interaction. The silica can then only interact with each other, resulting in aggregation process and in the formation of a gel network. In this case, low concentrations of silica is required (3-6% by total weight) to obtain a percolated network characteristic of a colloidal gel[7].

On the other hand, when a hydrophilic solvent (hydrogen-bonding-systems) is used to form gels, higher silica concentration is needed since the particles will be interacting not only with themselves but also with the liquid phase. The concentration range usually required to form gel in acids, alcohols, water and others is about 10-15%[7]. In general, the characteristics and quality of the gel formed by silica depends on the following parameters: nature of the pure liquid, nature and grade of gelling agent, concentration of gelling agent, degree of dispersion and temperature of the system. In practice, they affect directly the flow and mechanical properties of the final material. The hydrogen bonds between silica-silica particles in the solvent build up viscosity and affects viscoelastic properties of the system. In addition, fumed silica gels exhibit thixotropic behavior[8], which has been rarely reported despite of its importance on the performance of these systems.

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Thixotropy is a time dependent rheological phenomenon. It can be defined as a decrease of viscosity with time when a constant shear is applied[9]. A gradual recovery can be observed when the shear is removed. Different definitions of thixotropy have been proposed along years and sometimes it has been confused with shear-thinning behavior. Shear thinning fluids have their viscosity decreased when the shear rate applied is increased, which makes them function of shear rate only. Fig. 1 illustrates the typical behavior of a thixotropic fluid when a constant shear rate is applied. The viscosity decreases as the times goes on and a constant value is eventually reached.

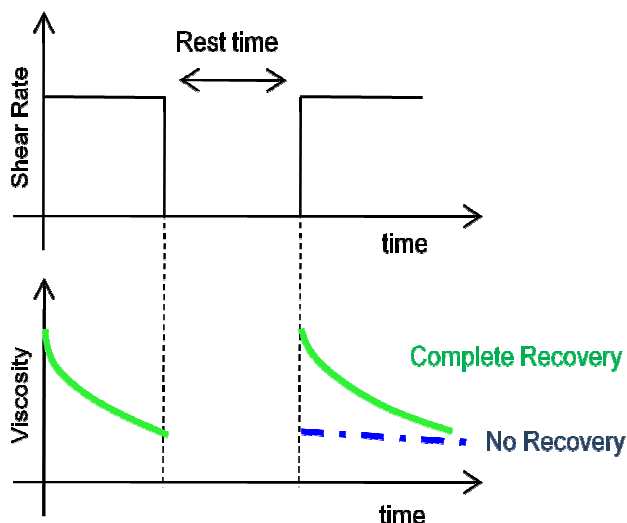


Fig.1 –Thixotropy in fluids.

The viscosity decrease with time due to the constant shear applied is related to microstructural changes in the material. Another simple and quick way to detect thixotropicity in fluids is by applying an up and down ramp of shear rates. Fig. 2 illustrates the expected behavior of a thixotropic material. If differences between the ramp measurements are observed, the fluid exhibits some degree of time dependency. The area of the hysteresis loop illustrates qualitatively evidence of thixotropicity in the fluid.

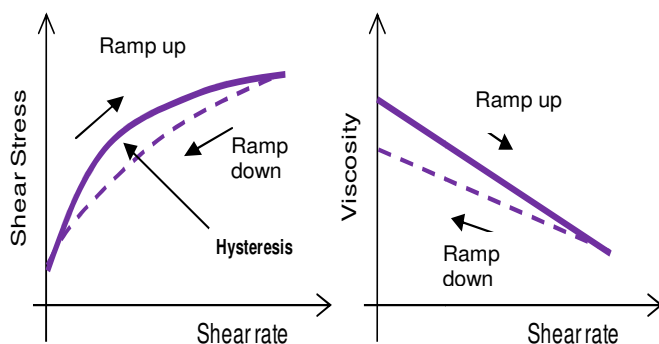


Fig. 2 – Common rheological test for thixotropic fluids.

For airbreathing and rocket propulsion systems, thixotropic gels would allow an efficient feeding control process, feeding pressure reduction and better atomization[9]. In addition to that, the rheological properties of gelled propellants influence flow, injection, atomization

and combustion processes. They provide basic information to storage and design rocket motor systems. A previous study focused on the determination of an optimal mixing process and how those parameters affect the viscosity and stability of gelled hydrocarbon fuels[11]. Since the degree of thixotropy depends on many variables such as type of gellant, concentration, solvent, among other parameters, the objective of this work was to investigate thixotropy in gelled propellant using silica as gellant agent.

II. MATERIALS AND METHODS

A. Gelled Jet Propellant

Fumed silica (CAB-O-SIL®, M-5, Cabot Corporation) was used as the gellant in the present study. The average particle size is 0.2-0.3 micrometer with significant high surface area (200 m²/g). As described before, the surface of fumed silica plays an important role in the formation of aggregates and gels. Different silica concentrations were investigated in the present study (4-7% total weight). Previous investigations showed that this concentration range is high enough to form a gel with hydrocarbon fuels[12]. Jet Propellant (JP-8) and Rocket Propellant (RP-1) were used as solvents.

The silica particles were then mixed with JP-8 using an acoustic mixer (ResodynResonantAcoustic®LabRAM). In order to form the gel, the silica particles have to be highly dispersed in the solvent to allow the formation of hydrogen bonds between them and consequently the network formation. This technique has some advantages since it is able to mix high viscous materials or even solids. In addition, the time required for the mixing is short. The shear applied to the system and the time for which this shear is applied also affects the rheological properties of hydrocarbon/silica gels. Based on previous investigations[11-12], the mixer acceleration for gel preparation was set at 100G during 60s. Those conditions were found to be the best taking into account flow properties and stability of the gels.

B. Rheological Characterization

The rheological behavior of the gelled JP-8 and RP-1 was performed by using a rotational AR-G2 Rheometer with Smart Swap™ Geometry (TA Instruments, Delaware, USA). A cone and plate geometry was used for the present investigations since it allows a homogeneous strain distribution in the sample. All measurements were carried out at constant temperature of 25°C. Different experiments were designed to detect and investigate thixotropy in the gelled fuel.

III. RESULTS AND DISCUSSIONS

For a non-Newtonian fluid, the viscosity is dependent on the applied shear rate. If the viscosity remains constant for a range of shear rate, the fluid is named as Newtonian (for fluids without yield point). If the increase in shear rate results in lower viscosity values, the fluid exhibits a shear thinning behavior whereas it is named shear thickening when higher values of viscosity is obtained. A similar experiment can be

carried out to qualitatively detect thixotropy in materials. Fig. 3 and 4 show viscosity data obtained for 4 and 7% gelled JP-8, respectively. The measurement was carried out by applying an up and down ramp of shear rate. First, the viscosity was determined varying the shear rate from 1 s^{-1} to 1000 s^{-1} (ramp up). Then, the same sample was used for an additional measurement performed by varying the shear rate from 1000 s^{-1} to 1 s^{-1} (ramp down). The concentration of silica affects the magnitude of the viscosity, as can be observed by comparing Fig 3 and 4. An increase in the silica concentration results in an increase in the viscosity of the gel.

From the ramp up measurement data, it is possible to say that the gelled propellant behaves as a Non-Newtonian fluid with its viscosity decreasing when shear rate is increased. In addition to that, there is a significant effect of silica concentration on the gel viscosity.

For both silica concentrations, there is a difference between the viscosity curves obtained from the ramp up and ramp down runs. The presence of hysteresis is a strong indication that the gel is a thixotropic fluid. The viscosity values determined in the ramp down measurements are lower than those observed in the ramp up run. The shear applied during the ramp up run affected the gel structure and consequently the viscosity of the “pre-sheared” gel. Fig. 3 and 4 also shows that the area size (hysteresis loop) relative to the 7% silica gel is larger than the 4% one. Even though this is a qualitative way to investigate thixotropy, it suggests that the 7% gel exhibits a higher degree of thixotropy than the 4% gel. Therefore, these results show that the amount of silica in the gels affects their viscosity and the degree of thixotropicity. The decrease in viscosity may be related to the shear thinning behavior of the gel combined with its thixotropic characteristics.

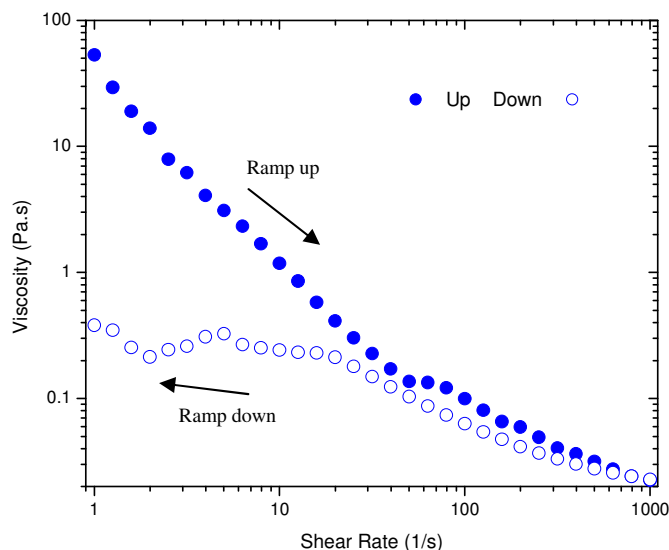


Fig 3 – Ramp up and down runs for viscosity measurement – 4% silica/Jp-8.

To show that the application of shear affects the viscosity values of these gels, 5% JP-8/silica intact sample was sheared at 1000 1/s for 2 minutes. After that, the flow curve for this pre-sheared gel was determined. Fig 5 presents the data obtained for both the intact and pre-sheared gel. The

application of constant shear for 2 minutes reduced the viscosity up to 10 times (at low shear rates).

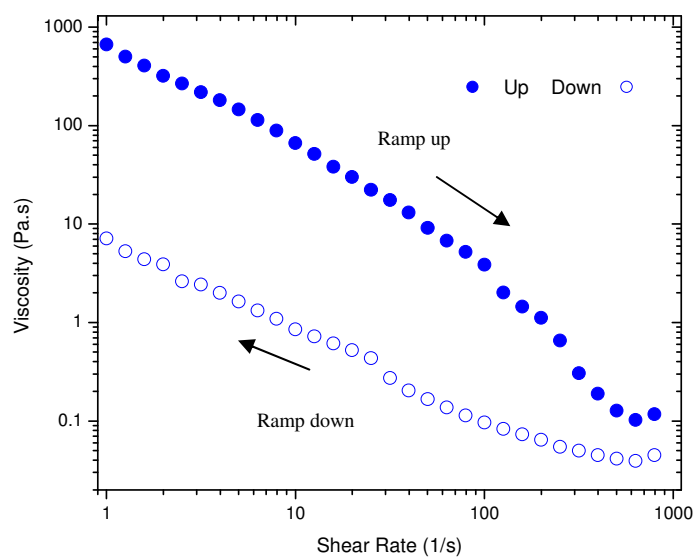


Fig. 4 - Ramp up and down runs for viscosity measurement – 7% silica/Jp-8.

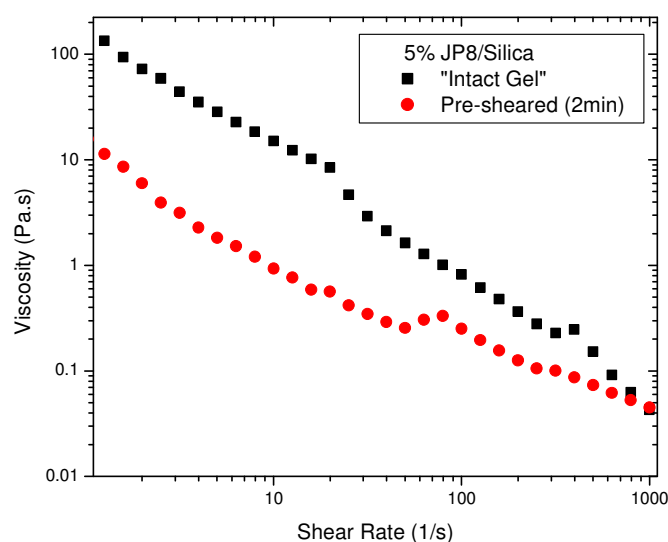


Fig. 5 – Viscosity of “intact” and pre-sheared gel (2 minutes at 1000 1/s) – 5% silica/Jp-8.

As described before, all the rheological characterization was carried out using a rotational rheometer. Rotational rheometers are commonly used to measure viscosity of fluids, mainly of those dependent on shear rate. Some devices, like the one used in this study (AR-G2 Rheometer, TA Instruments) allow one to use some parameter/conditions to carry out a measurement. For example, to measure viscosity at different shear rates, the equipment allows one to choose how many points to get from a range of shear rate and the “sample period”, i. e. the period of time that a constant shear is applied to the sample to get a single point. When time independent materials are studied, those parameters might not affect significantly the measurement, unless a steady state flow is not achieved during that time. However, if the fluid is time dependent, those two parameters may affect the measurement and consequently the data and its analysis. In those cases, a more detailed measurement procedure (listing

sampling period and number of experimental point) would be more appropriate to make the data more reproducible and consistent. To verify if sampling period is relevant to measure viscosity of gelled JP-8, different times were used. For all measurements, 10 points per decade were collected. In this case, the different sampling times include not only the effect of time on breaking the gel structure but also on the flow characteristics, since the calculation is based on the assumption of a steady state flow.

Fig.6 shows the viscosity measurement for 4% gelled JP-8 using 10, 30 and 60 seconds as sampling times. The measurements were carried out in triplicate, so the plot presents the average viscosity values. It can be seen that longer sampling time resulted in lower viscosity values. That could be related to the breaking down of the gel network during the application of shear for a longer time. The difference between 10 and 30 s does not seem to be very significant, especially at shear rates higher than 10 1/s.

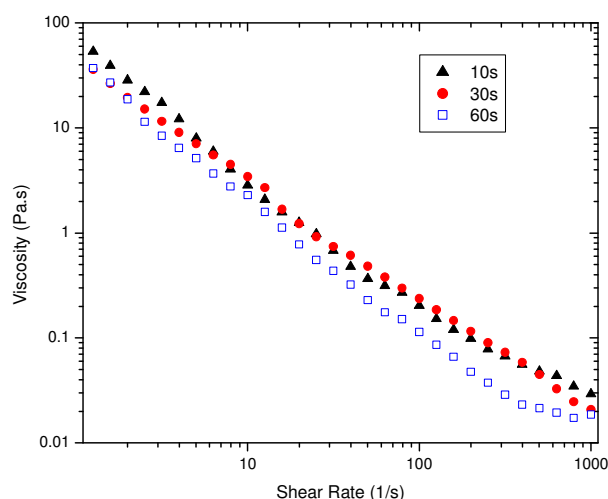


Fig. 6 – Viscosity measurements for 4% JP8 gels using different sampling times.

Further investigations were performed to study how viscosity is affected by time. For that, the following experiment was designed: application of a shear rate of 1000s^{-1} , followed by a resting period with no shearing for 480s and application again of a shear rate of 1000s^{-1} . The viscosity was measured as a function of time in the first and second parts, which allows the observation of changes during the application of shear and if there is any viscosity recovery during the rest time.

Figs.7 and 8 show the viscosity values of 4 and 7% silica/JP-8 gels as a function of time at a constant shear rate of 1000s^{-1} . The initial viscosity of both concentrations is reduced during time when shear rate is applied: there is a decay followed by a constant value at long times. In the case of 4% silica gel, at long times, the viscosity value observed was $\sim 0.02\text{ Pa.s}$, 50% lower than the initial value. A more drastic change is observed for the 7% gel. Its viscosity reaches a value of 0.05 Pa.s in a relative short period of time, which corresponds to a decrease of approximately 90%. Moreover, the viscosity plateau of 7% silica gel is reached at shorter time than the 4% one. For the higher concentration

investigated, the viscosity reached a constant value at approximately 25 s, whereas in the other case it took up to 150 s. No viscosity recovery was observed for the samples and conditions studied.

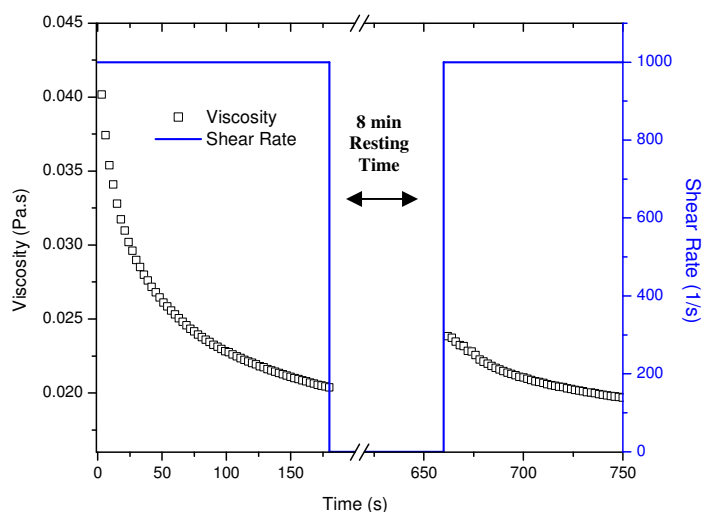


Fig. 7 – Viscosity as function of time for 4% JP8 gel at constant shear rate of 1000s^{-1} and resting time of 8 minutes.

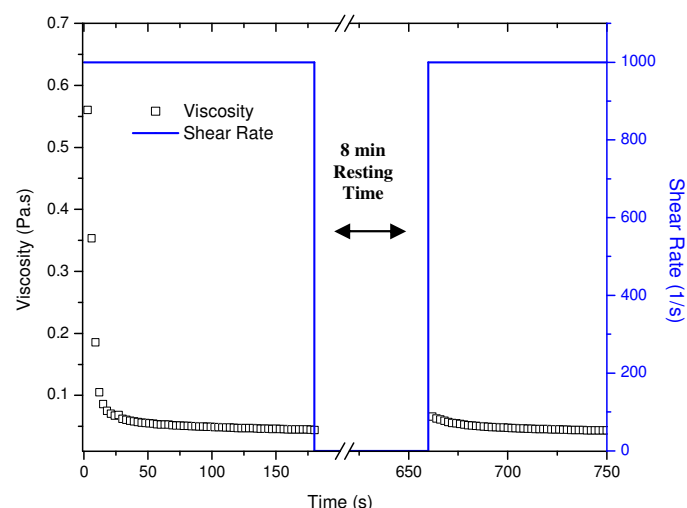


Fig. 8 – Viscosity as function of time for 7% JP8 gel at constant shear rate of 1000s^{-1} resting time of 8 minutes.

Additional measurements were carried out to evaluate how resting time affects the viscosity recovery. In this case, lower shear rates (100 1/s) and longer resting time (30 minutes) were considered. After the application of constant shear (100 1/s) for 180s, the samples were allowed to rest for 1800s (30 minutes). Therefore, lower shear was applied to see if the structure of the gels is less affected by it and longer resting time was used to allow any structural recovery to happen. Figs. 9 and 10 present the data obtained for 4 and 7% JP-8 gels, respectively. The same experiment was carried out using RP-1 propellant to see if similar behavior is observed for another hydrocarbon fuel. Figs. 11 and 12 depict the data for RP-1 gels. However, for both fuels and concentrations, the viscosity of the gels after shearing remained the same. Even at lower shear rate and longer resting time, the gel viscosity did not show significant recovery.

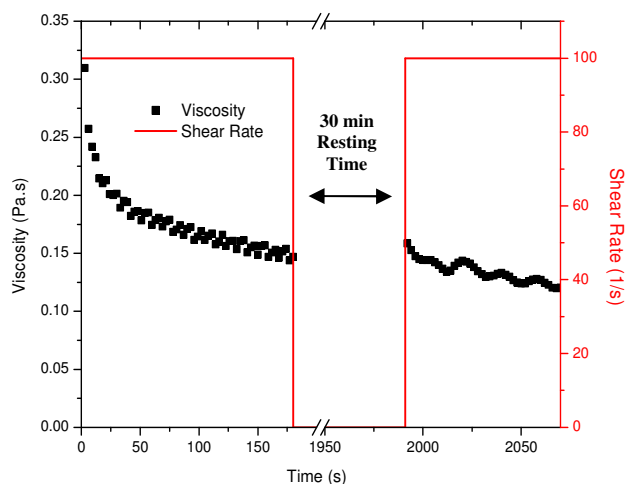


Fig. 9 – Viscosity as function of time for 4% JP8 gel at constant shear rate of 100s^{-1} resting time of 30 minutes.

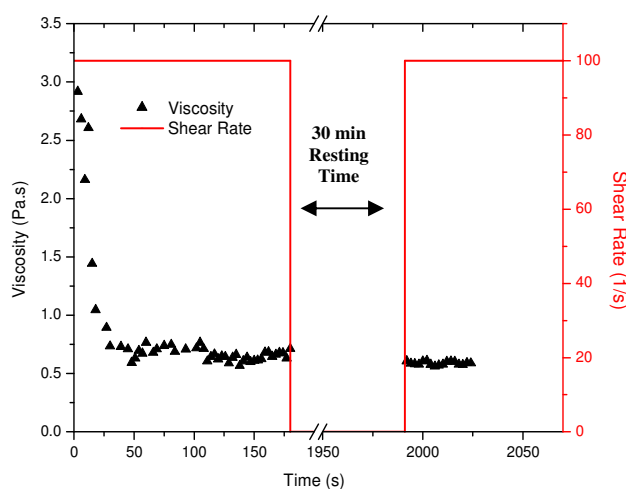


Fig. 10 – Viscosity as function of time for 7% JP8 gel at constant shear rate of 100s^{-1} resting time of 30 minutes.

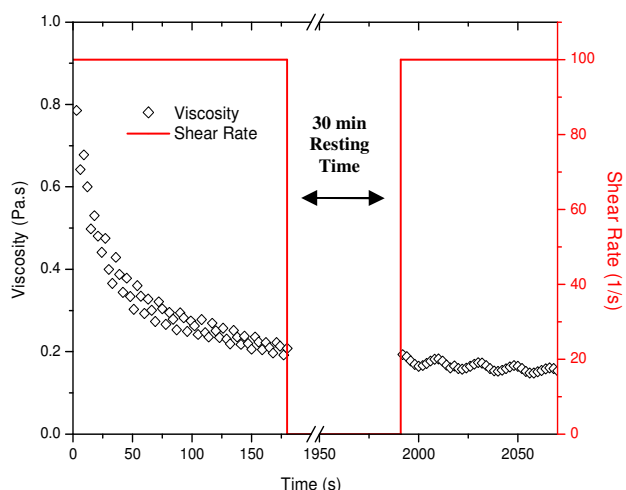


Fig. 11 – Viscosity as function of time for 4% RP1 gel at constant shear rate of 100s^{-1} resting time of 30 minutes.

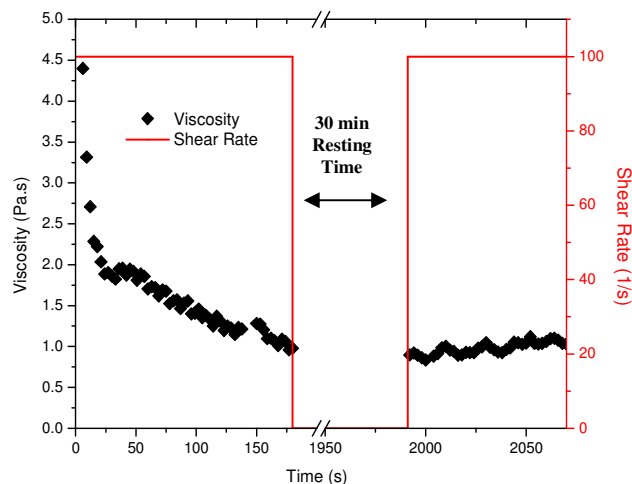


Fig. 12 – Viscosity as function of time for 7% RP1 gel at constant shear rate of 100s^{-1} resting time of 30 minutes.

The results show that the application of shear affects the gel structure, possibly destroying the 3D gel network formed by the silica particles. The network formation occurs when the particles are dispersed in the liquid and some mechanical energy is inputted. This network is responsible for the change in the flow properties of the pure fuel and also responsible for the gel like characteristic of the system. When shear is removed, the viscosity is far below the initial viscosity, showing an insignificant recovery degree for the conditions studied. Therefore, the viscosity decrease observed in the flow curve of the gels is due to the combined effect of shear thinning and thixotropy behavior that these fluids exhibit.

The effect of shear on gelled jet propellant with 7% silica can be seen in Fig. 13. The pictures were taken before and after the application of 1000s^{-1} shear for 180 s. The difference between the gelled fuel and the sheared sample can be visually observed. The gel before application of shear looks like a stiff material whereas the sheared one looks like more a viscous liquid. The excess of sample around the probe was intentionally left to show the difference between them.

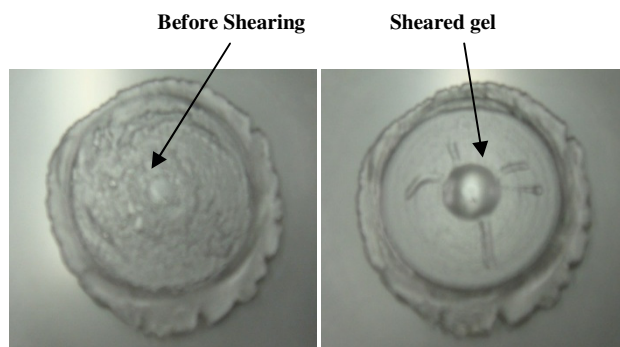


Fig. 13 – 7% Gelled JP-8 with silica before and after application of shear rate (1000s^{-1}) for 180 s.

In Figure 14 we show an illustration of what may happen to the silica gel network when shear is applied. Initially, to get a gel formed, the particles are added to the solvent and have to be highly dispersed. This allows the formation of hydrogen bonds between themselves (Fig. 14A). The solvent is then entrapped in a 3D network, which changes the flow

properties of the material. However, we observed that if a constant shear rate is applied to the gel, its viscosity is reduced during time. The application of shear might affect the 3D network, possibly breaking down the gel structure.

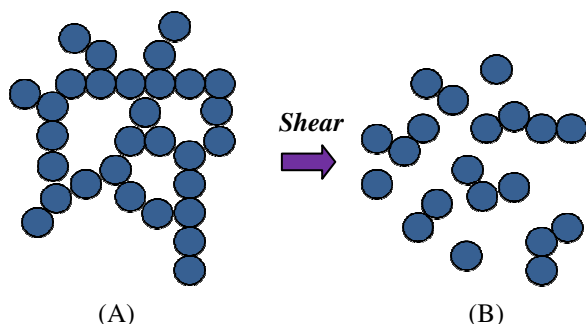


Fig. 14 – Illustration of a possible effect of shear on the fumed silica gel network.

As commented earlier, thixotropy is sometimes confused with shear thinning. For a timescale that rheometers can respond, a fluid can exhibit shear thinning behavior and not necessarily thixotropy. To illustrate this situation and to compare the different behavior of our gelled propellant to a purely shear thinning fluid, we run similar experiments using a 3% Xanthan gum water solution. Xanthan gum is commonly used as food ingredient in several formulations due to its rheological properties and because its viscosity is reduced when shear is applied. Fig. 15 shows the viscosity measurement for Xanthan gum solution for shear rate varying from 1 to 1000 s^{-1} . As can be seen, the viscosity decreases when shear rate is increased. However, when a constant shear rate is applied to the sample during a period of time (Fig. 16), the viscosity remains constant. For this case, the fluid shows a Non-Newtonian behavior but not time dependency. This material can be characterized as a shear thinning fluid.

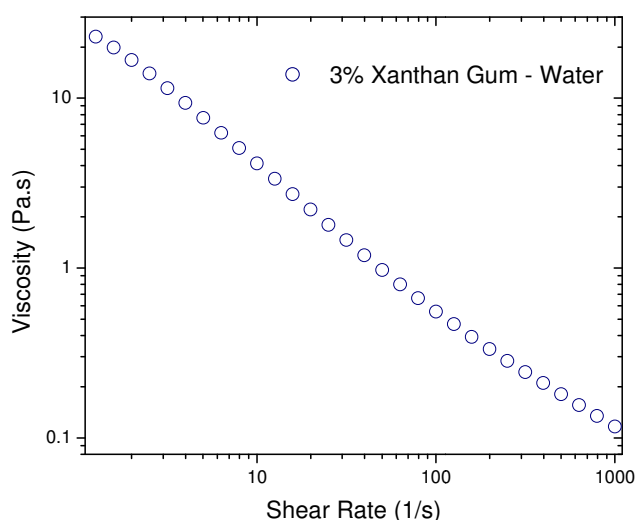


Fig. 15 - Viscosity as function of shear rate for 3% Xanthan gum solution.

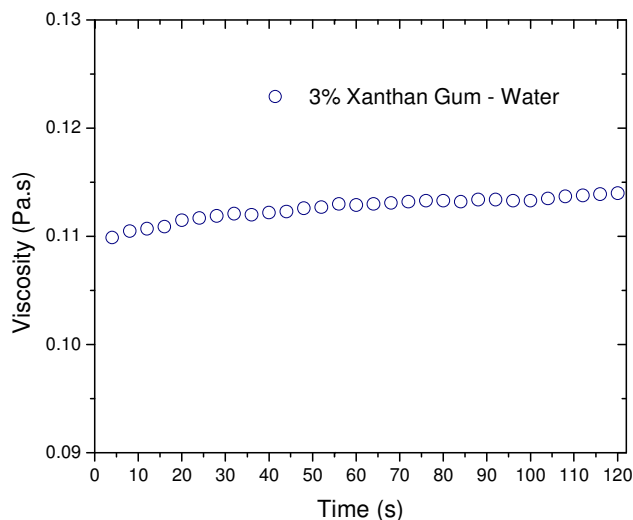


Figure 16 - Viscosity as function of time for 3% Xanthan gum solution at constant shear rate (1000 s^{-1}).

IV. CONCLUSIONS

The present paper investigated the thixotropic behavior of gelled jet propellant. The data obtained provide information for the design of next generation propulsion systems. Fumed silica gels exhibited irreversible thixotropicity, of different degrees. The amount of added gelling agent showed also a significant influence on the viscosity. The decrease in viscosity was attributed to the increase in shear rate and to a breakdown of their structure. This combined effect of shear thinning and thixotropy would lead to the use and development of appropriate rheological models that can describe flow behavior of these gels during deformation and flow.

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