

Flow and dynamic rheological characterization of ethanolamine gel propellant with hybrid gelling agent

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Abstract

In this paper, efforts are made to formulate and prepare ethanolamine gel system, using hybrid of paired gelling agent (PVP+SiO₂), that exhibit a measurable yield stress, thixotropic behavior under shear rate ranges of 1 to 20 and 1 to 1000s⁻¹ and a viscoelastic nature. To achieve these goals, multiple rheological experiments (including flow and dynamic studies) are performed. In this paper, results are presented from experiments measuring the apparent viscosity, yield stress, thixotropy, dynamic strain, frequency sweep and $\tan \delta$ behaviors, as well as the effects of the test temperature, in the gel systems. The results show that the formulated ethanolamine gel is thixotropic in nature with some yield stress. The apparent viscosity of the gel decreases as the test temperature increases, and the apparent activation energy is lower for the ethanolamine-(PVP+SiO₂) gel system. The dynamic rheology study shows that, the choice of hybrid gelling material, the applied frequency and the strain all vitally affect the viscoelastic property of the ethanolamine gel system. In the frequency sweep experiment, the ethanolamine gel to which PVP+SiO₂ was added behaves like a nearly frequency-independent viscoelastic solid.

Keywords : ethanolamine, gel, rheology, thixotropy, viscoelasticity

1. Introduction

Gel propellants are in the form of soft solids or highly structured liquids, thus showing the properties of yield stress materials. The most important characteristics of these materials are that they can behave as solids under small applied stresses and as liquids at high stresses. The strength of the gel skeleton is governed by the structure of the dispersed phase and its interactions. Normally, the continuous phase is low in viscosity; however, volume fractions of a dispersed phase and/or strong interactions between components can increase the viscosity by a thousand times or more and induce solid-like behavior at rest. This unique structure distinguishes these fluids from Newtonian liquids and makes a gel exhibit a complex rheology^{1),2)}. Most gel fuels can be rheologically categorized as pure shear-thinning fluids. Rheological

properties such as shear-thinning and thixotropy³⁾ and the viscoelastic properties of gels are of considerable interest during processing and manufacturing. Consequently, rheological characterization is an essential step for the better understanding of gel systems^{4) -6)}.

Several rheological properties play an important role in determining how a material behaves as it moves from a static to a dynamic environment and vice versa^{7) -15)}. For example, the force or stress required to initiate the flow of fluid and semi-solid materials plays a significant role in the storage, transportation, handling, sedimentation, leakage and end-use performance of those materials. Likewise, the force or stress level at which appreciable flow stops once initiated may also be of interest. The stress level required to initiate flow is usually referred to as the yield stress and is related to the level of internal structure in the material

that must be destroyed or overcome before flow can occur. Conversely, the stoppage of flow once the stress is removed is related to the rebuilding of the structure¹⁵. The yield stress and thixotropic behavior can be understood and modeled as two effects of the same cause^{17, 18}. This paper addresses phenomena such as thixotropy, yield stress, shear-thinning and structure rebuilding as well as viscoelastic properties.

The purpose of this paper is to examine the rheological properties of eco-friendly ethanolamine gel suitable for use as rocket propellant. We investigated hybrid of paired material (PVP + SiO₂) used as gelling agent for ethanolamine gel. The selection of hybrid of the two gelling agent was motivated by an attempt to produce a substantial yield stress and viscoelasticity in the ethanolamine gel propellant.

2. Materials and methods

2.1 Preparation of ethanolamine gel fuel system

In the present study, ethanolamine (99.5%) obtained from the Sigma Aldrich Corporation (CAS: 14-14-35) was selected as the base fuel. The critical concentrations of a hybrid gellant (also obtained from Sigma Aldrich) needed to gel ethanolamine were determined by conducting several sets of experiments in the range of 1 to 10 wt% of gellant. The gelling agents used for the gelation process were compatible and non-reactive with the base fuel. A uniform process was maintained during all experiments. The requisite concentrations of the gelling agents for gelation of the ethanolamine were as follows: in the case of hybrid gellant, 6 wt% PVP+6 wt% SiO₂ were the concentrations used.

Dispersions of hybrid gellant particles in ethanolamine fuel were prepared by mixing the ingredients thoroughly for 3 hours. The suspensions were stirred at room temperature (298 ± 1 K) at 3000 rpm to ensure complete dissolution of the gellant in the fuel. The mix was then left undisturbed for 24 hrs to allow gel network formation. In this case, stable gel of fuel could be prepared (Figure 1).

2.2 Rheological characterization

Rheological studies (including flow and dynamic studies) were performed on freshly prepared ethanolamine gel using a rotational rheometer (HAAKE RS6000). The rheometer was operated in controlled rate (CR) and controlled stress (CS) modes to characterize the rheological behavior of the gelled propellant. The rheometer imposed a strain on the fluid and measured the resulting stress at shear rates up to 10001/s. A 60 mm parallel plate configuration with a 1 mm gap height was used for all measurements in this study. A control system inside the rheometer ensured a constant temperature of 293 K during all rheological measurements. During the flow studies, the gel apparent viscosity measurement was performed with a 30 second sampling period. Each experiment was repeated at room temperature at least 3 to 4 times in each condition.

Shear-rate sweep experiments at up to 1000s⁻¹ were performed to characterize the shear-thinning behavior of



Figure 1 Ethanolamine - (PVP+SiO₂) gel.

ethanolamine gel formulation. The shear rate range for these experiments was selected to provide insight into the behavior of the gel under conditions such as tank filling, storage, transportation and low-speed propellant displacement within the injection feed system. The existence of yield stress and thixotropy in the ethanolamine gel system was also investigated. The yield stress and thixotropy experimental methods will be discussed in later sections.

Knowledge of the viscoelastic properties of a gel is desirable to understand the microstructural network of the gel system. The viscoelasticity of material is often determined under small strain (i.e., within the linear viscoelastic range). The linear viscoelastic region was identified by performing stress sweep at frequency of 1Hz. From this study, the elastic (storage modulus, G') and viscous (loss modulus, G'') components of the sample was estimated. Further detailed study of the G' and G'' properties of the sample was performed through frequency sweep study at 1 % strain.

3. Rheological results and discussion

3.1 Flow study

3.1.1 Determination of apparent viscosity (CR mode)

A CR-mode flow study was conducted on the prepared gel to measure the apparent viscosity as a function of the shear rate. In a non-Newtonian fluid, the viscosity is dependent on the applied shear rate. This study was conducted to investigate the shear-thinning property of ethanolamine-based gel propellant at shear rates in the ranges of 1 to 20 and 1 to 1000 s⁻¹ (Figure 2). This measurement provides an understanding of the variation of the fluid flow behavior with the yield stress, consistency, homogeneity and overall quality of the gel. The results clearly indicate that the apparent viscosity of ethanolamine gel decreases significantly with increasing shear rate. This observation can be explained by the assumption that as the shear rate is increased, the loosely associated three-dimensional network is disturbed. This

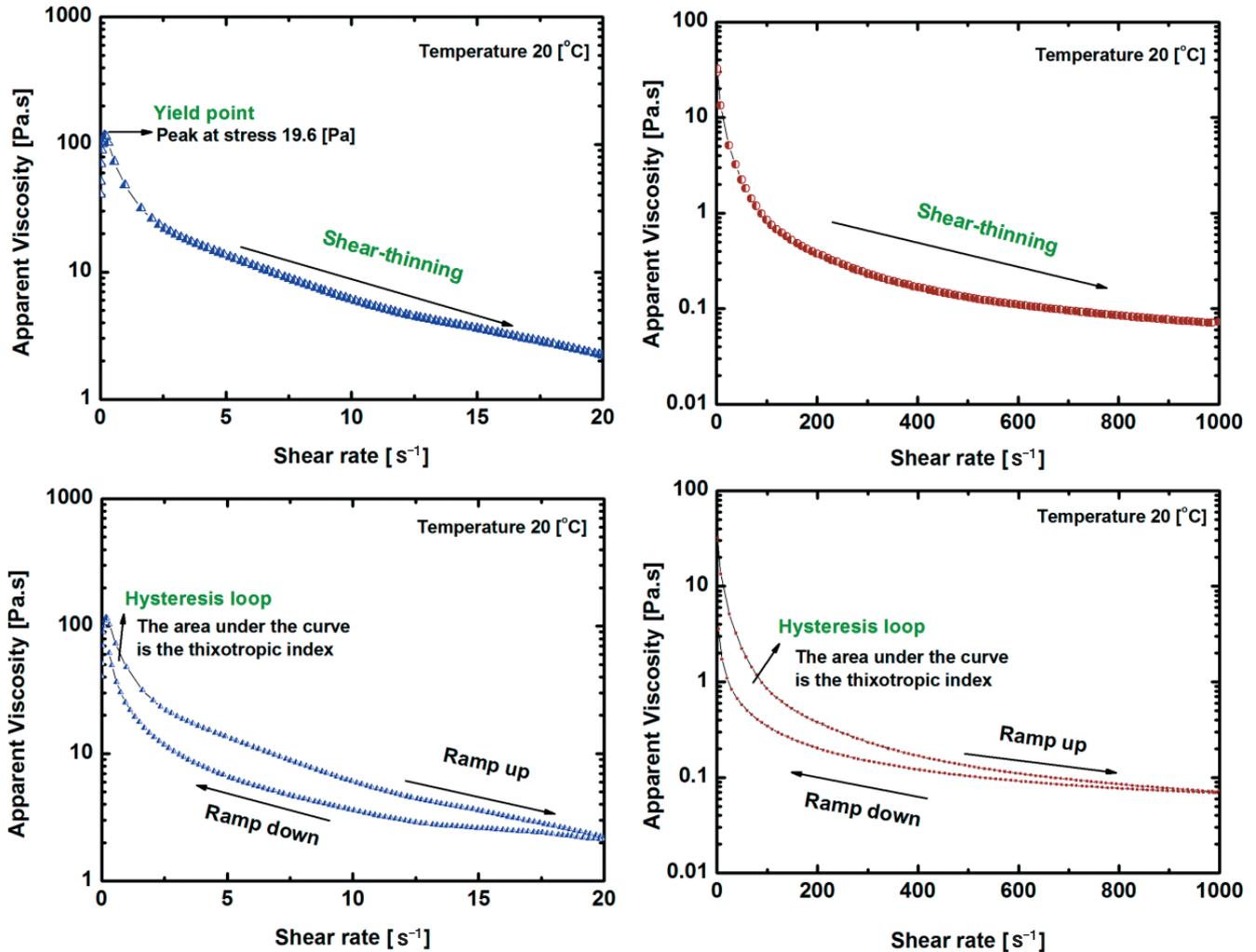


Figure 2 Rheogram study of ethanolamine - (PVP+SiO₂) gel system at shear rates of 1 to 20 and 1 to 1000 s⁻¹.

may lead to an alignment of the network elements that results in the release of the liquid entrapped within, offering less resistance to flow and, as a result, a reduction in the apparent viscosity.

From Figure 2, it can be observed that when gel is disturbed at very low shear rates, the flow is initiated at the yield stress (except at 1 to 1000 s⁻¹), and a further increase in the shear rate leads to a thinning of the gel in both of the shear rate ranges. This yield stress phenomenon shows that the gel will not flow unless they have reached a critical stress level, called the yield stress. Whereas below the yield stress the gel have solid-like behavior, above the yield stress, viscous flow (i.e., liquid-like behavior) occurs due to the breakdown of the three-dimensional network structure of the gel. In practice, this means that the material has to be pumped to break down its structure and initiate its flow. This static yield stress is defined as the stress required to initiate flow and is often higher in value. It is usually better to measure the static yield stress when investigating the initiating flow in a material, such as in pumping.

3.1.2 Determination of thixotropic behavior

In this experiment, the shear rate was increased systematically to a maximum level and then decreased in

similar steps to obtain the rheogram curve in both directions (Figure 2). In the ethanolamine-(PVP+SiO₂) gel, there is a difference between the viscosity curves obtained from the increasing and decreasing runs. The presence of hysteresis is a strong indication that the gel is a thixotropic fluid. The area within the loop provides a direct measure of the extent of the thixotropic behavior of the gel. It also reflects the reduction in the structural strength during the shear load phase, the completeness of the structural regeneration with time and the subsequent decrease in the shear rate due to the local spatial rearrangement of the molecules in the three-dimensional network. Although this is a qualitative way to study thixotropy, it suggests that ethanolamine gel exhibit greater thixotropy in the shear rate range of 1 to 1000 s⁻¹ than in the 1 to 20 s⁻¹ range. Therefore, these results show that the gel apparent viscosity and degree of thixotropy depend on the shear rate. The decrease in viscosity may be related to the shear thinning behavior of the gel, combined with its thixotropic characteristics. Additionally, the materials demonstrating a yield stress are typically thixotropic, meaning that their properties are dependent on the shear history of the sample and are susceptible to aging.

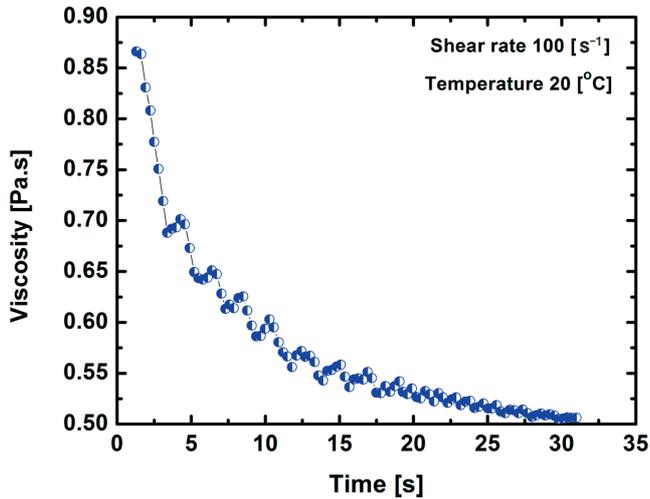


Figure 3 Time-dependent behavior of ethanolamine - (PVP+SiO₂) gel system at a constant shear rate (100 s⁻¹).

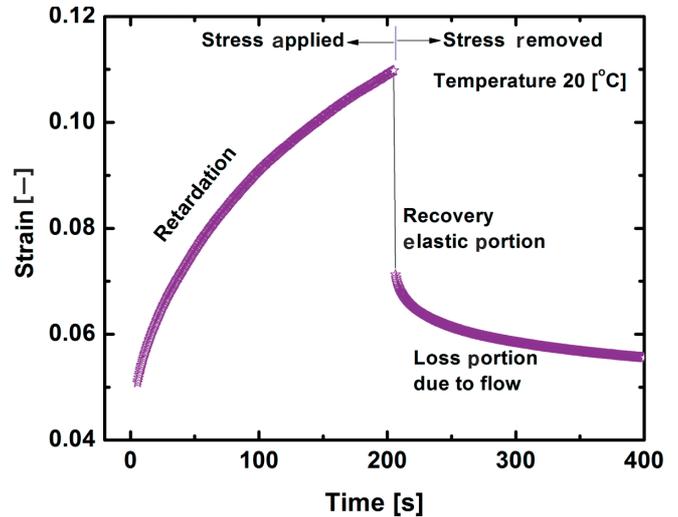


Figure 4 Creep-recovery behavior of ethanolamine-(PVP+SiO₂) gel system at a constant shear stress (10 Pa).

3.1.3 Time-dependent behavior of ethanolamine gel

In this test, the apparent viscosity of the ethanolamine gel with time was studied at a constant shear rate (100 s⁻¹).

In this experiment, a constant shear rate of 100 s⁻¹ was applied for 60 seconds to study the effect of low shear rate on time-dependent behavior of ethanolamine-(PVP+SiO₂) gel system (Figure 3). The critical behavior of the gel system can be determined primarily at the lower applied shear rates. The shear thinning response of the gel, which is the desirable feature of the gel system, can be achieved by altering the viscoelasticity of gel even at the low constant shear rate. During this process, the apparent viscosity of the gels was measured as a function of time. From Figure 3, it can be observed that the initial viscosity of the ethanolamine-(PVP+SiO₂) gel sample decreased over time. In the gel, the three-dimensional microstructure affects the time needed to move from one microstructural state to another, that is, from the rest state to the final state. The driving force for microstructural change during flow is the structural breakdown due to flow stresses. These effects determine the levels of viscosity and elasticity and the time to change from one state to another under the action of shear. The ethanolamine gel system might have a more substantial microstructural network due to random alignment and spatial distribution in the three-dimensional network, and there might also be a greater degree of entanglement. Both of these conditions would result in a shear thinning viscous response.

3.2 Creep-recovery test of ethanolamine gel

In this experiment, a constant shear stress (10 Pa) on the gel was instantly applied for 200 s and then removing the stress for another 200 s. The test condition was isothermal at 293 K. Constant shear stress of 10 Pa was applied to understand the effect of low shear stress over the viscoelasticity of ethanolamine-(PVP+SiO₂) gel system. From Figure 4 we can observe that elastic recovery is dominating over the viscous behavior of the gel even at low shear stress and thus this behavior is helping the gel

to behave as a viscoelastic solid. A creep experiment can be used where stress is applied to the material and strain (displacement) is monitored with time. The viscoelastic materials exhibit creep behavior. The resultant profile has three regions a initial elastic region, a transition region and a viscous region. The data obtained from this experiment is presented as strain versus time, as shown in Figure 4. Figure 4 shows that under shear stress, the ethanolamine-(PVP+SiO₂) gel behave as viscoelastic solid. The curve exhibits typical behavior for a viscoelastic material. The relative value of the initial and the recovery shear strain indicate that the ethanolamine gel propellant elastic branch is dominant, compared to the viscous branch under the applied shear stress.

3.3 Dynamic strain sweep test (CS mode)

Dynamic strain sweep measurements were used to determine the linear viscoelastic (LVE) range of the gel sample. This test involves monitoring the elastic modulus and LVE range at a constant frequency because the LVE range is frequency dependent. It can also be employed to determine the yield stress. To determine the critical strain of ethanolamine-(PVP+SiO₂) gel system at comparably lower frequency and to have the approximate extent of LVE range the experiment has been performed at constant frequency of 1 Hz. When gel sample was compared, the limit of the LVE region of the material may be differentiated, unlike in shear experiment.

At small stress amplitudes, the elastic modulus (G') is independent of the strain, whereas at higher strain, there is a sudden drop in the elastic modulus, indicating structural deformation and a transition from elastic to viscous behavior. This change can provide information about gel strength and stability. The strain value at the transition from the linear viscoelastic region to the viscous region represents the yield point (i.e., the critical strain point, γ_c : $G' \cdot \gamma = \tau_o$, where G' is the elastic modulus, γ is the strain and τ_o the yield point). The dynamic yield stress is defined as the minimum stress required to maintain flow. Consequently, the dynamic yield stress value may be

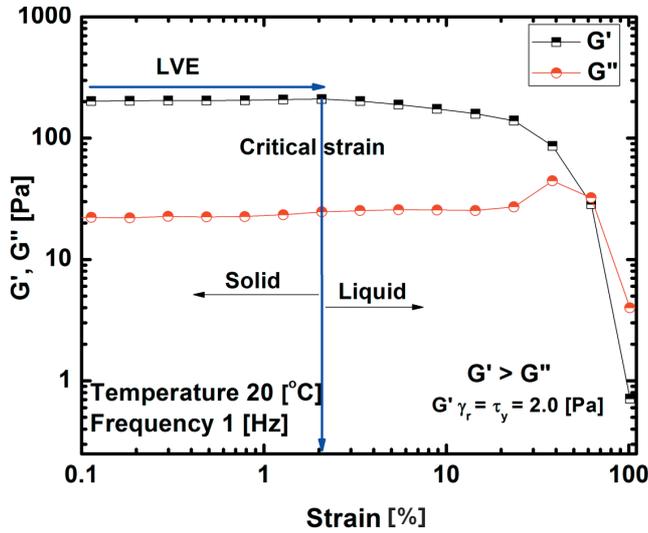


Figure 5 Dynamic strain sweep study of ethanolamine-(PVP+SiO₂) gel system at 1 Hz.

most useful in applications in which the flow is maintained or stopped after initiation, where lower dynamic yield stress values may be desirable (Figure 5). Figure 5 shows the limit of the LVE range for constant frequency of 1 Hz. The LVE plot enables one to distinguish network deformation in the gel. In Figure 5, it can be observed that the LVE of the ethanolamine gel with PVP+SiO₂ added are independent of strain between 0.1 to 2% in 1 Hz frequency condition. Below this strain level, the gel structure is intact, the material behaves like a solid, and G' is greater than G'' (for constant frequency of 1 Hz), indicating that the material is highly structured. Increasing the strain above the critical strain disrupts the network structure. The material becomes progressively more fluid-like, and the modulus declines.

3.4 Frequency sweep test (CS mode)

Frequency sweep test was performed below the critical strain of the ethanolamine gel sample to investigate the viscoelastic property of the gel network structure as a function of the gelling agent and to determine the frequency dependence of the elastic (G') and viscous (G'') moduli. This test provides information about unusual flow behavior. The shape of the material function curve reveals the structural characteristics of the material. These characteristics are useful because they describe the gel in terms of its strength and weakness. A high G' in comparison to G'' represents strong intermolecular interactions and results from the ability to resist intermolecular slippage due to the relative strength of the loosely associated gel structure occurring in the three-dimensional network.

Figure 6 shows the G' and G'' values for the ethanolamine gel sample, measured in the frequency range (ω) of 0.1 to 50 Hz. From Figure 6, it can be observed that for strain 1%, the G' and G'' moduli of the gel sample with PVP+SiO₂ added behaves consistently like a perfectly elastic gel, nearly independent of the frequency. Therefore, the critical gel concentration could be less than the gellant concentration used in the present study for the

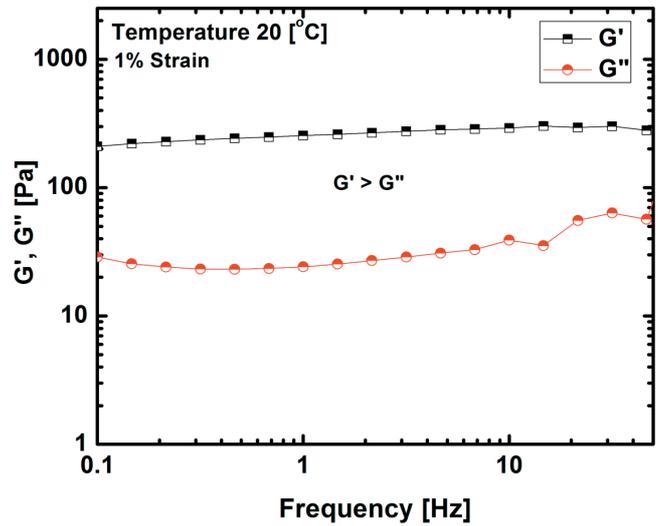


Figure 6 Frequency sweep study of ethanolamine-(PVP+SiO₂) gel system at 1% strain.

gelation of ethanolamine. This result provide key insight into the mechanism at work during propellant injection because at low frequencies, the strain simulates a disturbance during loading or storage and at higher frequencies, the tests may provide information about fast phenomena such as injection.

4. Conclusion

In this paper, efforts were made to understand the rheological properties required to make a ethanolamine gel suitable for use as a propellant. To achieve this goal, multiple rheological experiments (including both flow and dynamic studies) were performed to evaluate the gel apparent viscosity, shear-thinning, yield stress, thixotropy, dynamic strain, critical strain, LVE, storage modulus. The observed changes in the ethanolamine gel properties during the experiments were assumed to be solely due to the imposed conditions.

The gelation of ethanolamine fuel can be performed with hybrid gelling agent such as PVP+SiO₂ at reasonably low critical concentrations to obtain stable gel. The gel formulated exhibited shear-thinning, thixotropic behavior over the shear rate ranges of 1 to 20 and 1 to 1000 s⁻¹. The influence of the shear rate led to a reduction in the apparent viscosity with some yield stress behavior.

The dynamic rheology analysis showed that the type of gellant and its concentration plays a vital role in determining the viscoelastic properties of ethanolamine gel system. For the ethanolamine gel with PVP+SiO₂ added, G' was greater than G'' for the frequency range (1 Hz) covered in the present dynamic strain sweep study. Both the G' and G'' moduli of the ethanolamine gel with PVP+SiO₂ added behaved consistently like a perfectly elastic gel, independent of frequency, for strain cases 1%. These results enable the distinction of gel and their network deformation and, consequently, the microscopic structure of the material. The ethanolamine-(PVP+SiO₂) gel could be classified as weak physical gel with good cross-linking network. The shear rate range, temperature, frequency and strain, as well as the type of gellant and its

concentration, all play important roles and significantly influence the rheological properties of an ethanolamine gel propellant system.

The required properties of a useful gelled propellant that we intended to address in this work were the presence of yield stress to prevent sedimentation, the ability to flow during storage and handling, shear-thinning behavior for ease of flow in injection systems, thixotropic behavior for gel structural reformation and the gel three-dimensional network time response at constant shear. The microscopic gel structure provided information about the gel strength, weakness and stability. Although the viscoelastic measurements were performed at low shear strain and frequency, the results obtained under dynamic shear provided key insights into the mechanisms at work during propellant injection and disturbances during storage and loading.

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