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Rheological Behavior of Nitromethane Gelled with Nanoparticles

Ulrich Teipel* and Ulrich Förter-Barth†
Fraunhofer Institut für Chemische Technologie, 76327 Pfinztal, Germany

Gel propellants provide rocket propulsion systems of high specific impulse, low sensitivity, and low vulnerability in combination with the capability to control the thrust, that is, variation of thrust and thrust cutoff. The rheological characterization is essential for the development of adequate gel propellant formulations and, thus, for the design of an applicable propulsion system. The rheological behavior of a gel propellant consisting of nitromethane as fuel and nanoparticles of silicon dioxide as gelling agent was examined. The experiments were conducted under steady-state shear flow and oscillatory shear. The nitromethane/silicon dioxide gels exhibit non-Newtonian flow behavior over the whole concentration range examined. Additionally, a yield stress is determined for all of the gels. The viscoelastic properties are typically gellike in that the storage and the loss moduli are both independent of frequency.

I. Introduction

IN recent years, the challenge of achieving high performance while also improving the safety characteristics of rocket propellants has become an important goal within the industry. Gel propellants offer the potential to satisfy such demands because they combine certain advantages of liquid propellants with other attractive properties typical of solid propellants. Gel propellants can be designed as mono- or bipropellants. When used as a bipropellant, both the fuel and oxidizer can be prepared as gels. The safety of the system is improved by separating the fuel and oxidizer. In general, gel propellants exhibit a specific impulse comparable to liquid propellants, but their performance can be increased even further through the addition of additives such as metal particles. A significant advantage of gel propellants over solid rocket propellants is the ability to control the thrust by controlling the mass flow of propellant into the combustion chamber. The rocket motor can even be turned on and off or pulse driven as required. Furthermore, gel propellants are less sensitive than liquid propellants and can be handled, stored, and transported more securely because of their solidlike properties. This is especially important when, for instance, fissures or leakage sites develop within the combustion chamber of a gel propellant-driven rocket motor. The viscoelasticity of the gel propellant, that is, its unique rheological properties, significantly reduces the risk that the propellant will leak from the motor and inadvertently ignite.

The rheological properties of a gel propellant significantly affect a number of key operational and production requirements, including the propellant material behavior, casting and spraying operations, and combustion within the rocket motor. Rheological characterization of the gel provides basic information critical to the production and storage of gel propellants, rocket motor casting, as well as the design of the entire rocket motor system.

The rheological properties of gel propellants enhanced with metal particulate additives is described in the literature. Gupta et al.[1] characterized virgin and metallized unsymmetrical dimethyl hydrazine (UDMH) gel fuels with methyl cellulose as the gelling agent. The flow properties of this gel were determined as a function of time (in experiments conducted at various constant shear rates) and as a function of shear rate and temperature. At a given constant shear rate, the gel viscosity increased with time. As the shear loading was increased, the gels exhibited pronounced shear thinning behavior. At constant metal concentrations, shear thinning became less pronounced as the temperature increased, but at constant temperatures the shear thinning behavior became more pronounced with increasing metal concentration. Likewise, the yield stress of the gel increased with increasing metal concentration and decreased with increasing temperature. Rapp and Zurawski[2] examined the rheological behavior of gelled aluminum/kerosene fuels. They found that the yield point increased with increasing concentration of metal particles in the gel. During long-time storage, the yield stress of the gels decreased, a phenomenon that was attributed to physical, thermal, and chemical instability. Varghese et al.[3,4] investigated UDMH and kerosene gels with different gellants and metal ingredients. The material was subjected to a range of different shear stresses and temperatures. The gel fuels exhibited shear thinning and thixotropic behavior, which became more pronounced with increasing metal concentration and less pronounced at higher temperatures. Compared to the kerosene gels, the flow behavior of the UDMH gels was more strongly dependent on the shear loading applied. The particle size of the metal additive and characteristics of the other ingredients, such as the gellant, stabilizer, and wetting agent all have an important influence on the rheological properties of the gel. Rahimi et al.[5] examined fuels such as hydrazine (N_2H_4), monomethyl hydrazine (MMH), and kerosene, which were gelled using various cellulose compounds. They also examined the oxidizers inhibited red fuming nitric acid (IRFNA) and hydrogen peroxide (H_2O_2), which were gelled using silica particles. From these rheological studies, gel propellants can be divided into three categories depending on their degree of shear thinning behavior, their yield stress characteristics, and their viscoelastic and thixotropic properties.

This study examined the rheological behavior of nitromethane gelled with nanometer-sized silicon dioxide. In combination with suitable oxidizers and additives, nitromethane exhibits a specific impulse $I_s > 2400\ \mathrm{N \cdot s \cdot kg^{-1}}$ and is much less toxic than hydrazine derivatives, thus, providing environmental and handling advantages compared to such compounds.

II. Measurement Methods

A. Steady-State Shear Flow

The rheological behavior of the gels prepared was examined in steady state and oscillatory shear flow using a universal dynamic spectrometry 200 rotational rheometer manufactured by Physica Meßtechnik, GmbH. All rheological measurements conducted showed very good reproducibility, that is, the variation of the measured values was less than 0.5%. Cone and plate measurement fixtures were used.

Under steady-state shear flow, the characteristic material function can be described as follows:

$$\tau(\dot{\gamma}) = \eta(\dot{\gamma}) \cdot \dot{\gamma} \qquad (1)$$

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*Professor, Department of Energetic Materials, Joseph-von-Fraunhofer-Straße 7, D.

†Dipl-Inf., Department of Energetic Materials, Joseph-von-Fraunhofer-Straße 7, D.

Here $\eta(\dot{\gamma})$ is a characteristic material function that describes the flow properties when the fluid is subjected to a rheometric flow.

Various models are available in the literature[6] to describe the material behavior of fluids in stationary shear flow. Examples of several model functions[6,7] that describe nonlinear flow behavior are presented in this section.

The power law function of Ostwald–de Waele can be used to model shear thinning (pseudoplastic) or shear thickening (dilatant) flow behavior:

$$\tau = K_1 \cdot \dot{\gamma}^n \tag{2}$$

K_1 is the consistency coefficient and n is the flow index. Shear thinning behavior corresponds to $n < 1$, whereas shear thickening behavior exists when $n > 1$. Ideal viscous (Newtonian) behavior corresponds to $n = 1$. This model is unfortunately not effective in describing the flow behavior of many fluids at very small shear rates (near the limiting viscosity at zero shear rate) and at very high shear rates. The viscosity function for such power law fluids is expressed as follows:

$$\eta(\dot{\gamma}) = K_1 \cdot \dot{\gamma}^{n-1} \tag{3}$$

Sisko[6] expanded this model equation for the high shear rate region:

$$\eta(\dot{\gamma}) = \eta_\infty + K_1 \cdot \dot{\gamma}^{n-1} \tag{4}$$

The model presented by Ellis[7] is more suitable for describing flow behavior in the low shear rate region:

$$\eta(\tau) = \eta_0 \Big/ \left(1 + K_2 \cdot \eta_0 \cdot \tau^m\right) \tag{5}$$

where K_2 and m are fitted model parameters.

When the shear stress applied to a fluid must exceed a threshold value, that is, yield stress, before the onset of irreversible deformation, the material is said to exhibit plastic flow behavior. Below the yield stress, the fluid exhibits reversible (elastic) deformation. Highly concentrated disperse systems, in which the solid particulates tend to aggregate, exhibit such viscoplastic material behavior. Materials that exhibit a linear relationship between the shear stress and shear rate at stresses above the yield stress, τ_0, are known as Bingham[7] fluids and can be modeled using the following equation:

$$\tau = \tau_0 + \eta_B \cdot \dot{\gamma} \tag{6}$$

If the behavior at shear stresses above the yield stress τ_0 is nonlinear, the material can be described by the Herschel–Bulkley[7] equation:

$$\tau = \tau_0 + K \cdot \dot{\gamma}^n \tag{7}$$

This power law equation allows one to describe shear thinning or shear thickening fluids that exhibit a yield stress τ_0.

Besides shear rate dependence, non-Newtonian behavior can also manifest itself as shear time dependence. For instance, if a material's viscosity decreases with time at a constant shear rate, it is said to exhibit thixotropic behavior.

B. Oscillatory Shear Flow

In oscillatory shear flow (Fig. 1) the fluid is subjected to a periodic, for example, sinusoidal deformation $\gamma(t)$ with an amplitude $\hat{\gamma}$ at a radial frequency $\omega = 2\pi f$ (Ref. 6),

$$\gamma(t) = \hat{\gamma} \sin(\omega t) \tag{8}$$

At sufficiently small amplitudes, that is, in the linear viscoelastic range, subjecting the material to an oscillatory (sinusoidal) shear deformation results in a sinusoidal shear stress $\tau(t)$ output. Viscoelastic material behavior is characterized by the existence of a phase shift δ (Fig. 2) between the shear stress output $\tau(t)$ and the deformation input $\gamma(t)$,

$$\tau(t) = \hat{\tau} \cdot \sin(\omega t + \delta) \tag{9}$$

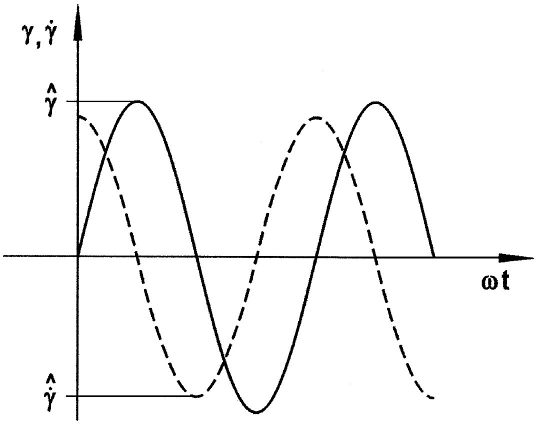

Fig. 1 Deformation and shear rate profiles in oscillatory shear flows: ---, $\dot{\gamma}$ and ——, γ.

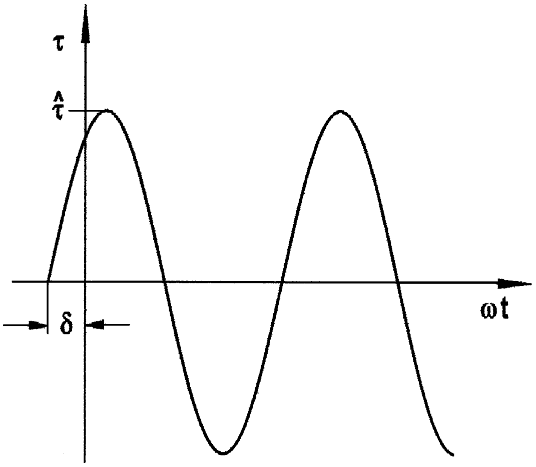

Fig. 2 Shear stress profile of a viscoelastic fluid resulting from an oscillatory shear deformation.

By definition, the phase shift δ of a perfectly elastic solid is zero and that of a purely viscous fluid is $\pi/2$, whereas for viscoelastic fluids $0 \leq \delta \leq \pi/2$.

The shear stress function can be described in terms of the frequency-dependent complex shear modulus $G^*(\omega)$,

$$\tau(t) = \hat{\gamma}|G^*(\omega)| \cdot \sin[\omega t + \delta(\omega)] \tag{10}$$

The complex shear modulus can also be expressed as

$$|G^*(\omega)| = \hat{\tau}(\omega)/\hat{\gamma} \tag{11}$$

The complex shear modulus $G^*(\omega)$ of a viscoelastic material is composed of two material functions, a real and an imaginary component, called the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$, respectively. The storage modulus $G'(\omega)$ is proportional to the deformation energy stored by the material (the elastic component), whereas the loss modulus $G''(\omega)$ is proportional to the amount of energy dissipated by the material (the viscous component),

$$|G^*(\omega)| = \sqrt{G'(\omega)^2 + G''(\omega)^2} \tag{12}$$

Oscillatory shear experiments must be conducted at deformations within the material's linear viscoelastic range. In this range, at a constant radial frequency ω, the deformation amplitude $\hat{\gamma}$ is proportional to the resulting shear stress amplitude $\hat{\tau}$, that is, $\hat{\tau} \sim \hat{\gamma}$. This is only the case at sufficiently small oscillatory deformations. Within the linear viscoelastic region, the moduli $G'(\omega)$, $G''(\omega)$, and $G * (\omega)$ are independent of the oscillatory amplitude in tests conducted at a constant frequency.

III. Materials

The gel propellants examined consisted of nitromethane as the continuous phase and nanometer-sized silicon dioxide particles as the dispersed phase. Nitromethane exhibits Newtonian flow behavior with a dynamic viscosity of $\eta\ (25°C) = 0.61$ mPa · s. Its density is $\rho = 1.139$ kg/m^3. The silicon dioxide particles were obtained from Degussa AG, Frankfurt, Germany, and had a density $\rho = 1.51$ g/cm^3 (determined by gas pycnometry) and a specific surface area $S_V = 260$ m^2/g (determined by gas adsorption). The mean size of the primary particles was $\bar{x} = 7$ nm.

IV. Results

A. Steady-State Shear Flow Behavior of the Nitromethane/Silicon Dioxide Gels

Before the rheological characterization, the nitromethane/silicon dioxide gels were stirred for several hours to deagglomerate the particles and homogenize the gel. The rheological properties were then determined under steady-state shear flow. Figure 3 shows the relative viscosity of the gel as a function of shear rate. The concentration of dispersed particles was varied from 4 to 8 vol%. Figure 3 also shows the viscosity function of pure nitromethane.

The relative viscosity η_{rel} is defined as the ratio of the gel viscosity to that of the matrix fluid at a constant shear rate $\dot{\gamma}$,

$$\eta_{\text{rel}} = \frac{\eta_{\text{gel}}|\dot{\gamma}}{\eta_{\text{nitromethane}}} \tag{13}$$

With the increase of silicon dioxide concentration, more pronounced shear thinning flow behavior is observed. This nonlinear material behavior of the gel can be attributed to particle–particle interactions as well as the changed hydrodynamics of the multiphase system compared to the single-phase fluid. This viscosity increase as a function of concentration is especially pronounced at low shear rates. In this shear rate region, the interparticulate interactions dominate compared to the relatively small hydrodynamic forces, so that the rheological properties of the suspension depend very strongly on the solids concentration and structural interactions within the suspension. Increasing the shear rate leads to an increase in the hydrodynamic forces, which in turn results in a shear-induced structuring of the nanometer-sized particles and a corresponding decrease in the viscosity at a given concentration. The viscosity difference as a function of concentration is, therefore, much smaller in the high shear rate region than in the low shear rate region, due to the hydrodynamic structuring that occurs in the system at higher shear rates.

Figure 4 shows how the viscosity of the gel depends on solids concentration at the limiting viscosity at zero shear rate ($\dot{\gamma} \to 0$) and at a shear rate $\dot{\gamma} = 1000$ s^{-1}. As the silicon dioxide concentration increases, the inner particulate structure of the system becomes ever more pronounced. This inner quiescent structure in the nitromethane/silicon dioxide gel leads to the limiting viscosity at zero shear rate behavior shown in Fig. 4. The viscosity difference between the suspension and the pure fluid is $\approx 10^9$ at a solids concentration $c_{\text{particle}} = 8$ wt.%. In contrast to the behavior of the limiting viscosity at zero shear rate, the slope of the relative viscosity function at the maximum shear rate is much lower. This relatively small increase in the viscosity of the nitromethane/silicon dioxide gel within this shear rate range arises because hydrodynamic effects are dominant and lead to development of a shear-induced structure within the silicon dioxide particles. The viscosity difference may also indicate that the gel's inner structure undergoes reversible breakdown at such high shear rates.[6]

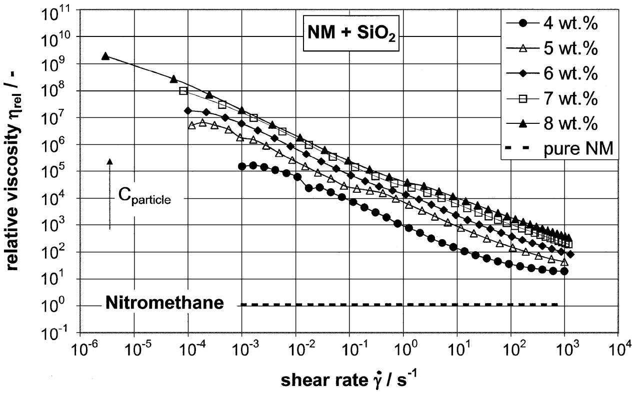

Fig. 3 Relative viscosity of nitromethane/silicon dioxide gels as a function of shear rate: ●, 4 wt %; △, 5 wt %; ◆, 6 wt %; □, 7 wt %; ▲, 8 wt %; and –––, pure nitromethane.

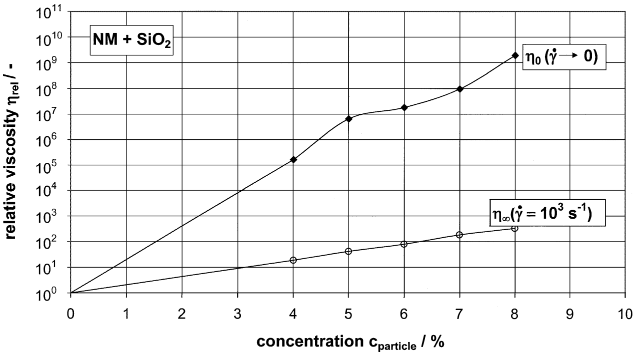

Fig. 4 Relative viscosity of the nitromethane/silicon dioxide gels as a function of particle concentration.

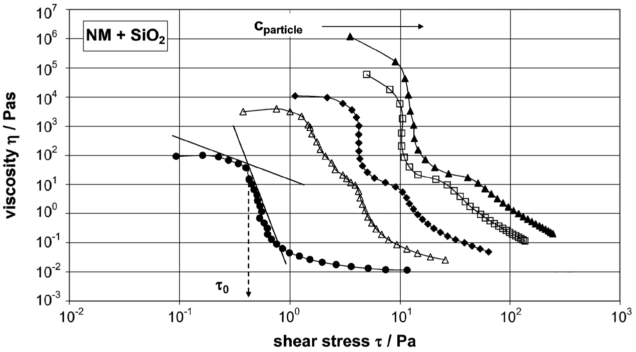

Fig. 5 Determination of yield stress of nitromethane/silicon dioxide gels.

Figure 5 shows the viscosity of the nitromethane/silicon dioxide gels as a function of shear stress. The yield stress of these suspensions was determined using the tangent method.[8] As seen in Fig. 5, all of the nitromethane/silicon dioxide gels examined exhibited a yield stress. For irreversible flow to occur, the stress applied must be above the yield stress value; at stresses below the yield stress the gel exhibits pure elastic deformation like a solid.

As described in the literature,[9] the flow behavior of gel propellants is characterized by using the power law of Ostwald–de Waele [see Eq. 2)]. Figure 6 shows the fit of the nitromethane/silicone dioxide gel by using the power law. An appropriate characterization is only given in the shear rate range between $10 \le \dot{\gamma} \le 100$ s^{-1}.

The flow behavior of the nitromethane/silicone dioxide gel can be described using the following equation for the shear stress:

$$\tau = \tau_0 - \eta_\infty \cdot \dot{\gamma} + \eta^* \cdot \dot{\gamma}^\alpha \tag{14}$$

Here τ_0 is the yield stress of the gel, η_∞ is the viscosity at a shear rate $\dot{\gamma} \to \infty$, η^* is the viscosity that characterizes structuring within the disperse system, and α is the exponent that characterizes structural changes within the system.

Figure 7 shows the measured shear stress values for the nitromethane/silicone dioxide gel with a concentration $c_{\text{particle}} = 8$ wt % compared with the shear stress function calculated from Eq. (14). There is good agreement between the calculated and measured values.

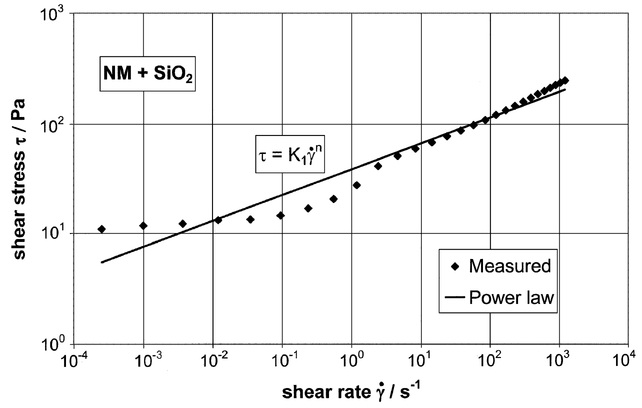

Fig. 6 Measured values and power law (Ostwald–de Waele) for the shear stress of nitromethane/silicon dioxide gel.

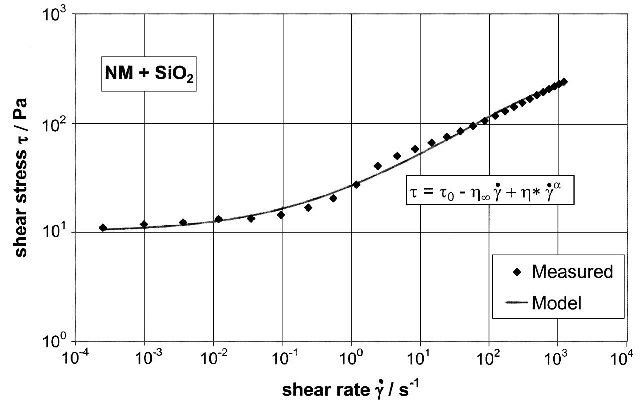

Fig. 7 Measured values and model for the shear stress of nitromethane/silicon dioxide gel.

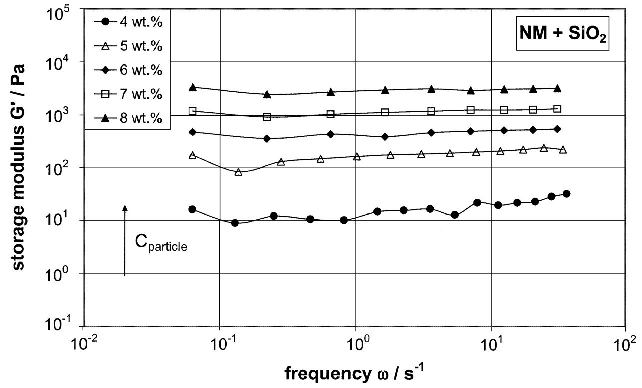

Fig. 8 Storage modulus as function of frequency of nitromethane/ silicon dioxide gels.

B. Viscoelastic Properties of Nitromethane/Silicon Dioxide Gels

Viscoelastic properties can be determined via oscillatory shear experiments. The complex shear modulus determined via dynamic experiments in the linear viscoelastic region can be separated into two material functions as shown in Eq. (12), the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$. Figure 8 shows the storage modulus of the nitromethane/silicon dioxide gel at various solids concentrations.

In the concentration region examined, the storage modulus was independent of the radial frequency, indicating the existence of a compact inner structure in the nitromethane/silicone dioxide gel. Figure 9 shows example results of the storage and loss moduli as a function of frequency for the gel with a solids concentration $c_{\text{particle}} = 8$ wt %. The moduli $G'(\omega)$ and $G''(\omega)$ are independent of frequency, meaning that within this frequency range the nitromethane/silicone dioxide gel exhibits elastic, solidlike behavior.

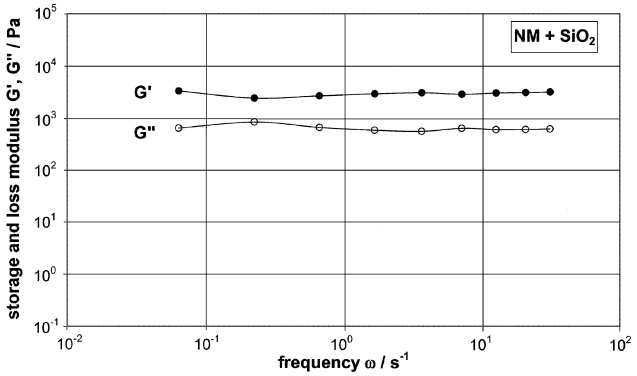

Fig. 9 Storage and loss modulus as function of frequency of a nitromethane/silicon dioxide gel ($c_{\text{particle}} = 8$ wt %).

From this rheological study the following hypothesis concerning the material behavior of gel propellants are proposed.

1) A gel propellant must exhibit shear thinning behavior when subjected to stationary shear flow.

2) The limiting viscosity at zero shear rate η_0 of a gel propellant should be as high as possible.

3) The shear viscosity at high shear rate η_∞ of a gel propellant should be sufficiently small.

4) A gel propellant should exhibit a yield stress τ_0.

5) The elastic component of the complex modulus must always be higher than the viscous component.

6) The moduli $G'(\omega)$ and $G''(\omega)$ should be independent (or nearly independent) of the oscillatory frequency ω.

V. Conclusions

The nitromethane/silicone dioxide gels examined in this study exhibited pronounced shear thinning behavior with a yield stress when subjected to stationary shear flow. This behavior is attributable to the inner structure of the gel, which leads it to exhibit solidlike properties. At high shear rates, the hydrodynamic forces exceed the interparticle interaction forces, producing flow-induced structuring of the nanometer-sized silicon dioxide particles and pronounced nonlinear flow behavior. The shear stress equation introduced in this work accounts for the change in the inner particle structure during stationary shear flow and, thus, provides a good description of the material behavior of this class of nitromethane gel propellants. The oscillatory shear experiments showed that the storage and loss moduli were independent of frequency in the range examined, meaning that the gel exhibits elastic behavior at low frequencies.

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