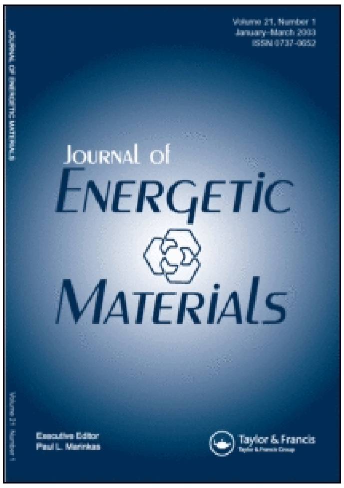

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Mechanical Properties of Gel Propellants with Nanoparticles

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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 characterization of the mechanical properties is essential for the development of gel propellant formulations and for the design of an applicable propulsion system. In this contribution the mechanical properties of a gel propellant consisting of nitromethane as fuel and nanoparticles of silicon dioxide as gelling agent are 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. The viscoelastic properties are typically gel-like in that the storage and the loss moduli are both independent of frequency.

Keywords: propellant, gel, nitromethane

Introduction

In recent years the challenge of achieving high performance while also improving the safety characteristics of rocket propellants

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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 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 solid-like 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 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. The characterization of the mechanical properties of the gel provides basic information critical to the production and storage of gel propellants and 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 and 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-term storage the yield stress of the gels decreased, a phenomenon 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), mono methyl 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 studies gel propellants can be divided into three categories depending on their degree of shear thinning behavior, yield stress characteristics, viscoelastic and thixotropic properties.

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

Experimental

Steady State Shear Flow

The rheological behavior of the gels prepared was examined in steady state and oscillatory shear flow using a UDS 200 rotational rheometer manufactured by Physica Messtecknik GmbH. Cone and plate measurement fixtures were used.

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

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

where $\eta(\dot{\gamma})$ 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:

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

where K_1 is termed the consistency coefficient and n is called the flow index. Shear thinning behavior corresponds to $n<1$, while 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:

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

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

$$\eta(\tau) = \frac{\eta_0}{(1 + K_2 \eta_0 \cdot \tau^m)}, \tag{4}$$

where K_2 and m are fitted model parameters.

When the shear stress applied to a fluid must exceed a threshold value (i.e., 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 fluids.

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

$$\tau = \tau_0 + K \cdot \dot{\gamma}^n. \tag{5}$$

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.

Oscillatory Shear Flow

In oscillatory shear flow the fluid is subjected to a periodic (e.g., sinusoidal) deformation $\gamma(t)$ with an amplitude $\hat{\gamma}$ at a radial frequency $\omega = 2\pi f$ [6]:

$$\gamma(t) = \hat{\gamma} \sin(\omega t). \tag{6}$$

At sufficiently small amplitude—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. Visocoelastic material behavior is characterized by the existence of a phase shift δ between the shear stress output $\tau(t)$ and the deformation input $\gamma(t)$:

$$\tau(t) = \hat{\tau} \cdot \sin(\omega t + \delta). \tag{7}$$

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, $0 \leqslant \delta \leqslant \pi/2$.

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

$$\tau(t) = \hat{\gamma}|G^*(\omega)| \cdot \sin(\omega t + \delta(\omega)). \tag{8}$$

The complex shear modulus can also be expressed as

$$|G^*(\omega)| = \frac{\hat{\tau}(\omega)}{\hat{\gamma}}. \tag{9}$$

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), while the loss modulus $G''(\omega)$ is proportional to the amount of energy dissipated by the material (the viscous component):

$$|G^*(\omega)| = \sqrt{G'(\omega)^2 + G''(\omega)^2}. \tag{10}$$

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.

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 $\eta(25°\mathrm{C}) = 0.61\,\mathrm{mPas}$. Its density is $\rho = 1139\,\mathrm{kg/m^3}$. The silicon dioxide particles were obtained from Degussa AG, Frankfurt, and had a density $\rho = 1.51\,\mathrm{g/cm^3}$ (determined by gas pycnometry) and a specific surface area $S_v = 260\,\mathrm{m^2/g}$ (determined by gas adsorption). The mean size of the primary particles was $\bar{x} = 7\,\mathrm{nm}$.

Results

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

Prior to the rheological characterization, the nitromethane/ silicon dioxide gels were stirred for 1–3 hr depending on the particle concentration to deagglomerate and homogenize the particles and to make the gel. The rheological properties were then determined under steady state shear flow. Figure 1 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 1 also shows the viscosity function of pure nitromethane.

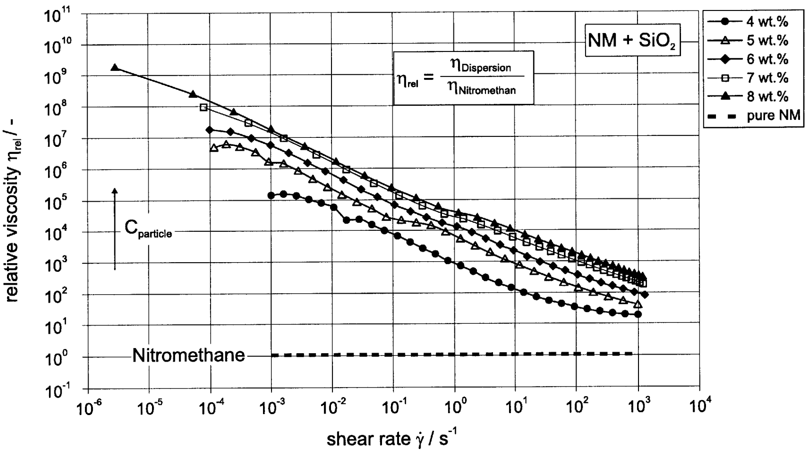

Figure 1. Relative viscosity of nitromethane/silicon dioxide gels as function of shear rate.

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

$$\eta_{\text{rel}} = \frac{\eta_{\text{gel}}|\dot{\gamma}}{\eta_{\text{nitromethane}}}. \tag{11}$$

With increasing 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 visocity at a given concentration. It has been described that spheres of nearly identical particle size, which are primarily distributed licentious, array to long catenarian structures when subjected to shear forces, for example, between two parallel plates [8]. 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, because of the hydrodynamic structuring that occurs in the system at higher shear rates.

Figure 2 shows how the viscosity of the gel depends on the solids concentration at the limiting viscosity at zero shear rate ($\dot{\gamma} \rightarrow 0$) and at a shear rate $\dot{\gamma} = 1000\,\text{s}^{-1}$.

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 Figure 2. The viscosity difference between the suspension and the pure fluid is $\approx 10^6$ at a solids

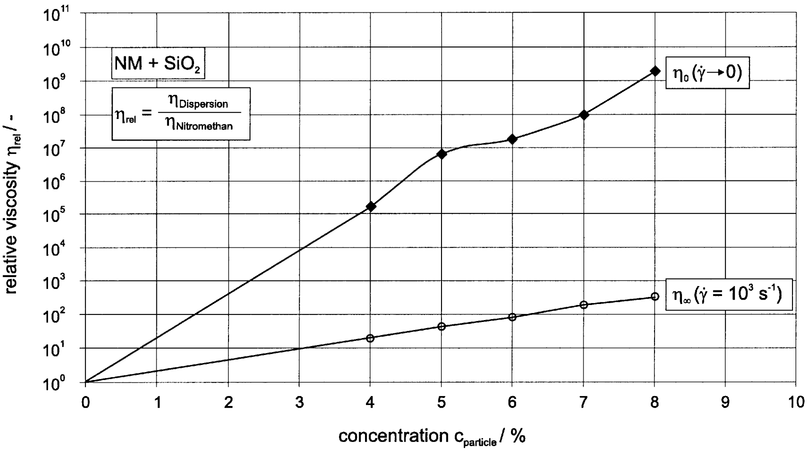

Figure 2. Relative viscosity of nitromethane/silicon dioxide gels as a function of particle concentration.

concentration $c_{\text{particle}} = 8\,\text{wt.\%}$. 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 effect 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 surface undergoes reversible breakdown at such high shear rates [6].

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

$$\tau = \tau_0 - \eta_\infty \cdot \dot{\gamma} + \eta^* \cdot \dot{\gamma}^\alpha. \tag{12}$$

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 3 shows the measured shear stress values for the nitromethane/silicone dioxide gel with a concentration

$c_{\text{particle}} = 8\,\text{wt.\%}$ compared with the shear stress function calculated from Equation (12). There is good agreement between the calculated and measured values.

Figure 4 shows the rate of the change in the viscosity due to the change of the inner structure of the gel. The interactions within the gel are characterized by the hydrodynamic forces described by the η^* term. Thus, a flow-induced structuring of the nanoparticle occurs. The formation of this structure is ever more pronounced with increasing particle concentration. The change in viscosity for a gel with a concentraion of $c_{\text{particle}} = 8\,\text{wt.\%}$ is in the range of 18 Pas.

Figure 5 shows the dependence of the exponent α, which is a measure of the change of the gel's inner structure, as a function of the particle concentration. The characteristics of the function clearly indicate the ever more pronounced change of the inner structure with increasing particle concentration. The hydrodynamic forces make the particles to adopt a flow-induced structure in the pseudoplastic region of the material. For high particle concentration, the particulate interactions increase

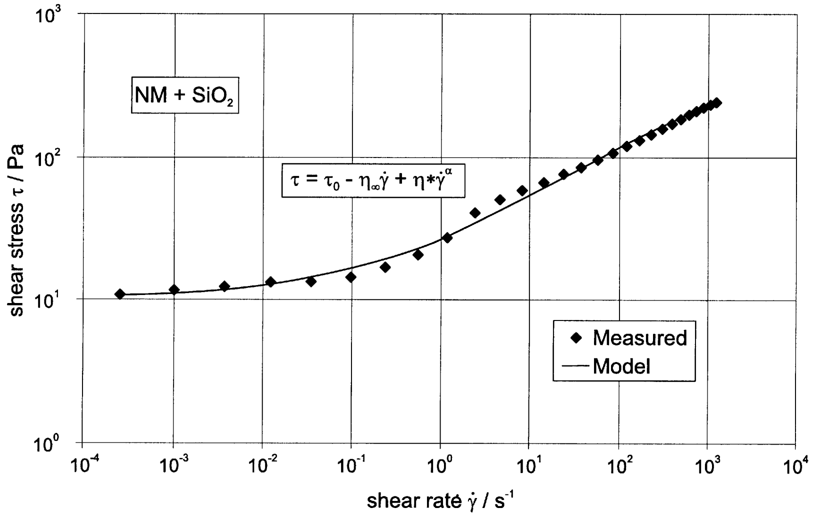

Figure 3. Measured values and model for the shear stress of a nitromethane/silicone dioxide gel.

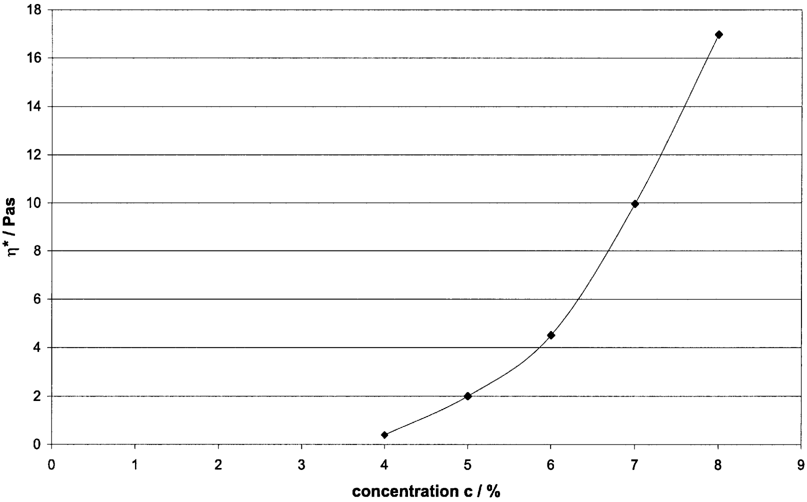

Figure 4. Viscosity term η^* as function of concentration.

which mean that the change of the inner structure grows less. This behavior is pointed out by the asymptotic characteristics of the function.

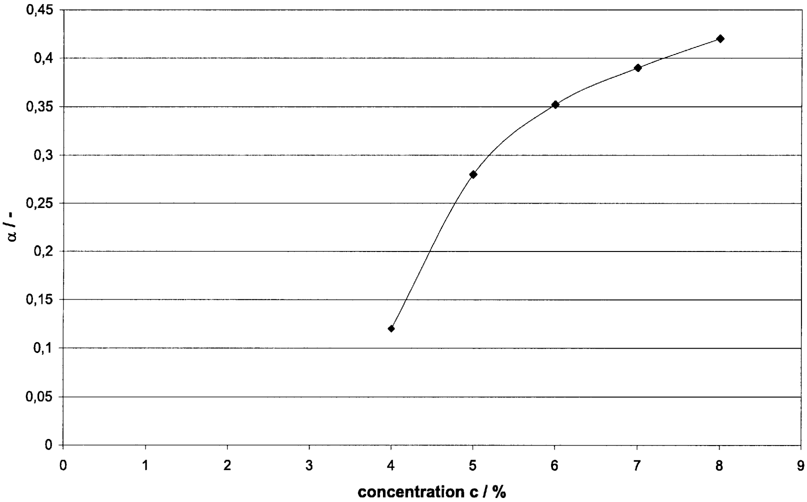

Figure 5. Exponent α as function of concentration.

Viscoelastic Properties of the 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 Equation (10): the storage modulus $G'(\omega)$ and the loss modulus $G''(\omega)$. Figure 6 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. This behavior is also known for rubbers and highly concentrated polymeric suspensions [7]. Figure 7 shows example results of the storage and loss moduli as a function of frequency for the gel with solids concentration $c_{\text{particle}} = 8\,\text{wt.\%}$. The moduli $G'(\omega)$ and $G''(\omega)$ are independent of frequency, meaning that within this frequency range the nitromethane/silicone dioxide gel exhibits more elastic, solid-like behavior.

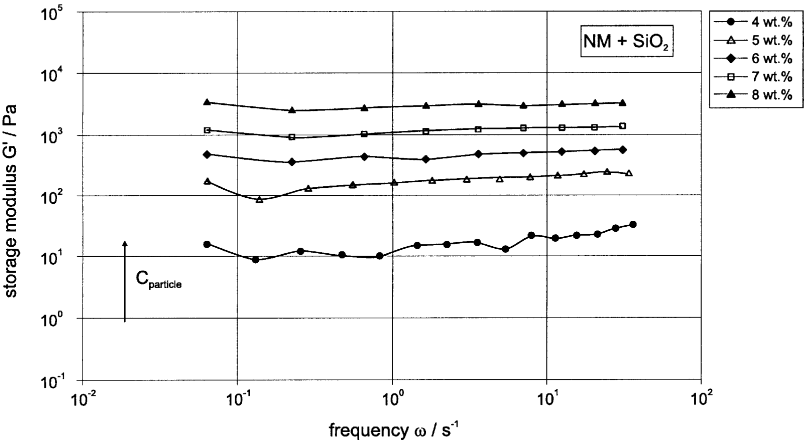

Figure 6. Storage modulus as function of frequency of the nitromethane/silicon dioxide gels.

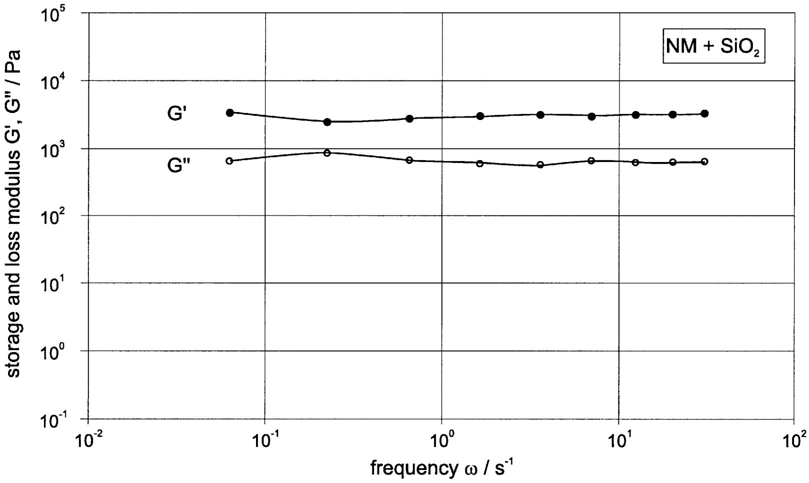

Figure 7. Storage and loss modulus as function of frequency of a nitromethane/silicon dioxide gel ($c_{\text{particle}} = 8\,\text{wt.\%}$).

From this rheological study the following hypotheses concerning the material behavior of gel propellants are proposed:

- A gel propellant must exhibit shear thinning behavior when subjected to stationary shear flow.
- The limiting viscosity at zero shear rate (η_0) of a gel propellant should be as high as possible.
- The shear viscosity at high shear rate (η_∞) of a gel propellant should be sufficiently small to be able to atomize the gel.
- A gel propellant should exhibit a yield stress τ_0.
- The elastic component of the complex modulus must be higher than the viscous component within the linear viscoelastic range, that is, the elastic properties of the gel are more pronounced than the viscous ones.
- The moduli $G'(\omega)$ and $G''(\omega)$ should be independent (or nearly independent) of the oscillatory frequency ω.

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 attribute to the inner structure of the gel, which leads it to exhibit solid-like 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.

References

[1] Gupta, B. L., M. Varma, and N. L. Munjal. 1986. *Propellant*, *Explosive*, *Pyrotechnics*, **11**: 45.

[2] Rapp, D. C. and R. L. Zurawski. 1988. Characterization of aluminium/RP-1 gel propellant properties. AIAA Paper 88–2821.

[3] Varghese, T. L., S. C. Gaindhar, J. David, J. Jose, R. Muthiah, S. S. Rao, K. N. Ninan, and V. N. Krishnamurthy. 1995. *Defense Science Journal*, **45**: 25.

[4] Varghese, T. L., N. Prabhakaran, K. P. Thanki, S. Subramanian, S. S. Rao, K. N. Ninan, and V. N. Krishnamurthy. 1997. *Defence Science Journal*, **49**: 71.

[5] Rahimi, S., D. Hasan, A. Peretz, Y. Benenson, and S. Weiner. 2001. Preparation of gel propellants and Simulants. AIAA paper 2001-3264.

[6] Teipel, U. 1999. Rheologisches Verhalten von Emulsionen und Tensidlösungen. Ph.D. thesis, University of Bayreuth. Scientific publication of Fraunhofer ICT, 22.

[7] Macosko, C. W. 1994. *Rheology*: *Principles*, *Measurements*, *and Applications*. New York: VCH Publishers.

[8] Giesekus, H. 1994. *Phänomenologische Rheologie*. Berlin: Springer-Verlag.