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Technical Note

TECHNICAL NOTES are short manuscripts describing new developments or important results of a preliminary nature. These Notes cannot exceed 6 manuscript pages and 3 figures; a page of text may be substituted for a figure and vice versa. After informal review by the editors, they may be published within a few months of the date of receipt. Style requirements are the same as for regular contributions (see inside back cover).

Thixotropic Effect of Inorganic Gel Fuels

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Introduction

GEL propellants seem to be attractive for many applications due to their performance characteristics and operational capabilities, which are similar to liquid propellants, as well as their high density, increased combustion energy, and long-term storage capability. Moreover, gels provide safety over conventional liquids and solid propellants.

Gel propellants are fuels and oxidizers whose rheological properties have been altered by the addition of gelling agents and metal loading additives, such that they behave as time-dependent non-Newtonian fluids. At rest, the viscosity of gel propellants is significantly higher than the viscosity of liquids[1] by several orders of magnitude.

One of the most important characteristics of gel propellants and fuels is that their viscosity is shear-rate dependent (non-Newtonian). When considering this rheological behavior of the gel propellants, by applying high shear rates during injection it is possible to reach low viscosities and even liquidification near the injector exit. The decrease in viscosity with increasing shear rate is referred to as shear thinning. The viscosity of gels is also affected by the temperature and by the mass fraction of metals in the gel mixture.

Another characteristic of gel propellants that has been reported in various studies[2–8] is the thixotropic behavior, which means that shear stress (and consequently viscosity) decreases with time under constant shear rate and temperature. Thixotropy is rather like pseudoplasticity in which the time required for the alignment of the polymeric chains is not negligible, and the difference is only a matter of degree.[7] Rapp and Zurawski[2] received thixotropic loops for aluminum–rocket propellant 1 gels; however, their measurements have mainly qualitative value.

In the feeding process of the propellant the gel fluid passes through a pipe and finally is injected to the combustion chamber. The injectors are small in both length and cross-section area size and the fluid stays there for a very limited time (fraction of 1 ms). The shear rates developed in the injectors due to the sudden decrease in the cross-section area are very large ($\geq 10^4\ \mathrm{s}^{-1}$) and the shear thinning effect is dominating. The thixotropic effect should be considered in pipes where the fluid flows through for a long time and the shear rates are considerably lower (500–5000 s^{-1}). Thus, the use of thixotropic models for the rheological constitutive equations of gel propellants is necessary for formulating the governing equations of the flow in uniform-cross-section pipes that connect the fuel and oxidizer tanks to the injectors. In these cases the diameter/length ratio of the pipe might be an important design parameter.

The behavior of gel fuels, as characterized by Rahimi,[8] can be viscoelastic or pseudoplastic. Organic gelled fuels are viscoelastic and exhibit both viscous and elastic behavior. Inorganic gelled fuels have an insignificant elastic branch; they are mainly viscous and their rheological character is similar to water gels.

In the present work an effort was made to investigate the significance of the thixotropic effect in inorganic gel fuels. The rheological behavior of water gels that resemble inorganic gel fuels was characterized experimentally, and the effect of thixotropy was evaluated for pure viscous gels.

Theoretical Analysis

To estimate the thixotropic effect on the effective viscosity resulting from continuous flow of gel in a uniform cross section pipe, the mathematical model of Tiu and Boger[9] is used. The shear stress τ as a function of the shear rate $\dot{\gamma}$ is described by the three-parameter Herschel–Bulkley constitutive model:

$$\tau = \lambda\left[\tau_0 + k(\dot{\gamma})^n\right] \tag{1}$$

where n is the power-law index, k is the viscous constant, τ_0 is the yield stress, and λ is a structural parameter that is a function of time. Before shearing, $t = 0$, and $\lambda = 1$, and after complete breakdown from shearing, $t = \infty$, an equilibrium value $\lambda = \lambda_e$ is obtained. The decay of the structural parameter with time is assumed to obey a second-order kinetic equation for $\lambda > \lambda_e$:

$$\frac{\mathrm{d}\lambda}{\mathrm{d}t} = -c(\lambda - \lambda_e)^2 \tag{2}$$

where c is the rate constant and is a function of the shear rate. Solving Eq. (2) considering the initial condition that at time $t = 0$, we have $\lambda = 1$, yields

$$\lambda = \frac{1 - c\lambda_e t(\lambda_e - 1)}{1 - ct(\lambda_e - 1)} \tag{3}$$

To find the rate constant c, parameters λ and λ_e are expressed in terms of the apparent viscosity η, which in this specific case is a function of both shear rate and time:

$$\lambda = \eta\dot{\gamma} \Big/ \left[\tau_0 + k(\dot{\gamma})^n\right] \tag{4}$$

Combining Eq. (2) with differentiation of Eq. (4) with respect to time at constant shear rate yields

$$\frac{\mathrm{d}\eta}{\mathrm{d}t} = -a(\eta - \eta_e)^2 \tag{5}$$

where

$$a = c\dot{\gamma} \Big/ \left[\tau_0 + k(\dot{\gamma})^n\right] \tag{6}$$

Integration of Eq. (5) at constant shear rate from $\eta = \eta_0$ at $t = 0$ to $\eta = \eta$ at $t = t$ results in the relation

$$1/(\eta - \eta_e) = 1/(\eta_0 - \eta_e) + at \tag{7}$$

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Function a can be determined experimentally, and rate constant c can be calculated from Eq. (6) based on knowledge of the Herschel–Bulkley rheological parameters, n, k, and τ_0. Thus, λ can be evaluated from Eq. (3) as a function of time and the rate constant c, which depends on the shear rate.

For power-law fluids, the shear rate at the wall is given by[10]:

$$\dot{\gamma}_w = [(3n + 1)/4n] \cdot (4\dot{V}/\pi R^3) \tag{8}$$

where $\dot{V}$ is the volumetric flow rate and R is the pipe radius.

To evaluate the upper limit of thixotropic effect in a pipe, the shear-rate value near the wall, which is maximum, is considered as the applied shear rate in the whole cross section. The apparent viscosity is calculated from Eq. (4).

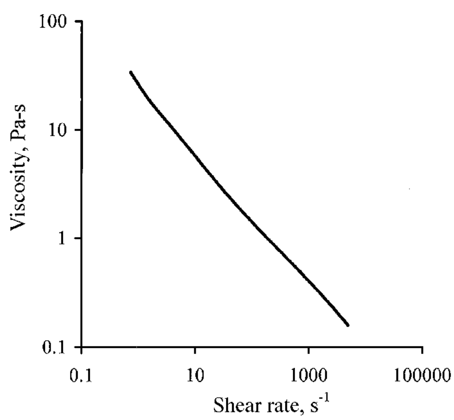

Fig. 1 Viscosity vs shear rate for a water gel.

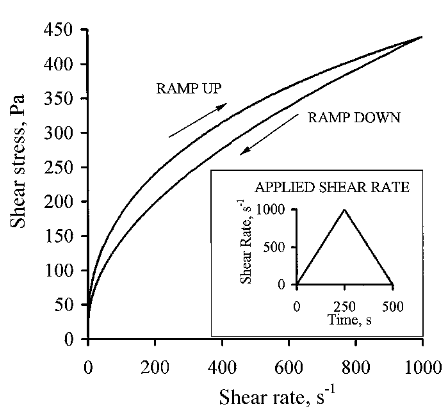

Fig. 2 Thixotropic loop.

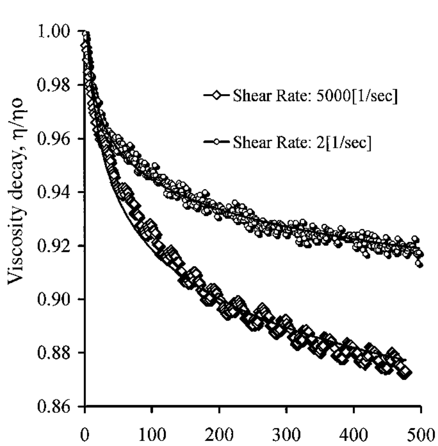

Fig. 3 Stress decay curves for two different shear rates.

Experimental

The purpose of the experimental investigation was to characterize the rheological behavior of water gels with various gellants. The reason to choose this kind of gels was to eliminate the effect of the elastic branch of viscoelasticity and concentrate on the pure thixotropic effects.

A TA Instruments CSL$^2_{100}$ Carri-Med rheometer was employed for the measurement of the rheological constants. Two gellant types, X and Z at various contents, were used for the investigation. The same gels were used in another study by the authors, and the rheological power-law parameters of these water gels appear in Ref. 11.

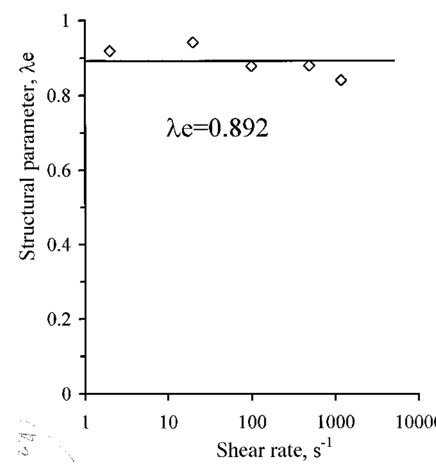

Fig. 4 Structural parameter at equilibrium.

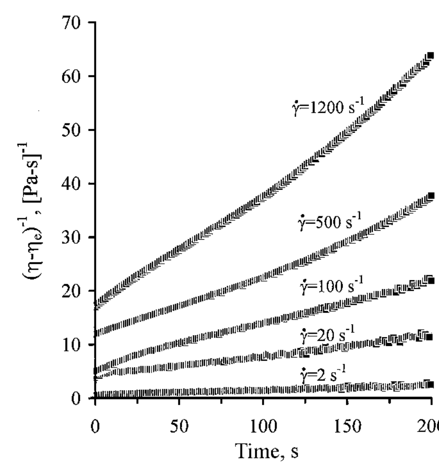

Fig. 5 Almost linear (experimental) behavior of $(\eta - \eta_0)^{-1}$ with time.

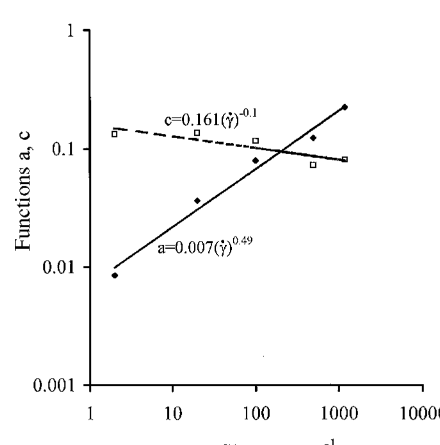

Fig. 6 Power correlation of functions a and c with shear rate.

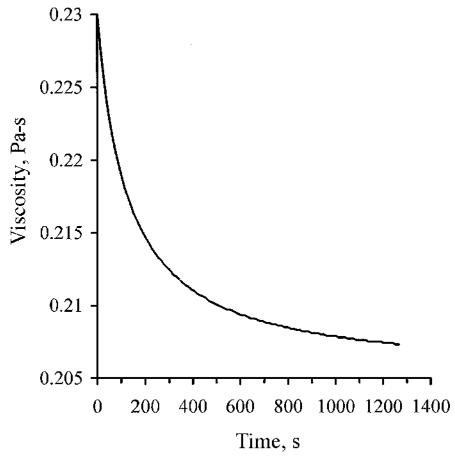

Fig. 7 Prediction of the viscosity of water gel for a $\frac{1}{4}$-in. pipe with flow rate of 50 cm^3/s.

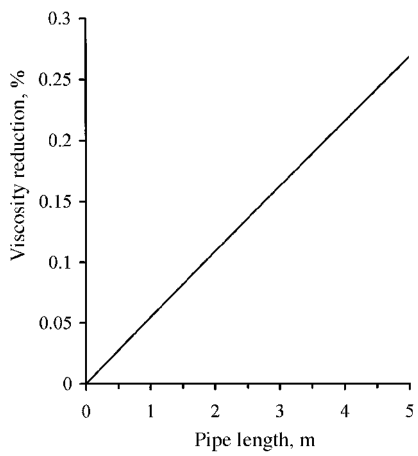

Fig. 8 Reduction in viscosity vs pipe length for a $\frac{1}{4}$-in. pipe with flow rate of 50 cm^3/s.

Creep tests were conducted to verify that the gels used behave as ideal viscous materials. Shear stress vs shear rate tests provided the flow curve shown in Fig. 1. The time-dependent thixotropic behavior of gel Z was received by applying an up and down ramp of shear rate and is presented in Fig. 2. The thixotropic loop (hysteresis loop) has only qualitative significance. Stress decay curves indicate the shear stress dependence on time for constant applied shear rate. A series of tests was conducted for various shear rates between 2 and 5000 s^{-1} to obtain stress decay curves. Figure 3 presents stress decay curves for the extreme shear rates. The results were processed to receive λ_e and the dependence of $1/(\eta - \eta_0)$ on time, shown in Figs. 4 and 5, respectively. The functions a and c are presented in Fig. 6.

Example of the Thixotropic Effect

The time dependence of the viscosity of water gel Z in a $\frac{1}{4}$-in. pipe for a volumetric flow rate of 50 cm^3/s is presented in Fig. 7 under the aforementioned assumptions. It is rather obvious that viscosity decreases with time due to the thixotropic effect; however, the decrease is very small. Considering a 5-m-length pipe, a reduction of 0.3% in the viscosity is received at the pipe end as shown in Fig. 8.

Conclusions

The significance of the thixotropic effect in inorganic gel fuels was examined in the present study. The thixotropic properties evaluation procedure is presented. The rheological parameters of water gels that resemble these fuels were experimentally measured.

A theoretical analysis on the effect of the thixotropy reveals that viscosity decreases insignificantly in typical pipe lengths in rocket motors.

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