

Rheological Behavior of DBS-induced Kerosene Gel Propellants

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Abstract: *The study reports the findings on gelation of rocket fuel kerosene using low molecular weight gelator (LMWG) 1,3:2,4-dibenzylidene-D-sorbitol (DBS) for the use in gel propulsion system. The rheological properties of the formulated kerosene gels are determined using shear flow test and dynamic oscillation tests. It is observed that over the range of applied shear rate ($0.1-1000\text{ s}^{-1}$) kerosene gel fuels exhibits a strong shear thinning-thixotropic behavior. Cross Law (CL) model is used to predict the zero shear viscosity and onset of shear thinning and found to describe the shear flow data perfectly. Below the critical stress, τ_c , the gel exhibits elastic dominant behavior ($G' > G''$) and found to be independent of applied shear stress in linear viscoelastic region. A key finding of this study reveals that all fuel formulations display solid-like characteristics under the test conditions as G' and G'' are nearly independent of the frequency range studied.*

Keywords: *Kerosene gel, dibenzylidene sorbitol, rheology, yield stress.*

1. Introduction

Kerosene based fuel and its derivatives are widely used in aerospace industry, either in aviation or in spacecraft industry. In aviation, JP-4 (Jet Propellant-4) and JP-8 are the main fuel for turbine engine. While in spacecraft, RP-1 (Refined Petroleum-1) is one of the most successful fuel in the liquid rocket engines (LRE). For safety and performance reasons, the idea of gellifying kerosene was taken into account by several research groups. Rahimi et al [1] worked on gel propellants in their study, one of them is JP-8 which used silica as its gelator. Silica is very good gelator and it will form gel in any compound immediately. However, silica has some drawbacks especially related to combustion since it is inorganic compound and will not take part in combustion. Varghese et. al. [2] introduced kerosene gel and found that the combination between organophilic clay complex (OPC) and propylene glycol (PG) resulting a consistent gel. However, clay, which contained in OPC is one of silica derivatives which reduce the combustion efficiency.

Dibenzylidene sorbitol (DBS) is one of the most common gellant used in cosmetic and healthcare industry [3]. DBS is a low molar weight organic gelator (LMWG) which have sorbitol body and two benzylidene attached as wings-like shape [4]. It is organic compound, which has the capability to self-assemble into long nano fibers depends on the polarity of the solvents [5]. The self-assembly capability of DBS can induce gelation by forming 3-D fibrillary network which entraps the solvent. Due to its ability to induce gelation by self-assembly, some research groups have reported DBS as an organogelator for gelling wide variety of organic solvents (alkanes, esters, alcohols, hydrocarbons, etc) and polymer (poly propylene-oxide, poly dimethyl-siloxane, poly propylene, poly methyl methacrylate, poly styrene, etc) [6] at a low concentrations. Diehn et. al. [7] predicted the gelling ability of DBS using Hansen solubility parameters and divided the solvent into 4 regions i.e., soluble, slow gel, instant gel, and insoluble region. They found that DBS is highly soluble in polar aprotic solvents (DMSO, DMF, etc), but insoluble in non-polar aliphatic liquid (n-alkane). Santos [8] revealed that DBS is miscible in kerosene based aviation fuel (JP-8), but does not form gel.

Furthermore, the favorable properties of gelled fuel are able to store in solid behavior, while acts as liquid in service. The best way for quantifying the properties of gelled fuel is through rheology. This study reports the

use of DBS as an organogelator in kerosene with the use of solvent and co-solvent, meanwhile rheological experiments were conducted to investigate the rheo-physical properties of the formulated kerosene gels. Simple shear flow test was used to determine the flow properties non-Newtonian fluid. The oscillation amplitude and frequency sweep test were used to probe the viscoelastic nature of the gel sample.

2. Experimental Section

2.1. Materials and Methods

Base fuel kerosene (CAS: 8008-20-6), organic solvent dimethyl sulfoxide (DMSO; CAS: 67-68-5) and cosolvent *l*-hexanol (CAS: 111-27-3) were obtained from Sigma-Aldrich Co., 1,3:2,4-dibenzylidene-D-sorbitol (DBS) (purity $\geq 97\%$) was supplied as a white crystalline powder by Milliken chemicals. All the chemicals were used without further purification.

2.2. Sample Preparations

The preparation of kerosene gel involves two steps: First, a predefined amount of DBS as the gelling agent was dissolved in DMSO to make a gellant solution. Separately, the pre-determined amount of hexanol and kerosene was mixed thoroughly. Secondly, the required amount of gellant solution was added to the kerosene-hexanol mixture. The solution was hand-stirred for 1 minute and stored at room temperature to complete the gelation process. The samples were stored for one week before the characterization. The formulation of the samples is detailed in table 1 and samples studied is shown in Fig. 1.

TABLE I: Composition of kerosene gel samples

Sample	Concentration (wt %)			
	Kerosene	Hexanol	DMSO	DBS
KD4	69	25	4	2
KD6	67	25	6	2
KD8	65	25	8	2
KD10	63	25	10	2

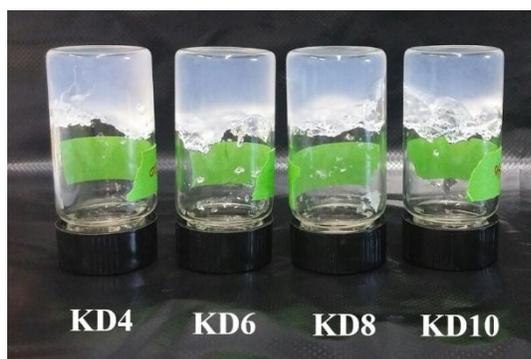


Fig. 1: Kerosene gel fuel.

2.3. Rheological Characterization

A HAAKE RS 6000 controlled-stress rotational rheometer (from Thermo Fisher Scientific) was used to characterize the rheological behavior of kerosene gels. The samples were loaded in a cone-plate configuration (plate diameter of 35 mm, cone angle 2°) with a minimum gap of 0.105 mm between the plates. The shear flow measurements were performed by varying the applied shear rate from 0.01 to 1000 s^{-1} to understand the flow behavior of the kerosene gels. The dynamic behavior of the gels was analyzed through oscillation amplitude sweep measurements that were carried out by varying stress at a constant frequency of 5 Hz. Finally, the frequency sweep tests were carried out at a frequency ranging from 0.01 to 100 Hz at the stress value

corresponds to 20% of the critical stress value obtained from amplitude sweep mode tests. All experiments were carried out at 20 ± 0.2 °C, and at least 3 trails were performed for each test.

3. Results and Discussion

3.1. Flow Study

In simple shear studies, the shear rate ($\dot{\gamma}$) applied to a sample alters its apparent viscosity (η_{app}). The gel samples were subjected to controlled rate (CR mode) in the range of 0.1 - 1000 s^{-1} to infer the flow properties of the sample. Fig. 2 illustrates that the η_{app} decreases monotonically with an increase in the applied shear for all the cases. This clearly demonstrates the shear-thinning behavior exhibited by gel fuels, which occur due to the gradual breakdown of the 3D microstructural nanofibrillar network.

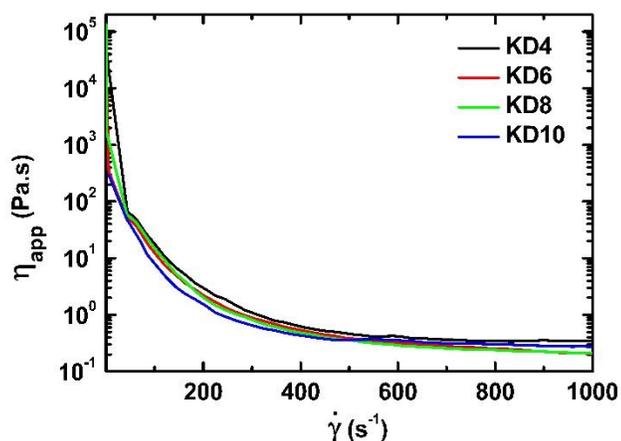


Fig. 2: Semi-log plot of apparent viscosity as a function of the applied shear rate of gel samples.

The 3D network breakdown completely and exhibits near Newtonian behavior when the applied stress reaches critical stress value called yield stress. From the Fig. 2, all the samples showed a similar trend of shear thinning, however, the magnitude of $\eta(\dot{\gamma})$ decreases with the concentration of DMSO (C_{DMSO}) solvent. This further justifies that the increase in C_{DMSO} in the solvent mixture affects gelation of DBS in kerosene.

To further investigate the flow characteristics of the formulated kerosene gel, the generalized Cross Law (CL) constitutive model was applied to the flow curves, which was found to be the most adequate for the gels studied. According to CL model, the shear stress (τ) as a function of shear rate ($\dot{\gamma}$) is expressed by:

$$\tau = \dot{\gamma} \left(\eta_{\infty} + \frac{\eta_0 - \eta_{\infty}}{1 + \left(\frac{\dot{\gamma}}{\dot{\gamma}_b} \right)^m} \right) \quad (1)$$

where η_0 is the zero shear viscosity, a critical material property, which estimates gel stability, η_{∞} is the infinite shear viscosity which predicts gel behavior at high shear situations like atomization, m is known as the Cross rate constant and $\dot{\gamma}_b$ is the critical shear rate which gives the onset shear rate for shear-thinning. Table 2 details the model parameters obtained from the curve fit using CL model. From the Table 2 it is noted that η_{∞} remains in the close range however the onset of shear-thinning ($\dot{\gamma}_b$) decreases with increase in C_{DMSO} in the solvent mixture.

In the practical application, flow properties play an important role in storage, handling, atomization and combustion process. The yield point represents the stability of the sample when it is stored for longer period, and the shear thinning property makes the gel flows under applies shear stress which makes the gel atomization simpler. Another important flow property of this sample which is also worthwhile is the reversible process which shown in thixotropic behavior. The sample can flow as a liquid when shear is applied, and once the shear is released, it backs to gel form as before after a while.

TABLE II: Parameters of Cross Law model obtained from the curve fit of flow measurements.

Sample	η_o (Pa.s)	η_∞ (Pa.s)	$\dot{\gamma}_b$ (s ⁻¹)	m (-)
KD4	96.96	0.30	59.70	2.9
KD6	138.00	0.22	41.46	2.6
KD8	276.60	0.20	38.35	2.9
KD10	993.70	0.27	16.92	2.7

3.2. Thixotropy

A simple shear flow test was performed to analyze the time-dependent thixotropic behavior of kerosene gel fuels. This provides insights on the structural integrity of the network when subjected to controlled shear rate over a prolonged period. A simple loop test is performed to estimate the thixotropic area (S_T), $S_T = S_{up} - S_{down}$ where, S_{up} and S_{down} respectively represent the area under ramp-up and ramp-down curves in the shear rate range of 0.1-1000 s⁻¹. These areas are calculated analytically as $\int_{\dot{\gamma}_{min}}^{\dot{\gamma}_{max}} \tau(\dot{\gamma}) d\dot{\gamma}$ where the hysteresis loop is given by $\tau = f(\dot{\gamma})$ is obtained using Cross Law model (Eq. 1). Table 3. shows the thixotropic area (S_T) for all the propellant formulation and found that KD4 samples showed highest thixotropic area. Thixotropy provides better possibility to liquefy the gel during feeding process, which in turn reduces the feeding pressure and better atomization. The thixotropic effect in inorganic gellant such as silica is insignificant. However, there is significant thixotropic effect in organic gellant [1] which makes kerosene-DBS gels superior over kerosene-silica gels.

TABLE III: Thixotropic area of gels obtained from the hysteresis loop test.

Sample	S_{up} (MPa.s ⁻¹)	S_{down} (MPa.s ⁻¹)	S_T (MPa.s ⁻¹)
KD4	0.49	0.27	0.21
KD6	0.44	0.24	0.20
KD8	0.46	0.25	0.20
KD10	0.41	0.28	0.12

3.3. Oscillation Test

3.4. Stress Amplitude Sweep Test

The amplitude sweep test is conducted to determine the viscoelastic properties of the gel samples in detail. The primary aim of the experiment is to identify two critical parameters: First, linear viscoelastic (LVE) region, and second, the critical stress (τ_c), the stress at which the initial breakage occurs in the internal structures of the sample. The gels were subjected to stress at a constant frequency of 5 Hz. Fig. 3. (a) shows the variation of dynamic parameters such as storage modulus (G'), loss modulus (G'') with applied shear stress. It is observed from the Fig. 3. (b) that, all the kerosene gel fuels exhibits a linear viscoelastic behaviour (independent of applied stress) for $\tau < \tau_c$ i.e., solid-like behaviour and a transition from LVE to non-linear range for $\tau > \tau_c$ i.e., viscous behaviour. In this regard, τ_c marks as the onset of initial structural breakage occurs in nanofibrillar network to exhibit flow behaviour under applied stress and beyond which G' decays. Within the LVE range, the elastic property of the gel samples is governed by G' is always found to be greater than G'' . Note that the

magnitude of τ_c was observed to be highest for KD8 sample indicating $C_{DMSO} = 8 \text{ wt}\%$ is the optimum concentration of solvent for DBS to gel kerosene-hexanol mixture.

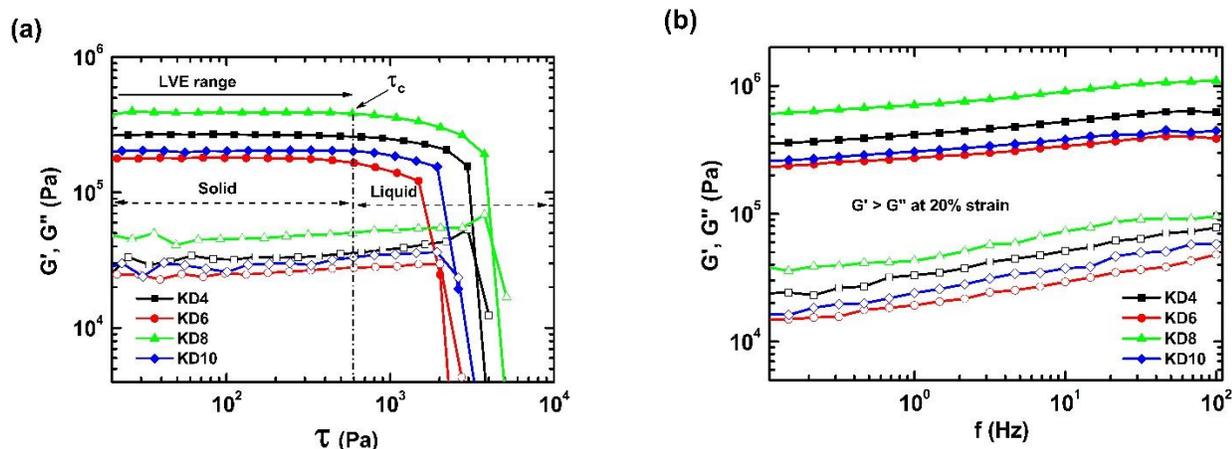


Fig. 3: Variation of dynamic rheological properties of kerosene gel samples: (a) as a function of shear stress and (b) as a function of frequency. Storage modulus (G'); solid marker with solid line; loss modulus (G''); open markers with solid line.

3.5. Frequency Sweep Test

The frequency sweep test is performed to establish the solid-like nature of gel samples and to understand their microstructural arrangements. Fig. 3. (b) illustrates the variation of dynamic properties with frequency ranging from 0.01-100 Hz at 20% of critical stress, τ_c (within LVE range). In Fig. 3. (b), all the gel samples observed to exhibit a plateau in the elastic regime with $G' \gg G''$ over several range of frequency studied. G' is ~ 11.5 - 13.5 times higher than G'' which indicates that the gel fuels are solid-like and displays viscous dominated nature when subjected to shear above the critical stress value.

4. Conclusion

In this work, gelation of liquid rocket fuel kerosene has been formulated using low molecular weight gelator (LMWG) 1,3:2,4-dibenzylidene-D-sorbitol (DBS) for use in gel propulsion systems. The rheology of kerosene gel was investigated using both shear flow tests and dynamic oscillation tests for the samples with 2 wt% DBS and varying concentration of solvent, DMSO (C_{DMSO}). Through shear flow test, it was observed that over the range of shear rate applied (0.1 - 1000 s^{-1}), the gel fuels exhibit strong shear thinning, thixotropic behavior. The degree of shear thinning increases with increase in C_{DMSO} . The Cross Law (CL) model was used to predict the zero shear viscosity and onset of shear thinning and found to describe the shear flow data perfectly. From the oscillation studies, it was found that, below critical stress (τ_c), the gel samples exhibit an elastic dominant behavior and found to be independent on applied stress in the linear viscoelastic zone. Moreover, the spectra of G' and G'' from the frequency sweep measurements indicates the solid-like nature of kerosene gels and are nearly independent of the applied frequency.

5. Acknowledgements

This work was supported by a National Research Foundation of Korea (NRF) grant funded by the Korea government (MEST) (No. 2014R1A2A2A01007347). Mr. Kurniawan Ardianto gratefully acknowledges Indonesian Endowment Fund for Education (LPDP) for providing scholarship in his study.

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