Comparative Study of Rheological Properties of Ethanol and UDMH based Gel Propellants

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Abstract
An experimental investigation on rheological properties of Ethanol and Unsymmetrical dimethyl hydrazine gels using methyl cellulose as gelling agent has been carried out. The gel fuels were rheologically characterized using a rheometer, in a low shear rate range. Ethanol and UDMH gels have been found to be thixotropic in nature. Their apparent viscosity values drastically fall with shear rate. It has been observed that apparent viscosity of gels gets significantly reduced at higher ambient temperatures. The up and down shear rate curves for both gels formed an hysteresis loop that showed no significant change with variation in temperature.

Keywords: ethanol, unsymmetrical dimethyl hydrazine, methyl cellulose, propellants, rheological property, gel

1 Introduction

The efficient and safe operational use, ease of handling and transportation of the propellants, eco-friendly characteristics, and relatively safer combustion products are some of the aspects that are considered before selecting a propellant for utilization in rocket engines. Conventional Unsymmetrical di methyl hydrazine (UDMH) and ethanol based propellants have long and illustrious service record as rocket fuels in liquid propulsion engines used in Proton Rocket, Ariane 1 first and second stages, PSLV (ISRO), MGM-52 Lance missile system, German V-2 missile, Jupiter C, American Redstone Rocket etc. However, conventional propellants have to be delicately handled; therefore it requires special care and system for storage, handling and transportation of such inflammable and hazardous liquids. Gelled fuel systems have arisen as a potential alternative to improve safety, handling, storage, transportation and sloshing related problems in many propulsion applications. In recent past, considerable research and development work has been done in the areas of formulation, preparation and rheological characterization of gel propellant systems [1-8]. Other areas of related studies focusing on performance evaluation, ignition and combustion, atomization etc. have also been attempted [9-11].

Gel propellants are modified conventional liquid systems whose mechanical properties can be altered by the addition of suitable gelling agent. The gellant particles or molecules when dispersed into the parent liquid form a three dimensional network that transform it into a gelled state by changing its properties from a free flowing liquid to a thick semi-solid [3,4]. Gels are non-Newtonian fluids and their rheological properties play a vital role in quality control during production and subsequent effective usage. Hence, rheological characterization is an essential step for better understanding of a gel system and serves multiple purposes. This helps to determine apparent viscosity at different shear rates and also to understand fluid's response to deformation when sheared. The obtained knowledge is essential in developing critical specifications for handling, transportation application and in determining the optimum conditions for the efficient injection of the system in a rocket engine. The clear understanding of fluid flow characteristics is vital for efficient combustion and finally to get optimum end use performance.

The selection of ethanol based gelled fuel for current study has been made due to its eco-friendly nature, cost-effectiveness and ease of availability. Even the combustion of ethanol based fuel does not produce any obnoxious or toxic gas emission such as nitrogen oxides. On the other hand, UDMH forms a hypergolic propellant system with many storable oxidizers with high performance and is widely used in liquid rocket propulsion systems. As a result, it is uniquely suited for spacecraft maneuvering. The present study aims to formulate suitable gels of ethanol and compare its rheological characteristics with UDMH using methyl cellulose (MC) as gellant. The effect of variation of ambient temperature on rheological properties of Ethanol-MC and UDMH-MC gelled systems has also been studied to compare their relative suitability.

2 Materials and Methods

2.1Preparation of Ethanol and UDMH Gel Fuel Systems

In present work ethanol (99.8%) and UDMH (propellant grade) were selected as base fuels. The critical concentrations of gellant required to gel ethanol and UDMH were determined by conducting several set of experiments between the range of 1 to 10 wt% of gellant. The gelling agent (particle size: 40 µm) was used for gelation process has been found to be compatible and non-reactive with base fuels. The gelation process is known to be affected not only by the type of gelling agent, but other parameters such as processing temperature; mixing time, particle size of gellant etc. also. Uniformity of process details was maintained during all experiments. Methylcellulose (Fig.1) in requisite concentrations (4.5 wt%) was used for gelation of ethanol and UDMH.

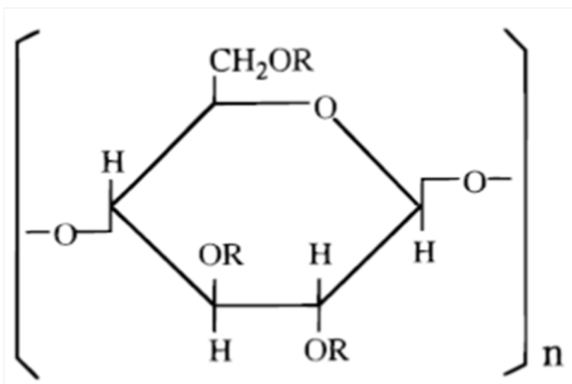


Figure 1: Methyl Cellulose Gelling Agent

The physico-chemical properties of both the fuels used are shown in Table 1 and Table 2.

Table1: Ethanol Properties (at 298K)

Molecular Formula	**C_2H_6O**
Boiling Point (K)	**352**
Vapor Pressure (kPa)	**5.95(at 293.15K)**
Flash Point, min. (K)	**286.15-287.15**
Density, liquid (g/cm3)	**0.789**
Viscosity, liquid (mPa.s)	**1.040**
Heat Capacity, liquid (J/(mol K))	**112.4**
Heat of Vaporization, at normal boiling point (kJ/mol)	**+38.56**
Heat of Combustion, min.(kJ/mol)	**-1370.7**
Auto ignition Temperature (K)	**635.15**

Table2: UDMH Properties (at 298K)

Molecular Formula	**$C_2H_8N_2$**
Boiling Point (K)	**147**
Vapor Pressure (kPa)	**13.7**
Flash Point, min. (K)	**-283.15**
Density, liquid (g/cm3)	**0.784**
Viscosity, liquid (mPa.s)	**0.56**
Heat Capacity, liquid (J/(molK))	**164.05**
Heat of Vaporization, at normal boiling point (kJ/mol)	**+35.22**
Heat of Combustion, min.(kJ/mol)	**-1982.3 ~ -1975.1**
Auto ignition Temperature (K)	**521.15**

Dispersions of methylcellulose particles in ethanol and UDMH liquid fuels were prepared by mixing the ingredients thoroughly for 5 minutes. The suspension was stirred at room temperature (298.15K ± 1K) to ensure complete dissolution of the gellant in the fuel. The mix was then kept undisturbed to allow the network formation. In both the cases, stable gels of fuels could be prepared.

2.2Rheological Characterization

Rheological studies on freshly prepared gelled ethanol and UDMH were carried out using a rheometer (HAAKE RS600) to determine the gel viscosity in low shear rate range (1 to 12 s^{-1}). This exercise is considered important for better understanding of the minimum stress required for initiating flow of the gels (yield stress) during. A set of parallel plates geometry was selected in the present investigation since it is more suitable for studying the rheological characteristics of Non-Newtonian linear visco-elastic fluids. A temperature control system present inside the equipment was used to ensure a constant fluid temperature during rheological measurements. The measurements were carried out at pre-selected temperatures (283.15, 288.15, 293.15, 298.15 and 303.15 K). The non- Newtonian fluids like gels exhibit a complex flow behavior unlike the conventional fluids that have a predictable variation in their flow properties with shear rate and temperature. Figure 2 depicts the variation of viscosity as a function of shear rate for different Newtonian and non-Newtonian fluids for the purpose of comparison. The experiments to study thixotropic character of respective gels were carried out by systematically increasing the shear rate to record the up-curve of the rheogram and then the shear rate was reduced in similar steps to capture the down curve.

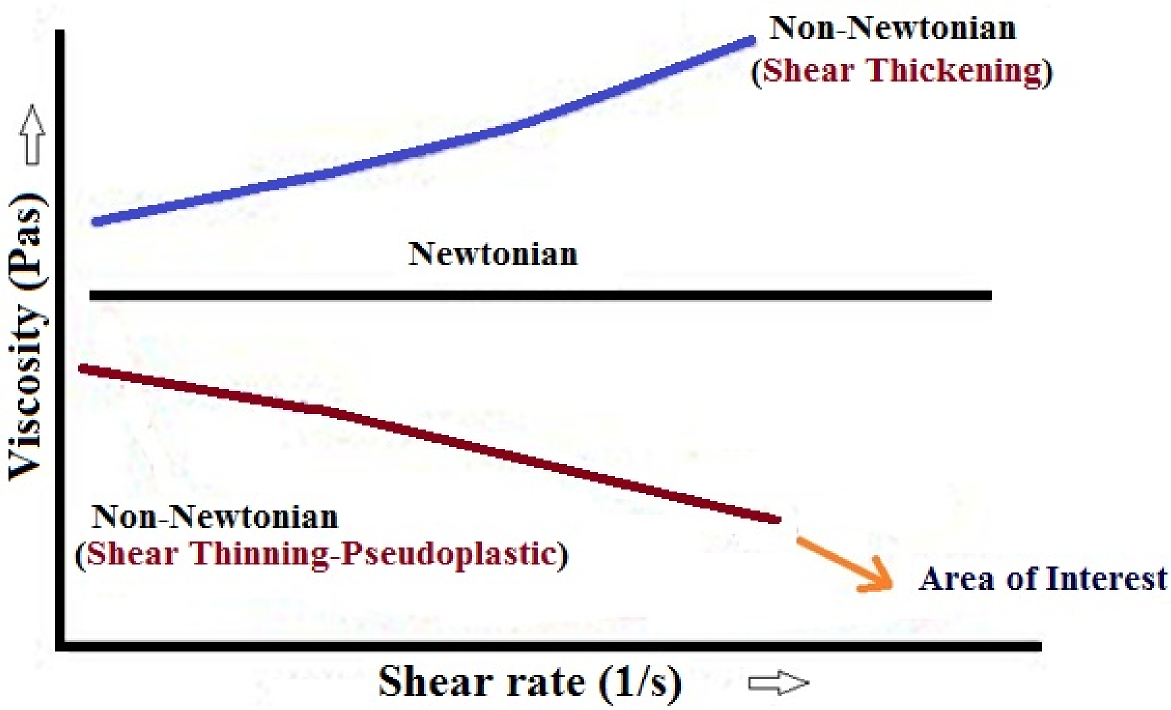
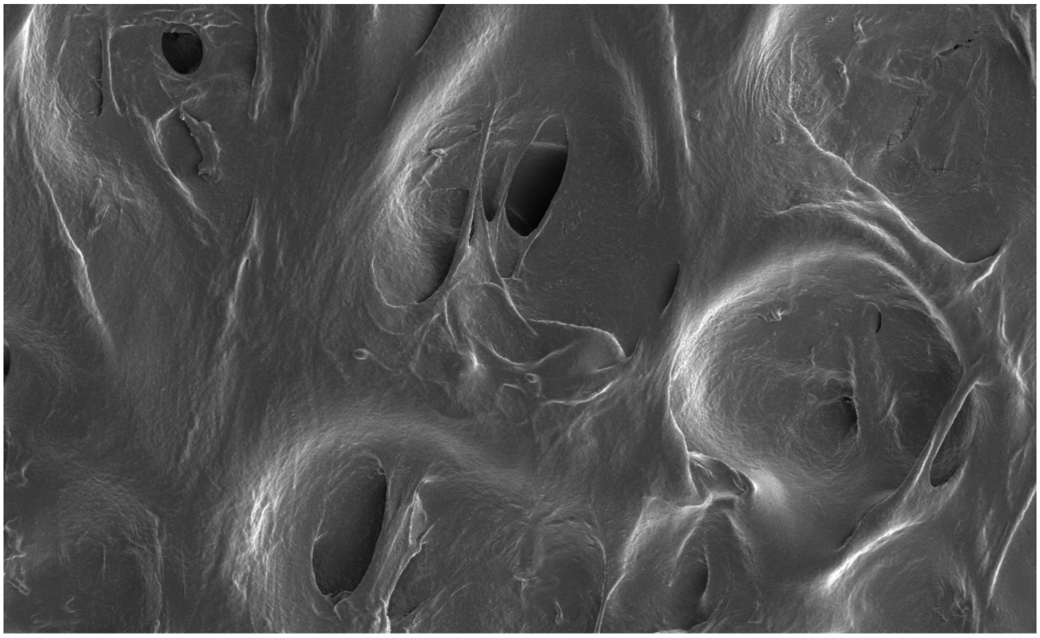


Figure 2: Typical Rheogram of Newtonian and non-Newtonian Fluids

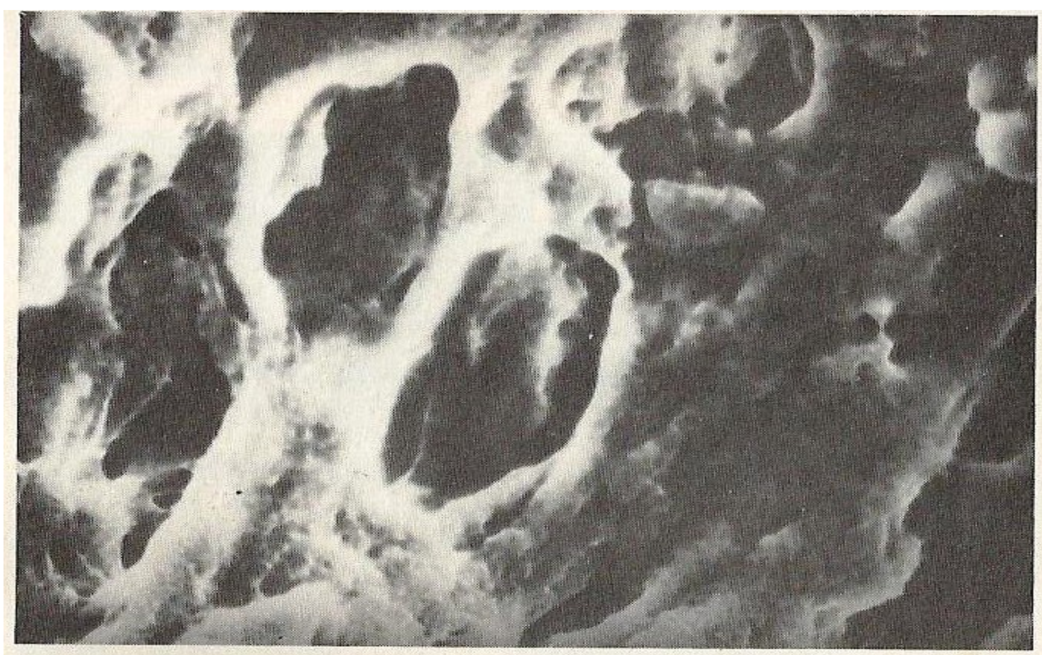
3 Results and Discussion

3.1Mechanistic Studies

The gelation of fuels with MC is mainly seen due to the manifestation of the hydrophobic effect. These hydrophobic repeat units in gellant act as physical "cross-linking loci" and hence form a three dimensional network with ethanol and UDMH fuels and ultimately this leads to gelation. The increase in the solution viscosity soon after dispersion of gellant at relatively low polymer concentration has been reported earlier [12] for MC. The micro-structural entities form in such a polymeric system due to their ability to give rise to weak intra and intermolecular hydrophobic interactions in the solution. These interactions form a temporary associating network which serves to reinforce the larger entangled network. The micrograph obtained using scanning electron microscope confirms that three dimensional miscelle formations take place in both the gels (Fig. 3). The quality of gel network obtained is usually dependent on – nature and purity of liquid, degree of substitution, grade, concentration and degree of dispersion of gelling agent and temperature involved. The uniformity in these critical aspects of gelation process was maintained during all experimentations in this study.



(A)



(B)

Figure 3: Scanning Electron Micrographs of (A) Ethanol-MC and (B) UDMH-MC Gels

3.2 Rheological Studies

The rheological study on the prepared gels is conducted to measure the apparent viscosity as a function of shear rate. The study was conducted to investigate the shear-thinning (thixotropic) properties of ethanol and UDMH based gel propellants in a low shear rate range (1-12 s^{-1}). The measurement of rheological properties provides a better understanding of consistency, homogeneity and overall quality of gels. The critical information can also be gathered about salient features of micro-structure deformation, fundamental characterization of the fluid behavior, ambient storage and ageing characteristics.

3.2.1 Determination of apparent viscosity

The results on the variation of apparent viscosity with shear rate at different temperatures (283.15, 288.15, 293.15, 298.15 and 303.15 K) for ethanol-MC and UDMH-MC gels are presented in Fig.4 and 5. The results clearly indicate that the apparent viscosity for gelled ethanol and UDMH decreases significantly with increasing shear rate. The observation can be substantiated by explanation that with increase in shear rate the weak intra and intermolecular hydrophobic interactions that form three dimensional gel networks get disturbed or broken. This may lead to alignment of network elements that results in the release of the entrapped liquid within, offering less resistance to flow and as a result, reduction in apparent viscosity. The results showing the effect of temperature on apparent viscosity variation at different shear rates clearly show a substantial decrease in gel viscosity with temperature.

Figure 4 shows that as soon as the Ethanol-MC gel is disturbed at a very low shear rate (less than 3 s^{-1}) the flow is initiated and further increase in shear rate leads to thinning of gel. The initial apparent viscosity of gel is seen to decrease with increase in test temperature (curves shift downwards). This magnitude of reduction in apparent viscosity with shear rate is seen to be more pronounced with increase in temperature possibly due to rapid breaking of gel network at elevated temperatures from temperature 283.15 to 303.15 K. In general, it is also seen that apparent viscosity decreases linearly with shear rate, indicating that the gel exhibits a pseudo-plastic character under the shear rate and temperature range covered under the present study. This further establishes that the formulated Ethanol-MC shows a shear thinning and pseudo-plastic character. The similar apparent viscosity measurement results of UDMH-MC gel are shown in Figure 5. The gels show an inherent lower viscosity in comparison to ethanol gels and results are quite similar at all the temperatures covered. The noteworthy feature is that the rate of reduction of viscosity for UDMH-MC is relatively lower than ethanol gel that exhibits a higher slope.

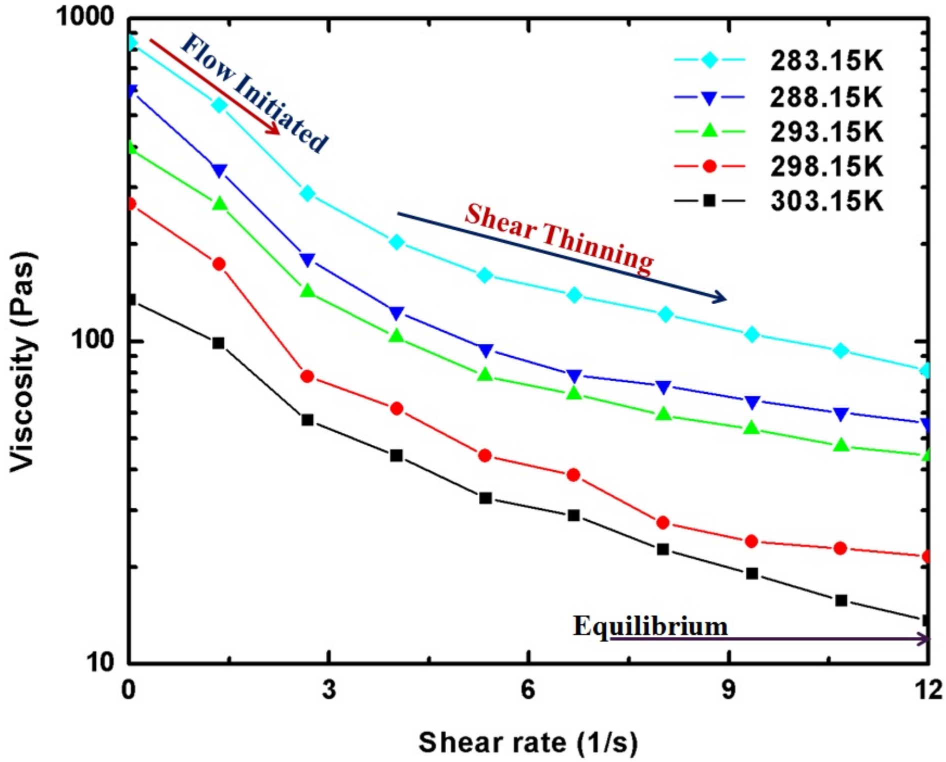


Figure 4: Ethanol-MC Gel Apparent Viscosity as a Function of Operating Temperatures

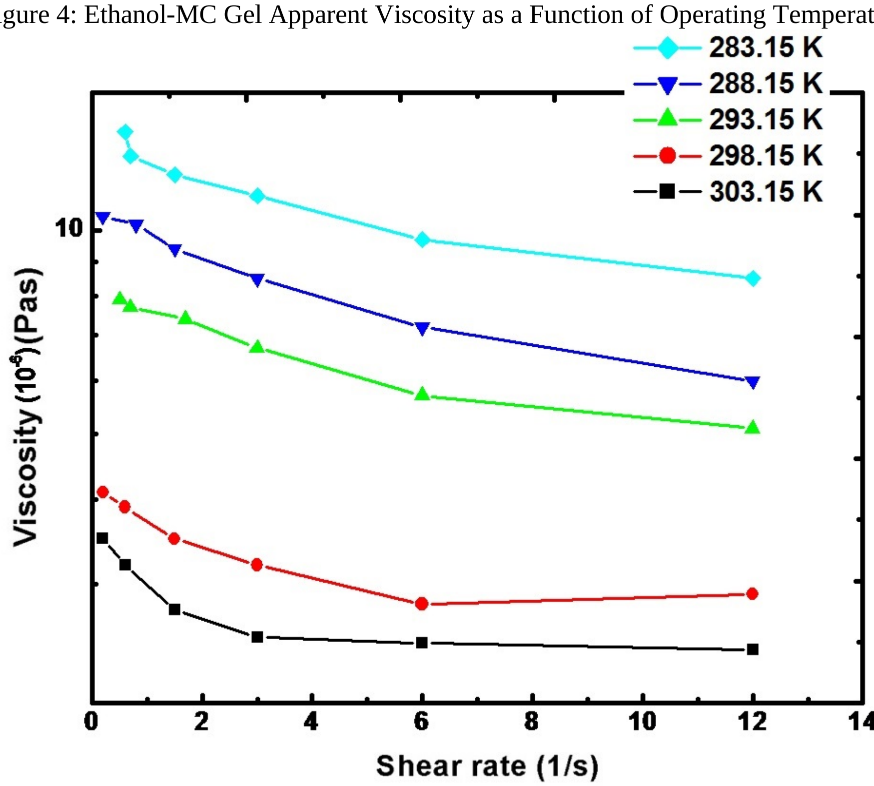


Figure 5: UDMH-MC Gel Apparent Viscosity as a Function of Operating Temperatures

A summary of the obtained results of apparent viscosity of both the gels at different temperatures is presented in Table 3. The data clearly show that the UDMH-MC gel has a very high initial viscosity at lower temperatures (283.15K) that finally drop down manifold at higher temperature in the shear rate range covered. It is evident that the gels started flowing at a nominal shear rate range of 1 to 12 s^{-1} with considerable reduction in viscosity as given in Table 3. The Ethanol-MC gel initially has a much higher viscosity value at all temperatures covered in this study in comparison to UDMH-MC gel but the viscosity reduction up to a level of approximately 10% w.r.t. initial viscosity (Column 4 & 5) can be achieved even in the very low shear rate range.

Table 3: Effect of Temperature on Apparent Viscosity of Ethanol and UDMH Gels

Temperature (K)	Apparent Viscosity (Pas)			
	Ethanol		UDMH (10^{-6})	
	Initial (η)	Final(η)	Initial (η)	Final(η)
283.15	843	81.3	14	8.5
288.15	601	55.8	10.5	6.0
293.15	394	44.2	7.9	5.1
298.15	266.8	21.5	4.1	2.8
303.15	134.5	13.6	3.5	2.4

Shear thinning pseudoplastic behavior is very important to ensure that with increase in shear rate to higher levels the viscosity of the fluid would drastically reduce to facilitate flow through injectors. This property of gel provides a unique advantage as the gels in the storage tank is much safer to transport and would not leak through minor cracks. Accidental spills on a naval ship or where the propellant is stored in close proximity of personnel will also not prove catastrophic due to high viscosity and reduced vaporization of fuel.

3.3 Assessment of Thixotropic Behaviour

The thixotropic character of Ethanol-MC and UDMH-MC gel fuels at different temperatures has been studied in the covered shear rate range. During the experiments, the share rate was increased systematically to a maximum level to trace the up curve and it was decreased in the similar steps to get the down curve of the rheogram (Fig.6 and 7). The data reveal that the apparent viscosity of the Ethanol-MC and UDMH-MC gel decreases significantly with shear rate, and because the shear stress values do not exhibit proportionality with shear rate, both up and down curves do not superimpose each other and enclose an area between them, referred to as 'hysteresis loop'. The area within the hysteresis loop provides a direct measure of the extent of thixotropic behavior of the gel. It can also reflect the reduction in structural strength during the shear load phase and the more or less rapid, but complete structural regeneration with time with subsequent decrease in shear rate due to local spatial rearrangement of the molecules in the three dimensional network. The presence of 'hysteresis loop' indicates that the breakdown of structure has occurred and the area within the loop may be used as an index of the degree of breakdown. The results shown in Fig.

6 and 7 reveal the phenomenon. This indicates that both Ethanol-MC and UDMH-MC gel exhibit a shear-thinning behavior i.e. thixotropic character. The results were also analyzed using Power law and the approach has been mentioned elsewhere [13]. The results of the computed consistency coefficient (K), a measure of consistency of the gel, show a reduced value at higher temperature whereas the thixotropic index is found to be more or less unaffected at higher temperature. The UDMH gels show a 'n' value closer to Newtonian fluids (n = 1), when sheared, however, ethanol-MC gels show a larger departure from unity indicating that much higher shear rates are required to facilitate the free flow for this gel (Table 4).

Table 4: Effect of Temperature on Thixotropic Index of Ethanol and UDMH Gels

	Consistency coefficient (K) (Pas^n)		Thixotropic index (n)	
Temperature (K)	Ethanol	UDMH	Ethanol	UDMH
283.15K	693.3	12.6	0.13	0.85
288.15K	437.5	10.0	0.12	0.81
293.15K	341.1	7.6	0.14	0.85
298.15K	230.9	3.6	0.13	0.89
303.15K	126.7	2.9	0.18	0.88

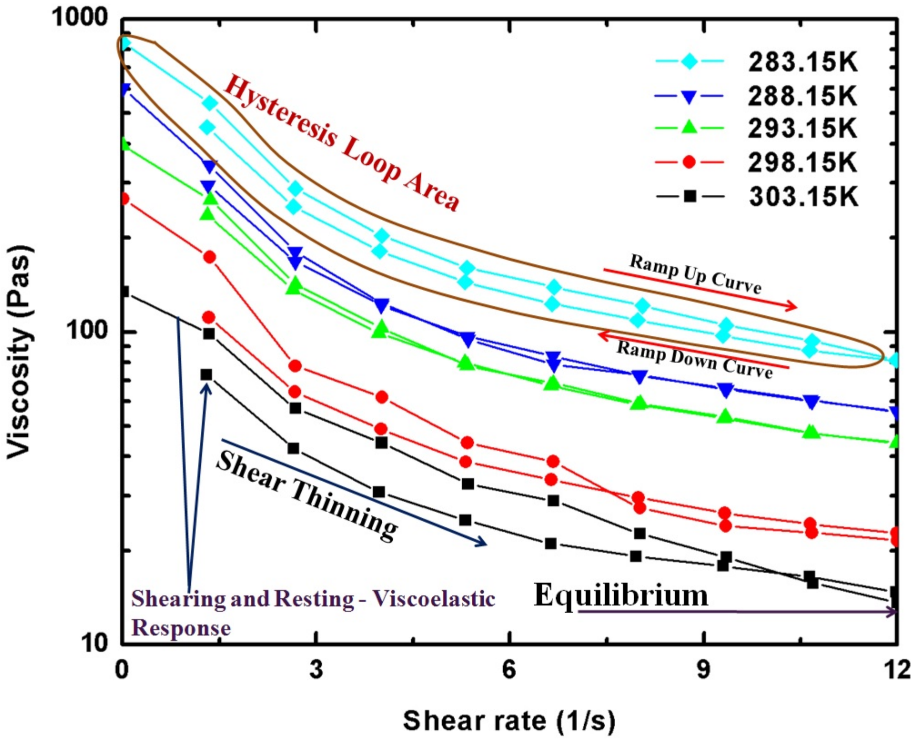


Figure 6: Rheograms of Ethanol-MC Gel Propellant at Different Temperatures

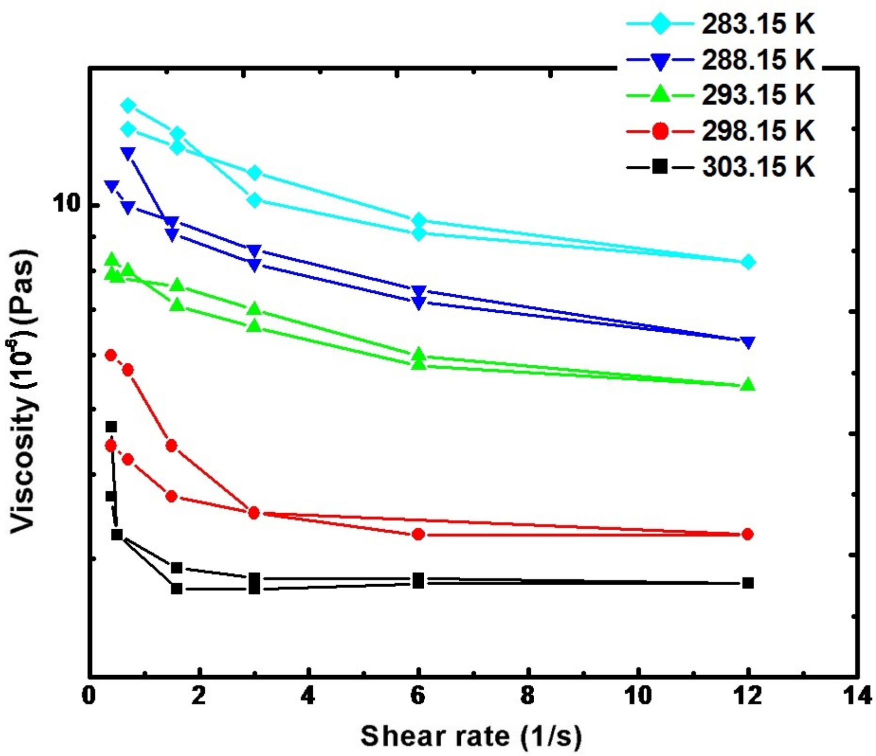


Figure 7: Rheograms of UDMH-MC Gel Propellant at Different Temperatures

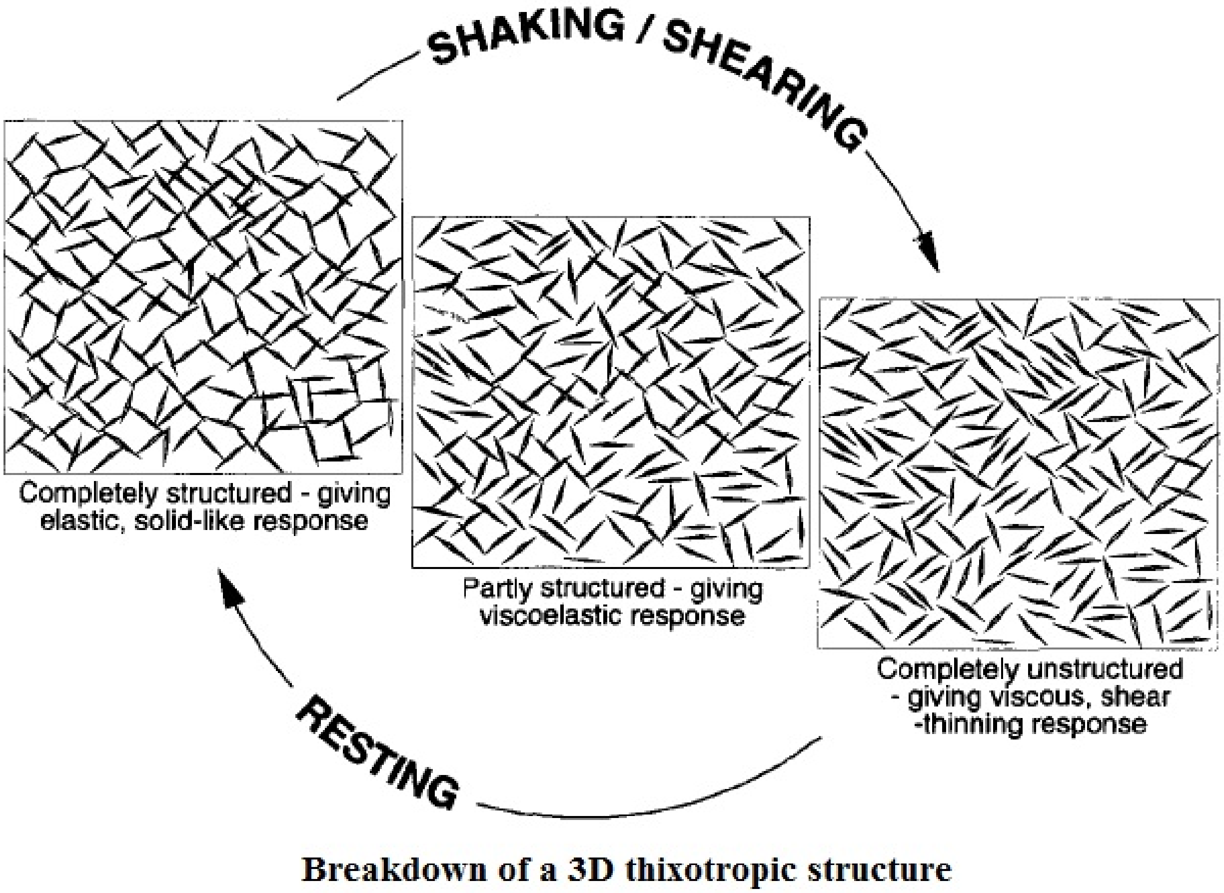


Figure 8: Breakdown of Three Dimensional Network and Regain

Figure 6 and 7 clearly reveal that with increase in operating temperature, the apparent viscosity profile of both the gels (up and down curve) is seen to shift to lower viscosity region. It can be attributed to the weakening of the structural strength that in turn is responsible for reduction of gel viscosity at elevated temperatures. It is interesting to note that the hysteresis loop area remains more or less the same in this shear rate range. The results confirm that the area enclosed in the hysteresis loop is just marginally affected by the variation in operating temperature at low shear rate range. Further, it is evident from the data that both the gels do not lead to a complete breakdown of gel structure. Figure 8 [14] attempts to explain the breakdown of three dimensional gel networks from stationary to sheared condition. The break down obviously becomes more pronounced at high shear rate and the re-gelation process of the gels is also found to be much slower when subjected to higher shear rates.

4 Conclusion

The gelation of conventional rocket fuels - ethanol and UDMH can be done with methyl cellulose as gelling agent at reasonably low concentrations to get stable gels. The mechanistic studies indicate the three dimensional micellar structure is responsible for gel formation and a large amount of fuel can be entrapped in it. The influence of shear rate led to reduction in apparent viscosity and the analysis of results reveal that both the gels exhibit shear-thinning i.e. thixotropic nature. Apparent viscosity of ethanol-MC and UDMH-MC gels were found to decrease with increase in shear rate at higher temperatures as well. The magnitude of apparent viscosity shifted to a much lower viscosity range with increase in operating temperature for both the gel propellant systems. No significant change in hysteresis loop and thixotropic index of gels, has been observed. The operating temperature and shear rate together play an important role and significantly influence the rheological properties of gel propellant systems.

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References

[1] Natan, B. and Rahimi, S. 2002. The status of gel propellants in year 2000. *International Journal of Energetic Materials and Chemical Propulsion*. 5: 172-194.

[2] Ciezki, H.K. and Natan, B. 2005. An overview of investigations on gel fuels for ramjet applications. *17th Int. Symposium on Airbreathing Engines*, Munich, Germany, September 4th- 9th.

[3] Munjal, N. L., Gupta, B. L. and Varma, M. 1985. Preparative and mechanistic studies on unsymmetrical dimethyl hydrazine - red fuming nitric acid liquid propellant gels. *Propellants, Explosives, Pyrotechnics*. 10: 111–117.

[4] Varma, M., Gupta, B. L. and Pandey, M. 1996. Formulation & storage studies on hydrazine based gelled propellants. *Defence Science Journal*. 46: 435–442.

[5] Gupta, B. L., Varma, M. and Munjal, N. L. 1986. Rheological studies on virgin and metallized unsymmetrical dimethyl hydrazine gelled systems. *Propellants*, *Explosives*, *Pyrotechnics*. 11: 45–52.

[6] Varma, M. and Pein, R. 2009. Optimization of processing conditions for gel propellant production, *International Journal of Energetic Materials and Chemical Propulsion,* 8 : 501-513.

[7] Teipel, U., and Forter-Barth, U. 2007. Rheological behavior of nitromethane gelled with nanoparticles. *J Propul Power*. 21: 40-43.

[8] Rahimi,S., Peretz, A. and Natan, B. 2007. On shear rheology of gel propellants. *Propellants,Explosives,Pyrotechnics.* 32: 165-174 .

[9] Gupta, B.L., Varma, M. and Munjal, N.L. 1992. Theoretical performance of metallized unsymmetrical di methylhydrazine - red fuming nitric acid system, *Ind.J. Technol*., 30: 234 – 244.

[10] Varma, M. and Jyoti, B.V.S. 2011. Ignition and Combustion Studies of Heterogeneous UDMH-RFNA Gel Propellants, *International Journal of Energetic Materials and Chemical Propulsion*, 10 : 259-275.

[11] Mallory, J. A. and Sojka, P. E., 2011. Impinging Jet Structure and Break-up Using Gelled Propellant Simulants, *European Conference on Liquid Atomization and Spray Systems*, Portugal.

[12] Kobayashi, K., Huang, C. and Lodge, T.P. 1999. Thermoreversible gelation of aqueous methylcellulose solutions. *Macromolecules*. 32: 7070-7077.

[13] Varma, M. 1986. Studies on UDMH - RFNA Gelled Propellant Systems, Ph.D. Thesis, Birla Institute of Technology, Ranchi, India.

[14] Howard A. Barnes. 1997.Thixotropy – a review. *J. Non-Newtonian Fluid Mech*. 70: 1-33.