Rheological Study of Solid Ethanol Using Different Solidifying Agents

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Abstract

The solidification of pure ethanol for hybrid rocket application using Methylcellulose (MC) and Hydroxypropyl methylcellulose (HPMC) as solidifying agent, and its rheological behavior are reported herein. The solidification experiment carried out at critical concentration of solidifying agent as low as 10 wt. % for HPMC and 14 wt. % for MC. The rheological study shows that, increasing shear rate (1 to 20 s⁻¹) reduces the apparent viscosity of the propellant for given yield stress. The varying concentration of solidifying agent significantly affects the propellant viscosity and yield stress. The oscillatory shear test proved the propellant samples exhibit viscoelastic nature with high storage modulus (G') and independent of strain percent (50 %–100 %). The G' values for all propellant samples depended on frequency ranges from 1 to 100 Hz, and exceeded the loss modulus (G'') values, which indicated propellants highly structured.

Introduction

In the recent past, considerable interest has been paid for identifying, and formulating novel propellants in order to achieve higher density, better regression rate, high specific impulse, and cost effective to other conventional hybrid rocket engines. Ethanol is a vital biofuel which is eco-friendly and cost effective to other conventional hybrid rocket fuels which are in current use. Ethanol also has a long and illustrious record as a rocket fuel and it is desirable for use in hybrid rocket. Hybrid rockets generally uses a liquid oxidizer and a solid fuel grain, so, in order to use ethanol in hybrid rocket, it must be converted into solid material. Solidification of ethanol will provide additional advantages, such as higher specific impulse, volumetric loading, reduced vaporization loss, and other etc. [1-3]. In order to use newly formulated propellants in the hybrid rocket engine, the details about their rheological behavior must be precisely understood.

The rheological properties of the propellants primarily depend on their formulation [4]. Only few studies have aimed to investigate the formulaion, the rheology, and the microstructure development behavior of solid ethanol fuels [5]. The present study aims to explore the critical concentration of MC and HPMC for converting ethanol water mixture into solid fuel. The structural features responsible for the viscoelastic behavior are also identified via dynamic and flow curve analysis. The decrease of viscosity increases the regression rate and the trend is connected to the increasing development of entrainment phenomena, which strongly increases the regression rate [6]. Oscillatory sweep test were performed to analyze the viscoelastic properties of the solid fuels for better understanding of micro structural network and transition point from elastic to viscous behavior. Steady shear experiments at shear rate ranges from 1 to 20 s⁻¹ and 1 to 1000 s⁻¹ were also conducted to determine the yield stress profile as a function of solidifying agent concentration at room temperature. The required properties for the use of formulated propellant in the hybrid rocket engine addressed in this study were yield stress over considerable range of shear rate, high elastic modulus, and viscoelasticity.

Materials and Methods

Formulation

All the chemicals were procured from Sigma Aldrich Corporation. Ethanol (99.8 %) was selected as the base fuel. Methylcellulose (~400 cP) and Hydroxypropyl methyl cellulose (~ 4000 cP) were selected as solidifying agent for formulating solid fuel. The critical concentration of solidifying agent required for solidification was determined by conducting several sets of experiments ranging from 10 wt. % to 15 wt. % of MC and 10 wt. % to 12 wt. % of HPMC. The solidifying agent was mixed with ethanol water mixture (15 wt. % of H₂O for MC, 10 wt. % of H₂O for HPMC) by dropping it slowly in the mixer as a free-flowing powder, and the mixture was stirred using a laboratory impeller at a fixed speed for approximately 5 minutes at room temperature to ensure a homogenous mixture. The homogenous mixture was then maintained for 4-5 hours to complete the solidifying process. The uniformity of the process details was maintained during all experiments.

Table 1. Ethanol solidification experiment using MC

<table>
<thead>
<tr>
<th>Propellant</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol+ 17% MC</td>
<td>Soft Solid, No phase separation</td>
</tr>
<tr>
<td>Ethanol+ 15% MC</td>
<td>Solid, No phase separation</td>
</tr>
<tr>
<td>Ethanol+ 14% MC</td>
<td>Solid, No phase separation</td>
</tr>
<tr>
<td>Ethanol+ 12% MC</td>
<td>Soft Solid, No phase separation</td>
</tr>
<tr>
<td>Ethanol+ 10% MC</td>
<td>Soft Solid, No phase separation</td>
</tr>
</tbody>
</table>
Table 2. Ethanol solidification experiment using HPMC

<table>
<thead>
<tr>
<th>Propellant</th>
<th>Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol-10wt.% HPMC</td>
<td>Soft solid, No phase separation</td>
</tr>
<tr>
<td>Ethanol-11wt.% HPMC</td>
<td>Solid, No phase separation</td>
</tr>
<tr>
<td>Ethanol-12wt.% HPMC</td>
<td>Solid, No phase separation</td>
</tr>
</tbody>
</table>

The solidification of ethanol water mixture with MC and HPMC is mainly due to the formation of strong hydrogen bond formed between two, which forms a three dimensional network. The strength of the hydrogen bond depends on the concentration of solidifying agent and ethanol water mixture. A weak hydrogen bond was observed for ethanol gel wherein, a strong hydrogen bond exist in the solid ethanol fuel.

Rheological Characterization

Rheological studies of freshly prepared samples were carried out with a rotational rheometer (HAAKE RS6000). The most common geometries for rotational rheometers are parallel plate and the cone plate configuration. The parallel plate geometry configuration was used for all the measurements in this study. For the flow study, the apparent viscosity was measured for a sampling time of 30 seconds; the number of experimental points set to 100. Each experiments was repeated for each condition at room temperature for reducing the error.

Results and Discussion

Flow Study

The flow study of the prepared samples were conducted to measure the apparent viscosity as a function of shear rate. For a non-Newtonian fluid, the viscosity depends on the applied shear rate. The shear rate used for this study were low shear (1 to 20 s⁻¹) and high shear (1 to 1000 s⁻¹) rates. This measurements provide better understanding of the flow behavior, consistency, homogeneity and quality of the formulation. The results clearly indicates that, the apparent viscosity of the Ethanol-MC and Ethanol-HPMC propellants significantly decreases with the increase of shear rate. This behavior is due to the disturbance or breakage of hydrogen bond associated with the three dimensional network in the response to the increased shear rate. The propellants remains solid unless they have reached critical stress level called yield stress. The solid ethanol propellants are fully elastic below this yield stress, the three dimensional network structure of the propellants breaks above this yield stress, and shows viscous behavior. Moreover, the concentration of gellant affects the magnitude of viscosity and yield stress of the propellant, as shown Fig. 3 to Fig. 7.
Jerin et al [5] have discussed the upper and lower limit critical concentration for MC for solidification of ethanol. They observed a good solidification at 15 wt. % and 14 wt. % of MC, and if the concentration of MC exceeds 17 wt. %, the formed propellant sample was powdery rather than elastic solid, and if it exceeds the lower limit of MC (14 wt. %), the samples behaved more like a gelled fuel than elastic solid. Using MC as solidifying agent for ethanol, there is a considerable sacrifice of active ethanol in the formed sample; the active ethanol in the solid samples varies from 70 wt. % to 75 wt. %.

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From the Fig. 3, Fig. 4, Fig. 5, the apparent viscosity for ethanol-MC and ethanol-HPMC decreased with the increase in shear rate, this behavior is generally observed in non-Newtonian fluids. The ethanol-HPMC samples showed a better performance over ethanol-MC samples under flow study. From the solidification experiment, using Hydroxypropyl methylcellulose, the lower limit for the solidification was 10 wt. % whereas, in MC it was found to be 14 wt. %. It was observed that, 3 wt. % less concentration of HPMC needed compared with MC to convert ethanol into viscoelastic solid. From Fig. 4, HPMC-12 wt. % sample proved a better one over MC-12 wt. % from the flow study.

Fig. 4 Apparent viscosity for Ethanol-HPMC formulation for low shear rate (1 to 20 s⁻¹)

Fig. 5 Apparent viscosity for Ethanol-MC, Ethanol-HPMC formulation for low shear rate (1 to 20 s⁻¹)

Fig. 6 Apparent viscosity for Ethanol-MC formulation for higher shear rates (1 to 1000 s⁻¹)

Fig. 7 Apparent viscosity for Ethanol-MC, Ethanol-HPMC formulation for higher shear rates (1 to 1000 s⁻¹)

In the coming analyses, we focused on ethanol-HPMC formulations and ethanol-MC (10 wt. % and 12 wt. %), as ethanol-MC case was studied in detail by Jerin et al [5].

Dynamic Strain Sweep Test

This experiment was performed on the formulated propellant to determine the critical strain ($\gamma_c$), to identify the upper limit of the Linear-Elastic range (LVE) of each formulation. The tests were carried on the solid propellant at a constant frequency of 1 Hz and 100 Hz. The LVE was determined from the strain region where $G'$ (storage modulus) is independent of the strain amplitude. Beyond the critical strain value,
the propellant behavior is non-linear and the storage modulus, $G'$, which give a detailed information in characterizing viscoelastic behavior of the propellants declines. The dynamic strain sweep test would establish the linearity of $G'$ of the propellants. The limit of the LVE range is shown in Fig. 8 and Fig. 9. These ranges gave the distinction between solid phase and network deformation, which indicated the microscopic structure of the propellants.

Frequency Sweep Test

Frequency sweep test were performed on the formulated samples below the critical strain to probe the viscoelastic properties as a function of solidifying agent concentration. These test will provides the information about the interaction of ethanol water mixture and MC, HPMC particles inside the formulated propellant; also helps to determine the frequency dependence on $G'$ and $G''$ values. Higher the $G'$ value stronger the intermolecular interactions.

On comparing Fig. 8 and Fig. 9, $G'$ values were greater than $G''$ values, indicates propellant samples were highly elastic in nature; HPMC samples were more elastic in comparison to MC samples. The point at which $G'$ and $G''$ values drops (dependent on shear stress/strain) called critical strain. Below this strain, propellant structure is rigid, the material behaves like elastic solid. The three dimensional network structure gets disrupted if the strain exceeds critical strain value and the $G'$ declines. The critical strain value and the yield stress is the upper limit value prior to the structural deformation.
As observed in the Dynamic Strain Sweep test, the HPMC samples have higher G' values compared with MC samples in Frequency Sweep test. The Fig. 10 and Fig. 11 shows the G' and G'' measured in the frequency range of 1 to 100 Hz for the propellant samples at 100% strain. It is observed that, G' and G'' values were nearly dependent of frequency range, and G'>G'', covered in the present study for all propellant samples.

From the Fig. 10 and Fig. 11, the G' values for Ethanol-HPMC (12 wt. %), Ethanol-HPMC (10 wt. %) were higher in comparison with Ethanol-MC propellants. The lower G' value for the Ethanol-MC samples may be due to weak three dimension network, due to lower concentration of methylcellulose.

The usage of Hydroxypropyl methylcellulose have progressively changed the fuel formulation as well as the mechanical properties of the solid ethanol fuel. This may be due to the development of much stronger connectivity across three dimensional network. This higher degree of the cross-linking capability of HPMC have decreased the concentration of solidifying agent resulted in increased active fuel content and more shear resistant propellant.

Conclusion

In this paper, efforts were made to understand the effects of two different solidifying agent and the rheological behavior of the formulated propellant samples for the use as a solid fuel in the hybrid rocket system. At this end, number of formulation experiments were carried out to find the upper and lower critical concentration of methylcellulose and Hydroxypropyl methylcellulose for the solidification of ethanol. Rheological experiments were performed to determine the apparent viscosity, yield stress, critical strain, LVE range, storage modulus and viscous modulus. The observed changes in the properties of the propellant samples during the experiments were assumed to be solemnly due to the imposed conditions.

The ethanol fuel can be solidified used appropriate concentration of MC and HPMC. All the formulated samples showed viscoelastic behavior over the shear rate of 1 to 20 s⁻¹ and 1 to 1000 s⁻¹. There is a greater influence on the yield stress for propellant samples having higher gellant concentration. The higher yield stress means the ease of handling, storage, transportation.

An oscillatory rheology analysis showed that, the different solidifying agent and its concentration play an important role in determining the viscoelastic properties of the solid ethanol fuel. Furthermore, Ethanol-HPMC propellants have higher LVE range over Ethanol-MC propellants over higher range of shear stress values. G' values were greater than G'' for all propellant samples over range of shear stress and frequency used in the present study. The HPMC concentration in the ethanol increased the viscoelastic nature of solid ethanol at lower concentration compared with MC. Overall, Hydroxypropyl methylcellulose found to be a better partner with ethanol, in solidifying ethanol; critical concentration for solidifying ethanol was lower for HPMC compared with MC, thereby more active fuel percentage in the solid ethanol.

Acknowledgments

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References

5) J. John, B. V. S. Jyoti, S. W. Baek, 30th International Symposium on Space Technology and Science, Kobe, Japan, July 4-8, 2015.
6) M. Boiocchi et.al, EUCASS Conference, 1199-1887, 2011.