Paraffin-based Solid Fuels Characterization and Effect of their Properties on Entrainment Phenomena

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Abstract

In this work paraffin-based fuels for hybrid rockets were investigated by means of experimental approaches in order to develop a new type of solid fuel combining at the same time good ballistic and suitable mechanical properties.

Three kinds of experimental investigations were performed in order to study the rheological, viscoelastic and mechanical properties of paraffin-wax based blends doped with thermoplastic polymers and metal powders so as to evaluate a formulation which fits best to requirements to be used as a fuel for hybrid rocket engines.

1. Introduction

A hybrid rocket has the advantages of high safety, thrust adjustment, re-ignition, low-cost, and low negative environmental impact. However, a hybrid rocket has technical problems of low fuel regression rate, low combustion efficiency, and low volume efficiency. Therefore, at present there are no practical examples of such rockets. Several studies have been performed to overcome the above-mentioned problems, especially the ones related to low regression rate. Karabeyoglu et al. at Stanford University studied paraffin-based fuels for hybrid rockets. In Japan, the study of the Cascaded Multi Impinging- jet was performed at Hokkaido University. Oxidizer swirling flow was investigated at Tokyo Metropolitan University. From previous researches, the paraffin-based fuel regression rate proved 3 to 4 times higher than that of conventional fuels such as HTPB. Paraffin waxes are inexpensive materials, soft and brittle. However, to use these materials in hybrid rockets propulsion systems the mechanical properties of waxes need to be improved because waxes are brittle due to the nature of the paraffinic material.

Some materials such as low density polyethylene (LDPE) [1], ethylene vinyl acetate copolymer (EVA) [2], octadecanoic acid (stearic acid) [3] and poly-urethane foam (PUF) [4] were investigated as possible strengthening additives.

In this experimental work, in order to improve mechanical and ballistic characteristics thermoplastic polymers were added and metal hydrides were used.

The original diffusion-limited model developed by Marxman and co-workers was developed considering polymeric fuels burning in oxygen [5][6][7]. Recent investigations, carried out at Stanford University by Karabeyoglu et al. highlighted the marked regression rate increase offered by particular solid fuels as solid paraffin wax and other alkanes [8][9]. The regression rate increase of these latter fuels is up to 400% with respect to (conventional) polymeric fuels. Paraffin burns faster because as the oxygen gas blows across the melted surface, waves form and are pulled off as a spray of droplets (Figure 1). That spray burns extremely fast, thus increasing the fuel combustion rate.

In general, the total regression rate of a hybrid motor is the sum of the evaporation regression rate that is generated by the vaporization of the liquid into the gas stream and the entrainment regression rate, which is related to the mass transfer mechanically extracted from the liquid surface.

$$\dot{r} = \dot{r}_v + \dot{r}_{ent} \quad (1)$$

The suggested general empirical expression for the entrainment rate of liquid droplets in terms of the relevant properties of the hybrid motor is the following [9]

$$\dot{m}_{ent} \infty \frac{P_d^{\widehat{\alpha}} h^{\widehat{\beta}}}{\mu_l^{\widehat{\gamma}} \sigma^{\widehat{\pi}}} \tag{2}$$

where P_d is dynamic pressure;
h is melt layer thickness;
μ is viscosity;
σ is surface tension.

Consequently, the lower viscosity a material has, the higher rate of the entrainment effect is expected. It was found that fuels that develop a melt layer of low viscosity could entrain liquid droplets under the influence of the shear stress of the gas flow in the port. It was shown that if the melt layer is sufficiently fluid, that is, with low viscosity and surface tension, then under a high gas flux environment, instability is created in the liquid layer, resulting in the formation of liquid droplets that are expelled from the surface. When liquid entrainment occurs, the resulting fuel flow from the surface is composed of a mixture of vapor and liquid droplets.
Alkanes are considered the best paraffin fuels due to the fact that their melt layers have low viscosity.

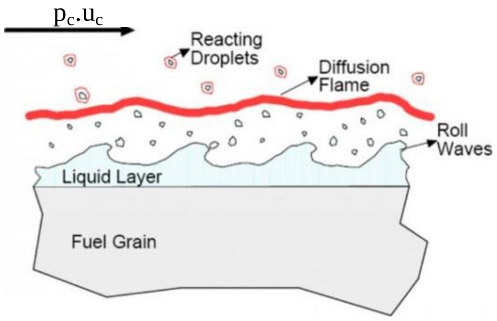

Figure 1: Entrainment of melted fuel droplets from surface melted layer of fuel grain by oxidizer flow

2. Investigated materials

The paraffin used as main ingredient in this work is supplied by Sigma Aldrich company with the melting point temperature around 55-60 °C, which means that the used paraffin-wax chemical formula is $C_{28}H_{58}$.
Paraffin-wax itself does not have sufficiently good mechanical properties so as to allow the solid fuel grain to remain in solid state under high temperature environment in the combustion chamber. As a consequence some kind of strengthening additive must be supplied.
Based on previous research works and looking for a suitable match, four thermoplastic polymers (TPP) were chosen:

- Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene-graft-maleic anhydride (SEBS);
- Polystyrene-block-polyisoprene-block-polystyrene (SIS);
- Ethylene vinyl acetate (EVA);
- Polyethylene (PE).

SEBS, SIS, EVA and PE are low molecular weight polymers and are expected to increase hardness, tensile strength and flexibility of paraffin-wax as well as polyethylene does [10].
One of the most important properties of these TPP is good compatibility with paraffin-wax. A homogeneous mixture is expected due to the presence of ethylene-butylene and isoprene blocks in their chemical formulas, which are similar to paraffin structure. The blend of TPP and paraffin forms a semi-crystalline thermoplastic structure and ensures low manufacturing costs, homogeneous fuels and possibility to use this kind of formulations in higher-scale tests.
Metal hydrides, simple as Magnesium hydride (MgH_2), or double as Lithium Aluminum hydride ($LiAlH_4$), were used as fillers in the paraffin matrix.
Metal additives - reactive metals such as aluminum, magnesium, lithium or beryllium can be easily included in the fuel grain thus increasing specific impulse (*Is*), density specific impulse, or both.
Lithium aluminum hydride (LAH) is an inorganic compound with the chemical formula $LiAlH_4$.

Regression rates for paraffin wax hybrids are high compared to other hybrid fuels; additives can be used with paraffin wax to tailor the regression rate and specific impulse (*Is*). Aluminum is a traditional solid rocket motor additive.

Adding metal hydrides to paraffin was found to increase the combustion temperature and regression rate. Metalizing the paraffin can also decrease the optimal oxidizer-to-fuel ratio, making it possible to reduce the volume of the oxidizer tank relative to straight paraffin hybrid rockets. The major difficulty (and advantage) of metal hydrides is that they are very reactive with water and therefore humid air. Metal hydride compounds need to be stored in a dry environment.

Carbon black powder is used in paraffin-based formulations in order to enhance the radiative heat transfer between flame zone and the regression surface [11], [12] and also to concentrate the radiation absorption in the thin layer under the regression surface.

Different compositions were manufactured and characterized, according to the list and the nomenclature of Table 1.

Table 1: Composition of studied pure paraffinic material, polymer-based and metal powder-added blends

Fuel	Composition
GW	Gelly Wax
S05G	SEBS 5% GW 94% CB 1%
S10G	SEBS 10% GW 89% CB 1%
S20G	SEBS 20% GW 79% CB 1%
S30G	SEBS 30% GW 69% CB 1%
S40G	SEBS 40% GW 59% CB 1%
S05GLAH5	SEBS 5% GW 89% LAH 5% CB 1%
S05GLAH10	SEBS 5% GW 84% LAH 10% CB 1%
S10GLAH5	SEBS 10% GW 84% LAH 5% CB 1%
S10GLAH10	SEBS 10% GW 79% LAH 10% CB 1%
S05GM5	SEBS 5% GW 89% M 5% CB 1%
S10GM5	SEBS 10% GW 84% M 5% CB 1%
SIS10GPE10	SIS 10% GW 79% PE 10% CB 1%
EVA10GPE10	EVA 10% GW 79% PE 10% CB 1%

3. Manufacturing procedure

Operating steps:

1. Required amounts of GW, TPP and carbon are placed in a Pyrex beaker (after check of static electric charge absence).
2. Pyrex beaker is placed in a heated oil bath (Figure 2) with temperature of 350 °C till complete melting of GW and TPP.
3. Compound is mixed for from 40 minutes to 4 hours depending on the composition by an impeller inserted in the beaker.
4. Energetic additive (if required) is added to the compound. The fuel formulation is then mixed again for a suitable amount of time. $LiAlH_4$ is added under the vacuum, as it is extremely reactive with the air.
5. Compound is gradually poured into molds (Figure 2). Operation is performed in multiple steps in order to avoid possible imperfections in the solid fuel grain.
6. After complete filling, the molds are left at ambient temperature for complete cooling of the material.

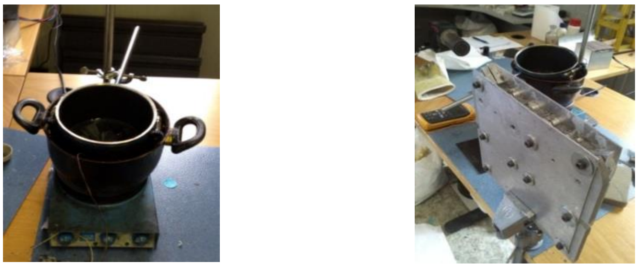

Figure 2: The preparation of the formulations

4. Rheological and mechanical characterization

Three kinds of experimental investigations were performed in order to study the rheological, viscoelastic and mechanical properties of paraffin-wax based blends doped with thermoplastic polymers and metal powders so as to evaluate a formulation which fits best to requirements to be used as a fuel for hybrid rocket engines.

The rheological characterization of thermoplastic polymers and its blends is a complex subject that requires careful test design in order to obtain the information needed to meet the investigator's requirements. A rotational rheometer was applied in order to obtain the viscoelastic behavior of the investigated formulations. A Couette apparatus was used for viscosity measurements on melted materials and a parallel plate to study the elastic and storage moduli (G´, G´´). All the experiments were carried out using a Rheometrics Dynamic Analyzer RDA II.

With the aim to determine the fuel formulations storage modulus, an investigation was carried out in oscillatory regime, at small strains, using a parallel-plate rheometer *Rheometrics Dynamic Analyzer RDA II TA Instruments*. Applying a sinusoidal deformation, a co-sinusoidal shear rate is obtained, allowing the measurement of viscoelastic properties such as the storage modulus G' and the complex viscosity η*. Tests were performed with the help of the TA Instruments apparatus.

Material samples for mechanical characterization were obtained by casting the melted mixture into a mold designed according to UNI-EN-ISO 527 norm for plastic materials. Material testing was performed with a PC-controlled uniaxial tensile test machine equipped with a load cell of 1KN (Instron Series 4302).

Tensile tests measure the force required to break a plastic sample specimen and the extent to which the specimen stretches or elongates to that breaking point. Tensile tests produce stress-strain diagrams used to determine tensile moduli. The tensile test data can help specify optimal materials, design parts to resist application forces, and provide key quality control checks for materials. Tensile tests were performed using MTS 858 Material Testing System and according to the standard ISO 527 "Plastics – Determination of tensile properties" [13], [14].

5. Results

5.1 Mechanical characterization

Using the processed data the comparison among the results obtained for different formulations is shown below. Figure 3 shows influence of content of polymer on elongation break. The higher the polymer fraction is, the higher is the elongation break. As the polymer fraction increases the elongation at break increases with a not linear trend. On the contrary as we can see from Figure 4 addition of $LiAlH_4$ causes quicker break of the sample.

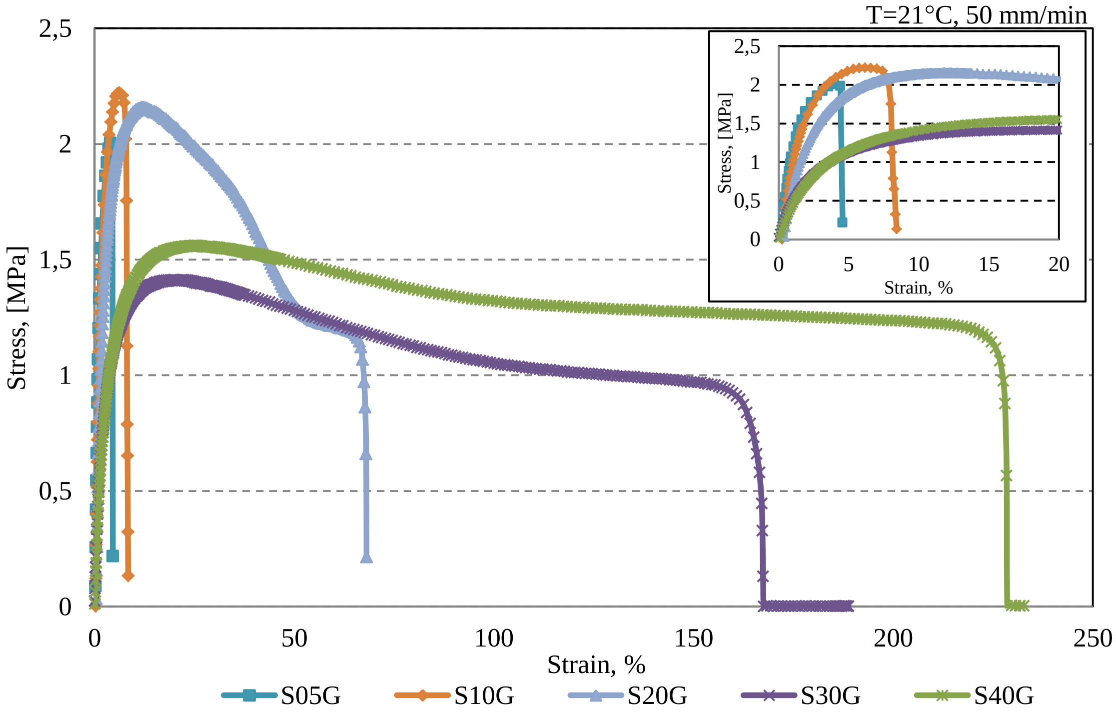

Figure 3: Influence of polymer mass fraction on Stress-Strain behavior

Considering content of $LiAlH_4$, as it can be seen in Figure 4, the higher $LiAlH_4$ content is the less is the elongation at break. So the higher the amount of $LiAlH_4$ is, the more brittle the material is - with the increasing of $LiAlH_4$ mechanical properties decrease. The sample without additive of metal powder has the highest elastic properties.

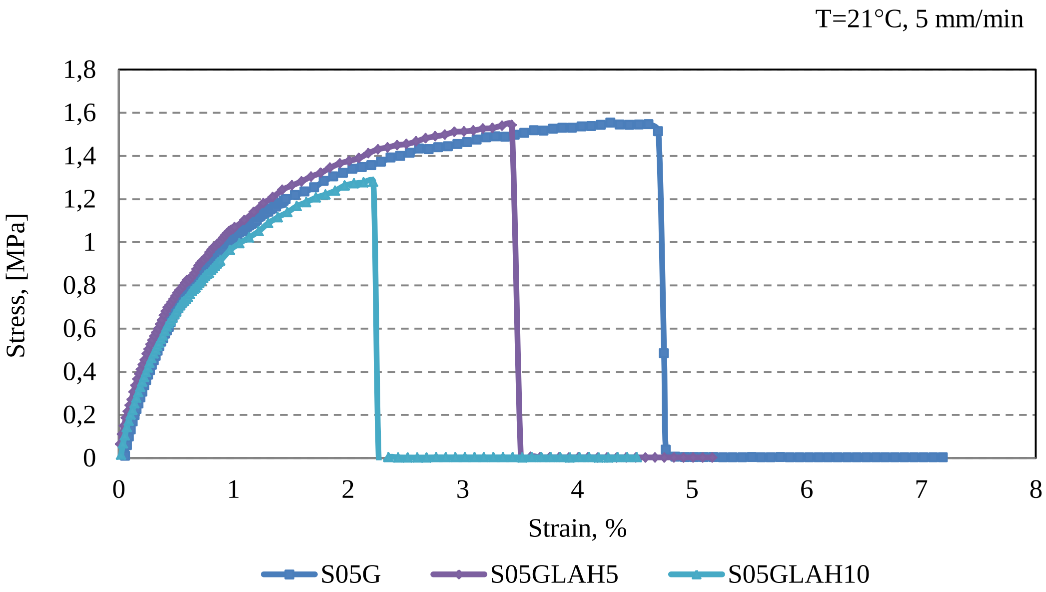

Figure 4: Effects of $LiAlH_4$ mass fraction on the elongation at break in S05G samples at 5 mm/min speed

Tables 2-4 present Young's Moduli values with standard deviation for all tested formulations at different conditions (speed and temperature).

In Table 3 and Figure 4 we can see the effect of the LAH addition to Young's Modulus which is decreasing with addition of LAH. Comparing S05G and S05G-LAH5 Young Modulus decreases significantly. Also the rate effect is seen. At low rates an increase of Young's Modulus occurs if mass fraction of LAH increases. But at higher rates the opposite occurs because Young's Modulus decreases when the rate increases.

Table 2: Young's Moduli for SEBS containing formulations and pure GW

Blend	**Young's Modulus (MPa) / Standard Deviation (MPa)**			
Rate (mm/min)/ $T_{storage}$ (°C)	**GW**	**S05G**	**S10G**	**S20G**
5 / 21	-	233,5±37,7	152±29,4	155±27,3
50 / 21	-	191,3±14	168,5±8,8	132±4,16
0.5 / 21	39,6±14,5	-	-	-
1.5 / 21	38,1±4,3	-	-	-
3 /21	42,8±2,6	-	-	-

Table 3: Young's Moduli for LAH containing formulations

Blend	**Young's Modulus (MPa) / Standard Deviation (MPa)**		
Rate (mm/min)/ $T_{storage}$ (°C)	**S05G-LAH5**	**S05G-LAH10**	**S10G-LAH5**
0.5 / 21	90,8±4,9	100,8±11,2	96,7±31
5 / 21	163,3±12,5	141,4±20,4	124,4±17
50 / 21	170,7±3,7	150±18,9	108,7±16,7

Table 4 shows the influence of the temperature of the S10G-M5 samples on maximum load and on the value of elongation at break. A possible explanation of this strong sensitivity to the temperature could be connected with the softening of the material.

Table 4: Young’s Moduli for SIS, EVA, PE and MgH_2 containing formulations

Blend	**Young’s Modulus (MPa) / Standard Deviation (MPa)**			
Rate (mm/min)/ $T_{storage}$ (°C)	**S05G-M5**	**S10G-M5**	**SIS10G-PE10**	**EVA10G-PE10**
0.5 / 8	82,51 ± 14,88	-	80,3 ± 9,1	60,9 ± 7,0
5 / 8	138,3 ± 17	100,0 ± 6,4	160,2 ± 7,5	114,7 ± 8,1
50 / 8	-	189,4 ± 21,1	-	-
0.5 / -19	138,1 ± 9,9	-	130,2 ± 1,8	107,2 ± 3,4
5 / -19	234,2 ± 35,2	287,5 ± 1,9	199,7 ± 15,7	162,7 ± 12,2
50 / -19	-	284,1 ± 13,2	-	-

Also Table 4 shows the influence of temperature and speed on samples, for example for samples containing two polymers - at T = -19 °C elongation at break increases from 2,3 % to 2,7 % for SIS10G-PE10 and from 2,8 % to 4% for EVA10G-PE10.

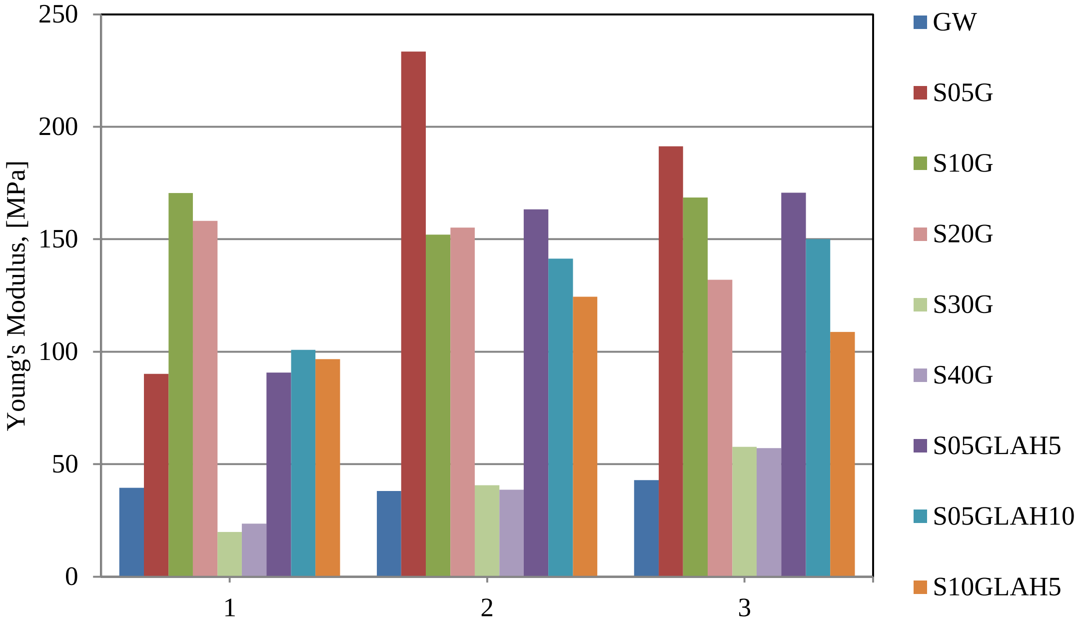

Figure 5: Young Modulus trend of paraffin-based formulations.
Axis X: “1” – 0.5 mm/min, “2” – 5 mm/min (1.5 mm/min for GW), “3” 50 mm/min (3 mm/min for GW)

In Figure 5 the comparison between Young’s Moduli values of tested formulations are presented. The highest Young’s Modulus has the blend with 5% of SEBS at 5 mm/min speed, whereas the composition with 30% SEBS polymer at 0,5 mm/min has the lowest.

5.2 Effect of viscosity

The investigations on viscosity were performed on a selection of previous materials. Figure 6 shows the viscosity behavior of melted SEBS-based blends (with 10% and 20% of SEBS) and one composition with metal hydride addition tested at 100 °C at different rates. Viscosity values of S20G are higher than that of S10G: increasing the rate viscosity decreases. The S10G shows a lower viscosity than S20G formulation.

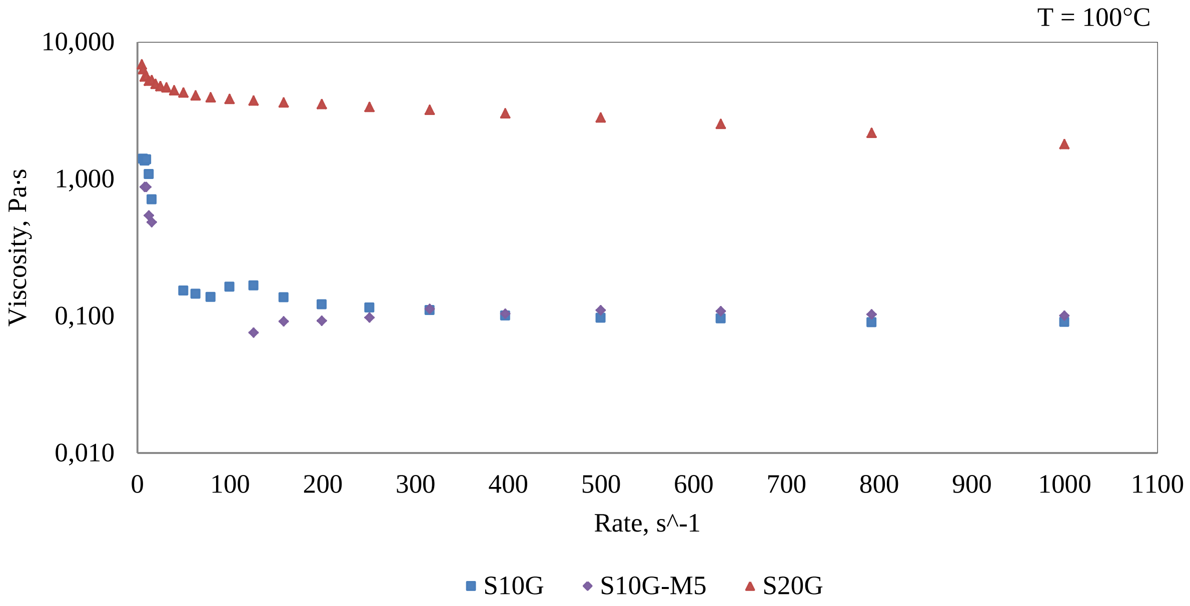

Figure 6: Viscosimetric behavior at the increasing of polymer mass fraction and addition of MgH_2 at 100 °C

Figures 7 and 8 show the viscosimetric behavior of the tested polymeric blends SIS10G-PE10 and EVA10G-PE10 in the temperature range 80 – 140 °C.

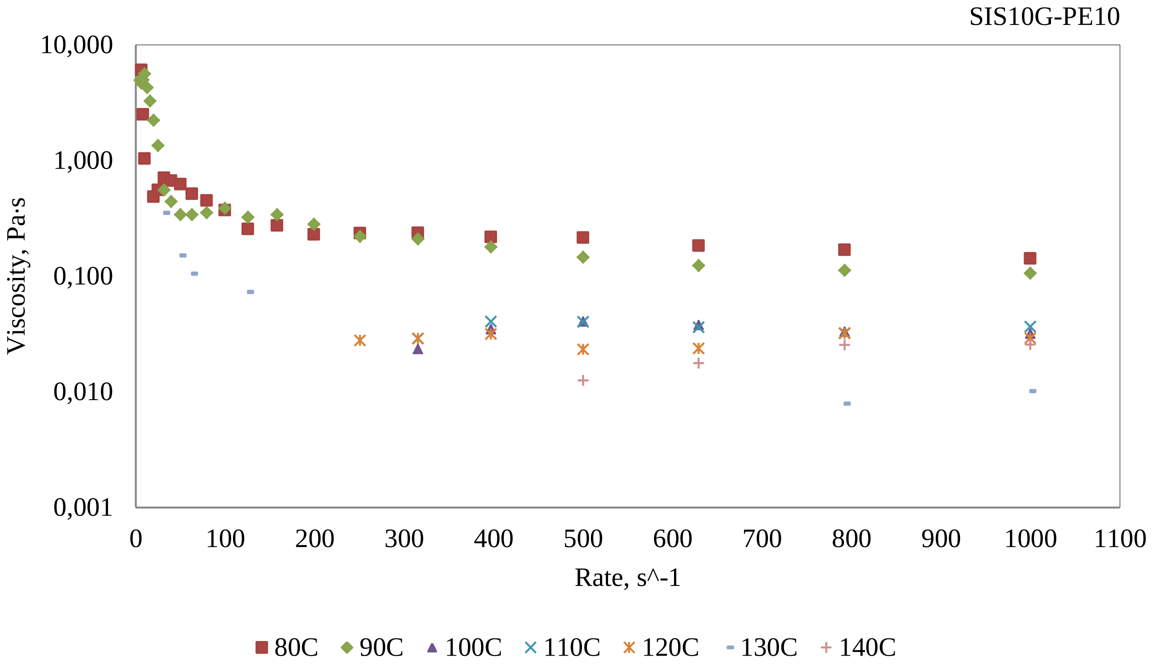

Figure 7: Temperature scan of viscosity in the range 80 °C – 140 °C for SIS10G-PE10 samples material

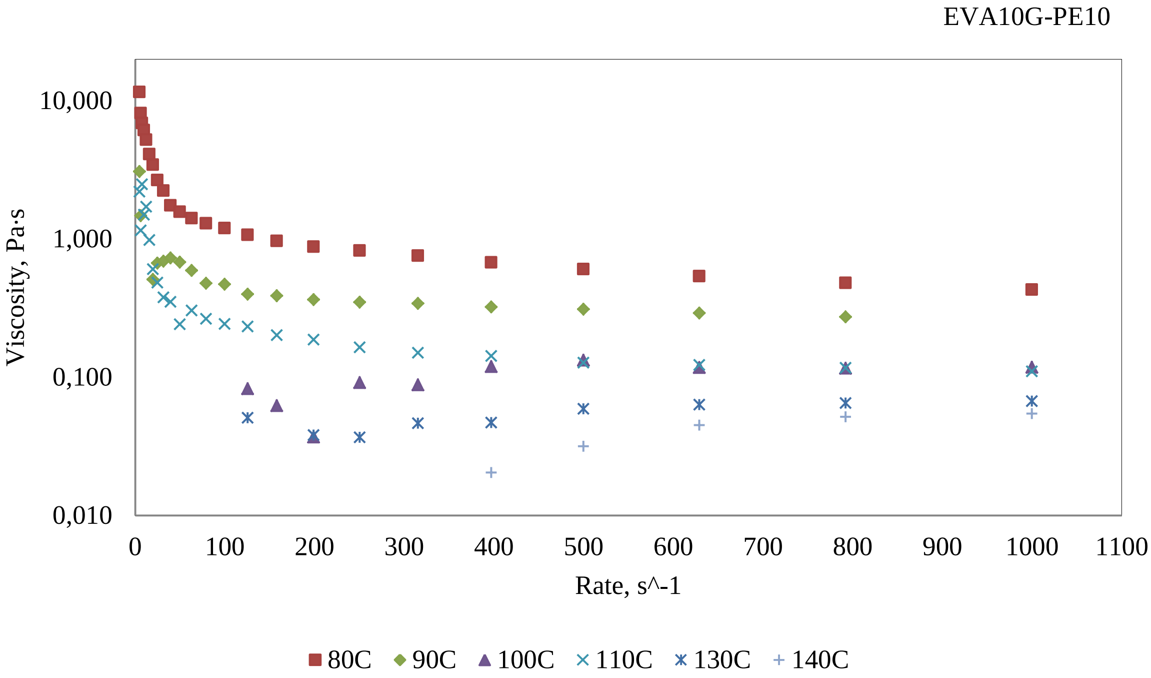

Figure 8: Temperature scan of viscosity in the range 80 °C – 140 °C for EVA10G-PE10 samples material

Considering the S20G tested at 90 and 100 °C, tests were interrupted (at 790 s^{-1}) because the limit of maximum torque was reached. For all other formulations torque values were always lower than the limit (≤ 450 g/cm). The investigation and comparison of two SEBS-based blends, containing MgH_2 metal hydride, one SIS and PE-containing one EVA and PE-based samples were made at the same experimental conditions like melting temperature and rate of the Couette apparatus. Table 5 shows viscosity values for all formulations obtained at 1000 s^{-1}.

Table 5 Viscosity values obtained with Couette rheometer tests at 1000 s^{-1}

Formulation	**Viscosity values at 1000 s^{-1}**								
Temperature	**80**	**90**	**100**	**110**	**120**	**130**	**140**	**150**	**160**
S20G	-	-	1,795	0,641	0,36	0,203	0,13	0,099	0,065
S10G	0,77	0,231	0,09	0,039	0,027	0,022	0,036	0,01	0,02
S10G-M5	-	0,186	0,101	0,054	0,026	0,013	0,023	0,021	-
S05G-M5	0,075	0,029	0,038	0,015	0,010	-	-	-	-
SIS10G-PE10	0,141	0,105	0,032	0,036	0,029	0,01	0,025	-	0,014
EVA10G-PE10	0,429	0,261	0,118	0,110	0,179	0,067	0,054	-	-

In Table 5 the effect of polymer mass fraction is shown, which is responsible for viscosity decrease going from S20G to S10G, S10G-M5 and S05G-M5. Comparing SIS and EVA containing formulations, the second one is characterized by a much higher viscosity.

The results show that increasing the rate the viscosity decreases. This trend is connected to the increasing development of entrainment phenomena, which strongly increases the regression rate. The lowest viscosity is shown by S05G-M5. And this blend tends to have high regression rate. The highest values of viscosity were observed in EVA10G-PE10.

5.3 Reology

Figure 9 allows us to see clearer trend of the G´ values. It is seen that EVA10G-PE10 and SIS10G-PE10 have so wide range of temperature (20 – 90 °C) and high melting point because of PE and two other different polymers (EVA and SIS) in the content.

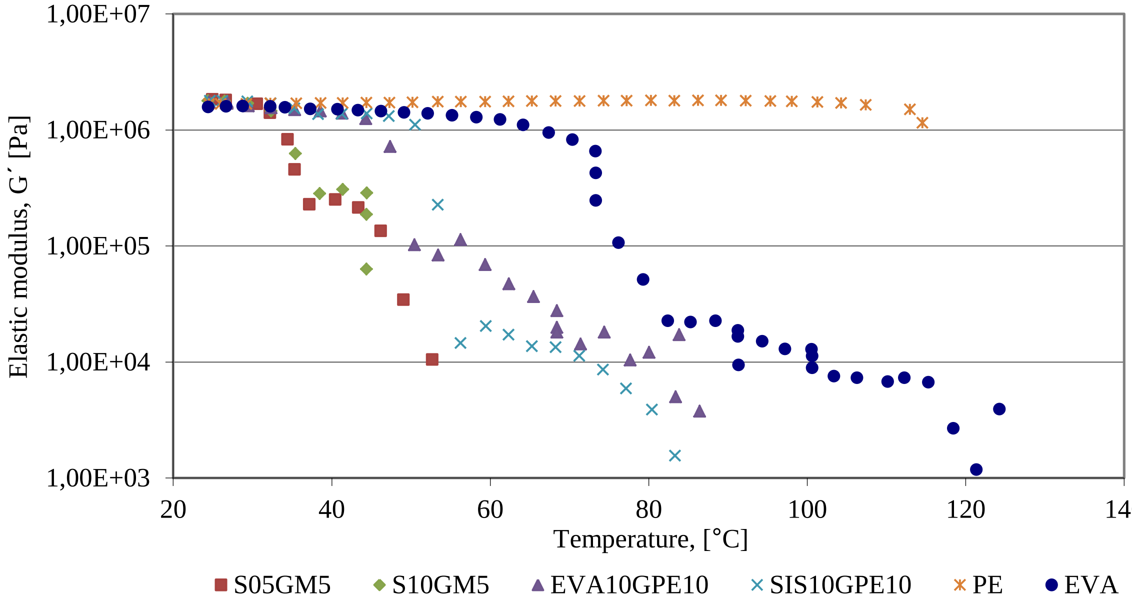

Figure 9: Trend of G´ for SEBS, SIS, EVA, PE-containing blends and for pure PE and EVA polymers at frequency 1 Hz

Figures 10 shows that the G´ is approximately the same for all blends presented on the plot. But from 40 °C the values of elastic modulus for the formulation containing MgH_2 significantly decrease.

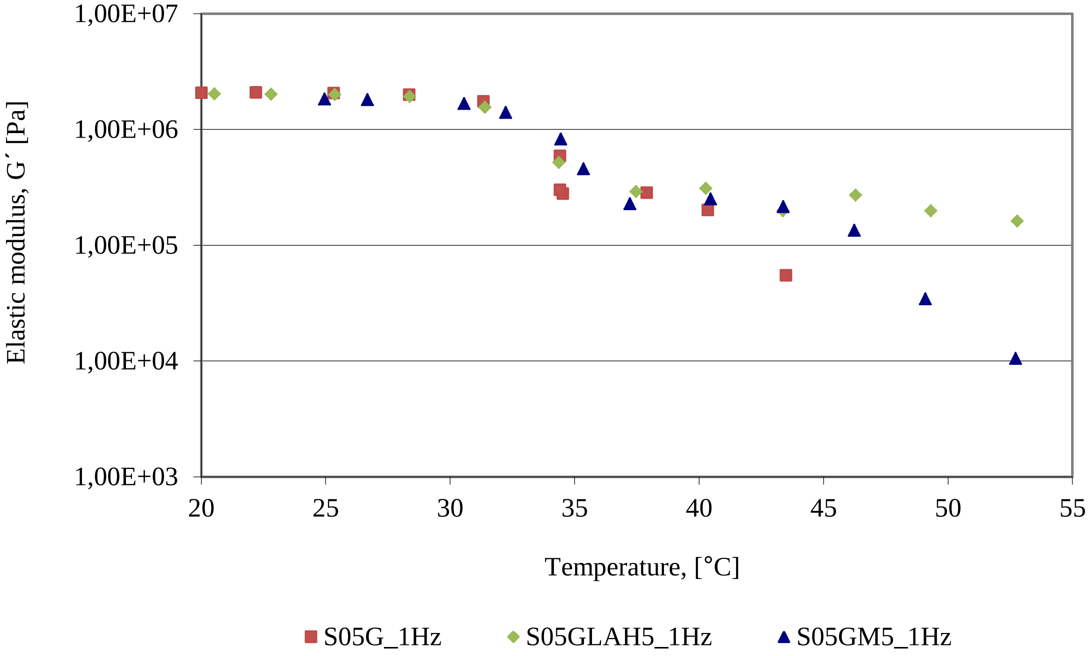

Figure 10: Trend of G´ for SEBS -based blends containing different additives of metal hydrides at 1 Hz

The addition of polymers increases the storage modulus value. Storage modulus for all investigated paraffin-based materials decreases with the increasing of temperature. The addition of polymers to paraffin causes the increasing of melting temperature.

6. Conclusions and future work

Paraffin waxes are inexpensive materials, soft and brittle. In order to use these materials in hybrid rocket propulsion systems the mechanical properties of waxes need to be improved.

Paraffin-based fuels for hybrid rockets were investigated by means of experimental approaches in order to develop a new type of solid fuel combining at the same time good ballistic and suitable mechanical properties.

As stated above strengthening of the paraffinic material was done by addition of different polymers (SEBS, SIS, EVA, PE). On the other hand for suitable ballistic properties samples with metal hydrides addition were tested as well.

EVA polymer was chosen as one of the most investigated material in the literature as additive to paraffin. SIS was previously investigated properly in our laboratory and it was investigated more than SEBS. So these two polymers were chosen in order to compare their properties. The investigations showed that EVA containing sample has higher viscosity but better mechanical properties than SIS containing.

Couette apparatus was used for investigation of viscosimetric behavior on melted materials and a parallel plate to study the elastic and storage moduli (G´, G´´). The results show that increasing the rate the viscosity decreases. This trend is connected to the increasing development of entrainment phenomena, which strongly increases the regression rate. The lowest viscosity is shown by S05G-M5; this blend tends to have high regression rate. The highest values of viscosity were observed in EVA10G-PE10.

To study rheology parallel-plate rheometer was used. The investigation on the rheological behavior of the selected materials was performed by determining the elastic moduli. The addition of polymers increases the storage modulus value. Storage modulus for all investigated paraffin-based materials decreases with increasing of temperature.

The addition of polymers to paraffin causes the increasing of melting temperature. The temperature up to which the material gives rheological response is important because it is linked with the material tendency to entrainment. The tendency to entrainment and regression rate are higher with lower maximum temperature at which a rheological response is obtained and lower viscosity. Despite the fact that polymers addition increases melting temperature of the sample it is lower than that for HTPB degradation. Therefore all tested paraffin-based materials, except that which contain two polymers (SIS10G-PE10 and EVA10G-PE10), are expected to show high regression rate.

Mechanical properties were investigated through uniaxial tensile tests. The influence of the thermoplastic polymers and metal hydrides was measured. A strong influence of temperature of the sample and of SEBS, other polymers and metal hydrides mass fraction on maximum load and elongation at break was observed.

Taking into account the significant improvement of mechanical properties when paraffin-wax is doped with a TPP, it can be concluded that such blends are quite promising for the use as hybrid rocket solid fuels. Except two blends with polyethylene (SIS10G-PE10 and EVA10G-PE10) addition because of their high viscosity, which determines low regression rate and not good mechanical properties.

Considering future work, combustion tests must be performed to obtain regression rate data of all paraffin-based samples in order to compare and correlate mechanical and ballistic properties of fuels.

References

[1] DeSain J.D., Brady B.B., Metxler K.M., Curtiss T.J., Albright T.V., *Tensile Tests of Paraffin Wax for Hybrid Rocket Fuel Grains,* AIAA 2009-5115, Joint Propulsion Conference & Exhibit, Denver, Colorado, 2 - 5 August 2009.

[2] Maruyama S., Ishiguro N., Shinohara K., Nakagawa I., *Study on Mechanical Characteristic of Paraffin-Based Fuel,* AIAA 2011-5678, Joint Propulsion Conference & Exhibit, San Diego, California, 31 July - 03 August 2011.

[3] Paravan C., *Ballistics of Innovative Solid Fuel Formulations for Hybrid Rocket Engines*, PhD Dissertation, Politecnico di Milano, Italy, 2012.

[4] Boiocchi M., Merotto L., Maggi F., Di Landro L., Galfetti L., *Rheological and Mechanical Characterization of Hybrid Rocket Solid Fuels,* EUCASS Conference, Saint Petersburg, Russia, 2011.

[5] Marxman G.A. and Gilbert M., *Turbulent Boundary Layer Combustion in the Hybrid Rocket,* 9th International Symposium on Combustion, Academic Press, Inc., New York, 1963, pp. 371-383.

[6] Marxman G.A., *Boundary Layer Combustion in Propulsion,* Proceedings of the 11th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pennsylvania, 1967, pp. 269-289.

[7] Marxman G.A. and Wooldridge C.E., *Research on the Combustion Mechanism of Hybrid Rockets,* Advances in Tactical Rocket Propulsion, edited by Penner, S.S., AGARD Conference Proceedings No. 1, 1968, pp. 421-477.

[8] Karabeyoglu M.A. and Cantwell B.J., *Combustion of Liquefying Hybrid Propellants: Part 2, Stability of Liquid Films,* Journal of Propulsion and Power, Vol. 18, No. 3, 2002.

[9] Karabeyoglu M.A., Altman D., and Cantwell B.J., *Combustion of Liquefying Hybrid Propellants: Part 1, General Theory,* Journal of Propulsion and Power, Vol. 18, No. 3, 2002.

[10] BennettH., *Industrial Waxes. Natural and synthetic waxes*, Volume 1., Chemical publishing company, INC. New York, 1975..

[11] Chiaverini M.J., *Review of Solid Fuel Regression Rate Behavior in Classical and Nonclassical Hybrid Rocket Motors,* Fundamentals of Hybrid Rocket Combustion and Propulsion, edited by Chiaverini M.J., and Kuo K.K., AIAA Progress in Astronautics and Aeronautics, Volume 218, Chapter 2, 2007, pp. 37-125.

[12] Paravan C., Viscardi M., DeLuca L.T., and Kazakov A., *Regression Rates and Anisotropy Effects in Hybrid Rockets Microburner,* 3rd EUCASS (European Conference for Aerospace Sciences) Conference, Versailles, France 04-07 Jul 2009.

[13] ISO 527-1:2012, *Plastics - Determination of tensile properties. Part 1: General principles*.

[14] ISO 527-2:2012, *Plastics - Determination of tensile properties. Part 2: Test conditions for molding and extrusion plastics.*