Rheological and mechanical characterization of hybrid rocket solid fuels

M. Boiocchi, L. Merotto, F. Maggi, L. Di Landro, L. Galfetti

Politecnico di Milano
Aerospace Engineering Department,
I-20156, Milano, MI, Italy

Abstract

Solid fuels for hybrid rockets were characterized in the framework of a research project aimed to develop a new generation of solid fuels, combining at the same time suitable ballistic and mechanical properties. Rheological and mechanical characterization of paraffin-based hybrid rocket solid fuels was performed, considering pure wax-based fuels and fuels doped with different additives.
Results of this investigation show a strong correlation between the measured viscosity of the melted paraffin layer, and the regression rate. Results show that a decrease of viscosity increases the regression rate. This trend has to be ascribed to the increasing development of entrainment phenomena, which strongly increases the regression rate.

Nomenclature

G'	=	Storage modulus, *Pa*	*GW*	=	Gel Wax
T_{mp}	=	Melting temperature, *°C*	*HEX*	=	CycloHexane
r_f	=	Regression rate, *mm/s*	*HTPB*	=	Hydroxyl-Terminated Poly-Buthadiene
η	=	Viscosity, *Pa s*	*KER*	=	Kerosene
η^*	=	Complex viscosity, *Pa s*	*LP*	=	Liquid Paraffin
			MA	=	Mahleic Anhydride
			MO	=	Mineral Oil
			PUF	=	Polymeric Foam
			SEBS	=	Styrene Polymer
			TPE	=	Thermoplastic Polymers

1. Introduction

The most limiting feature of hybrid rocket engines is the low regression rate of the standard solid fuels. Several researches were carried out along the last decades in order to develop innovative formulations for solid fuels, able to ensure suitable performance for hybrid propulsion missions. The methods investigated so far for regression rate enhancement through the development of new fuel formulations include energetic additives and liquefying fuels [1-2].
The inclusion of energetic particles into the solid fuel grain, such as metal or metal hydrides particles, provides not only higher regression rate and higher energy release[3-5] (corresponding to increased flame temperature and increased specific impulse), but also increased density impulse. Nevertheless, the regression rate increase obtained with this method is not

high enough to allow new propulsive mission to be performed with hybrid engines. New perspectives has been opened thanks to the development of liquefying fuels, which allows obtaining a 3-4 times increase in regression rates with respect to traditional HTPB-based fuels[6-8]. Despite the high performance, these fuels show an important drawback, *i.e.* unsatisfactory mechanical properties for rocket motors applications.
In order to develop innovative solid fuel formulations suitable for hybrid rocket engines, the need arises to ensure both good mechanical properties and high regression rate. For this purpose, in this work, the use of a strengthening structure in paraffin-based fuels was investigated. First, the strengthening with a Poly-Urethane Foam (PUF) structure was investigated. The PUF structure leads to a notable increase in the regression rate, but results in a heterogeneous composition, thus in non-isotropic mechanical properties. Figure 1 shows the PUF structure in the mould used for melted paraffin pouring in the reinforcing structure. A second type of strengthening structure involving thermoplastic polymers (TPE), soluble in paraffin (SEBS-MA), was then designed and tested, with the aim to increase the paraffin elasticity without any decrease in regression rate value and ensuring isotropic mechanical properties. The use of TPE reinforcing structure in paraffin results in lower manufacturing costs and in homogeneous fuels.

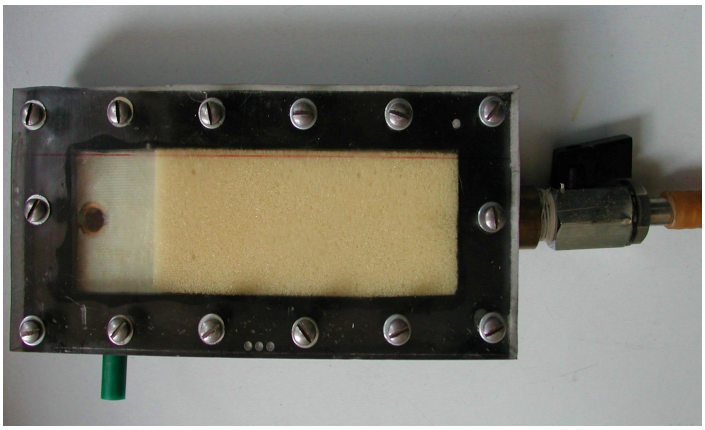

Figure 1: Sample mould and PUF strengthening structure for paraffin-based fuel formulations.

Moreover, melting point temperature and viscosity decrease through addition of kerosene was investigated for the GW-PUF formulation, with the aim to increase the fuel regression rate up to values similar to those typical of SW-PUF formulations.
A microscope picture of the formulation obtained adding a 3% mass fraction of PUF in paraffin doped with Lithium Aluminum Hydride (LAH) is shown in Figure 2.

2. Fuel Formulations and Experimental Methods

The experimental facilities used in this work are a Couette Viscosimeter (*TA Instruments*), and a plate-plate rheometer (*Rheometrics Dynamic Analyzer RDA II*) for viscosity and storage modulus measurement. In order to compare the formulation physical properties with the corresponding performance, the average regression rate r_f of the fuel formulations tested was measured performing firing tests in a 2D slab hybrid burner, designed and set up at SPLab. The experimental facility for firing tests is described in [9].
The fuel formulations manufactured and tested for this work include a group based on gel wax (GW-), and a group based on solid wax (SW-). The selected paraffin waxes GW and SW have chemical formula $C_{12}H_{26}$ and $C_{24}H_{50}$, respectively. Several other formulations were obtained through additive filling. GW- and SW-based fuels were added with LP and HEX. A third group of fuel formulations based on GW, PUF and KER was prepared (GWPK-). A fourth group is based on SEBS and LP, filled with SW, mineral oil (MO) and/or KER. Fuel nomenclature, composition, and density are presented in Table 1. The regression rate percentage increase with respect to pure HTPB (selected as reference formulation) is also reported for each formulation tested. Among the SEBS-containing formulations, only the most promising formulation from the mechanical properties point of view (SEBS-MO-SW-KER) was tested for the r_f measurement. Ballistic results will be presented in detail in the following section.
The physical-chemical properties of the ingredients used in the present work are summarized in Table 2. For each ingredient, the supplier is also indicated.

Table 1: Fuel formulations manufactured and tested in this work:
composition, density and regression rate increase with respect to pure HTPB.

Fuel Formulations	**Ingredients**		**Fuel Density g/cm^3**	**r_f increase with respect to pure HTPB**
GW	GW 100%	--	0.88	NAv
GWP	PUF + GW 3% + 97%	--	0.88	+48%
GWP-LP20	PUF + GW 3% + 77%	LP 20%	0.88	+84%
GWP-HEX20	PUF + GW 3% + 87%	CicloHexane 10%	0.88	+88%
GWPK	PUF + GW + KER 3% + 87.3% + 9.7%	--	0.87	+140%
GWPK_MGH3	PUF + GW + KER 3% + 84.6% + 9.4%	MGH 3%	0.88	+158%
SW	SW 100%	--	0.89	NAv
SWP	PUF + SW 3% + 97%	--	0.88	+200%
SEBS-MA	SEBS-MA 100%	--	0.90	NAv
SEBS-LP-SW	SEBS + LP 15% + 35%	SW 50%	0.88	NAv
SEBS-LP	SEBS + LP 15% + 85%	--	0.87	NAv
SEBS-LP-MO	SEBS + LP 15% + 35%	MO 50%	0.89	NAv
SEBS- MO-SW	SEBS + MO 15% + 35%	SW 50%	0.90	NAv
SEBS-MO-SW-KER	SEBS + MO 15% + 25%	SW + KER 50% + 10%	0.90	+158%

Table 2: Supplier and main features of the ingredients used in fuel formulations manufacturing.

Ingredient	**Supplier**	**Chemical-Physical Characteristics**
SEBS-MA	Sigma Aldrich	Styrene = 30%, MA = 2%
Polymeric Foam (PUF)	Commercial	Density ρ= 0.02 g/cm^3 Porosity distribution: 300 – 400 µm
Gel Wax (GW)	Commercial	Density ρ= 0.88 g/cm^3 Tmp= 45 - 55 °C
Solid Wax (SW)	Sigma Aldrich	Density ρ= 0.89 g/cm^3 Tmp= 58 – 62 °C
Liquid Paraffin (LP)	Carlo Erba Reagenti	Density ρ= 0.86 g/cm^3
CycloHexane (HEX)	Carlo Erba Reagenti	Density ρ= 0.78 g/cm^3
Kerosene (KER)	Commercial	Density ρ= 0.77 g/cm^3
Mineral Oil (MO)	Commercial	Density ρ=0.91 g/cm^3

3. Results Discussion

3.1 PUF reinforcing structure

In order to increase the GW-PUF formulation regression rate, the selected strategy was to decrease the formulation's melting point temperature and viscosity through additive inclusion. A lower viscosity is expected to lead to increased entrainment effect, thus resulting in higher average regression rate. A rheological investigation in continuous regime was performed using a Couette Viscosimeter, in order to investigate the viscosity of the modified material. The measured viscosity of GWP, GWPK and SWP at 70°C is shown in Figure 3. Table 3 reports the measured viscosity for the same fuel formulations at different temperatures.

Table 3: Measured viscosity of GWP, GWPK and SWP at different temperatures.

T [°C]	GWP viscosity [Pa*s]	GWPK viscosity [Pa*s]	SWP viscosity [Pa*s]
60	11.29	1.47	0.89
70	1.12	0.14	0.09
80	0.15	-	-

From the data reported in Figure 2 and in Table 3, it can be observed that GW displays the higher viscosity values (1.12 Pa s at 70°C), while SW shows notably lower viscosity (0.09 at 70°C). At the same temperature, the viscosity of GWPK is one order of magnitude lower than that of pure GW, thus showing the influence of aromaticity on the selected paraffin, as expected from literature analysis [10].
An interesting observation arises from the comparison of this result with the average regression rate of the fuel formulations. The average r_f measured for GWP at oxidizer mass flux of 150 kg/m^{2}s is 0.63 mm/s; at the same conditions, the r_f obtained is 1.28 mm/s for SW, and 1.02 mm/s for GWPK. Therefore, the kerosene addition to GW results in higher regression rate values, similar to those typical of SW.

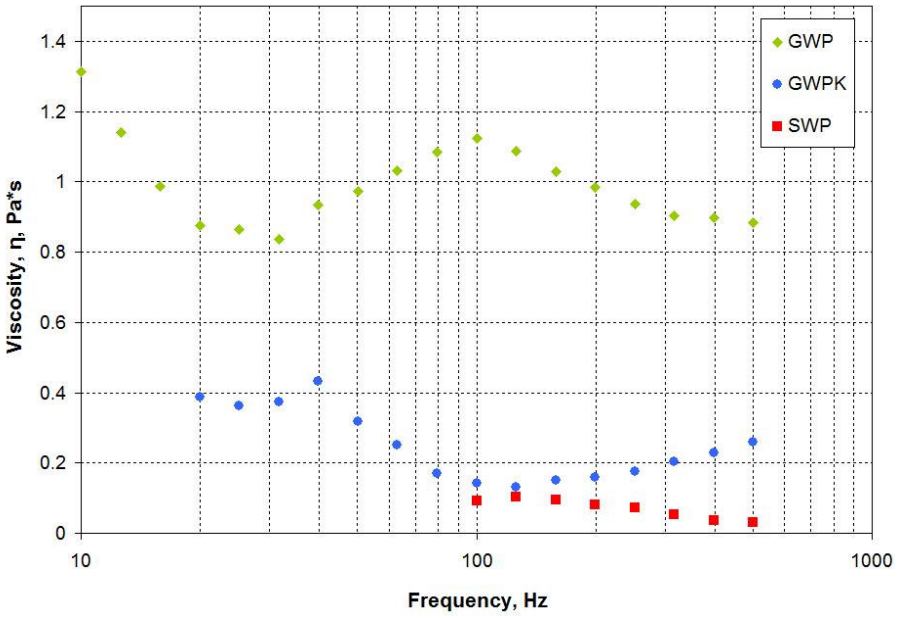

Figure 2: Measured viscosity (by Couette viscosimeter) of GW, SW and GW added with KER, showing the effect of kerosene addition and the very low viscosity of the melted SW, which is responsible for a large entrainment effect. Tests were performed at 70 °C.

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. Applying a sinusoidal deformation, a co-sinusoidal shear rate is obtained, allowing the measurement of visco-elastic properties such as the storage modulus G' and the complex viscosity η*. Tests were performed at constant strain, with a frequency sweep (0.5-50 Hz) and a temperature sweep (T>30°C). The sample thickness is 2.2 mm, while the diameter is 25 mm.
The comparison among the results obtained for GW, GWP and PUF is shown in Figure 3. The result for pure HTPB is also shown as a reference value.

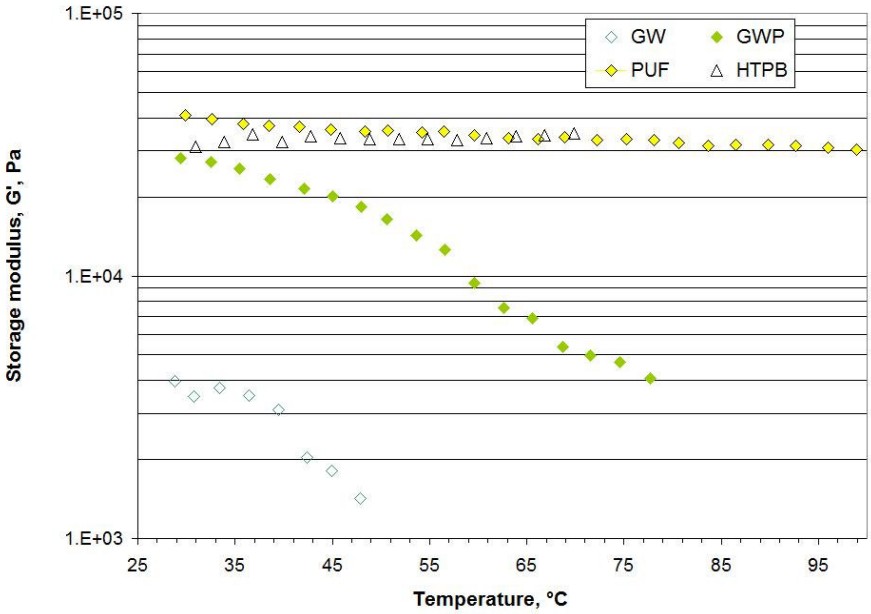

Figure 3: Storage modulus vs. temperature in a parallel-plate rheometer for GW, GWP and PUF. HTPB is shown as a reference value. Strain =5%.

From the data reported in Figure 3 the notable contribution of PUF to the overall formulation storage modulus can be observed. In particular, two consequences arise from PUF addition. The first one is an increase in the overall storage modulus, from a value of about 4000 Pa for GW up to about 30000 Pa for GWP, at the initial test temperature. The second effect is the enhanced temperature field in which the material gives a perceivable rheological response; this means that the PUF avoids paraffin from flowing, up to temperatures higher than the melting temperature of GW. For example, data reported in Figure 4 show that the last measurement point for GW is obtained at about 47 °C, while the last measurement point for GWP is at about 77°C. The temperature up to which the material gives a perceivable rheological response is important because it is linked to the material's tendency to entrainment: the lower the maximum temperature at which a rheological response is obtained, the lower the viscosity, thus the higher the tendency to entrainment and the regression rate.

Storage modulus measurements obtained for SW, PUF and SWP are shown in Figure 4. The G' increase due to PUF addition to SW is lower than that obtained for GW (Figure 3), thus a lower elasticity enhancement is obtained in this case: PUF addition does not solve the problem of SW fragility. It can also be noticed from Figure 4 that, like in the case of GW, the last measurement point for the material is obtained at higher temperatures when PUF is added (at 64°C, while the last point was obtained at 49°C for SW). Therefore, also in the case of SW-based formulations, PUF avoids paraffin from flowing up to temperatures higher than the melting temperature of the pure material.

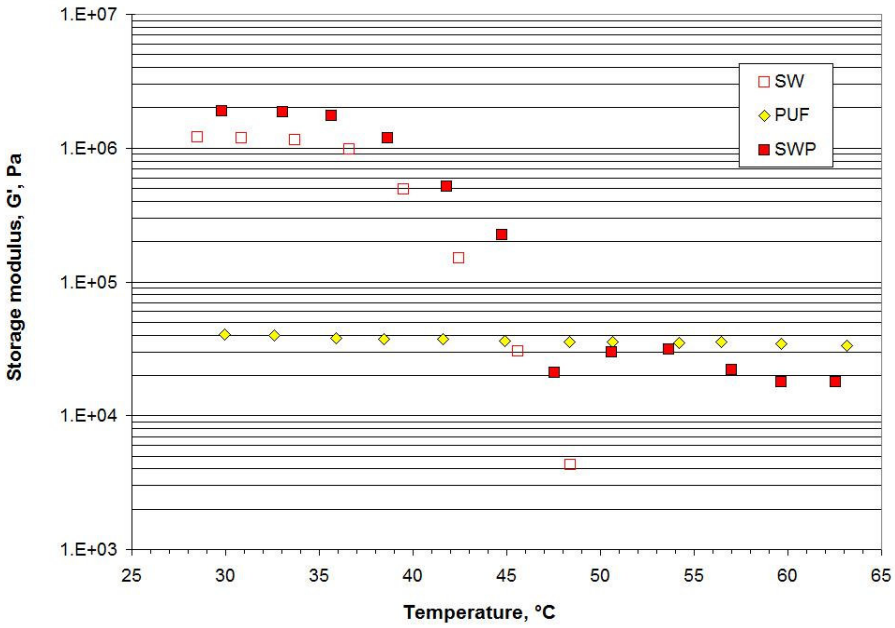

Figure 4: Storage modulus vs. temperature in a parallel-plate rheometer for SW, SWP and PUF. Strain =1%.

Data reported in Figures 3-4 are summarized in Table 4. The measured G' is reported, together with the melting point temperature, when available.

Table 4: Storage modulus measured for GW- and SW-based fuel formulations.

Fuel Formulation	**G' [KPa]**	**T_{mp} [°C]**
HTPB	30 - 35	-
PUF	40 - 30	-
GW	4 – 1.5	47
GWP	29 - 4	77
SW	1200 – 4	48
SWP	1900 - 30	54

3.2 SEBS-containing formulations

In order to increase SW elasticity without decreasing the solid fuel regression rate, PUF strengthening structure shows interesting results, but leads to heterogeneous fuel formulations. This, in turn, leads to non-isotropic mechanical properties. In order to avoid this problem, it was decided to test the possibility of ensuring paraffin-based formulations elasticity by using a thermoplastic elastomer (SEBS) instead of PUF reinforcement. This strategy ensures lower manufacturing costs, homogeneous fuels and possibility to use this kind of formulations in higher-scale tests.

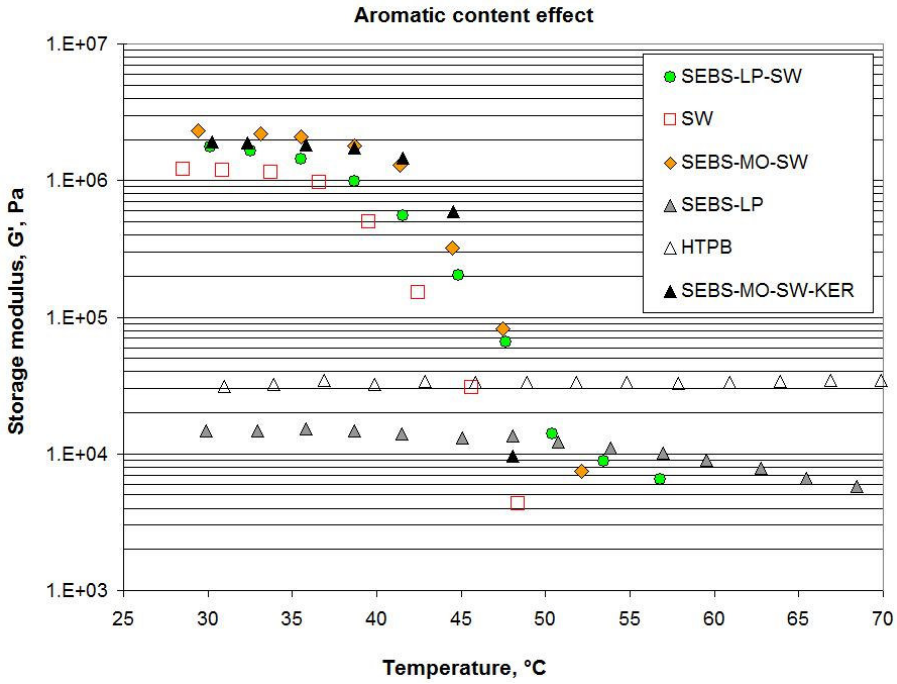

Figure 5: Storage modulus vs. temperature in a plate-plate rheometer for SEBS-containing fuel formulations. Strain=1%.

Figure 5 shows the storage modulus G' measured vs. temperature for the SEBS-based formulations. The results obtained for pure HTPB and SW are also reported, as reference values. It is worth noticing that in this case the whole material melts during the test, thus allowing a comparison among the whole material properties, while in the case of heterogeneous materials (PUF containing fuels), only the paraffin melts.
Several observations can be drawn from data reported in Figure 5. First, a notable increase in the G' value is observed when SW is added to SEBS-LP formulation (about $2x10^6$ Pa for SEBS-LP-SW and about $1.5x10^4$ Pa for SEBS-LP, at the initial test temperature); the curve obtained for the SEBS-LP-SW formulation is similar to that of pure SW.
The second observation concerns the aromatic content in the formulations: comparing the results obtained for increasing aromatic content (SEBS-LP-SW, SEBS-MO-SW, and SEBS-MO-SW-KER), it can be noticed that the predominant effect is that due to SW presence rather than to aromatic content. In fact, the three curves are very similar. A higher aromatic content results in a lower melting temperature of the material (about 57°C for SEBS-LP-SW, about 53°C for SEBS-MO-SW, and about 48°C for SEBS-MO-SW-KER). Moreover, approaching the T_{mp}, the drop in mechanical properties becomes steeper with increasing aromatic content. The measured storage modulus for the SEBS-based formulations is reported in Table 5.

Table 5: Storage modulus measured for SEBS-containing fuel formulations.

Fuel formulation	G' [KPa]
SEBS-LP	15 - 6
SEBS-LP-SW	1800 - 7
SEBS-MO-SW	2200 - 7
SEBS-MO-SW-KER	2000 - 15
SW	1300 - 4
HTPB	30

The complex viscosity represents the viscosity of the solid material, and it is linked to the viscosity of the melted material. The complex viscosity measured for the SEBS-containing fuel formulations is shown in Figure 6. The

reference formulation in this plot is SW, which starts melting at about 38°C and displays a steep decrease in complex viscosity (last measured point at 48°C).
The three formulations containing SEBS (SEBS-LP-SW, SEBS-MO-SW, and SEBS-MO-SW-KER) display a complex viscosity slightly higher than that of SW (about 3 x 10^5 Pa*s at initial test temperature, while the value obtained for SW is about 2 x 10^5 Pa*s), due to the polymer viscosity contribution.

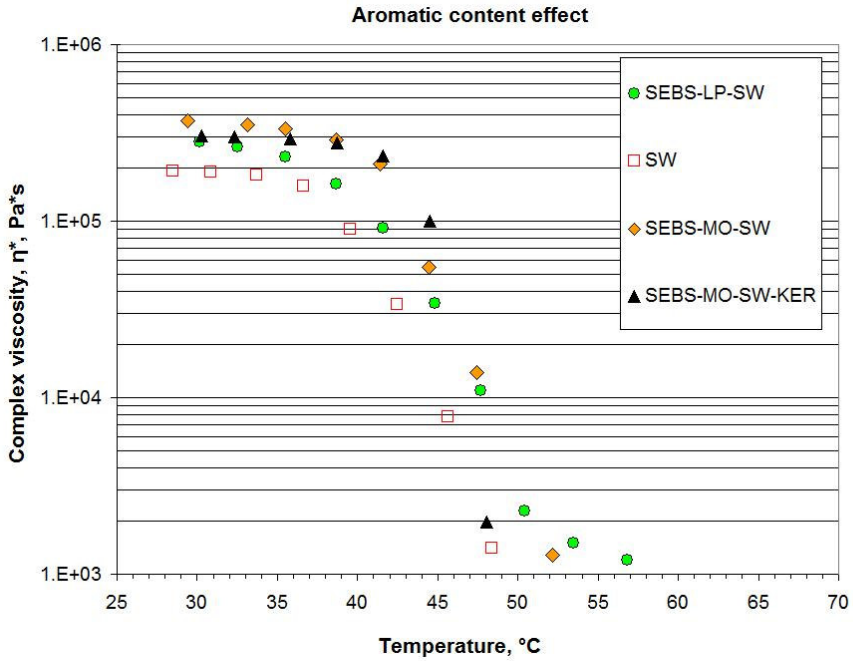

Figure 6: Complex viscosity vs. temperature for SEBS-containing formulations. Strain=1%.

Furthermore, at the last temperature at which SW gives rheological response (48°C), the complex viscosities of SW and SEBS-MO-SW-KER are very similar (about 2 x 10^3 Pa*s), while the other two formulations display complex viscosities higher than 1 x 10^4 Pa*s. This means that a higher aromatic content results in decreased complex viscosity, thus SEBS-MO-SW-KER is expected to show higher ballistic performance. On the basis of this consideration, among the SEBS-containing fuels only SEBS-MO-SW-KER was tested for regression rate measurements.

Table 6: Complex viscosity measured for SEBS-based fuels.

Formulazione	**T_{mp} [°C]**	**η* (48°C) [PA*s]**
SEBS-LP-SW	57	12000
SEBS-MO-SW	52	15000
SEBS-MO-SW-KER	47	2400
SW	47	1500

3.3 Ballistic performance comparison

The average regression rate of the tested fuel formulations was measured at a reference condition, corresponding to 150 kg/m^2s oxidizer mass flux and 1.5 bar operating pressure. Tests were performed in double slab configuration, with pure oxygen as oxidizer. The results of the ballistic characterization are shown in Figure 7, were the different formulations are compared to the reference formulation (pure HTPB). For the tested formulations, the regression rate percentage increase with respect to pure HTPB at the reference oxidizer mass flux is reported in Table 1.

As it can be seen, GWP-based formulations (green columns in Figure 7) allow obtaining r_f values higher than that typical of HTPB (up to +88% at the selected oxidizer mass flux). GWPK-based formulations (blue columns in Figure 7) allow obtaining higher performance (up to +158%), similar to those obtained with SWP-based fuels (red columns, r_f up to +200%). SEBS-based fuel gives an increase of +157%, thus similar to GWPK-based fuels. Results obtained suggest that kerosene addition is effective in enhancing GW-based fuels r_f, by decreasing their viscosity and thus increasing their tendency to entrainment.

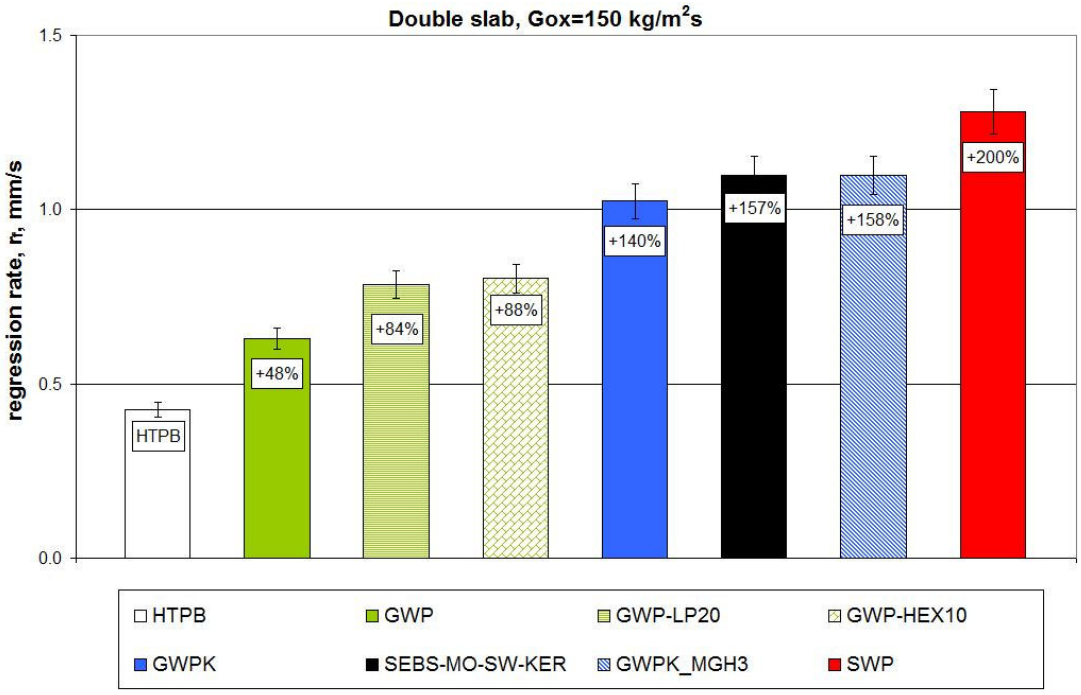

Figure 7: Regression rate comparison for different fuel formulations.
Oxygen mass flux: 150 kg/m^{2}s. Operating pressure: 1.5 bar.

4. Concluding Remarks

Paraffin-based solid fuels for hybrid rockets were characterized in the framework of a research project aimed to develop a new generation of solid fuels, combining at the same time good ballistic and suitable mechanical properties.
With this purpose, two strengthening strategies were investigated during this work, the PUF strengthening and the TPE addition.
PUF reinforced formulations show interesting results, but lead to heterogeneous solid fuels. Homogeneous fuels are obtained with SEBS-containing formulations, allowing isotropic mechanical properties.
The present investigation shows a strong correlation between the measured viscosity of the melted paraffin layer and the regression rate. Results show that a decrease of viscosity increases the regression rate. This trend is connected to the increasing development of entrainment phenomena, which strongly increases the regression rate. GWPK-based formulations allow increasing the regression rate up to 158% with respect to the reference formulation (pure HTPB), almost +37% with respect to the best result obtained with the GWP-based formulations. SWP formulation allows obtaining the best performance among the tested formulations (+200% with respect to pure HTPB).

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