Joint Propulsion Conferences
July 14 - 17, 2013, San Jose, CA
49th AIAA/ASME/SAE/ASEE Joint Propulsion Conference

10.2514/6.2013-4038

Experimental Study of Vegetal Based Polyurethane Fuel filled with Paraffin Particles for Hybrid Rocket Motors

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Experimental investigation was conducted to determine the relative propulsive and combustion behavior of a polyurethane-based solid-fuel formulations containing 30% w/w of paraffin. In total, 4 solid fuel formulations were investigated. The thermal decomposition of the solid fuels was studied at different heating rates in dynamic nitrogen. Fuel containing paraffin was investigated with electron microscopy, paraffin spheres were visualized and measured. Firing tests with 4 configurations were performed. Thrust measurements indicated that the addition of paraffin increased thrust at about 57% and regression rates at about 83%. It was found that increase in regression rate is proportional to paraffin content.

I. Introduction

Much work has been done on hybrid rocket motors, because of great technical interest in safety and mechanical simplicity of this system[1,2]. It has been shown[3-5] that liquefying fuels such as paraffin highly increase the regression rates. Once paraffin provides poor mechanical properties to sustain loads on flight condition, a binder is desirable. This work investigates the thermal behavior and regression rates of a solid fuel system composed of a polyurethane binder embedded with micron sized paraffin.

Researchers at Stanford University[1] discovered that paraffin-based fuels have regression rates that are 3-4 times higher than those of conventional hybrid fuels. This is largely due to the development of a thin liquid layer on the fuel grain surface which becomes instable: instability appears due to the incoming oxidizer flow pattern and liquid fuel droplets are injected into the boundary layer[4,5]. This enhanced mass-transfer mechanism increases fuel mass flow without the blocking effect typical of gaseous fuel blowing.

Paraffin presents poor mechanical properties; a binder is hence desirable to sustain loads on flight condition. Therefore, the purpose of this work was the thermal analysis of a developed polyurethane binder. This product is supposed to be applicable as a fuel binder or solid propellant binder formulations. The synthesized binder is embedded with paraffin. Synthesized fuels are tested to assess the improvement in combustion efficiency and regression rates.

In the binder, HTPB-hydroxyl-terminated polybutadiene was replaced with a modified soy bean (polyol) based pre-polymer with 6% of free NCO that was cured with 1,4 Butanediol for the production of polyurethane elastomers. Two types of polyurethane were synthesized, one plasticized with a mineral oil and the other with castor oil, both were tested and the one with castor oil was chosen for its performance.

A microcrystalline paraffin from petroleum (Petrobras 140/145-1) composed of saturated aliphatic hydrocarbons with melting point of 61,4° Celsius and boiling point of 290° Celsius at standard conditions was added to the synthesized PU. A treatment to change paraffin grain shape is used to improve fuel packaging, first paraffin is

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melted, then, a spray injector is used to solidify the particles in sphere shape. Firing tests with axial injector were done, the ballistic results were obtained and evaluated.

Kissinger[6], Ozawa[7] and Flynn[8] demonstrated that DSC technique, based on the linear relation between peak temperature and heating rate, can be used to determine the kinetics parameters of a thermal decomposition (activation energy, rate constant). The Ozawa method is one of the most popular methods for estimating activation energies by linear heating rate and it is the so-called isoconversional method.

In the present work, the DSC technique and the Ozawa dynamic method were used to determine the kinetic parameters of the solid fuel. Thermal analysis cannot be used to elucidate the complete mechanism of a thermal degradation but the dynamic analysis has been frequently used to study the overall thermal degradation kinetics of polymers and composites because it gives reliable information on the frequency factor (A), the activation energy (E) and the overall reaction order[9].

II. Solid Fuel Thermal Analysis

A. Binder thermal analysis

TG/DTG curves were obtained on a model TGA 50 Thermogravimetric Analyzer (Shimadzu) in the temperature range of 173 – 323 for TGA and 293 - 1200 K for TG with heating rates 10, 20, K min-1, under dynamic nitrogen atmosphere (100 mL min-1). Sample masses were about 10 mg each.

DSC analysis of the synthesized polyurethane PU-CTDIB1 was performed, Fig. 1. The material glass transition temperature -Tg was determined as 39°C. An endothermic peak occurred at approximately -20°C. This peak is a feature of incorporating the functional groups of the polyol chain that interact with other chains producing these peaks fusion, this polymorphism is also assigned to the triglyceride molecule[10]. The Tg of PU was close to the Tg of HTPB (-45°C) produced from PU with TDI. A larger value of Tg was expected due to the existing branches in the polymer chain, differently in the HTPB the linear structure gives more flexibility lowering Tg. caused this purpose since the structure more linear than the HTPB gives more flexibility which lowers the Tg[11].

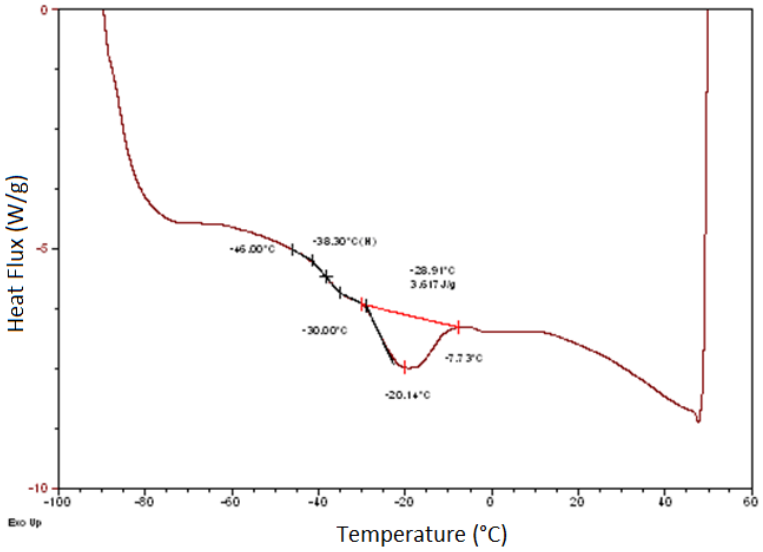

Figure 1. DSC curve of the sample PU-CTDIB1, determination of the glass transition temperature. Conditions: initial mass of 11,197 mg, inert atmosphere of N2 (50mL.min-1) and a heating rate of 10 K/min-1.

Determination of Activation Energy and Pre Exponential Factor with Flynn, Wall and Ozawa kinetic model by thermogravimetric analysis.

Figure 2 shows the TG curves of polyurethanes in different proportions under different heating ratios that were used for kinetic study. The analysis was performed based on the ASTM E2550-11 standard. Data were collected from conversion percentages as a function of heating rate. Conversional levels (α) of 5.0, 7.5, 10.0, 12.5, 15.0, 20.0, 25.0, and 30.0% were gathered.

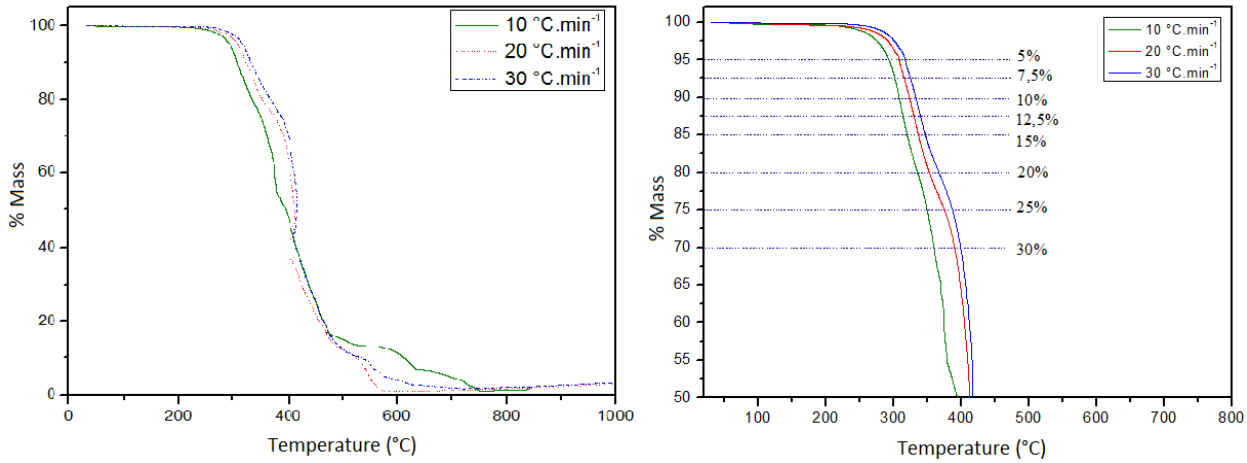

Figure 2. TGA curves of PU-CTDIB1. Conditions: Initial mass of 10 mg, synthetic air atmosphere (100ml/min). Heating rates of 10 °C/min, 20 °C/min and 30°/min. On the right, the degrees of conversion "α" for the kinetic model study are shown.

Activation energy and the pre-exponential factor were determined using ASTM E1641-07. Fig. 3 shows the logarithm of the heating rate as a function of inverse temperature for specific levels of mass conversion. Table 1 shows the activation energies and pre-exponential factors calculated for each conversion degree.

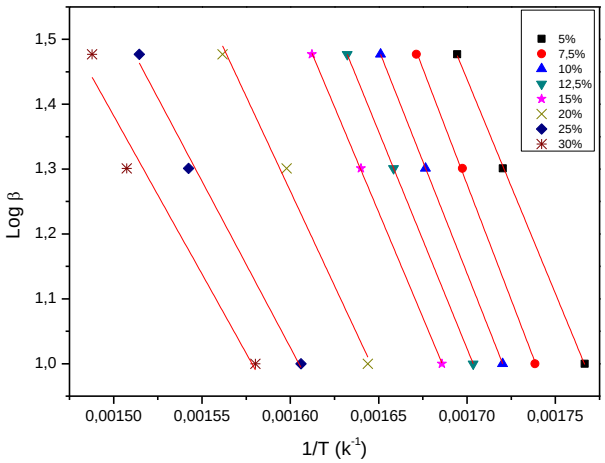

Figure 3. Logarithm of the heating rate as a function of inverse temperature for specific levels of mass conversion "α".

Table 1. Activation energies and pre-exponential factors for each α.

% Conversion degree	Activation Energy (kJ/mol)	Pre-exponential factor (s^{-1})
5	116,83	1,20E+12
7,5	126,88	4,16E+13
10	122,38	6,95E+12
12,5	118,33	5,17E+12
15	114,6	1,32E+12
20	101,75	7,76E+10
25	87,41	1,39E+09
30	82,66	5,94E+08

The relationship between activation energy and conversion degree was established on Fig. 4.

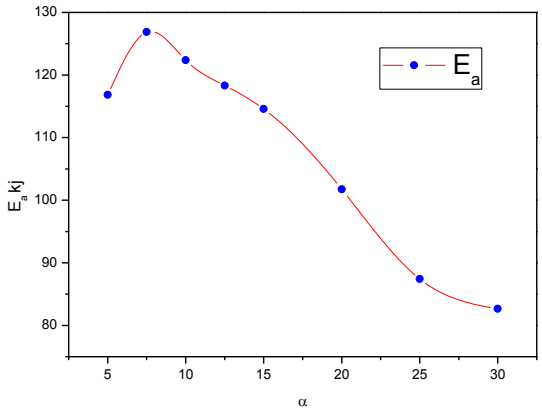

Figure 4. Curve of activation energy as a function of the polyurethane synthesized.

The activation energy values for polyurethane are much dependent on the degree of conversion, for the first step of degradation, the apparent activation energy increases from 116.83 $kJmol^{-1}$ at α = 0.05, reaches the value of 126.88 $kJmol^{-1}$ at α = 0.075, and then decreases to 122.38 $kJmol^{-1}$ at α = 0.1. The continuous decrease of apparent activation energy in degree of conversion range 0.1–0.9 indicates a two-step mechanism for thermal degradation. This increase in activation energy corresponds to cross-linking reactions during thermal degradation of polymer. Activation Energy values calculated using isoconversional methods are independent of degree of conversion in the range α=0.25–0.8 indicating that single mechanism is working during this range.

At low heating rates and low surface temperature, chemical processes such as polymer chain scission and cyclization, in the solid fuel decomposition zone just below the surface are kinetically limiting processes[12,13]. Arrhenius type expression is given by the following equation:

$$r = Ae^{\left(-\frac{E_a}{R_u T}\right)}$$

The logarithm of r values obtained from the intercepts of the straight lines of Fig. 3 are plotted against 1/T in Fig. 5. It can be observed a deviation of the straight line predicted by the Arrhenius equation. This is a positive suggestion that the observed ordering reaction is a composite one, made up of two or more concurrent reactions differently influenced by temperature[10]. Two or more simultaneous processes with different activation energies yield a plot which is concave upwards while consecutive processes are reflected in a plot which is concave downwards[14,15].

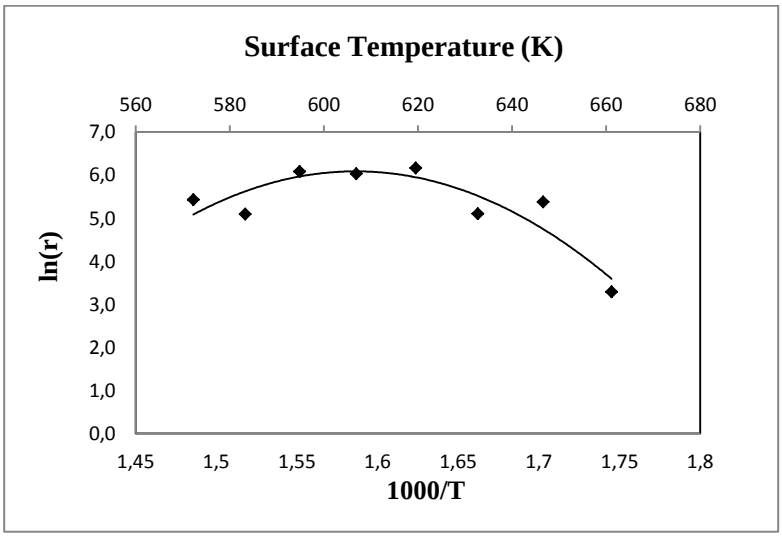

Figure 5. Curve of activation energy as a function of the polyurethane synthesized.

B. Paraffin analysis

The ASTM E-1641 method[16] requires at least four heating rates, Fig. 6, in this work[17] the mass loss curves of $140^0/145^0$ F wax were performed with heating rates of 10^0C/min, 20^0C/min, 30^0C/min and 40^0C/min. According to this method, the analysis of the activation energy displays significant values in the region of low mass loss, close to 15%, corresponding to the release of volatiles (hydrocarbons of low molecular weight) and hydration water. In order to facilitate the method interpretation, the region of interest is highlighted, Fig. 6 (right).

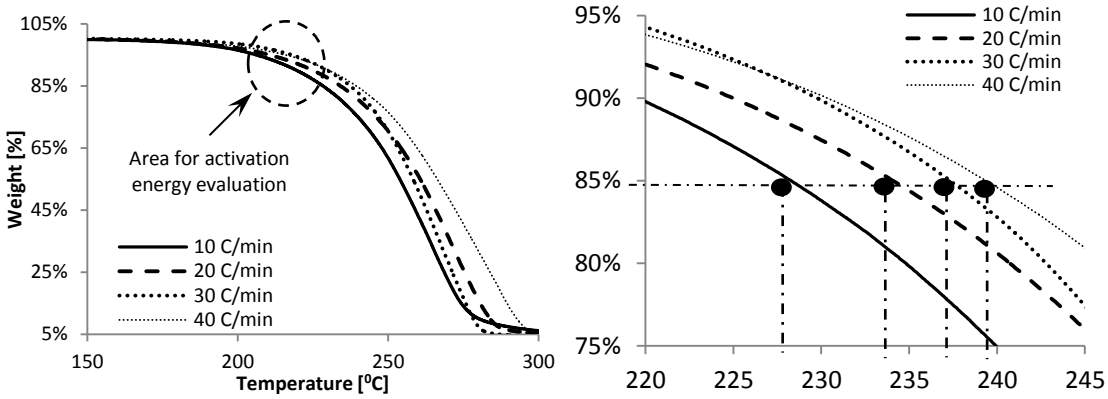

Figure 6. Left: Mass loss curves for heating rates of 10 °C/min, 20 °C/min, 30 °C/min e 40 °C/min. Right: Temperature distribution with paraffin mass losses of 15% for each heating rate.

The paraffin wax type $140^0/145^0$ F manufactured by Petrobras has an activation energy of 224 KJ/mol with a pre-exponential factor of $5.48x10^{22}$, in accordance to the ASTM-E-1641. Whereas the kinetics of paraffin decomposition follows first order reaction, the method for determining the kinetic parameters was used with the results of thermogravimetric analysis (TGA) carried out in the Chemical Analysis Laboratory from the Materials Division (AMR/IAE/CTA). The paraffin wax type $140^0/145^0$ F manufactured by Petrobras has an activation energy of 224 KJ/mol with a pre-exponential factor of $5.48x10^{22}$, in accordance to the ASTM-E-1641.

C. Blend of polyurethane and paraffin

A basic hybrid model of regression that uses traditional regression theory such as that for polyurethane and mixes in elements from entrainment dependent regression theory is used to try to establish a methodology for regression rate calculation based on fuel mass proportions.

The polyurethane is mixed with micron paraffin grains uniformly and cast into fuel cores. The two fuels are not thought to be molecularly bonded, except for small thin areas of contact. The fuel can be visualized in Fig. 7.

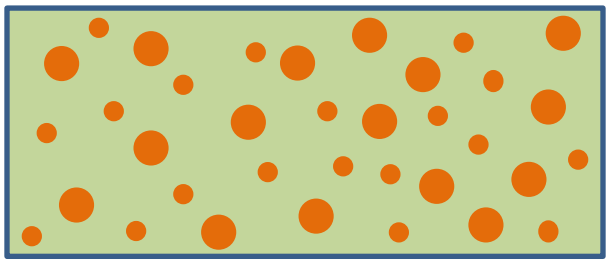

Figure 7. Representative cross section of a hypothetical heterogeneous fuel with paraffin spheres.

It is assumed that the initial process is polyurethane vaporization at the fue surface through pyrolysis. The second phase would be the entrainment of small droplets of paraffin in the flame zone due to the boundary layer viscous forces. These processes compete and the overall efficiency is increased. A first approximation would be to weight the each separate regression prediction by the % mass contribution near the surface of the fuel grain assuming an even distribution of paraffin spheres in the PU.

$$a.\dot{r}_{PU} + b.\dot{r}_{Paraffin} = \dot{r}_{total}$$

SEM images of the samples under 80 and 252 magnified, Fig 8. Paraffin spheres can be seen on both photos. They are blended in the polymeric matrix as expected in the theory, this improves fuel packaging, increasing bulk density. A general idea about sphere diameters is the range between 150 to 400 µm.

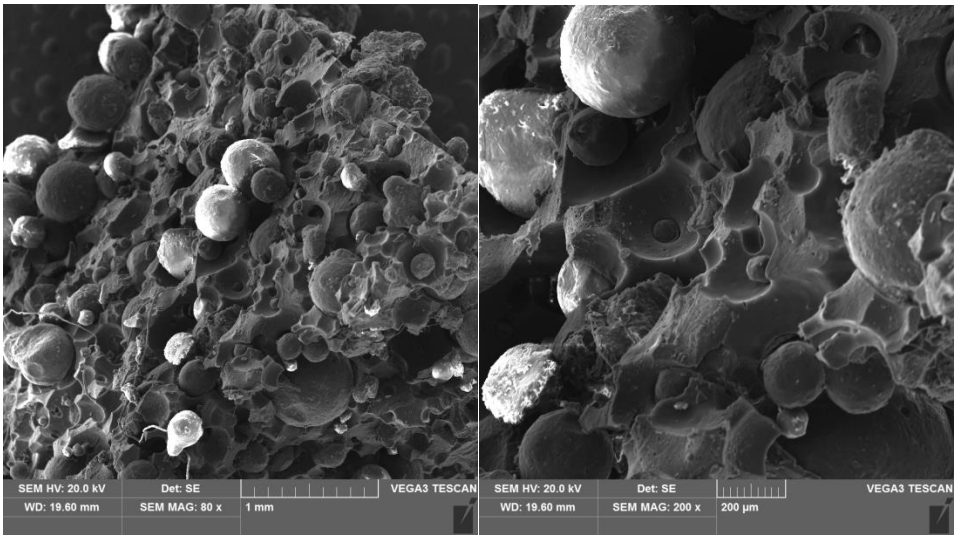

Figure 8. SEM micrographs of samples of polyurethane embedded with paraffin grains (30% w/w).

III. Static Firing Tests

A. Experimental setup

The baseline engine design was developed from a need for simplicity and flexibility; therefore a modular design was incorporated. The set could be assembled and disassembled in minutes allowing the practice of several tests per session.

The case and the flanges were made from stainless steel. The case was machined to fit between the steel flanges. The nozzle was adapted in the aft flange, to prevent nozzle escape. A hydraulic system was settled to perform the thrust measurements. A view of the motor attached to the test bench is shown in Fig. 9. Compression fitting valves were used in the oxygen feed line. A squib was used to achieve ignition.

Figure 9. Upper side view of the labscale hybrid rocket motor on the test bench.

B. Tests of PU fuels

First series of synthesis:

1) PU (polyurethane) plasticized with mineral oil;
2) PU plasticized with castor oil;
3) PU plasticized with castor oil containing 30% of paraffin;
4) PU plasticized with castor oil containing 50% of paraffin;

A series of tests with each synthesized fuel and one commercial polyurethane was performed with the axial injector, the gaseous oxygen mass flow rate was maintained constant at 40g/s. The thrust results are presented in Fig. 10.

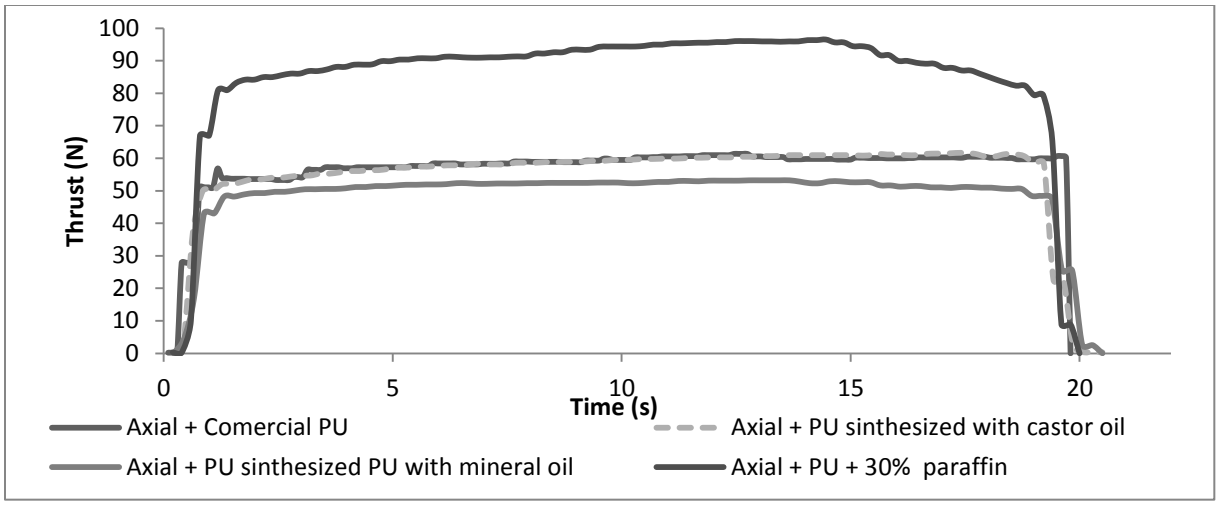

Figure 10. Thrust data of polymeric fuels and paraffin wax mixture with axial injector and 20 seconds tests.

The graph shows that the thrust obtained with the PU synthesized with mineral oil obtained the lowest thrust, followed by the commercial and PU synthesized with castor oil, both with the approximate same thrust of 62 N. The results obtained with the use of paraffin were the most promising reaching almost 100 N. Further data is show in Table 2.

Table 2. Experimental results for each fuel given the use of the axial injector.

	P(atm)	O/F	Thrust (N)	Isp (s)	$\dot{r}$ (mm/s)
PU + Paraffin 30%	13,98	1,63	98,5	177,9	0,97
PU w/o castor oil	8,11	3,72	52,7	121,1	0,50
PU with castor oil	8,94	3,23	62,9	140,0	0,53
Commercial PU	8,97	2,89	62,6	137,5	0,53

It was observed that the binder that contains castor oil had better performance and higher stability. It increased Isp in about 15,6% and thrust in about19,4%. The addition of 30% paraffin increased ISP in about 29,5% and thrust in about 56,9%, the pressure achieved with the same oxidizer mass flow rate is 58,8% higher. Regression rates in relation to the polyurethane synthesized with castor oil increased almost 70%. For the same oxidizer mass flow rate, pressure achieved was at least 70% higher when 30%w/w of paraffin is added.

Assuming an even distribution of paraffin spheres, and weighting the regression rate contribution of each fuel yields:

$$\mathrm{a}.\,\dot{\mathrm{r}}_{\mathrm{PU}} + \mathrm{b}.\,\dot{\mathrm{r}}_{\mathrm{Paraffin}} = \dot{\mathrm{r}}_{\mathrm{total}}$$

From Table 2, $\dot{r}_{PU} = 0.53mm/s$, $\dot{r}_{total-PU+paraffin} = 0.97mm/s$.

Karabeyoglu and coworkers[18] suggested that paraffin regression rates within O/F between 1.7 – 2.3 is $\dot{r}_{Paraffin} = 0.488\bar{G}_{ox}^{0.62}$

Using methodology of gaseous flux calculation from Altman[19]:

$$\bar{G}_{o3} = \frac{\bar{G}_{o1} + \bar{G}_{o2}}{2} = \frac{2\dot{m}_o}{\pi}\left(\frac{1}{D_1^2} + \frac{1}{D_2^2}\right) = 9.2\ g/cm^2s$$

Using regression rate equation for paraffin[18] and the calculated oxidizer flux, regression can be estimated as:

$$\dot{r}_{Paraffin} = 1.93mm/s$$

Then, weight factor a for paraffin becomes: a = 0.31, which means that the increase in regression rate is proportional to paraffin content in fuel mass as expected.

C. High temperature coating

Before the tests, a high temperature resistant coating was used as a thermal barrier of engine components, especially the metal case and the nozzle incoming area, which is exposed to temperatures higher than 2000 degrees

Celsius. This jacket is made from a silicate binder and loaded with silicon carbide (SiC) which has been specially developed for applications in combustion chambers for liquid propelled rocket engines. This research was funded by the Brazilian Space Agency, AEB. The "coating" is applied in the form of ink on the metal surface, curing takes place at 600 degrees Celsius. After this procedure the tests may be performed. Figure 11 - Left shows the ring prior to tests and Right presents the nozzle.

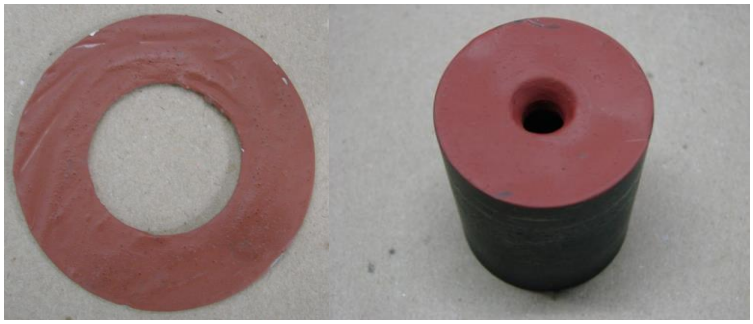

Figure 11. Left: Painted ring to prevent nozzle deterioration. Right: Painted nozzle prior to firings.

In order to assess the degree of thermal protection, a total of 28 firing tests were performed, 14 with painted ring and nozzle and 14 without any thermal protection. Stainless steel rings were used to protect aft flange and nozzle against deterioration and erosion, respectively.

Rings protected the aft flange and decreased throat widening. The initial throat diameter was 8 mm, the average final diameter without protection was 9.6 mm and with coating was 8.6mm, meaning an improvement of . 20% to 8% of diameter increase in average, Fig 12.

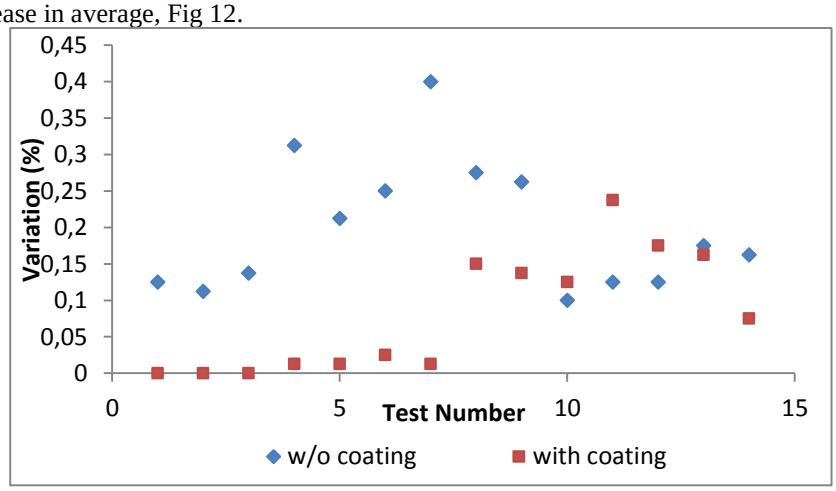

Figure 12. Nozzle diameter variation

Figure 13 shows how the ring looked after tests. A new ring is then used for each new test.

Figure 13. Painted ring after tests.

IV. Conclusion

The embedding of paraffin increased the overall ballistic parameters of the motor. The use of the binder is essential to structure and strengthen the paraffin in order to endure flight condition loads. A general idea about sphere diameters is in the range of 150 to 400 µm. Mixing ratio of 30% w/w of paraffin wax in the binder structure

yielded good results. Several additional tests must be performed to address the best mixing ratio. Rings painted with high temperature coating protected the aft flange and decreased throat widening. Regression rate results are proportional to paraffin content in the fuel.

Acknowledgments

The authors gratefully acknowledge financial support from CNPq (National Council for Scientific and Technological Development) and AEB (Brazilian Aerospace Agency).

References

[1]Altman, D., Rocket Motors, Hybrid. The Encyclopedia of Physical Science and Technology. Vol. 14, 2001.

[2]Altman, D., and Humble, R., "Hybrid rocket propulsion systems," Space Propulsion Analysis and Design, edited by R. Humble, G. Henry, and W. Larson, McGraw-Hill, New York, 1995, pp. 365-441.

[3]Karabeyoglu, M. A.; Cantwell, B. J.; Altman, D., "Development and testing of paraffin-based hybrid rocket fuels," in Proceedings of the 37th AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, July 2001, AIAA Paper 2001-4503.

[4]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, pp. 610–620, 2002.

[5]Karabeyoglu, M. A.; Cantwell, B. J.; "Combustion of liquefying hybrid propellants: part 2, Stability of liquid films," Journal of Propulsion and Power, vol. 18, no. 3, pp. 621–630, 2002.

[6] Kissinger, H. E., Anal. Chem., 29 (1957) 1702.

[7] Ozawa , T., J. Thermal Anal., 2 (1970) 301.

[8] Flynn, J. H., Thermochim. Acta, 4 (1966) 323.

[9] Park, J. W.; H. Lee, P.; Kim, H. T.; Yoo, K. O.; Polym. Degrad. Stabil., 67 (2000) 535.

[10]Guo, A.; Demydov, D.; Zhang, W.; Petrovic, Z. S. Polyols and Polyurethanes from Hydroformylation of Soybean Oil. Journal of Polymers and the Environment, v. 10, p. 49-52, 2002.

[11]Silva, G.; Matos, E. C.; Nakamura, N.; Iha, K. Aplicação da Calorimetria Exploratória Diferencial no Estudo da Cinetica de Transicao a → δ HMX. Química Nova, v. 27, p. 889, 2004.

[12]Arisawa, H., and Brill, T. B., "Flash Pyrolysis of Hydroxyl-Terminated Polybutadiene (HTPB) I: Analysis and Implications of the Gaseous Products," Combustion and Flame, Vol. 106, Nos. 1 and 2, 1996, pp. 131–143.

[13]Arisawa, H., and Brill, T. B., "Flash Pyrolysis of Hydroxyl-Terminated Polybutadiene (HTPB) II: Implications of the Kinetics to Combustion of Organic Polymers," Combustion and Flame, Vol. 106, Nos. 1 and 2, 1996, pp. 144–154.

[14] J.R. Mullet, Quart. Rev. 18 (1964) 227.

[15] A. Galwey, Thermochim. Acta 399 (2003) 1.

[16]ASTM-E-1641-04 Standard Test Method for Decomposition Kinetics by Thermogravimetry.

[17]Pimenta, G. S., Lacava, P. T., Rocco, J. A. F. F., Gomes, S., Kinetics Parameters Evaluation of Paraffin-Based Fuel.Proceeding of the International Mechanical Engineering Congress and Exposition IMECE2012, November, 9-15, Houston, Texas, USA. Paper number 86275.

[18]Karabeyoglu, A., Zilliac, G., Cantwell, B. J, Zilwa, S., Castelluci, P., Scale-Up Tests of High Regression Rate Liquefying Hybrid Rocket Fuels, 41st Aerospace Sciences Meeting and Exhibit, 6-9 January 2003, Reno, Nevada. AIAA 2003-1162.

[19]Altman, D. (2001). Rocket Motors, Hybrid. In R. A. Meyers (Ed.), Encyclopedia of Physical Science and Technology (3 ed., Vol. 14, pp. 303-321). Elsevier Science Ltd.