Copyright © 2007 by ABCM

PRODUCTION AND TESTING OF PARAFFIN GRAINS FOR HYBRID ROCKETS

Cesar Addis Valverde Salvador, salvador@lcp.inpe.br
Demétrio Bastos Netto, demetrio@lcp.inpe.br
Fernando de Souza Costa, fernando@lcp.inpe.br
Instituto Nacional de Pesquisas Espaciais
Rodovia Presidente Dutra, km 40, Cachoeira Paulista/SP, Brasil

Abstract. *Paraffin is a fuel used in hybrid thrusters which presents high regression rates. Addition of black pigments and carbon black darkens the paraffin thus reducing the internal heating of the paraffin grain by thermal radiation. This work describes the manufacturing process of paraffin grains with addition of a black pigment and carbon black. Several dispersants were tested to avoid sedimentation of the carbon black particles in the liquid paraffin. The effects of low pressure and low temperature on cylindrical paraffin grains were analysed, to allow good performance in space missions.*

Keywords*: paraffin, carbon black, fuel grain, dispersant, hybrid rocket*

1. INTRODUCTION

Hybrid rocket technology is known for more than 50 years, however only in the 1960's its safety characteristics motivated a significant research. Nowadays, the need for green propellants (propellants with low toxicity and low pollutant characteristics), the requirements of safe operation and storability, low cost missions, and the interest for launching small payloads and nanosats into LEO made hybrid rockets more attractive (Gouvêa et al., 2006, Kulkarni & Panda, 1980; Korting et al., 1987; Sparks, 1988; Chiaverini et al. 1999; Chiaverini et al. 2000; Chiaverini et al. 2001; George et al., 2001).

Hybrid propulsion systems employ propellants in different phases, being the most usual hybrid systems with a solid fuel and a liquid oxidizer.

The main disadvantage of hybrid rockets is the low thrust level attainable, due to the relatively low regression rates of the solid fuel grain, making necessary the use of a large number of ports (Karabeyoglu et al., 2003a). The control of the oxidizer flow rate allows several starts and an accurate control of the thrust level.

The safe operation of hybrid propulsion systems is related to the separation of fuel and oxidizer, differently from solid systems which mix fuel and oxidizer in the grain. Another important safety characteristic is the independence of the regression rate with respect to the chamber pressure, making hybrid systems safer than solid systems if pressure peaks do occur.

Hybrid systems have only one liquid propelllant, thus they require only one liquid line and a relatively simple injection system, as compared to liquid bipropellant systems which require two separate liquid lines and a complex injection plate in order to collide and mix the fuel and oxidizer jets.

The paraffin used as fuel, specially in candles, is part of human culture for hundreds of years, but only in the last years has been considered as a rocket fuel. Recently, it was developed in the Stanford University and in the Ames-NASA Research Center, both in the USA, a new paraffin-based fuel whose regression rate is approximately three times higher than conventional hybrid fuels (Karabeyoglu et al., 2003a,b, 2004). Promising results were obtained by several researchers (Brown and Lydon, 2005; Karabeyoglu et al., 2004; Santos et al., 2005; McCormick et al., 2005) using paraffin with different oxidizers – liquid oxygen (LOX), gaseous oxygen (GOX), nitrous oxide (N_2O) and hydrogen peroxide (H_2O_2).

Paraffin grains in hybrid rockets are under strong radiative and convective heating which can reduce the strength and even melt the whole grain. The use of additives can reduce the thermal radiation effects inside the grain. Carbon black is a common additive in explosives with a high pigmentation power and capable of increasing the mechanical strength of the paraffin grain.

Therefore this work presents a study of mixing carbon black and black pigment to paraffin, aiming to improve the mechanical strength and to increase the regression rate of paraffin grains used as fuel in hybrid systems.

2. METHODOLOGY

2.1. Physical and chemical characteristics of the solid paraffin used for testing

Paraffin is formed by a straight saturated chain of hydrocarbons, C_nH_{2n+2}. In this work, fuel grains of solid paraffin for testing were produced from commercial granular white paraffin supplied by the company Comarplast Aditivos. The granular paraffin came with a quality certificate and had a melting point varying from 60 to 62.8 ^oC, boiling point $T_b \approx$

259 ^oC, average molecular weight of 280 kg/kmol, density at 60 ^oC, $\rho \approx 0{,}78 - 0{,}80$ g/cm^3, and low oil content, approximately 0.62 %. Paraffins with an oil content lower than 1% present higher hardness and higher resistance to impact.

2.2. Physical and chemical characteristics of the black pigment and carbon black used for testing

The black pigment 33015-preto manufactured and supplied by the company Power Corantes Ltda was used to darken the paraffin. This pigment is oil based and is commonly used in decorative candles.

Several brands of carbon black supplied by the company Columbian Chemicals Brasil were used: Statex 125, Statex 300 and Raven 1255, all samples with particle diameter lower than 32 nm. Paraffin and carbon black can not be easily mixed, because paraffin is a non-polar substance and carbon black is a polar substance.

It should be mentioned that carbon black has not the same composition of soot, because soot contains poly-cyclical aromatic hydrocarbons (PAH) which can reach up to 30 % by weight, whereas carbon black has negligible PAH content.

2.3. Preparation of a cylindrical grain of paraffin with a black pigment

The first phase of the manufacturing process of a paraffin grain comprised the heating and melting of the granular paraffin. After the paraffin was completely melted a small amount of black pigment was added to the paraffin.

The mixing with a black pigment made the paraffin opaque, which is essential to make sure that the phase change in the fuel occurs only at the grain surface during the combustion process. As a consequence, a thin liquid layer is created along the grain surface and, consequently, small droplets are released at the gaseous flow of reactants and products.

It was verified that a minimum of 0.003 % in mass of the black pigment was required to obtain a uniform black color along the whole grain. Mass fractions of black pigment lower than 0.003 % produced blue grains. Therefore it was decided to add 0.005 % in mass of the black pigment to assure the paraffin was completely black. The black pigment allowed to solve the problem of melting by radiation throughout the grain during burning in the rocket chamber.

2.4. Preparation of a cylindrical grain of paraffin with carbon black

The carbon black was added to the liquid paraffin in temperatures between 15 and 25 ^oC above the melting point. This temperature range is important for two reasons: 1) A temperature lower than 15 ^oC above the melting point makes the mixing difficult because the paraffin is near the melting/solidification point; 2) At temperatures higher than 25 ^oC above the melting point the paraffin density is strongly reduced and, consequently, the carbon black particles settle down in the container bottom.

After mixing the liquid paraffin was poured into a PVC mold with length and internal diameter equal to the fuel grain length (110 mm) and to the grain external diameter (40 mm), respectively. The PVC mold was placed inside an aluminum tube with external threads at its ends. PMMA lids were placed on the top and on the bottom of the aluminum tube to avoid leaking, and were hold in place by two brass covers screwed on the aluminum tube. This aluminum container with brass covers was used as support in a lathe for the solidification process by centrifugation. After that the paraffin grain was drilled to obtain an internal diameter of 15 mm. Figure 1 shows the aluminum container and the accessories utilized. Figure 2 shows the centrifugation process of the paraffin grain in a lathe.

The rotation speed of the lathe was 1200 rpm during 40 minutes, allowing the paraffin to settle on the tube walls by the centrifugal forces. This process also improves the structural integrity of the grain, since the combustion port is formed without requiring the drilling of a hole. A minimum time of rotation of 40 minutes is important to guarantee complete cooling and, consequently, a complete solidification of the grain, avoiding the production of a fragile and low structural quality grain.

Contractions from 15 to 19 % were observed in the liquid paraffin volume during solidification. This contraction fraction is taken into account to calculate the amount of liquid paraffin required to yield a grain with a specified volume.

Eight cylindrical paraffin grains with 110 mm length, 40 mm external diameter and 15 mm internal diameter were prepared for tests, varying the carbon black mass fraction from 0.5 to 5 %. A percentage of 0.5 % of carbon black allowed obtaining a homogeneous dispersion of the paraffin. A larger fraction of carbon black causes the settling of carbon black particles in the bottom of the paraffin container.

A helix stirrer was used to disperse and to make uniform the distribution of particles in the liquid paraffin. Table 1 shows the influence of the carbon black mass fraction on carbon black sedimentation.

Figure 1: Brass covers with screws, aluminum tube and PMMA covers.

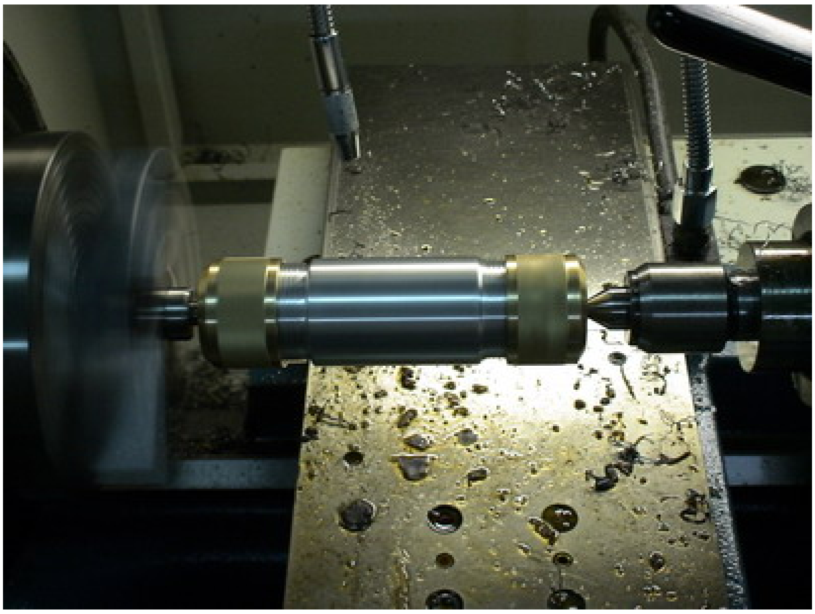


Figure 2: Paraffin centrifugation in a lathe.

Table 1: Effects of carbon black mass fraction on sedimentation.

Grain	Carbon black mass fraction, %	Sedimention
1	0.5	No sedimentation, but small aglomeration of solid particles
2	0.75	Light
3	1	Light
4	1.5	Medium
5	2	High
6	3	High
7	4	High
8	5	High

To reduce the agglomeration problem of the carbon black particles, several dispersants were tested: Byk-411, Byk-9076, Byk-9077, Antiterra U-80, Disperbyk-108, Disperbyk-2000 and Disperbyk-2150, all manufactured and supplied by the company Bandeirante Química (www.bandeirantequimica.com.br).

It was found that only the Disperbyk dispersants are soluble in paraffin. The Disperbyk-2150 dispersant allowed to obtain a dispersion larger than 50 % of the carbon black volume, delaying the sedimentation of the carbon black, and, consequently, it was chosen as the only dispersant for the paraffin grain preparation.

To avoid sedimentation of the paraffin containing 0.5 % in mass of carbon black, it was determined a minimum mass fraction of 1.5 % of Disperbyk-2150. It should be noted that grains with different mass fractions of carbon black can be produced, however higher carbon black contents require larger fractions of the dispersant.

The resulting grain is a mixture of paraffin, black pigment, carbon black and dispersant Disperbyk-2150. Table 2 shows the final composition of the grain.

Table 2: Final composition of the paraffin grains.

Substance	% mass
Paraffin	97.95
Black pigment	0.005
Carbon black	0.50
Disperbyk-2150	1.50

The addition of carbon black in the paraffin grain was made to improve the mechanical characteristics of the paraffin grain, to verify later its effects on the regression rates and on the overall performance during combustion, and, also, to compare with available results for paraffin grains mixed with black pigment (Karabeyoglu, 2004). It is expected that the carbon black increases the regression rate of the grain, since it is also a fuel material.

2.5. Fuel grain testing at low pressure and low temperature

In order to verify the possibility of using paraffin grains in space missions, it was necessary to verify their behavior in low pressures and low temperatures. To perform that, a paraffin grain was placed in a vacuum chamber during 6 periods of 24 hr. The vacuum pumps were turned on during 30 min each day until the pressure in the chamber reached 0.02 mbar. Figure 3 shows the chamber pressure variation during a 24 hr period. It is observed that after turning off the vacuum pumps, the pressure increases until to stabilize at 1 mbar.

At the end of testing at low pressure it was not observed any significant visible physical changes, such as fissures or cracking that can compromise the paraffin grain performance during burning. Figure 4 shows the grain and the vacuum chamber used for testing the effects of vacuum on grain integrity.

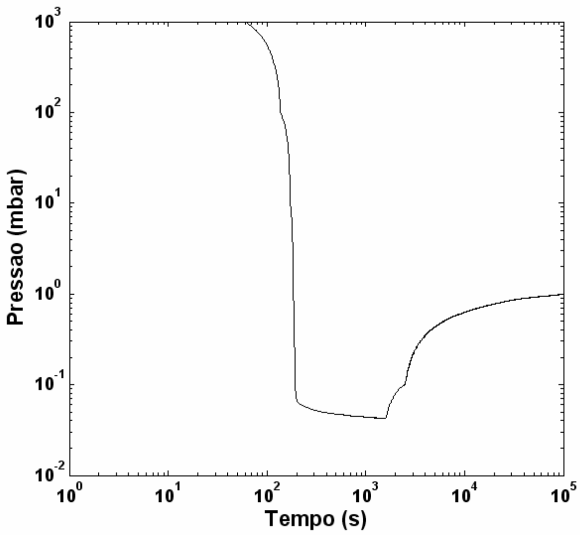


Figure 3: Pressure evolution in the vacuum chamber.

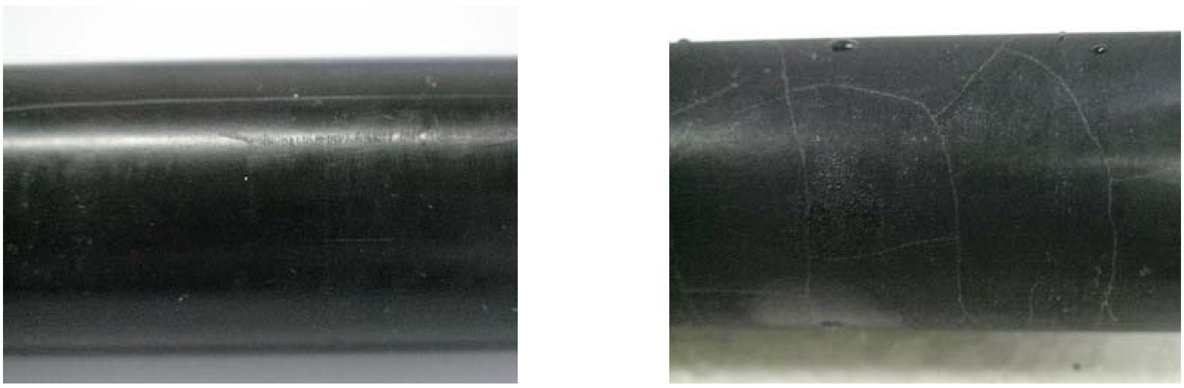
(a) (b)

Figure 4: (a) Paraffin grain for low pressure tests; (b) Vacuum chamber at LCP/INPE.

An analysis of the paraffin grain behavior at low temperature was also made in order to verify if its mechanical strength was affected at extreme conditions of operation. The grain was placed in a sealed glass container and then placed in tank with liquid nitrogen during a 24 hr period.

The sealed glass container was used to avoid direct contact with the liquid nitrogen, and thus to reduce the rates of convective heat transfer to the grain. The liquid nitrogen temperature was -195 ^{o}C and this was the final paraffin temperature after attaining thermal equilibrium. After 24 hr, and still inside the nitrogen tank, the grain was analysed.

It was observed no significant visible change in the paraffin grain, however after 5 minutes of the tank removal at ambient conditions (25 ^{o}C), the grain structure was modified, with the formation of cracks along the paraffin surface. Figures 5.a and b show the grain before and after testing at low temperature. It should be noted that during operation in space there is a sudden temperature increase at the grain surface just after ignition, avoiding the formation of cracks as observed in the low temperature test. Figure 6 also shows the paraffin grain after being taken out of the liquid nitrogen tank and the equipment used in the tests. Figure 7 shows the fuel grain tested in cold temperature. This grain had no dispersant mixed and therefore the carbon black was concentrated in the external region of the grain. It can be seen in Fig. 7 that the cracks occurred not only at the grain surface but were distributed inside all the grain volume.



(a) (b)

Figure 5: Paraffin grain used in the low temperature tests. (a) Before test; (b) After test.

Figure 6 - (a) Liquid nitrogen tank and glass container used in the low temperature tests;
(b) Paraffin grain after 24 hr at -196 ^{o}C.

Figure 7 - Paraffin grain prepared without dispersant and tested in low temperature.

3. CONCLUSIONS

This paper described the preparation process of paraffin grains (110 mm length, 40 mm external diameter, 15 mm internal diameter) to be used in hybrid rockets. The effects of low pressure and low temperature on paraffin grains are presented.

Several mixtures of paraffin with black pigment, carbon black and dispersants were tested. The black pigment was used for darkening the grain, the carbon black was used for multiple reasons: darkening the grain, to increase the grain hardness and to improve combustion characteristics, and the dispersant was required to mix the carbon black with the paraffin.

It was verified that a mass fraction of 0.005 % of black pigment oil based was required to create an opaque mixture and, consequently, to reduce the internal absorption of radiation heat during the combustion process. The temperature range appropriate for mixing and uniform distribution of carbon black with paraffin was determined as 15 to 25 ^{o}C above the melting point of the paraffin. A rotation of 1200 rpm in a lathe was used to provide fuel grains without internal bubbles and good structural integrity. There was a contraction of 15 to 19 % in volume of paraffin during solidification. It was found that the best dispersant agent for carbon black in paraffin was Disperbik-2150, among the dispersants tested, thus allowing to disperse 0.5 % carbon black in mass with 1.5 % of dispersant in mass.

There was no significant effect of low pressure (1 mbar) on structural integrity during and after tests. Exposition of paraffin grains to low temperatures (-196 ^{o}C) caused the formation of cracks inside the grain. The paraffin grains produced were later burned inside in a combustion chamber in a propulsion test bench.

4. REFERENCES

Brown, T. R., Lydon, M.C., 2005, "Testing of Paraffin-Based Hybrid Rocket Fuel Using Hydrogen Peroxide Oxidizer", AIAA Region 5 Student Conference, Wichita, USA.

Chiaverini, M.J., Harting, G.C., Lu, Y-C., Kui, K.K., and Peretz, A. , 1999, "Pyrolysis Behavior of Hybrid-Rocket Solid Fuels under Rapid Heating Conditions", Journal of Propulsion and Power, vol. 15, no. 6.

Chiaverini, M.J., Johnson, D.K., Lu, Y-C., Kui, K.K. and Risha, G.A. , 2000, "Regression Rate Behavior of Hybrid Rocket Solid Fuel", Journal of Propulsion and Power, vol. 16, no 1.

Chiaverini, M.J., Kui, K.K., Peretz, A. and Harting, G.C., 2001, "Regression-rate and Heat-Transfer Correlations for Hybrid Rocket Propulsion", Journal of Propulsion and Power, Vol. 17, No. 1, pp. 99-110.

George, P., Krishnan, S., Ravindran, M., Varkey, P.M. and Ramachandran, L., 2001, "Fuel Regression Rate in Hydroxyl-Terminated-Polybutadiene/Gaseous-Oxygen Hybrid Rocket Motor", Journal of Propulsion and Power, vol. 17, no. 1, pp. 35-42.

Gouvêa, L.H., Vieira, R., Costa, F.S., 2006, H2O2/Paraffin Hybrid Rockets for Launching Nanosats into LEO, 11th Brazilian Congress of Thermal Sciences and Engineering, ENCIT 2006, Paper CIT06-0913, Curitiba, Brazil.

Karabeyoglu, A., Zilliac, G., Cantwell, B.J., Dezilwa, S., Castellucci, P., 2003, "Scale-up Tests of High Regression Rate Liquefying Hybrid Rocket Fuels", 41st Aerospace Sciences Meeting and Exhibit. Nevada, USA.

Karabeyoglu, A., Zilliac, G., Cantwell, B.J., Dezilwa, S., Castellucci, P., 2004, "Scale-up Tests of High Regression Rate Paraffin-Based Hybrid Rocket Fuels", Journal of Propulsion and Power, v.20, n.6, pp. 1037-1045, November-December.

Karabeyoglu, M. A.; Cantwell, B. J.; Altman, D., "Development and Testing of Paraffin-Based Hybrid Rocket Fuels", AIAA Paper 4503, Joint Propulsion Conference and Exhibit, 37th, Salt Lake City, UT, July 8-11, 2001.

Karabeyouglu, M.A., Zilliac, G., Castellucci, P., Urbanczyk P., Stevens J., Gohkan I. and Cantwell B.J., 2003, "Development of High-Burning-Rate Hybrid-Rocket-Fuel Flight Demonstrators", *39th AIAA/ASME/ASEE Joint Propulsion Conference*.

Kulkarni, S.G., and Panda, S.P., 1980, "Role of Thermal Degradation of Hybrid Rocket Fuels in Hypergolic Ignition and Burning with RFNA as Oxidizer", Combustion and Flame, no. 39.

Korting, P.A.O.G., Schoyer, H.F.R., and Timmat, Y.M., 1987, "Advanced Hybrid Rocket Experiments", Acta Astronautica, vol. 15, no. 2, pp. 97-104.

McCormick, A., HultgreN, E., Lichtman, M., Smith, J., Sneed, R., Azimi, S., 2005, "Design, Optimization, and Launch of a 3" Diameter N_2O/Aluminized Rocket", AIAA/ASME/SAE/ASEE Joint Propulsion Conference and Exhibit, 41, Tucson, Arizona, USA.

Philmon, G. and Krishman, S., 2001, "Fuel Regression Rate in Hydroxyl-Terminated-Polybutadiene/Gaseous-Oxygen Hybrid Rocket Motors", Journal Propulsion and Power, vol.17, no.1, pp. 35-42.

Santos, L. M. C., Almeida, L.A.R, Veras, C.A.G., 2005, "Design and Flight Test of a Paraffin Based Hybrid Rocket", 18th International Congress of Mechanical Engineering, Ouro Preto, Brasil.

Sparks, D. R. , 1988, "Hybrid rocket propellants from lunar material", Acta Astronautica, vol. 17, no. 10.

5. RESPONSIBILITY NOTICE

The authors are the only responsible for the printed material included in this paper.