Characterization of HTPB-Based Solid Fuel Formulations: Performance, Mechanical Properties, and Pollution

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MOTIVATIONS

• Hybrid rocket engines are an attractive option for private space access:
  ✓ Safety,
  ✓ Low-cost,
  ✓ Throttleability, and
  ✓ Reduced (?) environmental impact.

• Solid fuel to be optimized: room for improvements.

OBJECTIVES

• Assess current state-of-the-art: good and weak points.
• Extend ballistic analysis to transient conditions.
• Point out a comprehensive strategy to enhance solid fuel formulation, manufacture, and burning.
Plan of Presentation

- Introduction and historical note
- Overview of hybrid propulsion
- Hints on propellant selection

- 2D radial burner and 2D slab burner
- Flame visualization in 2D radial burner
- Steady regression rate measurement
- Surface phenomena in 2D minislab burner
- Unsteady regression rate measurement

- Propulsive performance
- Mechanical properties
- Dispersion of fillers (cohesion)
- Environmental impact

- Conclusions and recommendations
Space Tourism

Started by Mr. Dennis Tito ten years ago, with an orbital mission combining Soyuz TM-32, ISS-EP1, and Soyuz-TM-31. 8 days at $20 million in Apr 01.

• $700 million industry by 2020, flying thousands of passengers per year, with Virgin Galactic offering six seats per flight at 200 k$ each.

• suborbital flights
• lunar flyby
• space stations
• space hotels
• and more.

Hybrid propellant HTPB/N_2O
suborbital flight: 100 km altitude.
Ansari X prize, 2004
LIQUID OXIDIZER

- Major driving feature for engine design (e.g., TP use)
- Technology borrowed from Liquid Propulsion

SOLID FUEL  C-based, inert, non toxic, safe, available

- HTPB: polymer featuring good mechanical and ageing properties but low regression rates
- Paraffin wax: solid form of saturated hydrocarbons featuring good regression rates but poor mechanical properties

SELECTION OF ADDITIVES

- Optimize regression rate vs. mechanical properties
- Increase specific impulse, density, combustion efficiency and stability
- Decrease nozzle erosion, identify optimum O/F ratio
- Transient operations?

Only solid fuel discussed here …
2D-Radial Burner

- Combustion chamber: stainless steel operating pressure up to 30 bar
- Injection of gaseous oxidizer and/or nitrogen for purge & cooling
- Oxidizer flow rate up to 250 Nlpm (about Gox = 400 kg/m²s)
- Controlled combustion pressure and oxidizer flow rate (separate)
- Laser ignition of primer charge
- Video camera with mirror allowing unique view of regressing central port
- Digital data acquisition
Example 1: pure HTPB
pressure: 10 bar; oxidizer: 100% O₂ @ 70 Nlpm
Ballistics: quasi-steady analytical

Time-Resolved Regression Rate (Continuous)

\[
\bar{D}(t) - D_0 = a(t - t_0)^n \\
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad t \geq t_{ign} > t_0
\]

\[
r_f(t) = \frac{1}{2} \frac{d[\bar{D}(t) - D_0]}{dt} = \frac{1}{2} an (t - t_0)^{n-1} \\
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad t \geq t_{ign} > t_0
\]

\[
< r_f(t - t_{ign}) >= \frac{\int_{t_{ign}}^{t} [r_f(t)]dt}{t-t_{ign}} = \frac{an}{2} \int_{t_{ign}}^{t} (t-t_0)^{n-1} dt \\
\quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad t \geq t_{ign} > t_0
\]
Ballistics: quasi-steady TOT

**TOT Regression Rate (Discrete)**

An alternative approach is to deduce the average regression rate, over each sampled time interval $t_{i+1} - t_i$, directly from the raw diameter data as a TOT (Thickness-Over-Time) ratio of sampled diameter difference over sampled time difference during combustion:

$$
\bar{r}_{f,i+1/2} = \frac{1}{2} \frac{\bar{D}_{i+1} - \bar{D}_i}{t_{i+1} - t_i}
$$

TOT measurement technique, often used in literature, quickly and easily provides a discrete set of data which, however, is intrinsically prone to larger errors since based on raw data handling prior to smoothing.
Average Regression Rates in GOX

- Operating conditions: 10 bar and 210 Nlpm pure oxygen mass flow rate
- Complete set of ensemble averages curves for 12 loaded HTPB
- For all tests, initial rate much faster than final rate (constant power law not valid)

Representative Results for Pure and Loaded HTPB
Single and double-slab (pure and loaded) HTPB burning in GOX. Initial oxidizer mass flux 120 kg/m²s and pressure 1.5 bar.
Incipient CCP formation and detachment (agglomerate ?) from the regressing surface of HTPB loaded with 5.0% μAl burning under 60% O₂ + 40% N₂ at 10 bar. [M. Manzoni, S. Romanò, S. Tarquini, and G. Vadalà]
Fuel fragments detach from the surface of HTPB burning under 60% O₂ + 40% N₂ at 10 bar. [M. Manzoni, S. Romanò, S. Tarquini, and G. Vadalà]
Exploratory tests conducted to assess the feasibility of transient regression rate measurements. Changes of pressure or oxidizer flow rate were imposed and the subsequent effects on regression rate monitored. Visualization of the sample central port during combustion performed using a High-Speed and High-Resolution Camera, with a recording frame rate of 250 fps and 1024 x 1024 pixels of resolution.

- **Changes of pressure** in the range 7 to 13 bar, up and down, with 210 Nlpm of oxidizer flow rate, brought only minor effects.
- **Changes of oxidizer flow rate** from 210 down to 130 Nlpm, at 13 bar, brought some perceivable effects.
- ** Interruption of the oxidizer flow rate** for 1 s revealed apparent extinction followed by reignition, triggered by hot spots at the sample head-end.
- Significant flame oscillations were visible during reignition.
Transient burning HTPB in GOX from 210 to 130 Nlpm; bottom time scale shifted by 1.7 s ignition time.
Extinction and reignition following oxidizer flow rate disruption.
# Hybrid propulsion performance

(courtesy of Mr. Calabro)

<table>
<thead>
<tr>
<th>Propellant</th>
<th>Mixture Ratio</th>
<th>Density kg/m³</th>
<th>Isv (ideal) 7 MPa, $\varepsilon=40$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid AP/Al/HTPB</td>
<td>68/18/14</td>
<td>1750</td>
<td>315</td>
</tr>
<tr>
<td>Hybrid LOX/HTPB</td>
<td>72/28</td>
<td>1060</td>
<td>354</td>
</tr>
<tr>
<td>Liquid Bi Propellant</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NTO/MMH</td>
<td>2.37</td>
<td>1200</td>
<td>341</td>
</tr>
<tr>
<td>H₂O₂/RP1</td>
<td>7.0</td>
<td>1320</td>
<td>314</td>
</tr>
<tr>
<td>LOX/RP1</td>
<td>2.77</td>
<td>1030</td>
<td>358</td>
</tr>
<tr>
<td>LOX/CH₄</td>
<td>3.45</td>
<td>830</td>
<td>369</td>
</tr>
</tbody>
</table>

![Graph showing Isv values for different propellants](image)

**INTRODUCTION**

**HISTORY**

**OVERVIEW**

**PROPELLANT**

**2D RADIAL**

**VISUALIZATION**

**BALLISTICS**

**REGRESSION**

**SURFACE**

**UNSTEADY**

**2D SLAB**

**PERFORMANCE**

**MECHANICS**

**DISPERSION**

**IMPACT**

**CONCLUSIONS**
HTPB is a polymer widely used for both solid propellants and hybrid solid fuels. This is due to HTPB ease of manufacturing and capability of providing good mechanical properties also for highly loaded grains. Here a characterization of mechanical properties based on uniaxial tensile stress test is provided for HTPB baseline and HTPB loaded with 2% C.

Comparative results show that loading polymeric matrix with Carbon enhance mechanical properties with respect to baseline values. Due to good adhesion characteristics of Carbon (an active filler), tangent elastic modulus, true stress, and elongation at break of the loaded formulations result higher than the corresponding values of the baseline fuel.
Difficult to disperse nano-powders through conventional mixing: Van der Waals forces and nano-particles high surface areas cause cohesion in large clusters, which prevents effective transfer of nano-materials properties to the composite.

How to obtain a homogeneous dispersion of nano-ingredients still is a challenge.

Most explored strategy based on sonochemistry, whereby chemical reactions are activated due to powerful ultrasound radiation (in the range 20 kHz – 10 MHz). The phenomenon responsible for sonochemical reaction is cavitation: creation, growth and explosion of bubbles can decrease intermolecular forces and chemical bonds.
Filler Dispersion 2/3

HTPB loaded with 1% nAl (100 nm) and 0.2% CB: possible formation of big clusters (cohesion).

HTPB loaded with 1% μAl (30 μm) and 0.2% CB: formation of big clusters (cohesion) not observed.
HTPB loaded with 1% nAl (100 nm) and 0.2% CB. Effect of sonication time on dispersion: a) no sonic, b) 1/2h sonic. Optical microscope, magnification 10X.

Sonicated samples show higher extensibility, but **time and frequency to be optimized**. CB further improves extensibility of sonicated samples.
According to Ross et al.*

• a fleet of 1000 launches/year of suborbital rockets would create a persistent layer of black carbon particles in the northern stratosphere that could cause potentially significant changes in the global atmospheric circulation and distributions of ozone and temperature.

• after one decade of continuous launches, globally averaged radiative forcing from the black carbon would exceed the forcing from the emitted CO₂ ... and would be comparable to the radiative forcing estimated from current subsonic aviation.

• The emission index (EI) of N₂O/HTPB assumed as 60 g per kg of propellant, much larger than the EI for LOX/RP1 set to 20-40 g/kg (due to lower carbon particulate oxidation rate in the hot plume).

Soot formation and destruction are complex kinetic processes that start in the combustion chamber where Polycyclic Aromatic Hydrocarbons (PAH) are generated, conglomerate into larger groups, grow, and are consumed by oxidizing species such as O, O₂ and OH. PAH are always present in nonpremixed flames within a specific temperature range (1000 to 2000 K) of fuel rich environments. These conditions commonly found close to the surface of regressing solid fuels.

Metals and organometallic compounds as well as turbulence and electrical fields known to decrease soot formation. Overall, soot formation in hybrid rockets is much complicated by peculiar and time-dependent flame structure. Systematic experimentation needed for reliable predictions.
Vacuum Is and exhaust carbon mass concentration for different liquid oxidizers burning pure HTPB solid fuel. Ideally, no C emission expected under optimum Is conditions for H$_2$O$_2$ and N$_2$O. Combustion pressure 30 bar, expansion ratio 10.
Conclusions and Recommendations

• Hybrid propulsion, so far limited to small-scale and suborbital flights, shows good potential also for space applications (lander and upper stage).

• Large-scale configurations need advanced fuels, but current TRL low
  – instantaneous regression does not obey standard const power law even ss
  – Transient regression to be fully investigated

• Required efforts for large-scale applications
  – innovative solid fuel formulations with/without entrainment
  – identify best energetic additives and best coating
  – realize more efficient nano ingredients dispersion
  – define amount, shape, and size distribution of possible CCP (agglomeration)
  – get deeper understanding of flame structure for soot formation
  – best combination of Is, good $\eta_{ls}$, regression rate, mechanical properties …
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