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Investigation of Thermoplastic Polymers and Their Blends for Use in Hybrid Rocket Combustion

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INVESTIGATION OF THERMOPLASTIC POLYMERS AND THEIR BLENDS FOR

USE IN HYBRID ROCKET COMBUSTION

By

Spencer D. Mathias

A thesis submitted in partial fulfillment of the
requirements for the degree

of

MASTER OF SCIENCE

in

Aerospace Engineering

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ABSTRACT

Investigation of Thermoplastic Polymers and Their Blends for Use in Hybrid Rocket

Combustion

by

Spencer D. Mathias, Master of Science

Utah State University, 2018

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Utah State University has developed a low cost, "green" hybrid rocket technology

as a drop in replacement for hydrazine propulsion supporting guidance and navigation

systems on small spacecraft. The current development is based on the thermoplastic

known as acrylonitrile butadiene styrene. This plastic was used because it was a

commercially available 3D printing plastic. To date, all of the hybrid fuel applications at

Utah State University have relied upon commercially-available feed stocks optimized for

structural properties. This thesis set out to find a blend of thermoplastics that had better

combustion properties than the current materials. These thermoplastics have

characteristics that allow for injection molding, extrusion forming and fused deposition

modeling. By investigating other thermoplastics and their blends there was a significant

theoretical improvement in combustion performance. In addition high and low density

polyethylene plastics were used because they are common plastics found in landfills,

possibly allowing for plastic to be recycled into rocket fuel and therefore do not

contribute to the waste stream. Three plastics were considered for replacement and as

mixture components with the acrylonitrile butadiene styrene, namely low and high density polyethylene, and high impact polystyrene. The low density polyethylene was tested using a static rocket firing stand at the following mixture ratios by weight: pure, 29%, and 50%. The high density polyethylene was tested in its pure form, and the high impact polystyrene was tested in its pure form as well as at an even mix with the acrylonitrile butadiene styrene. The documented test setup shows the measurements taken during testing. The results were analyzed to show properties not directly measured, such as regression rate, and characteristic velocity. These properties were searched to find trends. The trends show that optimal performance may be achieved using propulsion systems outside the scope of the current research area. The plastics studied failed to show superior combustion properties when used in rockets designed to achieve 12 pounds of thrust compared to the current acrylonitrile butadiene styrene plastic.

(54 pages)

PUBLIC ABSTRACT

Investigation of Thermoplastic Polymers and Their Blends

for Use in Hybrid Rocket Combustion

Spencer D. Mathias

This thesis set out to find a blend of thermoplastics that had better combustion properties than the current ABS (acrylonitrile butadiene styrene) plastic or "Lego ™ plastic" used by Utah State University. The current work is in an effort to eliminate toxic propellants from small space applications. High and low density polyethylene plastics were used because they are common plastic waste items. In this way rocket fuel can be made from these items to reduce the waste found in landfills. Three plastics were considered for replacement and as mixture components with the ABS plastic, namely low and high density polyethylene, and high impact polystyrene. These plastics failed to have superior combustion properties when used in rockets designed to achieve 12 pounds or less of thrust compared to the current ABS plastic.

ACKNOWLEDGEMENTS

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NOMENCLATURE

a	Scale Factor for Exponential curve fit
A^*	Nozzle Throat Area
A_b	Burn Area
A_c	Cross Sectional Area
ABS	Acrylonitrile Butadiene Styrene
CEA	Chemical Equilibrium with Applications
C^*	Characteristic velocity
C_{ac}^*	Actual Characteristic velocity
C_{th}^*	Theoretical Characteristic velocity
D	Diameter
DOT	Department of Transportation
EPA	Environmental protection agency
FDM	Fused Deposition Modeling
G_{ox}	Gaseous oxygen
γ	Ratio of specific heats
HDPE	High Density Polyethylene
HIPS	High Impact Polystyrene
HTPB	Hydroxyl Terminated Polybutadiene
L	length
LDPE	Low Density Polyethylene
m	Burn Exponent
$\dot{m}$	Mass Flow Rate

MMH	Monomethyl Hydrazine
n	Burn Exponent
η^*	Normalized Characteristic velocity
NOAA	National Oceanic and Atmospheric Administration
P_c	Chamber Pressure
P&ID	Piping and Instrumentation Diagram
PET	Polyethylene Terephthalate
PMMA	Poly methyl methacrylate
ppm	Parts per million
PT	Pressure transducer
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
$\dot{r}$	Regression Rate
R_g	Specific Gas Constant
ρ_f	Fuel Density
SLS	Selective Laser sintering
T_0	Stagnation Temperature
TC	Thermocouple
USU	Utah State University

CHAPTER 1

INTRODUCTION

The typical in-space propulsion systems used by spacecraft guidance and

navigation systems have monomethyl hydrazine (MMH) as at least a partial fuel source.

This propellant is autocatalytic, meaning that it will ignite in the presence of most

oxidizers. MMH has a specific impulse of 225-250[1] and is highly toxic; so much so that

the Environmental Protection Agency (EPA) has given a peak exposure limit of 16 parts

per million (ppm) in a 10 minute time period[2]. It also has a vapor pressure of 49.6

mmHg, meaning that when equilibrium is reached the air above the fuel is greater than

one tenth or 100,000 ppm MMH. If anyone is in contact with this substance severe

reactions to skin, eyes and respiratory systems will occur. NOAA (National Ocean and

Atmospheric Administration) and the DOT (Department of Transportation) give MMH a

health rating of 4, the most dangerous rating, indicating possible lethality. They also list

ratings of 3 for flammability and 2 for instability. MMH has a flash point of 75 degrees

Fahrenheit in ambient pressure and can explode at higher temperatures and pressures.[3]

These problems have given the European Union cause to ban the parent chemical

hydrazine which has been classified as a carcinogen and is not legal to sell in Europe[4].

To prevent further use of this dangerous chemical, money and time have been invested

into finding any propellant combination that is less toxic.[1] In general, anything that

meets this description --less toxic than hydrazine--is considered green.

Solutions have been varied, but Utah State University has proposed hybrid rocket

technology as a possible solution. Hybrid rockets are good solutions because they have

the simplicity of a monopropellant system, have no risk of detonation, are throttleable,

and can stop and restart on demand[5]. The classical hybrid rocket has the oxidizer in fluid form and the fuel in solid form. A heat source causes the fuel to change into a gaseous form, then the oxidizer is added causing a flame to propagate down the fuel in the boar of the fuel grain inside the combustion chamber. At the small scales needed for spacecraft, the heat source can be electrically powered. Thus the valve for the oxidizer is the only moving part of the system, just as in a monopropellant system. The fuels in this study are common thermoplastics which have no DOT restrictions on handling. Fuel is burned off of the surface proportional to the amount of oxidizer added to the combustion chamber, so when a lower thrust is desired a lower amount of oxidizer is added. When there is no oxidizer added the combustion process stops. The rocket can then be relit using the methods used to ignite it in the first place, without requiring any physical resetting.

While researching various 3D printable plastics as alternatives to legacy solid propellant binders like hydroxyl terminated polybutadiene (HTPB) [6], the Propulsion Research Laboratory at Utah State University (USU) discovered that employing a type of additive manufacturing known as Fused Deposition Modeling (FDM) with certain printable materials like acrylonitrile butadiene styrene (ABS) allows manufacture of a structural matrix with unique electrical breakdown properties. This discovery has allowed the development of a unique on-demand ignition technology for hybrid rockets. [7]

Thermoplastic manufacturing techniques

ABS is a thermoplastic that will deform when sufficient heat is applied. Thermoplastic is the term given to all polymers that when heated the molecules are freed and can slide past each other. This movement allows the thermoplastics to be repeatedly formed and recycled time and time again. Examples of this type of plastics are poly

methyl methacrylate (PMMA) otherwise known as Plexiglas; acrylonitrile butadiene styrene (ABS); low density polyethylene (LDPE); high density polyethylene (HDPE); high impact polystyrene (HIPS); polyvinyl chloride (PVC); polypropylene (PP); and Polyethylene terephthalate (PET)[8]. Polymers that are not thermoplastics are referred to as thermoset. Thermoset polymers are created at the time that they are shaped. The molecules in the material create bonds that hold the structure together in all directions, forming a single large molecule. Examples of thermoset polymers are epoxy, polyurethane, and hydroxyl terminated polybutadiene (HTPB). These polymers will burn before they become malleable. In this thesis only thermoplastic polymers are used because of the ease with which they are formed into the shapes needed.

The processes commonly used to shape thermoplastics are extrusion blow molding, vacuum forming, injection molding, extrusion molding, and some forms of additive manufacturing.[9] Extrusion blow molding is useful for making bottles but not rocket fuel grains, and is therefore irrelevant to this study. Vacuum forming is what is typically used for making packaging and all kinds of thin plastic shapes. Because the fuel grains are not thin, this method is also a poor choice for this study.

Extrusion molding is a method used to create a part with a constant cross section. The process starts with plastic pellets in a hopper. These pellets then flow into an auger that pushes them into a heating chamber where they soften or melt. The pressure created by the addition of more plastic to the chamber pushes the plastic out a die that creates the final shape.[10] This method is a good candidate for creating fuel grains. The speed of this operation is directly proportional to the speed of the auger that is adding the plastic. The extruded plastics are nonporous meaning that the grains can be burned without an

exterior case. The plastic can be shaped into a tube with helical shapes on the interior using a mandrel. These helical shapes have been shown to increase the fuel regression of the hybrid rockets.[11] The current restriction in using this technology at USU is the size of the present extruding system, which has a 5/8ths of an inch diameter extrusion opening. The current size range for USU thrusters is between 1 and 4 inches in diameter.

Injection molding is where an auger pushes the plastic through a heater and out into a mold. The mold has the profile of the final shape and is removed after the plastic has cooled. The mold is typically made from high temperature materials using subtractive manufacturing methods such as milling and lathing. This method is faster than additive or subtractive manufacturing of individual parts. The process is typically factory-based and produces thousands of parts every hour.

The additive manufacturing methods that use thermoplastics are selective laser sintering (SLS) and fused deposition modeling (FDM). SLS melts the plastics to the point at which they fuse together into a solid piece that is in the shape sent to the printer by the computer. In FDM processing, a plastic filament is unwound from a coil that supplies material to an extrusion nozzle[12]. This nozzle is similar to the extrusion forming process, except the nozzle is smaller and contacts the surface of the part that it is building, adding a thin bead of material to the surface as moved by the computer numerically controlled (CNC) in three dimensions using a robotic mechanism. The nozzle is heated to melt the feed-stock, then the nozzle extrudes the filament in thin layers to build a structure according to a programmed design.

Because of this layered build pattern, when exposed to an electrostatic charge the layered structure containing electrically conductive particles allows a current to arc near

the surface, and the dissipated energy results in a surface char layer, or "arc-track." Joule heating along this surface arc-track allows sufficient fuel material pyrolysis so that combustion occurs spontaneously once a local oxygen partial pressure of approximately two atmospheres is reached. The high oxygen concentration is provided by an external oxidizer flow. [13]

Through the course of several research programs, this physical property has been developed into a simple, low-wattage, on-demand hybrid ignition system with a moderately-high Technology Readiness Level (TRL). Using this enabling discovery direct on-demand ignition has been demonstrated using ABS and gaseous oxygen (*GOX*) for multiple motor configurations with thrust levels varying from less than 5 Newtons to greater than 900 Newtons. [14][15] Figure 1 shows some of the scales of hybrid rocket

Figure 1: Scalable Thruster Sizes Possible Through Additive Manufacturing

fuels that have been successfully designed, fabricated, integrated, and test fired using FDM additive manufacturing and arc-ignition technology in the USU Propulsion Lab. Each of the pictured motors uses identical technologies with the only tangible differences being the scale of the motor mold lines. This reliable method of ignition was used as a

standard to compare the steady state burning of the new plastics without changing this important variable.

To date, the feed stock used to print this propellant has been based only on commercially available products. These commercial materials are optimized for strength and durability and not combustion performance. In fact, most of the commercial FDM feed stocks incorporate some measure of burn retardance. Thus, there exists the potential to blend the commercial feed stocks with enhancement materials that will significantly improve their performance as rocket fuels while still maintaining sufficient structural integrity.

Plastic Chemistry

ABS is a copolymer meaning that it is made when two or more distinct polymers are created in the same place and time. The monomers added before polymerization are: acrylonitrile which has a formula of C_3H_3N[16], 1, 3-butadiene with formula C_4H_6[17], and finally styrene with formula C_8H_8[18]. When these monomers polymerize they mix together and entangle themselves creating a blend that is inseparable but still a thermoplastic. The focus of this study is to improve the performance of the fuels burned. To find the most efficient hybrid rocket fuel, inspiration was taken from the combustion of hydrogen and oxygen, which produce the most thrust when normalized by the weight of propellant. The theory guiding material selection was that the most hydrogens per molecular weight is the most important parameter; then the least number of double and triple bonds is the second most important parameter for increasing performance. Looking at constituents of abs one of them was chosen for study. Butadiene has a higher hydrogen ratio than the others of 3/5, however it is not produced as a thermoplastic because it is too

soft to be useful. The next highest hydrogen ratio monomer is styrene with a ratio of 1/2. This plastic is commonly available as it has a recycle symbol 6 and can be purchased from commercial FDM filament vendors as HIPS. HIPS is sold as an expendable support material for home 3D printing, dissolving in limonene. The last is acrylonitrile which has a hydrogen ratio of 3/7. It also has a triple bond, which lowers the energy that can be extracted from this reaction. The monomer is formed from a vinyl group and a hydrogen cyanide. When incomplete combustion occurs hydrogen cyanide is the fifth most common product. Thus, the polymer chosen from the constituents of ABS was styrene.

Expanding the search to all available polymers the monomer ethylene has the formula C_2H_4 which gives two hydrogens for every carbon or a 2/3 hydrogen ratio. When this monomer is polymerized it creates polyethylene which has no double or triple bonds in its repeating structure and therefore is fully saturated with hydrogen.

Miscible and Immiscible Polymer Blends

Blending of plastic materials to form alloys is more complicated than just throwing the materials together into a pot and melting them. Very seldom do different types of polymers blend well together. Polymers that mix well together to form a homogeneous blend are referred to as "miscible." Polymers that do not mix well together are referred to as immiscible.

Miscible blends are rare because plastic molecules are so big that they have a high innate entropy. Miscible blends are formed when the plastic has electronegative groups, or when it is a copolymer with segments that dislike the presence of neighboring copolymer parts more than it dislikes the plastic it is being mixed with. These blends are

easily made using a solvent to form a stirrable liquid. Then the solvent will evaporate off leaving a homogeneous mixture.[19]

Immiscible blends are more common. When immiscible plastics are mixed the result is a two-phased alloy in which the minor blended component exists as small lumps within the major component. The plastics in this study are categorized into two families: the styrene family and the ethylene family. These families are immiscible with each other. When mixed, separated alloys always result.

Background on Hybrid Fuel Regression Rate Modeling

Hybrid rocket motors generate combustion through processes that are intrinsically linked to the oxidizer mass flow. Marxman and Gilbert[20], and Marxman et al. [21] initially developed a hybrid model where the rate of fuel pyrolysis results from diffusion of the radially-emanating fuel flow into the core oxidizer flow along a combustion layer or flame sheet. Figure 2 presents a schematic of this diffusion process.

Figure 2: Hybrid Rocket Motor Combustion Concept.

In the Marxman model, the rate of fuel pyrolysis results from a balance of all of the energy sources, where the net energy influx into the fuel surface equals the required enthalpy for pyrolysis of the fuel material. Marxman's model predicts that the radial

outflow of the pyrolyzed fuel pushes the combustion layer away from the fuel surface, insulating the fuel surface, reducing heat transfer, and decreasing the efficiency of the material diffusion at the flame sheet. This phenomenon is termed "wall blowing" and it is the main reason that hybrid fuels have low fuel regression rates compared to solid rocket propellants.

With the current state of the art, three distinct hybrid combustion regimes have been identified and characterized as a function of the oxidizer mass flux *Gox* through the fuel port. These combustion regimes are generally characterized by low, medium, and high mass flux levels. Table 3 summarizes the expected flow characteristics in each of these regions of operation.[22]

Table 1: Hybrid Rocket Combustion Characteristics as a Function of Oxidizer Mass flux

Mass flux Level G_{ox}	Low	Medium	High
Description	Radiative heat transfer dominates due to optical transmissivity of propellant particles	Convective diffusion dominates as well as fully turbulent heat and mass transfer	Gas-phase kinetics on chemical reactions become more apparent
Mass flux Level	Less than *15 g/cm²-sec*	*15-75 g/cm²-sec*	Greater than *75 g/cm²-sec*

To date, most hybrid rocket applications have concentrated on launch-operations, and as such, have predominately operated within the medium-to high level mass flux regimes.

In this flow regime, the high mass flux regime, the regression rate can be simply modeled by an exponential curve fit of the form

$$\dot{r} = a \ G_{ox}^{n} \ x^{m} \tag{1}$$

where G_{ox} is the oxidizer mass flux, x is the longitudinal position on the grain, a is a scale factor, and n, m are the burn exponents. Typically, the regression rate data tend to fit a trend where $m = n\text{-}1$.

The exponential-fit regression rate model of Eq. (1) assumes that the preponderance of the fuel regression rate results from convective heat transfer from the flame zone to the fuel wall, depicted in Fig. (2). Because the radiation heat transfer from the flame zone to the fuel wall are considered to be negligible, motor scale effects are minimal, and the burn exponents are typically treated as constants that are matched to a given propellant combination.

Oxidizer to Fuel Ratio Shift

The Oxidizer to Fuel Ratio (O/F) is a key parameter that determines the efficiency of hybrid fuel combustion. Hybrid motors tend to operate at "best performance" when O/F ratio operates slightly richer than the stoichiometric point where the reacting propellants are consumed entirely during the combustion reaction. Unlike solid propellant rockets, hybrid systems do not burn at a constant O/F ratio. Instead the O/F ratio shifts throughout the motor burn.[23] The burn exponent of each motor directly correlates to a shift in the oxidizer-to-fuel ratio (*O/F*) over the burn lifetime of each motor. For a single cylindrical fuel-port the *O/F* ratio can be written as

$$O/F = \frac{\dot{m}_{ox}}{\dot{m}_f} = \frac{G_{ox} A_c}{\rho_f \, \dot{r} \, A_b} = \frac{G_{ox} D}{4 \rho_f \, \dot{r} \, L} \tag{2}$$

and when Eq. (1) is substituted for regression rate, $\dot{r}$, the expression further reduces to

$$O/F = \frac{G_{ox}^{1-n} D}{4 \, a \, \rho_f \, L^{m+1}} = \frac{1}{4^n \, \pi^{1-n}} \left(\frac{\dot{m}_{ox}^{1-n} D^{2n-1}}{a \, \rho_f \, L^{1+m}} \right) \tag{3}$$

Analysis of Eq. (3) shows that when the burn exponent is greater than one-half ($n>1/2$), the O/F ratio is progressive and the motor burns increasingly leaner as the fuel grain burns and the port diameter widens. When the burn exponent is exactly equal to one-half ($n=1/2$), the burn rate is neutral and implies no O/F ratio shift during the burn. Conversely, when the burn exponent is less than one-half ($n<1/2$), the O/F ratio is regressive and becomes increasingly fuel rich as the port diameter widens. Clearly, a neutral burn exponent with no O/F shift is a very desirable burn property.

Table 2 summarizes curve-fit results for several different oxidizer/fuel combinations, the classical legacy fuel material hydroxyl terminated polybutadiene (HTPB) as well as those for newly emerged fuels based on paraffin wax. Also listed are burn parameters for hybrid motors using 3-D printed ABS fuel.[24] Finally, the exponential curve fit parameters for Low Density Polyethylene (LDPE) and GOX are presented. Hybrid rockets based on classical hybrid rocket fuels such as hydroxyl terminated polybutadiene and polyethylene have all exhibited burn exponents greater than 0.5[25]. Utah State University has measured FDM acrylonitrile butadiene styrene (ABS) to have a variety of burn exponents that vary from 0.2 to 0.46 depending on the motor size. [26] The ABS fuel motors exhibited a strong correlation to the motor diameter.

Table 2. Summary of regression rate fit-parameters for 5 commonly-used hybrid propellants, and GOX/ ABS for different motor diameters.

Propellant Combination	Oxidizer	Fuel	Scale factor, a $\left(\dfrac{cm^{2n+1}-s^{n-1}}{g^n}\right)$	Burn Exponent, n
1	Gox	HTPB	0.0144	0.686
2	LOX	HTPB	0.0146	0.681
3	LOX	HTPB-Escorez	0.0099	0.680
7	GOX	ABS (98 mm)	0.0480	0.460
8	GOX	LDPE (35 mm)	0.0542	0.3944[i]

Karabeyoglu, et al.,[27] have investigated a class of hybrid fuel materials based on paraffin wax formulations. These paraffin-based fuels melt before vaporizing, and a properly formulated wax mix produces a melt layer with a low viscosity and high surface tension. When the oxidizer flows at high speed over the upper side of the melting fuel surface, the liquid layer becomes unstable and minute surface waves are formed. The resulting fluid boundary layer is hydro-dynamically unstable and allows fuel droplets to be entrained into the core flow.

Uniquely, these authors have discovered that certain paraffin formulations, when burned with nitrous oxide, exhibited a burn exponent that was almost exactly n = 0.5;

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[i] See Figure 19 Curve Fits of the Regression Rate with Respect to the Oxidizer Mass Flux in this thesis for curve fit details

with the result motors based on these propellants exhibited no explicit O/F shift during the burn lifetime. Unfortunately, paraffin has several undesirable thermodynamic and structural properties that make it less than an ideal propellant.

Due to the fuel drop entrainment, significant unburned materials are ejected from the nozzle, and combustion efficiencies for paraffin-based fuels are inherently lower. More significantly, the properties that allow the fuel droplet entrainment in paraffin-based fuels introduce mechanical and structural problems that reduce the fuel grain integrity as the propellant burns. Solid phase paraffin is rather brittle and is easily cracked when subjected to launch vibration loads. As the paraffin melts the material softens and tends to flow and "sluff" under axial launch loads. Thus, paraffin based fuels require either special additives or a support lattice to keep the grain structure intact under launch loads.

Several strengthening materials have been tested in hybrid motors.[28] Polyurethane foam (PUF) strengthening structure shows promising results, but leads to heterogeneous fuel formulations that are difficult to manufacture with any degree of consistency. To avoid this problem and ensure paraffin-based formulations with sufficient elasticity to survive launch vibration levels, a miscible thermoplastic elastomer Styrene-Ethylene-Butylene-Styrene (SEBS) was tested as a strengthening alternative to PUF. Mixing SEBS into the paraffin fuel produces a homogenous fuel grain and offers significantly lower manufacturing costs. During the combustion of the homogeneous material the material melts; when using heterogeneous materials only the paraffin melts. Unfortunately, both the SEBS fuel additive and PUF structural support materials reduced the burn effectiveness and performance of the hybrid motor.

Blending Thermoplastic Polymers to Limit or reduce Hybrid Fuel O/F Shifts

This thesis will investigate an alternative approach to reducing the O/F shift by blending polymers with known burn properties to create a propellant that produces a burn exponent approaching the critical $n=0.5$ value. For example, as shown by Table 2 when LDPE is burned in the presence of gaseous oxygen (GOX), then a burn exponent of approximately 0.55 results. When 3-D printed ABS was burned with GOX in a similar motor, the resulting burn exponent was approximately 0.46. Thus, it is entirely feasible that a blend of materials would result in a burn exponent that can be engineered to approach the critical value of $n=1/2$, required for a static O/F value throughout the burn lifetime. This thesis will determine if the combining of plastics yields a linear change in this and other key properties. If such a linear blending trend results, then it may be possible to produce "designer" plastic alloys that optimize desirable thermodynamic or structural properties.

CHAPTER 2

DESCRIPTION OF MANUFACTURING METHODS AND TEST APPARATUS

In order to study the effects of various polymer blends that are not commercially available, non-standard polymers and blends of polymers first needed to be made into the appropriate feed stock shape for the 3D printer. A standard shape for the fuel grain was created using a computer-aided design program. The file was saved to a format that the 3D printer, a MakerBot® Thing-O-Matic[29], could use. The ABS fuel was then printed using FDM techniques, as described above.

Table 3: Materials studied in this research

ABS		
LDPE	28% LDPE 71%ABS	50% LDPE 50% ABS
HDPE		
HIPS	50% HIPS 50% ABS	

Pure Polyethylene Fuel Grain Manufacture

Purchased Low Density Polyethylene (LDPE) pellets were passed through a commercially-available Filabot® extruder[30]. The Filabot is a hobby scale extrusion forming machine that uses a circular die to create the 1.75 mm filament required for the MakerBot®. The filament was fed into the printer and was found to be flexible, so a flexible filament modification was made to the printer[31]. This modification consisted of adding a Polytetrafluoroethylene (PTFE) tube to the extruder system. The tube is 2 inches

long with a circular cut in it for the extruder gear to contact the filament inside. The

PTFE tube channels the filament from the inlet of the extruder past the gear and into the

heating chamber. This modification will wear out faster if stiffer plastics are used[32];

however, it works perfectly for pure HDPE and LDPE. The print temperature of the

LDPE was found using a printed thermal bench test[33]. This test consists of printing a

series of overhanging steps with a half inch bridge to a secondary strait tower. Each

increment decreases in temperature until the printer no longer extrudes plastic. The

quality of each of the steps is examined and compared to the other steps to identify the

best print temperature for each of the nonstandard filaments. LDPE and HDPE were

found to have an optimal print temperature of 205 degrees Celsius. This information was

programmed into the printer file and successfully printed fuel grains were produced.

Some difficulties were caused by the ignition sections because the extrusion speed was

difficult to set as the filament did not have a constant diameter. This caused the print to

be less dense than expected. When heat was applied the plastic melted and clumped

together with the arc moving through the molten clump. When the spark turned off the

plastic cooled and formed a non-conductive surface. An LDPE grain was tested in the test

combustion chamber with a carbon doped spark shelf, to decrease the arc track resistance.

This addition of carbon allowed the LDPE motor to light and the products of combustion

left carbon on the surface of the test grain, allowing for subsequent ignitions. The HDPE

grain had similar issues, however, in the one test preformed the carbon layer did not form

properly and no subsequent relight events could be performed. These problems led to the

use of a standard ABS ignition cap, with the plastic in question making up the main

combustion area, consisting of the bottom 4/5 of the original design. Rods of LDPE and

HDPE were ordered and machined or "subtractive manufactured" to the appropriate shape. This consisted of the using a lathe to turn the rod to the appropriate diameter and drilling the center port.

LDPE blend

Of the blends studied in this project, LDPE and ABS are immiscible with each other. When these plastics are placed in the Filabot, the resulting filament has the average hue of the constituents, is flexible and soft, and buckles under minimal load. It was discovered that the first pass through the Filabot typically produces a filament that, when crushed, forms curled sheets

Figure 3: Immiscible Plastic Filament Breaks into Small Sheets Because of Low Level Forces

about 1 to 2 cm in length. With each subsequent pass through the machine, the sheet sizes become smaller. However, as shown by Figure 3, the immiscible filament exhibits low resistance to shearing forces.

Once the sample filaments were extruded, an attempt was made to print fuel grains using the samples. Because of the flexibility of the blend, the MakerBot® extruder gear would buckle the filament when trying to extrude it. The same flexible filament modification was applied; however, the added friction caused the gear to shear through the filament, indicating that a different mechanical setup was required for processing this, and possibly most, immiscible plastic blends.

The solution to this problem was to make a mold for injection forming. This mold was made from a large piece of machined ABS, as shown in Figure 4. The Filabot extruder was used to push molten plastic into the mold. Then the cast rod was removed using conventional machining techniques. The rudimentary grains were machined to the same dimensions as the LDPE that came from the bar stock, and the same ABS cap design was used to ensure reliable ignition.

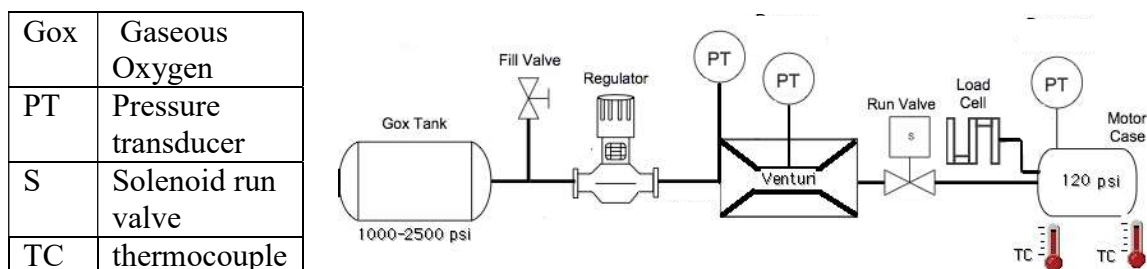**Figure 4: Mold for Casting LDPE/ABS Mix**

HIPS Construction

HIPS is sold as a standard printing material and has specifications for printing which are similar in temperature to ABS[34]. This allows for standard FDM printing like ABS. This plastic has similar electrical properties as ABS and sparks well every time ignition is tried. An excellent example of a miscible blend is High Impact Polystyrene (HIPS) and ABS plastic. When extruded out of the Filabot the plastics mixed easily and detection of grain boundaries was not noticeable. A blend of 50% HIPS and 50% ABS filament printed easily on the 3D printer. This blend also did not have any sparking issues and was used in this state for testing.

Hot Fire Test Setup

For the hot fire testing campaign a well-characterized 38-mm hybrid motor system was used. Figure 5 shows the test article assembly. Gaseous oxygen was used as the system oxidizer. The oxidizer was fed into the motor through a single orifice injector. The case was the Aerotech ARO-3812M bought from Apogee Components. It is made

from 6061 T-6 Aluminum with a wall thickness of 1.42mm, length of 8.23cm and a weight of 37.2 grams.

Figure 5: Hot-Fire Test Assembly

Instrumentation on the system included a load cell for thrust, a pressure transducer for the motor chamber, and a Venturi flow meter on the oxygen feed. A National Instruments Data Acquisition system was used to read the transducers and record the values measured for further calculations. By weighing the propellant grain before and after each burn, the instrumentation allowed for the calculation of both oxidizer and fuel flow rates, as well as thrust, total impulse, fuel regression rate, specific impulse and characteristic velocity. Figure 6 shows the Piping and Instrumentation Diagram (P&ID) of the test system

Gox	Gaseous Oxygen
PT	Pressure transducer
S	Solenoid run valve
TC	thermocouple

Figure 6: Piping and Instrumentation Diagram of Test Apparatus

Two graphite nozzle expansion ratios, 2.90:1 and 2.07:1 were available for these tests. The 2.90:1 ratio nozzle had a smaller throat area creating higher pressure in the chamber while burning. This higher pressure caused the oxidizer to change its mass flow as the chamber came up to pressure. The equilibrium pressure was determined by the amount of fuel regression at the current time. Each evaluation burn using this nozzle lasted one second.

The 2.07:1 ratio nozzle was designed to have a chamber pressure that causes a choked flow at the orifice injector. This allows for control of the oxidizer flow rate using an adjustable pressure regulator. The regulator holds a constant upstream pressure, keeping a steady oxidizer flow of 3.25 grams per second.

CHAPTER 3

HOT FIRE TEST RESULTS

An analysis program was created in LabView to calculate properties not directly recorded. The premise of the program was that what came into the rocket had to leave it. The compressible mass flow equations for choked and unchoked flow were used and integrated to find the total mass leaving the nozzle. The fuel mass leaving the motor was calculated by subtracting the total oxygen used from the total mass. This value was determined by the temperature, pressure and the ratio of specific heats caused by the combustion of the fuel. These parameters were set by the O/F ratio input, to look up the values needed at the pressures that existed in the motor at each time step. The temperature was further modified by the efficiency input parameter, by which the temperature was multiplied. A rough estimate of the O/F was made by dividing the total oxygen used by the total fuel loss measured. The efficiency was then adjusted until the calculated value and measured value for the amount of fuel used became the same.

The characteristic velocity (C^*) is a critical performance parameter that quantifies the velocity of the exhaust products when accelerated in an isentropic way to Mach 1. This allows the efficiency of various propellant combinations to be compared, independent of the motor geometry. As shown by Figure 7, for a given propellant combination, the optimal O/F ratio tends to exhibit a distinct peak as a function of the O/F ratio. The theoretical characteristic velocity (C^*_{th}) can be calculated from combustion product properties by Eq. (4)

$$C_{th}{}^* = \sqrt{\dfrac{R_g \cdot T_0}{\gamma \cdot \left(\dfrac{2}{\gamma + 1}\right)^{\frac{\gamma + 1}{\gamma - 1}}}} \qquad (4)$$

In Eq. (4) R_g is the gas constant for the combustion products, T_0 is the combustion flame temperature, and γ is the combustion product ratio of specific heats. In this formula the Generally, the achieved performance of the propellants is lower than the theoretical value, and the actual characteristic velocity (C_{ac}^*) can be calculated from measured data by:
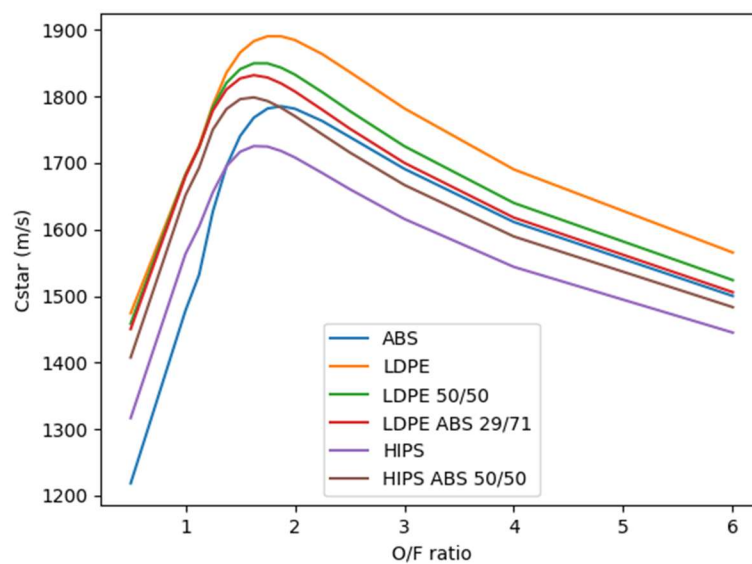
$$C_{ac}{}^* = \dfrac{P_c \cdot A^*}{\dot{m}} \qquad (5)$$

In Eq. (5) P_c is the pressure in the combustion chamber and A^* is the nozzle throat area, and $\dot{m}$ is the propellant mass flow. The continuity equation can be rearranged, assuming that the gas is calorically perfect, that the flow is isentropic and the velocity of the flow is the same as the speed of sound in the flow, to give equation 4 is equal to equation 5.
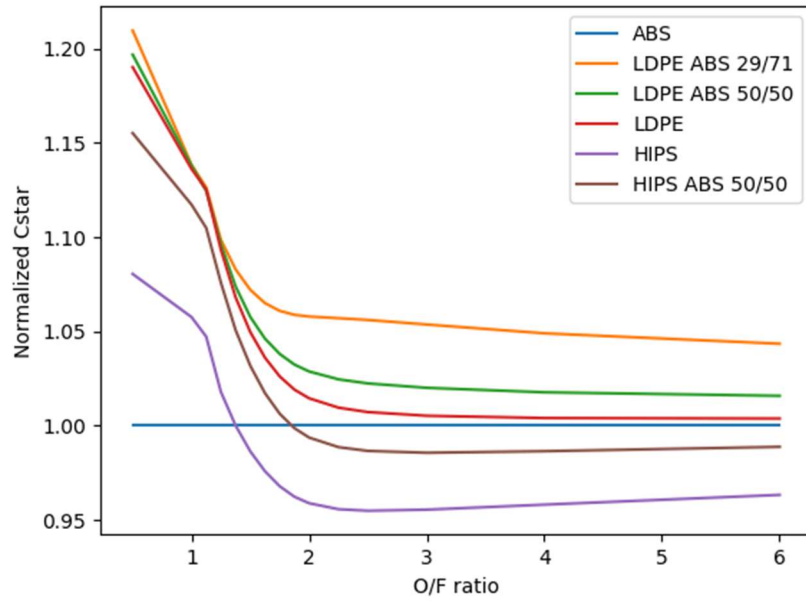
Figure 7 compares the theoretical C^* values for a variety of printable plastics and plastic blends when burned with GOX. These values were calculated using the industry standard NASA chemical equilibrium program "Chemical Equilibrium with Applications," (CEA).[35] These materials include ABS, LDPE, a 50/50 mass-blend of LDPE and ABS, a 29/71 blend of LDPE and ABS, High Impact Polystyrene (HIPS), and a 50/50 mass-blend of HIPS and ABS.

Taking ABS as the reference standard, Figure 8 compares the C^* curves for each of the plastics of Figure 7, normalized by the C^* curve for ABS. Except at very low O/F

ratios, the LDPE based plastics exhibit superior performances. The HIPs and HIPS blends

exhibit the poorest performances.

Figure 7: Theoretical C* Curves for Various Propellant Burns at 120 PSI

Figure 8: Normalized Characteristic Velocities for the Various Plastics Used
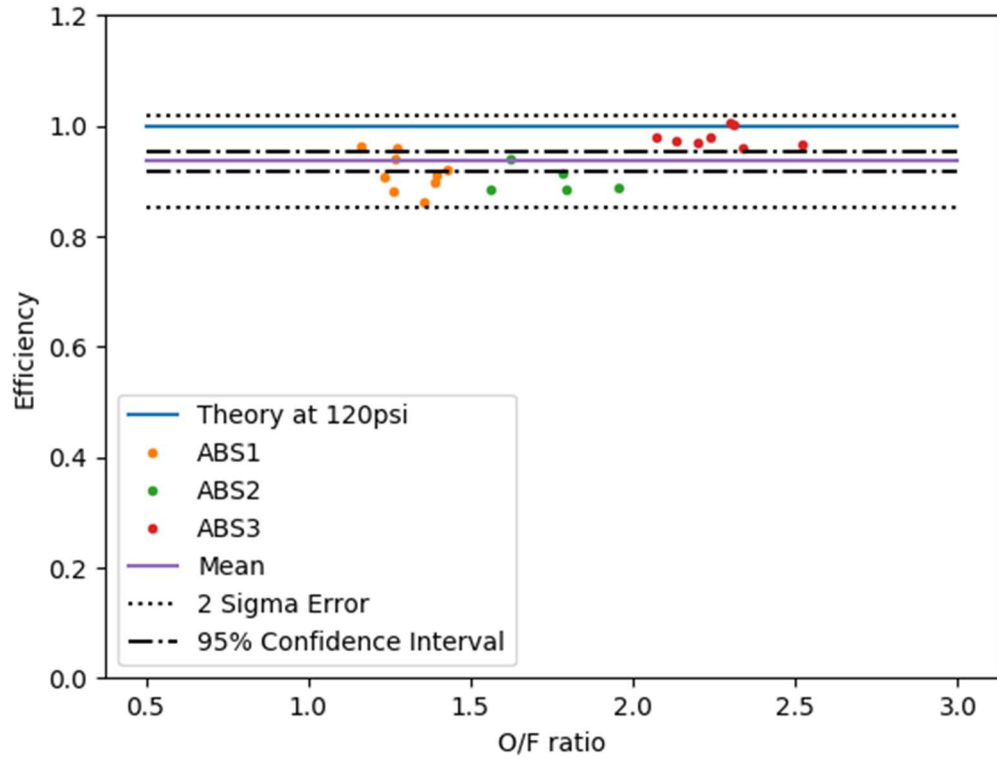
ABS Control Tests

In practice the achieved C^* is always lower than the theoretical value, and the ratio of the achieved and theoretical values

$$\eta^* = \frac{C_{ac}^{\ *}}{C_{th}^{\ *}}.$$

(6)

η^* is a measure of the combustion efficiencies. Figure 9 plots the achieved combustion efficiencies resulting for 22 different GOX/ABS fuel burns. Here the mean combustion efficiency is calculated as 93.6% with a standard deviation of 4.1%. ABS 1, 2 and 3 are the names of the test runs and are made from the same materials and are tested in identical setups except as noted. ABS 1 and ABS 2 had the different nozzle sizes which changed the O/F ratio, but did not change the efficiency of the burn. ABS 3 had a longer burn time

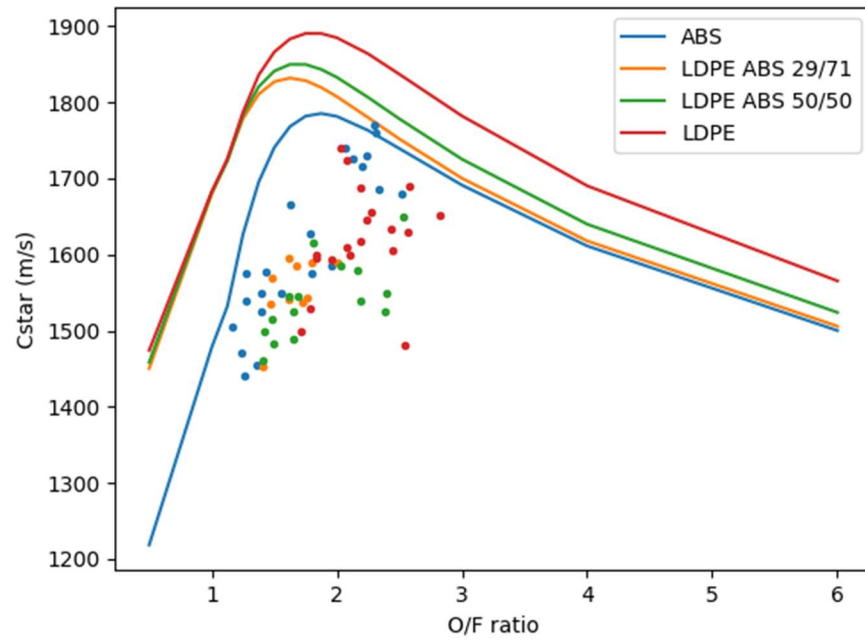which caused a slightly improved efficiency and the O/F ratio to be shifted to a higher value.

Figure 9: Ensemble Efficiency of Three different Hybrid Motors Burned with ABS and GOX.
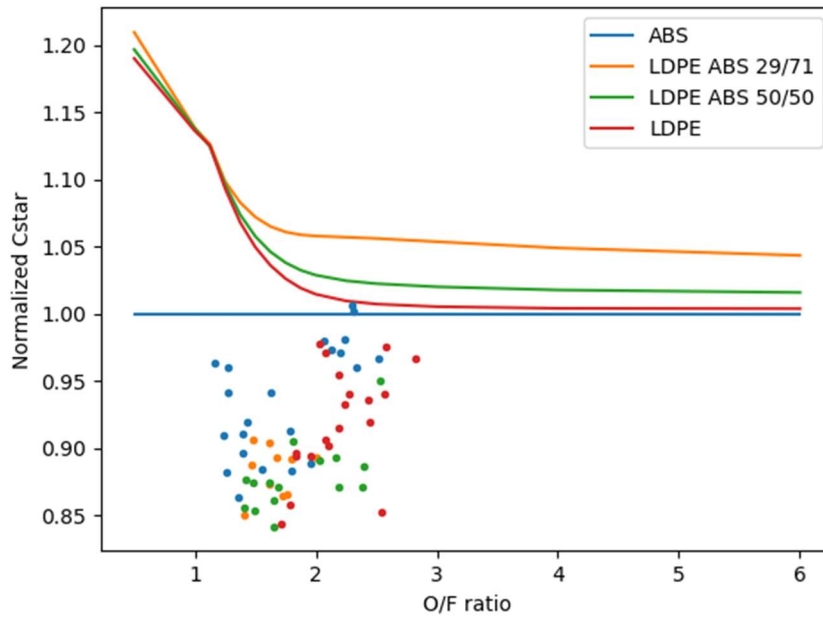
LDPE and ABS Continuum Blend Tests

As described earlier LDPE was investigated as a potential additive because of its theoretical performance-enhancing abilities. Figure 10 presents these test results. Here the calculated C^*_{ac} values blended propellants are compared against the theoretical curves. Figure 11 plots the normalized C^* values.
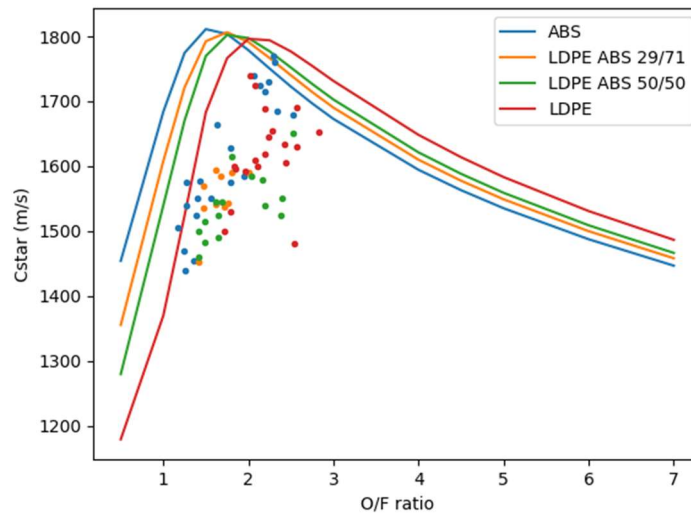
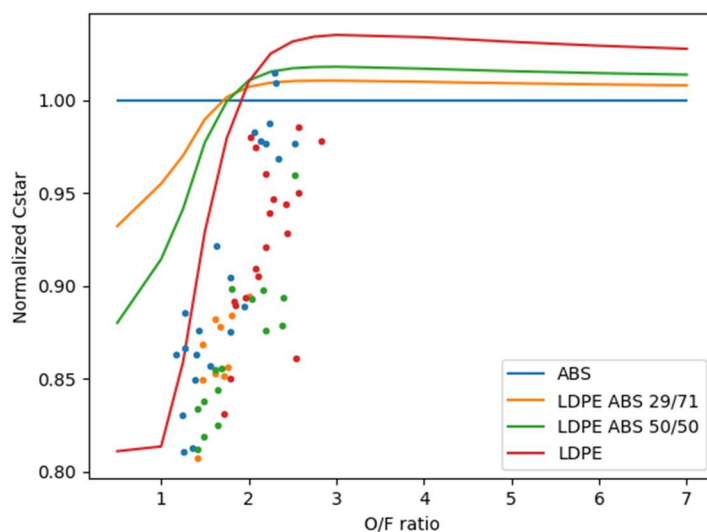**Figure 10: LDPE/ABS C^* Values Change with LDPE Concentration**

Figure 11: Normalized Characteristic Velocity of ABS/LDPE Concentrations

Originally, the achieved C^* data were found to lie significantly below the theoretical values; however, it was discovered that the original theoretical calculations did not consider the energy of polymerization and the resulting predictions were optimistically high. When the energy of polymerization was factored into the theoretical calculations, the achieved and theoretical comparisons become significantly better. Figure 12 and Figure 13 show these revised comparisons. The energy-of-polymerization corrections procedures are described in the next section.

Figure 12: Characteristic Velocity Comparisons for of ABS LDPE with Theoretical Curves Adjusted for Energy of Polymerization at 120 psi

**Figure 13: Normalized ABS LDPE Characteristic Velocity Comparisons
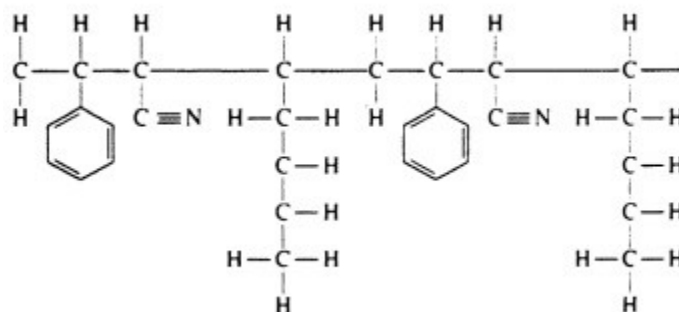Theoretical Curves Adjusted for Energy of Polymerization.**

Polymerization Impact on Combustion Properties

The NASA program Chemical Equilibrium with Applications (CEA) calculates

the important values using the Gibbs free energy. Gibbs free energy uses the enthalpy of

formation and the change in entropy of the molecules present. The non-polymerized

version used the enthalpy of formation values found on the NIST website.[36]

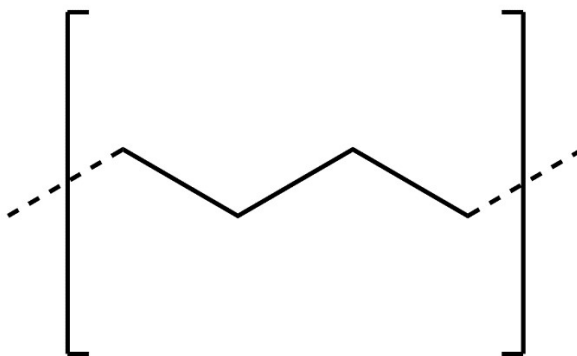**Table 4: Enthalpy of Formation for Various Monomers Relevant to This Study**

Molecule	Enthalpy of Formation (kJ/mol)
Acrylonitrile	179.7[37]
Butadiene	111.9[38]
Styrene	146.9[39]
Ethylene	52.4[40]

From these values the enthalpy of formation can be calculated using bond energies. To find the bond energy the shape of the polymer must be correctly constructed. The molecule for ABS that is used in this thesis is shown in Figure 14
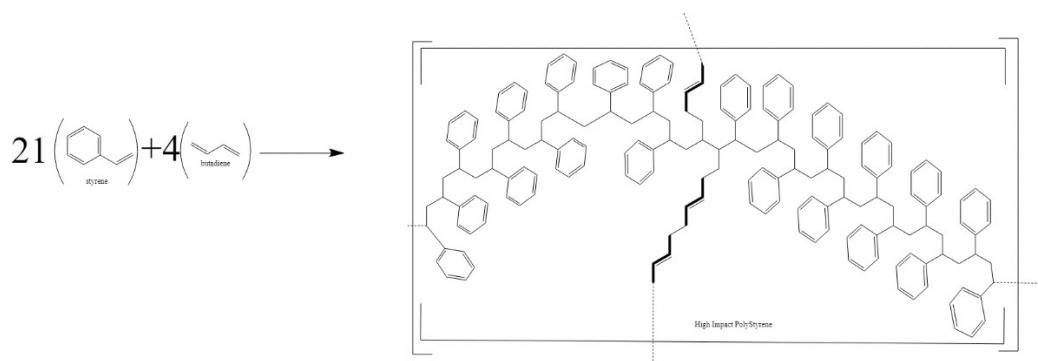

Figure 14: Two Units of ABS Molecular Structure [41]

In this structure 4 carbon-carbon single bonds were formed and 3 carbon-carbon double bonds were broken. For every mole of single bonds made 347 kJ of energy is released, and for every mole of double bonds broken 614 kJ of energy is absorbed by the reaction.[42] However, a single bond is almost always formed when this happens, giving a net absorbance of 267 kJ for every mole of double to single bond reactions. This bond energy is added to the constituents to give a final enthalpy of formation for abs to be 553.6 kJ/mol. For ethylene, the structure is shown in Figure 14 and has 1 double bond to single and one single bond formed to give an enthalpy of formation of -27.6 kJ/mol. This value is in the same range as found from other sources. The final value used in this thesis was -25.6kJ/mol.[43] This significantly lowers the expected energy of combustion leading to a lower characteristic velocity.
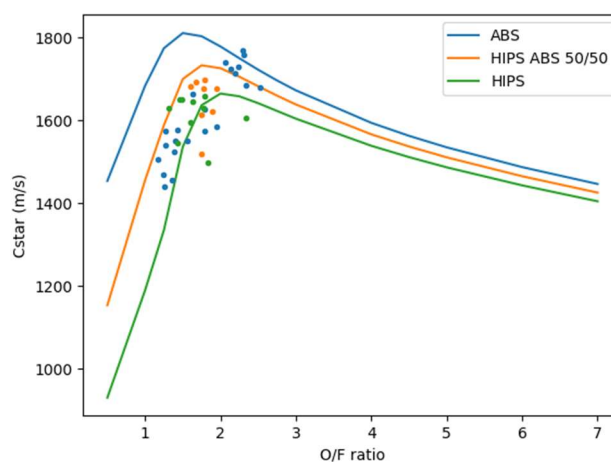
Figure 15: Two Units of Polyethylene Molecular Structure.

The last polymer studied was HIPS. The structure chosen for this molecule is shown in Figure 16. The ratio of styrene to butadiene was hard to find as it is proprietary information; however, one patent held by Asahi Kasei Corp[44] stated that HIPS was composed of "styrene having dissolved therein 2 to 20% by weight of one or more polybutadienes". In this thesis the styrene to butadiene ratio will be 90 to 10 by weight. The structure also was difficult to discern so the structure used in this thesis is shown in Figure 16. The mole fraction of reactant is 21 to 4 because styrene is about twice as heavy as butadiene.

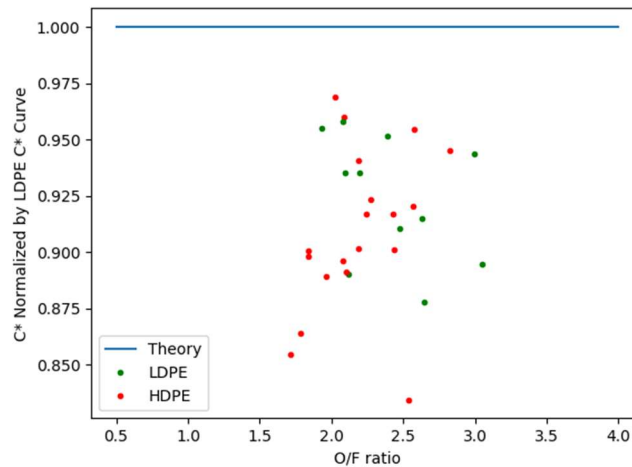**Figure 16: HIPS Molecular Structure and Formulation.**

This molecule has long chains of polybutadiene going vertically and poly styrene going horizontally. The crosslinking of this molecule is widely debated, so the structure above may be over crosslinked. The process to find the energy of formation was the same as above, yielding -7169.7 kJ/mol with the molecular formula of $C_{184}H_{192}$. This can be simplified to $C_{23}H_{24}$ with an enthalpy of formation of -899.6 kJ/mol. These results were used to as inputs to CEA which generated the needed values for the theoretical C* equation and the analysis program. The new C* curves for HIPS are shown with the experimental data in Figure 17. The experimental data lines up well with the polymer values. Because the theoretical values for HIPS are all less than ABS this fuel is not a good candidate for replacing ABS.

Figure 17: HIPS ABS C* Comparisons

LDPE and HDPE Comparisons

As testing continued the differences between Low and High density polyethylene were discussed. It was decided to use the same combustion properties for HDPE as LDPE and look at the change in efficiency to determine if there was a difference in those properties. In Figure 18, the tests that were performed show that the higher density polyethylene has similar properties to the lower density version.
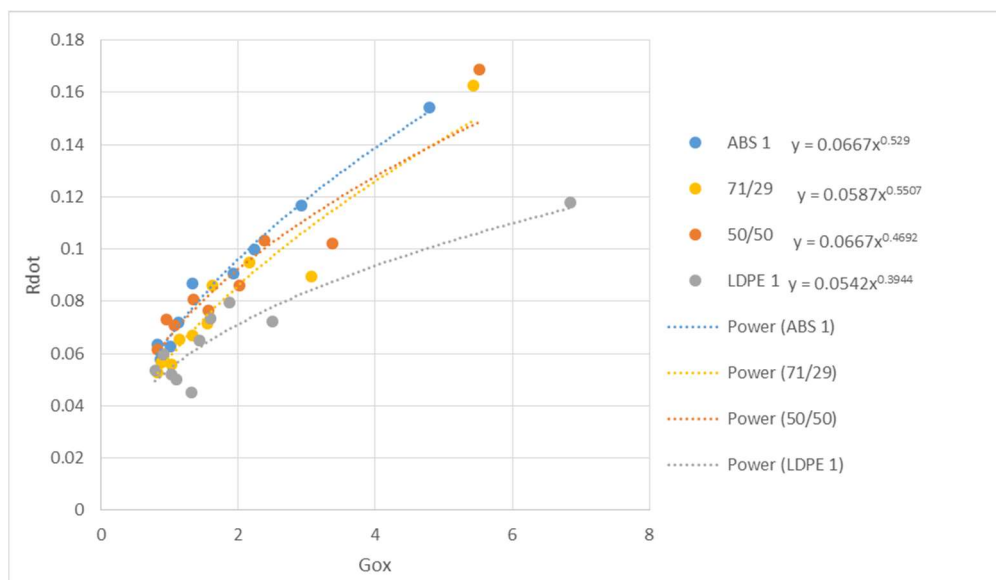

Figure 18: Normalized Characteristic Velocity of LDPE and HDPE Compared to Theoretical Values for LDPE

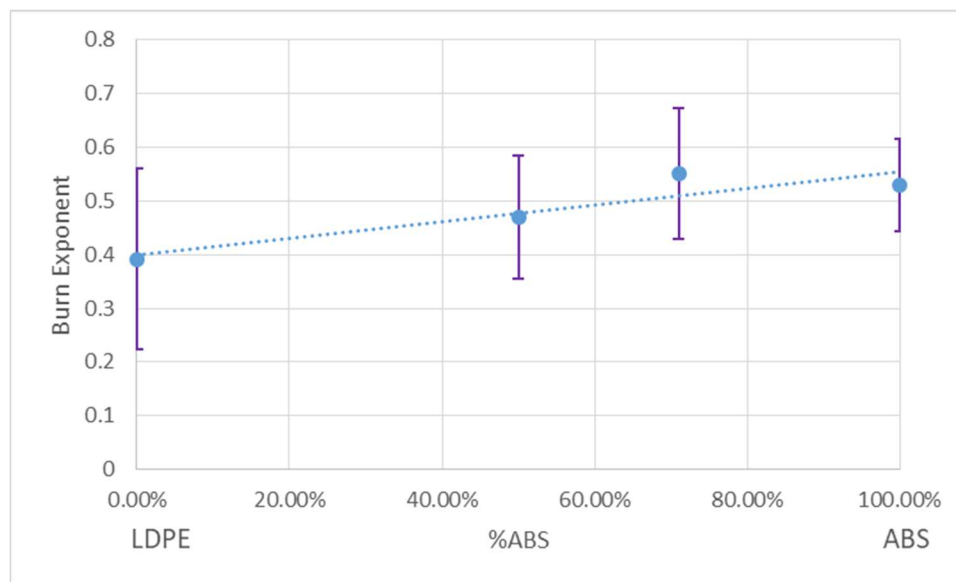**Finding Optimal Performance through Modeling Combustion**

As described in the introductory sections of this paper a major objective of this research was to develop a 3-D printable plastic alloy that exhibited good combustion properties but also resulted in a critical burn exponent of $n = 1/2$. At this critical value the motor would not exhibit an O/F shift over the burn lifetime. Assuming a linear property

trend, models predicted that a blend consisting of 71% ABS and 29% LDPE by mass would achieve this result.

Figure 19 compares the resulting regression rate curves developed from a series of experimental tests using 100% ABS, a 29/71 LDPE-ABS blend, a 50/50 LDPE-ABS blend, and 100% LDPE. Figure 20 plots the resulting burn exponents as a function of O/F ratio with each of the plotted data points showing 95% confidence error bars. The resulting curve clearly demonstrates that the 4 fuel materials "bracket" the critical $n=1/2$ value, and that a linear trend exists. However, the predicted optimal 29/71 blend resulted in an exponent of 0.55 rather than the targeted 0.5 value. Based on the data of Figure 20, the optimal "zero-shift" fuel blend would consist of approximately 60% ABS and 40% LDPE. Figure 21 shows the results of a similar analysis that was performed using the HIPS/ABS fuel blends. The HIPS/ABS fuel blend was not able to achieve the critical $n=1/2$ exponent value. In fact, adding HIPS to the fuel blend lowers the burn exponent, indicating a plus-rich O/F shift with time.
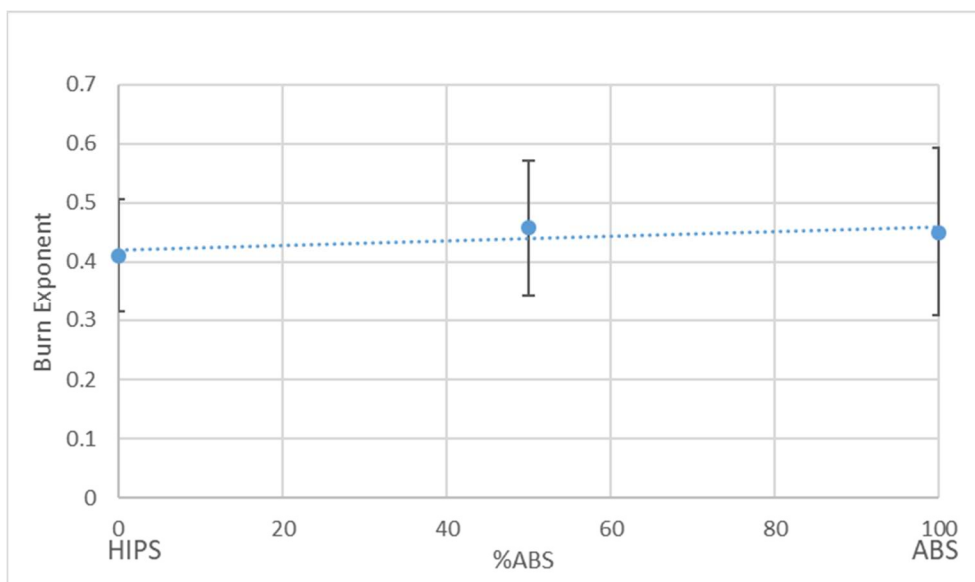
Figure 19: Curve Fits of the Regression Rate with Respect to the Oxidizer Mass Flux

Figure 20: LDPE/ABS Burn Exponent Correlated with ABS Fuel Mass Fraction

Figure 21: Adding HIPS to Fuel Lowers the Burn Exponent

In spite of the pre-test modeling errors, the major thesis of this research is proven. The linear trend of Figure 21 shows that it is entirely feasible that the burn properties of the plastic alloys can be engineered to give the desired low O/F shift result. The addition of LDPE to ABS not only shapes the burn profile; but, as exhibited by Figure 12 and Figure 13 also has the effect of improving the propellant performance. This result is a "win-win" scenario.

CHAPTER 4

CONCLUSION

This study has surveyed the uses of thermoplastic blends to replace hydrazine in

small spacecraft applications. The blends were thought to be a method of adding to the

chemical energy of the system. The extra hydrogen was theorized to give the system

better efficiencies. Methods of manufacture were created to solve some of the difficulties

associated with making the blended fuel grains. The results of the testing show that the

blends did not increase the efficiencies of the rockets, because the energy of

polymerization was far greater than expected. Also the theory that the fuel could be

blended to achieve a burn desired exponent was shown to have significant limitations

because in the tests conducted for this thesis the burn data has wide scatter. In the future

new blends should be tested to characterize the burn properties as a function of blend

constituents.

Manufacturing Processes

Manufacturing methods discussed in this thesis are new alternatives for the hybrid

rocket community. The FDM method is a way to create complex internal structures with

standard filaments that can be blended with miscible plastics. This allows for designing

potentially better rocket fuels; however, this has drawbacks in that scalability is not

profitable for industry. Each new blend will need to be approved for printing in each new

facility. The cost of integrating new filament types in standard business printing setups is

large and unlikely to occur for use as a rocket fuel. The blending of filaments is in the

range of people who hobby 3D print; however, the standards of manufacture that the

aerospace industry expects will not be created for this type of work, because of unique

settings and quality differences in each of the printers used to print non-standard filaments. Therefore, at this time, it is not a wise choice for the hybrid rocket community to invest in this method of manufacture.

The extrusion molding process is the best for making immiscible plastic parts. It is a fast process that can produce thousands of parts. For a lab-scale operation the amount of time and cost prohibits the use of this technology. Furthermore, the mixed plastics would not be allowed in a commercial setup due to contamination issues. Therefore the use of non-standard plastics in commercial injection molded fuel grains should not be used at laboratory scales.

Polymerization energy

The heat released when forming polymers cannot be used to propel gases out of the rocket. Each bond made is energy lost and each bond that is formed during polymerization adds energy to the combustion process. After including this factor the characteristic velocity drops, decreasing performance. With the error found in the measurements of each of the fuels in this study, even the theoretical values do not exceed the efficiency of the standard ABS plastic.

Future Work

The burn exponent in the hybrid rocket model was looked at to try to establish the 0.5 condition to prevent shifting properties as the burn continues. The data in this study showed that the recommendation of 71% ABS did not perform as predicted, and that a 40/60 blend would more closely achieve the desired critical burn exponent value. However, in spite of the pre-test modeling errors, a major conclusion of this work is that the burn exponent of the fuel blends can clearly be manipulated and that the original goal

of developing "designer blends" that minimize the O/F shift is entirely feasible. Future work should include the study of LDPE mixes at 5% increments to search for the point of no O/F shift. The HIPS/ABS blends should also be studied at 5% increment mix ratios. Until the variation in the data can be explained, none of the plastic blends will have superior combustion compared to the current ABS plastic fuel.

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