

Review on the Fundamentals of Polymer Combustion and Flammability Characteristics for Hybrid Propulsion

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Abstract Hybrid Propulsion is an attractive alternative to conventional liquid and solid rocket engines. This is an active area of research and technological developments. The potential wide application of the hybrid engines opens the possibility for safer and more flexible space vehicle launching and manoeuvring. The fundamental combustion issues related to further development of hybrid rockets are discussed in the present paper. The emphasis is made on the properties of the potential polymeric fuels and their modification. The fundamentals of polymeric fuel combustion and the flammability Characteristics are discussed.

Keywords: Polymer Combustion, Flammability Characteristics, Hybrid Propulsion, polymeric fuels, Combustion Characteristics

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1. Introduction

In recent years, the revived interests in hybrid propulsion systems have become apparent [1]. It is well known that traditional solid and liquid rocket engines suffer from certain drawbacks. For example, liquid systems, while providing high performance, require quite complex and costly plumbing. Solid systems, on the other hand, are inherently unsafe due to uniform mixing of fuel and oxidizer. Besides, there are difficulties with thrust control and termination in such engines.

Hybrid systems aim to provide alternative to both above-mentioned technologies by executing combustion in diffusion mode, and therefore with initial separation of fuel and oxidizer. In a classical design, solid fuel and liquid oxidizer are used. Such arrangement provides operationally flexible, safe and reasonably priced solution. A variety of solid fuels, such as metals and hydrocarbons, and a wide range of liquid oxidizers can be used.

At the present, various modifications of the basic idea have been proposed, such as reverse hybrid, solid-fuel ramjet, tribrid, and the ducted rocket. Reverse hybrids use solid oxidizer and liquid fuel. The solid oxidizer has to be mixed with either an inert filler or a small percentage of fuel. The tribrid systems use bipropellant combustion with a third component being metalized fuel. The solid-fuel ramjet utilizes a solid fuel and rams air as an oxidizer. Finally, the ducted rocket uses fuel rich solid propellant to generate a flame, which mixes downstream with the ram air to achieve optimum performance.

The classical hybrid rocket propulsion possess a number of very attractive features. Its advantages over

solid and liquid propulsion technologies can be summarised as follows [2]:

- Operating issues. Engine throttling and shutdown are significantly simplified by this technology. Throttling is achieved by liquid flow rate modulation, which is considerably simpler in this case compared to a liquid rocket engine where two liquid streams have to be synchronised. Termination is accomplished by cutting of the liquid flow rate. This opens possibility of quick and robust abort procedure.
- Safety. The solid fuel is inert, therefore it can be manufactured, transported and handled safely. In addition, because an intimate mixture of oxidizer and fuel is not possible, it is non-explosive.
- Cost. Operational costs are obviously of great importance. In this regard hybrid systems benefit from simplified manufacturing procedures, due to their inherent safety. Consequently, fabrication (and therefore operation) costs are reduced.
- Choice of fuel. A wide range of easily available solid fuels can be used, giving wider design flexibility compared to liquid or solid motors. Combustion performance of solid fuel is also more reliable since in a hybrid mode it is not sensitive to fuel-grain cracks.

As for the disadvantages, the major of them areas follows [2]:

- Combustion efficiency is lower compared to liquid or solid engines, due to non-premixed nature of combustion.
- Low regression rate. This is a major obstacle for a wide use of Hybrid Rocket Engines. Essentially non-energetic nature of fuels gives rise to requirement of very high regression rates, in order to achieve

required thrust. In practice it leads to necessity to use multiple ports, and other modifications that complicates design.

- Ignition transient and thrust response to throttling is slower than in solid or liquid motors.

Despite the above-mentioned shortcomings, hybrid propulsion technology enjoys quite versatile application potential. They include, but are not limited to, for example, sounding rockets, auxiliary power units, tactical rockets, space engines, thrust augmentation, and large launch boosters. In particular, research on Hybrid Propulsion Engines is concentrated within several research clusters around the world [2].

As indicated, enhancement of regression rates is a primary obstacle for wide spread of technology. Consequently, significant research efforts are currently concentrated in this area.

Further progress requires, first of all, advanced understanding of combustion properties of various polymeric fuels, and potential ways of their modification. Secondly, regression rates and overall Hybrid Engine performance are determined by the global dynamics of combustion process in the engine. This process also has to be understood quite well. Computational Fluid Dynamics (CFD) modelling becomes increasingly important tool for such understanding [2]. The challenge of predicting combustion process in Hybrid Engine (Figure 1) from the first principles is quite challenging.

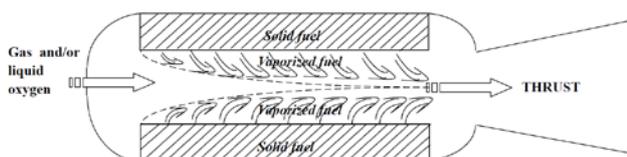


Figure 1. Schematic of the combustion process in a Hybrid Rocket Engine

According to the above considerations, the purpose of this paper is to discuss properties of polymeric fuels, relevant to their implementation in hybrid propulsion. The paper is arranged in the following manner: fundamentals of polymer combustion are discussed as follows.

2. Flammability Characteristics of Polymer

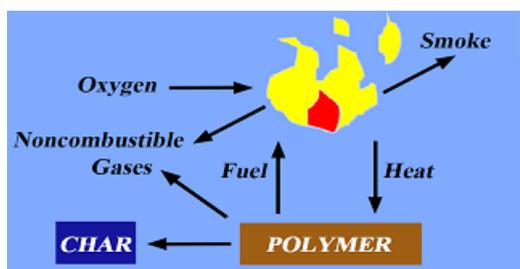


Figure 2. Combustion cycle of Polymer

When subjected for a sufficient length of time to an external heat source, organic polymeric materials undergo thermal degradation, generating various products in varying concentrations over different temperature ranges. The nature and amount of the volatile combustible products depend on the chemical structures of the

polymers undergoing degradation. If the gaseous mixture resulting from the mixing of degradation volatiles with air is within the flammability limits, and the temperature is above the ignition temperature, then combustion begins (Figure 2). The combustion of a polymeric material is a highly complex process involving a series of interrelated and/or independent stages occurring in the condensed phase and the gaseous phase, and at the interfaces between the two phases [3].

The chemical reaction steps leading to the formation of volatiles may be homolytic or heterolytic, i.e., be radical or ionic [4]. The three overall processes implicated in the thermal degradation of most thermoplastic polymers are as follows [2]:

- Random chain cleavage followed by chain unzipping is characterized by high monomer yields and a slow decrease in the molecular weight of the polymer, e.g., poly (methyl methacrylate), poly (α -methylstyrene), polystyrene, polytetrafluoroethylene.
- Random chain cleavage followed by further chain scission is characterized by very low monomer yields amongst the degradation products and a rapid drop in molecular weight, e.g., polyethylene, polypropylene, poly (methylacrylate), polychlorotrifluoroethylene.
- An intra-chain chemical reaction followed by cross-linking reaction and formation of a carbonaceous residue, or random chain cleavage. This generates a relatively high yield of volatiles from the intra-chain reaction, but produces little monomer, and produces, no, or only a very slight, reduction in molecular weight during the initial stages of degradation, e.g., poly (vinyl chloride), poly (vinyl alcohol), polyacrylonitrile.

In some cases, several of these processes occur simultaneously, depending on the sample size, heating rate, pyrolysis temperature, environment, and presence of any additives. Although polymer degradation schemes can be greatly altered by the presence of comonomers, side-chain substituents, and other chemical constituent factors, the ultimate thermal stability is determined by the relative strengths of the main-chain bonds. Many additives and comonomers employed as flame retardants are thermally liable; as a result the thermal stability of the polymer system is reduced. In order to reduce the observed effects of the flame retardant additives on the thermal stability of the polymeric materials, more thermally stable and hence inherently fire-resistant polymers are of increasing interest.

Thermosets, on the other hand, owing to the highly cross-linked three dimensional structural attribute, have much lesser propensity to thermally degrade (especially at lower temperatures) to yield flammable volatiles. The rupture of bonds does not initially generate combustible gases, and carbonisation is usually promoted. Ladder polymers, in which the main chains are bonded together at each repeat unit by a cross-link, serve the same purpose. Polymers with relatively strong main chain bonds and/or with aromatic and heterocyclic structural units, are also inherently thermally stable [5]. There are several classes of polymers, such as polyphenylenes, poly(p-phenylene oxide)s, polybenzimidazoles, polybenzamides, that have relatively high thermal decomposition temperatures coupled to low levels of fuel production on degradation.

The ability to form char is related to the flammability of a polymer. The higher the amount of residual chars after

combustion, the lower the amount of combustible material available to perpetuate the flame and greater is the degree of flame retardance of the material [6]. Therefore, one of the ways to achieve high degrees of flame retardancy or non-combustibility of polymeric materials is to increase the amount of char produced on combustion. This is illustrated by the fact that aromatic polymers, e.g., polycarbonate and poly (phenylene oxide), have lower flammabilities than purely aromatic polymers. The greater thermal stability of cross-linked and aromatic structures in thermosets gives rise to greater degree of condensation into aromatic chars, and therefore only relatively low levels of flammable gases are available to feed the flame.

As a consequence of the complex nature and pure reproducibility of fire, there are many techniques for estimating the flammability characteristics of polymeric materials. The most widely used laboratory test is the Limiting Oxygen Index (LOI) measurement, which is a very convenient, precise and reproducible technique [7]. The LOI is a measure of the volume percentage of oxygen in a mixture of oxygen and nitrogen gas stream that just supports candle-like combustion of a polymer mixture. This value therefore enables the combustibility of a polymer to be expressed and compared with that of other material (Table 1) [2]. However, the relatively high concentrations of oxygen used in making measurements of LOI are unrepresentative of a real fire, and generally there is a lack of correlation between most of the small-scale test and full-scale tests [2].

Table 1. Limiting oxygen indices of some polymers

Polymer	LOI
Polypropylene	18
Poly (butylene terephthalate)	20
Poly (ethylene terephthalate)	21
Nylon-6,6	24
Nylon-6	21
Cotton	16
Polyester fabric	21
Wool	24
Polyacrylonitrile	18
Polyaramid	38

Table 2. Some representative peak heat release rates obtained by cone calorimetry

Polymer	Peak Heat Release Rate (kW m ⁻²)
Polypropylene	1095
Poly(butylene terephthalate)	1313
Isophthalic polyester	985
Nylon-6,6	1313
Nylon-6	863
Wool	307
Acrylic fibres	346

Medium-scale experiments, based on oxygen consumption calorimetry, such as the cone calorimetric measurements, are generally considered to generate parameters that are more relevant to real fire scenarios involving polymeric materials [8]. The measured parameters include time to ignition, heat release rate, total heat released, mass loss rate, effective heat of combustion, smoke specific extinction area, smoke production rate and total smoke production (Table 2) [2]. The central objective in carrying out the oxygen consumption calorimetric techniques is to obtain parameters that represent the true nature of the fire hazards possessed by the materials under investigation such as the heat release rates (as well as the total heat released) and production of smoke and CO [9].

The measurements should be carried on sufficiently thick samples to avoid thermally thin behaviour, by and using sample holder with minimum heat losses so as to minimize the effects of the apparatus employed on the values of the parameters obtained. This will ensure that the values collected through such measurements are in turn more global in nature [10].

Similar parameters, as obtained through a cone calorimeter, can be collected from much lesser quantities of materials (ca. 5 mg or so), with a Pyrolysis Combustion Flow Calorimeter (PCFC) which is based on the principle of oxygen depletion calorimetry [11]. Here the influences of sample size, thickness and morphological features are essentially eliminated. Accurately weighed solid samples (ca. 5 mg) are first heated to about 900°C at constant heating rate of 1 Ks⁻¹, in a stream of nitrogen flowing at a rate of 80 cm³ min⁻¹. The thermal degradation products, thus obtained, were then mixed with a 20 cm³ min⁻¹ stream of oxygen prior to entering a combustion chamber maintained at 900°C. Each sample is run in triplicate and the data obtained are averaged over the three measurements [12]. The instrument also generates plots of the Heat Release Rates (HRR) against the temperature and gives values for the maximum amount of heat released per unit mass per degree of temperature (i.e., heat release capacity measured in Jg⁻¹ K⁻¹), the latter being a reliable indicator regarding flammability of a material (Table 3) [13].

Table 3. Heat release capacity, total heat released, and char yield of selected polymers

Polymer	Heat Release Capacity (J g ⁻¹ K ⁻¹)	Total Heat Released (kJ g ⁻¹)	Residue (wt.%)
Polypropylene	1571	41.1	0
Polyethylene (LDPE)	1676	41.6	0
Polystyrene	927	38.8	0
Poly (butyleneterephthalate)	474	20.3	1.5
Poly (ethyleneterephthalate)	332	15.3	5.1
Polymethylmethacrylate	376	23.2	0
Polyoxomethylene	169	10	0
Polyvinylchloride	138	11.3	15.3

Net heats of combustion of polymeric materials are a good indicator of their combustibility (assuming complete combustion), and therefore a good indicator of the total heat released. Heats of combustion are usually measured using an oxygen bomb calorimetric technique, where the sample is burned in an atmosphere of excess and hyperbaric oxygen [14]. A similar parameter can be also deduced from PCFC runs (Table 4) [15].

Table 4. Net heats of combustion of selected polymers by PCFC and oxygen bomb calorimetry

Polymer	Net Heat of Combustion (kJ g ⁻¹)	
	PCFC	Oxygen Bomb
Polyethylene	44.1	43.3
Polystyrene	40.1	39.8
Polycarbonate	29.1	29.8
Poly (butyleneterephthalate)	26.3	26.7
Poly (ethyleneterephthalate)	23.2	21.8
Polymethylmethacrylate	25.0	25.4
Polyoxomethylene	15.0	15.9

3. Representative Polymer Combustion

3.1. Polyolefins

Polyolefins are among the most important polymers in terms of production volume. By copolymerization of ethylene and propylene with higher n-olefins, cyclic olefins, or polar monomers, product properties can be varied considerably, thus extending the range of possible applications [16]. Polyethylenes (PE) are manufactured in the largest tonnage of all thermoplastic materials. Several well-established families of polyethylenes are now available on the market, each having a different molecular architecture and different behaviour, performance and applications, e.g., low-density polyethylene (LDPE), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), very low-density polyethylene (VLDPE), and high and ultra-high molecular weight polyethylenes [17]. The main structural features of that determine the properties of PE are the degrees of short- and long-chain branching, the average molecular weight and polydispersity [18].

Generally, polyolefins are highly flammable. The principal mechanism of thermal degradation being homolytic chain scission, followed by inter- and intramolecular chain transfer, resulting in the formation of volatile fragments [19]. The long-chain fragments and the soot-like products formed by cyclization dehydrogenation, contribute to smoke development. Carbon dioxide and water are also formed during combustion. Polyolefins burn readily in air (LOI = 18) with melting and dripping, and produce little or no residual char [20].

3.2. Acrylics

Acrylic polymers are obtained from derivatives of acrylic and methacrylic acids; the group includes also their copolymers with various vinylic and allylic monomers. The largest applications of acrylic polymers in terms of tonnages used are in moulded and fabricated plastic articles of many kinds made from poly(methyl methacrylate) (PMMA) [21]. On heating PMMA undergoes extensive chain unzipping or depolymerisation to produce quantitative yield (>90%) of monomers and is, as a consequence, highly flammable (LOI = 18). The oxygen of the ester group assists complete combustion of the pyrolysis products and is the reason for the low smoke production of the burning polymer. The material melts and volatilises so that no residue remains [22].

3.3. Elastomers

The common form of polyisoprene is cis-1,4-polyisoprene, which occur in the latex of many plants and trees as natural rubber [23]. The trans isomer can be isolated from some plants as gutta percha or balata. Both these forms, and their derivatives, may also be synthesised by the use of stereospecific catalysts. Generally, natural rubber and other related polydienes such as poly-1,3-butadienes burns readily in air (LOI = 17) [24].

4. Enhancement in Degradation and Regression Rates in Hybrid Fuels

The overriding principle here is to obtain, as fully as possible, the structure property relationships of some novel materials to be tested as components of hybrid fuel systems for rocket propulsion that have enhanced

degradation/regression rates as compared to the unmodified counterparts. Synthetic strategies for making these materials could include copolymerization reactions, grafting reactions and other post-chemical modifications on preformed precursor polymers [25,26,27].

The characterization techniques employed, on recovered and purified materials, could include [2,28,29,30]:

- Spectroscopic (NMR and FT-IR) and elemental analyses: high field (500 MHz) solution state ¹H- and ¹³C-NMR for deciphering the microstructures of the polymers (this includes tacticity, composition, monomer sequencing, minor structures including structural defects, etc.). Limited, but complementary, information regarding the structural features of the polymer could also be obtained from the FT-IR spectra and heteroatom elemental analyses.
- Chromatographic and related techniques: these are primarily aimed at obtaining the molecular weights and their distributions. For polyolefin based-polymers, optionally melt-flow index measurements could be carried out.
- Thermo-gravimetric analyses (TGA): TGA runs need to be carried out on ca. 10-15 mg of the resin in nitrogen, air and in oxygen atmospheres, say, at 10°C min⁻¹, and from 30 to 1000°C. The idea behind these runs is to get the general thermal- and thermo-oxidative degradation profiles of the material (i.e., under different oxidative atmospheres).
- Differential Scanning Calorimetry (DSC): here, milligrams of samples are heated in sealed aluminium pans, under a nitrogen atmosphere and usually at a heating rate of 10°C min⁻¹, up to a point where substantial thermal degradation starts. This is a very useful technique that often yields information regarding melting behaviours, glass transition temperatures, etc. that the material might undergo under the heating conditions imposed.
- Parallel Plate Rheometry: here again the sample, ideally in the shape of thin films, is heated whilst sandwiched between two heated parallel plates, at the same time a sinusoidal mechanical stress is applied. Generally, this constitute a good method for determining the moduli of elasticity (store and loss), the glass transition temperatures, and more importantly the melt flow behaviour of the resin.
- Combustion Bomb Calorimeter: this instrumentation is used to determine the heats of combustion (ΔH_{comb}) of the resin. This parameter is a good indicator of the maximum heat out put on complete oxidation of the polymeric material in question.
- Pyrolysis Combustion Flow Calorimetry (PCFC): this piece of instrumentation, often dubbed as the micro cone calorimeter, produces plots of Heat Release Rates against time, as well as generates parameters like the heat release capacity on milligrams of a material (i.e., the maximum amount of heat released per unit mass per degree of temperature (Jg⁻¹ K⁻¹, is a material property that appears to be a good predictor of flammability).
- Hyphenated techniques: attempts to identify the volatiles formed from thermal degradation of the materials could be made by hyphenating the TGA to

an FT-IR or to a GC/MS. Such hyphenated technique is also available in a larger scale that, primarily, involves two consecutive tube furnaces in connected in series. Optionally, some of the gaseous-products formed upon degradation, in ambient atmosphere, collected through by using proprietary containers, will be subjected to GC/MS.

The main areas of interest here are as follows [2,31,32,33,34]:

- Try to find the influence of the molecular weights (i.e., the chain lengths, or the degree of polymerization), structural defects and other microstructure on the thermal/thermo-oxidation behaviours.
- Gauge the “ease” of thermal/thermo-oxidative degradation, and thus hopefully leading to correlations with the regression rates.
- Estimate the influences of combustion energetics (such as the heats of combustion, the heat release and its rate, residue left), the effects of the heteroatom bearing groups/transition metal (Si and B, or V), the morphology, melt-drip behaviours, etc. on the overall performance of the material as a rocket fuel d) carryout further chemical modifications, in the wake of the results obtained through c, with a view to improving the overall performance of the polymeric substrates as components of hybrid rocket engine systems.

5. Conclusions

The main objective of the paper has been review of fundamental problems related to further polymer fuel application in Hybrid Rocket Engines. Fundamental flammability characteristics of polymeric fuels have been discussed. Success of polymer fuel applications to Hybrid Propulsion depends on further improvement of their combustion characteristics. In the context of hybrid propulsion, this effectively means enhancement of regression (and therefore burning) rates. This problem is not an easy one since estimations suggest that regression rate needs be increased dramatically (possibly by an order of magnitude). Chemical fuel modification is one promising route to overcoming the problem. Some suggestions for potential modifications of basic polymer fuels have been presented.

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