

Novel, High-Regression Rate Fuels For Hybrid Rocket Motors

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Abstract

A series of fuels for hybrid rocket engine of our design were developed and tested. Poly(methylene oxide), paraffin wax and epoxy-based compositions were made, characterized by means of measured thrust, c^* , I_{sp} , thermal stability (DSC, TG) and chemical composition (FTIR). Various techniques of fuel casting which enabled us to obtain free of cracks and defects grains of paraffin wax and homogenous emulsion of paraffin in epoxy resin have been proposed.

1. Introduction

The work presented here has been performed by the students from AGH Space Systems Student's Association. Our team has been working on small sounding rockets, which we use to test our CanSat lander, perform in-flight measurements and achieve higher and higher apogees. Our most current project is focused on construction of a 2-stage sounding rocket, capable of beating Poland's current 12.3 km altitude record for amateur rocket flight. All of our rockets up to now have been propelled by N₂O hybrid rocket engines, especially a small 'B2' engine. Likewise, the main stage of our new rocket is also designed to be a larger version of B2. Since the very beginning we have been using commercially available poly(propylene) water pipes as fuel. PP was chosen because of its low price, suitable dimensions and heat of combustion even as high as a 45.8 kJ/g [1]. However, because pipe industry exclusively utilizes the high-molecular-weight isotactic PP, the material is quite resistant to decomposition and the molten phase is highly viscous, which limits the regression rate of the fuel. High viscosity of the melt limits the entrainment mechanism, as the mass flux associated with the transportation of unevaporated droplets has been found to be inversely proportional to the viscosity [2]. Because of these inherent drawbacks of highly-crystalline polymers, we came up with several ideas for high regression rate fuels not containing them, and designed in a way which, in our opinion, would promote faster regression.

Poly(oxymethylene) was chosen as a very promising candidate for a high regression fuel, because of its ability to almost entirely decompose to gaseous formaldehyde. Thermal degradation proceeds upon heating even at temperature as low as 87 °C. However, to enable technological processing of POM, end-chain hydroxyl groups are protected, which leads to more heat resistant, highly crystalline polymer [3]. Because the POM pipe was purchased as an off-the-shelf product, thermal analysis have been performed to estimate its melting point and heat and temperature of depolymerization. High density of crystalline POM (1.41 g/cm³) and 53 % (w/w) oxygen content are features that made it a very interesting material, worth of further research. What is more, to the best of our knowledge, there are no scientific reports on POM application in hybrid rocket engines.

Poly(ethylene) is usually used as a reference fuel for hybrid rockets engines. It has even higher combustion heat compared with poly(propylene) i.e. 47.7 kJ/g [1]. However, since Ziegler-Natta catalyst development, most of the PE products which are available on the market are made by coordination polymerization, which results in high molecular weight and leads to the same drawbacks as in the case of PP. It has been reported in literature that it is beneficial for the fuel regression to use low-MW versions of PE, namely paraffin waxes. They provide a compromise between low molten phase viscosity and high heat of combustion. However, during our preliminary tests, paraffin (candle wax) was found to be ejected through the nozzle in unburned form. What is more disturbing, explosion-like work has been noticed for this kind of material during experiments. In order to tackle these problems, we have decided to use pure

poly(ethylene) wax (PEWAX). It is a cheap, nontoxic oligomer, characterized by a convenient melting point of around 100°C, density of 0.91 g/cm³ and low viscosity in molten state – usually sold as wax candle hardener. It is much more resistant to deformation and has been found as a good additive for improving tensile strengths of low-melting paraffins [4]. However, as PE polymers exhibit one of the largest density changes upon liquid to solid transition, there is a largely unsolved problem of cracking of cast samples. We hoped to alleviate this problem by incorporating a layer of non-woven PP fabric, spirally-wound around the core when casting PEWAX.

Another type of researched fuels were epoxy resin based compositions. It was speculated, and verified by DSC, that the amount of the hardener used for curing can affect the heat of combustion. This led us to use a lowered amount of hardener for our compositions, resulting in less-densely crosslinked material. We have also examined the addition of an oxidizer (ammonium nitrate) and liquid fuel (refined mineral oil). Use of appropriate surfactant turned out to be essential for liquid emulsion preparation. We also came up with a unique idea of impregnating natural fiber fabrics with our compositions, and forming the fuel grains by winding them around a solid core. The presence of fabric was hoped to introduce turbulence and help to expose larger surface area during burn time.

In this paper we report the results of thrust and pressure measurements for eight different fuel compositions.

2. Materials and methods

Tab. 1. Prepared fuel samples

Sample	Composition	Method of preparation	Density [g/cm ³]
1	polypropylene	-	0.9
2	polyoxymethylene	-	1.5
3	polyethylene wax wrapped on polypropylene fabric	wrapped	0.9
4	83% EPIDIAN 601/17% TFF	casting	1.2
5	76% EPIDIAN 601/15% TFF/9% NH ₄ NO ₃	casting	1.2
6	53% EPIDIAN 601/16% TFF/31% liquid paraffin	casting	1.0
7	83% EPIDIAN 601/17% TFF/jute	wrapped	0.7
8	53% EPIDIAN 601/16% TFF/31% liquid paraffin/jute	wrapped	0.9

Eight fuel compositions were prepared. All grains were made to match the B2 engine dimensions (Fig. 2.). All blocks cast or wrapped by us (except PEWAX) were made to fit inside PVC pipe, to ensure mold release and tight fit in the chamber. PP and POM were used as-received, and PEWAX grain has been cast directly to a 40 mm aluminum pipe, since no problems with release were expected. All compositions and their basic properties (sample No., composition, preparation method, density) have been presented in table 1.

Fuel blocks 3, 4, 5, 6 were prepared by casting, where the liquid composition was poured into a vertical mold of our design. In the case of PEWAX grain (no. 3, Fig. 1.) the aluminum core was first wrapped with a few layers of thin polypropylene fabric. The fuels were left to fully set and harden overnight and then taken out, cut to length and weighed.

Fuel blocks containing jute fabric (i.e. samples no. 7 and 8) were prepared in a following way. First, a liquid composition was prepared, and dry jute fabric was spread out on a flat surface. Next, the composition was slowly poured all over the fabric, ensuring good infiltration. Finally, an aluminum pipe serving as a port template was placed at the edge, and the soaked fabric was tightly wound in a parallel fashion around it. The assembly was secured with stretch wrap and left to harden overnight. The amount of fabric was chosen so that it would fit snugly inside the PVC pipe, but to ensure perfect fit and account for unevenness of the surface, the block was glued inside with epoxy.

2.1. Materials

2.1.1. Epoxy resins

The composition for these experiments was a commercially available Epidian 601 composition, consisting of Bisphenol A + epichlorohydrin condensation product and a reactive solvent for viscosity control - cresyl-glycidyl ether. TFF epoxy hardener was used, which consists of phenol and triethyltetraamine reaction product with formaldehyde. Both materials came from Ciech Organika Sarzyna, Poland. “Light epoxy” refers to a composition made with Epidian 601 and TFF hardener added in amount equal to 66% that of recommended by the distributor.

2.1.2. Other materials

Jute fabric used was plain weave raw jute, typically used for vegetable sacks, with area density of 270 g/m^2 . Polyethylene wax (PEWAX) had melting point at $94 - 100^\circ\text{C}$ and was purchased as candle wax hardening additive. Ammonium nitrate was purified by recrystallization, dried, ground and coated with acetone-based spray paint to prevent water uptake and limit reactions with epoxy resin. Liquid nitrous oxide was purchased from Air Liquide.

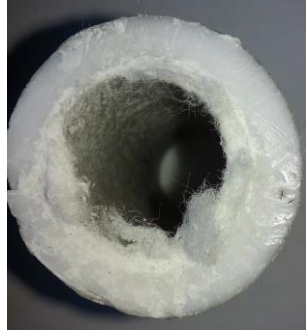


Fig. 1. PEWAX cross-section

2.2. Methods

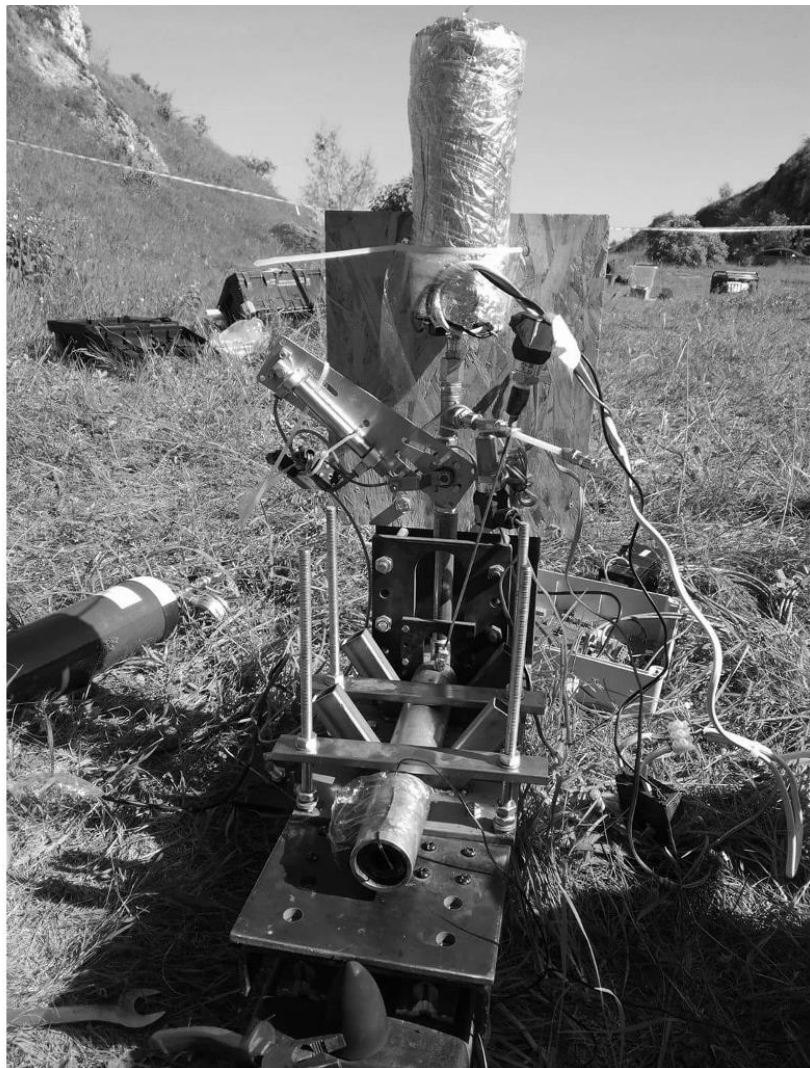
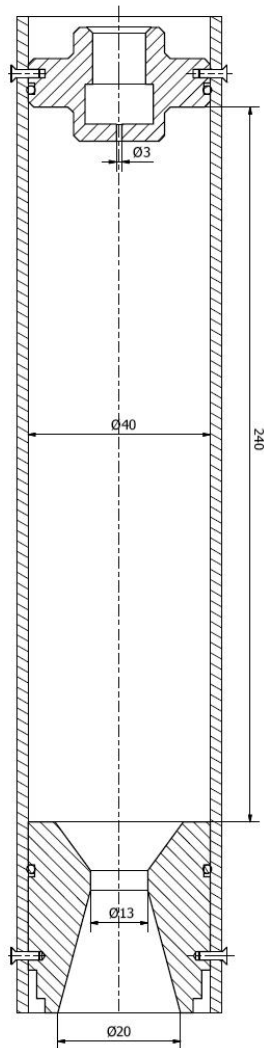


Fig. 2. B2 engine dimensions (left) and static test stand (right)

The main point in evaluating obtained fuel materials was a static test on experimental stand of our design and construction. The system allowed for measurement of thrust, chamber pressure and N₂O tank pressure. The static test stand is based on bridging plate to which the engine is mounted. The thrust is measured with a strain gauge. All the sensors were hooked up to a custom electronic sensing board (sampling frequency 600 Hz). Pressure sensors were placed near the injection area inside the chamber and a few centimeters downstream from N₂O tank valve to estimate the pressure inside the tank. The tank was connected to the injector by a joint with ball valve operated by pneumatic arm.

Thermogravimetry and Differential Scanning Calorimetry measurements (TG/DSC) were performed on NETZSCH STA 449 F3 Jupiter, under Ar atmosphere. Fourier Transform Infrared Spectroscopy (FTIR) were carried out on Bruker 70V, using KBr pellet technique. The SEM measurements were done with Nova NanoSEM 200 FEI apparatus, using LVD detector.

3. Experimental

Tab. 2. Experimental test parameters

Sample	N ₂ O mass [g]	igniter delay [s]	engine working time (liquid N ₂ O) [s]
1	320	2.5	1.5
2	312	2.0	1.6
3	373	2.0	1.8
4	370	2.0	1.6
5	330	3.0	1.6
6	340	2.5	1.6
7	422	2.5	1.6
8	380	2.5	1.5

Prior to the engine ignition on the test stand, the 0.35 L aluminum pressure tank was weighed empty, filled with liquid N₂O from a large storage steel cylinder and weighed again to estimate the mass of the oxidizer for each test. The full tank, after being mounted to the stand was thermostated at 30°C by means of an electric heater. The igniter, composed of a ~20 g block of epoxy-based pyrotechnic mass and resistance wire was placed inside the port, close to the injector. The electronic system was programmed to first set off the igniter, wait a prescribed amount of time, and open the pneumatic N₂O valve, allowing the tank to be completely emptied. Igniter burn time was set taking into account the type of fuel, how easily it decomposes and whether or not there is a danger of excessive melting. This and other experimental parameters are listed in Table 2.

4. Results and discussion

4.1. Static engine test

The thrust curves on Fig. 3. show that all the burns lasted for around 3 - 4 seconds; however, the engine only worked on liquid N₂O for below 2 seconds in each case. The initial tank pressure was always above 60 bar, indicating proper operation of the heating device and thermostat.

The most noticeable difference between some of the thrust-time curves are the initial spikes. Their presence indicates large amounts of combustible gases in the chamber prior to N₂O injection. Here, the formation of formaldehyde during decomposition of POM is clearly visible. What is surprising, is the fact that almost every epoxy-based composition also produced very significant spikes, often lasting quite a bit longer than in the case of POM. The only epoxy composition without a spike is composition 5, containing ammonium nitrate. This is possibly due to a fairly large moisture content, introduced during grinding. Also, surprisingly, the PEWAX grain produced no spike. This most likely can be attributed to a high heat of fusion of paraffins, and generally to the fact that in this case the generation of gases is a result of a phase transformation, rather than an irreversible decomposition. This can be further backed up by looking at the case of PP, which decomposes rather than melts, and which has a visible spike in its thrust curve. The thrusts (during the liquid phase interval), are relatively stable, with slight downward trend, indicating n parameters in regression rate law to be equal, or greater than 0.5. This is fortunate, as such behavior is more suitable for long-burning main stage engines.

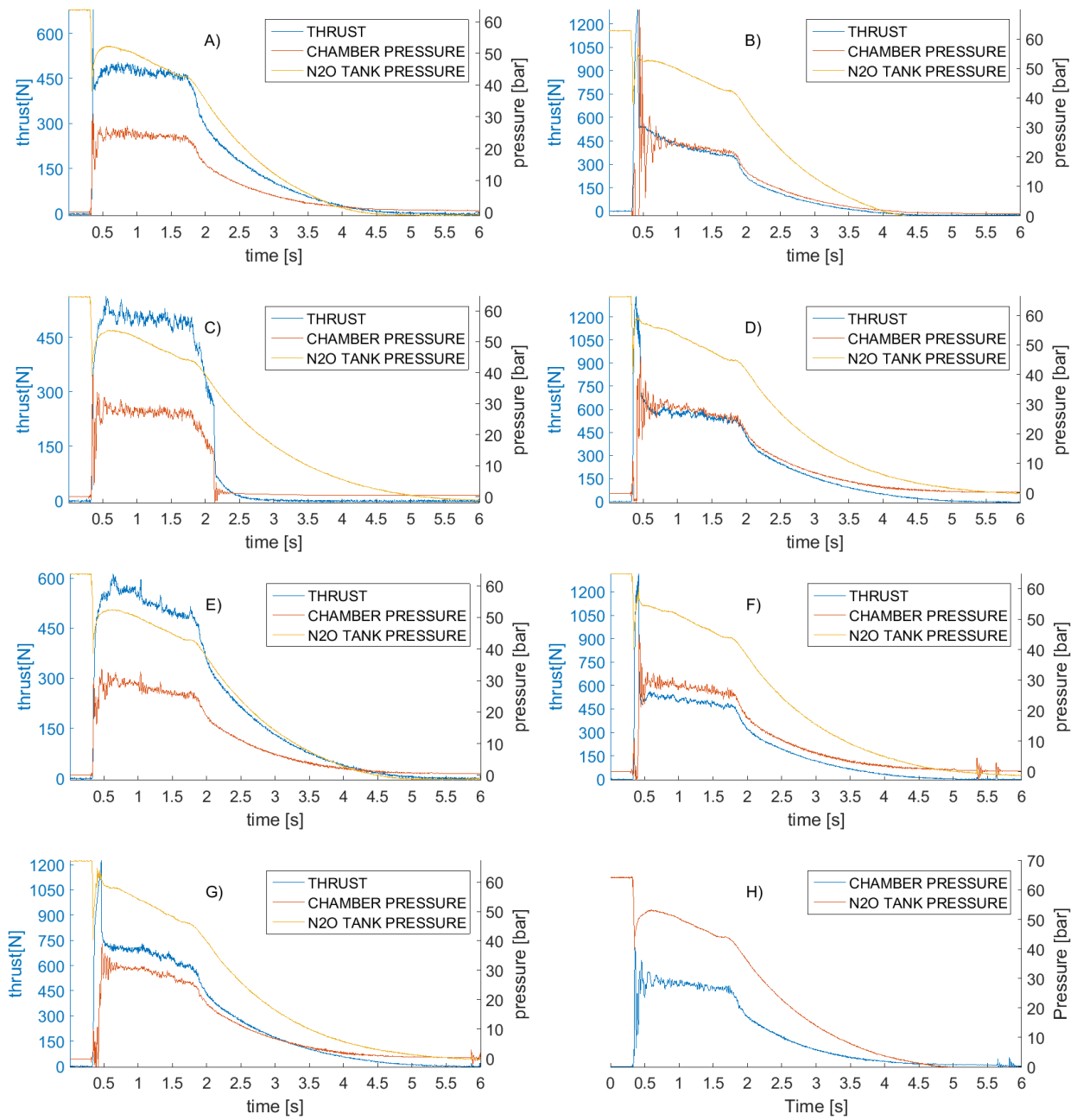


Fig. 3. Thrust and pressure in time. A-H correspond to 1-8 compositions respectively. Thrust for fuel 8 has not been measured.

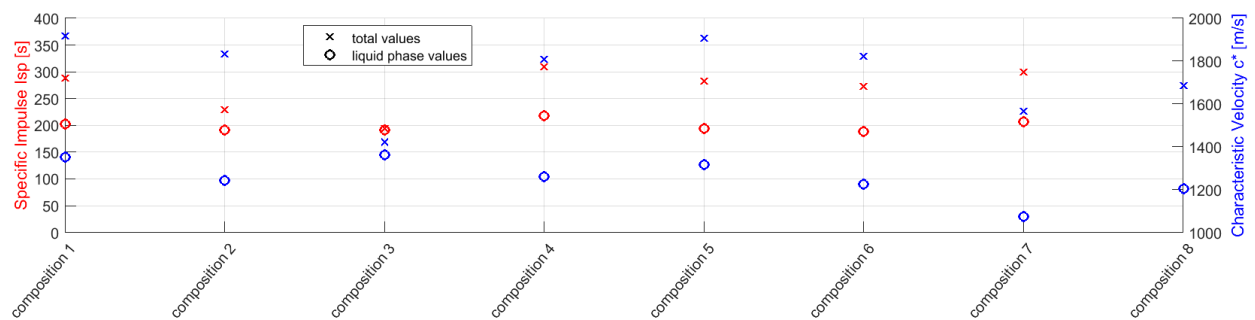


Fig. 4. Specific impulse and characteristic velocity calculated using the whole curve and only liquid N_2O interval.

The I_{sp} and c^* values have been calculated as follows: ‘total values’ are the values obtained by using the thrust-time integral, the average chamber pressure and the total mass flow taken from the moment of ignition to the moment when the thrust falls down to zero again in the calculations. The ‘liquid phase values’ only take these values in the range from engine ignition to the moment where there is no more liquid N_2O left. What is more, the propellant masses lost during the gaseous N_2O ‘tail’ are neglected, therefore the average mass flow rates are calculated by dividing the mass of spent propellant by the width of the ‘liquid phase’ interval.

When testing multiple fuel compositions using one engine with fixed design, it is natural that some propellants will be favored. Even taking the nozzle parameters out of consideration by operating on c^* values, still, the injector cross sectional area is fixed, and therefore in all cases the mass flow rate of N_2O would be similar. When testing fuels within a broad range of optimal O/F ratios, this can be attributed to have even a prevailing effect on the outcome. At this point it must be said that the B2 engine has been made such as to use PP as its fuel, and therefore the injection system is designed to provide an optimal O/F ratio for a fuel with a very low oxygen balance. This could explain the poor performance of POM, which has a lot of oxygen atoms in its chains, and therefore its optimal O/F ratio would be much lower. An indication of POM burning with a significant excess of oxidizer is its almost invisible exhaust flame. Another important factor could be the lack of post-combustion chamber, i.e. the empty space just upstream from the nozzle, which would provide an opportunity for all the gases to mix and combust. This again decreases the performance of fuels generating large volumes of gases, such as POM, as these gases can easily escape the chamber, rather than burn inside. The PEWAX propellant was most likely affected by this as well, as waxes are known for burning with the entrainment mechanism, spraying liquid droplets from their surface into the port. However, if these droplets are not given the chance to fully combust, they will escape through the nozzle, dramatically reducing I_{sp} and c^* . This is possibly also the case for the propellants no. 6 and 8, whose parameters do not stand out despite containing significant amounts of liquid mineral oil dispersed in the resin. The entrainment mechanism also most likely caused the PEWAX fuel to extinguish as soon as the liquid N_2O stopped flowing, which was clearly visible during the test and also can be seen on the thrust curve. This is the reason why the ‘total’ and ‘liquid phase’ values of I_{sp} and c^* are very close in this case. The large values of I_{sp} and c^* for PP are to be attributed to the said design of the injection system, which clearly promotes this kinds of fuels. What is interesting, is that epoxy-based compositions achieved similar or even higher I_{sp} despite having a much more positive oxygen balance. This indicates that the performances could be much better when applied in a more suitable engine. The presence of jute fabric (propellant no. 7) was hoped to promote turbulence and reveal more surface area for combustion. The downside is that a thermally stable fiber takes place of the resin, which is reflected in I_{sp} remaining at the similar level to propellant no. 4. On the other hand, the total impulse (and thrust) are the largest for this particular fuel, which indicates high volumetric impulse (or, in other words, total impulse delivered by the B2 size engine). We were hoping that propellant no. 8 would be one of the best. Unfortunately, due to an error in our electronic system, the thrust curve has not been recorded. However, judging by the average chamber pressure, this propellant did not stand out. Again, this might be because the full potential of liquid paraffin could not be utilized or because of the fact that we used highly crosslinked epoxy in this case, to prevent emulsion destabilization upon too long setting time.

4.2. TG/DSC

In this method thermal properties of three samples were outlined (Fig. 5. A-C). Charts A and B show two resin samples’ TG and DSC curves. A difference in DSC measurement pinpoints that the amount of curing agent does affect the materials’ thermal effects. By reducing hardener content we achieved more energetic propellant – it exhibits quantitatively smaller endothermic effects at lower temperatures and greater exothermic effects at elevated temperature, though both resin’s degradation proceed similarly. On the other hand, POM started to decompose into formaldehyde at approx. 320°C, whereas resin samples display slight mass reduction onset at 180°C. This indicates higher thermal stability of POM over epoxy resin, and is a good reason to believe that the POM indeed was of the stabilized kind. DSC curve of POM shows large endothermic depolymerization effects that may lower the chamber temperature and thus its performance as a fuel. Very strong endothermic effects in POM hint that by absorbing the heat the material itself slows down its combustion process, and hence regression rate. This unfortunate thermal effects, combined with the incorrect O/F ratio, caused the overall poor performance of POM.

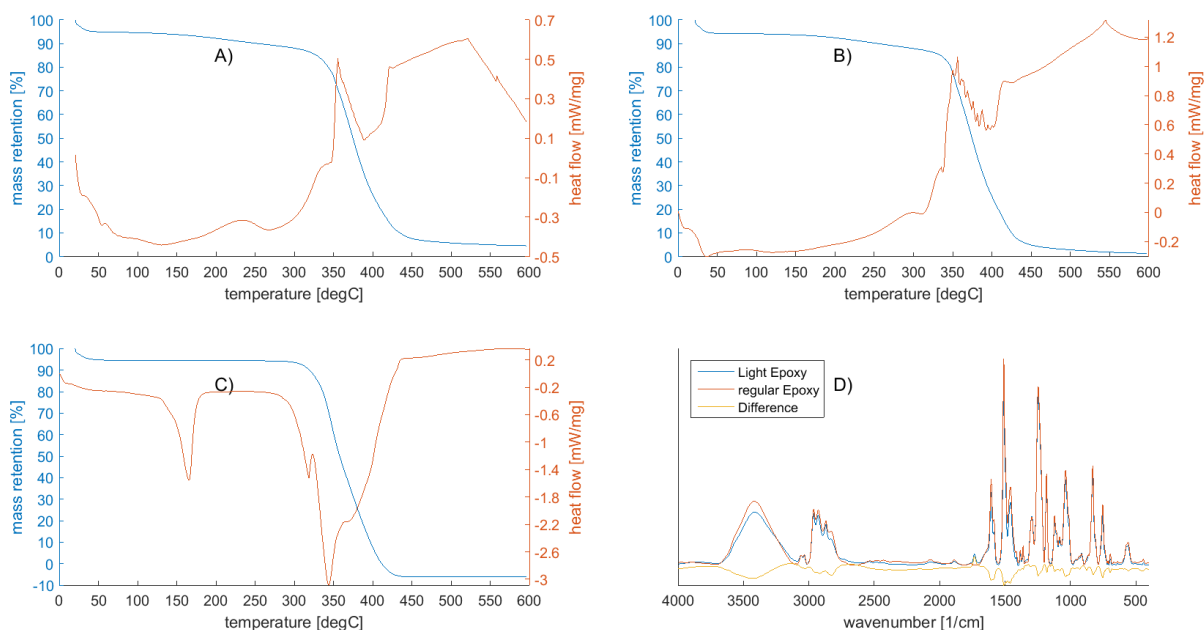


Fig. 5. TG/DSC curves (A-C): A – regular epoxy resin, B – light epoxy, C – POM; D – stacked FTIR curve for light and regular epoxy samples.

4.3. FTIR

Two epoxy samples, regular and ‘light’ were analyzed using FTIR spectroscopy. The spectra (Fig. 5.D) are very similar, characteristic broad band of OH groups are observed in the range between 3100 cm^{-1} and 3700 cm^{-1} . Ether groups can be recognized on the spectra as peaks between $1085\text{--}1150\text{ cm}^{-1}$. Both groups increase oxygen balance which is very important for fuel combustion, as it has been already said. Absorptions of aliphatic resin part and aromatic rings are observed between 2800 and 3000 cm^{-1} . Due to their high heat of combustion such groups have a positive impact on the performance of fuel. In the spectrum of light resin sample additional peak of oxirane rings should appear due to incomplete crosslinking as assumed from sample’s rubbery-like mechanical behavior. However, basing on FTIR spectra, no expected peaks from oxirane rings were detected. It might be due to the fact that the samples were stored for more than a week before performing the FTIR analysis. The epoxy groups could have been consumed in various side reactions during that time. Judging solely by the FTIR results, there is not much evidence for ‘light’ epoxy actually being a better fuel than a regular one. The only premise comes from differences in DSC behavior, which do not seem to be a result of variations in chemical composition.

4.4. SEM

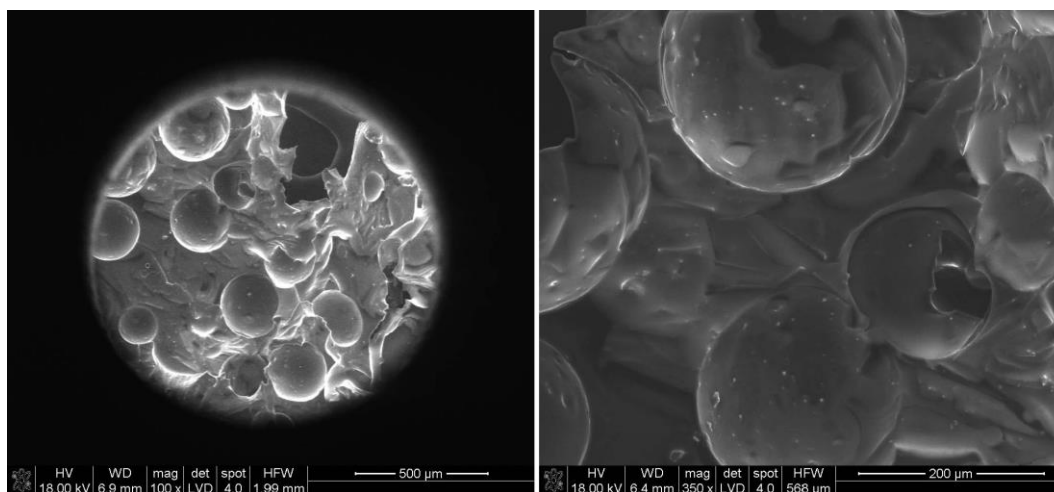


Fig. 6. SEM microphotographs of composition no. 6 (epoxy resin + liquid paraffin).

Scanning electron microscopy confirmed that emulsion of liquid paraffin in epoxy was successfully prepared; in the fig. 6 well-defined spherical pores of average size 200 μ m are visible in the microphotograph of fractured material, which indicates a perfect choice of surfactant for this system. The presence of room temperature liquid paraffin should increase overall regression rate due to entrainment of droplets, without the negative effects of endothermic melting.

5. Conclusions

The main conclusion from this work is that better propellants than PP are quite easily produced, and are within our reach. Regarding the introduction, the propellant which will most likely be used in the main stage of our record-breaking rocket is composition no. 7, containing epoxy and jute fabric. Other epoxy resin-based compositions are also very promising. The ammonium nitrate composition could possibly do better if other oxidizer was used. We chose NH_4NO_3 because of its ability to fully decompose into gases of low molecular weight, but the hygroscopicity seems to limit the performance of such materials. The stable epoxy/liquid paraffin emulsion stabilized by BRIJ L-23 are very promising. The solid block containing only such emulsion (i.e. sample no. 6) after the resin has set was quite elastic and mechanically weak. It managed to withstand the chamber pressure, but any increase in the paraffin content could weaken in to the point where it does no more. On the other hand, by using a jute fabric and a technique of winding with the same composition, we were able to form quite stiff blocks. In this way we might be able to incorporate even more liquid into the fuel grain. Even though we had much higher expectations concerning POM as a high regression hybrid fuel, these results are not enough to decide whether or not the poor performance is POM's inherent property related to its high crystallinity. Perhaps, if given the right conditions (namely lower oxidizer mass flow rate and a post-combustion chamber), POM would outperform most of the fuels tested. On the other hand, the ability to perform well without a bulky post-combustion chamber (and, in general, to perform well in any engine) is another important property, especially from the standpoint of designing the whole rocket, as it allows for better propellant packing. The same goes for PEWAX fuel, in which high regression was balanced by quite low burn efficiency. As for the problem with PEWAX blocks cracking, we were able to successfully block crack propagation by incorporating layers of PE fabric. It remains to be tested whether or not this measure will be enough for scaled-up grains, as the stresses increase with increasing volume.

For future research ideas we plan to experiment more with paraffin emulsions and try to incorporate as much liquid as it is possible without compromising the mechanical strength. We have an idea to make use of the swelling phenomenon in polymers to store volatile liquids in the grain, such as flammable solvents. This idea could work well with another one, which is to use polyHIPE materials as fuel grains, to dramatically increase the burn area.

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