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Low reaction-to-fire polymer filament : formulation, 3D printability modeling and fire testing

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ABSTRACT:
Additive manufacturing and especially Fused Filament Fabrication (FFF) technology is mature enoughfor industrialisation. Indeed, many works about new composite filaments for 3D-printing and3D-printability are reported1,2.However most of them only focus on one specific aspect such as temperature changes3, bond formation4 or rheology5instead of performing a systemic approach. In addition to this, fewpapersdeal with 3D printing and fire properties6.

The objective of this studyis to develop new filament for FDM/FFF with low reaction to fire in order to fulfil the rail and aeronautic fire requirements. First, the development of a proper definition of 3D-printability and of a mathematical model to determine this 3D-printability was investigated. All the parameters influencing the 3D-printability were determined and the Buckingham theory was applied to determine the dimensionless numbers influencing this 3D-printability.The impact of the 3D-printing parameters on the fire performances was then evaluated via UL94 (standardized vertical flame propagation) and cone calorimeter (heat release rate under radiative heat flux) tests. Finally, formulations were developed in order to satisfy all requirements in rail and aeronautic industry.

3D printing company, Formalloy, is producing parts using a laser-based process because of its ability to create new advantageous shapes. "Our technology is known as LMD. That's a method where you blow power and heat it with a laser.

Keywords: 3D printability, Fire retardancy, FDM, FFF, adimensioned number

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INTRODUCTION

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Introduction:

Plastics (polymers) are a large and growing fraction of the fire load in homes, commercial environments, and transportation [1-5]. Moreover, the plastics that are most widely used are the least expensive and tend to be the most flammable. Flammability, which generally refers to the propensity of a substance to ignite easily and burn rapidly with a flame, is one indicator of fire hazard. Figure 1 shows the relationship between two measures of flammability: heat release capacity (section 4.6) and flame resistance (section 5.4) versus the truckload price of commercial polymers. Flammability and cost span over two orders of magnitude. The commodity polymers costing less than about $1/pound comprise over 95% of the polymers in use, and these will continue to burn after brief exposure to a small flame. Engineering and specialty plastics costing over $2/pound are typically polymers with aromatic backbones and fluoropolymers, which selfextinguish or resist ignition because of high thermal stability or low fuel value. Figure 1 shows that the flame resistance of polymers does not always correlate with cost but does correlate reasonably well with heat release capacity.

Printability Check

Anyone who has operated any type of 3D printer is aware that printing an object requires more than just designing a model and clicking on “print”. There are several variables that will impact the quality and success of a printed part. In some occasions, even the most experienced engineer, designer or 3D printing enthusiast, will end up with a failed print. Obviously, there are ways to maximize the success rate of 3D printed parts such as using conceptual frameworks for designing printable objects like Design for Printability (DFP). But even then, sometimes printed parts will simply not come out right. Having several years of combined experience in Additive Manufacturing, Beamler’s team also had its fair share of 3D print failures. When we started building a platform that enables manufacturers and engineers to print industrial parts anywhere in the world, we made it a priority to provide our customers with a fully automated testing tool that analyses each 3D model’s printability.

One of the greatest benefits of 3D printing is the ability to build highly customized products and components. In fact, every 3D model is unique by design. For that reason, it is important to assess the printability of your file to ensure that it can be successfully 3D printed, with quality. Our software performs an automated check of all uploaded files. The algorithm of the tool considers all the variables that determine whether a print will succeed or fail in order to run an effective printability check. To ensure the most reliable and optimal results we broke down the printability check into two stages. Each stage is at the two opposite ends of ordering parts on our platform:

File upload – Once a printable file is uploaded, our software will run a Geometric Check of the file to identify the following characteristics of the object:

- Size
- Width
- Depth
- Height
- Volume
- Area

This will allow Beamler’s proprietary software to identify the most appropriate materials, technologies and printers for the production of the object. It also provides an overview of the amount of locations where the file can be 3D printed.

After check-out – The exact material and printer type to build the custom part is confirmed only after check-out. At that moment, the tool will test the uploaded file for specific design guidelines such as:

- Wall thickness
- Bounding Box Size
- Model Density
- Model Integrity
- Orientation
- Holes
- Area
- Strength (based on material properties)
- Other variables

THE BURNING PROCESS:

Gases and volatile liquids are small molecules that are held together by weak (< 1 kJ/kg) secondary chemical bonds. These volatile compounds spontaneously form combustible mixtures with air that ignite easily and burn with a high velocity. Polymers are very large (macro) molecules with the same intermolecular and intramolecular forces as low molecular weight compounds, but their boiling temperature is essentially infinite because of their high molecular weight. Consequently, both intermolecular and intramolecular (backbone) chemical bonds of polymers must be broken to generate volatile fuel species. This process requires a large (≈ 2 MJ/kg) and continuous supply of thermal energy for ignition and sustained burning. Flaming combustion can be roughly divided into physical and chemical processes taking place in each of three separate phases: gas, mesophase, and condensed (liquid/solid) phase [6,7, and 10- 16]. The mesophase is the interface between the gas and condensed phase during burning. Figure 2 shows a schematic diagram of a horizontal polymer slab that is burning with a diffusion flame. The physical processes are shown on the left-hand side of figure 2, which include (1) energy transport by radiation and convection between the gas phase (flame) and the mesophase and (2) energy loss from the mesophase by mass transfer (vaporization of the pyrolysis gases) and conduction into the solid. At typical burning rates, the polymer surface (mesophase) recedes at a velocity of about 10-6 m/s. Conservation of momentum at the gas-mesophase boundary shows that fuel gases evolve at a relatively low velocity (≈ 10−3 m/s) compared to the burning velocity of these gases when mixed with air (≈ 1 m/s). Consequently, fuel generation is the ratelimiting step in polymer flaming combustion, and it is governed primarily by the rate at which heat and mass are transported to and from the polymer, respectively. The important chemical processes are shown on the right-hand side of figure 2, which include (1) thermal degradation of the polymer in a thin surface layer (the mesophase) as a consequence of the physical (energy transport) processes, (2) mixing of the volatile pyrolysis products with air by diffusion, and (3) combustion of the fuel-air mixture in a combustion zone that produces radiant energy over a spectrum of wavelengths including visible. The combustion zone is bounded by a fuel-rich region on the inside and a fuel-lean region on the outside. Increasing the concentration of oxygen in the environment is known to increase the flame heat flux, either due 2 to a higher flame temperature, an increase in the volume of the combustion zone, or an increase in the soot concentration (luminosity) of the flame. The chemical and physical processes of flaming combustion particular to each of the gas, meso, and solid phases are treated separately below.

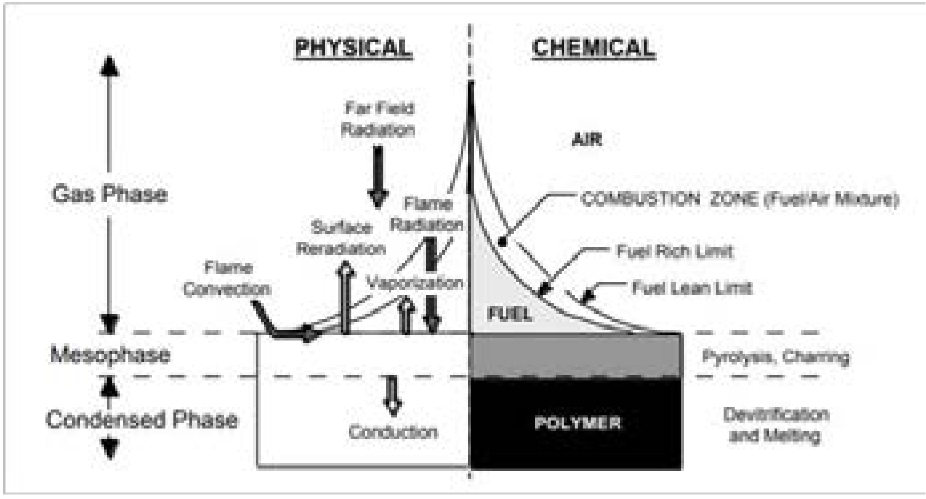

FIGURE 1. PHYSICAL AND CHEMICAL PROCESSES IN THE FLAMING COMBUSTION OF POLYMERS

Material Selection

The initial series of fuel grains tested were manufactured from commercially available ABS, ASA, PLA, AL, PETG, Nylon, and PP. ABS has been selected as it has been shown to perform as well as HTBP at lab-scale static fire tests [2,9], while ASA was selected due to its similarities to ABS. The PLA was selected as a benchmark with which to test the Al, as there is currently no commercially available aluminum-doped ABS. PETG and Nylon were selected due to their excellent mechanical properties, which would be beneficial if they were used as a structural component of the rocket, and finally, PP was selected due to its low price and because it is a highly crystalline material.

The small-scale fuel grains were designed to be 100 mm long and 20 mm in diameter with a 6 mm diameter combustion port. It is typical for HRM fuel grains to have high aspect ratios in order to achieve the desired oxidizer to fuel (O/F) ratios, and it was believed that this combination of port diameter and fuel grain length would provide that. A straight, circular combustion port was selected for the small-scale motor case verification testing and for the material selection testing, as this is the simplest and easiest to manufacture, as well as the simplest to evaluate. A series of ABS grains were printed using a Prusa i3 MK2 FDM 3D printer (Prusa Research s.r.o., Prague, Czech Republic) that were used to verify the operation of the test stand and small-scale motor case.

Testing of Fuel Grains

The testing regime was separated into two main rounds conducted at small-scale. Within these tests, there was an apparatus verification component and a fuel grain testing component. The first round of small-scale testing was designed to confirm the operation of the existing small motor casing and to verify the operation of the newly constructed test stand (Figure 1), sensors, and data logger. Several verification burns were conducted using circular, straight port ABS fuel grains. The purpose of these initial tests was to ensure that motor and nozzle were operating in the choked condition and that the chamber pressure was within the operating limits of the motor case and associated plumbing. These initial tests also allowed the data logger code to be tested and modified as required, and the correct operation of the sensors to be verified. The fuel grains of the seven different materials were then subjected to a single, three-second burn each. The testing regime consisted of: • Measuring and recording the initial weight of the fuel grain • Measuring and recording the initial weight of the oxidizer bottle • Placing the fuel grain in the testing apparatus and subjecting it to a three-second burn • Removing the fuel grain and measuring and recording the final weight • Measuring and recording the final weight of the oxidizer bottle These measurements allowed for the determination of the fuel and oxidizer and total mass flow rates, O/F ratio, and the fuel regression rate. To measure chamber pressure, an analogue gauge was initially mounted to a brass outlet tube plumbed to the mixing chamber at the fore of the motor case. Once the correct operation of the rocket motor was confirmed, a digital pressure transducer was used in place of the analogue gauge, allowing much more accurate measurement and recording, as well as the option to plot the pressure chamber throughout the duration of each burn. A Honeywell heavy duty, 10 BAR ratiometric pressure sensor was chosen for its robust construction and represented an excellent compromise between performance and price. Protection from over pressurization was via a 1.0 MPa pressure relief valve that was installed in-line with both the analogue gauge and pressure transducer. Temperature protection was provided via the installation of a thermocouple below the pressure measurement devices. This thermocouple provided real-time feedback on the temperatures being experienced by gauges, allowing the burn to be stopped prematurely if temperatures approached or exceeded the maximum operating temperatures of the unit.

The Fire Products Collector

The first industrial-size calorimeter for fires into the megawatt (MW) range was built at Factory Mutual (currently FM Global) around 1980. This calorimeter, also referred to as the FM Fire Products Collector, was designed to measure heat and other fire products from test fires up to a size associated with sprinkler activation in commodity warehouse storage and other representative occupancies. Approximately 10 years later, a similar industrial-size calorimeter for HRR measurements up to 10 MW was constructed at SP National Testing Laboratory in Sweden. Since then several other laboratories, such as the National Research Council of Canada, the Fire Research Station in the UK, Underwriters Laboratories and Southwest Research Institute in the U.S. developed the capability of measuring HRR from large fires into the MW range.

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