Flammability of 3-D Printed Polymers – Composition and Geometry Factors

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Abstract

The focus of this paper is to evaluate the comparative flammability of additively manufactured (AM) and conventionally molded polymers. Flammability of objects is dependent on two main factors: material composition and object geometry. To evaluate effects of material composition, experiments on polymer samples made via conventional molding and via AM were performed using an ASTM E1354 cone calorimeter to measure and compare material ignitability and heat release rate. ULTEM™ (amorphous thermoplastic polyetherimide) and PPSF/PPSU (polyphenylsulfone) heat release rates were about 10 times lower than ABS (acrylonitrile butadiene styrene). This was in part due to the large char layer formed by these materials during burning. Comparisons between conventional molded and AM materials revealed slight differences in heat release rate. Additively manufactured ABS sheets had about a 17% higher mean average heat release rate (MAHRR). Conversely, the characterization of ULTEM 9085™ sheets revealed the MAHRR of the AM samples were 13% lower than the molded samples. This is attributed to additives in the material used for extrusion AM as well as the build process itself. Effects of geometry were assessed using material cribs, which were composed of layers of rectangular prisms separated by air gaps, with prisms on consecutive layers being orthogonal. Cribs were constructed with three to ten prisms per layer to evaluate the effects of varying the internal material surface area. Below a specific threshold, the burning mass loss rate per unit area of the cribs decreased with an increase in internal material surface area; this agrees with trends predicted using a theoretical model previously developed for wood cribs.

1. Introduction

1.1 Motivation

Originally founded on the concept of providing a means for prototyping design iterations, additive manufacturing (AM) systems are now being used to fabricate end-use products from both metals and polymers. In addition, a number of companies now produce desktop-scale, inexpensive, extrusion-based AM systems that process polymers such as ABS (acrylonitrile butadiene styrene) and Nylon. 278,000 of such systems were sold in 2015 [1]. In addition, the list of processable polymers for industrial-grade AM systems has also expanded in recent years including both low temperature (such as Nylon and ABS) to high temperature polymers such as ULTEM™ and Polyphenylsulfone (PPSF). In addition, systems with larger build volumes have been developed to enable both large scale prototyping and manufacturing large end use components. One such printer can produce objects as large as a car, 10 m by 4.3 m by 3.8 m[2]

While additively manufactured polymers are often very similar to those typically used in traditional polymer processing (e.g., extrusion and injection molding), the formulations are often modified to be better suited for the printing process. For example, Stratasys’ “Digital ABS,” one of a variety of polymers for material jetting platform, has a distinct chemical formulation that
requires combination of two separate acrylate-based photopolymers that approximate the mechanical properties of ABS, according to its manufacturer[3]. Extrusion AM systems [4] use a thermoplastic form of ABS, but even these formulations are slightly different than those used in injection molding to accommodate specific needs of AM including modified rheology and robustness to humidity.

AM technology allows easy formulation of materials with various additives. Most research in AM materials has been focused on improving mechanical properties. However, Lao et al. performed thermal and flammability testing on custom formulations of polyamide 11 nanocomposites, and demonstrated that improved flammability properties can be obtained with specific compositions of fire retardant additives[5]. Their work studied the addition of nanoclays, carbon nanofibers, and nanosilicas into polyamide 11 for production using selective laser sintering.

Since AM parts are composed of different formulations of materials, and have different build characteristics (e.g., porosity, poor interlayer adhesion, etc.), than parts made by conventional means, flammability characterization is needed to ensure that AM parts are not significantly different (e.g., more hazardous). As the use of additively manufactured parts increases, and the use of AM becomes more prevalent in end use applications, the fire safety industry will need to assess fire properties accordingly. Such knowledge is needed to assist designers in specifying the use of printed components for end use products. For example, one area of consideration is the large effort by the U.S. Navy to use 3D printed parts on ships[6]. The program, called “Print the Fleet,” aims to significantly save time and resources by allowing replacement parts to be printed on-board (or at a nearby dock) during naval assignment, thus minimizing time invested in resupply. While this may indeed improve the efficiency of ships by allowing longer time on the sea, fire hazards are tightly controlled on ships due to the potential for accidents. Ensuring that AM components will not cause a greater hazard is important to this effort.

1.2 Context

The overall goal of this work is to compare the fire performance of additively manufactured and conventionally produced materials. Heat release rate is often the most important parameter in characterizing the fire hazard of a material or object[7]. The first objective, therefore, is to explore potential differences between the heat release rate of AM parts and conventionally fabricated (e.g., injection molded) parts. Another objective is to investigate the geometric aspects of flammability. To determine the effect of geometric spacing, the fire performance of material cribs in various configurations will be compared using a theoretical model. Since one benefit to additive manufacturing is the ability to create parts with complex and sparse geometries to save weight, it is important to know to what extent this increases flammability.

An overview of the theory of fire safety testing and the model used to correlate the geometric cribs study is shown in Section 2. Tests to perform this characterization use a cone calorimeter, performed according to ASTM E1354[8]. The device test method is explained further in Section 3. The heat release rate results and discussion of the material comparison are presented in Section 4. Section 5 contains the conclusion and recommendations based on the results of this work.
2. Theory and Modeling

2.1 Fire Safety of Plastics

The heat release rate of an object in a fire will directly contribute to the hazard. Some materials with fire resistant properties inhibit fire spread, and this corresponds to a low heat release rate. Other materials, often with high carbon, oxygen, and hydrogen compositions, readily burn and cause an even greater hazard once ignited.

Fire safety engineers use the heat release rate of objects and components to predict and model fire spread in a room. Buildings and other room-type enclosures (e.g. buses and trains) can then be designed accordingly. For example, egress time is sometimes calculated based on how fast a room fire attains full involvement. The heat release rate of objects in a room will dictate how fast the area becomes untenable.

Cone calorimeter testing allows characterization of ignition time, heat release rate, smoke release rate, and mass loss of samples exposed to a heat flux. A cone heating element provides a radiative flux to a sample. The combustion gases are extracted and their concentrations analyzed. The depletion of oxygen and the mass flow rate of the combustion gases allows the calculation of heat release rate. Full size objects can be tested in a furniture or other large calorimeter to measure heat release rate and other fire hazard information. However, since those tests are expensive, researchers have developed methods to relate bench-scale results to full scale predictions. Details on the cone calorimeter used in this study are provided in Section 3.1. The simplest way to extend bench-scale results to larger objects is to use a surface area ratio[9]. Empirical correlations can also be determined using statistical analysis.

2.2 Material Flammability

The two materials selected for this comparative study are ABS and ULTEM™. ABS (acrylonitrile butadiene styrene) is selected since it may be the most widely used material in AM. Much data on fire properties of ABS are available, and its heat release rate is relatively high compared to many plastics[10][11]. For this reason fire retardants are often added to ABS, and researchers continue to develop new formulations[12][13]. ULTEM™ (amorphous thermoplastic polyetherimide) was developed for high temperature use and good fire resistance, but cone calorimeter data are not readily available. ULTEM™ 9085, the material tested in this study, has been used to demonstrate additively manufactured aircraft seats[14], and the material has passed the Federal Aviation Regulation (FAR) for fire resistance[15].

Flammability characterization of the material itself does not provide a full prediction of the hazard. Air gaps and internal geometry are process and design dependent, and they can both promote or inhibit fire spread. This is an important characteristic to measure with parts made via AM, since the process is often used to produce highly complex geometries that feature purposefully designed porosity for lightweighting.
2.2 Examining Geometry Effects on Flammability with Cribs

In fire testing, objects with regular air gap spacing and equally dimensioned prisms are termed “cribs.” Much characterization has been done on wooden cribs, most notably by Gross and Block[16][17]. (An example crib is shown in Figure 1.) Researchers have also characterized polymers when burned in a crib configuration[18][19][20]. However, a thorough investigation of most polymers' fire performance when burned in the crib configuration is lacking in the literature. This may be due in part to difficulties with burning polymers in a structured configuration. For example, some materials intumesce before and during ignition. In addition, most thermoplastics will melt or collapse before, or during, burning. The second goal of this paper is to investigate the fire performance of the geometry of additively manufactured cribs made from ABS plastic.

Figure 1: Crib structure with parameters: square prism (or stick) member has thickness $b$, spacing $s$ between sticks, number of sticks per layer is $n$, and number of layers $N$ (the pictured example 4 layers with 7 sticks)

The model used in this work is based on Block's theoretical investigation on wood cribs[17]. Block's study on free burning wood crib fires defines a porosity factor to separate two distinct burning regimes, namely the porosity controlled regime and the surface area regime. In the porosity controlled regime the spacing between the rectangular prisms, as well as the number of layers of prisms, controls the burning rate. In the surface area controlled regime, the spacing does not have an effect, and the burn rate is only dependent on how much of the surface is exposed to the air. Figure 2 contains Block’s data, which is organized into what he calls the densely and openly packed regimes.
The theoretical model by Block [17] is based on the approximation that the vertical shaft of the crib can be modeled as a porous tube. After performing a thermodynamics and fluids analysis on this porous tube and wood structure, he found that in the densely pack burning regime the burn rate is a function of the crib height, vent area of the shaft, and cross sectional area of the shaft. These parameters are completely controlled by the square prism (or stick) dimensions, the spacing between the prisms, and the number of layers of prisms. Within a material, all other parameters are constant. These terms are the variables to control the porosity. Above a certain porosity factor, the theory predicts no increase in burn rate when scaled by surface area.

Block performed his study comparing mass loss rate (kg/m$^2$·s) for various crib configurations to porosity factor. This work uses a cone calorimeter apparatus to perform the experimentation, and measure the heat release rate, which is the more important parameter in a fire hazard. Heat release rate can be related to mass loss rate by the heat of combustion of the material.

This study seeks to apply this porosity model to AM polymer cribs of similar configuration. Specifically, the burning of ABS cribs is dictated by a porosity controlled regime and a surface area controlled regime. The burning of an object with internal spacing is expected to obey the same physics, whether of wood or polymer construction. Although the pyrolysis properties of wood and polymers differ in terms of char layer development, the general pyrolysis process and fluid flow through the crib is expected to be the same.

3. Experimental Methods

3.1 Test Method and Apparatus

Testing on the plastics was done on a bench-scale cone calorimeter largely according to the ASTM E1354-15a standard[8]. The bench-scale unit was developed to use oxygen consumption calorimetry to acquire heat release data for materials[21]. The device uses the changes in the oxygen concentration (as well as other combustion gases) to determine the heat release of the fire. Cone calorimeters are typically used 1) to provide a comparison of material performance, 2) for
obtaining material property data, 3) to provide inputs to numerical fire models, and 4) to prove regulatory compliance[21].

The apparatus used in this work is shown in Figure 3. The major components of the instrument are identified in the figure. The cone shaped heating element is controlled by a PID controller to provide a constant irradiance to the specimen via an electric resistance heater. A load cell measures the transient mass. The exhaust duct vents the combustion gas mixture from the fire, and part of this stream is sampled for analysis in a paramagnetic gas analyzer. Temperature probes and a pressure transducer on the exhaust stream allow for the calculation of mass flow rate of combustion gases.

Figure 3: This photo shows the cone calorimeter used in the ExtReMe Lab at Virginia Tech. The major components are identified in the photo. Crib samples are placed on the sample holder under the cone heater for testing. Tests are performed to ASTM E1354.

The testing closely conformed to the ASTM E1354 standard[8]. The apparatus was calibrated each day before testing with a methane burner providing a known 5 kW heat release rate. The samples were placed in a holder with insulation backing. The molded and printed sheet specimens were 4” × 4” (100mm × 100 mm) and 0.236” (6mm) thick. Before the samples were inserted into the apparatus, the cone heater was raised to a steady temperature that provides the desired heat flux. Data were collected for 120 s prior to testing to ensure an accurate pre-ignition state.

After the sample was inserted, ignition time was determined by visual observation. This allows for accounting of the delay of the gas analyzer so the heat release rate can be compared to other parameters such as mass loss rate. Flame-out time was recorded, also by visual observation, and the data acquisition system was left on for at least 120 seconds after extinguishment.
No pilot ignition system was used in this study. Ignition of the sample was due to the sample reaching its autoignition temperature after being heated with a predetermined irradiance. Common irradiiances are 20 kW/m$^2$ for items near a small fire, to over 90 kW/m$^2$ for room fires that are in the post flashover stage\[9\]. The heat flux value selected for this study was 40 kW/m$^2$. Preliminary testing at 20 kW/m$^2$ revealed inconsistent ignition time.

3.2 Material Preparation

*Evaluating Heat Release Rate*

To compare printed and molded polymers, three samples of each type were tested. Molded ABS specimens were cut from larger sheet. The printed sheets were made from extruded black and white ABS-M30 in a Stratasys Fortus 400 mc system. Likewise, the ULTEM™ 9805 sheets were printed with the same Fortus printer. The Ultem 9805 molded plaques were obtained from colorxpress.com. All sheets were 6mm thick.

*Evaluating Geometric Effects on Flammability*

The geometric flammability study was done using ABS plastic. Crib samples made from molded ABS plastic were manually constructed. Printed crib samples were made using the Fortus described earlier. Support material SR-30 was used in the printing process to scaffold the overhanging features; it was dissolved in a sodium hydroxide solution according to manufacturer’s specifications. The samples were then flushed with tap water to eliminate the solution, and dried before undergoing testing.

To ignite the cribs, the top of the crib was exposed to 40 kW/m$^2$ heat flux in the cone calorimeter. The testing done with the plastic cribs was the same as that for the sheet samples. During crib burn testing, mass loss caused the height of the crib to decrease. Since the height of the cone heater was not changed during the test, this increased distance between the cone heater and the sample caused a decrease in the heat flux from the original 40 kW/m$^2$.

ABS has a low glass transition temperature of about 100 °C. At this temperature ABS does not melt into a liquid, but, nevertheless, demonstrates viscous flow. ABS is considered an amorphous polymer, and, as such, it does not have a true melting point. When ABS is burned in a structured configuration, it collapses due to the high temperature. In the experiments performed, all ABS cribs tested did eventually collapse. The cribs with a denser porosity factor maintained their structure longer than the sparsely constructed cribs. To lengthen the time before collapse for lower density cribs, wire supports were constructed (examples of these supports can be seen in Figure 4-b). Collapse was determined by visual inspection to occur from about 20 seconds to over 1 minute.

The porosity study was performed with both printed ABS cribs and with cribs made from injection molded plastic. Examples of AM cribs made for the experiments are shown in Figure 4.
4. Results and Discussion

4.1 AM Sheet Polymer Comparison

Figure 5 shows an overall flammability comparison between the heat release rate curves of three additively manufactured polymers, ABS-M30, ULTEM™ 9085, and PPSF/PPSU. All samples were tested according to ASTM-E1354, as described in Section 3.1. It is apparent that the ULTEM™ and PPSF are developed as heat and fire resistant plastics. Evaluating the respective fire hazards reveals that ABS is about 10 times more hazardous in terms of heat release rate. Testing was performed at 40 kW/m² irradiance, and more testing at different heat flux levels is needed to fully ascertain the relative hazard between these materials. Ignition times between the samples were 20 s for the ABS, 60 s for ULTEM™, and 340 s for the PPSF. The ULTEM™ and PPSF samples displayed intumescent behavior by developing a large char layer as they burned. This both inhibited efficient heat transfer into the material, as well as restricted the upward flow of combustion gases through the cone heater.
Figure 5: ASTM-E1354 cone calorimeter results for three additively manufactured polymer sheets. Testing was done at 40 kW/m$^2$ irradiance. Flaming for PPSF and ULTEM™ samples did not cease until 1700 s, but steadily decreased during that portion.

4.2 AM and Molded Polymer Sheet Heat Release Comparison

Figure 6 shows the comparison of the heat release rate of the AM ABS sheets and conventional molded ABS sheets. The difference between the average values of peak heat release rate is 134 kW/m$^2$.

Table 1 shows the comparison of the test averaged heat release rate. The AM sheets had a higher mean average heat release rate by about 80 kW/m$^2$. Since none of the specimens burned longer than 300 s, the average is for the entire portion of the heat release curve.
Figure 6: ASTM-E1354 cone calorimeter results for 6mm thick 3D printed and molded ABS sheets at 40 kW/m\(^2\) irradiance. The mean peak heat release rate for the 3D printed and molded sheets are represented as the dashed lines in the figure. The average for the 3D printed and molded sheets are 1067 kW/m\(^2\) and 933 kW/m\(^2\), respectively.

Table 1: Average ABS heat release rates for molded and AM sheets. Data were integrated over 300 s. Units are kW/m\(^2\).

<table>
<thead>
<tr>
<th>Test</th>
<th>Molded Sheet</th>
<th>FDM Sheet</th>
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<tbody>
<tr>
<td>Test 1</td>
<td>485</td>
<td>537</td>
</tr>
<tr>
<td>Test 2</td>
<td>470</td>
<td>523</td>
</tr>
<tr>
<td>Test 3</td>
<td>487</td>
<td>631</td>
</tr>
<tr>
<td>Average</td>
<td>480</td>
<td>564</td>
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The resultant ash from each of the molded and printed ABS sheets measured approximately 0.6 g. Each process produced about the same amount of ash. However, the appearance of each of the resultant ash was markedly different. The ash produced from the molded sheets was whitish in color, while the ash produced from the AM sheets appeared blue. The comparison between the ash samples is shown in Figure 7.

This difference between the results for the AM and molded ABS sheets could primarily be due to the distinct chemical formulations. Since the ABS used in the Fortus has been modified for optimal processing via extrusion AM, increased flammability may occur. The density of the molded sheets was greater than the density of the printed sheets by 7%. However, internal density differences between the injection molded and additively manufactured ABS sheet is not believed to have an effect. Patel et al. performed a numerical study to investigate the effect physical material properties have on cone calorimeter results[22]. Changes in density did not affect peak heat release rate. However, more testing is required to validate this assumption.
In most cases, the differences observed between the AM and molded material flammability are not significant to warrant extra controls for fire safety reasons. However, in some applications this trend towards increased flammability of printed ABS may become a more serious consideration, and a better understanding of what causes these materials to exhibit different performance should be studied.

Figure 7: ABS sheet combustion ash: (a) AM sheet ash, (b) Injection molded sheet ash.

Figure 8: ASTM-E1354 cone calorimeter results for 6mm thick AM and molded ULTEM™ 9085 sheets at 40 kW/m² irradiance. Only the first 1150 s of data are shown. The mean average heat release rate for the first 1000 s is plotted as a dashed line, with the mean average heat release rate of the 3D printed and molded sheets being 61 kW/m² and 69 kW/m², respectively.
Figure 8 shows the comparison of AM and molded ULTEM™ 9085 sheet heat release rates. The average peak heat release rate is only 2 kW/m² higher for the printed sheet. However, the average heat release rate of the molded sheets is 13% higher than the AM sheet over the first 1000 seconds of burning.

The ash of the samples is shown in Figure 9. The molded sheets all generally expanded uniformly upward into the cone heater during the test. The AM sheets, however, sometimes seemed to delaminate and expanded erratically. This behavior is likely what caused the lower overall heat release rate in the AM sheets. The figure shows the unburned material which spilled over the side of the sample holder. Although aluminum foil was used to contain the plastic in the sample holder, the aluminum foil was insufficient to prevent this expanded material from flowing off of the sample holder.

During the test the material expanded into the cone heater. This intumescent behavior was significant, and caused the material to contact the bottom of the cone heater. This inhibited the combustion gases from escaping the top of the cone heater. The large char prevented efficient heat transfer from the cone to the unburned material, and this caused the heat release rate to be low for both AM and molded sheets.

4.3 Flammability Dependence on Geometry

Figure 10 contains the results from the flammability study on the ABS crib tests. The porosity factor from Block's work[17] is plotted against heat release rate. The maximum heat release rate of the portion of the burning before collapse was used, since the airflow properties will change after collapse. CAD images of the cribs used in this study, which demonstrate different porosity factors, are shown in Figure 11.
ABS crib pre-collapse heat release rate are graphed as a function of Block’s porosity factor. The cribs were tested at 40 kW/m$^2$ irradiance, and both molded and AM produced materials are included in the graph.

![Figure 10](image)

The initial tests of the cribs with the larger porosity factors resulted in very short collapse times, and full ignition of the entire crib may not have been realized. This is believed to be the cause of the lower heat release rate values for the molded cribs at porosity factors greater than 1. The wire supports did prolong the structured burn. Most crib configurations were not repeated, but the general trend of the data indicates the applicability of the use of Block’s porosity factor to predict two regimes of burning of plastic cribs.

![Figure 11](image)

Figure 11: Cribs used in porosity study, using ABS material; (a) Porosity factor $\varphi = 1.46$, (b) $\varphi = 0.81$, (c) $\varphi = 0.33$
The constants used in the calculation of the porosity factor were estimated based upon limited data available in the literature. Values of porosity greater than one indicate the burning is in the surface area controlled regime. However, more testing is required to determine exactly how the porosity should be scaled to accomplish a proper quantitative determination of each regime. Ultimately, the data seem to indicate the presence of two distinct regimes of burning, which demonstrates the importance of designing structures for fire safety performance independent of material characterization.

Due to the many factors governing the burning of polymer cribs, the differences between the burning of the AM and molded cribs is not deemed significant. As shown in Figure 6, the initial burning of the AM and molded ABS sheets display similar performance. Only pre-collapse heat release data was used for the porosity model. Most cribs collapsed within 30-50 s, and most of the peak heat release rate values were obtained before 60 s of flaming. The sheet data is varied within this region, and differences in material properties therefore do not have as much effect on crib flammability.

The data indicate the presence of a porosity controlled regime, and this provides a basis for designing polymer parts for fire performance using geometry. Increasing the resistance to airflow by decreasing the spacing between structural members will reduce the initial heat release rate, and lower the fire hazard of the object. While there are many benefits to creating a sparse structure in terms of material usage, weight reduction, and speed of manufacturing, in certain instances slightly more material being used to block airflow may substantially increase the fire safety of a design.

5. Conclusion

As more designers look to AM as a means of fabricating end use parts, understanding printed parts' fire safety performance becomes imperative. While designers know not to assign material properties of conventionally processed parts to those that are printed (i.e., due to part anisotropy), there remains uncertainty about the flammability of printed materials and their differences with conventionally processed materials.

Two tests were performed in this study: AM polymers were compared with their respective molded counterparts, and cribs of various porosities were compared using a theoretical model. Peak heat release rate and average heat release rate comparisons between conventional injection molded and AM parts reveal different behavior between the two processes. The AM produced ABS sheets had an 80 kW/m² (17%) higher mean average heat release rate than the injection molded pieces. The ULTEM™ AM sheet had a 13% lower mean average heat release rate, but its behavior as shown during the test may cause other issues during a fire, as the AM sheets displayed substantial dripping from the holder. The molded sheets did not display this behavior. More testing is needed to fully understand why the AM sheets differ in fire performance than conventionally produced parts.

The porosity study revealed two distinct regimes in free burning structures made from ABS plastic. This result indicates that structures may be able to be designed to inhibit fire hazard, even without material controls. Further study is required to fully define the transition point between the porosity controlled regime and the surface area controlled regime. Impeding the airflow into the structure will lessen the fire hazard, and this should be a design consideration for AM parts.
References
