



United States

Consumer Product Safety Commission

Lifecycle Evaluation of 3D Printers

September 2022

Table of Contents

Preface..... 4

Executive Summary 5

Introduction 7

Background 8

Design Selection 9

 Design Selection 9

 Design and Printer Limitations 11

Fabrication 11

 Summary 16

Chemical Analysis 17

 Test Method 17

 Resin Analysis 17

 3D printed children’s products 18

 Results 18

 Resins 18

 3D printed children’s products 21

 Conclusions 27

Flammability Analysis 28

 Test Method 28

 Results 28

 Conclusions 32

Mechanical Analysis 33

 Test Method 33

 Results 34

 Bubble Toy Performance Analysis 34

 Rattle Performance Analysis 36

 First Puzzle System Performance Analysis 38

Conclusions.....40

Data Analysis of 3D Printed Children’s Products.....41

 Test Method41

 Results42

 Conclusions.....45

Summary46

References46

Preface

This technical report was prepared by the “3D Printer Project Team,” led by Sayon Robinson, Ph.D., Chemist, Laboratory Sciences Chemistry Division (LSC).¹

The 3D Printer Project Team consisted of the following participants:

- Sayon Robinson, Ph.D., Chemist, LSC
- Zachary Goldstein, Mechanical Engineer, Laboratory Sciences Mechanical Engineering Division (LSM)
- Emily Maling, Textile Technologist, Division of Engineering, Directorate for Laboratory Sciences (LSE)
- Alisa Hwang, Mathematical Statistician, Division of Hazard Analysis, Directorate for Epidemiology (EPA)
- Andrei Komarov, M.D., Ph.D., DABT, Physiologist, Division of Pharmacology and Physiology Assessment, Health Sciences (HSPP)
- Benjamin Mordecai, Mechanical Engineer, LSM
- Brandy Bucher, Chemist, LSC
- Emily Matthews, Chemist, LSC
- Greg Ota, Mechanical Engineer, LSM
- Julio Alvarado, Compliance Officer, CRE
- Mark Bailey, Economist, Economic Analysis (EC)
- Mary Pigott, Product Safety Investigator (CFI)
- Matthew Roemer, Chemist, LSC
- Tammy Massie, Ph.D., Mathematical Statistician, Division of Hazard Analysis, EPA
- Treye Thomas, Ph.D., Program Area Risk Manager, Chemical, Nano, and Emerging Materials
- Zachary Foster, Industrial Engineer, Directorate for Engineering Sciences, Division of Human Factors (ESHF)

¹ This report was prepared by CPSC staff. The report has not been reviewed or approved by, and does not necessarily represent the views of the Commission.

Executive Summary

In recent years, 3D printers² have become inexpensive and easier to operate, which has led to an increased use among consumers. Specifically, consumers now have access to a range of 3D printer technologies in homes, schools, libraries and makerspaces. Furthermore, through small home-based businesses, consumers can order customized 3D printed products via the Internet.

In this project, CPSC staff investigated potential hazards associated with 3D printers and 3Dprinted children's products. The findings in this report present a lifecycle evaluation of consumer interactions with 3D printers, from potential material handling and fabrication hazards to consumers, to the mechanical, flammability, and chemical hazards associated with the final 3Dprinted products.

CPSC staff selected five printers, based on target market cost and availability to consumers, to conduct this study. This selection of printers includes three different 3D printing technologies: Stereolithography (SLA), Liquid Crystal Display (LCD), and Fused Deposition Modeling (FDM). The three techniques are also representative of the most common 3D fabrication modes available among low-cost desktop consumer printers.

The specific designs selected for fabrication using the various 3D printers were determined based on a review of banned and regulated products, infant products, and children's toys that represent the online marketplace and imported products. CPSC's staff targeted designs that met the age-grading criteria for the 0-35 month age-range, as well as designs that best suited mechanical testing of the finished product, while considering the physical limitations of the 3D printers themselves.

Staff settled on three designs for the fabrication stage: a toy rattle, a bubble toy, and a multi-component first puzzle system. The 3D printed products were subjected to the applicable flammability testing, heavy metal content, and use-and-abuse testing from ASTM F963-17. In addition, staff investigated the chemical content of the feedstock resins, as well as their compliance with relevant federal regulations under The Federal Hazardous Substances Act (FHSA). The 3D printed toys were also tested to determine compliance with the relevant federal regulations for lead and phthalates covered under both the Consumer Product Safety Improvement Act of 2008 (CPSIA) and the FHSA.

Staff characterized the resins and found that all the 3D printed products analyzed in this study were compliant with the lead and phthalate limits specified in the CPSIA and FHSA. In addition, no migratable heavy elements were found in violation of federal regulation limits. Staff has not reached a conclusion whether any foreseeable consumer exposures during use of 3D printers or 3D printed products would result in a substantial risk of serious illness or injury. This study also

² ISO (International Organization for Standardization)/ASTM. 2016. Standard terminology for additive manufacturing – General principles – Terminology. ISO/ASTM 52900:2015(E). Conshohocken, PA. ASTM International.

suggests that toys made using consumer 3D printers do not pose an inherent flammability hazard, although flammability will depend on the shape of the printed toy.

Finally, although the specific designs selected and printed in this study met chemical and flammability requirements, in some cases, the printed products liberated small parts during use-and-abuse performance testing. Staff recommends that consumers be cautioned about the risks of 3D printing children's products using incorrect printing parameters or materials. Printer conditions may need to be optimized to improve mechanical hazards associated with the build of the designs and lead to the fabrication of more durable and safer products for children to use.

In addition, staff recommends future work to investigate and gather data regarding the chemical and particulate emissions during the 3D printing process. The data provided would allow a more complete assessment of potential consumer exposures to particles and vapors generated during the printing process.

Introduction

Three-dimensional (3D) printing, also known as additive manufacturing (AM), describes the family of processes that are used to build three-dimensional objects from computer aided design (CAD) files and similar user-input designs. These processes typically build the objects by adding materials sequentially in a layer-by-layer methodology. These 3D printing processes have been around since the 1980s; however, recent advances in technology, materials, and equipment have made 3D printing more accessible to a wider range of businesses and consumers. There has been a rapid increase in availability of low-cost, consumer-grade desktop printers. This has led to a rise in the use of 3D printers in homes, schools, libraries, makerspaces, and small home-based businesses.

As 3D printers have become more readily available, consumers are now able to print various consumer products covered by U.S. Consumer Product Safety Commission (CPSC) regulations, either for personal use or for sale on a small scale by microbusinesses. Small-scale, low-cost production by microbusinesses is a growing trend and is commonly referred to as distributed manufacturing. Consumer products, in particular children's products, produced by such means may not meet applicable regulations or voluntary standards, because consumers or microbusinesses may be unaware of federal regulations and voluntary standards applicable to such products. Past CPSC reports³ have highlighted the potential hazards associated with the use of 3D printers and 3D printed consumer products, including fire and combustion hazards, mechanical hazards, and chemical hazards. Currently, CPSC is developing guidance on safety procedures for consumers.⁴

As such, CPSC staff investigated hazards associated with 3D printers and 3D printed children's products. The findings in this report present a lifecycle evaluation of consumer interactions with 3D printers, from potential material handling and fabrication hazards to consumers, to the mechanical, flammability, and chemical hazards associated with the final 3D printed products. Staff evaluated mechanical performance of 3D printed children's products and their compliance with ASTM F963-17, *Standard Consumer Safety Specification for Toy Safety*.⁵ Staff also conducted flammability testing of 3D printed children's products in accordance with 16 CFR § 1500.44, Method for Determining Extremely Flammable and Flammable Solids, to ensure they were not classified as flammable solids, as described in 16 CFR § 1500.3(c)(6)(vi) and to ensure

³ CPSC Report on Safety Concerns Associated with 3D Printing and 3D Printed Consumer Products, May 2020, <https://www.cpsc.gov/s3fs-public/Safety-Concerns-Associated-with-3D-Printing-and-3D-Printed-Consumer-Products.pdf>

⁴ CPSC Staff proposed and led a UL 2904 Working group to develop guidance on safety procedures for consumers.

⁵ ASTM F963-17 Standard Consumer Safety Specification for Toy Safety.

compliance with 16 CFR § 1500.3(c)(6)(vi). Staff, in addition, analyzed the chemical composition of the raw materials and the chemical content of the final printed products for lead and phthalate limits established by the CPSIA and FHSA.

Background

Advances in 3D printing technology over the last decade continue to lower the price threshold of 3D printers, increasing their presence in home and school settings. According to the 2021 Wohlers⁶ report, in 2020, desktop 3D printer sales grew by 6.7 percent to more than 750,000 units sold, after sales increases of 19.4 percent in 2019, and 11.7 percent in 2018.

Five printers were identified by LS staff to conduct this study (**Table 1**). The selection of printers represents two different AM processes, namely, material extrusion (ME) and vat polymerization (VP). The 3D printing technologies used by the printers include stereolithography (SLA), liquid crystal display (LCD), and fused filament fabrication (FFF), also known as fused deposition modeling (FDM). Although this is not an exhaustive list of all possible 3D printer types, LS staff determined that these five printers are representative of this study's target market cost (under \$4,000) and availability to consumers. The three 3D technologies are also representative of the most common 3D fabrication modes of available consumer-grade 3D printers.

Table 1: 3D Printer Technologies and Processes Evaluated

| Printer | Brand | Technology | Process |
|-----------|---------|------------|---------|
| Printer A | Brand A | FDM | ME |
| Printer B | Brand B | FDM | ME |
| Printer C | Brand C | SLA | VP |
| Printer D | Brand D | LCD | VP |
| Printer E | Brand E | LCD | VP |

FDM printing is the most common form of consumer-grade 3D printing. Structures are built by heating up a solid plastic feedstock, called filament, to a malleable state and extruding it through a nozzle onto a print bed or onto the previous layer of deposited material. The print bed may also be heated, depending on the requirements of the material being used. Most FDM printers typically rely on a form of G-Code⁷ to control the movement of either the nozzle, the print bed, or both, to layer the extruded material and form the final structure.

⁶ Wohlers Report, 3D Printing and Additive Manufacturing, Global State of the Industry, 2021 pp 118-122.

⁷ G-code. A computer numerical control programming language.

SLA and LCD printing both operate similarly to each other. Both methods use a liquid photopolymer feedstock called resin. The print bed is vertically dipped into a resin tank, where the liquid resin is hardened and adhered to the print bed, or to the previous layer of cured material. SLA printers use a laser beam to stencil the design of the current layer, while LCD printers use UV light to flash the entire image of the current layer all at once.

Despite SLA printing being developed before FDM printing, SLA technology has not been adapted as easily into the consumer world, due to its greater complexity and lower-user friendliness, compared to FDM. However, as the technology becomes more affordable, consumer-grade 3D printers utilizing SLA and LCD are beginning to appear in the market.

Design Selection

LS staff considered a variety of designs based on banned products, infant products, and children's toys that represent the online marketplace and imported products.

Design Selection

CPSC's staff researched 16 different 3D printer toy designs. These designs were refined, based on staff recommendations, as well as design and printer limitations. Ultimately, we selected three designs: the Rattle (**Figure 1**), the Bubble Toy (**Figure 2**), and the multi-component First Puzzle System (**Figure 3**).



Figure 1: The Rattle. This design has been age graded as <3 years, 0-35 months.



Figure 2: The Bubble Toy. This design includes five components (bubble cup, bubble wand, two wings and cap), and has been age graded as <3 years, 19-35 months.

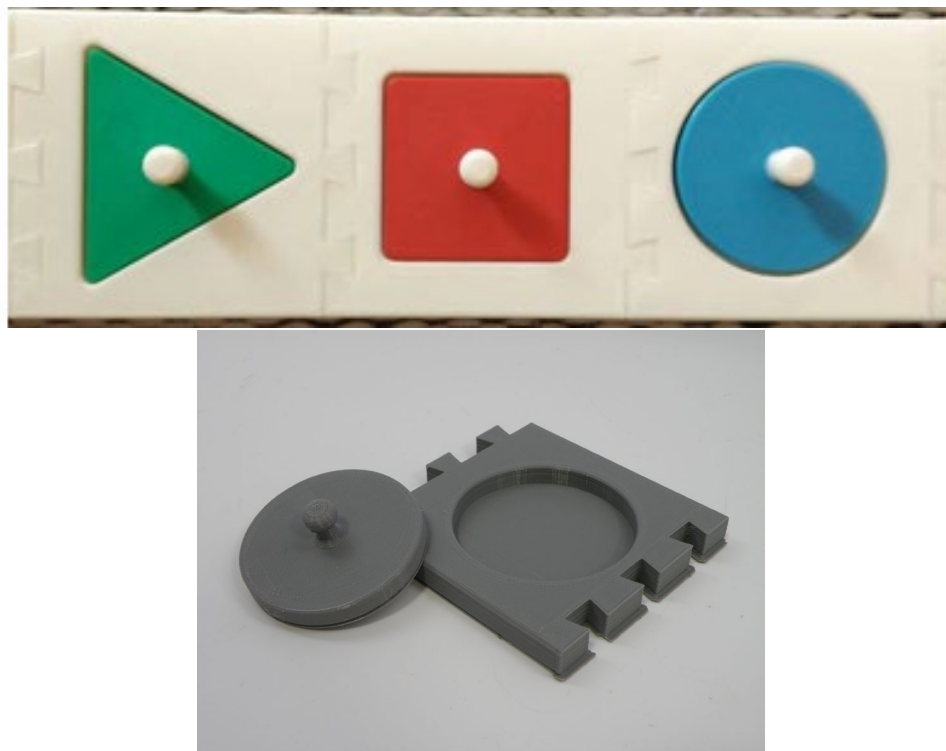


Figure 3: The First Puzzle System. This design includes eight components (three shape pieces, three shape inlays with jigsaw connectors and two endcaps with jigsaw connectors), and has been age graded as <3 years, 19-35 months.

Design and Printer Limitations

Design selections were required to meet the age grading criteria for the 0-35 month age-range in order to conduct the required toy testing according to ASTM F963-17, *Standard Consumer Safety Specification for Toy Safety*. This influenced the final selection of toy designs and helped narrow the potential list of designs.

The major design limitations were the specific capabilities of the set of printers evaluated. Another design limitation was staff's ability to restock reliably consumable material for the project. Designs with too many components or with multiple overhanging features, both of which greatly increase the amount of material required per print, had to be eliminated. Printer limitations included the available print volume, print speed, and material consumption. The print volume of a 3D printer is defined by the area of its print bed, multiplied by the total height of either the bed or the nozzle's z-axis, depending on which component moves in a particular printer. Since every 3D design chosen in this study had to be replicated on every printer, final design selection was limited by what could fit on the smallest print bed. In this study, this limiting size factor was determined by Printer E, which has the smallest print volume in this study. Some flexibility was gained through creative orientation of the models in 3D space to fit more than would fit if oriented flat across the print bed area. Beyond this size exception, given enough material and time, there are few physical limitations to what any 3D printer can produce.

Fabrication

Printers were purchased, assembled, and set up in stages to ensure that all machines were functional. Each printer was operated only with its own brand's source materials. Staff did not use third-party feedstock materials or use one brand's resin/filament on another brand's printer, due to known or potential compatibility issues. For example, if either LCD printer used another brand's resin, it would not fully harden. This may be influenced by a difference in UV intensity produced by both printers in this study, despite the resin listing the same activation wavelength. In the case of the SLA printer, Printer C utilizes a unique resin cartridge system rendering the printer incompatible with other pourable liquid resins, and the cartridge incompatible with other printers. Though it is possible to interchange FDM printers and brands, for consistency across the study, both FDM printers also only used their own brand's filament material, summarized in **Table 2**.

Table 2: 3D Material Samples

| Printer | Source Material | Material Type | Number of Variants |
|-----------|-----------------|------------------|--------------------|
| Printer A | Filament | PLA | 11 |
| | | Tough PLA | 4 |
| | | ABS | 10 |
| | | PP | 1 |
| | | Nylon | 2 |
| | | CPE | 9 |
| | | TPU95A | 4 |
| | | PC | 3 |
| | | | Total: 44 |
| Printer B | Filament | PLA | 11 |
| | | Tough | 4 |
| | | | Total: 15 |
| Printer C | Resin | Standard | 4 |
| | | Tough/Durable | 3 |
| | | Flexible/Elastic | 2 |
| | | Rigid | 3 |
| | | Specialty | 2 |
| | | | Total: 14 |
| Printer D | Resin | Plant-based | 3 |
| | | Basic | 2 |
| | | | Total: 5 |
| Printer E | Resin | Standard | 10 |
| | | Water Washable | 2 |
| | | ABS-Like | 2 |
| | | | Total: 14 |

Three Rattles, two complete Bubble Toys, and two extra sets of Bubble Toy Accessories (every Bubble Toy component minus the liquid soap cup), were printed for every feedstock material sample in the study, (**Figure 4**). Two Rattles and the two complete Bubble Toys were designated for mechanical testing; the third Rattle and one Bubble Toy Accessories set was designated for flammability testing, and the final Bubble Toy Accessories set for chemical testing. Only one color of each material sample type was used to print the two subs of the First Puzzle System design (**Figure 5**), because chemical analysis of the Rattle and Bubble toys indicated that there would likely not be any mechanical differences based on resin and filament color. The First Puzzle System was only printed for mechanical testing. In total, 692 individual samples, comprised of more than 2,000 individual components, were fabricated for evaluation.

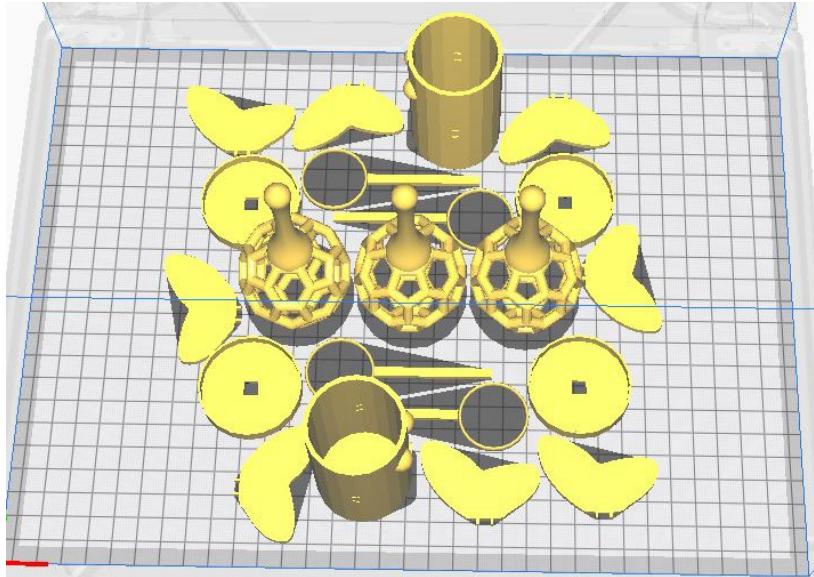


Figure 4: An example of the total number of Rattle and Bubble Toy/Bubble Toy Accessory sets printed per material sample, as modeled on Printer A's printing bed.

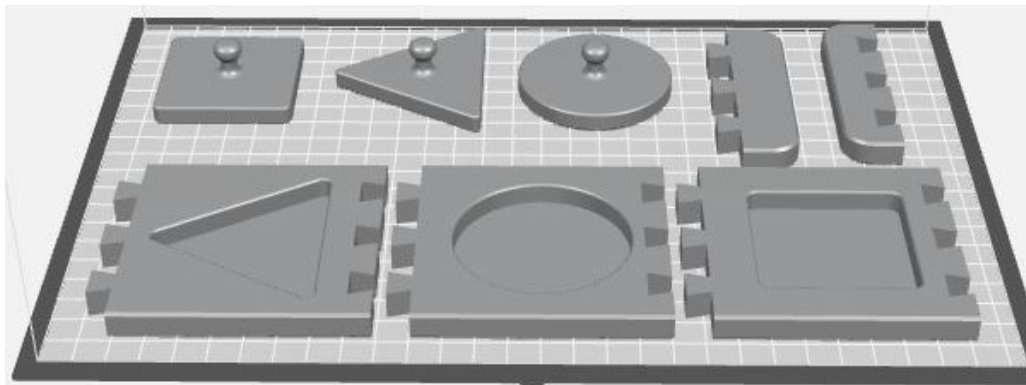


Figure 5: An example of a complete First Puzzle System sub, as modeled on Printer B's printing bed.

In between each material change the LCD printer beds and resin tanks were cleaned (for purposes of this testing) in an alcohol bath to remove all traces of the previous material. The printer bed of the SLA printer was cleaned in an alcohol bath between material changes; however, its resin tank and cartridge system allowed new tanks to be assigned to operate with specific resins, and swap in and out, as needed. In addition, all SLA and LCD printers evaluated include a post-processing step for printed structures that the filament printers evaluated do not. Once the FDM printers complete the final layer, the product is immediately ready for evaluation, and the next sample can be loaded into the printer. Resin structures were first washed in an alcohol bath to remove any excess liquid polymer that has adhered to the sides of the structure while not being

hardened. After washing and drying, the structures were then left under UV light to finish setting the polymer, according to manufacturer-recommended procedures.

FDM Printer Notes

While there are a variety of sizes to choose from, in general, consumer-level FDM printers typically provide the largest print volume, compared to other consumer-grade printers. In addition, FDM printers' earlier availability in the consumer market means there is a larger hardware and software support network, as well as multiple different vendors and price ranges to choose from. While not examined as part of this study, most FDM nozzles and printers are not restricted to using only their own brand specific filament. The general physical limitations are whether the nozzle and bed can produce enough heat to manipulate that material type, and the diameter of that filament. Filament diameter is typically standardized across the different material providers.

Both FDM printers in this study functioned as expected throughout the course of fabrication. Regular maintenance was required to correct some issues with the print beds and the nozzles. However, all adjustments were considered acceptable, based on the volume of work performed with those devices.

Staff performed periodic maintenance to replace worn parts and clear blockages from nozzles, as well as replace worn printer parts, such as nozzles and glass plates, at times during the study, with no defects seen related to the wear and tear.

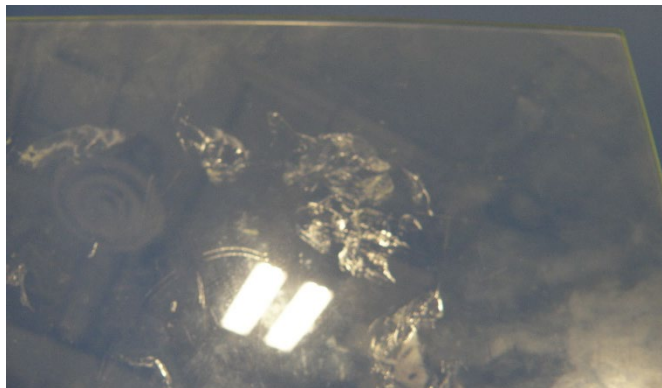


Figure 6: Chipping and peeling that Printer A's glass printing plate experience during the fabrication stage.

Printer B used a semiflexible print bed. No damage to the bed was observed. However, it did cause some variability in the base layer of structures printed on it, depending on their location on the plate (**Figure 7**). Staff determined that this was caused by the restraint system used to attach the bed to the printer. Steps were taken to adjust it, and the base level improved across the bed. All issues noted with the base layer only affect how the bottom surface of the structure appears. Staff determined that the structure of the base layer was still mechanically sound and was not any cause to doubt the structural integrity of the part.



Figure 7: An example of different bottom layer finishes based on the structure's printing location on the flexible bed.

SLA Printer Notes

Printer C monitors itself to level the print bed ahead of prints, and its exchangeable resin cartridges and resin tanks made it very easy to handle the liquid polymer safely. A notable printing failure of this printer occurred with its elastic sample material. In one case after attempting to print, the resin tank appeared to be a collection of partially cured globs of resin (**Figure 8**). The printer continued to follow this method of printing even after the printer bed had risen high enough that the bottom layer no longer contacted the resin, leaving a collection of partially cured globs of resin in the tank. Such a print defect could cause exposure to slightly different resin materials. A reprint of this material was not attempted, and the partially completed structures were divided for flammability and chemical examination.

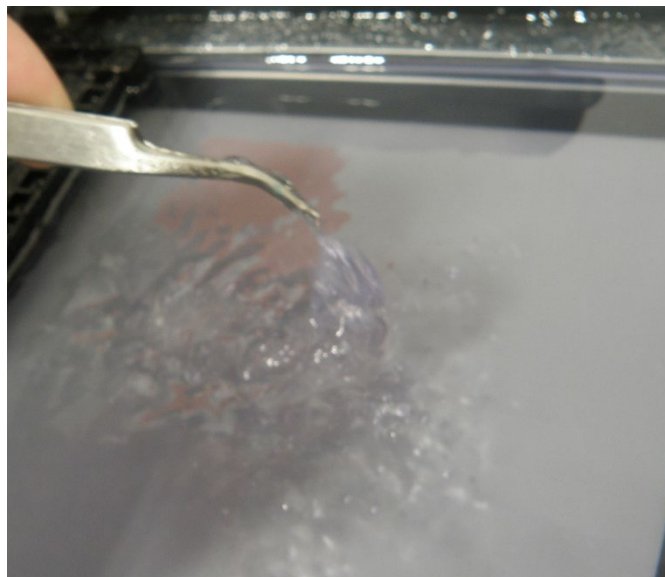


Figure 8: The elastic resin tank, post printing. Some of the elastic resin in the tank has coagulated.

LCD Printer Notes

The LCD printer resin tanks must be adequately filled prior to each job. There is no system in place for either LCD printer used in this study to refill itself to complete the job if the resin tank runs empty, which will result in an incomplete print. Additionally, although all resin printers are fully enclosed units, the resin bottles and tanks of the LCD printers used here must be handled manually. The resin tanks also must be manually cleaned between each sample material change. Skin protection measures must be always taken while operating the liquid polymer printers.⁸

Finally, although proper ventilation is a safety concern with both solid filament⁹ and liquid polymer¹⁰ 3D printers, the amount of standing volatile liquids used for both SLA and LCD printers, including the liquid polymer itself and the alcohol required for post-processing, makes proper fumigation and storage of chemicals a concern for SLA and LCD printers even while they are on standby between jobs.

Summary

Five 3D printers were selected for this study, covering three different types of AM technologies: FDM, SLA, and LCD. Over 2000 total components for almost 700 toy assemblies were fabricated across all five printers. Relative to their own AM type, each printer performed this task equivalently. Even across all five printers there were no notable performance deviations. The FDM and SLA printers each had larger print volumes allowing them to produce more components in a single print. The LCD printers, however, demonstrated faster print speeds due to curing the entire next layer to be added to the structure all at once. Between these differences, each printer ultimately produced finished components at roughly the same rate. These toy samples were then distributed for chemical, flammable, and mechanical analysis.

Chemical hazards associated with the fabrication process were also assessed. All fabrication methods reviewed in this study can release fumes as a byproduct of their processes. FDM printers can produce and release fumes while melting the solid plastic. SLA/LCD printers can produce fumes from the liquid resin tanks and from the alcohol used in post-processing. These fumes can pose a health hazard; however, the hazard can be mitigated using an appropriate ventilation system while the machines are in use. SLA/LCD printers pose an additional chemical hazard due

⁸ <https://radtech.org/safe-handling-of-3d-printing-resins/>.

⁹ Yi J, Duling MG, Bowers LN, Knepp AK, LeBouf RF, Nurkiewicz TR, Ranpara A, Luxton T, Martin SB Jr, Burns DA, Peloquin DM, Baumann EJ, Virji MA, Stefaniak AB. Particle and organic vapor emissions from children's 3-D pen and 3-D printer toys. *Inhal Toxicol.* 2019 Nov - Dec;31(13-14):432-445.

¹⁰ Stefaniak AB, Bowers LN, Knepp AK, Luxton TP, Peloquin DM, Baumann EJ, Ham JE, Wells JR, Johnson AR, LeBouf RF, Su FC, Martin SB Jr, Virji MA. Particle and vapor emissions from vat polymerization desktop-scale 3-dimensional printers. *J Occup Environ Hyg.* 2019 August ; 16(8): 519–531

to the potential of skin contact during handling of the resins and alcohol washes and require additional precautions.

Chemical Analysis

Test Method¹¹

Resin Analysis

A total of 25 liquid resins consisting of various colors and polymer matrices were purchased from four different photopolymer resin manufacturers (Brand 3, 4, 5, and 6¹²). Different types of resins, when available, were analyzed from each brand. The resin types studied included the commonly found Standard resins, as well as specialty resins such as Clear, Tough, Flexible, Plant-based, Water-Washable, ABS-Like and Hi-temp liquid resins. The resins are composed of a variety of monomers and functionalized oligomers and contain a photoinitiator to facilitate the UV curing process. Solid filaments have been researched and characterized by academia, industry, and other federal agencies, resulting in numerous publications. Therefore, the characterization of the solid filament feedstock materials was not included in this report.

The resins were evaluated by Division of Chemistry (LSC) staff to ensure their compliance with relevant federal regulations for chemical content covered by the FHSA and CPSIA. This includes the total lead content, phthalates, and the presence of regulated extractable elements (antimony, arsenic, barium, cadmium, chromium, lead, mercury, and selenium). In addition, staff investigated the chemical composition of the resins.

The photopolymer resins were screened and quantified for elemental content using high-definition X-ray fluorescence (HDXRF) and inductively coupled plasma-optical emission spectrometry (ICP-OES), respectively.

Gas Chromatography-Mass Spectrometry (GC-MS) was used to determine the individual chemical components of these resins. A method was developed after determining the optimum solvent and temperature conditions. Duplicate samples were dissolved in appropriate solvents and injected into the GC-MS for the analysis of the resins. The solvents methylene chloride, acetonitrile, acetone, ethanol, isopropanol, tetrahydrofuran, and cyclohexane were all evaluated for each resin. Direct Analysis in Real Time Mass Spectrometry (DART-MS) was also used to

¹¹ The instruments and materials are identified in this report in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the Consumer Product Safety Commission, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose.

¹² Brand 6 resin was analyzed for chemical content and not used to print any products.

corroborate the chemical content of the resins. Headspace GC-MS was used to test the resins for the presence of any volatile organic compounds (VOC).

Bulk polymer identification was conducted using Fourier-Transform Infrared (FTIR) spectroscopy. An IR profile spectrum for each resin sample was obtained by analyzing a neat sample (*i.e.*, liquid phase, without solvent) of the liquid resin on an FTIR spectrometer at room temperature. The IR profile of each of the samples was compared to a library of chemical standards. The chemical standard library was built by collecting the IR profile of chemicals reported as present in the safety data sheet (SDS), documents provided by the liquid resin manufacturers, as well as published literature.

Finally, flashpoint testing was performed following ASTM D7236 method. Flashpoint testing determines the lowest temperature a chemical can vaporize to form an ignitable mixture in air if an ignition source is provided. Instrument parameters and detailed test methods for each analysis method can be found in **Appendix A and B**.

3D printed children's products

LSC staff analyzed 188 specimens obtained from the 3D printed toys fabricated using the five different 3D printers (resin and filament). Various color and polymer matrix combinations were used to print the same two toy designs, resulting in 94 unique toy samples. The samples were evaluated by LSC staff to ensure their compliance with the relevant federal regulations for lead, phthalates, and the presence of F963 elements covered by the CPSIA and the FHSA.

Qualitative chemical analysis was performed using GC-MS to identify extractable components in each of the printed toys. Isopropyl alcohol (IPA) was used as the extraction solvent of choice. FTIR and pyrolysis GC-MS analysis were used to identify the major polymer components in the printed products. Potential volatile organic compounds present in the samples were tested for using Headspace GC-MS. Finally, the elemental content of the printed products was determined using ICP-OES (quantitative) and HDXRF (qualitative).

Results

Resins

GC-MS, FTIR and DART-MS results identified tri(propylene glycol) diacrylate as one of the major components in Brand 4 and 5 resins. Another common monomer identified across the two brands was 4-acryloylmorpholine. FTIR results indicated that the standard type of Brand 5 resin also contained bisphenol A ethoxylate diacrylate. Brand 6 resins were found to contain 4-acryloylmorpholine, 2-hydroxyethyl acrylate and 1,6-hexandiol diacrylate. FTIR data found that the SLA printer resin, Brand 3, generally contained diurethane dimethacrylate isomers. GC-MS analysis identified isophorone diisocyanate in all the different types of Brand 3 resins analyzed, in addition to some form of hydroxy-“alkyl” dimethacrylate. This reinforces the FTIR data, as the reaction of isophorone diisocyanate with hydroxyethyl methacrylate is known to synthesize polyurethane resins. The complete data tables for FTIR, GC-MS, and DART-MS can be found in **Appendix B**. Flashpoint testing revealed that none of the resins tested ignited below 212 °F.

ICP-OES data indicated that all Brand 3 resins contained phosphorous and tin. Several of the resins also contained titanium. **Tables 3 and 4** show the concentration of the elements found in the different types of Brand 3 resins. Resins with special material properties are indicated in the tables below. Complete ICP-OES tables containing all the elements tested for, including the elements not detected, can be found in **Appendix B**.

Table 3: Elemental content of Brand 3 liquid resins by ICP-OES analysis (mg/Kg)

| Element | C1 (R-Grey) | C2 (R-White) | C3 (T-Grey) | C4 (T-Dark Grey) | C5 (F-Clear) | C8 (Sp-Clear) |
|--------------|----------------|-----------------|----------------|------------------------|-----------------|------------------|
| Arsenic | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Cadmium | <i>nd</i> | <i>nd</i> | <i>nd</i> | 10.0 | <i>nd</i> | 159.8 |
| Lead | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 4.4 |
| Phosphorous* | 1146 | 700.5 | 332.9 | 236.4 | 835.3 | 1124 |
| Tin | 13.0 | 13.4 | 19.0 | 12.3 | 10.2 | 5.4 |
| Titanium | 87.9 | 17.1 | 77.5 | 46.0 | 25.2 | <i>nd</i> |
| Zinc | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 34.1 | <i>nd</i> |

*above highest calibration point (>750 ppm)

R-Rigid resin, T- Tough resin, F-Flexible resin, Sp-Specialty (Hi-Temp) resin, nd-not detected

None contained the following elements: aluminum, antimony, barium, calcium, cobalt, copper, chromium, iron, magnesium, manganese, mercury, molybdenum, nickel, selenium, vanadium

Table 4: Elemental content of Brand 3 liquid resins by ICP-OES analysis (mg/Kg) cont.

| Element | C9 (Light Grey) | C15 (Dark Grey) | C16 (Black) | C17 (Clear) | C19 (R-Grey) |
|--------------|--------------------|--------------------|----------------|----------------|-----------------|
| Arsenic | 1.0 | <i>nd</i> | <i>nd</i> | <i>nd</i> | 1.1 |
| Cadmium | <i>nd</i> | 730.2 | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Phosphorous* | 552.6 | 755.9 | 265.3 | 444.6 | 657.7 |
| Tin | 22.4 | 33.1 | 3.3 | 34.7 | 13.1 |
| Titanium | 113.6 | 187.9 | 148.4 | 3.4 | <i>nd</i> |
| Zinc | <i>nd</i> | <i>nd</i> | 59.1 | <i>nd</i> | <i>nd</i> |

*above highest calibration point (>750 ppm)

R-Rigid resin, nd-not detected

None contained the following elements: aluminum, antimony, barium, calcium, cobalt, copper, chromium, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, selenium, vanadium

Brand 4 resins contained chromium, phosphorous, and tin. In addition, one of the Brand 4 resins also contained aluminum and titanium. **Table 5** shows the concentration of the elements found in the different types of resins.

Table 5: Elemental content of Brand 4 liquid resins by ICP-OES analysis (mg/Kg)

| Element | D1 (P-Translucent Green) | D2 (P-Black) | D3 (P-White) | D4 (Green) | D5 (Clear) |
|--------------|-----------------------------|-----------------|-----------------|---------------|---------------|
| Aluminum | <i>nd</i> | <i>nd</i> | 9.36 | <i>nd</i> | <i>nd</i> |
| Barium | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 36.29 |
| Chromium | 10.00 | 7.66 | 7.48 | 1.96 | <i>nd</i> |
| Iron | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Phosphorous* | 2497 | 3301 | 2434 | 2722 | 4248 |
| Tin | 18.99 | 17.46 | 12.01 | <i>nd</i> | <i>nd</i> |
| Titanium | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> |

*above highest calibration point (>750 ppm)

P- Plant based resin, *nd*-not detected

None contained the following elements: antimony, arsenic, calcium, cadmium, cobalt, copper, lead, magnesium, manganese, mercury, molybdenum, nickel, selenium, vanadium, zinc.

Several of Brand 5 resins contained aluminum, antimony, chromium, copper, tin, and titanium. In addition, one of Brand 5 brand resins contained barium. All Brand 5 resins contained phosphorous. **Tables 6 and 7** show the concentration of the elements found in each of the resins.

Table 6: Elemental content of Brand 5 liquid resins by ICP-OES analysis (mg/Kg) cont.

| Element | E1 (Clear Green) | E2 (Clear Red) | E3 (Grey) | E4 (Skin) | E5 (Maroon) | E6 (Black) | E7 (Translucent) |
|--------------|---------------------|-------------------|--------------|--------------|----------------|---------------|---------------------|
| Aluminum | <i>nd</i> | <i>nd</i> | 9.79 | 10.18 | 8.75 | <i>nd</i> | <i>nd</i> |
| Barium | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 36.29 | <i>nd</i> | <i>nd</i> |
| Chromium | 1.78 | 3.55 | 3.00 | <i>nd</i> | 9.80 | <i>nd</i> | <i>nd</i> |
| Copper | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 2.14 | <i>nd</i> |
| Phosphorous* | 2651 | 2511 | 4446 | 4317 | 3667 | 3689 | 4257 |
| Tin | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 4.14 | <i>nd</i> | <i>nd</i> |
| Titanium | 10.45 | 4.69 | 4.32 | 4.09 | 26.85 | <i>nd</i> | <i>nd</i> |

*above highest calibration point (>750 ppm)

nd- not detected

None contained the following elements: antimony, arsenic, calcium, cadmium, cobalt, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, selenium, vanadium, zinc.

Table 7: Elemental content of Brand 5 liquid resins by ICP-OES analysis (mg/Kg)

| Element | E8 (White) | E9 (Yellow) | E10 (Blue) | E11 (WW- Clear Green) | E12 (WW- Black) | E 13 (ABS- Grey) | E14 (ABS- Clear Blue) | E15 (WW- Clear Red) |
|--------------|---------------|----------------|---------------|--------------------------------|-----------------------|------------------------|--------------------------------|------------------------------|
| Aluminum | 15.09 | 11.74 | 11.73 | nd | nd | 8.01 | nd | nd |
| Antimony | nd | nd | nd | 70.12 | 35.93 | nd | nd | 35.25 |
| Chromium | nd | nd | nd | 2.01 | nd | 11.27 | nd | 4.06 |
| Copper | nd | nd | 1.44 | nd | 2.72 | nd | nd | nd |
| Phosphorous* | 4548 | 4542 | 4506 | 2058 | 3154 | 2624 | 4430 | 1978 |
| Tin | nd | nd | nd | 7.59 | 6.65 | 22.19 | 17.07 | 8.14 |
| Titanium | 2.55 | 3.82 | 4.31 | nd | nd | nd | 21.27 | nd |

*above highest calibration point (>750 ppm)

WW-water washable resin, ABS- ABS-like resin, nd- not detected

None contained the following elements: arsenic, barium, calcium, cadmium, cobalt, iron, lead, magnesium, manganese, mercury, molybdenum, nickel, selenium, vanadium, zinc.

Complete HDXRF data tables containing the elemental contents of the sun cured solid resins are found in **Appendix B**. HDXRF analysis allowed for the quick semi-quantitation of the total elemental content of the resins. Results were consistent with those determined by ICP-OES analysis. A wide variety of elements were found across the different brands of resins as well as across the various resin types within the brands.

HS-GC-MS data tables located in **Appendix B** give the results for VOCs in each of the resins. HS-GC-MS analysis confirmed the presence of toluene in all the resins; however, the concentration was less than 2 µg/mL (determined by comparing to the VOC spiked resin samples). Two of the resins (**D4-green** and **E9-yellow**) also contained trace levels of xylenes. In addition, cyclohexane was also confirmed in all Brand 4, 5, and 6 resins.

3D printed children’s products

GC-MS results tables identifying extractable components in each of the printed toys can be found in **Appendix B**. No chemical components were identified (no NIST library match) in the extract solutions of the resin-based Printer D toy pieces. Ten out of the 14 resin-based Printer E prints had no identifiable chemical components in the solution extracts as well. However, 4-acryloylmorpholine and tripropylene glycol diacrylate were present in the solution extracts of the remaining four toy prints. Eight out of 16 SLA toy prints still had isophorone diisocyanate. The majority of solid filament-based toy prints (Printer A and B) had no identifiable chemical components in the solution extract. No phthalates were detected by GC-MS analysis.

Pyr-GC–MS qualitative result tables can be found in **Appendix B**. The results were used to confirm the polymer type for each of the 3D printed toys produced using the solid filaments (Printer

A and B). The major components were identified by comparing the mass spectra in question with the mass spectra from the NIST MS library, followed by polymer identification using a reference book¹³ to confirm the polymer type (acrylonitrile butadiene styrene (ABS), polylactic acid (PLA), nylon, and poly carbonate (PC)).

Pyr-GC–MS qualitative results for the thermal decomposition of the 3D printed toys produced using the liquid resins (Printers C, D and E) can be found in **Appendix B**. The major components were identified by comparing the mass spectra of compounds detected with the mass spectra from the NIST MS library. Bisphenol A (CAS# 80-05-7) was identified as a major component in each of the 3D printed products produced using the liquid resins. FTIR corroborated the presence of Bisphenol A in Printer E resin printed toys and in two of Printer D toy prints. However, the majority of Printer C’s 3D toy prints had diurethane dimethacrylate identified as a major component. No phthalates were detected by FTIR screening.

ICP-OES data tables **8-19** found below present the elemental content of each of the toy prints tested. Complete ICP-OES tables containing all the elements tested for, including the elements not detected, can be found in **Appendix B**. None of the toy prints contained lead (Pb) and no F963 elements were found above the adjusted limits stated in the ASTM F963-17 Standard Consumer Safety Specification for Toy Safety with one exception. Antimony was found at ~90 ppm in one Printer E toy print (E11); however, once the adjustment factor was applied the amount of extractable antimony fell to 36 ppm which is well below the regulatory limit of 60 ppm.

Table 8: Elemental content of Printer A printed children’s products by ICP-OES (mg/Kg)

| Element | A1 | A2 | A3 | A4 | A5 | A6 | A7 | A8 | A9 | A10 |
|------------|-------|-------|-------|------|--------|--------|-------|------|-------|-------|
| Aluminum | 51.6 | 939.1 | nd | nd | 3930.5 | nd | 753.3 | nd | nd | nd |
| Calcium | nd | nd | 299.5 | nd | nd | nd | nd | nd | nd | nd |
| Copper | nd | nd | nd | nd | nd | nd | 41.1 | nd | 11.6 | nd |
| Iron | nd | 76.3 | nd | nd | 44.6 | 137.60 | 10.8 | nd | nd | nd |
| Magnesium | nd | 43 | nd | nd | 85.5 | nd | nd | nd | nd | nd |
| Phosphorus | nd | nd | nd | nd | nd | 28.2 | nd | nd | nd | nd |
| Tin | 43.4 | 58.4 | 41 | 44.5 | 68.7 | nd | 30.6 | 21.7 | 44 | 33.8 |
| Titanium | 185.7 | 295.1 | 35.2 | 1.1 | 282.3 | 151.8 | 121.2 | 40.3 | 136.5 | 153.9 |
| Zinc | nd | nd | nd | nd | nd | 34.9 | nd | nd | nd | nd |

¹³ Shin T, Hajime O, Chuichi W. Pyrolysis-GC-MS data book of synthetic polymers: pyrogram, thermograms and MS of pyrolyzates; Burlington, Elsevier Science, 2011.

Table 9: Elemental content of Printer A printed children’s products by ICP-OES (mg/Kg)

| Element | A11 | A12 | A13 | A14 | A15 | A16 | A17 | A18 | A19 | A20 |
|------------|-------------|--------------|--------------|-------------|-------------|--------------|--------------|--------------|--------------|--------------|
| Calcium | <i>nd</i> | <i>nd</i> | 26.0 | 11.2 | 4.1 | <i>nd</i> | 24.0 | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Copper | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 2.6 | 2.2 | 2.0 | 2.6 | 2.7 |
| Magnesium | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 141.0 | 128.0 | 113.3 | 138.9 | 108.6 |
| Phosphorus | <i>nd</i> | 7325* | 5877* | 23.9 | 23.8 | 57.8 | 78.2 | 42.8 | 45.9 | 63.8 |
| Selenium | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 1.1 | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Tin | 34.1 | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 4.3 | 1.2 | <i>nd</i> | <i>nd</i> | 0.4 |
| Titanium | 0.7 | <i>nd</i> | <i>nd</i> | <i>nd</i> | 60.7 | 115.6 | 137.5 | 13.9 | 152.6 | 136.5 |

*above highest calibration point (>750 ppm)

Table 10: Elemental content of Printer A printed children’s products by ICP-OES (mg/Kg)

| Element | A21 | A22 | A23 | A24 | A25 | A27 | A28 | A29 | A30 | A31 |
|------------|--------------|--------------|--------------|----------------|---------------|-----------|--------------|-------------|--------------|--------------|
| Aluminum | 65.1 | <i>nd</i> | 51.9 | 3865.8* | <i>nd</i> | <i>nd</i> | 46.3 | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Calcium | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 63.0 | 38.7 | <i>nd</i> | <i>nd</i> |
| Cobalt | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 2.6 | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Copper | 2.6 | 2.3 | 3.0 | 2.8 | 2.7 | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Chromium | <i>nd</i> | <i>nd</i> | <i>nd</i> | 2.2 | 38.9 | <i>nd</i> | <i>nd</i> | <i>nd</i> | 10.6 | 2.3 |
| Iron | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 35.7 | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Magnesium | 140.5 | 141.2 | 112.3 | 146.2 | 595.5 | <i>nd</i> | <i>nd</i> | <i>nd</i> | 0.5 | 1.4 |
| Manganese | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 40.7 | 40.5 |
| Molybdenum | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 1.0 |
| Nickel | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 1.9 | <i>nd</i> | <i>nd</i> | <i>nd</i> | 0.9 | <i>nd</i> |
| Phosphorus | 69.4 | 76.4 | 51.7 | 43.5 | 92.0 | <i>nd</i> | <i>nd</i> | <i>nd</i> | 70.4 | 79.9 |
| Selenium | <i>nd</i> | <i>nd</i> | <i>nd</i> | 1.0 | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 1.1 | <i>nd</i> |
| Titanium | 150.3 | 45.5 | 159.0 | 78.2 | 131.0 | <i>nd</i> | 179.4 | <i>nd</i> | 129.2 | 120.9 |
| Vanadium | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 697.0 |
| Zinc | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 1662.1 | <i>nd</i> | <i>nd</i> | <i>nd</i> | 36.6 | <i>nd</i> |

Table 11: Elemental content of Printer A printed children’s products by ICP-OES (mg/Kg)

| Element | A32 | A33 | A34 | A35 | A36 | A37 | A38 | A39 | A40 | A41 |
|------------|-------|-------|------|------|-------|-------|------|-------|-------|--------|
| Aluminum | 233.5 | nd | nd | nd | 107.9 | 78.5 | nd | nd | nd | nd |
| Calcium | nd | nd | nd | nd | nd | 91.1 | nd | nd | nd | 905.6* |
| Chromium | 15.3 | nd | nd | nd | nd | nd | nd | nd | nd | nd |
| Iron | nd | nd | 32.9 | nd | nd | nd | nd | nd | nd | nd |
| Magnesium | 2.6 | 0.6 | nd | nd | 1.6 | 0.5 | nd | nd | nd | 9.5 |
| Manganese | 40.2 | 41.5 | 20.8 | 42.3 | 40.6 | 39.2 | 40.1 | nd | nd | nd |
| Phosphorus | 70.1 | 72.0 | 36.4 | 70.5 | 74.6 | 90.5 | 69.3 | nd | nd | nd |
| Selenium | nd | 1.1 | nd | nd | 1.1 | 1.1 | nd | nd | 1.1 | 1.2 |
| Tin | nd | nd | nd | nd | nd | nd | nd | 0.1 | nd | 0.2 |
| Titanium | 135.7 | 121.1 | 90.8 | 30.8 | 150.1 | 166.5 | 41.5 | 125.8 | 182.2 | 83.4 |

*above highest calibration point (>750 ppm)

Table 12: Elemental content of Printer A printed children’s products by ICP-OES (mg/Kg)

| Element | A42 | A43 | A44 | A45 |
|------------|-------|-------|-------|------|
| Aluminum | 575.4 | nd | nd | nd |
| Calcium | nd | 46.7 | nd | 36.4 |
| Chromium | 13.8 | nd | nd | nd |
| Magnesium | 4.3 | nd | nd | nd |
| Phosphorus | nd | nd | 5969* | nd |
| Selenium | nd | nd | 1.2 | nd |
| Tin | 0.3 | nd | nd | nd |
| Titanium | 65.9 | 159.8 | 14.3 | nd |

*above highest calibration point (>750 ppm)

Table 13: Elemental content of Printer B printed children’s products by ICP-OES (mg/Kg)

| Element | B1 | B2 | B3 | B4 | B5 | B6 | B7 | B8 |
|----------|-------|-------|-------|------|-------|-------|-------|-------|
| Aluminum | 174.7 | 123.6 | 117.6 | 14.6 | 31.1 | 161.3 | 247 | 56.4 |
| Copper | nd | nd | 93.4 | nd | nd | nd | 63.7 | nd |
| Tin | 39.8 | 38.2 | 38.9 | 38.3 | 39.7 | 39.1 | 39.5 | 37.6 |
| Titanium | 149.3 | 144.8 | 148 | 50.7 | 128.3 | 148.5 | 152.7 | 163.4 |

Table 14: Elemental content of Printer B printed children's products by ICP-OES (mg/Kg) cont.

| Element | B9 | B10 | B11 | B12 | B13 | B14 | B15 |
|------------|-------|-------|-------|-------|--------|-------|-------|
| Aluminum | nd | 43.7 | nd | 54.3 | 49.7 | 16.8 | nd |
| Barium | 543.6 | nd | nd | nd | nd | 74.1 | nd |
| Calcium | 4.6 | nd | nd | nd | 56.6 | 215.5 | nd |
| Chromium | nd | nd | nd | nd | nd | nd | 0.6 |
| Iron | nd | 760.3 | nd | 122.8 | 997.6* | nd | nd |
| Magnesium | nd | nd | nd | nd | 1.2 | 2.2 | 0.6 |
| Manganese | nd | 3.3 | nd | 29.4 | nd | nd | nd |
| Phosphorus | nd | nd | 522.6 | 249.5 | 252.5 | 251.3 | 246.4 |
| Tin | nd | 31.1 | nd | 10.4 | 12.8 | 10.0 | 10.6 |
| Titanium | nd | 171 | 88.5 | 197.3 | 183.5 | 141.8 | 3.0 |
| Zinc | nd | nd | nd | nd | 366.1 | nd | nd |

*above highest calibration point (>750 ppm)

Table 15: Elemental content of Printer C printed children's products by ICP-OES (mg/Kg)

| Element | C1 | C2 | C3 | C4 | C5 | C6 | C7 | C8 |
|------------|--------|-------|-------|-------|-------|--------|--------|-------|
| Aluminum | nd | nd | 127.5 | 107.4 | nd | 15.5 | nd | nd |
| Chromium | nd | nd | nd | nd | 29.3 | 10.6 | nd | nd |
| Iron | 15.1 | nd | nd | nd | nd | nd | nd | nd |
| Magnesium | nd | nd | nd | nd | nd | 0.6 | nd | nd |
| Phosphorus | 921.0* | 641.7 | 2654* | 534.6 | 283.0 | 833.4* | 871.4* | 2898* |
| Tin | 46.8 | 30.3 | nd | nd | nd | 34.2 | 26.3 | nd |
| Titanium | 89.5 | 5.5 | 104.7 | 56.7 | 87.0 | 10.0 | 146.7 | nd |

*above highest calibration point (>750 ppm)

Table 16: Elemental content of Printer C printed children's products by ICP-OES (mg/Kg) cont.

| Element | C9 | C10 | C11 | C12 | C14 | C15 | C16 | C17 |
|------------|------|---------|--------|--------|--------|--------|-------|-------|
| Aluminum | nd | nd | nd | nd | 14 | nd | nd | nd |
| Calcium | nd | nd | nd | nd | 1493.1 | 1576.3 | nd | nd |
| Copper | nd | nd | nd | 5.7 | nd | nd | nd | nd |
| Iron | nd | nd | nd | nd | nd | nd | nd | 3.7 |
| Phosphorus | 32.9 | 1159.8* | 598.8* | 697.9* | 634.7 | 647 | 357.9 | 518.8 |

| | | | | | | | | |
|----------|-----------|-------------|--------------|-------------|-------------|--------------|--------------|-------------|
| Tin | <i>nd</i> | 11.1 | 15.5 | 16.2 | 72.7 | 71.9 | 22.1 | 68.9 |
| Titanium | <i>nd</i> | 19.3 | 124.6 | 42.8 | 143 | 105.2 | 115.2 | 46.4 |

*above highest calibration point (>750 ppm)

Table 17: Elemental content of Printer D printed children’s products by ICP-OES (mg/Kg)

| Element | D1 | D2 | D3 | D4 | D5 |
|------------|--------------|--------------|--------------|--------------|--------------|
| Copper | <i>nd</i> | 1.3 | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Phosphorus | 2459* | 3437* | 2441* | 2752* | 4242* |
| Tin | 28.6 | 33.7 | 19.4 | <i>nd</i> | <i>nd</i> |
| Titanium | 17.9 | 40.3 | 32.4 | <i>nd</i> | 11.6 |

*above highest calibration point (>750 ppm)

Table 18: Elemental content of Printer E printed children’s products by ICP-OES (mg/Kg)

| Element | E1 | E2 | E3 | E4 | E5 | E6 | E7 | E8 |
|-------------|-------------|---------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Aluminum | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 692.4 | 32.6 | 196.3 | <i>nd</i> |
| Arsenic | <i>nd</i> | 0.52 | <i>nd</i> | 0.52 | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Barium | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 263.1 | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Calcium | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 133.3 | <i>nd</i> | 4.9 | <i>nd</i> |
| Iron | <i>nd</i> | 8.9 | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Magnesium | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 303.0 | <i>nd</i> | <i>nd</i> | 8.4 |
| Phosphorus* | 2755 | 2754.2 | 4058.2* | 4196.4* | 2107.1* | 3719.4* | 3821.2* | 4458.1* |
| Titanium | 19.9 | <i>nd</i> | 8.1* | 13.3* | <i>nd</i> | 59.2 | <i>nd</i> | 55.6 |

*above highest calibration point (>750 ppm)

Table 19: Elemental content of Printer E printed children’s products by ICP-OES (mg/Kg) cont.

| Element | E9 | E10 | E11 | E12 | E13 | E14 |
|-----------|--------------|--------------|------------|------------|-------------|-----------|
| Aluminum | 235.7 | 286.5 | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Antimony | <i>nd</i> | <i>nd</i> | 87.8 | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Calcium | 4.4 | 9.1 | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Cobalt | <i>nd</i> | <i>nd</i> | 2.1 | <i>nd</i> | 10.9 | <i>nd</i> |
| Chromium | <i>nd</i> | <i>nd</i> | 2.6 | 1.2 | <i>nd</i> | 1.1 |
| Iron | <i>nd</i> | 23.9 | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> |
| Magnesium | <i>nd</i> | <i>nd</i> | <i>nd</i> | 2.5 | 6.6 | <i>nd</i> |

| | | | | | | |
|-------------|----------------|----------------|----------------|----------------|----------------|----------------|
| Phosphorus* | 2895.2* | 4465.1* | 2010.1* | 3073.9* | 2295.7* | 4449.4* |
| Selenium | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | <i>nd</i> | 1.1 |
| Tin | <i>nd</i> | <i>nd</i> | 5.3 | 5.6 | 15.5 | 14.0 |
| Titanium | <i>nd</i> | 76.4 | 11.7 | 5.6 | 58.8 | 4.8 |

*above highest calibration point (>750 ppm)

Conclusions

Qualitative analysis of the photopolymer resins samples via FTIR, GC-MS, and DART-MS identified several monomers and oligomers. Results were found to be consistent across the three different methods and confirmed the presence of tri(propylene glycol) diacrylate, 4-acryloylmorphiline, 2-hydroxyethyl acrylate and urethane dimethacrylate in a number of resins. The laboratory chemical safety summary datasheets for tri(propylene glycol) diacrylate, 4-acryloylmorphiline and 2-hydroxyethyl acrylate confirm that these compounds are irritants, corrosive, and toxic in some cases. The Safety Data Sheets (SDS) for several photopolymer resins indicate that the hazards associated with the use of the resins include: skin corrosion/irritation, serious eye damage/eye irritation, skin sensitization, and harmful if swallowed. The exact compositions of the resins are not reported in the SDSs due to the proprietary nature of the materials.

Elemental analysis via HDXRF and ICP-OES detected trace amounts of metals, such as aluminum, antimony, chromium, copper, tin, and titanium. It is unclear if some of the elements identified by ICP-OES or HDXRF analysis were intentionally included as photoinitiators or are contaminants from catalysts used during the formulation process. Another possibility is the transfer of elements from the printer to the 3D print during the printing process.

All the 3D printed toys analyzed in this study were found to be compliant with the lead and phthalate limits specified in the CPSIA and FHSA. In addition, no ASTM F963 elements were found in violation of federal regulation limits for migratable heavy elements. No marked difference was observed between the different colors of the resins. However, more work is needed to determine the exact nature of the chemicals and particulates emitted during the printing process. Staff has not reached a conclusion whether any foreseeable consumer exposures during use of 3D printers or 3D printed products would result in a substantial risk of serious illness or injury. CPSC staff is currently working through various interagency agreements to analyze and characterize 3D printer emissions, as well as exposure from 3D printed products, including during printing and post-processing phases.

Flammability Analysis

Test Method

The 3D printed toys were tested according to the Method for Determining Extremely Flammable and Flammable Solids, 16 CFR § 1500.44, to ensure they are not flammable solids. A flammable solid is defined in 16 CFR § 1500.3(c)(6)(vi) as “a solid substance that, when tested by the method described in § 1500.44, ignites and burns with a self-sustained flame at a rate greater than one-tenth of an inch per second along its major axis.” 16 CFR § 1500.44 is a method used to determine the burn rate of a solid along its major axis when the solid is exposed to a candle flame for 5 seconds. ASTM F963-17 Standard Consumer Safety Specification for Toy Safety Annex 5 Flammability Testing Procedure for Solids and Soft Toys gives more detailed procedures to test toys to meet the requirements of 16 CFR § 1500.3(c)(6)(vi).

In this study, samples were supported using a ring stand and clamps while a candle flame was applied to the specimen for 5 seconds at one end of the major axis of the toy. The specimen was allowed to burn for 60 seconds or until it self-extinguished, whichever was shorter. For specimens that burned, a burn rate was calculated from the burn time and the measured burn length along the major axis of the specimen. No burn rate was calculated for specimens that did not ignite. These specimens are considered passing.

Specimens are designated to be in compliance with 16 CFR § 1500.3(c)(6)(vi) and not classified as a flammable solid if the calculated burn rate is less than or equal to 0.1 inches per second.

A total of 185 specimens representing 93 different polymer printing materials, both resins and filaments, and two different toy designs (rattle and bubble wand shown in **Figures 9** and **10**), were printed on five different printers to be used for flammable solids testing.

Results

Burn rates for 3D printed rattles and bubble wand toys are shown in **Table 22**. For rattle specimens, the candle flame was applied to the handle end, unless otherwise noted. For bubble wand specimens, the flame was applied to the circular end, *i.e.*, the end opposite the handle. Test setup for rattle specimens and bubble wand specimens are shown in **Figures 9** and **10**, respectively.

Table 22: Burn Rates for 3D Printed Toys Tested According to 16 CFR 1500.44

| ID# | Material Description (Feedstock type/color) | Rattle Burn Rate (inches/second) | Bubble Wand Burn Rate (inches/second) |
|-----|--|--|---|
| A1 | Filament PLA White | Did Not Ignite | 0.03 |
| A2 | Filament PLA Pearl White | Did Not Ignite | 0.03 |
| A3 | Filament PLA Yellow | Did Not Ignite | 0.03 |
| A4 | Filament PLA Black | Did Not Ignite | 0.03 |

| | | | |
|-----|------------------------------|-----------------|----------------|
| A5 | Filament PLA Silver Metallic | Did Not Ignite | 0.03 |
| A6 | Filament PLA Red | Did Not Ignite* | 0.03 |
| A7 | Filament PLA Blue | Did Not Ignite | 0.03 |
| A8 | Filament PLA Transparent | Did Not Ignite | 0.03 |
| A9 | Filament PLA Green | Did Not Ignite | 0.03 |
| A10 | Filament PLA Magenta | Did Not Ignite | 0.03 |
| A11 | Filament PLA Orange | 0.02 | 0.03 |
| A12 | Filament Tough PLA Black | Did Not Ignite | 0.04 |
| A13 | Filament Tough PLA Green | Did Not Ignite | 0.04 |
| A14 | Filament Tough PLA Red | Did Not Ignite | 0.04 |
| A15 | Filament Tough PLA White | Did Not Ignite | 0.05 |
| A16 | Filament ABS Blue | Did Not Ignite | 0.04 |
| A17 | Filament ABS Green | Did Not Ignite | 0.04 |
| A18 | Filament ABS Black | Did Not Ignite | 0.04 |
| A19 | Filament ABS Gray | Did Not Ignite* | 0.04 |
| A20 | Filament ABS Yellow | Did Not Ignite | 0.04 |
| A21 | Filament ABS White | Did Not Ignite | 0.04 |
| A22 | Filament ABS Red | Did Not Ignite | 0.04 |
| A23 | Filament ABS Orange | Did Not Ignite | 0.04 |
| A24 | Filament ABS Silver | Did Not Ignite | 0.04 |
| A25 | Filament ABS Pearl Gold | Did Not Ignite | 0.03 |
| A27 | Filament PP Natural | Did Not Ignite* | 0.03 |
| A28 | Filament Nylon Transparent | Did Not Ignite | Did Not Ignite |
| A29 | Filament Nylon Black | Did Not Ignite | Did Not Ignite |
| A30 | Filament CPE Red | Did Not Ignite | 0.04† |
| A31 | Filament CPE Green | Did Not Ignite | 0.03† |
| A32 | Filament CPE Blue | Did Not Ignite | 0.04 |
| A33 | Filament CPE Yellow | Did Not Ignite | 0.04† |
| A34 | Filament CPE Light Gray | Did Not Ignite | 0.01† |
| A35 | Filament CPE Transparent | Did Not Ignite | 0.01† |
| A36 | Filament CPE Dark Gray | Did Not Ignite | 0.04† |
| A37 | Filament CPE White | Did Not Ignite | 0.02† |
| A38 | Filament CPE Black | Did Not Ignite | 0.03 |
| A39 | Filament TPU95A Black | Did Not Ignite | 0.03† |
| A40 | Filament TPU95A White | Did Not Ignite | 0.01† |
| A41 | Filament TPU 95A Red | Did Not Ignite | 0.02† |
| A42 | Filament TPU 95A Blue | Did Not Ignite | 0.01† |
| A43 | Filament PC Black | Did Not Ignite | 0.01 |

| | | | |
|-----|-------------------------------------|----------------------|----------------|
| A44 | Filament PC White | Did Not Ignite | Did Not Ignite |
| A45 | Filament PC Transparent | Did Not Ignite | Did Not Ignite |
| B1 | Filament PLA True Red | 0.02 | 0.03 |
| B2 | Filament PLA True Orange | Did Not Ignite | 0.03 |
| B3 | Filament PLA True Blue | 0.03 | Did Not Ignite |
| B4 | Filament PLA True Black | Did Not Ignite | 0.03 |
| B5 | Filament PLA True Purple | Did Not Ignite | 0.03 |
| B6 | Filament PLA True Yellow | 0.03 | 0.03 |
| B7 | Filament PLA True Green | Did Not Ignite | 0.02 |
| B8 | Filament PLA True White | 0.03 | Did Not Ignite |
| B9 | Filament PLA Warm Gray | Did Not Ignite | 0.02 |
| B10 | Filament PLA Cool Gray | 0.03 | 0.03 |
| B11 | Filament PLA Natural | Did Not Ignite | 0.03 |
| B12 | Filament Tough Stone White | 0.03 | 0.04 |
| B13 | Filament Tough Slate Gray | 0.02* | 0.04 |
| B14 | Filament Tough Safety Orange | Did Not Ignite | 0.04 |
| B15 | Filament Tough Onyx Black | 0.03 | 0.04 |
| C1 | Resin Grey Pro | 0.01 | 0.02 |
| C2 | Resin Rigid White | Did Not Ignite | 0.02 |
| C3 | Resin Tough A Grey | Did Not Ignite | 0.02 |
| C4 | Resin Tough B Grey | Did Not Ignite | 0.02 |
| C6 | Resin Castable Wax Dark Purple | Did Not Ignite | 0.02 |
| C7 | Resin Model Orange | Did Not Ignite | 0.02 |
| C8 | Resin High Temp Clear | Did Not Ignite | 0.02 |
| C9 | Resin Light Grey | Did Not Ignite | 0.02 |
| C10 | Resin Durable Clear | Did Not Ignite | 0.02 |
| C11 | Resin Flexible Grey | Did Not Ignite | 0.02 |
| C12 | Resin Tough Blue | Did Not Ignite | 0.02 |
| C14 | Resin White | No Specimen Received | 0.02 |
| C15 | Resin Grey | Did Not Ignite | 0.02 |
| C16 | Resin Black | Did Not Ignite | 0.02 |
| C17 | Resin Clear | Did Not Ignite | 0.02 |
| D1 | Resin Plant-based Translucent Green | Did Not Ignite | 0.02 |
| D2 | Resin Plant-based Black | Did Not Ignite | 0.02 |
| D3 | Resin Plant-based White | Did Not Ignite | 0.02 |
| D4 | Resin Green | Did Not Ignite | 0.02 |
| D5 | Resin Clear | Did Not Ignite | 0.02 |

| | | | |
|-----|---------------------------|----------------|------|
| E1 | Resin Green | Did Not Ignite | 0.02 |
| E2 | Resin Red | Did Not Ignite | 0.02 |
| E3 | Resin Grey | Did Not Ignite | 0.02 |
| E4 | Resin Skin | Did Not Ignite | 0.02 |
| E5 | Resin Maroon | 0.05* | 0.02 |
| E6 | Resin Black | Did Not Ignite | 0.02 |
| E7 | Resin Translucent | Did Not Ignite | 0.02 |
| E8 | Resin White | Did Not Ignite | 0.02 |
| E9 | Resin Yellow | Did Not Ignite | 0.02 |
| E10 | Resin Blue | Did Not Ignite | 0.02 |
| E11 | Resin WW Green | Did Not Ignite | 0.02 |
| E12 | Resin WW Black | Did Not Ignite | 0.02 |
| E13 | Resin ABS-Like Grey | Did Not Ignite | 0.02 |
| E14 | Resin ABS-Like Clear Blue | Did Not Ignite | 0.02 |

† These specimens self-extinguished before 60 seconds.

* These rattle specimens were all broken during printing (usually handle broken off with sphere of rattle remaining), and as a result, these specimens had a different sample geometry than other rattle specimens and were ignited at different places based on the longest axis for the specimen.

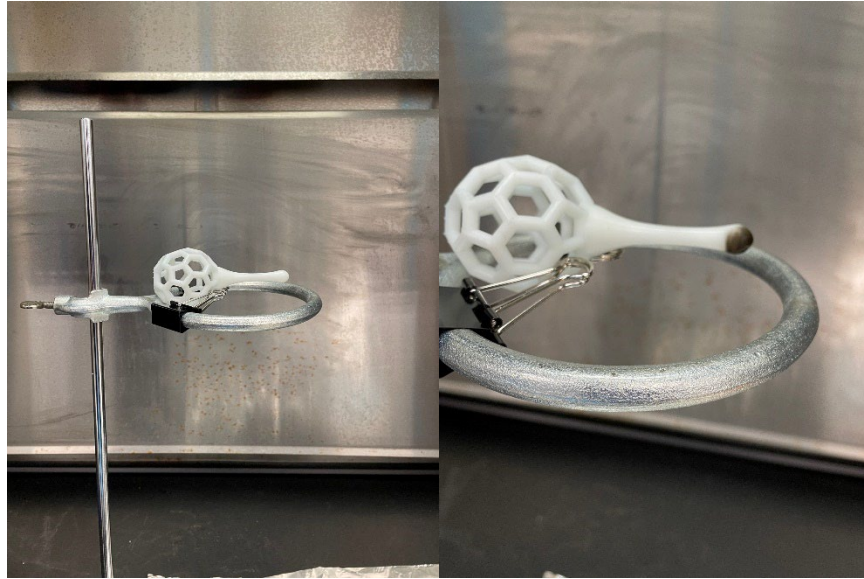


Figure 9: Rattle Specimen Test Setup

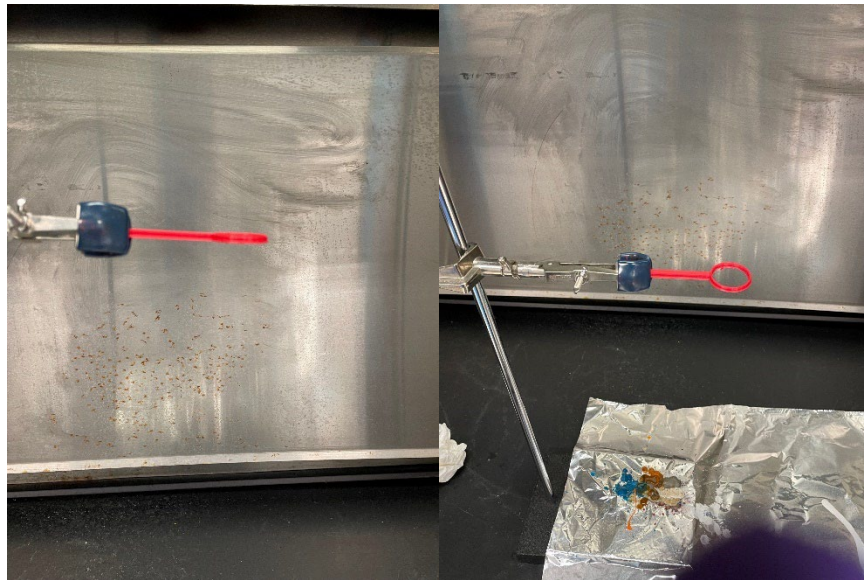


Figure 10: Bubble Wand Specimen Test Setup

Conclusions

All specimens tested were well below the 0.1 inches/second burn rate threshold for classification as flammable solids. As expected, the shape of the toy had an impact on the flammability of the toy, with the thinner bubble wand design being more likely to ignite than the thicker rattle design

made from the same material. None of toys from the materials and designs selected are considered flammable solids, according to 16 CFR § 1500.3(c)(6)(vi). This testing suggests that toys made using evaluated consumer 3D printers do not pose an inherent flammability hazard, although flammability will depend on the shape of the printed toy.

Mechanical Analysis

Test Method

The 3D toy samples were mechanically tested according to the drop test described in ASTM F963-17, Section 8.7.1. The specifics of the test plan were developed with LSM and CPSC Epidemiology (EPI) staff. EPI's analysis of the test results can be found in the following chapter, "Data analysis of 3D printed children's products."

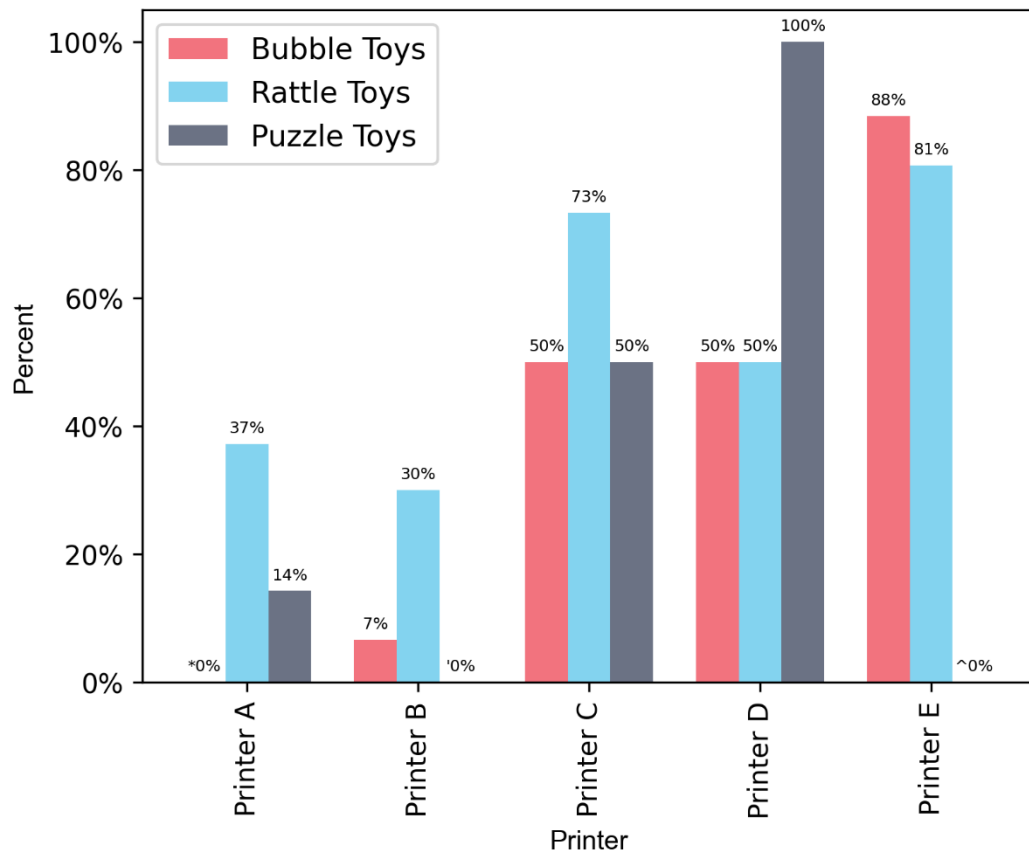
The designs were selected as discussed previously based on what fell within the 0-35 month age range according to HF staff's age determination. The applicable use and abuse testing from ASTM F963-17 primarily tests for the liberation of small parts, sharp edges, or sharp points. Although sharp edges and sharp points are a potential hazard for toys in the age range above 35 months, sharp edges are only considered for products made from metal or glass¹⁴. The focus of general use and abuse testing for these plastic products was narrowed down to only the small parts examination, requiring the age range cap.

The overall performance of toy types by printer is shown in **Figure 11**¹⁵. In general, both FDM printers produced fewer samples that liberated small parts than the SLA and LCD printers. Printer D had comparable results to Printer C, and Printer E produced the most samples that did not meet the safety criteria.

¹⁴ ASTM F963-17 Standard Consumer Safety Specification for Toy Safety

¹⁵ Based on the statistical analysis of the data

Percent of Toys That Did Not Meet Criteria by Toy Type and Printer



Notes:

^ No samples of Printer E-Resin tested for Puzzle Toys.

* One sample that experienced liberation of a part, not small, and was considered to have “met” the criteria.

^ One sample had components broken prior to testing, but the main component was tested and was considered to have “met” the criteria.

Figure 11: Percent of toys that did Not meet criteria by toy type and printer

Results

Bubble Toy Performance Analysis

With an age grading of 19-35 months, the Bubble Toys were all dropped from three feet above the testing surface a total of four times¹⁶. LSM staff attributes the performance of the bubble toy to the differences between solid and liquid source material fabrication processes, rather than

¹⁶ From ASTM F963-17

difference between the specific source material. FDM printers extrude everything in layers; however, they do not extrude to completely fill the volume of an enclosed shape. While different fill designs can be selected before uploading the design from the computer to the printer, most fill patterns involve the use of a lattice structure to only partially fill any enclosed space. This is done to both conserve material, and to decrease the time required per print by only completely extruding the exposed surfaces. By contrast, the SLA and LCD printers flash the complete image of the object to the bottom surface of the structure of the print, completely filling any internal space.

The result is that the FDM components are typically hollow, with an internal lattice support structure, while the SLA/LCD are completely solid. The relative density of the liquid polymer components is higher than their otherwise identical solid filament components. This means that the resin components impact the testing surface with more force than the filament ones, as demonstrated by **Table 23** and **Table 24**. Using the average of both resin and filament source types, the potential energy of the resin Rattles is more than 1.4 times greater than the filament Rattles, and the potential energy of just the triangle peg from the First Puzzle System is more than 1.8 time greater.

Table 23: Potential Energy Difference Between Filament and Resin Samples: Rattle

| Printer | Material | Mass (g) | PE (J) | Average PE (J) by Source Type |
|-----------|----------|----------|--------|-------------------------------|
| Printer A | PLA | 14.00 | 0.1884 | 0.1775 |
| Printer B | PLA | 12.37 | 0.1665 | |
| Printer C | Standard | 18.51 | 0.2491 | 0.2563 |
| Printer D | Basic | 20.51 | 0.2761 | |
| Printer E | Standard | 18.10 | 0.2436 | |

Table 24: Potential Energy Difference Between Filament and Resin Samples: First Puzzle System, Triangle Peg

| Printer | Material | Mass (g) | PE (J) | Average PE (J) by Source Type |
|-----------|----------|----------|--------|-------------------------------|
| Printer A | PLA | 7.000 | 0.0628 | 0.1775 |
| Printer B | PLA | 9.150 | 0.0821 | |
| Printer C | Standard | 13.92 | 0.1249 | 0.2563 |
| Printer D | Basic | 15.74 | 0.1412 | |

On impact, because of the layering process, there are more avenues for the filament models to disperse the force along its internal lattice, while the internal structure of the resin models provides no mechanical shock absorption advantage. The layers at the point of impact on the filament model separate from the rest of the impacted face due to the force but can otherwise remain intact

because each layer can individually separate or distribute the force along its lattice. On the resin model, however, if the impact is enough to cause fracturing, then that area of the model has no option but to separate from the rest of the model (**Figure 12**).



Figure 12: Example of Bubble Toy sets which fractured. Top; A Printer C resin sample which liberated a part that did not meet the requirements of ASTM F963-17. Bottom; Printer A filament sample which fractured at approximately the same point but distributed the force such that the split portion still met the same requirements.

Rattle Performance Analysis

The Rattles were all dropped from 4.5 feet above the testing surface a total of 10 times¹⁷.

The primary failure mode of FDM Rattles was at the interface between the handle and the bulb. Only two FDM Rattles, both printed with Printer A, broke at the bulb. The primary failure mode of SLA and LCD Rattles were at the bulb.

LSM staff interpret this as another result of the respective fabrication processes. The interface of the handle and the bulb of the Rattle design occurs at an opening between one of the hexagon patterns in the bulb. On FDM printers, this means that the first layer sealing that hexagon closed

¹⁷ From ASTM F963-17

to complete the rest of the handle takes place on an open space in the air. The first layer at that point comes out looking “stringy”, which is a term used to describe when a mid-print layer does not fully adhere to the previous layer (**Figure 13**). This problem may have been mitigated by adding support structure to that location during the print, but since the instructions that accompany the Rattle design explicitly state to not use any supports inside the bulb, this modification to the design was not made for this study. In the SLA/LCD Rattles, because that interface is flashed at/very nearly the same time while still within the resin tank, the connection at that point is as solidly filled as the rest of the resin model is.

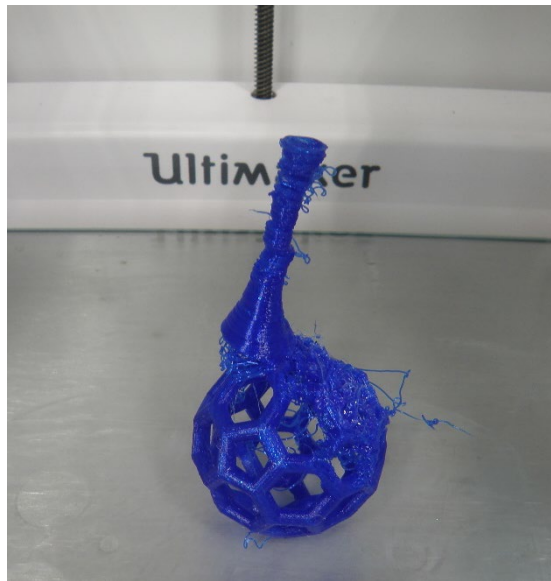


Figure 13: An extreme example of stringing in FDM models, ultimately resulting in this failed print. Stringing did not occur until the handle-bulb interface.

Compared to the bulb structure, the handle is a longer and denser feature which relies on the strength of the handle-bulb interface to keep it in one piece. When the FDM Rattles impact the testing surface, stress concentrates at the handle-bulb interface, which is already compromised, and ultimately the impact force is dissipated through dislodging the handle.

Since the handle is better supported in the SLA/LCD Rattles, impact stresses do not concentrate at a singular point. Its solid fill method also subjects it to the same lack of internal force dissipation methods seen in the Bubble Toy. The impact forces rise to a level above the strength of the material or the strength of the joints between hexes, and it fractures (**Figure 14**).

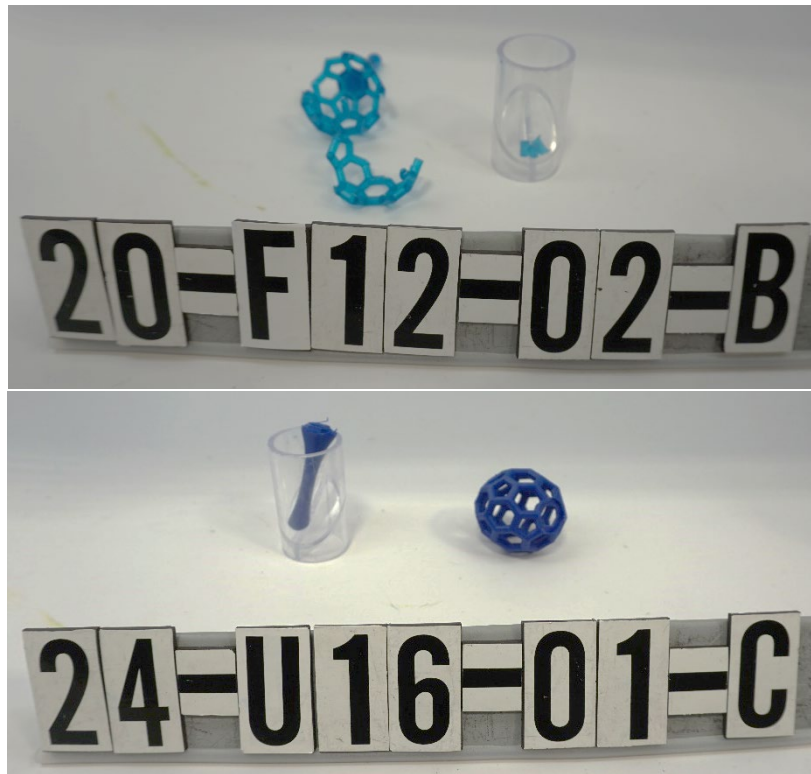


Figure 14: Examples of Rattles which fractured during testing. Top; A Printer C resin sample with bulb fractures at the joints between hexes. Bottom; Printer A filament sample which fractured at the handle-bulb interface.

First Puzzle System Performance Analysis

The First Puzzle Systems were all dropped from 3 feet above the testing surface a total of 4 times¹⁸.

The First Puzzle System components were the largest of all toys tested. Like the previous toy samples, the SLA/LCD printers produced First Puzzle Systems that are heavier than their FDM counterparts. The back wall of the mold pieces that the pegs fit into are the thinnest wall section of the set, and these components were the first to liberate small parts during testing. For FDM First Puzzle Systems, the interface between the knob on the peg and the rest of the shape insert was the weakest connection point, and this was where the most damage occurred during testing (**Figure 15**).

¹⁸ From ASTM F963-17



Figure 15: Examples of First Puzzle System sets which liberated small parts that did not meet the requirements of ASTM F963-17. Top; A Printer D resin sample with spider cracks originating from the center of its thinnest wall. Bottom; Printer A filament sample which fractured at the knob-peg connection point.

Interestingly, one of the two Printer A First Puzzle System samples split apart at one of the bottom layers (**Figure 16**). While it's not the most likely fracture point, and both pieces were large enough to meet the requirements of ASTM F963-17, it is representative of delamination failures and other layer adhesion issues that can arise from FDM fabrication.



Figure 16: Example of a unique structural failure of an FDM model First Puzzle set which liberated parts that did meet the requirements of ASTM F963-17.

Conclusions

Through use and abuse testing, as dictated by ASTM F963-17, LSM staff observed that more resin-based samples did not meet the small parts criteria compared to identical filament-based samples. No statistical comparisons were conducted. LSM staff finds this is likely because the resin samples experienced greater impact forces than their filament counterparts and that the solid fill of the resin samples is unable to distribute the impact force as well as the lattice fill of the filament samples. LSM staff conclude that material type does play a role in the samples' performance, however the consistency demonstrated across different filament and resin materials indicates these construction failures are more likely the immediate cause for the samples' performances.

LSM staff tested 182 Bubble Toys, 182 Rattles, and 34 First Puzzle Systems, for a total of 398 children's products to ASTM F963-17's use and abuse testing. Of these almost 400 products only the four First Puzzle Systems from Printer B demonstrated a 100% passing rate. The failure rate for all children's products printed is 36.7%. Separating the products by 3D printer, on average each printer saw 45% of the products it produced fail. Based on these results, LSM staff recommends developing a consumer notification of the possible danger that 3D printing their own children's products might pose if incorrect printing parameters or materials are used. The samples made for this project utilized default settings, with support structure modifications made only to ensure that the print could be completed. This decision was made to ensure uniformity across samples to draw valid comparison in testing data. However, there are a vast number of settings which a consumer can alter before initiating a print. An end user may adjust the infill percentage, the extrusion speed, the thickness of each layer, the shapes used in the lattice of FDM models, the scaling factor for the entire part, or just a portion of the parts, size, etc. Even altering the temperature of the nozzle and bed can have an immense impact on the final product. Consideration of these factors by consumers when printing products will be important for safety.

Consumers should be cautioned that successfully 3D printing a children's product does not mean that the product is durable enough to meet the use and abuse performance requirements of ASTM F963-17. While it may be possible to alter the parameters of a print to produce a more durable product that can meet those requirements, users experiment at their own risk. Any children's products produced for consumer use through 3D printing should be verified against ASTM F963-17, as is required of all toy products per 16 CFR 1500 and 16 CFR 1501

While this study seems to indicate that SLA/LCD printed children's products are less likely to meet the use and abuse small parts requirements compared to FDM printed children's products, end users can and should optimize the parameters discussed above and the related part files to improve the durability of the printed items. Thus, LSM staff caution readers against interpreting the results from this study as meaning that SLA/LCD children's products are less safe than FDM children's products. Instead, LSM staff suggest that that without further optimization the FDM children's products fabricated during this study tend to perform better against ASTM F963-17

compared to their SLA/LCD counterparts, which illustrates the need for careful optimization by users when 3D printing children’s products.

Data Analysis of 3D Printed Children’s Products

Testing was performed by CPSC staff to identify issues with 3D printed toy products that may break during normal usage and render the products unsafe for infants and toddlers. This section of the report summarizes the data collected from the use and abuse testing on toy products created by a select combination of 3D printers and feedstock materials. Details about the testing plan or process, including the use and abuse tests of primary interest, can be found in the mechanical hazard analysis section.

Test Method

The printer/feedstock material combinations tested were: Printer C-Resin, Printer D-Resin, Printer E-Resin, Printer A-Filament, and Printer B-Filament. These will be referred to as “printers” in the rest of this discussion. The toys printed and tested were: bubble toys, puzzles, and rattles. Two replicates of each toy, printer, color and feedstock material combination were printed by LS staff during FY 22 Q1/Q2. Data collection from the tests on the three types of toys was conducted during FY22 Q3.

This section provides descriptive statistics of data collected on the various printer, resin and toy type combinations that were subjected to the use and abuse test. No statistical inference was requested.

Summary statistics were calculated for the various printer, feedstock material and toys combination based on the use and abuse test. The “Met” or “did not meet” criteria have been described in detail in the mechanical hazard analysis section. In short, a sample was considered to have met the testing criteria if no small parts were liberated or if the liberated part did not fit into the small parts cylinder. In addition to the overall use and abuse test for “Met” and “did not meet” criteria:

- a. A small part was defined as a liberated part that fit into a specified small parts cylinder.
- b. If a sample experienced liberation of a small part, then the sample was annotated as such. However, if a sample experienced liberation of a part but the liberated part did not fit into the small parts cylinder, then the sample was defined to have “Met” the testing criteria, and was annotated as “Parts, Not Small.”

Results

Bubble Toys

The first toys tested were Bubble toys. A total of 182 toys were tested across five printers. Drops were completed until there was liberation of a small part, or until the maximum number of drops (for the Bubble toy the maximum number of drops is four) was reached. The number of drops completed is listed in **Table 25**. The percentage and count of toys that met the requirement for each printer is listed in **Table 26**. The total number of drops differ due to differences in the number of samples per type of printer and resin combination.

Table 25: Bubble Toy-Number of Drops

| Printer | Number of Drops | | | | Total |
|--------------------|-----------------|---|----|-----|-------|
| | 1 | 2 | 3 | 4 | |
| Printer A-Filament | 0 | 0 | 0 | 86 | 86 |
| Printer B-Filament | 0 | 1 | 0 | 29 | 30 |
| Printer C-Resin | 7 | 2 | 3 | 18 | 30 |
| Printer D-Resin | 2 | 1 | 1 | 6 | 10 |
| Printer E-Resin | 12 | 5 | 6 | 3 | 26 |
| Total | 21 | 9 | 10 | 142 | 182 |

Table 26: Distribution of Bubble Toy Test Outcomes

| Printer | Outcome | | | Total |
|--------------------|----------|-------------------|------------|-------|
| | Met | Parts, Not Small* | Small Part | |
| Printer A-Filament | 97% (83) | 3% (3) | 0% (0) | 86 |
| Printer B-Filament | 93% (28) | 0% (0) | 7% (2) | 30 |
| Printer C-Resin | 43% (13) | 7% (2) | 50% (15) | 30 |
| Printer D-Resin | 60% (6) | 0% (0) | 40% (4) | 10 |
| Printer E-Resin | 12% (3) | 0% (0) | 88% (23) | 26 |

*Liberation of parts, not small, are considered to have met the criteria.

Of the five types of printers, only Printer A-Filament printer did not produce any toys that experienced a liberation of a small part. Printer C-Resin and Printer A-Filament did experience liberations of parts, but these were not small and are considered to have “Met” the requirements.

Printer A-Filament had the highest percentage of Bubble toys meet the requirements (100%), while Printer E-Resin had the lowest percentage of Bubble toys meet the requirements (12%).

Rattle Toys

The second type of toys tested were rattle toys. A total of 182 toys were tested across five printers. As done for Bubble toys, drops were completed until there was liberation of a small part, or until the maximum number of drops (for the rattle toy was ten) was reached. The number of drops completed is listed in **Table 27**. The percentage and count of toys that met the requirement for each printer is listed in **Table 28**. The total number of drops differ due to differences in the number of samples per type of printer and resin combination.

Table 27: Rattle Toy-Number of Drops

| Printer | Number of Drops | | | | | | | | | | Total |
|--------------------|-----------------|----|----|---|---|---|---|---|---|----|-------|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | |
| Printer A-Filament | 24 | 14 | 5 | 3 | 1 | 1 | 0 | 2 | 0 | 36 | 86 |
| Printer B-Filament | 2 | 1 | 0 | 1 | 1 | 3 | 0 | 1 | 0 | 21 | 30 |
| Printer C-Resin | 15 | 6 | 3 | 0 | 0 | 0 | 2 | 0 | 0 | 4 | 30 |
| Printer D-Resin | 3 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 5 | 10 |
| Printer E-Resin | 4 | 5 | 2 | 3 | 2 | 0 | 1 | 0 | 3 | 6 | 26 |
| Total | 48 | 26 | 11 | 7 | 4 | 5 | 3 | 3 | 3 | 72 | 182 |

Table 28: Distribution of Rattle Toy Test Outcomes

| Printer | Outcome | | | Total |
|--------------------|----------|-------------------|------------|-------|
| | Met | Parts, Not Small* | Small Part | |
| Printer A-Filament | 41% (35) | 22% (19) | 37% (32) | 86 |
| Printer B-Filament | 70% (21) | 0% (0) | 30% (9) | 30 |
| Printer C-Resin | 13% (4) | 13% (4) | 74% (22) | 30 |
| Printer D-Resin | 50% (5) | 0% (0) | 50% (5) | 10 |
| Printer E-Resin | 19% (5) | 0% (0) | 81% (21) | 26 |

*Liberation of parts, not small, are considered to have met the criteria.

Of the five printers, Printer B-Filament had the highest percentage of samples meet the requirements (70%), while Printer E-Resin had the lowest percentage of samples meet the requirements (19%).

Puzzle Toys

The last toys tested were puzzle toys. A total of 34 toys were tested across four printers. Drops were completed until there was liberation of a small part, or until the maximum number of drops (for the puzzle toy was 10) was reached. The number of drops completed is listed in **Table 29**. The percentage and count of toys that met the requirement for each printer is listed in **Table 30**. The total number of drops differ, due to differences in the number of samples per type of printer and resin combination.

For the puzzle toys, some toys had components of the toy already broken prior to testing. These components were not included in testing and are considered as “Other” in **Table 30**.

Table 29: Puzzle Toy-Number of Drops

| Printer | Number of Drops | | | | Total |
|--------------------|-----------------|---|---|----|-------|
| | 1 | 2 | 3 | 4 | |
| Printer A-Filament | 1 | 0 | 0 | 13 | 14 |
| Printer B-Filament | 0 | 0 | 0 | 4 | 4 |
| Printer C-Resin | 3 | 2 | 0 | 7 | 12 |
| Printer D-Resin | 1 | 2 | 0 | 1 | 4 |
| Total | 5 | 4 | 0 | 25 | 34 |

Table 30: Distribution of Puzzle Toy Outcomes

| Printer | Outcome | | | Total |
|--------------------|----------|------------|---------|-------|
| | Met | Small Part | Other* | |
| Printer A-Filament | 79% (11) | 14% (2) | 7% (1) | 14 |
| Printer B-Filament | 75% (3) | 0% (0) | 25% (1) | 4 |
| Printer C-Resin | 50% (6) | 50% (6) | 0% (0) | 12 |
| Printer D-Resin | 0% (0) | 100% (4) | 0% (0) | 4 |

*Other: components that were already broken prior to testing were removed, but the main component was still tested and was considered to have “Met” criteria.

Among the four printers, Printer A-Filament printer had the highest percentage of toys meet the requirements (79%). Printer D-Resin printer had no toys meet the criteria, as all experienced liberation of small parts.

Limitations

This study examined specific printers, resins and toys based on products selected by CPSC LS staff. The results, including the descriptive statistics provided here, would not necessarily be representative of all 3D printers, resins, printer settings, and toy types. Randomization of order

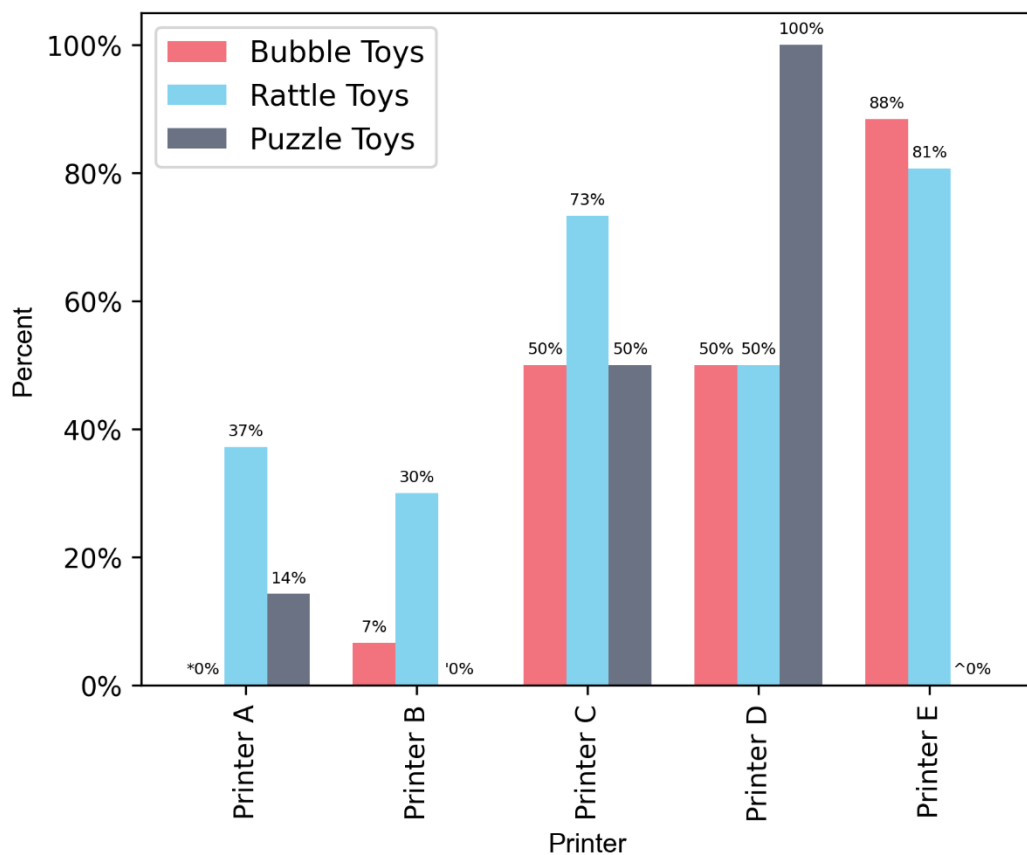
was limited by restrictions, as advised by testing staff; and there may have been differences between testers or samples that could not be accounted for. As no statistical test were pre-specified or conducted, there was no statistical evidence to suggest that any printers produced toys that performed better overall, or by toy type.

Conclusions

A multiple bar graph representing the percent of toys that did not meet the criteria by toy type and printer is shown below.

Figure 17: Percent of Toys that Did Not Meet Criteria by Toy Type and Printer

Percent of Toys That Did Not Meet Criteria by Toy Type and Printer



Notes:

^ No samples of Printer E-Resin tested for Puzzle Toys.

* One sample that experienced liberation of a part, not small, and was considered to have “met” the criteria.

‘ One sample had components broken (but not into small parts) prior to testing, but the main component was tested and was considered to have “met” the criteria.

Based on the observations above, it seems that Printer A-Filament and Printer B-Filament performed better across all three toy types, as they have a lower percentage of toys that did not meet the criteria. However, no statistical tests were conducted to compare the percent of toys that did not meet the criteria, due to the limitations described above.

Summary

3D/AM printing technologies have become readily accessible to the general public. 3D printers can now be found in use in schools, libraries, and homes. Free, open-source software, affordable printers and readily available 3D model files have aided in the proliferation of 3D printer usage. Staff did not identify any fire and combustion hazards; however, some potential chemical and mechanical hazards were found. This includes the presence of certain VOC's (e.g., toluene) detected by headspace and trace amounts of metals (aluminum, antimony, chromium, copper, tin, and titanium). Chemical analysis of the bulk resin materials indicated the presence of skin irritants and reinforced the need for PPE as recommended in all material safety data sheets(SDS). Staff did not determine whether reasonably expected exposures to these chemicals pose a substantial risk of serious illness or injury. Mechanical hazards, such as small parts and sharp points, were found through use-and-abuse testing. Staff observed that the FDM children's products fabricated through this study tend to liberate fewer small parts, compared to their SLA/LCD counterparts; however, staff made no attempt to improve specific designs or printer parameters to address compliance with use-and-abuse requirements. Proper guidance is needed to ensure that the consumers are well informed of the potential hazards associated with the use of the printers and for microproducers of 3D printed children's products to consider the design and printing parameters needed to ensure compliance with small parts regulations. Proper ventilation and personal protection equipment are recommended when handling liquid resins and during the printing and post-printing phases. Home-printed toys may not meet all industry and CPSC safety standards. Consumers should be aware of the risks associated with printing and using printed children's toys, while manufacturers should ensure that 3D printed toys and children's products meet all applicable requirements.

References

ASTM F963-17 Standard Consumer Safety Specification for Toy Safety.

Bharti N., and S. Singh [2017]. Three-dimensional (3-D) printers in libraries: Perspective and preliminary safety analysis. J. Chem. Educ. 94(7):879–885.

<https://pubs.acs.org/doi/abs/10.1021/acs.jchemed.6b00745>

CPSC Report on Safety Concerns Associated with 3D Printing and 3D Printed Consumer Products, May 2020.

CLEAPSS [2020]. Consortium of Local Education Authorities for the Provision of Science Services and the Health and Safety Executive (HSE). 3D Printing In Schools and Colleges: Managing the Risks <http://dt.cleapss.org.uk/Resource-File/3D-printing-in-schools-and-colleges-managing-the-risks.pdf>

Hoffman T [2018]. 3D Printer Filaments Explained. PC Magazine April 28. <https://www.pcmag.com/how-to/3d-printer-filaments-explained>

ISO (International Organization for Standardization)/ASTM. 2016. Standard terminology for additive manufacturing – General principles – Terminology. ISO/ASTM 52900:2015(E). Conshohocken, PA. ASTM International.

Moorefield-Lang, H [2014]. Makers in the library: Case studies of 3-D printers and makerspaces in library settings. Library Hi Tech. 32(4):583–593. <https://www.emerald.com/insight/content/doi/10.1108/LHT-06-2014-0056/full/html>

Shin T, Hajime O, Chuichi W. Pyrolysis-GC-MS data book of synthetic polymers: pyrogram, thermograms and MS of pyrolyzates; Burlington, Elsevier Science, 2011.

Stefaniak AB, Bowers LN, Knepp AK, Luxton TP, Peloquin DM, Baumann EJ, Ham JE, Wells JR, Johnson AR, LeBouf RF, Su FC, Martin SB Jr, Virji MA. Particle and vapor emissions from vat polymerization desktop-scale 3-dimensional printers. J Occup Environ Hyg. 2019 August; 16(8): 519–531.

<https://doi.org/10.1080/15459624.2019.1612068>

Yi J, Duling MG, Bowers LN, Knepp AK, LeBouf RF, Nurkiewicz TR, Ranpara A, Luxton T, Martin SB Jr, Burns DA, Peloquin DM, Baumann EJ, Virji MA, Stefaniak AB. Particle and organic vapor emissions from children's 3-D pen and 3-D printer toys. Inhal Toxicol. 2019 Nov - Dec;31(13-14):432-445.

<https://doi.org/10.1080/08958378.2019.1705441>

Wohlers Report, 3D Printing and Additive Manufacturing, Global State of the Industry, 2021 pp 118-122.