ASHRAE Conference Abstract Submission
June 22-26, 2019, Kansas City, MO

Particle and Chemical Emissions from 3D Printers and Their Potential Health Impacts

Qian Zhang, PhD **Aika Davis, PhD** **Marilyn Black, PhD**
Fellow ASHRAE

Rodney Weber, PhD

ABSTRACT

Fused filament fabrication 3D printers, which are commonly used in non-industrial indoor environments, emit gases and particles that may deteriorate indoor air quality, and adversely impact human health. This study characterized particle and chemical emissions from various 3D printers using an established test method and controlled environmental chamber. High concentrations of ultrafine particles, and numerous hazardous volatile organic compounds were observed during printing. The emissions are due to heating of the filament and varied depending on print conditions and filament and printer properties. Particle toxicity was assessed using various methods, and exposure concentrations were estimated using a model.

INTRODUCTION

Fused filament fabrication (FFF) 3D printers work by heating a coil of filament and extruding it from a nozzle onto a moving platform to build an object in layers. Commonly used filaments are thermoplastics such as polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), and nylon. Emissions of particle and volatile organic compounds (VOC) have been observed during 3D printing. Ultrafine particles (UFP, less than 100 nm in size) are hazardous to human health since they are capable of penetrating into the bloodstream and cells. Some gaseous emissions may be irritants and/or carcinogens. The wide use of FFF 3D printers in small-scaled indoor environments has raised concern of potential health impacts of emissions, especially for vulnerable populations such as children. Therefore, a systematic characterization of emissions and a standard test method are needed, given the emissions are dependent on operating conditions and experimental setup. Previous studies did not investigate in depth key parameters that affect emissions. In addition, research on the potential health impacts is limited. In this study, we developed a method for characterizing and quantifying particle and VOC emissions from 3D printers, and tested emissions for varying print conditions, including filament material, color and brand, extrusion temperature and printer brand. Assessment of health impacts and indoor exposure were also performed.

Qian Zang is a post-doc researcher at Underwriters Laboratories Inc., Marietta, GA. **Aika Davis** is a research scientist at Underwriters Laboratories Inc., Marietta, GA. **Marilyn Black** is a VP & Senior Technical Advisor at Underwriters Laboratories Inc., Marietta, GA. **Rodney Weber** is a professor in the Department of Earth and Atmospheric Sciences, Georgia Institute of Technology, Atlanta, GA.

METHODS

Emission characterization was performed using a 1 m^3 stainless steel chamber with clean air supply system, designed and evaluated following the ASTM standard D6670 (ASTM, 2013) and UL GREENGUARD Certification 2823 (UL, 2014). Ultrafine, fine and coarse particle number concentrations and size distributions were measured online with a scanning mobility particle sizer, a condensation particle counter and an optical particle counter. Individual VOC (IVOC) and aldehyde samples were collected onto solid sorbent cartridges and then analyzed by gas chromatography-mass spectrometry (GC/MS) and high-performance liquid chromatography separately, following US EPA Compendium Method TO-11A and 17 (USEPA, 1999a; b) and ASTM standard D6196 (ASTM, 2009). Total VOC (TVOC) was calculated from all detected IVOC and presented in a toluene equivalent. Test procedures followed BAM (2012), developed for testing emissions from laser printers. Particle composition was analyzed online by aerosol mass spectroscopy, and filament/particle composition by pyrolysis GC/MS. Toxicity tests focused on particle oxidative potential or oxidative stress responses. Particle samples were collected onto filters during chamber experiments and filter extracts were assessed with various cellular and acellular assays.

Six commercially available desktop FFF 3D printers were tested, with ABS, PLA, and nylon filaments from ten different manufacturers; the extrusion temperature ranged from 210 to 270°C. The emission rates and yields (total number of emitted particles per mass of filimant consumed) were calculated following BAM (2012). An indoor exposure model was based on calculated emission rates from chamber tests and applied to different scenarios.

RESULTS

Particle and VOC Emissions

With various combinations of different printers and filaments, a wide variability of emissions was observed. Particle number concentrations typically peaked at the beginning of the printing process, reaching 10^3 to 10^6 particles/cm^3, then dropped and achieved steady-state as printing continued. UFPs contributed approximately 70% of total particle number concentrations, which was associated with particles formed from a new particle formation process involving semi-volatile compounds emitted from heated filaments. TVOC concentrations increased during printing and reached steady-state later into print run, with over hundreds of IVOC species detected. Frequently detected species included styrene, ethylbenzene, and benzaldehyde from ABS filaments; lactide, benzaldehyde, and methyl methacrylate from PLA, and caprolactam from nylon.

Emission profiles and total emissions largely depended on filament materials. ABS had much higher particle number yields compared to PLA and nylon filaments. ABS filament also had the largest number of IVOCs and higher TVOC emission rates. For the same filament bulk material, some specific filament brands resulted in large differences in both particle emission concentrations and IVOC species, which were interpreted to be due to different minor additives in filaments utilized by different manufacturers. Filament color variation of the same brand generally had smaller impacts than among filament brands. In addition, higher extrusion temperatures were associated with higher emissions of both particles and VOCs; the impact of extrusion temperature on particle emissions was exponential, while linear for TVOCs.

Potential Health Impacts

The mass spectra of ABS emitted particles did not show similar composition to any of the ABS monomers, indicating that minor additives may control the formation and composition of particles. Therefore, the toxicity of particles may not be obtained directly from the raw filament material. Multiple approaches were explored to assess particle toxicity, including in vivo animal exposure, in vitro cell viability, cell death type, and intracellular reactive oxygen species (ROS) generation, in addition to a chemical (dithiothreitol, DTT) ROS assay. Results showed 3D printer emitted particles from ABS, PLA and nylon filaments all induced toxic responses, with different response levels according to applied methods. However, the overall toxicity levels of different filaments were difficult to compare, as their emissions varied largely.

VOC emissions were largely associated with filament material monomers. The top five VOC emissions from ABS filament were styrene, ethylbenzene, benzaldehyde, acetaldehyde, and phensuximide, three out of which (styrene, ethylbenzene, and acetaldehyde) are recognized as carcinogens in either the Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65) and/or Candidate Chemical List by California Department of Toxic Substances Control. Formaldehyde and acetaldehyde, both listed as carcinogens, were detected from all three filament materials VOC emissions. The dominant VOC emitted from nylon, caprolactam, has an ocular and respiratory toxicity. Methyl methacrylate, one of the top five IVOC detected from PLA emissions, is known to be carcinogenic. The exposure model results showed concentrations of certain hazardous species may exceed recommended levels when considering personal exposures.

CONCLUSION

High levels of particles and chemicals are emitted during 3D printing; the emission rates and profiles depended on print conditions, and are largely controlled by filament material, filament brand and extrusion temperature. Overall, particle emission rates from high emitting materials like ABS were comparable to those from laser printers. VOC species detected during 3D printing were associated with filament thermoplastics. Particles emitted from different filaments were found to induce toxic responses based on various toxicity assessment methods, while further research is needed to better understand the mechanism and compare effects among filaments. Some major detected VOC species were known or suspected to be irritant or carcinogenic to humans, the concentrations of which may exceed acceptable levels when a person is close to an operating 3D printer. As 3D printers are sources of high levels of ultrafine particles and hazardous gases, the emissions should be mitigated and regulated. However, consumers are unable to identify which printer or filament is safer to operate due to the lack of information in the current market. A standard on 3D printer emissions is beneficial to regulate emissions in the market and notify users of potential emission and hazard levels during 3D printing.

ACKNOWLEDGMENTS

This study is funded by the not for profit Chemical Safety Research Program of Underwriters Laboratories Inc.

REFERENCES

ASTM. 2009. ASTM D6196-03, *Standard Practice for Selection of Sorbents, Sampling, and Thermal Desorption Analysis Procedures for Volatile Organic Compounds in Air*. West Conshohocken, PA: American Society for Testing and Materials International.

ASTM. 2013. ASTM D6670-13, *Standard Practice for Full-Scale Chamber Determination of Volatile Organic Emissions from Indoor* Materials/Products. West Conshohocken, PA: American Society for Testing and Materials International.

BAM. 2012. *Test Method for the Determination of Emissions from Hardcopy Devices within the Award of the Blue Angel Ecolabel for Equipment with Printing Function according to RAL-UZ-171*. St. Augustin, Germany: Federal Institute for Materials Research and Testing.

UL. 2014. UL 2823, *GREENGUARD Certification Program Method for Measuring and Evaluating Chemical and Particle Emissions from Electronic Equipment Using Dynamic Environmental Chambers*. Northbrook, IL: Underwriters Laboratories.

USEPA (U.S. Environmental Protection Agency). 1999a. Compendium method TO-11A, Determination of formaldehyde in ambient air using adsorbent cartridge followed by high performance liquid chromatography (HPLC) [active sampling methodology].

USEPA (U.S. Environmental Protection Agency). 1999b. Compendium Method TO-17 determination of volatile organic compounds in ambient air using active sampling onto sorbent tubes. U.S. EPA Technical Assistance Document. EPA/625/R-96/010b.