2019 EXECUTIVE SUMMARY REPORT

3D Printer Emission Research

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INTRODUCTION

Previous studies have found that high levels of particles and numerous volatile organic compound (VOC) are emitted from fused filament fabrication (FFF) 3D printers and a standardized method was developed for testing 3D printer emissions. In 2019, this established method was applied to the investigation of additional FFF 3D printers and new filaments, including six PLA (polylactic acid)-based filaments, three nylon-based filaments, two ABS (acrylonitrile butadiene styrene), and one metal filament. The study aimed at characterizing particle and VOC emissions from new printers and filaments and investigating the effects of filament base material, additives and print nozzle temperature on particle and VOC emissions, as well as analyzing toxicity and metal composition of emitted particles.

KEY FINDINGS

Particle and chemical emissions from 3D printers were studied following the standard method described in ANSI/CAN/UL 2904, using an exposure chamber, particle measuring instruments and VOC and aldehyde collection and analysis systems. Online particle number concentration measurements covered ultrafine (less than 0.1 µm), fine (less than 2.5 µm) and coarse (2.5 to 10 µm) sizes.

- Thermoplastic filaments typically had an initial peak in particle number concentrations when filament started to be extruded, and thereafter concentrations decreased to a steady state concentration during the remaining printing. Particle geometric mean diameter was typically less than 100 nm, with some exceptions up to 160 nm.
- Metal filaments showed a different particle concentration trend during printing, suggesting a different particle formation mechanism than typical thermoplastic filaments. Lower concentrations of particles with larger sizes were formed when printing at a comparable nozzle temperature with thermoplastic filaments, with mean particle size to be 338 nm. This resulted in significantly higher mass concentration emissions than other thermoplastic filaments.
- Thermoplastic based filaments that contained various additives were often operated at differing nozzle temperatures, which affected particle emissions, but in some cases additives had additional effects and in other cases no effects.
- Green PLA filaments were found to emit more particles than a red PLA filament at 5 °C higher nozzle temperature. The metal PLA printing at a higher nozzle temperature was found to have higher particle number emissions than the other PLA-based filaments.
- Flame retardants present in a filament resulted in an increase in particle number emission rate and a slightly decrease in particle mean size when printing at the same nozzle temperature as the same base material filament without flame retardants.
- Nylon filament with chopped carbon fibers was found to have comparable particle number emissions as a pure nylon filament running at a comparable nozzle temperature, but higher than a nylon filament running at a lower nozzle temperature.

VOCs and aldehydes collected on sorbent tubes were then analyzed offline by a gas chromatography-mass spectrometry (GC-MS) for C_6 – C_{16} VOCs, and a high performance liquid chromatography (HPLC) for formaldehyde and other low-molecular weight carbonyl compounds.

- Total VOC emission rates were associated with filament material and nozzle temperature, with the highest for nylon-based filaments run at 275 °C (> 75% of previous data), and then PLA-based filaments run at 210 – 230 °C (50% – 75% of previous data), and lowest for the metal filament run at 220 °C (< 50% of previous data).
- Most detected individual VOCs were associated with filament base material, including lactide from PLA-based filaments and caprolactam from nylon-based filaments.
- Acetaldehyde, a possible carcinogen, was the chemical of concern with the highest emission rates for all 5 PLA-based filaments, and it was also emitted from the metal filament.
- Formaldehyde, a known human carcinogen, was detected from all 5 PLA-based filaments, 2 nylon-based filaments and the metal filament, with emission rates ranked at least the 4th highest.
- Other common emitted VOCs with health concern were decanal and nonanal from all tested filaments, siloxanes from the metal filament, the nylon with carbon fibers filament, and 25% bronze PLA filament, and caprolactam from nylon-based filaments.
- 6 VOCs with health concern not seen from the previous study were detected, which included 2 possible carcinogens, tetrahydrofuran (THF) and benzene, 1-methoxy-2-nitro-.
- In general, emission rates of total VOC and individual VOCs were lower than the criteria listed in ANSI/CAN/UL 2904.

Particle toxicity was assessed using a chemical (dithiothreitol, DTT) assay for particles collected on filters.

- Particles emitted from ABS, PLA and nylon filaments were found to induce adverse health impacts with response levels comparable for similar doses.

- When considering emission levels, ABS filaments had higher responses than the PLA filament due to their much higher emission rates.

- Results combining indoor air modeling showed exposure to 3D printer emitted particles can be a more significant health concern than outdoor ambient fine particulates when operating in poorly ventilated or confined spaces.

Metal analysis via inductively coupled plasma mass spectrometry (ICP-MS) was applied to particles collected on filters, as well as raw filament materials, which included a pure PLA with added metallic coloring, PLA with 25% bronze powder added and PLA with 80% bronze powder added.

- For the pure PLA filament, Fe and Si were detected with relative high concentrations. Copper and tin were detected in raw filaments with added bronze powder. In addition, Zn was detected at relatively high concentrations in 25% bronze PLA, and P and Ni in 80% bronze PLA. However, metals in particles were not necessarily consistent with those detected in raw filament materials.

- B, Si, Cu, and Sn were detected with higher concentrations than other metals in particle samples from the pure PLA and both PLA filaments containing a bronze additive, with concentrations of Si significantly higher than other elements. Boron, which was not detected in any of the filament raw materials, was present in all particle samples. Other sources, such as components of the 3D printer itself, or chemicals may contribute to particle composition like boron and silicon.

- The partition ratio of metal from filament to particle was found to be very low for copper (0.001 – 0.08 ppm) and tin (0.004 – 21 ppm), indicating they were not likely to drive particle formation for PLA filaments containing a bronze additive.

FUTURE RESEARCH

Future studies on 3D printer emissions will focus on:

- Metal analysis on particles emitted from metal filaments and the differences between a polymer based filament and a metal powder based filament.

- Particle toxicity analysis and the relationship between particle metal composition and particle toxicity.

- Data analysis of larger data sets to sort out which parameter have the greatest effect on particle and VOC emissions.

- Characteristics of particle and VOC emissions from SLA (stereolithography) 3D printing.

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