Proceedings/Publication
32nd International Conference on Digital Printing Technologies
Printing for Fabrication
Manchester, United Kingdom
September 2016

Fine particulate and chemical emissions from desktop 3D printers

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Abstract

Fused deposition modeling (FDM) printers, the more common type of desktop 3D printers, emit volatile gases and particulates that may deteriorate indoor air quality. The developed method for characterizing and quantifying emissions from an operating 3D printer measures fine particulate and volatile organic compound (VOC) concentrations over time using an environment controlled testing chamber.

All tested printers emitted ultrafine particulates (UFP). Approximately 70% of the particulates released from the printers were less than 50 nm in diameter. Emitted UFPs increased in size over time by coagulating with other particles and condensation of printer-generated vapors. Chemical compositions of the released gases varied depending on the filament material. Volatile chemicals such as styrene and ethylbenzene were released from acrylonitrile butadiene styrene (ABS) filament. Caprolactam, originating from a nylon filament, was a predominant released gas. Though polylactic acid (PLA) filament is thought to be safer since it is biodegradable, PLA still released chemicals such as methyl methacrylate. Acetaldehyde and formaldehyde were released from all the studied filaments. ABS emitted more particles than PLA or nylon filaments.

The extrusion nozzle temperature on the printer had the greatest effect on both particles and VOC emissions; the emissions increased as the temperature of the nozzle increased. Depending on the maker of the filaments, the total particle number emissions varied by a factor of 20. Filament colors had minor effects on emissions compared to other parameters studied.

Introduction

The 3D printer market is estimated to grow at a compound annual rate of 44% [1]. Among diverse 3D printers on the market, fused deposition modeling (FDM) 3D printers are relatively inexpensive and convenient to use, making them accessible to the general public. FDM 3D printers heat a filament to a semi-liquid state and deposit it to build a 3-dimensional object by layers [2]. In particular, desktop-sized 3D printers are often used in educational institutions (from primary schools to universities), design offices, libraries, and within homes [3]. Many of these locations have the potential to expose susceptible populations, such as children, to any toxic emissions generated in the printing process. It is known that commercial extrusion processing of thermoplastics generates both particles and volatile organic compounds (VOCs) [4], and some of the thermal decomposition products are recognized to be toxic [5, 6]. FDM 3D printers are potentially hazardous to operate in certain indoor environments. Due to the increasing usage of 3D printers and past experience with laser printer emissions, characterization of 3D printer emissions is necessary to assess human exposure and potential health impacts.

A number of studies have recently reported emissions from commercial 3D printers [7, 8, 9, 10, 11], but the use of differing characterization methods make it difficult to compare and contrast factors influencing emissions reported amongst the previous studies. In order to address this limitation and to understand the factors that drive emissions, a standard testing and evaluation method is essential. Consistent characterization of particle emissions according to printer and filament combinations and operation conditions would then be possible and could be provided to consumers when considering purchasing these printers.

Methods

We have developed a methodology for characterizing and quantifying ultrafine particle (UFP) and VOC emissions from operating 3D printers that involves operation inside a specially designed environmental chamber. To investigate factors that influence 3D printer emissions, numerous combinations of printers and thermoplastic filaments were tested. The following printer parameters and their effects on UFP and VOC emissions were studied in a systematic way: filament type, filament brand, filament color, print object shape, extrusion nozzle temperature, printer platform temperature, and printer brand. Each 3D printer was tested in an environmental chamber 1 cubic meter in volume that is specially designed for quantifying emissions in a well-mixed clean environment. Chamber operation and control measures used in this study complied with GREENGUARD Method and Laboratory Quality Requirements [12] and ASTM Standard D 6670 [13]. The chamber is made of stainless steel to minimize particle wall losses and contaminant adsorption. Air-flow through the chamber enters and exits through an aerodynamically designed air distribution manifold, also manufactured of stainless steel. Supply air to the chamber is stripped of particles, VOCs, formaldehyde, and other contaminants so that any contaminant background present in the empty chamber fall below strict levels. UFPs within the chamber were quantified with a range of online state-of-the-art particle sizers and counters. VOCs were collected on absorption columns for off line analyses.

Results

All tested printers emitted UFPs. Approximately 70% of the particulates generated from the printers were less than 50 nm in diameter. With various combinations of different printers and filaments, a wide variability of particle emissions was observed. Typically, the number concentration spiked to 10^3 to 10^6 particles/cm^3, and then gradually decreased over time until the print ended. This pattern is seen in Figure 1, which shows number concentration over time for a 7 hour print using acrylonitrile butadiene styrene (ABS) filament. The instantaneous increase in number concentration to 1.4×10^6 particles/cm^3 (emissions of 1.4×10^{12} particles/min) is enough to exceed the criteria set for laser printers by Blue Angel ($<3.5 \times 10^{11}$/10 min) and likely results from homogeneous nucleation of semi-volatile organic compounds (SVOCs) emitted near the extrusion nozzle. While number concentration starts decreasing, the mass concentration continues to increase (Figure 1), due to particle growth resulting from condensation of vapors on the newly formed particles. Initially, particles are in the size rage of 40 to 80 nm in diameter. Over time, the particles emitted from the printer interact through coagulation with particles generated earlier, and along with vapors continually being generated in the chamber by the printer, resulting in an increase in particle diameters to 100 to 250 nm. Despite the duration of print time, total particle emission was dominated by particles less than 50 nm, total surface area emission by particle sizes of 50 to 200 nm, and total mass emission by particles sizes of 100 to 300 nm.

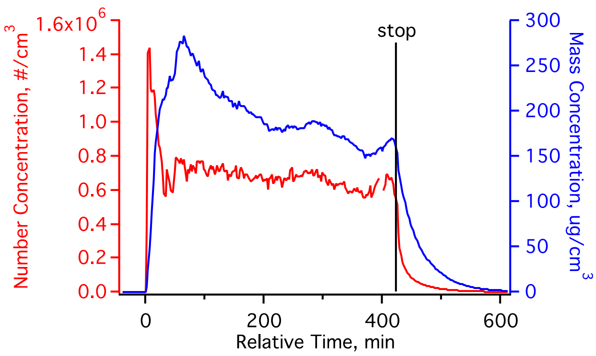

Figure 1. *Particle number and mass concentrations for a 7 hour print job using ABS filament on a consumer 3D printer in a well mixed 1 cubic meter environmental test chamber with continuous addition of clean air, resulting in an air exchange rate of 1 chamber volume per hour. Print started at time 0 min.*

Filament coloring pigment showed only slight differences in particle and VOC emissions. However, filament brand had a large effect. For the various ABS brand filaments used on a single printer, brand differences resulted in larger differences between particle emissions than color differences. One brand had approximately ten times higher particle emissions than other ABS brands tested. Printer brand differences also contributed up to an order of magnitude difference in particle number emissions. One cause for this was differences in the manufacturer-set extrusion nozzle temperature for use with a given type of filament. Tests showed that total particle number emissions increased exponentially with nozzle temperature. This also accounted for differences in emissions when using different filament types. For example, ABS filament generally runs at higher extrusion nozzle temperatures than for polylactic acid (PLA) filament. ABS emitted more particles than PLA or nylon filaments. Printer platform temperature (plate the print object is built on) was found to only increase the mass of emitted particles, and not number of particles emitted. This is apparently due to the lower platform temperature, compared to the extrusion nozzle, was insufficient to produce SVOCs at a level needed for homogeneous nucleation of new particles. Instead, the released vapors condensed on the particles originally formed near the nozzle and increased the overall mass of the emitted particles.

VOC emissions varied depending on the filament material. Formaldehyde and acetaldehyde, both listed as carcinogens, were detected in all three materials tested (ABS, PLA, and nylon). Nylon had the largest total VOC (TVOC) emission factor. Most of TVOC emission from nylon was caprolactam, which has an ocular and respiratory toxicity. Caprolactam has a low 8 hour chronic reference exposure level of 7 µg/m^3 (1.4 ppb) according to California's Office of Environmental Health Hazard Assessment (OEHHA). Methyl methacrylate, second most abundant emission from PLA, is an irritant according to USEPA [14]. Lactic acid is known to be released but was not detected in our analysis since our analysis covers mostly greater than C_6. Therefore, TVOC for PLA is likely to be underestimated. ABS had the largest number of identified VOCs. Styrene, released from ABS, is listed as a possible human carcinogen by International Agency for Research on Cancer. ABS emitted ethylbenzene, acetaldehyde, formaldehyde, and 4-vinylcyclohexene, which are recognized as carcinogens in the Safe Drinking Water and Toxic Enforcement Act of 1986, also known as California Proposition 65, and/or Candidate Chemical List by California Department of Toxic Substances Control.

Conclusion

Potentially hazardous levels of UFP, up to 1.4×10^{12} particles/min, were generated from tested desktop 3D printers. Chemicals unique to thermoplastics are released while operating the printer. Many are known or suspected irritants and carcinogens; therefore exposure to 3D printer emissions should be minimized. Nozzle temperature, filament type, filament and printer brand, and filament color all affect particle and VOC emissions, but to varying degrees. Yet, consumers cannot determine which printer or filaments are safer to operate with currently provided information, such as material safety data sheets (MSDS). Nozzle temperature, one parameter that users may have control over, should be set at a lower end of the suggested temperature range for a filament material to minimize direct exposure from 3D printer emissions. 3D printers should be used with caution in a well-ventilated area and special consideration given to potential exposures to susceptible populations.

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