

Phase 1 Research on Chemical and Particle Emissions from 3D Printing

Introduction

The 3D printing market is expected to grow at a compound annual growth rate of 23% by 2024. 3D printing technology is widely used in various fields, including electronics, medicine and medical sciences, aerospace and defense, automotive and manufacturing industries, consumer products, entertainment and education. Fused filament fabrication (FFF), a material extrusion-based 3D printing technology, works by heating a filament thermoplastic to a semi-liquid state, and depositing it through an extrusion nozzle onto a moving build plate, thus creating a 3D object layer by layer. Consumer-level 3D printers using FFF technology are popular and accessible to general public and widely used in small scale environmental settings, like school classrooms, institutional labs, design offices and residences, due to their relatively low cost and ease to operate. The most commonly used materials are acrylonitrile butadiene styrene (ABS), a cost-effective petroleum-based polyamide polymer, and polylactic acid (PLA), a compostable and biodegradable material produced from renewable sources.

As 3D printing technologies have become popular and available to the general public, concerns have been raised on the emissions and potential health impacts of operating 3D printers, especially in small or poorly ventilated indoor environments, and when susceptible people like children are involved. Studies have shown that the operation of an FFF 3D printer emits high levels of particles and numerous chemicals. However, due to the previous lack of a standardized testing method, the emissions are not consistently characterized nor can they be compared among published data. In addition, the potential health impacts of exposure to 3D printing emissions are not well known.

A study on emissions from 3D printing, being conducted by UL Chemical Safety and Human Health in partnership with Georgia Institute of Technology and other stakeholders, aims at understanding and characterizing the emissions from 3D printing and their potential health impacts. In Phase 1 research, a methodology was developed to identify and quantify emissions from 3D printers and to evaluate the emissions hazards. Particle concentrations and size distributions of particles from 10 nm to 10 µm are measured online, and volatile organic compounds (VOCs) and aldehyde samples are analyzed offline by analytical chemical instruments. Key findings from the Phase 1 research are presented below.

Key Facts

- 3D printing generates a complex mixture of airborne particles and volatile organic compounds (VOCs) during operation.
- Over 200 different VOCs have been identified from fused filament fabrication (FFF) 3D printing, many of which are known irritants, carcinogens, and odorants.
- Some specific VOCs include styrene, formaldehyde, methyl methacrylate and caprolactam, and they are dependent on the filament (feedstock) composition as well as printer operational parameters.
- Many of the measured VOCs during printing such as vinyl cyclohexene, caprolactam, and acetophenone, are not commonly found in the indoor air.
- Some of the most frequently detected and highest emitting VOCs include styrene, caprolactam, benzaldehyde, ethyl benzene, and acetaldehyde.
- Some measured VOCs during printer operation, including caprolactam and 2-butenal, may exceed current recommended exposure guidelines for acceptable indoor air.

a 2211 Newmarket Parkway, Suite 106, Marietta, Georgia 30067 Wulchemicalinsights.org e chemicalinsights@ul.org

© 2020 Underwriters Laboratories Inc. TB 120



- Personal exposure levels for people close to an operating printer are greater than exposure levels in a further surrounding space.
- Particle emissions reach up to 1012 particles per hour, and they are dominated by ultrafine particles (UFPs) that are smaller than 100 nanometers (nm) in size.
- UFPs present a health concern since they can be inhaled and penetrate deep into the lung, resulting in adverse cardiovascular and pulmonary health effects.
- Printer operational parameters such as printer brand, print filament material, brand and color, extrusion and build plate temperature have a measurable impact on emission levels of particles and VOCs.
- Filament material composition and extrusion temperature play important roles on particle and VOC emissions; acrylonitrile butadiene styrene (ABS) material, which works at a higher extrusion temperature, emits orders of magnitude more particles and higher levels of VOCs than polylactic acid (PLA). Some specific brands of filament with unknown additives can generate much higher particle emission levels than other filaments with the same bulk material.
- According to an aerosol dynamic model, particles are formed from nucleation of semi-volatile vapors emitted during heating of the filament, and they grow by vapor condensation and particle coagulation, which happen within a small volume near the extrusion nozzle.
- A way to remove the newly formed small particles before they are dispersed into surroundings may be thermophoresis, which is a phenomenon of particles in a mixture with a temperature gradient tend to move toward the region with lower temperature.
- The aerosol dynamic model relates particle emissions to the properties of precursor vapors, which indicated the particle formation may not necessarily be associated with bulk filament material but potentially the additives.
- The mass spectra of emitted particles are unlike those of the raw filament material monomers for ABS, but similar for PLA. This agrees with the model results that particle formation may be associated with the minor additives added into filaments.
- Multiple approaches assessing toxicity effects of particles emitted during 3D printing are applied, including mice exposure, in vitro cell viability, cell death type, and intracellular reactive oxygen species (ROS) generation, and a chemical (dithiothreitol, DTT) ROS assay. All show toxic responses when exposed to 3D printer emitted particles.
- The chemical DTT assay shows comparable toxic responses on a particle mass basis for ABS, PLA and nylon filaments, however ABS filaments show much higher exposure hazards due to their much higher emission levels.
- Potential exposure to styrene from ABS, methyl methacrylate from some PLA, and caprolactam from nylon filaments may present a human health hazard. All print feedstock studied release formaldehyde (a known human carcinogen (International Agency for Research on Cancer)) and toluene (a developmental toxicant (Proposition 65)).
- Exposure models can be used to predict human exposure concentrations to be expected in schools, homes, offices, and other environments during the operation of 3D printers. These exposure levels can be evaluated for chronic and acute health hazards.
- A stakeholder consensus ANSI (American National Standards Institute) standard that addresses the test method, measurement and hazard assessment of 3D printer emissions, ANSI/CAN/UL 2904, was developed and approved. This standard allows for consistent and accurate measurements of particle and chemical emissions from defined printers and print media, and provides acceptance criteria for indoor air.
- Suggestions for mitigating exposure to 3D printer emissions include: operating 3D printers at the lowest extrusion temperature possible without sacrificing quality; placing 3D printers in a well-ventilated large space or applying local exhaust close to the printers; minimizing direct contact with operating 3D printers when possible; and using printers and print material that have been tested and verified to have low chemical and particle emissions.

a 2211 Newmarket Parkway, Suite 106, Marietta, Georgia 30067 W chemicalinsights.org € chemicalinsights@ul.org

© 2020 Underwriters Laboratories Inc.

TB 120