

Particle and Chemical Emissions from a Vat Photopolymerization 3D Printer

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# 1. INTRODUCTION

Chemical Insights, with our research partner Georgia Institute of Technology, School of Civil and Environmental Engineering and School of Earth and Atmospheric Sciences, has been conducting leading research on the characterization and potential health impacts of chemical and particle emissions from 3D printers. These efforts have been presented in various <u>publications</u> and <u>reports</u> (more resources on <u>website</u>). In addition, a consensus standard, "<u>Standard Method for Testing and Assessing Particle and Chemical Emissions from 3D Printers</u>", has been developed from the research, establishing test protocols and acceptable emissions criteria for 3D printers. Primary research findings show that emissions released during fused filament fabrication (FFF) 3D printing process include large numbers of volatile organic compounds (VOCs) and particles, primarily in the ultrafine size range. Toxicity responses have also been obtained. Since these studies demonstrate the potential for adverse human health effects, research is continuing to further assess toxicity of emissions and to evaluate options for reducing emission exposures.

This study is an extension of the research initiative on characterizing emissions from 3D printing, further focusing on vat photopolymerization 3D printing technology, also called stereolithography (SLA) or resin printing. Unlike FFF or material extrusion 3D printing, SLA technology prints a 3D object by shining an ultraviolet (UV) light on a vat of photopolymer resin and cure (or harden) the resin via photochemical processes selectively by layers. This report presents the preliminary findings of particle and chemical emissions from a desktop SLA 3D printer during printing, as well as associated post-processing treatments, in accordance with ANSI/CAN/UL 2904.¹ Emissions from SLA 3D printing are compared to previously obtained results from FFF 3D printing using the same testing method.

#### 2. METHODS AND MATERIALS

Emission measurements were made in a 1 m<sup>3</sup> exposure chamber with the 3D printer placed in the middle. There were accessible ports with gloves on the side walls of the chamber to enable operation with the printer inside, without opening the chamber or changing the air conditions inside the chamber. The interaction chamber was validated for its air-tightness, mixing and air exchange rate according to standards.<sup>2,3</sup>

The studied SLA 3D printer has an enclosed design; a clear resin from the printer manufacturer was loaded in the printer tank when the printer was loaded in the chamber. The printer was heated to 31°C before print process started, followed with a 4-hour print, with the printer enclosed for the entire process. The post-processing treatments included a wash and a cure process. The wash unit is enclosed with the washing reagent of isopropyl alcohol (IPA); the lid was only open when loading/unloading the printed object. The time for wash treatment was 15 min. The cure unit is also enclosed with a 405 nm light; the lid was only open when loading/unloading the printed object. The treatment time for cure was 10 min.

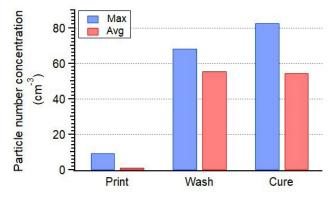
Particles with diameters from 7 to 300 nm were measured using a scanning mobility particle sizer spectrometer, and particles with diameters from 0.3 to 10 µm were measured by an optical particle sizer.<sup>4</sup> Particle emission rate (emission per print time) and particle yield (emission per mass of filament extruded) during printing and post-processing were calculated according to the methods in ANSI/CAN/UL 2904.¹ VOCs as well as formaldehyde and other low-molecular weight carbonyl compounds were collected onto sorbent media separately, and then analyzed by gas chromatography - mass spectrometric or high performance liquid chromatography, respectively.<sup>5</sup> Sampling time (i.e., target sampling volume) was adjusted according to the chemical levels in the chamber during printing and the shorter processing time for post-processing treatments. Emission rates for individual VOCs and total VOC (TVOC) were calculated based on the methods in ANSI/CAN/UL 2904.¹

# 3. RESULTS

Overall, preliminary findings on emissions from the studied SLA 3D printer and post-processing processes showed very limited particle emissions but high levels of VOC emissions. The total VOC emission rates from SLA 3D printing were higher than the average from FFF 3D printing by a factor of 3 to 6. Individual VOCs emitted differed from those measured with FFF 3D printing due to the differences in print technologies and materials. Detailed emission results are shown below.

#### 3.1 Particle emissions

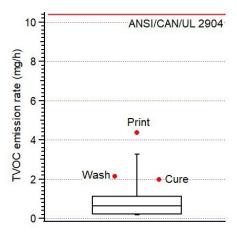
The particle emissions from SLA 3D printing, including post-processing processes, were very low (Figure 1); the particle concentrations remained similar to levels of the chamber background concentrations. The maximum particle number concentration was below 100 cm<sup>-3</sup> for all processes studied, which was typically in the order of 103 – 105 cm<sup>-3</sup> for FFF 3D printers under the same chamber conditions.



**Figure 1.** Maximum (Max) and average (Avg) total particle number concentrations for print, wash and cure processes.

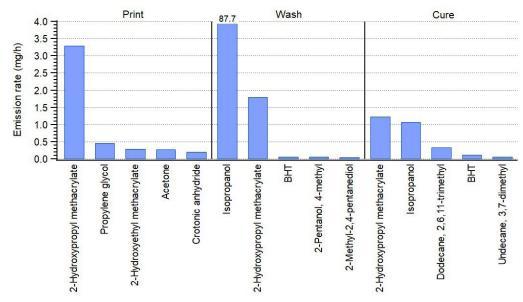
#### 3.2 VOC emissions

TVOC results are shown in Figure 2, along with the statistics of TVOC data from previously studied FFF 3D printing, which included 32 tests with thermoplastic materials. TVOC emission rates from all processes were below the maximum allowable emission criterion listed in ANSI/CAN/UL 2904 (10.4 mg/h), see Figure 2.



**Figure 2.** TVOC emission rates from this study (markers), compared to existing database (boxplot) and the maximum allowable level in ANSI/CAN/UL 2904 (red line). The box indicates 25% quartile, median and 75% quartile; the whiskers indicate the minimum and maximum values.

There were 40 individual VOCs detected from printing, 34 from wash post-processing and 42 from cure post-processing; note the air sampling volumes in this study were smaller than those for FFF 3D printing due to the differences of concentration levels and operation times. The top five chemicals with the highest emission rates are shown in Figure 3; they accounted for 88%, 100% and 91% of the sum of VOC emissions for print, wash and cure processes respectively. 2-Hydroxypropyl methacrylate was detected from all processes with the highest or second highest emission rates (Figure 3), which was associated with the resin chemical compositions. The studied resin is composed with 55% – 75% of urethane dimethacrylate, 15% – 25% of methacrylate monomers and photoinitiators according to manufacturer safety data sheet. Isopropanol accounted for over 97% of the sum of VOC emission rates for wash treatment, which was due to the use of isopropyl alcohol as the was reagent that was filled in the wash tank. The washed part was further treated with light (i.e., cure post-processing), therefore, isopropanol was also detected at a relatively high emission rate for cure treatment (Figure 3). Other top emitting chemicals included hydrocarbons, alcohols, and esters.



**Figure 3.** Top five of the most emitted chemicals from each process (Print, Wash, Cure) with their emission rates.

These highly emitted chemicals from SLA 3D printing (Figure 3) were not commonly observed from previously studied FFF 3D printing. Only BHT (2,6-di-tert-butyl-4-methylphenol) was detected at a frequency of 15% among 39 FFF prints, while the rest of the VOCs listed in Figure 3 had less than 10% detect frequencies. Among the top 10 individual VOCs detected from SLA 3D printing, 1-butanol was detected with a frequency of 72% for FFF prints, and the rest were below 50% detect frequency. Previous study showed VOC emissions from FFF 3D printing were mainly associated with the filament materials and additives, 5 therefore, the most commonly observed VOCs from FFF 3D printing were not detected or in low emission rates for SLA 3D printing, given the differences of print technologies and materials applied.

Chemicals of concern are VOCs listed in health-related regulation and guidance. There were 17, 16 and 12 chemicals of concern detected from print, wash and cure processes separately. Among them, formaldehyde is a human carcinogen according to International Agency for Research on Cancer (IARC) and it was detected from all 3 processes, at emission rate levels of 0.01 mg/h or lower. Other chemicals of concerns include acetaldehyde from printing, methyl isobutyl ketone (MIBK) and naphthalene from washing. Although the emission rates and estimated office exposure levels for chemicals of concern were below those indicated in regulation and guidance, this complex mixture of alcohols, aldehydes and acrylates could present a strong irritation response among those exposed.

# 4. FUTURE RESEARCH

Future research will explore how emission characteristics change for different print materials, i.e., resins, such as different manufacturers, polymer formulars, colors, etc.

# 5. REFERENCES

- 1. ANSI. ANSI/CAN/UL 2904 Standard Method for Testing and Assessing Particle and Chemical Emissions from 3D Printers. American National Standards Institute: Washington DC, US 2019.
- ASTM. ASTM D6670-13 Standard Practice for Full-Scale Chamber Determination of Volatile Organic Emissions from Indoor Materials / Products. ASTM International: West Conshohocken, PA 2013.
- 3. ISO. ISO 16000-9 Indoor Air Part 9: Determination of the Emission of Volatile Organic Compounds from Building Products and Furnishing Emission Test Chamber Method. International Organization for Standardization: Geneva, Switzerland 2007.
- 4. Zhang, Q.; Wong, J. P. S.; Davis, A. Y.; Black, M. S.; Weber, R. J. Characterization of Particle Emissions from Consumer Fused Deposition Modeling 3D Printers. Aerosol Science and Technology 2017, 51 (11), 1275–1286. https://doi.org/10.1080/02786826.2017.1342029.
- 5. Davis, A. Y.; Zhang, Q.; Wong, J. P. S.; Weber, R. J.; Black, M. S. Characterization of Volatile Organic Compound Emissions from Consumer Level Material Extrusion 3D Printers. Building and Environment 2019, 160, 106209. https://doi.org/10.1016/j.buildenv.2019.106209.
- 6. CDPH. Standard Method for the Testing and Evaluation of Volatile Organic Chemical Emissions from Indoor Sources Using Environmental Chambers Version 1.2. California Department of Public Health: Sacramento, CA 2017.
- ACGIH. TLVs® and BEIs®: Threshold Limit Values for Chemical Substances and Physical Agents Biological Exposure Indices.; Signature Publications: Cincinnati, OH, 2018.
- AgBB. Health-Related Evaluation Procedure for Volatile Organic Compounds Emissions (VVOC, VOC and SVOC) from Building Products 1. February 1, 2015.



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