Chemical Insights
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SUMMARY REPORT

Effects of a Filter Setup on Particle and Chemical Emissions from a 3D Printer

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1. INTRODUCTION

1.1 Objectives

This study was done as a research initiative to evaluate a design of filter setup on mitigating emissions from 3D printers. The 3D printer was tested for emissions of particles (ultrafine, fine and coarse) and volatile organic compounds (VOCs) in a controlled exposure chamber according to ANSI/CAN/UL 2904.[1] Measured emission data were used to estimate emission rate, yield, and exposure concentration levels. Furthermore, the results obtained from 3D printing with and without the filter setup were compared to evaluate the performance of the filter on mitigating particle and chemical emissions from 3D printing.

1.2 Print conditions

The tested print filament materials included Nylon black color (extruder nozzle temperature 250°C), ABS (acrylonitrile butadiene styrene) natural color (245 °C), ASA (acrylonitrile styrene acrylate) black color (245°C), PC-ABS (polycarbonate-ABS) black color (260 °C), and PC-ABS-FR (PC-ABS with flame retardants, FR) black color (260°C). All studied filaments were printed on the same printer. Support materials included PVA (polyvinyl alcohol) natural color (210°C) for Nylon filament and SR-30 natural color (245°C) for other filaments, which were extruded at the beginning of print with limited amount of filaments. The printer chamber temperature was 30°C for Nylon, 85°C for ABS and ASA, and 95°C for PC-ABS and PC-ABS-FR.

Each filament was tested once without the installation of the filter and again with filter installed. The filter setup was comprised of a carbon filter, a HEPA (high-efficiency particulate air) filter, and a fan. The same print file (40mmcube.stl) was applied for all prints, which was scaled and adjusted to an approximate 4-hour print time according to ANSI/CAN/UL 2904,[1] while actual print time and object mass might vary.

2. METHODS

Measurements were made in a 6 m^3 exposure chamber at 1 air exchange rate. The inflow air controlled by an air supply system containing an air compressing unit and VOC and particle removal media, resulted in an air exchange rate of 1 per hour. The design and the characterization of the chamber have been previously described in ISO 16000-9.[2] During the experiment, the 3D printer was placed in the middle of the chamber; sampling tubes for air collection and particle measurements were located approximately 10 cm from the printer to the instruments outside of the chamber.

The number distributions of particles with diameters from 7 to 300 nm were measured using a scanning mobility particle sizer (SMPS) spectrometer. An optical particle sizer (OPS) was used to measure fine and coarse particles with diameters from 0.3 to 10 µm. For each test, particle measurement started about 10 min before the print started; the background total particle number concentration was controlled to be less than 10 cm^{-3}. The measurement continued through printing period until 1-hour after print stopped or when particle concentrations decreased to background levels. Particle emission rate (emission per print time) and particle yield (emission per mass of filament extruded) during printing were calculated according to 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 (GC/MS) or high performance liquid chromatography (HPLC), respectively. The VOC analysis follows US EPA Compendium Method TO-173 and ASTM D 61964 and is generally applicable to C_6 – C_{16} organic chemicals with boiling points ranging from 35ºC (95°F) to 250ºC (482°F). Selected aldehydes were measured following ASTM D 5197[5] and US EPA Method TO-11A[6]. Each sample was collected through a mass flow controller for air volume collections of 12 L for VOCs and 30 L for aldehydes.

Emission rates for individual VOC and total VOC were calculated using a box model time-varying mass balance equation with first order total sink factor in accordance to ANSI/CAN/UL 2904. Predicted air concentrations for personal exposure were evaluated for a typical office, the default environment in ANSI/CAN/UL 2904. The office was assumed to have a volume of 30.6 m^3 with an air exchange rate of 0.68 h^{-1} and one 3D printer operating. Estimated air concentrations were based on the research measurements which do not consider other environmental conditions or pre-exiting air pollutants.

3. RESULTS

3.1 Emission summary

A comparison of overall particle, total VOC (TVOC) and VOC emission results for with and without filter are shown in Table 1, as well as the criteria listed in ANSI/CAN/UL 2904[1] as a reference.

TABLE 1. SUMMARY OF EMISSION RESULTS

Material		Particle			TVOC	VOC
		Emission rate (h^{-1})	Yield (g^{-1})	Within 2904	Emission rate (mg/h)	Within 2904
ANSI/CAN/UL 2904		3×10^{11}	2×10^{10}	-	10.4	
ABS	No filter	-	-	√	3.17	× (formaldehyde and phenol)
	Filter	-	-	√	3.14	× (phenol)
Nylon	No filter	4.6×10^{11}	5.7×10^{10}		0.19	√
	Filter	-	-	√	0.32	√
ASA	No filter	2.9×10^{9}	3.0×10^{8}	√	3.16	× (formaldehyde and phenol)
	Filter	-	-	√	4.48	× (phenol)
PC-ABS	No filter	2.1×10^{8}	1.5×10^{7}	√	2.90	× (formaldehyde and phenol)
	Filter	-	-	√	4.24	× (phenol)
PC-ABS-FR	No filter	8.7×10^{8}	5.4×10^{7}	√	1.26	× (phenol)
	Filter	-	-	√	2.65	× (phenol)

Note: "-" indicates particle concentrations were too low for emission calculations; chemicals inside brackets are above associated criteria in ANSI/CAN/UL 2904.

In summary, the filter setup was effective in reducing particle emissions across all filament types. With the filter, particle emissions from all filaments were reduced to low levels that were below quantitative emission rate determinations. ABS filament emissions were low with and without the filter. For Nylon filament, both particle emission rate and yield were above standard criteria without use of the filter; but fell below the maximum acceptable criteria when the filter was used.

All TVOC emission rates were below the maximum allowable criteria in ANSI/CAN/UL 2904 with and without use of the filter. However, evaluating the filter efficacy of removing VOCs was difficult as the filter materials themselves appeared to be contributors of VOCs. There was indication that plastic related VOCs such as phenol and various acrylates as well as numerous heavy hydrocarbons were associated with the filter materials.

3.2 Effects of filter on particle emissions

Particle emissions for prints without the filter setup are compared to our existing particle emission database of 372 tests, which includes 184 tests of ABS filaments, 157 tests of PLA filaments, 15 tests of Nylon filaments, 6 tests of HIPS (high impact polystyrene) filaments, 7 tests of PVA (polyvinyl alcohol) filaments, and 3 tests of metal filaments, as shown in Figure 1. In general, particle emission rates and yields were low except the Nylon filament in this study. Emissions from ASA, PC-ABS and PC-ABS-FR filaments were below 25th percentiles of the database, while Nylon filament emissions were near 75th percentiles of the database. Particle emissions from ABS filament were too low for calculations, thus no data was shown for ABS filament.

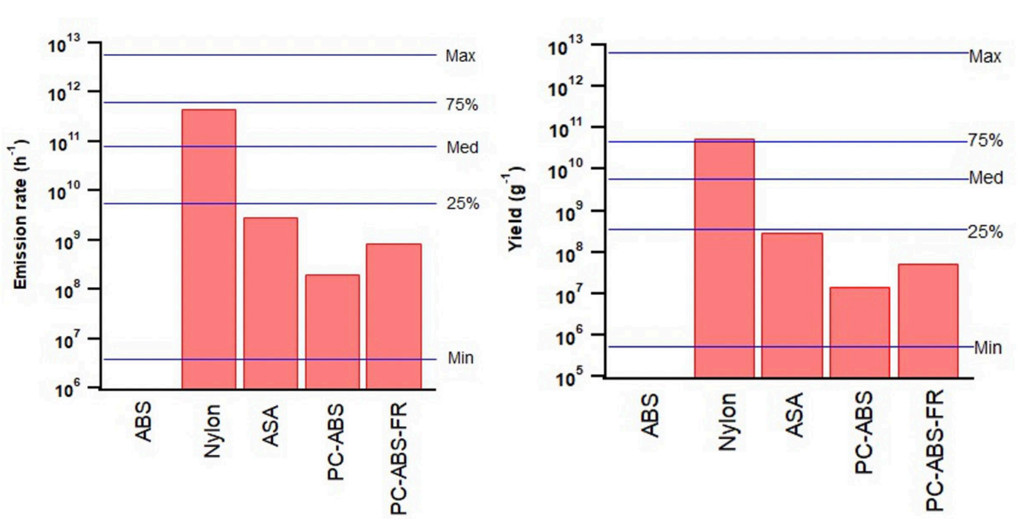

FIGURE 1. PARTICLE EMISSION RATE (LEFT) AND YIELD (RIGHT) FOR PRINTS WITHOUT THE FILTER SETUP, COMPARED TO PREVIOUS DATABASE. LINES INDICATE THE MAXIMUM (MAX), MEDIAN (MED), MINIMUM (MIN) AND 25TH AND 75TH PERCENTILES OF THE DATABASE.

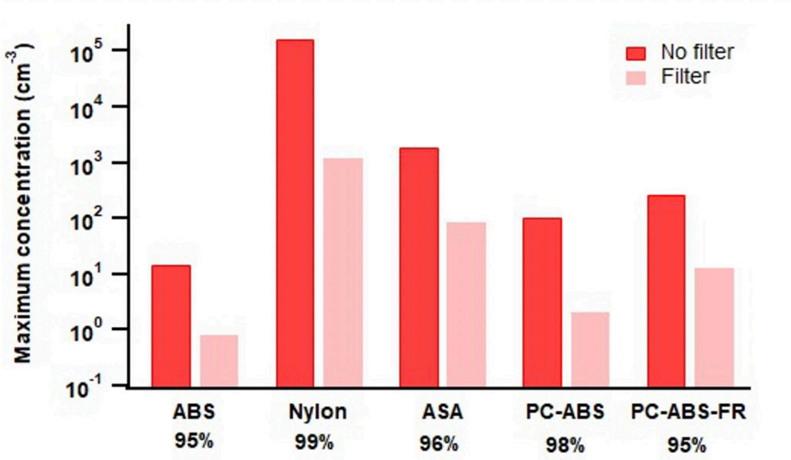

FIGURE 2. PARTICLE MAXIMUM CONCENTRATION DURING PRINTING FOR WITH AND WITHOUT THE FILTER SETUP. PERCENTAGE INDICATES THE REDUCTION DUE TO USE OF FILTER.

The geometric mean diameter (GMD) for Nylon filament did not change for with and without filter (21 – 22 nm), while that for ASA filament was reduced from 118 nm for without filter to 68 nm for with filter. In addition, GMD for ABS, PC-ABS and PC-ABS-FR filaments were 110 – 117 nm for without filter, but the size distribution information for those with filter were not available due to the low concentration measured. This indicated the filter was effective in removing all size of measured particles (7 nm to 10 μm) and tended to be more effective in removing larger size particles.

3.3 Effects of filter on VOC emissions

Total VOC emission rates shown in Table 2 were compared to previous dataset that included 33 tests of 3D printers operating with ABS (12 runs), PLA (14), Nylon (4), HIPS (1), PVA (1) and metal (1) filaments, see Figure 3.

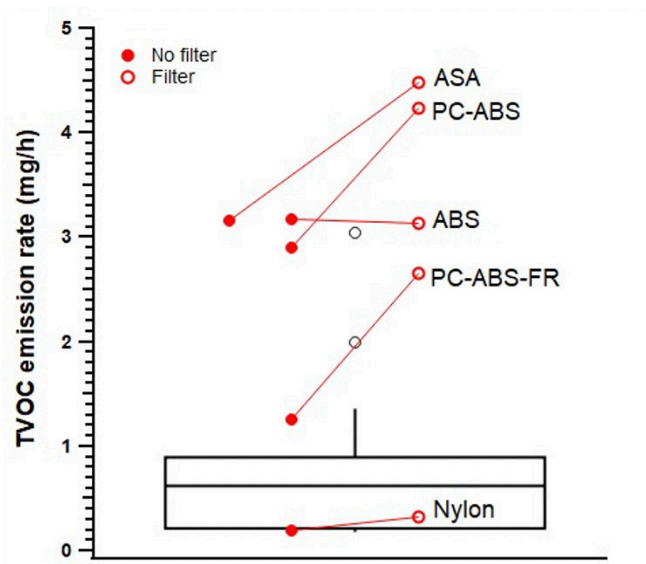

FIGURE 3. TVOC EMISSION RATES FOR EACH FILAMENT WITH AND WITHOUT FILTER, COMPARED TO EXISTING DATABASE. THE MIDDLE LINE IN THE BOX INDICATES THE MEDIAN; THE TOP AND BOTTOM OF THE BOX INDICATE THE 75% AND 25% QUARTILE; THE TOP AND BOTTOM OF WHISKERS INDICATE THE 90% AND 10% VALUES; THE OUTLIERS ARE LARGER THAN 1.5 TIMES OF WHISKER LENGTH.

The use of the filter setup showed an increase in TVOC emission rates for all filaments except ABS (Figure 3). However, all TVOC emission rates were within the criteria in ANSI/CAN/UL 2904.[1]

The effect of filtration on individual VOCs was not conclusive and depended on properties of each chemical. A summary of statistics of individual VOC emissions is shown in Table 2. The numbers of chemicals were categorized by those detected, chemicals of concern, and those exceeding ANSI/CAN/UL 2904 criteria. Chemicals of concern are VOCs listed in health-related regulation and guidance, including ANSI/CAN/UL 2904,[1] the California Department of Public Health Specification 01350 Standard Method (CDPH SM),[7] the American Conference of Governmental Industrial Hygienists (ACGIH®) Threshold Limit Values (TLVs®) and Biological Exposure Indices (BEIs®) Guidance,[8] and the German Ausschuss zur gesundheitlichen Bewertung von Bauprodukten (AgBB) Health-related Evaluation Procedure.[9] Comparisons of emission rates for with and without filter were also listed in Table 2, categorized as increased by filter (detected for both conditions and with filter > without filter), generated by filter (only detected for with filter), decreased by filter (detected for both conditions and without filter > with filter), and removed by filter (only detected for without filter).

TABLE 2. SUMMARY OF VOC EMISSION STATISTICS

Material	ABS		Nylon		ASA		PC-ABS		PC-ABS-FR	
# of chemicals	No filter	Filter	No filter	Filter	No filter	Filter	No filter	Filter	No filter	Filter
Detected	105	92	15	42	103	90	107	90	75	82
Chemicals of concern	38	34	5	20	36	36	38	36	33	35
Exceed criteria	2	1	0	0	2	1	2	1	1	1
Increased by filter	16		4		19		30		26	
Generated by filter	47		33		40		36		36	
Decreased by filter	29		5		31		24		20	
Removed by filter	60		6		53		53		29	

Note: for # of chemicals exceed criteria, "2" indicates formaldehyde and phenol exceeded the criteria, "1" indicates phenol exceeded.

Individual VOC emissions from ABS, ASA, PC-ABS and PC-ABS-FR filaments shared 4 out of 5 chemicals in common for the top 5 detected chemicals, which were styrene, phenol, formaldehyde and 1-propanol, 2-methyl (isobutyl alcohol). In addition, ethylbenzene was in top 5 chemical lists for ABS and ASA filaments. While Nylon filament had relatively different emitted VOC profiles; the top 5 detected chemicals were caprolactam; 1,2,3-propanetriol, 1-acetate; octanal; 5,9-undecadien-2-one, 6,10-dimethyl-, (E)-; and hexadecane.

Use of the filter reduced the emission rates of styrene, formaldehyde, ethylbenzene, and 1-propanol, 2-methyl, but tended to increase that of phenol. In addition, the filter tended to increase or introduce the emission of some chemicals, those common ones found in top 5 detected chemicals with filter were hexadecane, tetradecane, and trichloroacetic acid, 2-(1-adamantyl) ethyl ester.

For the top 5 chemicals of concern, ABS, ASA, PC-ABS, and PC-ABS-FR filaments had 4 chemicals in common (styrene, phenol, formaldehyde and 1-propanol, 2-methyl). Among them, styrene is categorized as a possible carcinogen by International Agency for Research on Cancer (IARC) and is a typical emission from ABS and ASA polymers; formaldehyde is carcinogenic to humans according to IARC and has been found emitted from most polymer-based materials including nylon; phenol is known for developmental and reproductive toxicity and was detected from all filaments except Nylon. Additionally, ethylbenzene was a common chemical of concern for ABS and ASA filaments, and 1-butanol (n-butyl alcohol) for PC-ABS and PC-ABS-FR filaments. Caprolactam is an irritant and usually found emitted from Nylon filaments. Acetaldehyde, a possible carcinogen by IARC, was one of the top 5 chemicals of concern for Nylon filament; it was also detected from all the rest filaments but at relatively lower emission rates. The filter was found to decrease emission rates of most of the top 5 chemicals of concern, including styrene, formaldehyde, ethylbenzene, 1-propanol, 2-methyl, and 1-butanol, while tended to increase emission rates of phenol, 1-hexanol, 2-ethyl and 2,6-di-tert-butyl-4-methylphenol (BHT).

The emission rates and estimated office concentrations of chemicals of concern were compared to regulation and guidance, including ANSI/CAN/UL 2904;[1] the California Specification 01350 Standard Method for the Testing and Evaluation of Volatile Organic Chemical Emissions from Indoor Sources using Environmental Chambers, V1.2;[7] occupational exposure threshold values (TLV®s) published by the ACGIH®;[8] Lowest Concentration of Interest (LCI) values published by the AgBB;[9] and other VOCs found in 3D printer emissions with carcinogenicity, irritation/odor or other unknown health impacts. In general, most of chemicals of concern had emission rates and estimated concentrations below recommended levels. However, emission rates of formaldehyde from ABS, ASA, and PC-ABS filaments were above the criteria in ANSI/CAN/UL 2904 (0.187 mg/h) and estimated office concentrations were higher than CDPH SM allowable concentration (9 $\mu g/m^3$). In addition, emission rates of phenol from all filaments except Nylon were above the ANSI/CAN/UL 2904 criteria (0.208 mg/h) and the estimated office concentrations were above the AgBB LCI (10 $\mu g/m^3$). The filter was able to reduce emission of formaldehyde to below the criteria while not for phenol.

To summarize, filaments except Nylon were found to emit relatively high TVOC and some specific individual VOCs. Use of the filter setup tended to increase TVOC emission rates but still below the standard criteria. Though the filter appeared to reduce some of the VOC species, some individual VOCs increased most likely due to filter material emissions or reactions forming VOCs during the filtration process. More research is needed to evaluate the filtration ability to remove VOCs.

4. 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.
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