Chemical Insights
An Institute of Underwriters Laboratories Inc.

3D PRINTER RESEARCH

Filtration Strategies for Reducing Chemical and Particle Emissions from 3D Printing

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1. INTRODUCTION

1.1 Background

Chemical Insights, with our academic research partners, has conducted discovery research on the characterization of chemical and particle emissions from operating 3D printers and their potential health effects. These efforts have been presented in various publications and reports (more resources on website). In addition, a consensus standard, "Standard Method for Testing and Assessing Particle and Chemical Emissions from 3D Printers," was developed by an expert standards group. This standard establishes testing and data assessment methodologies, as developed during the research, and defines acceptable emissions criteria for volatile organic compounds (VOCs) and particles. Primary research findings show emissions released during the 3D printing process include large numbers of volatile organic compounds (VOCs) and particles, primarily in the ultrafine size range. Toxicity responses of the particles demonstrated the potential for adverse human health effects. As a result of these findings, research is continuing to further assess toxicity and to evaluate options for reducing emission exposures through filtration of the emissions.

Recent research has focused on the use of local filtration as a means of reducing exposure risks of the emitting aerosols and chemicals. Using a readily available desktop 3D printer, emissions were evaluated during operation with a series of filaments, including ABS (acrylonitrile butadiene styrene), Nylon, ASA (acrylonitrile styrene acrylate), PC-ABS (polycarbonate-ABS), and PC-ABS-FR (PC-ABS with flame retardants). Testing included measurement of ultrafine, fine and coarse particles and VOCs in a controlled exposure chamber according to ANSI/CAN/UL 2904.[1] Emission data were obtained with and without the use of local filtration devices for comparison purposes. Multistage filtration consisted of a package containing a carbon bed filter, a HEPA (high-efficiency particulate air) filter, and a fan pulling air through the filters, housed by a plastic cover on top of the printer. Two separate filtration packages or sets were used with different filter brands in each.

1.2 Key Findings

In general, the combination of a HEPA filter and carbon bed filter was efficient in removing particle emissions, but this was not true for VOCs. There were variances in VOC removal rates, and in some cases the filter materials themselves appeared to contribute VOCs. Removal rates of emissions for the two filter sets are summarized in Table 1.

Filtration successfully removed particle emissions during printing for the two different filter packages (each containing different manufacturers of filters). Differences between the two filter packages for maximum particle concentration reduction were within 10%. Nylon filament particle emissions exceeded the maximum allowable criteria in ANSI/CAN/UL 2904[1]. But with the addition of filtration, emissions reduced to levels close to background.

The effect of filtration on VOC reduction was chemical and filter set dependent. Filter sets were found to add VOCs to the emissions and in some cases, addition of these VOC emissions and low efficacy of the filters themselves resulted in emission levels for specific VOCs above the criteria allowed in ANSI/CAN/UL 2904.[1] Filter set I was found to increase total VOC (TVOC) emission rates for four of the five filaments studied. The filaments ABS, ASA, PC-ABS and PC-ABS-FR all had individual VOC emissions of formaldehyde and phenol above the allowable criteria in ANSI/CAN/UL 2904[1] when printing without filtration. Filter set I failed to reduce phenol levels to below the criteria, while filter set II successfully reduced formaldehyde and phenol to allowable levels. In addition, filter set II was able to reduce TVOC emissions for the three filaments tested. Therefore, application of filtration does not always lead to reduction of VOC emissions; filter materials could present as VOC sources, which potentially increases VOC emissions. The differences of removal efficacy between the two filter sets used in this study emphasize the significance of filter specification in filtration design and verification testing prior to use.

TABLE 1. SUMMARY OF REMOVAL RATES FOR PARTICLE AND CHEMICAL EMISSIONS WITH FILTRATION FOR VARIOUS FILAMENT MATERIALS

Material	Maximum particle removal		Total VOC emission rate		Meets ANSI/CAN/UL 2904	
	Filter Set I	Filter Set II	Filter Set I	Filter Set II	Filter Set I	Filter Set II
ABS	95%	86%	1%	64%	×	√
Nylon	99%	100%	(66%)	21%	-	√
ASA	96%	-	(42%)	-	×	-
PC-ABS	98%	94%	(46%)	63%	×	√
PC-ABS-FR	95%	-	(110%)	-	×	-

Note: "-" indicates not tested; "()" indicates emissions increased due to filtration.

2. METHODS AND MATERIALS

Emission measurements were made in a 6 m^3 exposure chamber with the 3D printer placed in the middle of the chamber. The design and the characterization of the chamber have been previously described in ISO 16000-9.[2]

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.[3] 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 or high performance liquid chromatography, respectively.[4] Emission rates for individual VOC and total VOC were calculated in accordance to ANSI/CAN/UL 2904.[1]

The tested print filament materials included Nylon black color (extruder nozzle temperature 250 °C), ABS natural color (245 °C), ASA black color (245 °C), PC-ABS black color (260 °C), and PC-ABS-FR black color (260 °C). All studied filaments were printed on the same printer. Support materials were loaded and 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 without the installation of the filter set and again with filter set I installed. Additional tests with filter set II were carried out to investigate the effect of filter differences, which applied to Nylon, ABS and PC-ABS filaments. Filter set I included filters noted as HEPA I and CF (carbon filter) I and filter set II as HEPA II and CF II.

3. DISCUSSION

3.1 Effect of Filtration on Particle Emissions

Particle emission rates without filtration ranged from 2.1×10^8 to 4.6×10^{11} h^{-1} and particle yield ranged from 1.5×10^7 to 5.7×10^{10} g^{-1}, excluding ABS filament that had very low particle emissions. These emissions were below 25th percentiles of our existing research database except Nylon, which were near 75th percentiles of the database. See Report 170 for details.

The use of filtration significantly reduced particle emissions for all filament types studied. With the filter, particle emissions from all filaments were reduced to levels below quantitative emission rate determinations. For the Nylon filament, both particle emission rate and yield exceeded the maximum acceptable criteria in ANSI/CAN/UL 2904[1] without filtration; but fell below the criteria when a filter set was used. Figure 1 shows a comparison of maximum particle concentrations during print. Filtration (both filter sets) was able to reduce maximum particle concentrations by at least one order of magnitude, and the reduction rates were 86% or greater. There was generally no difference between the two sets of filters used regarding particle removal, the differences in maximum particle concentration reduction rate were within 10%.

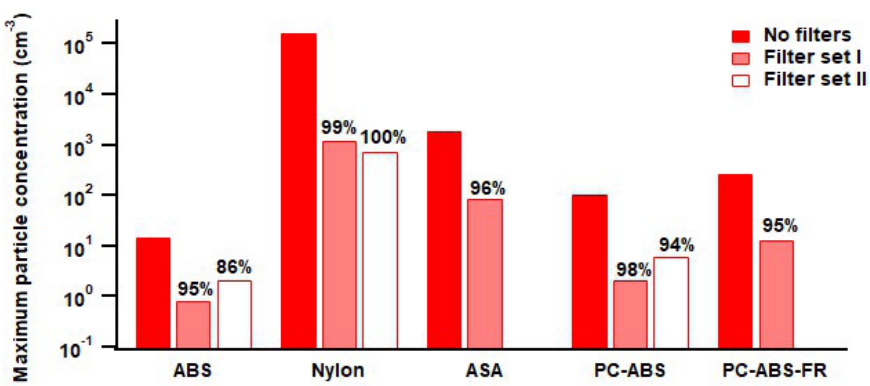

FIGURE 1. PARTICLE MAXIMUM CONCENTRATION DURING PRINTING FOR WITH AND WITHOUT FILTRATION.

3.2 Effect of Filtation on VOC Emissions

Total VOC (TVOC) emission rates measured in this study were compared to our research dataset that includes 33 tests of 3D printers operating with ABS (12 runs), PLA (polylactic acid, 14), Nylon (4), HIPS (high impact polystyrene, 1), PVA (polyvinyl alcohol, 1) and metal (1) filaments, see Figure 2. All TVOC emission rates, with or without filtration, fell below the maximum acceptable TVOC criteria in ANSI/CAN/UL 2904 (10.4 mg/h).[1] Filter set I only slightly reduced the TVOC emission rate for ABS filament by 1%, while it increased the emission rates for the rest four filaments by 42% to 110%. This indicated filter materials themselves could contribute additional VOC emissions while in use. On the other hand, filter set II was found to successfully reduce the TVOC emission rates for all three filaments applied, 64% for ABS, 21% for Nylon and 63% for PC-ABS. This difference in filtration efficacy was likely associated with the filter make and materials.

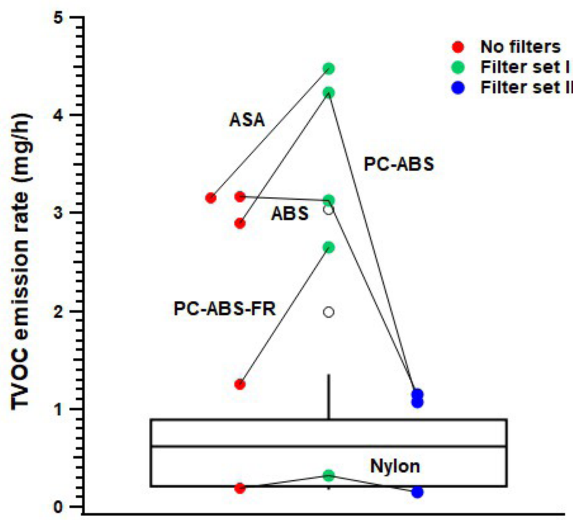

FIGURE 2. TVOC EMISSION RATES FOR EACH FILAMENT WITH AND WITHOUT FILTRATION, COMPARED TO EXISTING DATABASE. THE BOX INDICATES 25%, MEDIAN AND 75% QUARTILE; THE WHISKERS INDICATE 10% AND 90% VALUES; THE OUTLIERS ARE LARGER THAN 1.5 TIMES OF WHISKER LENGTH.

There were more than 300 individual VOCs detected during printing, many of which have been listed as chemicals of concern and health hazards. Table 2 summarizes the number of chemicals detected with and without filtration for each filament. Chemicals of concern are VOCs listed in health-related regulations and guidance documents, including ANSI/CAN/UL 2904,[1] the California Department of Public Health Specification 01350 Standard Method (CDPH SM),[5] the American Conference of Governmental Industrial Hygienists (ACGIH®) Threshold Limit Values (TLVs®) and Biological Exposure Indices (BEIs®) Guidance,[6] and the German Ausschuss zur gesundheitlichen Bewertung von Bauprodukten (AgBB) Health-related Evaluation Procedure.[7]

In general, Nylon filament emitted fewer VOCs than the rest four filaments, and it was associated with fewer VOCs of health concern. Without filtration, PC-ABS had the greatest number of VOCs detected; ABS and PC-ABS had the greatest numbers of chemical of concern (Table 2). Filter set I seemed to reduce or remove some VOCs, while it increased or introduced some other VOCs, which could result in an overall elevation of VOC emissions. Specifically, filter set I decreased the number of VOCs emitted for ABS, ASA, and PC-ABS, while they increased for Nylon and PC-ABS-FR; similar trends were found for specific chemicals of concern (Table 2). Filter set II was found to decrease the number of VOCs emitted for ABS, Nylon and PC-ABS filaments, as well as certain chemicals of concern (Table 2), and it tended to reduce more VOCs than were increased, resulting in an overall decrease of VOC emissions.

TABLE 2. NUMBERS OF VOC DETECTED FOR EACH CONDITION AND THE EFFECTS OF FILTRATION

Material	Filter condition	Number of Chemicals			
		Detected	Chemical of concern	Increased or generated by filter	Decreased or removed by filter
ABS	No filters	105	38		
	Filter Set I	92	34	63	89
	Filter Set II	56	21	35	102
Nylon	No filters	15	5		
	Filter Set I	42	20	37	11
	Filter Set II	14	4	12	11
ASA	No filters	103	36		
	Filter Set I	90	36	59	84
PC-ABS	No filters	107	38		
	Filter Set I	90	36	66	77
	Filter Set II	53	20	28	102
PC-ABS-FR	No filters	75	33		
	Filter Set I	82	35	62	49

Furthermore, the top five individual VOCs with highest emission rates from each filament type are listed in Table 3 for different filter sets used. Individual VOC emissions were associated with filament materials.[4] 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), since these filaments share similarities in polymer components. The Nylon filament had a different VOC emission profile, with caprolactam as the most emitting VOC, which was associated with the nylon polymer.

Filtration was found to reduce the emission rates for most of the top 5 emitting VOCs, however the removal efficiency depended on specific filter set and VOC species. Filter set I generally reduced the emission rates for styrene, formaldehyde, ethylbenzene, 1-propanol, 2-methyl, and caprolactam, while increased those for hexadecane, tetradecane, and trichloroacetic acid, 2-(1-adamantyl) ethyl ester, as well as for phenol except ABS (Table 3). These elevated VOCs were likely associated with the filtration materials, since they were found with elevated emission rates for different filaments but all with filter set I. For a same specific VOC, filter set II tended to always have a higher removal rate than set I; it was able to remove phenol, ethylbenzene, 1-propanol, 2-methyl, hexadecane in some cases (Table 3). However, filter set II also contributed some VOC emissions, like tetradecane and 1,4-methanobenzocyclodecene, 1,2,3,4,4a,5,8,9,12,12a-decahydro-.

TABLE 3. COMPARISON OF FILTER EFFECT ON THE TOP FIVE EMITTING VOCS

	No Filters	Filter Set I	Filter Set II
ABS	Styrene	↓ 24%	↓ 76%
	Phenol	↓ 37%	↓ **100%**
	Formaldehyde	↓ 20%	↓ 60%
	Benzene, ethyl	↓ 31%	↓ 100%
	1-Propanol, 2-methyl	↓ 80%	↓ 100%
		Hexadecane	1,4-Methanobenzocyclodecene, 1,2,3,4,4a,5,8,9,12,12a-decahydro-
		Tetradecane	Tetradecane
		Trichloroacetic acid, 2-(1-adamantyl) ethyl ester	Hexadecane
Nylon	Caprolactam	↓ 70%	↓ 75%
	1,2,3-Propanetriol, 1-acetate	↓ 58%	↓ 100%
	Octanal	↓ 6%	↓ 100%
	5,9-Undecadien-2-one, 6,10-dimethyl-, (E)-	↑ 16%	↓ 100%
	Hexadecane	↑ 756%	↓ 100%
		1-Hexanol, 2-ethyl	1,1',3-Tribenzoyl-2,3-dihydro-2,2'-biimidazole
		Trichloroacetic acid, 2-(1-adamantyl) ethyl ester	1,4-Methanobenzocyclodecene, 1,2,3,4,4a,5,8,9,12,12a-decahydro-
		Tetradecane	Acetaldehyde
		Acetaldehyde	Tetradecane
ASA	Styrene	↓ 39%	
	Phenol	↑ 169%	
	Formaldehyde	↓ 27%	
	1-Propanol, 2-methyl	↓ 75%	
	Benzene, ethyl	↓ 47%	
		Hexadecane	
		Trichloroacetic acid, 2-(1-adamantyl) ethyl ester	
		Tetradecane	
PC-ABS	Phenol	↑ 8%	↓ 87%
	Styrene	↓ 35%	↓ 74%
	1-Propanol, 2-methyl	↓ 83%	↓ 100%
	Formaldehyde	↓ 14%	↓ 26%
	Hexadecane	↑ 292%	↓ 100%
		1,4-Methanobenzocyclodecene, 1,2,3,4,4a,5,8,9,12,12a-decahydro-	1,4-Methanobenzocyclodecene, 1,2,3,4,4a,5,8,9,12,12a-decahydro-
		Tetradecane	Tetradecane

PC-ABS-FR	Phenol	↑ 41%	
	Formaldehyde	↓ 8%	
	Styrene	↓ 39%	
	1-Propanol, 2-methyl	↓ 81%	
	Glycerin	↓ 100%	
		Hexadecane	
		1,4-Methanobenzocyclodecene, 1,2,3,4,4a,5,8,9,12,12a-decahydro-	
		Trichloroacetic acid, 2-(1-adamantyl) ethyl ester	
		Tetradecane	

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), see Table 4. Among them, styrene is a possible carcinogen according to International Agency for Research on Cancer (IARC); formaldehyde is carcinogenic to humans according to IARC; phenol is known for developmental and reproductive toxicity. 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.

Without filtration, there were some VOCs exceeding the maximum allowable criteria in ANSI/CAN/UL 2904;[1] these included formaldehyde and phenol from ABS, ASA and PC-ABS filaments, and phenol from PC-ABS-FR filament. Filter set I was able to reduce formaldehyde from ABS and ASA to below the criteria, while not for phenol. In addition, filter set I tended to increase emissions of phenol (except for ABS), 1-hexanol, 2-ethyl and 2,6-di-tert-butyl-4-methylphenol (BHT). Filter set II had higher removal efficiency than set I and all chemicals of concern were within the criteria with filter set II. It reduced all of the top 5 chemicals of concerns except formaldehyde and acetaldehyde from Nylon filament. In fact, filter set II increased the emission rates of acetaldehyde, a possible carcinogen by IARC, for all three filaments.

TABLE 4. COMPARISON OF FILTER EFFECT ON THE TOP 5 CHEMICALS OF CONCERN

Material	No filters	Filter Set I	Filter Set II
ABS	Styrene	↓ 24%	↓ 76%
	Phenol	↓ 37%	↓ 93%
	Formaldehyde	↓ 20%	↓ 60%
	Benzene, ethyl	↓ 31%	↓ 79%
	1-Propanol, 2-methyl	↓ 80%	↓ 100%
		1-Hexanol, 2-ethyl	Acetaldehyde
Nylon	Caprolactam	↓ 70%	↓ 68%
	Octanal	↓ 6%	↓ 100%
	Formaldehyde	↑ 33%	↑ 41%
	Acetaldehyde	↑ 6%	↑ 35%
	Cyclopentanone	↓ 15%	↓ 100%
		1-Hexanol, 2-ethyl	1-Hexanol, 2-ethyl
		Cyclotetrasiloxane, octamethyl	

ASA	Styrene	↓ 39%	
	Phenol	↑ 169%	
	Formaldehyde	↓ 27%	
	1-Propanol, 2-methyl	↓ 75%	
	Benzene, ethyl	↓ 47%	
		1-Hexanol, 2-ethyl	
		2,6-Di-tert-butyl-4-methylphenol	
PC-ABS	Phenol	↑ 8%	↓ 87%
	Styrene	↓ 35%	↓ 74%
	1-Propanol, 2-methyl	↓ 83%	↓ 76%
	Formaldehyde	↓ 14%	↓ 26%
	1-Butanol	↓ 25%	↓ 100%
		2,6-Di-tert-butyl-4-methylphenol	Acetaldehyde
		1-Hexanol, 2-ethyl	
PC-ABS-FR	Phenol	↑ 41%	
	Formaldehyde	↓ 8%	
	Styrene	↓ 39%	
	1-Propanol, 2-methyl	↓ 81%	
	1-Butanol	↓ 20%	
		1-Hexanol, 2-ethyl	
		2,6-Di-tert-butyl-4-methylphenol	

Note: arrow and percentage indicate change of emission rate when filtration applied; chemicals listed under filtration scenarios were new chemicals that were not in top 5 chemical of concern list for the no filtration condition.

The effect of filtration on individual VOC removal depended on the property of each specific VOC, as well as the specific filter set used. In general, for high emitting VOCs, filtration appeared to decrease emission rates of styrene, formaldehyde, ethylbenzene, 1-propanol, 2-methyl, and 1-butanol, while the removal efficacy varied by filter set. Some VOCs tended to have elevated emission rates, likely associated with the filter materials, including phenol, hexadecane, tetradecane, acetaldehyde, 1-hexanol, 2-ethyl and 2,6-di-tert-butyl-4-methylphenol, some of which were listed as health-related VOCs. A successful filtration design could bring VOC emissions below the maximum acceptable VOC criteria in ANSI/CAN/UL 2904, while this may not be true for all filtration design. Since filter material themselves appear to be sources of VOCs that contribute to VOC emissions, this should be taken into consideration when designing filtration systems and verifying their performance.

4. REFERENCES

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