VOC Emissions Influenced by Polymer Additives in 3D Printing

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Introduction

There is a growing concern over hazardous emissions from 3D printing as printers become more affordable and enter more workplaces and consumer households. Printing emissions containing volatile organic compounds (VOCs) and particulate matter (PM) are still a potential threat to user health. While some studies quantify total VOCs, there have been just a few attempts to fully characterize and quantify VOC emissions[1-5].

3D Printer Filaments and Additives

3D printing filaments often contain additives to adjust their physicochemical properties. Common additives include: structural fillers, azo-dyes, plasticizers, stabilizers, wood fiber, metal particles, and carbon allotropes. While some of these additives may be advertised to the consumer, many more are not and can contribute to VOC formation.

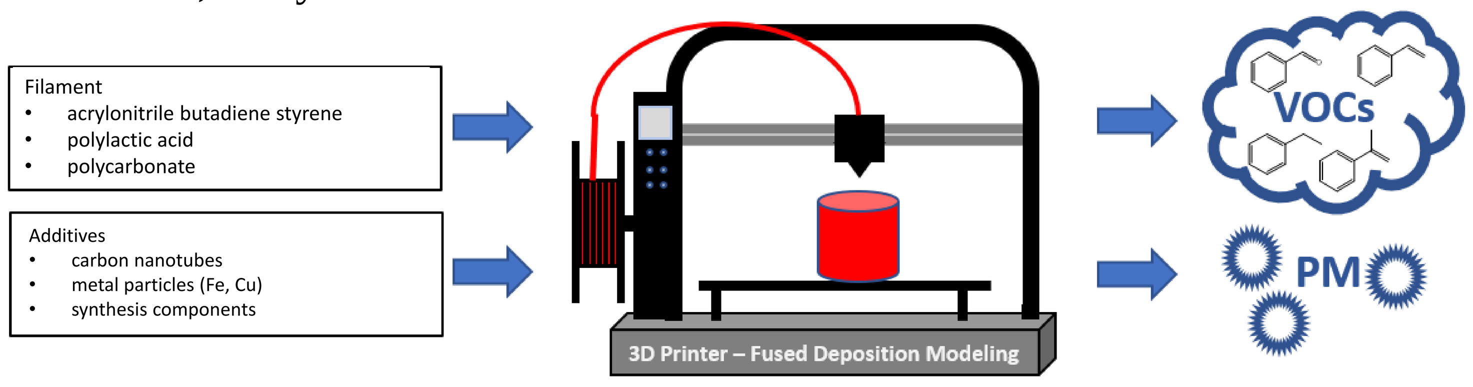

Figure 1. Polymer type and filament additives influence hazardous emissions from 3D printing.

In this work, six commercially-available 3D printer filaments are shown as examples of additives (advertised or not) affecting VOC emissions during 3D printing. The filaments are: acrylonitrile butadiene styrene (ABS) with carbon nanotubes (CNTs), polycarbonate (PC), polylactic acid (PLA), PLA + copper, PLA + bronze, and PLA + stainless steel.

Methods

All degradation experiments were performed using the System for Thermal Diagnostic Studies (STDS). The STDS is a custom-built, modular instrument shown below.

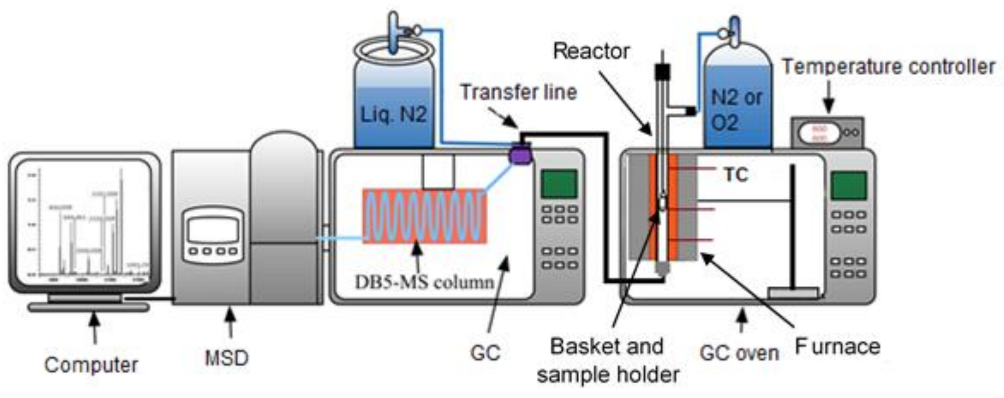

Figure 2. System for Thermal Diagnostic Studies (STDS)

Reaction Conditions

- Temperature – 180 - 280˚C
- Residence time – 1 & 3 min
- Reaction gas – O_2 and N_2

Results

Acrylonitrile butadiene styrene + carbon nanotubes

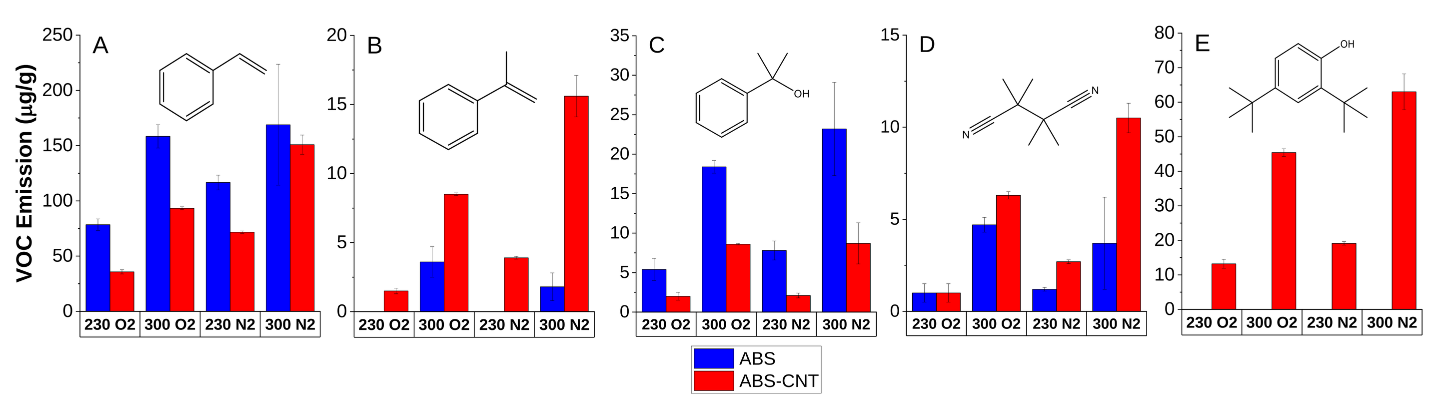

Figure 3. Influence of CNTs on emission of A) styrene, B) α-methylstyrene, C) 2-phenyl-2-propanol, D) tetramethylsuccinonitrile, and E) 2,4-di-tert-butylphenol. Error bars = ± 1 SD.

- presence of CNTs slightly lowers total VOC emissions
- CNTs also increase emission of more toxic components, e.g., α-methylstyrene
- emits VOCs that were not seen in plain ABS, e.g., 2,4-di-tert-butylphenol

Polylactic acid (PLA)

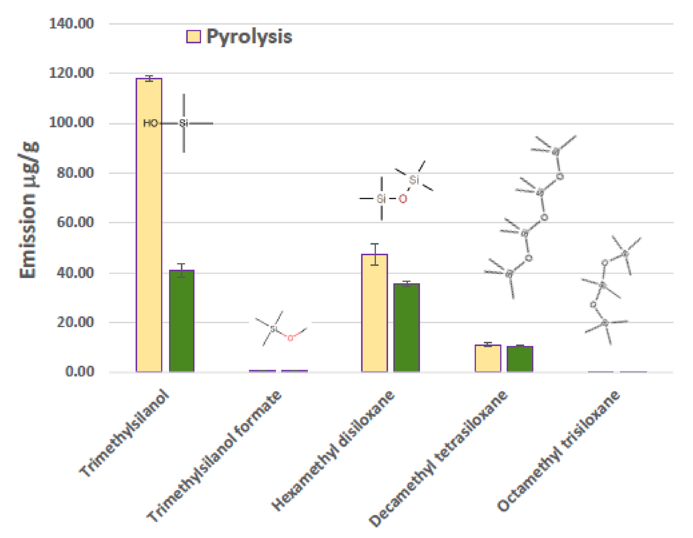

Figure 4. Silanol and siloxane emissions from PLA filament at 180 C. Error bars = ± 1 SD.

- PLA with no advertised additives
- VOC emissions include various silanols and siloxanes
- Silanol copolymers used in some PLA for increased structural integrity

PLA with copper, bronze, and stainless steel

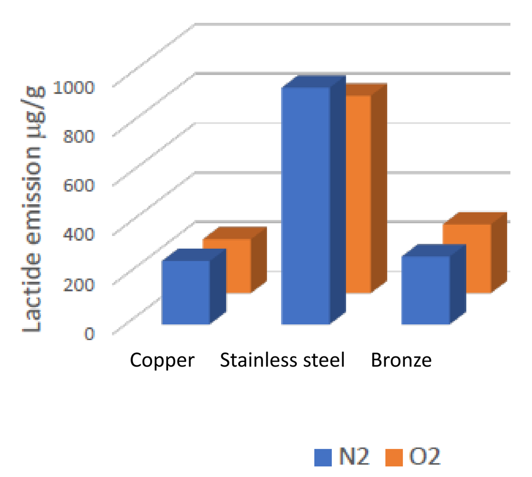

Figure 5. Lactide emissions from three metal-containing PLA filaments at 180 C.

- Lactide emission varied greatly based on the metal additive
- Iron-containing steel filament was most active in thermal degradation

Results (cont.)

Polycarbonate (PC)

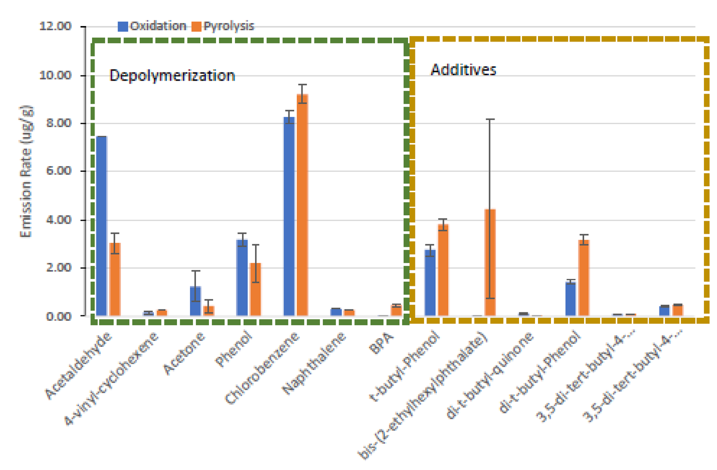

Figure 6. VOC emissions from thermal degradation of a PC filament at 280 C. Error bars = ± 1 SD.

- PC with no advertised additives
- presence of halogenated aromatics
- potential chlorine source is unreacted phosgene ($CHCl_2$), which is commonly used in PC synthesis

Environmentally Persistent Free Radicals (EPFRs)

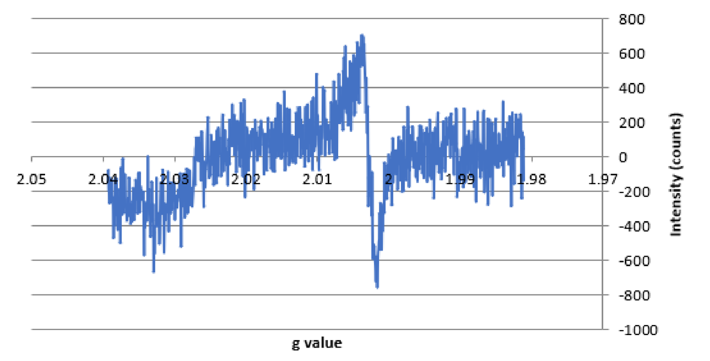

Figure 7. Electron paramagnetic spectrum of printed residue.

- substituted aromatic + metal oxide surface = surface-bound radicals that can have half-lives of days or weeks
- PLA + copper yielded organic radicals that could pose an additional inhalation risk to particulate matter

Conclusions

Table 1 shows the inhalation reference concentration (RfC) of five VOCs from various filaments. The amount of filament that would need to be printed to achieve these concentrations in a poorly-ventilated, 37.5 m³ room is also shown. These amounts are easily achieved during any type of residential or industrial printer use.

filament	compound	RfC (mg/m³)	printed filament mass to achieve RfC (g)
ABS-CNT	styrene	1	222.0
ABS-CNT	ethylbenzene	1	2451.0
ABS-CNT	cumene / isopropylbenzene	0.4	2586.0
PC	acetaldehyde	$9x10^{-3}$	112.5
PC	naphthalene	$3x10^{-3}$	375

Table 1. Integrated Risk Information System (IRIS) RfC values for VOCs emitted during 3D printing. Calculated 'printed mass to achieve RfC' values based on highest emission of individual VOC and a 37.5 m³ unventilated room. RfC = reference concentration for inhalation exposure

- filament additives, such as CNTs and metal particles, can directly influence VOC emissions and their use in 3D printing should be reevaluated
- filaments that do not advertise additives may contain reactants or other synthesis components that could also contribute to total VOC emissions
- some additives are not advertised and the consumer cannot expect the added risk of increased VOC emission
- some filaments can form surface-bound EPFRs with relatively long half-lives (days/weeks) and can generate reactive oxygen species in biological conditions

As the popularity of 3D printing grows, and applications spread from industry to the household, there is a critical need to investigate filament additives to assess their health risks. Future work will investigate other additives (dyes, metals, wood fiber) and involve characterization of both VOCs and particulate matter.

Acknowledgments

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