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VOC Emissions and Formation Mechanisms from Carbon Nanotube Composites During 3D Printing

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Introduction

There is a growing concern over hazardous emissions from 3D printing using fused deposition modelling (FDM) as they become more affordable and enter more workplaces and consumer households. Despite design efforts to limit exposure, printing emissions containing volatile organic compounds (VOCs) and particulate mater (PM) are still a potential threat to user health. While some studies quantify total VOCs, there have been few attempts to fully characterize and quantify VOC emissions.

3D Printers and Filaments

3D printing filaments often contain additives to adjust their physicochemical properties. Common additives include: azo-dyes, plasticizers, stabilizers, wood fiber, metal particles, phosphorescent compounds, and carbon allotropes. Many of these additives can either degrade into VOCs or contribute to their formation. The effects of many filament additives on VOC emissions during FDM has not been studied.

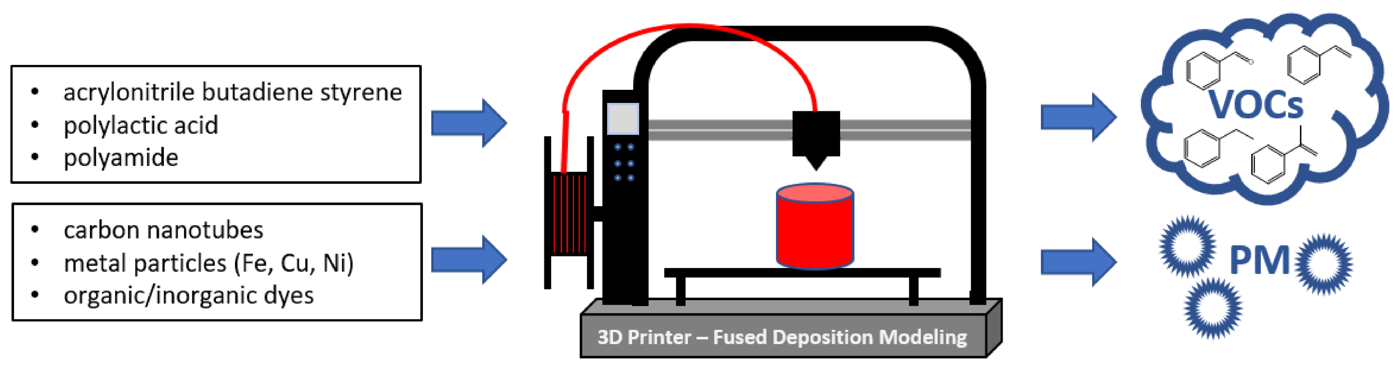


Figure 1. Polymer type and filament additives influence hazardous emissions from 3D printing.

In this work, two commercially-available 3D printer filaments, consisting of an acrylonitrile-butadiene-styrene – carbon nanotube (ABS-CNT) nanocomposite (0.7% CNTs by weight) and a plain ABS, were subjected to thermal conditions that simulate FDM. VOC emissions from the simulated printing were quantified and characterized to determine the effect of CNTs on hazardous emissions.

Methods

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

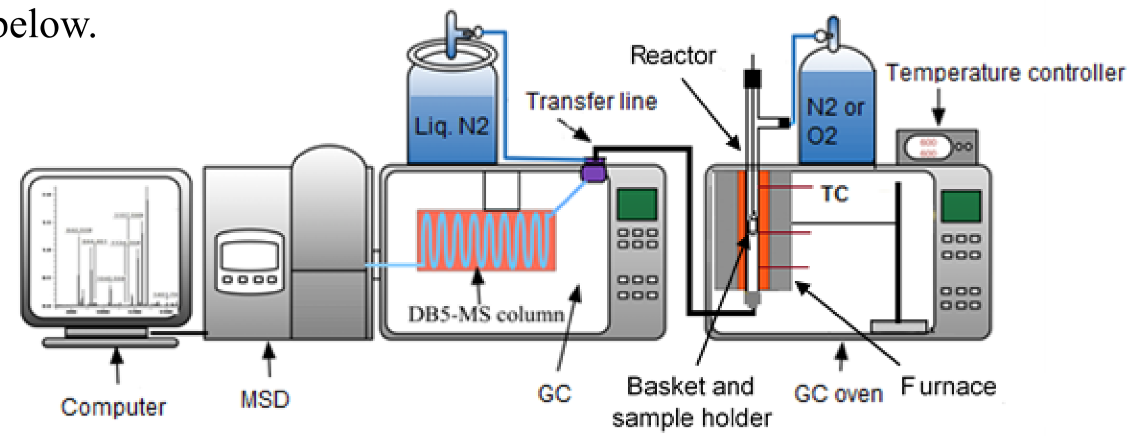
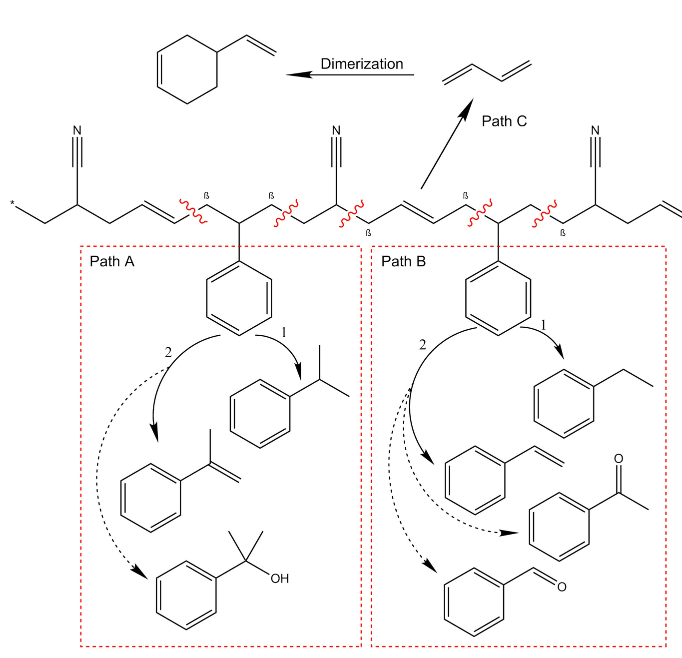


Figure 2. System for Thermal Diagnostic Studies (STDS)

Reaction Conditions

- Temperature – 200, 230, 300 ° C
- Residence time – 1 & 3 minutes
- Reaction gas – O_2 and N_2

Results



compound	source
4-vinylcyclohexene	butadiene monomer dimerization
ethylbenzene	polymer backbone cleavage
styrene	unreacted monomer / backbone cleavage
isopropylbenzene	polymer backbone cleavage
benzaldehyde	oxidation of backbone cleavage intermediate
α-methylstyrene	polymer backbone cleavage
tetramethylsuccinonitrile	polymerization byproduct
acetophenone	oxidation of backbone cleavage intermediate
2-phenyl-2-propanol	oxidation of backbone cleavage intermediate
2,6-di-tert-butylquinone	2,4-di-tert-butylphenol degradation
2,4-di-tert-butylphenol	polymer UV-stabilizer

Table 1. (above) Primary VOCs emitted from thermal degradation of ABS filament.

Figure 3. (left) Reaction pathways for the low temperature depolymerization of ABS filament.

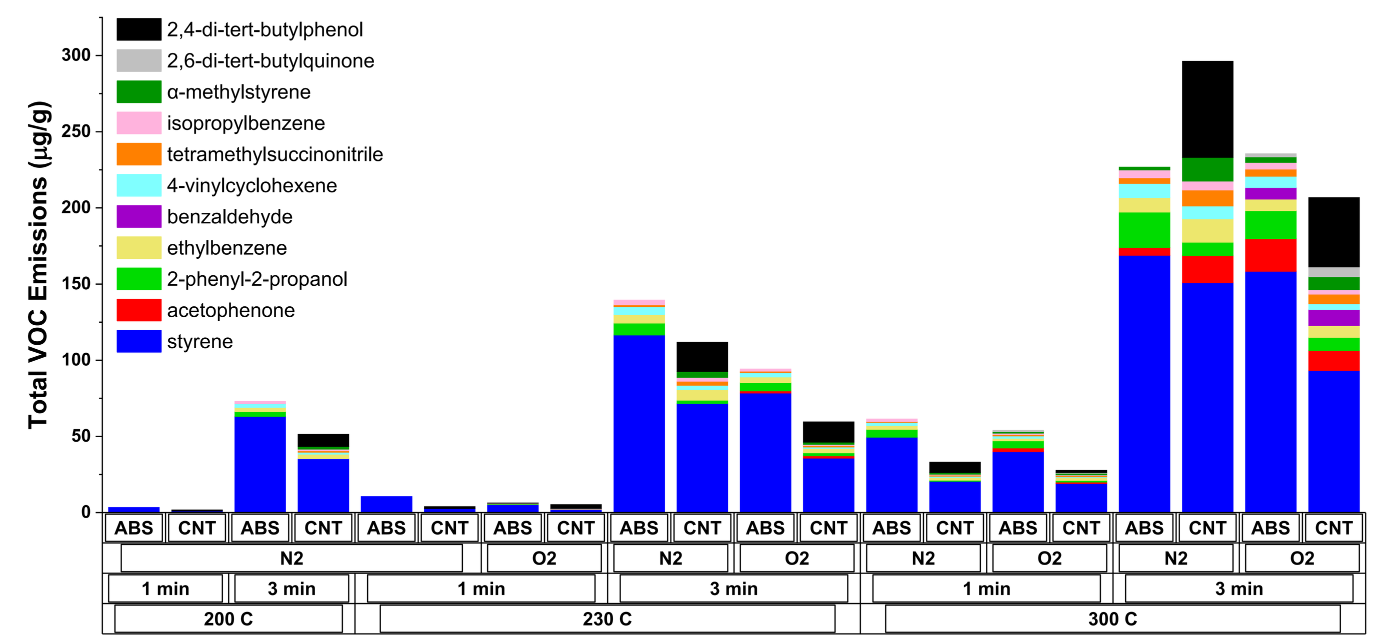


Figure 4. Total VOC emissions from thermal degradation of ABS and ABS-CNT at relevant printing conditions.

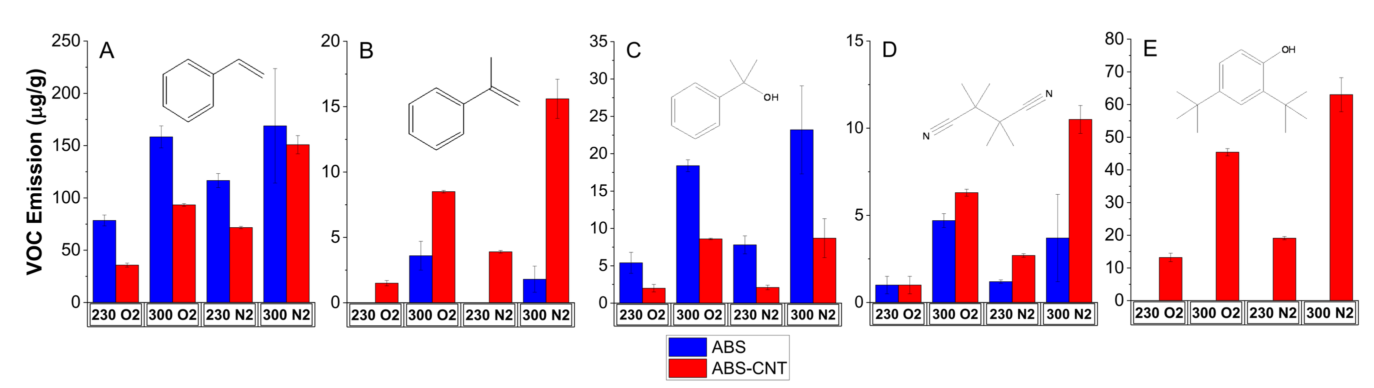


Figure 5. Influence of CNTs on emission of A) styrene, B) α-methylstyrene, C) 2-phenyl-2-propanol, D) tetramethylsuccinonitrile, and E) 2,4-di-tert-butylphenol. Error bars = ± 1 SD.

	Total VOCs	# of VOCs	styrene (ug/g)	other VOCs (ug/g)
Temperature	↑	↑	↑	↑
O_2	↓	↑	↓	↓
CNTs	↓	↑	↓	↑

Table 2. Effect of experimental conditions on various VOC emission parameters. Size of arrow signifies magnitude of effect.

Conclusions

There is evidence that three types of surface interactions may be responsible for the effect of CNTs on VOC emissions. These three interactions can occur independently, compete, or even exhibit synergy in altering VOC emissions:

1. strong adsorption of O_2 on CNTs lowering the amount of O_2 available for reaction with polymer backbone cleavage intermediates
2. adsorption of unreacted monomer styrene to CNTs yielding different products compared to Path A and B
3. increased affinity for certain aromatics leading to CNTs acting as sinks for particular VOCs

compound	RfC (mg/m^3)	printed mass to achieve RfC (g)
styrene	1	222.0
ethylbenzene	1	2451.0
cumene / isopropylbenzene	0.4	2586.0

Table 3. 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 m^3 unventilated room. RfC = reference concentration for inhalation exposure

This work has shown that filament additives such as CNTs can influence VOC emissions and their use in 3D printing should be reevaluated. CNTs increase formation of more hazardous VOC emissions and, if emitted in particulate, pose an added inhalation hazard as adsorption sites for VOCs. 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) and involve characterization of both VOCs and particulate matter.

Acknowledgments

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