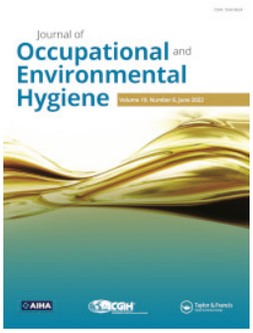

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Volatile organic compound and particulate emissions from the production and use of thermoplastic biocomposite 3D printing filaments

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ABSTRACT

Biocomposites (BCs) can be used as substitutes for unsustainable polymers in 3D printing, but their safety demands additional investigation as biological fillers may produce altered emissions during thermal processing. Commercial filament extruders can be used to produce custom feedstocks, but they are another source of airborne contaminants and demand further research. These knowledge gaps are targeted in this study. Volatile organic compound (VOC), carbonyl compound, ultrafine particle (UFP), and fine ($PM_{2.5}$) and coarse (PM_{10}) particle air concentrations were measured in this study as a filament extruder and a 3D printer were operated under an office environment using one PLA and four PLA-based BC feedstocks. Estimates of emission rates (ERs) for total VOCs (TVOC) and UFPs were also calculated. VOCs were analyzed with a GC-MS system, carbonyls were analyzed with an LC-MS/MS system, whereas real-time particle concentrations were monitored with continuously operating instruments. VOC concentrations were low throughout the experiment; TVOC ranged between 34–63 $\mu g/m^3$ during filament extrusion and 41–56 $\mu g/m^3$ during 3D printing, which represent calculated TVOC ERs of $2.6–3.6 \times 10^2$ and $2.9–3.6 \times 10^2$ $\mu g/min$. Corresponding cumulative carbonyls ranged between 60–91 and 190–253 $\mu g/m^3$. Lactide and miscellaneous acids and alcohols were the dominant VOCs, while acetone, 2-butanone, and formaldehyde were the dominant carbonyls. Terpenes contributed for ca. 20–40% of TVOC during BC processing. The average UFP levels produced by the filament extruder were $0.85 \times 10^2–1.05 \times 10^3$ $\#/cm^3$, while the 3D printer generated $6.05 \times 10^2–2.09 \times 10^3$ $\#/cm^3$ particle levels. Corresponding particle ERs were $5.3 \times 10^8–6.6 \times 10^9$ and $3.8 \times 10^9–1.3 \times 10^{10}$ #/min. $PM_{2.5}$ and PM_{10} particles were produced in the following average quantities; $PM_{2.5}$ levels ranged between 0.2–2.2 $\mu g/m^3$, while PM_{10} levels were between 5–20 $\mu g/m^3$ for all materials. The main difference between the pure PLA and BC feedstock emissions was terpenes, present during all BC extrusion processes. BCs are similar emission sources as pure plastics based on our findings, and a filament extruder produces contaminants at comparable or slightly lower levels in comparison to 3D printers.

KEYWORDS

3D printing; emissions; particulate matter; terpenes

Introduction

The additive manufacturing (AM) industry is an expanding consumer of energy and plastics which contribute to some of the most important environmental issues of recent times. Sustainable polymers derived from renewable sources and polymer composites reinforced with natural fibers referred to as biocomposites (BCs) gain popularity as environmentally friendly alternatives for petroleum-based pure polymers. The advantages of BCs include lightweight, reduced production costs, environmental friendliness, improved dimensional stability and stiffness (Ford and Despeisse 2016; Peng et al. 2018; Calí et al. 2020; Calvino et al. 2020), and even increased processability without affecting processing parameters (Mazzanti et al. 2019; Vaidya et al. 2019). The AM industry can play a role in energy conservation through a shortened supply chain as localized production and the use of sustainable feedstocks become increasingly commonplace. One way to support sustainability is the

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wider use of BCs which reduces the demand for unsustainable polymers (Ford and Despeisse 2016; Peng et al. 2018; Calí et al. 2020; Calvino et al. 2020).

Commercially available three-dimensional (3D) printer filament extruders have been introduced to consumer markets over the past few years. These extruders can produce custom 3D printer feedstocks from thermoplastic polymers, and additives or fillers, e.g., wood particles, if desired, but they are another source for polymer thermal degradation products. The emissions from such machines have been documented only once so far by Byrley et al. (2020). Their findings indicate the emissions are similar in composition when compared to those produced by material extrusion (ME) 3D printers, but this was not confirmed by using the produced filaments in a 3D printer. Principally, a thermal extruder can produce a wide range of emissions, mainly chemical species including volatile organic compounds (VOCs), ultrafine particles (UFPs), and to a smaller extent, fine ($PM_{2.5}$) and coarse (PM_{10}) particles (Kim et al. 2015a, Azimi et al. 2016; Stabile et al. 2017; Steinle 2016; Yi et al. 2016; Floyd et al. 2017; Kwon et al. 2017; Mendes et al. 2017; Rao et al. 2017; Stefaniak et al. 2017, 2021; Vance et al. 2017; Byrley et al. 2019, 2020; Du Preez et al. 2018; Davis et al. 2019; Väisänen et al. 2019, 2021a; Jeon et al. 2020). These emissions can induce adverse health impacts in humans after exposure, including respiratory symptoms, depression of the central nervous system, irritation, inflammation or sensitization, and they may exacerbate preexisting health conditions, e.g., asthma (WHO 1995, 2006; Van Kampen et al. 2000; Pope and Dockery 2006; Wolkoff et al. 2006; Mossman et al. 2007; Sarigiannis et al. 2011; Weschler 2011; Shahnaz et al. 2012; Klaasen et al. 2013; Rohr 2013; House et al. 2017; Chan et al. 2018).

Additionally, wooden products and BCs have been documented to emit distinctive chemicals that include various terpenes (Roffael 2006; Kim et al. 2006; Höllbacher et al. 2015; Pohleven et al. 2019). BCs can therefore produce altered emissions in comparison to pure plastics when used as filament extruder or 3D printer feedstocks. To be noted, a wide range of VOCs and certain terpenes are classified as irritants or sensitizers (Kasanen et al. 1999; Van Kampen et al. 2000; Kim et al. 2013; Wolkoff et al. 2006; Mossman et al. 2007; Shahnaz et al. 2012; WHO 2021), while terpenes are identified as precursors for secondary reactive chemical species and UFPs in the air phase in the presence of ozone. (Sarwar et al. 2004; Rohr 2013; Kim et al. 2015b; Wolkoff 2020). Indoor terpenes can potentially impair indoor air quality further on this basis. However, terpenes have widely been applied in consumer products, e.g., fragrances for decades without widespread adverse impacts while being present in both indoor and outdoor environments throughout history (Sarwar et al. 2004; Roffael 2006; Wolkoff 2020), and thus their contribution to indoor air quality must be evaluated carefully. In contrast, volatile terpenes are also associated with various health benefits, e.g., anti-inflammatory potential, further challenging their perception as mere pollutants (Kim et al. 2020).

The evaluation of safe use of alternative, sustainable materials is needed to justify the encouraging shift toward BCs. Therefore, multiple relevant indoor exposure agent parameters are sampled or monitored in this study while (poly)lactic acid (PLA) based BC filaments, and a reference PLA filament are produced with a commercial filament extruder and used as an ME 3D printer feedstock. The main aims of this study are to (1) discover how the introduction of wood (and cellulose) content affects the emission composition of 3D printer feedstocks, (2) to estimate how hazardous the produced emissions are in comparison to a pure plastic, (3) to establish if terpenes or other wood-related compounds are commonly produced during thermal processing of BCs, and (4) to document how the emissions from a filament extruder compare to a 3D printer when equivalent feedstocks are used in both machines. VOCs and particles originated from BC processing, and especially their small-scale production has not previously been investigated thoroughly from a safety perspective and the impacts of the introduction of bio-content on emission compositions are not previously discussed in the AM field. Although BC filaments have occasionally been used in ME printer emission studies as a subsidiary material (Azimi et al. 2016; Stabile et al. 2017; Kwon et al. 2017; Vance et al. 2017; Väisänen et al. 2019; Jeon et al. 2020), they have not been a central material of interest and the postulated terpene emissions have not been previously targeted. This study aims to fill in the remaining data gaps.

Materials and methods

Feedstock production and 3D printing

Wood powder used for custom BC filament production was prepared by grinding dried, mixed sawdust (including ca. 40% birch, 40% spruce, and 20% aspen) with an A10 analytical grinder (IKA-Werke GmbH & Co. KG., Staufen, Germany). The powder was sifted with a 250 µm mesh sieve and the larger particles were disposed of. Transparent PLA granules (3devo B. V., Utrecht, The Netherlands) and the wood powders were mixed and heated in a portable oven at 180 °C

Table 1. Material compositions and filament extruder zone temperatures.

Material	Composition	Temperature settings (°C)
Transparent PLA	100 w-% PLA	180/185/190/180
Formi 20	20 w-% cellulose fibers, 80 w-% PLA	180/185/180/170
Formi 40	40 w-% cellulose fibers, 60 w-% PLA	180/185/180/170
BC 15%	15 w-% wood powder, 85 w-% PLA	195/185/185/185
BC 30%	30 w-% wood powder, 70 w-% PLA	200/195/185/185

w-% = percentage in weight.
BC = custom biocomposite.

for 10 min. Two BC batches were produced, one with 15 and the other with 30 percentage in weight (w-%) wood content. For comparison, commercial BC filaments often contain 15–40 w-% wood or cellulose content. The composite mixes were cut into smaller pieces and shredded with a SHR3D IT plastic shredder (3devo B.V., The Netherlands). A total of five different 3D printable filaments with target thicknesses of 1.75 mm were extruded with a Filament Composer 450 extruder (3devo B.V.) using the BC shreds, the aforementioned PLA granules, and commercially available PLA-based Formi 20 and Formi 40 BC granules (UPM-Kymmene Corp., Helsinki, Finland) containing 20 and 40 w-% cellulose fibers, respectively. The filament extruder consisted of four temperature-adjustable heating zones, a feeder screw, an extruder nozzle, and filament puller and roller systems. The filament extruder heating zone temperatures and the compositions of all feedstocks used in this study are presented in Table 1.

The filament extruder was purged by extruding 250 mL of the transparent PLA granules between each feedstock material. Two-hundred-fifty (250) mL of the feedstock was also initially rejected from the spooling process to prevent filament contamination. Filament production lasted for 100–110 min. The filaments were used in an open Ender-3 ME 3D printer (ShenZhen Creality 3D Technology Co. Ltd, Shenzhen, China) to produce sets of eight $4 \times 4 \times 1$ cm plates over 110–120 min. The same printer specifications were used throughout the experiment; 200°C nozzle and 50°C bed temperatures, 0.2 mm layer thickness, 0/90° raster angle, and 1 mm path width as the printer was equipped with a 1 mm diameter nozzle to prevent fiber blockages. No adhesion enhancers were used on the build plate.

Emission and exposure agent measurements

The exposure and emission measurements were performed in a mechanically ventilated office room with floor area of 38.5 m^2, room height of 2.7 m, a total volume of 104 m^3, and a calculated ventilation rate of 3.6 air exchanges per hour (ACH) resolved by measuring air velocity from nine points at the exhaust vent interface after the measurement campaign using a 3000 md micromanometer (Swema AB, Farsta, Sweden). The ACH was calculated using the following equation:

$$ACH = \frac{CFM \times 60}{A \times h}$$

where *CFM* is the volumetric air flow per minute (m^3/min) calculated using the micromanometer readings and the area of the exhaust vent, while *A* and *h* represent the room dimensions (area and height). Air mixing factors or other contributors to the exhaust rate or infiltration were not identified.

A process operator was always present in the room, while a person responsible for the measurements visited the room twice an hour. Sampling was performed at a stationary point; the altitude of the breathing zone (height of 1.5 m) and one-meter distance from the emission sources. Background samples which were used to correct the results were also collected from this point. The room was ventilated between each set of collected samples and the absence of contaminants was verified by UFP concentration reduction down to background level, followed with ventilation for an additional hour. The ANSI/CAN/UL 2904 standard for 3D printer emission sampling was not followed in this study as the collected data sets were intended to represent real-life exposure circumstances, and because the filament extruder could not confidently be operated in a closed chamber.

VOC exposures were also sampled personally. Three parallel samples were collected from both the stationary point and the breathing zone of the process operator. The process operator ensured no errors were occurring during the extrusion processes while performing other tasks in the room which did not produce airborne contaminants. Sample collection time of 45 min was used to ensure the collection of sufficient amounts of compounds with Tenax TA adsorption tubes and SKC 222 pumps (SKC Inc., Eighty-Four, PA) using a calibrated flow rate of 150 mL/min. Background VOC samples were collected like the actual VOC samples, but before the initiation of thermal processes. The samples were analyzed and the mass concentrations (C_m) of individual compounds were calculated according to the ISO 16000-6:2011 standard using a gas chromatography-mass spectrometry system consisting of a TD100 thermal desorber (Markes International Inc., Sacramento, CA), 7890 A gas chromatograph equipped with an HP-5ms

UI column with 60 m length, 0.25 mm internal diameter and 0.25 μm film thickness, and 5975 C mass spectrometer (all manufactured by Agilent Technologies Inc., Santa Clara, CA) operating on scanning mode. The MSD ChemStation software (version F.01.00.1903, Agilent Technologies Inc.) paired with NIST20 database (National Institute of Standards and Technology, Gaithersburg, MD) was used for VOC identification based on compound retention times and ion fingerprints. Concentrations of individual compounds were calculated as toluene equivalents with the assistance of four-point toluene standard curves constructed with standard HC 48-component 40353-U VOC samples (Supelco Inc., Bellefonte, PA). A limitation of the toluene equivalent method is that the sensitivity of the mass spectrometer may be different for the individual chemical species which can lead to result distortion. The VOCs present in at least two of the three parallel samples were included in the results and their presented concentrations are background-corrected. For further details, please see our previous study (Väisänen et al. 2019).

Carbonyl compound air concentrations were sampled by collecting Sep-Pak 2,4-dinitrophenylhydrazine (DNPH) Silica cartridge samples (Waters Corp., Milford, MA) over the full duration of the thermal processes at a calibrated flow rate of 2 L/min using an N022.AN.18 pump (KNF Neuberger Inc., Trenton, NJ). The samples were selectively quantified using an LCMS-8040 triple quadrupole mass spectrometer (Shimadzu Corp., Kyoto, Japan) containing a Kinetex reversed phase C18 column with 1.7 µm pore size, 100 mm length, and 3 mm internal diameter (Phenomenex Inc., Torrance, CA). Acetonitrile and water were used as the eluents. The compounds were identified and quantified with the assistance of four-point standard curves constructed by running Carbonyl-DNPH Mix 1 certified reference material samples compromised of 13 common carbonyls (Sigma-Aldrich Corp., Saint Louis, MO) among the collected samples. The LabSolution Insight program (Shimadzu Corp.) was used to for compound identification and corresponding C_m calculations. Any carbonyls not included in the reference material evaded the analysis method. Background carbonyl samples were collected for 360 min when no operations were performed in the room. The presented results are background-corrected. For further details, please see our previous study (Väisänen et al. 2022).

Exposure levels to particulate matter were determined with two continuously operating devices; the number concentrations (C_n) of UFPs were measured with a P-Trak 8525 device (particle size range 20–1000 nm, TSI Inc., Shoreview, MN) and C_m of coarse (PM_{10}) and fine ($PM_{2.5}$) particles were measured with an Optical Particle Sizer (OPS) 3330 instrument (16 channels, particle size range 0.3–10 µm, TSI Inc.). The OPS instrument neglects the impact of UFPs on the particle air mass concentrations because of the smallest observable particle size of 0.3 µm, which likely results in underestimated mass concentrations. Ten-second logging intervals were used in both, and the devices were zero-calibrated before each measurement set. Background concentrations were measured for 30 min before any extrusion processes were initiated, and actual sampling lasted for the full duration of an extrusion process. The presented particle concentrations are background-corrected. This study was performed in duplicate to prevent VOC sampling from being influenced by isopropyl alcohol, the working fluid emitted by the P-Trak device.

Emission rates (ERs) for TVOC and UFPs were calculated using the simplistic equation:

$$S = ((C_{out} - C_{in}) \times Q)/60$$

where S is ER per minute, C_{out} represents the average C_n of UFPs or C_m of TVOC in m^3, C_{in} equals the measured background C_n of UFPs or C_m of TVOC, and Q is the volumetric flow rate (m^3/h) of exhaust air. Using background-corrected values for C_{out}, the equation can be further simplified:

$$S = (C_{avg} \times Q)/60$$

where C_{avg} is the average C_n of UFPs or C_m of TVOC after background-correction. These calculations are rough estimates which neglect particle losses, agglomeration, and other factors which can impact the evolution and decay of C_n of UFPs or C_m of TVOC as well as assumes complete mixing of air and constant rates for UFP and TVOC productions.

Indoor air quality (IAQ) parameters including carbon dioxide (CO_2), temperature, and relative humidity (RH) were monitored with a continuously operating IAQ-Calc 7525 device (TSI Inc.) using a 30-sec logging interval. The main purpose of these measurements was quality control, but the readings were also used to discover the plausible CO_2 emissions from the extrusion processes as the introduced wood content may burn in the extruder nozzles more easily than the base polymer. These parameters are not background-corrected in the results.

Table 2. The average air concentrations of the most common VOCs, cumulative other VOCs and TVOC (μg/m^3), and TVOC emission rates (S_{TVOC}, μg/min).

Description	1-Nonanol	1-Propanol	Acetic acid	Furfural	Lactide	Hexanal	3-Carene	α-Pinene	D-Limonene	Isoprene	p-Cymene	Other	TVOC	S_{TVOC}
Filament production: PLA	3 (3)	2 (0)	3 (2)	0 (0)	22 (16)	0 (2)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	17 (13)	42 (34)	2.6×10^2
Filament production: Formi 20	2 (5)	0 (2)	10 (11)	2 (0)	10 (9)	2 (2)	3 (2)	2 (3)	0 (2)	0 (0)	4 (3)	15 (14)	48 (48)	3.0×10^2
Filament production: Formi 40	3 (3)	2 (3)	5 (5)	3 (6)	13 (13)	0 (3)	6 (3)	5 (5)	3 (5)	3 (2)	4 (2)	11 (18)	56 (62)	3.5×10^2
Filament production: BC 15%	3 (2)	2 (0)	6 (4)	3 (0)	15 (18)	2 (2)	5 (5)	3 (3)	0 (2)	2 (0)	2 (3)	7 (13)	46 (48)	2.9×10^2
Filament production: BC 30%	2 (2)	0 (2)	12 (8)	4 (5)	16 (14)	2 (0)	6 (6)	4 (5)	3 (3)	3 (3)	3 (4)	5 (14)	58 (63)	3.6×10^2
3D printing: PLA	8 (7)	5 (6)	4 (7)	0 (0)	16 (14)	3 (3)	0 (0)	0 (0)	0 (0)	0 (0)	0 (0)	21 (22)	55 (56)	3.4×10^2
3D printing: Formi 20	3 (4)	4 (5)	4 (4)	2 (0)	7 (6)	2 (3)	3 (3)	7 (3)	3 (3)	0 (0)	0 (0)	23 (17)	54 (45)	3.4×10^2
3D printing: Formi 40	3 (4)	4 (4)	5 (4)	0 (2)	9 (7)	3 (3)	2 (2)	4 (2)	6 (6)	2 (2)	2 (2)	13 (4)	50 (41)	3.1×10^2
3D printing: BC 15%	5 (4)	5 (2)	4 (3)	0 (2)	9 (8)	3 (2)	2 (2)	3 (2)	5 (3)	0 (2)	2 (3)	19 (17)	54 (44)	3.4×10^2
3D printing: BC 30%	4 (4)	3 (3)	4 (4)	2 (0)	15 (8)	3 (2)	3 (2)	4 (3)	5 (5)	2 (2)	2 (3)	15 (8)	47 (39)	2.9×10^2

Average concentrations of personal samples shown in parentheses.
All presented values are background-corrected.
S_{TVOC} is calculated using the TVOC values obtained from a stationary point (the values without parentheses).

Results

Production of the custom BC filaments was empirically successful. All the studied materials, including the custom BC shreds were pulled into filaments with ease and 3D printing with the filaments demonstrated no malfunctions, nozzle blockages, or other critical errors and the surface qualities of the 3D printed plates were good.

The indoor air parameters were not markedly affected by the thermal processes. Room temperatures ranged between 21.2–22.8 and 19.8–20.6 °C during filament extrusion and 3D printing processes, respectively. Relative humidity is a plausible confounding factor when chemical emissions are sampled; lower RH levels are associated with diminished emissions (Manoukian et al. 2016), which might have had an impact on the overall VOC levels. Corresponding RH ranges were 17–27% and 27–35%. CO_2 was not found to be produced in noteworthy quantities during the measurements; the highest measured single value was 860 ppm (parts per million) during 3D printing, while a peak filament extrusion concentration was only 660 ppm. Corresponding average CO_2 concentrations ranged at 770–830 and 460–570 ppm during 3D printing and filament extrusion processes. These values exceed the background levels only marginally. Detailed air quality parameter results are presented in Supplementary Table 1.

VOCs and carbonyls

The main VOC results are presented in Table 2 and all the detected compounds are listed in Supplementary Tables 2 and 3. The background concentrations for VOCs and carbonyls are presented in Supplementary Table 4. The same compounds were detected during filament extrusion and 3D printing processes, and the total VOC (TVOC) concentration ranges were 34–63 μg/m^3 during filament extrusion and 41–56 μg/m^3 during 3D printing. Lactide, commonly encountered in thermal processing of PLA, was the most abundantly detected compound (peak concentrations were 24 and 16 μg/m^3 during filament extrusion and 3D printing, respectively), followed by various alcohols, acids, and aldehydes. The following terpenes were found in low concentrations: 3-carene, α-pinene, d-limonene, and p-cymene. Isoprene, the base unit of terpenes, was also detected. Cumulative terpene concentrations, including isoprene, ranged between 9 and 22 μg/m^3, while the peak concentration of any single compound (3-carene and α-pinene) was only 8 μg/m^3. The personal and stationary VOC results are indistinguishable as the operated machines were open and did not have any emission control mechanisms which resulted in free diffusion of the gaseous contaminants in the air. The concentrations of non-terpene VOCs were lower when wood or cellulose was present in the feedstock, but terpenes were

Table 3. The measured carbonyl compound air concentrations (μg/m^3).

Description	Formaldehyde	Acetaldehyde	Acetone	2-Butanone	Hexanal	Other	Total
Filament production: PLA	6	6	25	20	2	1	60
Filament production: Formi 20	7	5	47	16	2	1	78
Filament production: Formi 40	7	3	40	18	1	1	70
Filament production: BC 15%	6	5	42	15	1	2	71
Filament production: BC 30%	8	3	54	24	1	1	91
3D printing: PLA	40	27	83	70	16	17	253
3D printing: Formi 20	37	24	69	73	13	14	230
3D printing: Formi 40	32	20	55	58	12	13	190
3D printing: BC 15%	41	32	67	52	18	19	229
3D printing: BC 30%	36	27	70	53	15	15	216

All presented values are background-corrected and obtained from a stationary point.

Table 4. The measured particle air concentrations and UFP emission rates (SUFP).

	UFP C_n (#/cm^3)					$PM_{2.5}$ C_m (μg/m^3)				PM_{10} C_m (μg/m^3)			
Description	Min	Max	Average	SD	S_{UFP} (#/min)	Min	Max	Average	SD	Min	Max	Average	SD
Filament production: PLA	0.15×10^2	2.30×10^2	0.85×10^2	0.45×10^2	5.3×10^8	0.1	2.8	0.5	0.4	5	85	10	15
Filament production: Formi 20	1.35×10^2	2.00×10^2	1.65×10^2	0.20×10^2	1.0×10^9	0.1	1.0	0.4	0.2	<5	75	10	10
Filament production: Formi 40	0.65×10^2	1.85×10^2	1.30×10^2	0.40×10^2	8.1×10^8	0.1	0.5	0.2	0.1	<5	60	5	10
Filament production: BC 15%	5.60×10^2	7.65×10^2	6.55×10^2	0.50×10^2	4.1×10^9	0.2	0.5	0.3	0.1	<5	60	20	10
Filament production: BC 30%	8.00×10^2	1.25×10^3	1.05×10^3	1.00×10^2	6.6×10^9	0.3	2.1	0.6	0.3	<5	60	10	10
3D printing: PLA	0.20×10^2	1.41×10^3	6.25×10^2	3.30×10^2	3.9×10^9	1.2	2.9	2.0	0.3	<5	10	5	<5
3D printing: Formi 20	0.15×10^2	2.89×10^3	1.20×10^3	8.90×10^2	7.5×10^9	0.1	2.5	1.2	0.6	<5	10	5	<5
3D printing: Formi 40	1.00×10^3	2.78×10^3	1.74×10^3	4.30×10^2	1.1×10^{10}	1.0	2.6	1.7	0.3	<5	20	5	<5
3D printing: BC 15%	0.20×10^2	3.42×10^3	2.09×10^3	8.10×10^2	1.3×10^{10}	1.4	3.1	2.2	0.3	<5	5	5	<5
3D printing: BC 30%	3.50×10^2	7.60×10^2	6.05×10^2	0.75×10^2	3.8×10^9	0.2	3.1	1.4	0.7	<5	10	5	<5

All presented values are background-corrected and obtained from a stationary point.

introduced as new emission products. Hence, the TVOC levels were equal between the different feedstocks, but their VOC profiles were different. Terpenes contributed for 17–39% of TVOC during filament extrusion and 21–36% during 3D printing. The increase in wood content was associated with higher terpene portions of TVOC roughly equivalent for the wood or cellulose content, while no terpenes were encountered during processing of pure PLA. The TVOC ERs ranged between 2.6 and 3.6×10^2 μg/min during filament extrusion, and between 2.9 and 3.4×10^2 μg/min during 3D printing, and no consistent emission differences were found between the pure PLA and BC feedstocks.

The concentrations of carbonyl compounds were notably affected by the higher extrusion temperature of the 3D printer in comparison to the lower processing temperature used during filament production. The measured carbonyl concentrations are presented in Table 3. 2-Butanone, acetaldehyde, acetone, and formaldehyde were the most abundantly encountered carbonyls which together contributed for 84–98% of the cumulative carbonyl concentrations which ranged between 60–91 μg/m^3 during filament extrusion and 190–253 μg/m^3 during 3D printing. Acetone was detected in the highest concentration, at 83 μg/m^3 level during 3D printing of pure PLA. Peak concentrations for 2-butanone, acetaldehyde and formaldehyde were 73, 32, and 41 μg/m^3, respectively, measured while printing different BC feedstocks. Several other carbonyls (acrolein, methacrolein and benzaldehyde) were detected at low (below 5 μg/m^3) concentrations as well. The following carbonyls were detected at below 5 μg/m^3 levels in the background: 2-butanone, acetaldehyde, acetone, acrolein, formaldehyde, hexaldehyde, and propionaldehyde. The used analysis method was selective and only the compounds in the reference material were able to be identified, and other carbonyls evaded the method. However, no distinct phantom peaks representing unidentified compounds were found in the chromatograms.

Particulate matter

The obtained particulate matter concentrations and ERs for UFPs are presented in Table 4, and background particle concentrations are listed in Supplementary Table 5. Filament extrusion and 3D printing processes produced rather constant amounts of particles as no major concentration peaks were recorded and the concentrations fluctuated only mildly. Time series data illustrating the evolution of particle (UFP, $PM_{2.5}$, and PM_{10}) concentrations during thermal processing of pure PLA, Formi 20, and BC 30% are presented in Supplementary Figures 1–3. The top UFP concentrations were 2.30×10^2 and 1.41×10^3 #/cm^3 for pure PLA during filament extrusion and 3D printing, respectively, while the

corresponding peak values were 1.25×10^3 and 3.42×10^3 #/cm^3 for BC feedstocks. Pure PLA was documented to produce slightly lower amounts of UFPs than BCs during filament extrusion but not during 3D printing; the respective average concentrations for PLA were 0.85×10^2 and 6.25×10^2 #/cm^3 (which represent ERs of 5.3×10^8 and 3.9×10^9 #/min). The corresponding C_n ranges were 1.30×10^2–1.05×10^3 and 6.05×10^2–2.09×10^3 #/cm^3 for BC materials, which represent ER ranges of 8.1×10^8–6.6×10^9 during filament extrusion and 3.8×10^9–1.3×10^{10} during 3D printing. Overall, only moderate UFP concentration or ER differences are observable between the commercial and custom feedstocks, and the 3D printer produced principally more UFPs than the filament extruder.

$PM_{2.5}$ and PM_{10} particles were also produced during the extrusion processes. $PM_{2.5}$ particles were documented at the average C_m range of 0.2–0.6 µg/m^3 during filament extrusion, and between 1.2–2.2 µg/m^3 during 3D printing. C_m peaks for the respective processes were 2.8 and 3.1 µg/m^3 and no coherent differences were identified between the feedstocks. The highest C_m of PM_{10} particles (85 µg/m^3) was detected during pure PLA filament extrusion, while the top C_m measured during the production of BC filaments was 75 µg/m^3 (Formi 20). Mild concentration fluctuations were observed, but not in a consistent manner. The highest average filament extrusion PM_{10} C_m was 20 µg/m^3, measured during BC 15% processing. 3D printing produced lower amounts of PM_{10} particles, and the highest peak value was only 20 µg/m^3 recorded using Formi 40 feedstock. Otherwise, the average PM_{10} concentrations ranged between 5–10 µg/m^3 during both filament extrusion and 3D printing processes.

Discussion

The production of functional custom 3D printable filaments using only raw materials and commercial level machines was achieved in this study. An open 3D printer and a filament extruder produced particulate matter and chemical compounds at fair concentration levels when the machines were operated at reasonable temperatures in a medium-sized and adequately ventilated office space. The measured contaminant concentrations and calculated ERs were generally at anticipated levels based on the existing literature.

The measured CO_2 values were far from air quality compromising levels despite the occasional exceeding of the background concentrations by a few hundred ppm (FMSAH 2015, 2020). The elevated concentrations can be explained with the presence of the 3D printer and measurement personnel. The feedstocks were not noticed to burn in the extruder nozzles during the experiment, which is a relatively common malfunction in ME 3D printing. This is supported by the measured moderate UFP levels which are known to increase drastically in such situations and thus, the extrusion processes as the sources for CO_2 are unlikely. The other air quality parameters remained constant and therefore the operated machines had a negligible influence on them. The recorded low RH levels may have diminished the total production of VOCs. Regardless, internal VOC results comparison is unperturbed by the RH levels owing to their consistency.

VOCs and carbonyls

The VOC concentrations measured during the filament extruder and 3D printer operations were very analogous. Lactide was the most abundant compound detected throughout the experiment and a common thermal degradation product of PLA. It does not have an official occupational exposure limit (OEL) value. Evidence for its toxicity was found only after 2 weeks of daily high (≥1,000 mg/kg body weight) oral dosing in an animal study (Hébert et al. 1999), while no human toxicity data was found by the authors. Thus, the measured exposure levels are not expected to be hazardous for humans, despite the concentration being calculated as a toluene equivalent. Majority of the other VOCs found at the highest concentrations (acetic acid and various aldehydes or alcohols) corresponded with existing literature as well (Kim et al. 2015a, Azimi et al. 2016; Steinle 2016; Stefaniak et al. 2017; Davis et al. 2019; Pohleven et al. 2019; Väisänen et al. 2019, 2021a). These compounds are not particularly harmful for human health at the measured concentration levels either, as they do not possess eminent hazardous properties which is reflected by their high OELs (FMSAH 2020), or maximum acceptable workplace concentrations (MAKs, DFG 2021). A limitation of this study is that the presented compound concentrations are calculated as toluene equivalents and the administrative guideline values are derived using the response curves of the individual compounds. Therefore, the concentrations acquired in this study do not perfectly match the true concentrations of the compounds in the air. Examples of these values are 500 mg/m^3 for 8-hr exposure to 1-propanol, and 42 mg/m^3 for acute exposure to hexanal (FMSAH

2020). Like lactide, 1-nonanol has no established OEL, but exposure to the recorded levels (2–8 $\mu g/m^3$) are unlikely to produce adverse health impacts based on the available toxicity data (PubChem 2022). Furfural, a compound originating from heat-treating of wood (Pohleven et al. 2019) was inconsistently detected during BC extrusion processes at up to 6 $\mu g/m^3$ level. It has a lowest health-based concentration of interest (LCI) value of 10 $\mu g/m^3$ in the air because of its hepatotoxic properties (WHO 1995; EC 2020), thus making it the only compound which approached its available official limit value in the current study. Acetic acid is another wood-originated compound, but its measured concentration is likely underestimated because the used VOC sampling method is most accurate for the collection of compounds in 6–16 carbon atom range. Its OEL of 13 mg/m^3 for 8-hr exposure is, however, far higher than the recorded concentration magnitude (FMSAH 2020). The measured TVOC levels correspond rather well with the previously documented concentrations obtained using PLA and BC feedstocks in 3D printers (Kim et al. 2015a; Azimi et al. 2016; Floyd et al. 2017, Mendes et al. 2017, Stefaniak et al. 2017, Du Preez et al. 2018; Väisänen et al. 2019, 2021a). The TVOC levels were also low in comparison to the proposed occupational indoor air guidelines in Finland; 3000 or 250 $\mu g/m^3$ for industrial workplaces, or office and analogous environments, respectively (Tuomi and Vainiotalo 2016). Similarly, TVOC values fell below the Finnish residential space threshold TVOC value of 400 $\mu g/m^3$ and the individual non-health-based compound limit of 50 $\mu g/m^3$ was not exceeded, either (FMSAH 2015). While TVOC is not a health-based parameter, it is an applicable indicator of indoor air quality (Tuomi and Vainiotalo 2016). The indoor air quality of an adequately ventilated medium sized office space is not jeopardized by operation of a single 3D printer or filament extruder using PLA or PLA-based BC feedstocks on this basis. TVOC ERs calculated for PLA and BC feedstocks in previous studies (Azimi et al. 2016; Steinle 2016; Floyd et al. 2017; Stefaniak et al. 2017, 2019; Davis et al. 2019) express remarkable differences. Stefaniak et al. (2017) calculated a TVOC ER of ca. 2 $\mu g/min$ for a closed printer in a chamber, but in a later study Stefaniak et al. (2019) documented up to 4.4×10^4 $\mu g/min$ ER using an open printer in a laboratory with a ventilation rate of 2 ACH. The documented TVOC ERs have been more modest, around 10–50 $\mu g/min$ in chamber studies (Azimi et al. 2016; Steinle 2016; Floyd et al. 2017). The ERs calculated in the current study represent the chamber studies more accurately than those obtained in the laboratory study, suggesting moderate TVOC emissions. The different research methods and environments contribute to the diversity of the results, as for example, a real-time TVOC sensor has been used in multiple studies as opposed to adsorption tube sampling made use of in others, like the current one.

Terpene compounds were found on all occasions when wood or cellulose was present in the feedstock material, even though pure cellulose should not contain terpenes. In contrast, no terpenes were present during processing of pure PLA. Drying sawdust for 3 months likely contributed to the fair obtained terpene levels as a portion of the compounds had time to spontaneously depart the wood matter (Roffael 2006; Höllbacher et al. 2015). Nonetheless, terpenes contributed to ca. 20–40% of the TVOC levels. While not particularly toxic, they may impair indoor air quality as they are precursors for air quality deteriorating secondary chemical reactions and UFP formation in the presence of ozone (Sarwar et al. 2004; Weschler 2011; Rohr 2013; Kim et al. 2015b; Wolkoff 2020). Secondary compounds produced in the chemical interactions in air include reactive species and carbonyls of low molecular weight, e.g., carcinogenic formaldehyde (Weschler 2011; Rohr 2013; Kim et al. 2015b; Wolkoff 2020). However, many terpenes are purposefully used in significant quantities in various consumer products, such as fragrances, and some of their benefits have also been recognized (Kim et al. 2020). The measured air concentrations were low in comparison to their LCI or MAK values (2.5 mg/m^3 for α-pinene, 1.5 mg/m^3 for 3-carene, 28 or 5 mg/m^3 for d-limonene, 1 mg/m^3 for cymene, and 8.5 mg/m^3 for isoprene) and, thus, they are expected to have a minute impact on indoor air quality or little contribution to the induction of adverse health impacts in 3D printer operators (EC 2020; DFG 2021).

3D printing with PLA and PLA-based composite filaments have previously been documented to emit various carbonyls, e.g., acetaldehyde, acetone, and formaldehyde in moderate concentrations (Kim et al. 2015a; Mendes et al. 2017; Stefaniak et al. 2017; Du Preez et al. 2018; Davis et al. 2019; Väisänen et al. 2019). Unexpectedly, the filament extruder and 3D printer produced similar levels of VOCs, but the carbonyl concentrations were substantially higher, ca. two- to four-fold from the 3D printer in comparison to the filament extruder. The obtained levels were not affected by the feedstock material. It should be noted that the filament extruder operates at the lowest

temperature settings that makes feedstock extrusion and spooling plausible, which is lower than the temperatures used in 3D printers. The applied temperature is one factor which contributes to the higher carbonyl levels from the 3D printer in comparison to the filament extruder. Despite existing at moderate levels at highest, all carbonyls fell below their OELs (FMSAH 2020), MAK values (DFG 2021), LCIs (EC 2020), and residential space threshold values given by WHO (2018) and FMSAH (2015). The lowest official (long-term) limit value of 50 μg/m^3 given for formaldehyde in residential spaces in Finland was almost exceeded during 3D printing (FMSAH 2015). The lowest corresponding reference values given for acetaldehyde (300 μg/m^3, EC 2020), acetone (120 or mg/m^3, EC 2020), and 2-butanone (20 mg/m^3, EC 2020) are notably higher than the concentrations obtained in this study. Long-term exposure to formaldehyde and acetaldehyde still cannot be deemed completely innocuous due to their toxic properties (WHO 2006; Sarigiannis et al. 2011; Klaasen et al. 2013). Otherwise, the compounds are not expected to be hazardous for 3D printer personnel at the recorded levels. In addition to being more readily volatilized than VOCs, carbonyls are formed in secondary chemical interactions in the air as described above. It is plausible that these factors contributed to the unexpectedly high carbonyl levels.

Particulate matter

3D printers are identified as significant UFP emitters, but the obtained concentration levels were far below a proposed lightweight UFP exposure reference value of 4×10^4 #/cm^3 given for manufactured nanomaterials (Van Broekhuizen et al. 2012), the only available reference as no authoritative OELs exist. PLA and BC feedstocks have been recorded to emit UFPs with an aerodynamic diameter of 20 nm and above mainly in 5×10^2–5×10^4 #/cm^3 concentration levels when 200–220 °C temperatures are used (Kim et al. 2015a; Yi et al. 2016; Azimi et al. 2016; Floyd et al. 2017; Kwon et al. 2017; Mendes et al. 2017; Vance et al. 2017; Du Preez et al. 2018; Väisänen et al. 2019, 2021a; Byrley et al. 2019; Jeon et al. 2020). These concentration ranges represent calculated ERs of ca. 10^8–10^{11} #/min (Kwon et al. 2017; Vance et al. 2017; Byrley et al. 2019; Jeon et al. 2020). The concentrations documented in the current study are equivalent to the lower end of the documented concentration spectrum, while the calculated UFP ERs also fall within the previously reported ER ranges. The ERs calculated in the current study are, however, very likely underestimated because of the used calculation method. The studied BC feedstocks are, nevertheless, very similar UFP emitters as pure PLA feedstocks based on the results and previous literature. The filament extruder produced slightly lesser amounts of UFPs in comparison to the 3D printer, which is a consistent finding with the carbonyl levels. A filament extruder can be identified as an equivalent or a slightly lesser UFP emitter as a desktop ME 3D printer. In addition to VOCs, a higher 3D printer nozzle temperature is documented to increase UFP emissions by several studies (Yi et al. 2016; Byrley et al. 2019; Jeon et al. 2020; Stefaniak et al. 2021), and the findings of the current study reflect that (except the case of BC 30% which produced the most particles during filament extrusion). The obtained UFP levels were stable, and the absence of concentrations peaks indicates that the extrusion processes were principally undisturbed by the wood or cellulose particles.

To the best knowledge of the authors, $PM_{2.5}$ levels from the operation of ME 3D printers have been only studied once in a chamber, and only using ABS as the feedstock. $PM_{2.5}$ levels were documented to gradually increase from zero to as high as 900 μg/m^3 level in the study by Rao et al. (2017). Higher RH was associated with higher particle levels; the highest concentration was achieved at 80% RH. A concentration level of 600 μg/m^3 was reached at 40% RH. These values are far higher than those found in the current study, but neither the study designs nor used feedstocks are comparable. WHO (2021) has introduced a 24-hr average $PM_{2.5}$ guideline value of 15 μg/m^3 for ambient air, which is a suitable reference for comparison. This limit value was not reached during the current study using the CPC instrument, as the highest observed peak value was only 3.1 μg/m^3, and only up to 2.2 μg/m^3 average $PM_{2.5}$ levels were recorded over full thermal processes. It must be emphasized that the CPC instrument could not detect particles smaller than 0.3 μm in diameter and thus the true $PM_{2.5}$ (and PM_{10}) concentrations in the air are greater than what was detected in the current study, as the UFPs were not included in the recorded mass concentrations. Larger particles are occasionally documented to be emitted by 3D printers at fair to moderate, up to 100 μg/m^3 concentrations, if at all (Kim et al. 2015a; Yi et al. 2016; Väisänen et al. 2019; Mendes et al. 2017; Kwon et al. 2017; Byrley et al. 2019). The PM_{10} concentrations measured in this study correspond with the previously documented levels. No official OELs are established for PM_{10} particles, either, but

they can be substituted by guideline values for ambient air and residential indoor environments. These established health-based values are almost universally set at 50 µg/m^3, while WHO suggests a stricter long-term value of 20 µg/m^3 for residential spaces (EU 2008; FMSAH 2015; WHO 2018, 2021). The PM_{10} guideline of 50 µg/m^3 was temporarily exceeded during filament extrusion processes, but all average concentrations were below it. The closest comparable Finnish OEL is the one for total inhalable organic dust set at 5 mg/m^3 (FMSAH 2021), which is far higher than the measured PM_{10} concentrations. The exposure levels to $PM_{2.5}$ and PM_{10} particles are therefore not a significant concern for a process operator, albeit the machines temporarily produced particles at concentrations that exceeded the established PM_{10} guideline values.

The filament extruder

Similar UFP ERs, but far higher particle concentration levels for PLA feedstocks were documented in a study by Byrley et al. (2020) in comparison to this experiment. The extruder was in a chamber unlike in the current study, which naturally resulted in different particle concentration readings. A pulverized PLA feedstock produced as high UFP concentration peak as 3.5×10^5 #/cm^3, while a granulated PLA feedstock peaked at 2.5×10^4 #/cm^3. No as radical concentration differences and peaks were found in the current study. The ERs reported by Byrley et al. (2020) were 1.7×10^9 and 5.6×10^{10} #/min for the granulated and shredded feedstocks, respectively. In comparison, the calculated ER for PLA was 5.3×10^8 #/min in the current study, while the commercial BC granules produced fairly higher emissions, and the custom BC shreds emitted the most particles (up to 6.6×10^9 #/min), which is a consistent finding with the previous study. Additionally, Byrley et al. (2020) calculated C_m for $PM_{2.5}$ using resolved UFP size distributions and feedstock densities. In this study, C_m of $PM_{2.5}$ was sampled directly with the OPS instrument. The results are not comparable though, as the minimum detection limit of the OPS instrument is 0.3 µm, and thus, the majority of particles went undetected by the device in this experiment. The previously reported $PM_{2.5}$ concentrations were ca. 35 µg/m^3 for granulated PLA, and ca. 125 µg/m^3 for shredded PLA. The highest C_m peak of $PM_{2.5}$ particles during filament extrusion processes was a mere 2.8 µg/m^3 in the current study, while the average concentrations were below 1 µg/m^3 throughout the experiment. Also, no $PM_{2.5}$ C_m differences existed between the studied feedstocks. Similarly, the obtained PM_{10} C_m values were indifferent between the used feedstocks in the current study, with the highest peak value reaching 85 µg/m^3 and the highest average concentration being 20 µg/m^3. The VOCs detected by Byrley et al. (2020) included lactide, benzene derivates, and various acids and alcohols among others. These compounds correspond well with previous 3D printer emission literature and the findings of the current study, which supports the emission similarity assumption between filament extruders and 3D printers using similar feedstocks. Byrley et al. (2020) ultimately identified filament extruders and desktop 3D printers as very similar emission sources, and the findings of the current study support the claim.

Conclusions

It was demonstrated in this study that functional and 3D printable BC feedstocks can be produced from commercially available plastic granules and raw wood fibers without expensive and technically advanced machines. The airborne contaminant compositions, levels, and ERs produced by a filament extruder resemble those from an open ME 3D printer when equivalent feedstocks are used in both. This was the first time this was confirmed. Emission products originated from PLA-based BC feedstocks could not be identified as severely more hazardous than those from a pure PLA feedstock, albeit some differences in chemical compositions existed. Certain compounds that originate from thermal treatment of wood, including terpenes and furfural were the most obvious differences. Terpenes can impair indoor air quality through secondary chemical reactions and UFP formation, but their impact on air quality is not expected to be significant based on the concentration levels obtained in the current study. Furfural may produce toxic effects in prolonged exposure, but it was found inconsistently and only at low concentration levels. PLA-based BC materials can be identified as environmentally friendly feedstocks which express similar hazardous properties in comparison to traditional petroleum-derived polymers based our findings as the addition of bio-content both reduced the portion of plastic-originated emission products and introduced new chemical emission products, while no major impact was observed on the produced particle levels. Nonetheless, emission control measures should be always applied when thermal extruders are operated.

Findings by Byrley et al. (2020) were mostly confirmed in this study. The emissions from a filament extruder resemble those from a 3D printer accurately, for both the composition and magnitude. Filament extruders are often operated at lower temperature settings than 3D printers which contributes to slightly reduced emissions. This was observable in this study on behalf of carbonyls and UFPs. On the other hand, PM_{10} particles were observed at slightly greater concentrations when a filament extruder was operated, while the recorded VOC and $PM_{2.5}$ particle levels were identical between the machines. The contaminant concentration levels were mostly low or moderate based on the previous literature and administrative guidelines, indicating that emissions produced by a single 3D printer or filament extruder are not excessive in a moderately sized, well-ventilated office space. Further suggested research topics include the expansion of the studied feedstocks in a filament extruder, and the examination of the mechanical properties of (customized) BCs feedstocks which could further support the transition toward sustainable 3D printer materials.

Recommendations

Similar emission and exposure control measures can and should be applied on filament extruders as on 3D printers. These measures include the use of machine enclosures, local exhaust systems and lowest functional temperature settings, and spending the least possible time in the same premises with the operated machines to prevent exposure to their emissions. The use of wood-containing BC materials does not require further protective measures than generic feedstocks.

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Conflicts of interest

The authors declare no conflict of competing interest.

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Data availability statement

The authors confirm that the data supporting the findings of this study are available within the article and its supplementary materials and are shared upon request.

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