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Journal of Toxicology and Environmental Health, Part A
Current Issues

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/uteh20

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To cite this article: Antti Väisänen, Lauri Alonen, Sampsa Ylönen & Marko Hyttinen (2021): Organic compound and particle emissions of additive manufacturing with photopolymer resins and chemical outgassing of manufactured resin products, Journal of Toxicology and Environmental Health, Part A, DOI: 10.1080/15287394.2021.1998814

To link to this article: https://doi.org/10.1080/15287394.2021.1998814

JOURNAL OF TOXICOLOGY AND ENVIRONMENTAL HEALTH, PART A
https://doi.org/10.1080/15287394.2021.1998814

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Organic compound and particle emissions of additive manufacturing with photopolymer resins and chemical outgassing of manufactured resin products

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ABSTRACT

Photopolymer resins are applied at an increasing rate in additive manufacturing (AM) industry as vat photopolymerization (VP) and material jetting (MJ) methods gain more popularity. The aim of this study was to measure volatile organic compound (VOC), carbonyl compound, ultrafine particle (UFP), and particulate matter (PM_{10}) air concentrations emitted in 3D printer operations. Individual chemicals were identified when multiple photopolymer resin feedstocks were used in various VP and MJ printers. The size distributions of UFPs, and indoor air parameters were also monitored. Finally, the VOC outgassing of the cured resin materials was determined over 84 days. The data demonstrated that 3D printer operators were exposed to low concentrations of airborne exposure agents as follows: average concentrations of VOCs were between 41 and 87 μg/m^3, UFP number levels ranged between 0.19 and 3.62 × 10^3 number/cm^3; however, no impact was detected on air parameters or PM_{10} concentrations. A majority of the UFPs existed in the 10–45 nm size range. The identified compounds included hazardous species included sensitizing acrylates and carcinogenic formaldehyde. The outgassed products included similar compounds that were encountered during the AM processes, and post-processing solvents. Products heated to 37°C emitted 1.4–2.9-fold more VOCs than at room temperature. Total emissions were reduced by 84–96% after 28 days roughly from 3000–14000 to 100–1000 μg/m^2/hr. In conclusion, resin printer operators are exposed to low concentrations of hazardous emissions, which might result in adverse health outcomes during prolonged exposure. Manufactured resin products are suggested to be stored for 4 weeks after their production to reduce potential consumer VOC hazards.

KEYWORDS

3d printing; chromatography; material jetting; ultrafine particles; vat photopolymerization; volatile organic compounds

Introduction

The popularity of additive manufacturing (AM), usually referred to as three-dimensional (3D) printing, has risen over the past few decades as availability of 3D printers increased (Stefaniak, Du Preez, and Du Plessis 2021; Wohlers et al. 2017). Commercially available and cheap AM machines, often classified as desktop AM machines, were introduced into various indoor environments, including libraries, schools, and homes. It is also of interest that professional scale AM machines are being used ever more frequently and pervasively as the demand for custom and on-demand products increases (Wohlers et al. 2017). Consequently, an increasing number of individuals are exposed to the emissions of AM machines in their lives, both at work and on spare time (Chan et al. 2020; Short et al. 2015; Yi et al. 2016).

Vat photopolymerization (VP) and material jetting (MJ) 3D printers are gaining popularity as these AM technologies evolve, diversify, and become increasingly available for consumers. Wohlers et al. (2017) described the common AM production methods in detail, but in brief, MJ and VP machines use photosensitive resins or inks as their production feedstock material. The feedstock is either deposited on-demand, layer upon layer by an ink jet nozzle and cured with a light source, traditionally with a UV-light rail (MJ method), or a build platform is lowered in a resin tank where a light source, generally a UV-laser, cures the resin layer by layer as the build platform is gradually lifted from the resin vat (VP method). The main advantages of VP and MJ printers include (1) exceptional surface quality, (2) wide range of applicable materials, (3) large build volumes, and

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(4) swiftness of production. However, products manufactured with the VP, and occasionally with the MJ method, demand post-processing which involves removal of support structures and excess resin from the surface of an item before the product is ready to use. The supports are either removed manually or are chemically dissolved. The excess resin is removed from the surfaces of VP manufactured items with a solvent either manually, or by submerging the product in a solvent bath after which the products require surface finishing post-curing with a UV-light.

Different materials may be used concurrently with MJ machines that utilize multiple-ink jet nozzles, and several other AM methods. The simultaneous application of multiple materials is referred to as multi-material AM. Multi-material technologies enhance the diversity and capabilities of manufactured products and designs, as the applied feedstocks might exhibit various colors, different flexibilities or surface qualities, and other properties (Wohlers et al. 2017). Few investigations were apparently conducted on multi-material 3D printers and their emissions and thus, little is known regarding how the application of multiple materials affects the 3D printer emissions. The material extrusion (ME) method has been almost exclusively studied out of all the available AM methods. A scarce amount of emission and occupational safety studies were performed with VP or MJ printers. Thus far it is known that the VP and MJ machines both emit volatile organic compounds (VOCs) and ultrafine particles (UFPs), which are recognized as major occupational exposure agents of concern within the AM industry (Chan et al. 2020; MacCuspie et al. 2021; Petretta et al. 2019; Roth et al. 2019; Ryan and Hubbard 2016; Yi et al. 2016). These emission studies include our preliminary study (Väisänen et al. 2019), and research conducted by Yang and Li 2018; Stefaniak et al. 2019a; 2019b; Zisook et al. 2020; Hayes et al. 2021. The accumulated data are still insufficient for comprehensive safety evaluation of these methods, and more exposure data are needed. In addition, the composition of chemical emissions needs to be determined.

The mechanisms of emission production are fundamentally different between various AM technologies. Yang and Li (2018) noted that VOCs are emitted directly from the resin tank when the VP method is applied following spontaneous surface evaporation and occasional resin tank heating. Additional VOC species are produced during the photocuring processes. UFPs are formed through condensation and agglomeration of VOCs and semi-VOCs, regardless of the applied AM method (Pope and Dockery 2006; Shahnaz, Hayes, and Dechsakulthorn 2012; Yi et al. 2016). VOC emissions are presumed to be produced during the jetting process when MJ method is applied, where the feedstock is deposited with a high pressure onto the build platform, producing airborne VOCs (Hayes et al. 2021; Stefaniak, Bowers, and Knepp 2019b).

Photopolymer resins, which have been applied widely before commercialization of AM, consist of reactive acrylates and/or epoxies, other monomeric and (volatile) organic substances, additives, and photoinitiators (Alifui-Segbaya et al. 2020; Bettencourt, Neves, and De Almeida 2010; Jorge et al. 2003; Lago et al. 2015; Short et al. 2015; Stansbury and Idacavage 2016). The listed substances might exhibit toxic properties and induce adverse health effects following inhalation or dermal exposure. Major health risks of acrylates include cytotoxicity, induction of allergies and respiratory symptoms, including asthma, irritation, sensitization, dermatoses, and teratogenicity (Fukumoto et al. 2013; Savonius et al. 1993; Suojalehto, Suuronen, and Cullinan 2020; Van Kampen, Merget, and Baur 2000; Voller and Warshaw 2020; Walters et al. 2017). VOCs and carbonyls, which are compounds that belong to the very diverse groups of carbon-based chemicals, induce respiratory symptoms, central nervous system (CNS) depression, irritation, sensitization, and inflammatory effects, produce localized organ damage, or display carcinogenic and mutagenic risks, depending upon the individual compound and its properties (World Health Organization (WHO) 2006; Wolkoff et al. 2006; Barro et al. 2009; Mendes et al. 2011; Unwin et al. 2013; T-t et al. 2013; He et al. 2015; Cipolla, Bruzzone, and Stagnaro 2016; Janssens, Van Meerbeeck, and Lamote 2020; Ó, White, and Fraga-Iriso 2020). The effects induced by VOCs need to be evaluated through individual compounds as total VOC (TVOC) concentration is not an applicable measure of exposure based upon differing toxicities

attributed to exposure to various VOC species. However, TVOC may serve as an indoor air quality indicator as proposed by Tuomi and Vainiotalo (2014).

In addition to the exposure to VOCs and acrylates, UFP exposure is a major health concern when AM machines are operated. These particles of submicron scale are classified as nanoparticles with an aerodynamic diameter of ≤100 nm, which can deposit deep in the alveolar region of the lungs, penetrate biological membranes, and translocate to vital organs within the body. UFP exposure is associated with increased cardiovascular and respiratory morbidity and mortality, hypertension, reduced respiratory function, cytotoxicity, localized organ and CNS damage, and irritation or inflammatory symptoms (Leikauf, Kim, and Jang 2020; Ohlwein et al. 2019; Peters, Veronesi, and Calderón-Garcidueñas 2006; Schraufnagel 2020; Shkirkova, Lamorie-Foote, and Connor 2020). Particles can also act as a vehicle for chemicals or be dissolvable, thus increasing the chemical burden of the body (World Health Organization (WHO) 1999; Oberdörster 2001; Pope and Dockery 2006; Mossman et al. 2007; Lee, Kim, and Lee 2014). Larger particles deposit in the upper lung regions where individuals may develop respiratory symptoms including coughing, wheezing, shortness of breath, or produce short-term or chronic inflammation and irritation. Prolonged particle exposure may also induce pervasive lung diseases, such as asthma or chronic obstructive disorder (COPD), exacerbate preexisting respiratory diseases, and even promote cancer (World Health Organization (WHO) 1999; Mossman et al. 2007; Faustini, Stafoggia, and Colais 2013; Lee, Kim, and Lee 2014; De Oliveira et al. 2014; Costa, Ferreira, and Silveira 2014; Almetwally, Bin-Jumah, and Allam 2020).

The consumer safety of 3D-printed products is also yet to be thoroughly investigated (Stefaniak, Du Preez, and Du Plessis 2021). Several investigators noted that items manufactured with an ME printer and UV-cured products continue outgassing volatile substances (Damanhuri, Subki, and Hariri 2019; Du Preez et al. 2018; Lago et al. 2015). The diminished supply chain is a major benefit of AM, but may lead to unexpected risks. As known, building materials emit more gases when they are new and emission rates are reduced over time. 3D-printed products are expected to behave similarly. Thus, a recently 3D-printed product may pose a hazard for a consumer, as uncured volatile resin components depart the polymer matrix. Polymers might also experience blooming where unbound compounds travel to the surface of a product through diffusion, acting as a secondary source of VOCs (Nouman et al. 2017). Blooming might also result in unexpected contact exposure to resin components when present in dental products made of photopolymer resins are worn. A cautionary study performed by Petrofsky et al. (2014) found indicators of plausible kidney damage after allegedly biocompatible acrylate-based prosthetics were worn by patients.

The aim of this study is to (1) gain insights regarding 3D printer operator safety through the investigation and identification of toxicologically relevant 3D printer emission products and their indoor air concentrations when photopolymer resins are used for AM, and (2) determine how simultaneous application of multiple materials affects the emissions of a 3D printer. In addition, this study may serve as a preliminary investigation for 3D-printed product consumer safety assessment through measurements involving outgassed substances and TVOC emission rates, with assessment of a plausible safety period following the manufacturing of a product.

Materials and methods

Volatile organic compounds (VOCs), carbonyls, and UFPs were identified as the main emission products formed during AM with VP and MJ methods in our preliminary study, while no larger particles were produced in substantial quantities (Väisänen et al. 2019). These findings are supported by Ryan and Hubbard (2016), Yang and Li (2018), Stefaniak, Johnson, and Du Preez (2019a; 2021), Zisook, Simmons, and Vater (2020), and Hayes et al. (2021). Consequently, VOCs, carbonyls, and UFPs were selected as the main exposure agents of interest in this study. In addition, airborne particles and indoor air parameters including carbon dioxide (CO_2), temperature (T), and relative humidity (rH) were monitored.

The occupational exposure agent measurements were performed over the course of 4 days. For clarity, the 3D printers and feedstocks were divided into three categories: traditional and dental VP, and MJ, even though the two VP methods are fundamentally not different in their functioning principles. Two traditional VP printers (model Form 2 by Formlabs Inc., Somerville, MA, and model NXE400 by Nexa3D Inc., Ventura, CA) were sampled on 1 day, an MJ printer (model J735 by Stratasys Ltd., Eden Prairie, MN) on 1 day, and two dental VP printers (model PrograPrint PR5 by Ivoclar Vivadent Inc., Schaan, Liechtenstein, and model Varseo by Bego GmbH & Co., KG, Bremen, Germany) were examined over 2 days. The emissions were sampled at two locations: (1) traditional VP and MJ machine emissions were measured at the 3D printing lab of Savonia University of Applied Sciences and (2) dental VP machine emissions were measured at a commercial dental lab. Both locations were in Kuopio, Finland. Detailed 3D printing specifications and sampling location information are presented in Table 1. Miscellaneous products and a 3 × 3 × 3 cm cube with a surface area of 54 cm^2 were produced during each 3D print job. These cubes were used for material outgassing measurements as described later.

Exposure agent samples were collected from the height of the breathing zone (approximately 1.5 m) roughly from a 1-m distance from the 3D printers. In addition, chemical and particle samples were collected from the in-built ventilation duct of the Stratasys 3D printer, the only machine in this study with an emission elimination system. Background samples were collected before the 3D print jobs started, and background concentrations of chemicals and particles subtracted from the presented results. The used measurement apparatuses and devices were factory and/or zero calibrated before the sampling campaign began, and the measurement spaces were thoroughly ventilated before each 3D print job. Multiple measurements were performed daily, and the absence of the contaminants was ensured by allowing room UFP number concentration to reduce to background levels and ventilating the space for an additional hr. The background concentrations were measured by imitating an actual sample collection, but without active 3D printing.

Gaseous organic substances were measured using two methods. VOCs were sampled with Tenax® TA adsorption tubes (Markes Inc., Sacramento, CA) containing 200 mg sorbent, and AirChek 3000 pumps (SKC Inc., Eighty-four, PA) calibrated with a mini-BUCK Calibrator (A. P. BUCK Inc., Orlando, FL). The sampling lasted for 30 min at a calibrated flow rate of 0.2 L/min, commencing 30 min after a 3D print job initiation. This sampling design was adopted to ensure gaseous emissions are present in the air and adequate amounts of VOCs collected. Three parallel VOC samples were collected in all cases, and an additional three samples were collected from the ventilation duct of the Stratasys printer. The collected samples were analyzed according to the ISO 16000–6:2021 standard (International Organization for Standardization 2021) with a TD100 thermal desorber (Markes Inc.), 7890A gas chromatography system with an HP-5 ms UI column (60 m length, 0.25 mm internal diameter and 0.25 µm film thickness, Agilent Technologies Inc., Santa Clara, CA) and 5975 C mass spectrometer running on SCAN mode (Agilent Technologies Inc.). The individual compounds were identified by retention times and MS-library (NIST02, National Institute of Standards and Technology, Gaithersburg, MD, USA) identification with an MSD ChemStation software (version F.01.00.1903, Agilent Technologies Inc.). The compound concentrations were calculated as toluene equivalents and 4-point standard curves were constructed by running HC 48 component 40,353-U standard solution (Supelco Inc., Bellefonte, PA) samples along with each set of collected samples.

Carbonyls were sampled over the duration of complete 3D print jobs with Sep-Pak DNPH-Silica cartridges (Waters Corp., Milford, MA) containing 350 mg sorbent and an N022.AN.18 pump (KNF Neuberger Inc., Trenton, NJ). The air collection rate of 1.5 L/min was calibrated with the mini-BUCK Calibrator. A single sample was collected during each 3D print job, except for the Stratasys printer where a second sample was collected from the ventilation duct. The 2,4-dinitrophenylhydrazine (DNPH) derivates of the compounds were analyzed with a liquid chromatography-mass spectrometer system that consisted of a Nexera X2 LC-30AD pump, Nexera X2 SIL-30AC autosampler,

Table 1. 3D printer, feedstock, and measurement location specifications.

3D printer (AM method)	Feedstock	3D print duration (minutes)	Max build dimensions (mm)	Layer thickness (µm)	Post-processing device(s)	Post-processing method	Location and room volume	Ventilation and air exhanges per hour (ACH 1/h)
Formlabs: Form 2 (traditional VP)	Formlabs: Clear resin	145	145x145x175	50	Formlabs: Form Wash, Form Cure	Submersion in isopropanol for 10 min, followed with UV-curing at 60°C for 15 min	3D printing lab, 52 m^3	Mechanical: HEPA-filtered inlet, outlet assisted by fume hood; ACH 7/h
	Formlabs: Castable Wax resin	280				Submersion in isopropanol for 10 min, drying at room temperature for 60 min		
Nexa3D: NXE400 (traditional VP)	Nexa3D: xGPP-Translucent resin	55	280x165x400			Submersion in isopropanol for 10 min, followed with UV-curing at 35°C for 45 min		
Stratasys: J735 (MJ)	Stratasys: VeroCyan-V, VeroMagenta-V, VeroYellow-V, VeroPureWhite, and VeroClear ink-like resins	115	350x350x200	27	-	Rinsing with water, brushing	3D printing lab, 36 m^3	Mechanical: HEPA-filtered inlet, outlet assisted by local 3D printer exhaust; ACH 7/h
	VeroBlackPlus ink-like resin	130						
Ivoclar Vivadent: PrograPrint PR5 (dental VP)	Ivoclar Vivadent: ProArt Print Model resin	170	Area 125x78, height not reported	50	Ivoclar Vivadent: PrograPrint Cure	Submersion in isopropanol for 10 min, followed with UV-curing at room temperature for approx. 5 minutes	Dental lab, 70 m^3	Mechanical: HEPA-filtered inlet, outlet assisted by a nearby fume hood, and an air purifier; ACH unknown
	Ivoclar Vivadent: ProArt Print Splint resin	140						
Bego: Varseo (dental VP)	Bego: VarseoWax Model resin	135	96x54x85	50	Generic ultrasonic bath, Bego: Octoflash	Submersion in ethanol ultrasonic bath for 15 minutes, followed with UV-curing under nitrogen atmosphere at room temperature for approx. 7 minutes		
	Bego: VarseoWax Tray resin	155		100				

DGU-20A5R degassing unit, CTO-20AC column oven, LCMS-8040 triple quadrupole mass spectrometer (all manufactured by Shimadzu Corp., Kyoto, Japan), and Kinetex® reversed phase C18 column with 1.7 µm pore size, 100 mm length, and 3 mm internal diameter (Phenomenex Inc., Torrance, CA). Water and acetonitrile (ACN) were used as eluents; the initial portion of ACN was 30%, which steadily increased to 90% over 20 min, then reducing back to 30% over 1 min. The duration of a single run was 25 min. The collected compounds were selectively quantified with assistance of 4-point standard curves constructed with Carbonyl-DNPH Mix 1 certified reference material samples (Sigma-Aldrich Corp., Saint Louis, MO) containing DNPH derivates of 2-butanone, acetaldehyde, acetone, acrolein, benzaldehyde, butyraldehyde, crotonaldehyde, formaldehyde, hexaldehyde, methacrolein, propionaldehyde, tolualdehyde, and valeraldehyde. The individual compounds were identified by their retention times and produced ions. A LabSolution Insight software (Shimadzu Corp.) was employed for compound identification and quantification.

Airborne particulate matter (PM) concentrations were monitored with multiple continuously running instruments over the course of the complete 3D print jobs. The mass concentrations of airborne particles (particle size range 0.3–10 µm, hereafter referred to as PM_{10}) were monitored with an Optical Particle Sizer 3330 (hereafter referred to as OPS; TSI Inc.). The UFP number concentrations were monitored with two instruments; the total UFP number concentrations (particle size range 7–3000 nm) were monitored with a Condensation Particle Counter 3022A (hereafter referred to as CPC; TSI Inc.), while the size distributions of the UFPs (particle size range 5.6–560 nm, 16 standard size channels) were monitored with a Fast Mobility Particle Sizer 3091 (hereafter referred to as FMPS; TSI Inc.). A 10s logging interval was applied in all the listed devices. The indoor air quality parameters were monitored over the course of the measurements with an IAQ-Calc 7545 device (TSI Inc.) applying a 30s logging interval. Contrary to all other measurements, these indoor parameter results are not background-corrected, as the IAQ-Calc readings were mostly used for quality control.

Material outgassing measurements were performed by placing the 3D-printed cubes inside a Micro-Chamber/Thermal Extractor M-CTE250 apparatus (chamber volume of 114 mL, Markes Inc.) from which Tenax® TA samples were collected. Nitrogen carrier gas was applied at a calibrated flow rate of 75 mL/min. Two consecutive samples were collected, at 20°C and 37°C, of which the first represents normal room condition, while the latter simulates human body temperature. The 3D-printed cubes, placed on tinfoil plates, were purged at 20°C for 5 min before collection of the first sample. The temperature was then increased to and upheld at 37°C for 5 min prior to collection of the second sample. The sample collection lasted initially for 5 min (samples collected on days 1, 7 and 14). The duration was first rose to 10 min (samples collected on days 28 and 56), and ultimately up to 15 min (samples collected on day 84), to ensure the collection of a sufficient quantity of VOCs. Day 1 of sample collection stands for samples collected at 24 hr post-production. Control tinfoil plate VOC samples were collected concurrently during each set of samples, and the detected emission products were subtracted from the presented results. The samples were analyzed, identified, and calculated as described above in the VOC sampling section. The cubes were stored in a condition equilibrated room in an open glass container on tinfoil plates under an average temperature of 21.2°C and mean humidity of 30%.

Results

The results are presented as per applied feedstock material. Data regarding the multi-material 3D printing with multiple Stratasys ink resins is referred to as "Multi." Further, and the Stratasys printer findings are presented based upon sampling source, where applicable.

3D printer emissions

The measurements were collected during winter, under particularly cold and dry weather. The indoor air parameter results are provided in Table 2; indoor rH readings were consistently low, ranging from 1% to 11.6%. The measured air

temperatures were stable, except for the room in which the traditional VP printers resided, where the temperature steadily rose over time. Further, CO_2 concentrations were not significantly affected by the 3D printing processes, as the largest variance in CO_2 concentration was only 130 ppm during 3D printing with Stratasys machine. It is worth mentioning that several investigators reported that indoor air conditions influence VOC emission rates (Manoukian et al. 2015; Markowicz and Larsson 2015; Wolkoff 1998). Low rH has been associated with reduced indoor VOC emissions, which needs to be considered when chemical emission results are discussed later.

The average concentrations of the three most common VOCs per feedstock material and the measured TVOC levels are presented in Table 3 with ranges shown in parentheses. The measured TVOC concentrations were low, considering the Finnish occupational TVOC guideline value of 3000 μg/m^3, or even the 250 μg/m^3 office space guideline value as suggested by Tuomi and Vainiotalo (2014). No noteworthy differences were detected in the mean room TVOC concentrations, which ranged from 41 to 87 μg/m^3. However, the MJ printer produced markedly more emissions, as the TVOC levels measured from the ventilation duct were up to 40-fold higher than room concentrations, while the MJ room quantities corresponded with other locations. The most abundantly detected compounds were diverse. Little similarities existed among the different 3D printers, but differing feedstocks applied in the same 3D printer did produce similar emission products, except for the Form 2 printer. The compound concentrations were not significantly high, excluding those measured from the MJ printer's ventilation duct. As presented, acrylates and reactive VOC species were commonly encountered during 3D printer operations. Isobornyl acrylate, found predominantly during MJ printer operations, was detected at the highest average level of 38 μg/m^{3,} followed by methyl isobutyl ketone with a mean concentration of 24 μg/m^3, detected during dental VP printer operations. Several additional hazardous compounds were found at low levels, including other acrylates, ketones, and cyclic hydrocarbons. The full emission profiles and background VOCs are presented in Supplementary Tables 1–4.

Most of the selectively quantified carbonyls were detected at low concentrations, as noted in Table 4. Acetone, 2-butanone, acetaldehyde, and formaldehyde were found at in the highest levels; 2–37 μg/m^3, <1–35 μg/m^3, <1–14 μg/m^3, and <1–12 μg/m^3, respectively. The traditional VP and MJ printers emitted lower amounts of carbonyls (9–43 μg/m^3) than the dental VP printers (52–98 μg/m^3). Of these compounds, formaldehyde and acetaldehyde are of the highest concern due to their carcinogenic

Table 2. Background and 3D printing of indoor air parameter readings.

Parameter	Background (traditional VP)	Clear	Castable Wax	xGPP-Translucent	Background (MJ)	Multi	VeroBlackPlus	Background (dental VP)	ProArt Print Model	ProArt Print Splint	VarseoWax Model	VarseoWax Tray
CO_2 average (ppm)	500	440	455	450	500	525	460	570	555	550	595	535
CO_2 min (ppm)	480	425	430	430	440	490	420	530	520	525	575	525
CO_2 max (ppm)	515	515	480	500	535	580	550	610	600	580	630	555
CO_2 SD	11	24	21	20	26	27	42	23	27	26	25	18
T average (°C)	18.2	18.7	21.1	22.0	21.2	21.3	21.6	20.8	21.7	20.7	21.2	20.7
T min (°C)	17.8	18.6	20.7	21.7	20.7	20.7	21.4	20.5	21.6	20.6	21	20.6
T max (°C)	18.5	18.9	21.5	22.1	21.4	21.8	21.8	20.9	21.9	20.9	21.4	20.9
T SD	0.2	0.1	0.2	0.2	0.2	0.3	0.1	0.1	0.1	0.1	0.1	0.1
rH average (%)	5.7	3.3	3.1	1.8	1.7	1.3	1.8	10.1	11.1	10.1	12	7.4
rH min (%)	4.4	2.9	2.8	1.2	1	0.7	1.4	9.7	10.6	9.6	11.4	7.1
rH max (%)	7	4.9	3.7	2.6	2.6	1.9	3	10.9	11.6	10.6	13.5	7.6
rH SD (%)	0.8	0.5	0.3	0.5	0.4	0.4	0.5	0.4	0.3	0.3	0.6	0.2

Table 3. Three most common VOCs and the TVOC emission measured during 3D printing of each resin (μg/m^3).

Compound	Clear	Castable Wax	xGPP-Translucent	Multi, room	Multi, air duct	VeroBlackPlus, room	VeroBlackPlus, air duct	ProArt Print Model	ProArt Print Splint	VarseoWax Model	VarseoWax Tray
1,3-Dioxolane	-		-	-	-	-	-	-	-	-	7 (2–10)
2-Ethoxypropane	-		-	-	-	-	-	-	8 (6–10)	-	
2-Ethylpiperazine	-	4 (4–5)	-	-	-	-	-	-	-	-	-
2-Hydroxypropyl methacrylate	6 (2–8)	-	-	-	-	-	-	-	-	-	-
4-Acryloylmorpholine	-	-	-	-	-	-	205 (178–231)	-	-	-	-
Alpha-pinene	-	6 (5–7)	8 (7–8)	-	-	-	-	-	-	-	-
Benzoic acid	-	-	5 (5)	-	-	7 (6–8)	-	-	-	-	-
Ethyl methacrylate	4 (4–5)	-	-	-	-	-	-	-	-	-	-
Isobornyl acrylate	-	-	-	38 (33–41)	2017 (1858–2157)	17 (16–18)	1582 (1371–1772)	-	-	-	-
Isopropyl alcohol	-	-	-	4 (4)	94 (75–113)	-	-	15 (11–19)	22 (19–26)	18 (16–20)	15 (13–19)
Methacrylic acid	-	-	5 (4–6)	-	-	-	-	-	-	-	-
Methyl isobutyl ketone	-	-	-	-	-	-	-	24 (24–25)	15 (13–17)	7 (6–8)	
Methyl methacrylate	6 (5–7)	-	-	5 (4–5)		-	-	-	-	-	-
Nonanal	-	13 (11–14)	-	-	-	-	-	-	-	-	-
Propylene glycol	-	-	-	-	334 (325–344)	11 (10–11)	316 (306–325)	-	-	-	-
tert-Butyl alcohol	-	-	-	-	-	-	-	12 (11–13)		12 (11–15)	17 (13–23)
TVOC	41 (32–48)	46 (43–51)	45 (43–47)	70 (67–72)	2967 (2725–3209)	70 (63–77)	2207 (2041–2372)	75 (66–86)	66 (64–68)	55 (50–64)	87 (81–99)

Average concentrations of three parallel samples are shown above, concentration ranges are shown below in the parentheses.

Table 4. Carbonyl concentration emission during 3D printing of each resin (μg/m^3).

Compound	Clear	Castable Wax	xGPP-Translucent	Multi, room	Multi, air duct	VeroBlackPlus, room	VeroBlackPlus, air duct	ProArt Print Model	ProArt Print Splint	VarseoWax Model	VarseoWax Tray
2-Butanone	6	<1	10	1	4	<1	3	11	7	35	15
Acetaldehyde	2	1	<1	3	7	2	7	11	3	14	4
Acetone	3	2	12	14	22	2	8	37	28	25	26
Benzaldehyde	<1	<1	<1	5	8	<1	2	1	<1	1	1
Butyraldehyde	4	3	3	3	6	3	7	4	3	3	2
Formaldehyde	1	1	<1	12	20	11	17	11	8	12	4
Hexaldehyde	4	1	2	4	7	4	9	5	3	5	1
Propionaldehyde	1	1	1	1	3	1	4	2	1	3	1
Total	21	10	29	43	77	24	57	82	53	98	54

potential. The background carbonyl concentrations are provided in Supplementary Table 5. The application of multiple materials produced roughly twofold higher the amounts of carbonyls in comparison to the single material. The compound concentrations were also approximately twofold higher when measured from the ventilation duct in comparison to room quantities of the Stratasys printer. These are inconsistent findings in comparison to VOC results, which were much higher when measured from the ventilation duct than from the room air.

The VP and MJ printers did not emit particles in the PM_{10} size range. The measured concentrations did not exceed background amounts as presented as background-corrected values in Table 5. The mean measured PM_{10} concentrations ranged from 0.5 to 1.7 μg/m^3, while the highest single measured value was only 5.4 μg/m^3. These results indicate that the particles emitted during photopolymer resin 3D printing are smaller in size. As noted in Table 5, the studied 3D printers did emit UFPs. Both traditional VP and MJ printing rooms of the 3D printing lab were supplemented with HEPA-filtered air, but the background UFP number concentration in the traditional VP printer room was approximately twofold higher than the MJ printer room. The inactive 3D printers or post-processing devices may have acted as secondary UFP sources. However, this does not affect the presented background-corrected findings. The measured average UFP number concentrations, which ranged between 0.19 and 3.62 × 10^3 number/cm^3 during 3D printing were relatively low, considering the occupational lightweight UFP reference value of 4 × 10^4 number/cm^3 suggested by Van Broekhuizen et al. (2012). Not a single peak exceeded that reference value. The MJ printer emitted particularly low amounts of UFPs into the room and the concentrations measured from the ventilation duct were also low but comparable to the room quantities detected during VP printer operations. The application of multiple materials did not affect UFP emissions. No significant high peaks were observed during the measurements, which are common when traditional material extrusion 3D printers are operated (Du Preez et al. 2018).

The UFP size distributions, including backgrounds, are illustrated in Figure 1. The size distributions of UFPs emitted by the same 3D printer resembled each other, and most of the size distributions exhibited one notably high concentration peak accompanied by at least one lower peak. Particles emitted from traditional VP printers were numerically smaller than those emitted from dental VP and MJ printers; the concentration peaks were located at 10.8–19.1 nm size range for traditional VP machines. In contrast, the peaks were at 19.1–45.3 nm range for dental VP and MJ printers, but at 80.1 nm for Stratasys VeroBlackPlus room measurement. A tiny portion of particles were greater than 100 nm in size.

Outgassing emissions

The material TVOC emissions are presented in Figure 2. Interestingly, the non-solvent-washed cubes manufactured with the MJ printer emitted equal amounts of VOCs as solvent-washed cubes produced with the VP printers. However, the main compounds were different in comparison; the MJ cubes initially emitted high quantities of propylene glycol, while the post-processed cubes emitted predominantly the solvent they were treated with. The cubes manufactured from Bego feedstocks emitted

Table 5. Measured background and background-corrected UFP and PM_{10} concentrations (CPC and OPS).

UFP number concentration (number/cm^3, CPC).														
	Background (traditional VP)	Clear	Castable Wax	xGPP-Translucent	Background (MJ)	Multi, room	Multi, air duct	VeroBlackPlus, room	VeroBlackPlus, air duct	Background (dental VP)	ProArt Print Model	ProArt Print Splint	VarseoWax Model	VarseoWax Tray
Average	1.85×10^3	1.27×10^3	1.40×10^3	2.23×10^3	8.30×10^2	2.50×10^2	6.60×10^2	1.90×10^2	6.05×10^2	1.35×10^3	1.99×10^3	2.93×10^3	1.21×10^3	3.62×10^3
Min	1.73×10^3	0.75×10^2	0.50×10^2	0.80×10^2	8.00×10^2	0.10×10^2	1.45×10^2	0.15×10^2	1.45×10^2	3.20×10^2	3.45×10^2	6.05×10^2	3.20×10^2	9.65×10^2
Max	2.10×10^3	3.86×10^3	3.94×10^3	3.67×10^3	9.45×10^2	5.25×10^2	1.49×10^3	6.75×10^2	1.88×10^3	4.25×10^3	5.28×10^3	6.62×10^3	5.20×10^3	7.23×10^3
SD	0.80×10^2	6.60×10^2	6.90×10^2	6.70×10^2	0.55×10^2	1.05×10^2	3.65×10^2	1.25×10^2	4.00×10^2	1.85×10^2	4.40×10^2	7.10×10^2	5.85×10^2	1.65×10^3
PM_{10} mass concentration (µg/m^3, OPS).														
Average	1.7	1.0	0.9	1.0	1.6	1.3	0.9	1.7	1.0	0.5	0.5	1.0	0.6	1.3
Min	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Max	4.6	4.4	4.4	4.6	3.7	4.9	3.1	5.4	3.0	2.1	2.0	3.6	2.2	3.7
SD	0.9	0.8	0.8	0.7	0.6	0.6	0.6	0.8	0.5	0.3	0.3	0.3	0.3	0.6

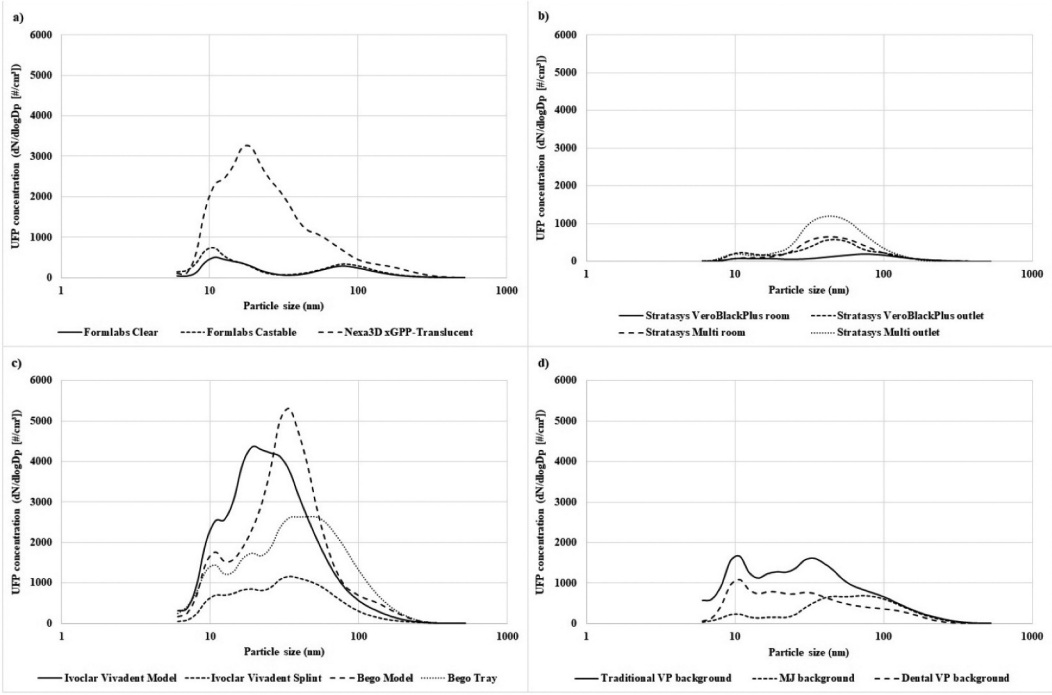

Figure 1. Background and 3D printing UFP size distributions: (a) traditional VP resins, (b) MJ resins, (c) dental VP resins, and (d) backgrounds.

markedly less VOCs than all other cubes, regardless of the solvent-washing, and despite Ivoclar Vivadent feedstocks resembling the Bego resins. In addition to solvents, acrylates, and oxygenated hydrocarbons, such as aldehydes, alcohols, and acids were commonly encountered emission products, as presented in Supplementary Tables 6–8. It is noteworthy that the actual emissions of solvents of such a low molecular weight as ethanol and isopropyl alcohol are most likely higher than measured, as the VOC collection method used best suits the sampling of compounds in the 6–16 carbon atom range. The VOC emission measurements were based upon production date, and thus, multiple-tinfoil control samples were collected for each elapsed measurement day. However, the control results were consistent, and the combined findings are presented in Supplementary Table 9. The TVOC emission rate was initially significantly higher, 1.5–2.7-fold, when the 37°C sample collection temperature was applied, in comparison to the sample collection temperature 20°C. This ratio remained rather constant through the experiment, as the emission rate of 37°C samples was still 1.4–2.9-fold higher after 84 days in comparison to the samples collected at 20°C. The steepest reduction in TVOC ranged between 40% and 75%, which was found between samples collected on days 1 and 7. The reduction rate was still 28–72% between days 7 and 14, after which the emissions diminished at a significantly slower rate. By day 28, total emissions were decreased by 84–96%.

Discussion

3D printer emissions

The non-standardized 3D printing process and different manufactured products during each set of sampling may exert an impact on emission results. However, the manufactured products always covered the majority of the build area in the cases of the VP printers, and one nozzle rail path width in the case of the MJ printer. Henceforth, it is considered that these results represent emissions under normal 3D printer operation.

A change in increasing temperature trend was observed in the room where traditional VP printers were located. Both the operated 3D printers heated

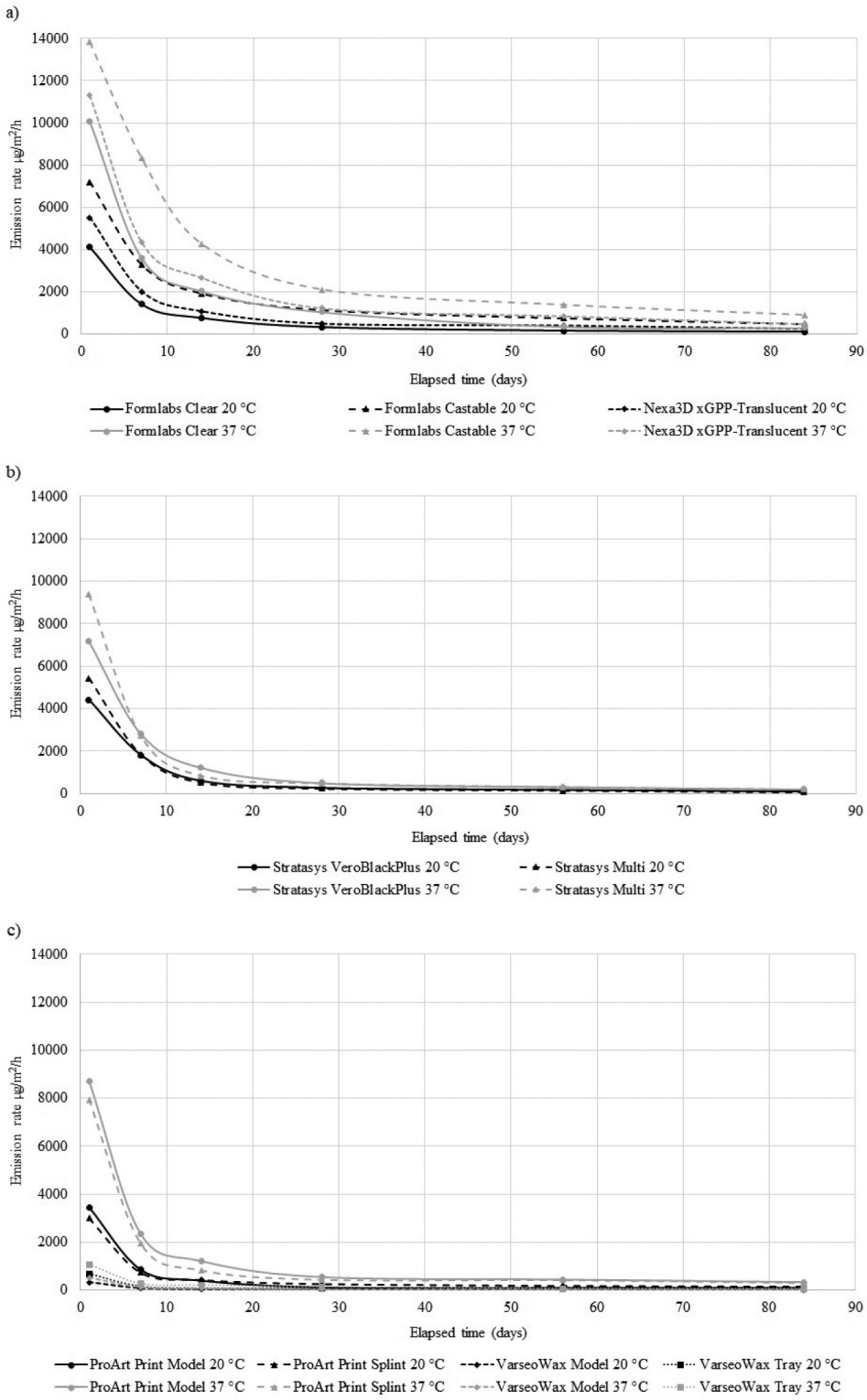

Figure 2. Total VOC outgassing of the resin products: (a) traditional VP resins, (b) MJ resins, and (c) dental VP resins.

their resin tanks up to 35°C before the manufacturing process was initiated. No similar alteration was detected with the other 3D printers that did not heat their printing chambers to a set target temperature. Thus, the operation of resin heating 3D printers may increase the operation at room

temperature. The CO_2 concentrations were found to remain stable during measurements, indicating that no CO_2 was emitted in the 3D printing process. Machine operators and measurement personnel might be attributed for the occasionally elevated CO_2 readings. Thus, VP and MJ printers appear to exert a low or negligible impact on the measured indoor air parameters.

As stated earlier, the measured TVOC concentrations do not raise concerns, but these values alone are not applicable for a health risk evaluation as different VOCs express varying hazardous characteristics. In comparison to existing literature (Hayes et al. 2021; Stefaniak, Bowers, and Knepp 2019b; Yang and Li 2018) and our preliminary study, the measured VOC concentrations were also low. As mentioned previously, low indoor rH has been associated with reduced indoor VOC emissions, but the emission differences cannot be completely explained by the particularly low rH. Other factors may have affected the results, including different operated machines, effective ventilations, different room setups, small build volumes, and short 3D print durations, which allowed for only low amounts of emissions to be present in the air.

Even the VOC compounds measured at the highest concentrations were far below (<1%) the Finnish occupational exposure limits (OELs, Finnish Ministry of Social Affairs and Health 2020). However, chronic VOC exposure might lead to unexpected health hazards (Manisaldis et al. 2020; Ran, Kioumourtzoglou, and Sun 2020). Certain identified compounds, classified as acrylates, carbonyls, and cyclic hydrocarbons, express hazardous properties through sensitization potential and the linear dose–response relationships of certain health effects, including carcinogenic risk (Savonius et al. 1993; Barro et al. 2009; Sarigiannis et al. 2011; Unwin et al. 2013; Janssens, Van Meerbeeck, and Lamote 2020; Ó, White, and Fraga-Iriso 2020). The identified VOC species were also diverse in comparison to the existing literature attributed to utilization of different analytical methods. Most of the compounds were dissimilar to what resins are known to be consisted of, and thus, chemical interactions within the resin followed by volatilization might be source for these compounds. However, many of the compounds are not particularly dangerous for human health and the measured exposure levels are not concerning, even if short-term effects, including irritation, fatigue, and discomfort may occur. The multi-material AM process was found to emit numerically more VOCs than deployment of a single material, as seen from the samples drawn from the MJ printer's ventilation duct. However, the measured TVOC concentrations were equal in the room. These samples are not sufficient to confirm if multi-material AM produces excess emissions but indicates that emission rates may be influenced by application of multiple materials. In the case of an MJ printer, this may be due to the use of multiple ink jet nozzles that enable emissions to be generated by multiple sources.

Few comparable investigations exist for the evaluation of carbonyls that originate from similar sources as VOCs, in addition to chemical interactions in the air (Barro et al. 2009). In comparison to our preliminary study, the measured concentrations were similar (Väisänen et al. 2019). Ryan and Hubbard (2016) and Zisook, Simmons, and Vater (2020) detected acetone and 2-butanone in <250 ppb-range during VP and MJ machine operations. Stefaniak, Johnson, and Du Preez (2019a) detected acetone and acetaldehyde in numerically higher concentrations, while Hayes et al. (2021) measured markedly higher, up to 610–1950 $\mu g/m^3$ amounts for acetone during VP and MJ machine operations. While our measured formaldehyde and acetaldehyde levels were low (highest measured concentrations were 12 $\mu g/m^3$ and 14 $\mu g/m^3$, respectively), a low carcinogenic risk resulting from exposure to them exist as carcinogenesis incidence following exposure to carcinogenic substances is linear. Exposure duration and concentration of a carcinogen are the main affecting risk factors, and thus, exposure to these compounds demand control measures (World Health Organization (WHO) 2006; Sarigiannis et al. 2011). Formaldehyde was also detected at the highest concentration (3%) in relation to its Finnish OEL of 370 $\mu g/m^3$. Exposure to the measured concentrations of the other detected compounds has not been documented to induce adverse health outcomes in humans, as these exhibit only low toxicity. However, the mentioned OELs are given for singular compounds and synergistic effects induced by

co-exposure to multiple VOC species can cause unexpected hazards. Furthermore, application of no-observed-adverse-effect levels (NOAELs) or lowest-observed-adverse-effect levels (LOAELs) on evaluation of VOC and carbonyl effects on human health is justified as they are based on a concentration threshold above which adverse effects may or are known to manifest. Henceforth, the concentrations falling below OELs do not outright signify an exposure to be risk-free.

The mass concentrations of PM_{10} emitted by both VP and MJ printers were practically zero and consistent with previous findings, as no elevated airborne particle levels beyond ultrafine size range were documented in VP or MJ printer operations (Hayes et al. 2021; Ryan and Hubbard 2016; Väisänen et al. 2019). The measured values are well below the European PM_{10} threshold value of 50 $\mu g/m^3$ (European Union 2008) even before background correction, and therefore of little concern for the 3D printer personnel. There were only small differences in the emitted UFP number concentrations among the different feedstocks and no distinct UFP peaks were detected. The measured UFP emissions of VP machines were also low in comparison to Stefaniak, Johnson, and Du Preez (2019a), albeit their documented emission rates were moderate or high in comparison to previous literature. The UFP values were relatively low when compared to the proposed occupational UFP reference value of 4×10^4 number/cm^3, even though UFPs are a contaminant group that does not have an established lowest safe limit and induction of adverse health effects follows a linear pattern (Pope and Dockery 2006; Shahnaz, Hayes, and Dechsakulthorn 2012). Henceforth, the measured values cannot be deemed explicitly hazard-free, but rather, the magnitude or probability of a health hazard induction is low. However, the composition and surface chemistry of particulate matter are major factors that affect their hazardous properties (Barro et al. 2009; Oberdörster 2001). The UFPs are formed through condensation and agglomeration of VOCs and semi-VOCs, and thus, their potential for adverse health outcome induction is real, given that several detected VOCs were highly irritating or otherwise hazardous to human health. Most emitted particles fell roughly in the 10–80 nm size range and particles of such size are readily inhaled into the alveolar region of the lungs, where they translocate into systemic circulation (Lee, Kim, and Lee 2014; Peters, Veronesi, and Calderón-Garcidueñas 2006; Puisney, Baeza-Squiban, and Boland 2018). The largest UFPs were observed in room air during 3D printing with Stratasys VeroBlackPlus. It is plausible that the particles grew in size following particle agglomeration in the air, as these were smaller when sampled from the ventilation duct. However, no similar behavior was found during multi-material 3D printing. Simultaneous application of multiple resins may exert an impact on air flow within the 3D printer, which might affect particle agglomeration. This is supported by the particle number measured in the 3D printer room where the MJ printer emitted numerically fewer, but larger particles when VeroBlackPlus material was applied, as opposed to when multiple materials were utilized.

The emissions originating from AM with photopolymer resins applying VP and MJ technologies appear to be relatively low based upon the measured exposure agent concentrations. However, exposure to specific organic compounds and UFPs might be considered a health hazard, and adverse health outcomes might be induced in prolonged exposure to VP and MJ printer emissions. Exposure control measures always need to be applied, following the hierarchy principle: eliminate, substitute, control, and personal protection. Further research is required to understand the long-term impact of 3D printing emissions and the emission characteristics of multi-material AM. Certain differences were noted during the application of multiple materials in comparison to a single material, but data are insufficient for in-depth evaluation of the emissions. In addition, the dermal health aspect of the AM industry requires more attention from the scientific community as resins might induce various dermal health hazards (Creytens et al. 2017).

Outgassing emissions

3D-printed products using ME method, and other consumer plastics have been reported to outgas VOCs (Du Preez et al. 2018; Even et al. 2020; Stefaniak, Du Preez, and Du Plessis 2021; Stefaniak, LeBouf, and Yi 2017) after their production. No apparent research data were available

regarding 3D-printed photopolymer resin products. The evaluation of VOC outgassing levels is difficult, as no safety limits or regulations exist for material VOC emissions of consumer products (Even et al. 2020), even though VOC contents of certain products, including paints and coatings in the EU, or individual compounds, such as formaldehyde, are regulated (European Union 2004). Dental and medical devices, materials, and products are also under regulation in the EU, but the regulation does not consider outgassing, only material safety through product composition and exposure evaluation. These regulations only bind material producers (European Union2017; International Organization for Standardization 2017). National material emission classifications and EU-wide lowest concentrations of interest exist which addresses outgassing of construction or surface materials (European Commission 2020). In Finland, a TVOC emission threshold value for the least-emitting class (M1) is set at ≤200 μg/m^2/hr (The Building Information Foundation 2021). However, the reliance on only TVOC emission is a limitation of the M1-classification, as it disregards the hazardous properties of individual compounds.

Only VarseoWax Model and VarseoWax Tray feedstocks achieved the M1-classification emission value; on days 7 and 14, respectively. Other dental resins achieved this threshold on days 28 (ProArt Print Model), and 56 (ProArt Print Splint), when samples were collected at 20°C. Both materials exceeded the threshold even on day 84 when a 37°C collection temperature was applied. The Stratasys feedstocks and the Clear resin expressed similar emission profiles as Ivoclar Vivadent feedstocks, while Castable Wax and xGPP-Translucent feedstocks emitted excess amounts of VOCs even after 84 days. However, the cubes manufactured from Ivoclar Vivadent feedstocks might have performed better if post-cured more. These cubes were slightly sticky even after post-processing, indicating that the post-curing was not complete even though the instructions given by the manufacturer were followed. As Stansbury and Idacavage (2016) indicated proper post-curing is necessary to ensure the safety of photopolymer resin products.

Outgassing results in direct dermal or mucous membrane exposure when a product is used in contact with biological tissues, in addition to secondary inhalation exposure. Inhalation exposure is likely a lesser concern, given the quickly diminishing outgassing levels. Dermal and mucous membrane exposures are more concerning, as resin materials were reported (Alifui-Segbaya et al. 2018; Creytens et al. 2017; Fukumoto et al. 2013; Heratizadeh et al. 2018; Petrofsky et al. 2014) to induce cytotoxic and immunostimulatory effects and various adverse dermal effects including dermatoses and sensitization. In addition, they might induce organ damage. Considering the documented emission rates and toxicity of the resin materials, a safety period preceding application of resin products might be recommended. The emission rate was reduced by roughly 90% after 28 days, after which the decreased rate was slow. A precautionary safety period of 28 days and a complete surface photocuring is advised prior to the photopolymer resin products being used to diminish the likelihood of sensitivity reactions and toxic responses initiated by application of these products, such as dental crowns, removable braces, or prosthetics. However, as Even et al. (2020) indicated individual measurements similar to ours are only valid as a single point of emission reference, as no standardized method for consumer product VOC emission measurement or safety evaluation exist. Further research is also suggested on the biocompatibility and consumer safety of various feedstocks applied in different AM machines. As documented, biodegradation might occur following application of polymeric products in contact with biological tissues, leading to unexpected exposure to the polymer components and toxic responses (Bettencourt, Neves, and De Almeida 2010; Jorge et al. 2003).

Conclusions

Several relevant occupational exposure agent concentrations were examined in this study when multiple photopolymer resins were applied to different AM machines. The measured exposure levels were relatively low in general. However, multiple hazardous VOC and carbonyl species were found at low concentrations during 3D printing with every applied feedstock

material, including sensitizing agents, carcinogenic compounds, and CNS depressants. Furthermore, all the operated 3D printers emitted UFPs at concentrations that notably exceeded background levels. The monitored air quality parameters were principally unaffected by the 3D printer operations, and no altered PM_{10} concentrations were detected during the measurements. In conclusion, VP and MJ printer operators might face occupational risks in their occupations using AM machines that utilize photopolymer resins as their feedstocks following exposure to chemical and particulate exposure agents, but the probability for an acute or severe adverse health outcome is low. However, repetitive, and long-term exposures might result in unexpected health hazards. Henceforth, emission control and exposure reducing actions always need to be applied when AM machines are operated. These include the deployment of emission capture or containment applications, proper ventilation, and use of personal protective equipment, in addition to reducing time spent in the same space with the AM machines. Further, a safety period is suggested preceding the application of 3D-printed resin products, especially those which are employed in contact with biological tissues. Based upon our findings, a 4-week storage period is sufficient to markedly decrease VOC outgassing, and thus, the likelihood of adverse biological responses from occurring.

Acknowledgments

The authors would like to thank M.A. Ari-Pekka Väisänen for proof-reading the manuscript.

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. The permanent address of this publication is http://dx.doi.org/10.1080/15287394.2021.1998814.

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

This work was supported by the Kuopio Area Respiratory Foundation.

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