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Additive Manufacturing: Possible Problems with Indoor Air Quality

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Abstract

This study deals with Additive Manufacturing and the possible problem of Indoor Air Quality pollution due to the melting process of 3D printers, during which materials such as plastics emit gaseous substances, commonly called Volatile Organic Compounds (VOCs). Assessing that the quantity of substances emitted does not exceed threshold levels is important for the health and safety of those using such digital tools. Therefore it has been performed air sampling of indoor air environments, while a 3D printer was under function, with different types of plastic in order to understand and assess the potential dangerousness to human health of this technological tool. Data collection in the research was performed by means of a membrane pump through an activated carbon vial (following the line of the ISO 16000-3:2011 standard), on plastics such as Polylactic Acid (PLA), Polyethylene Terephthalate (PET) and Acrinolitrile Butadiene Styrene (ABS). The results are in line with what has been previously found in literature and indicate that ABS is more toxic than PLA, but that the PLA under certain conditions is not free from harmful emissions to health issues, especially if melted at temperatures over 200°C. What is more adding PET to the comparison, this is the material which emitted less substances.

Keywords: Indoor Air Quality; 3D printing; Volatile Organic Compounds.

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1. Introduction

Three-dimensional (3D) printers are gaining popularity as rapid prototyping and small scale manufacturing devices. The development of low-cost desktop versions has made this technology widely accessible for use in home and office settings. Even if there are several types of 3D printing technologies, most desktop printers use the Fused Deposition Modeling (FDM) technique in which a heated nozzle melts a solid thermoplastic filament, usually Acrylonitrile Butadiene Styrene (ABS) or Polylactic Acid (PLA), and deposits multiple thin layers of extruded plastic to form a solid three-dimensional shape [1]. During the melting process of 3D printers, plastics both emit gaseous substances, commonly called Volatile Organic Compounds (VOCs), and Ultra Fine Particles (UFP) of size order of several tens of nanomillimeters. Through laboratory tests the variation of VOC concentration during the printing process of plastics has been monitored and studies have shown that ABS is more toxic than PLA, but that PLA under certain conditions is not free from harmful emissions to health issues, especially if melted at temperatures over 200 °C [2]. Non-manufacturing environments such as offices, homes, classrooms, and libraries are usually designed for occupant comfort, not exposure mitigation. Hence, use of 3D printers in non-manufacturing or private settings potentially represents another contribution to UFP exposure for indoor workers and the general public to particles with potentially unique physicochemical properties from these other known sources [3]. Since most desktop 3D printers are not equipped with exhaust ventilation or filtration accessories and users in home and public settings typically do not utilize appropriate personal protective equipment, it is important to characterize the physicochemical properties of 3D printer emissions to understand exposure potential and risk as early on as possible in the adoption of this technology to non-industrial settings. To this end, in collaboration with the laboratory Cosmob S.p.A., this study performed air sampling of indoor air environments, while a 3D printer was under function, with different types of plastic materials (PLA, ABS, PET) in order to understand and assess the potential dangerousness to human health of this technological tool.

2. Literature review

2.1 Primary Air Pollutants: Volatile Organic Compounds

Volatile Organic Compounds (VOCs) comprise a very wide range of hydrocarbons, oxygenates, halogenates and other carbon compounds existing in the atmosphere in the vapour phase. The predominant source is typically through leakage from pressurized systems (e.g. natural gas, methane) or evaporation of a liquid fuel such as benzene from the fuel tank of a vehicle. However, also organic solvents, used for example in paints and adhesives, are designed to disperse in the atmosphere to allow the active ingredients to dry [4]. In Western Europe people may be exposed to indoor air for more than 20 hours per day. The quality of indoor air has a non-negligible impact on human comfort and even health. These two facts explain the growing interest in making available simple yet effective ways for the characterisation of the air indoors. In fact the widespread use of new products and materials in our days has resulted in increased concentrations of indoor pollutants, especially of VOCs, that pollute indoor air and maybe affect human health [5]. In many scientific publications dealing with VOCs a tendency can be observed not to report the concentrations of all analysed VOCs individually but rather to indicate the total concentration of VOCs under the term "Total Volatile Organic Compounds" (TVOC). One of the reasons is that the interpretation of one single parameter is simpler and faster than the interpretation of the concentrations of several dozens of VOCs typically detected indoors [6]. Literature shows that there is a large variety of ways to calculate a TVOC value from the results of an analysis [7, 8]. In addition to the mere calculation procedure, differences may arise from the influence of the analytical system including the adsorbent used for sampling, the sampling rate and volume, and the separation and detection system. For all these reasons, published TVOC data are often not comparable and, consequently, there is a need for an agreement on what "TVOC" means from the standpoint of the analyst. Although there is not an agreed definition for TVOC, this entity is often used in the literature to describe indoor air exposures and to estimate health consequences and risks.

The justification for this is mostly derived from the work of Mølhave et al., [9], who studied the health and comfort effects of a mixture of 22 VOCs, and the subsequent complementing work carried out at the laboratories of the US Environment Protection Agency (US-EPA) using almost the same mixture [10]. In view of the large number of known organic chemicals in indoor air there is a tendency to divide them into several classes for easier handling. Following the classification given by the World Health Organization (WHO) working group on organic indoor air pollutants [11], it has become common practice to divide organic chemicals according to boiling point ranges (lower limit between 50-100° C and an upper limit between 240-260° C) and to discriminate between Very Volatile Organic Compounds (VVOC), Volatile Organic Compounds (VOC), Semi Volatile Organic Compounds (SVOC) and Particulate Organic Matter (POM).

Table 1. Classification of indoor organic pollutants [11].

Category	*Description*	*Abbreviation*	*Boiling-Point Range**	*Sampling media tipically used in field studies*
1	Very Volatile (gaseous) Organic Compounds	VVOC	< 0 to 50-100	Batch sampling; adsorption on charcoal
2	Volatile Organic Compounds	VOC	50-100 to 240-260	Adsorption on Tenax, graphitized carbon black or charcoal
3	Semivolatile Organic Compounds	SVOC	240-260 to 380-400	Adsorption on polyurethane foam or XAD-2
4	Organic Compound associated with Particulate matter or particulate organic matter	POM	>380	Collections on filters

* Polar compounds appear at the higher end of the range

If a VOC mixture is analysed in indoor air, the result is often expressed as TVOC. This means that one single value is taken to represent the VOC mixture (Table 1). Unfortunately, there is no general agreement on which compounds should be included in the procedure to generate the TVOC value. Hence, the number and the nature of VOCs on which the TVOC value is based varies between studies reported in the literature. This is also one of the problems if the TVOC value is used as an indicator of health effects [6]. Further agencies, in addition to WHO have proposed different definitions of VOC; the European Concerted Action (ECA) in the document “Evaluation of VOC emissions from building products: solid flooring materials” gives a classification of VOC according to the chromatographic retention time: "all volatile organic compounds, eluted in a capillary column coated with 100 % of dimethylpolysiloxane, in the range of retention between the n-hexane (C6) and hexadecane (n-C16)"; this range corresponds to boiling points between 50-290° C. The UNI EN ISO 16000-5 Part 5: Sampling strategy for volatile organic compounds (VOCs) takes over the classification of VOC according to the WHO, while the European Union (EU) with Directive 1999/13/EC on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and in certain facilities, implemented in Italy by Ministerial Decree 44/04, defines VOCs as "any organic compound having at 293.15 K a vapor pressure of 0.01 kPa or more, or having a corresponding volatility under the particular conditions of use". Subsequently in the EU Directive 2004/42 on the limitation of emissions of volatile organic compounds due to the use of solvents in certain paints and varnishes, as well as for vehicle refinishing products, implemented in Italy with Legislative Decree 161/06, defined as VOCs "any organic compound having an initial boiling point less than or equal to 250 °C measured at a standard pressure of 101.3 kPa" [12]. Some VOCs, such as benzene and formaldehyde are classified by International Agency for Research on Cancer (IARC) as carcinogenic - Group 1: Carcinogenic to humans found [13]. Moreover the WHO in the guidelines for indoor air quality indicates guide values for a number of pollutants, including certain VOCs, such as benzene, formaldehyde, trichlorethylene, tetrachlorethylene, and naphthalene in addition to nitrogen dioxide, carbon monoxide, polycyclic aromatic hydrocarbons (particularly benzo[a]pyrene) [11]. In Table 2, the main substances which compose the Total Volatile Organic Compounds (TVOC) are shown. These are divided into three different type of dangerous substances: carcinogens substances defined with the code HP7, that are substances that can cause cancer; teratogenic substances (HP10) which can cause fetal malformations and finally mutagenic substances (HP11) that can cause mutations or alterations in the genetic material. As it can be seen in Table 2 some of the substances which compose TVOC are not considered dangerous at all for human health and therefore they do not fall into these three categories listed above.

Table 2. TVOC: nocives substances

	Carcinogens (HP7)	Teratogenic substances (HP10)	Mutagenic substances (HP11)
Volatile Organic Compounds (TVOC)			
Benzene	X		X
Toluene		X	
Ethylbenzene			
Styrene		X	
Xylenes			
N-Hexane		X	
Cyclohexane			
1,2-Dichloroethane	X		
Trichlorethylene	X		X
Tetrachlorethylene	X		
Dichloromethane	X		
Ethanol			
Isopropanol (Isopropyl alcohol)			
Isobutanol			
N-Butanol (n-butyl alcohol)			
Ethyl acetate			
Isobutyl			
N-Butyl acetate			
Acetone			
Cyclohexanone			
Methyl isobutyl ketone (MIK)			
Methylethylketone (MEK)			
2-Metossietilacetato		X	
1,4-Dioxane			
4-Fenilcicloesene			

HP7 = substances that can cause cancer

HP10 = substances that can cause fetal malformations

HP11 = substances that can cause mutations or alterations in the genetic material

2.2 Indoor Air Qualiy and 3D printing

Most desktop 3D printers use the Fused Deposition Modeling (FDM) technique melting a thermoplastic filament, (usually ABS or PLA), and deposits thin layers of material to form a solid object [1, 14, 15]. Primary differences between ABS and PLA based printers are feedstock origin and nozzle and baseplate temperatures during operation. PLA is a biodegradable, corn-based plastic that prints at nozzle temperatures of ∼180 °C and baseplate temperatures near room temperature. ABS is a stronger thermoplastic that typically prints at ∼220 °C nozzle temperatures and ∼80 °C baseplate temperatures in most commercially available devices [1]. Other thermoplastic feedstock sources include Polyvinyl Alcohol (PVA), Polycarbonate (PC), and High-Density Polyethylene (HDPE), although they are not widely used in commercially available devices [15]. It is well known that office equipment such as laser printers and photocopiers that consume thermoplastic toner powder are emitters of Ultrafine Particles (UFP) with a diameter of less than 100 nm and various chemicals [16].

Already in the mid-90s the study of Contos et al., [17] has shown that moderately high temperature (e.g., 170–240 °C nozzle temperatures) thermal processing of thermoplastics in large scale industrial extrusion equipment, both gases and particles are emitted during operation and these findings have been confirmed in recent studies [18, 19]. Primary gas-phase products of ABS thermal decomposition at very high temperatures have been shown to include carbon monoxide and hydrogen cyanide, as well as a variety of volatile organics [20]. Exposure to thermal decomposition products from ABS has also been shown to have toxic effects in both rats and mice [21].

Through laboratory tests [21] the variation of VOC concentration during the printing process of plastics has been monitored and studies have shown, that ABS is more toxic than PLA, but that the PLA under certain conditions is not free from harmful emissions to health issues, especially if melted at temperatures over 200 °C [2, 20, 22]. The work of Stephens et al., [1] compared the amount of nanoparticles produced in a first case in which there were two printers with only PLA filaments with another case in which the same two printers were together with three printers employing filaments of ABS. The results of this comparison showed that the concentration of particles emitted in the second case ranged from about 3 to 30 times the concentration of particles emitted from only printers working with filaments of PLA. The test also wanted to highlight that after the shutdown of the printers, the decay time, that is the time necessary for halving the concentration of particulate matter in the environment, varied according to the size of the nanoparticles and that such period ranged between about 10 to 30 minutes to get a healthy "enough" environment. Toxicological studies confirmed that UFP penetrate into the alveolar region of the lungs and produce inflammatory responses, headache, and cardiovascular effects [23]. Further studies [24, 25] have shown that the nanoparticles are able to enter the bloodstream in the human blood system in under a minute. Once absorbed at a respiratory, cutaneous and gastrointestinal level, the particles may reach the systemic circulation and subsequently migrate in different organs and tissues.

3. Methodology

Data collection was performed by means of a membrane pump through an activated carbon vial (following the line of the ISO 16000-3:2011 standard), on plastics such as Polylactic Acid (PLA), Polyethylene Terephthalate (PET) and Acrinolitrile Butadiene Styrene (ABS). The pump was positioned above the base of the printer, which is a Delta Wasp 202040 Model, inserting the air extraction tube directly into the printer chamber. This implies that the presence of VOCs emitted may certainly be higher than those that will then be then dispersed in the air of the room in which the printer works. The sampling was carried out firstly when the 3D printer was on and brought to the temperature required for use, with the material inserted in the extruder but not in operation (it is said that the sampling was done in a white environment), and later while the same was working.

Since the objective of the study is the knowledge of the maximum concentration value of VOCs when the 3D printer is working, short-term sampling was carried out, thus performing short-term monitoring (80 minutes for each sampling). As regards this activity, an initial screening was carried out on different types of materials (PET, ABS, PLA, and PLA layer ABS) for the identification of critical emissions. Subsequently 5 vials of ABS, PLA and PET were sampled in the white environment, in such a way as to be able to compare such data with those present when the printer is operating. Therefore the air was sampled when the printer was working, while it was making objects both with PET plastic material, with PLA and then with ABS, sampling 5 vials for each type of material.

Approximately 3 samples were made per week, while the 3D printer was printing small objects (weighing no more than 50g). As previously indicated, the samplings were of the fixed duration of 80 minutes each, although the printing of the objects required different timing depending on the object printed and in each sampling the membrane pump was operated from the moment the printer started printing material and for the next 80 minutes.

Sampling was carried out from November 2016 to September 2017. The data sampled by the vial, were then sent to the laboratory for analysis. The obtained data were elaborated, trying to figure out the average composition of substances emitted during the 3D printing process of these plastics, making a comparison between the values of the "white environment" and those of the printer in operation. It has also been compared the values obtained with those present in the French decree concerning VOC emissions [26], so as to be able to understand if these values are above or below the threshold values defined by the decree. It has been taken as reference the values of the French decree, since there is not an European reference legislation that defines threshold values for indoor environments. Finally, it has been tried to identify for each sampled material its "fingerprint", considering the percentages of presence of the substances analyzed on each, taking into the fingerprint only those materials that are present for a percentage that is higher or equal to 5%, with the possibility to carry out an evaluation of the harmfulness of the material.

4. Results

The analysis of the presence of VOC on the plastic materials used to print objects with 3D printing has started with a preliminary analysis made on four different plastic materials, that is ABS, PLA, PET and a fourth material that is a PLA with some features of hardness of ABS, called PLA layer ABS.

This initial screening has been performed for the identification of the critical emissions of each material, to subsequently evaluate if these values were stable on multiple production batches. At the end of the screening it was decided to focus on the three pure materials for the next analysis, leaving the evaluation of the composite materials (i.e. PLA layer ABS) to a subsequent step. After this first step, the complete analysis on the materials was done.

4.1 VOC comparison with the French decree

To have an order of comparison of the emission levels with reference legislation, the French decree *"Arrêté du 19 avril 2011 relatif à l'étiquetage des produits de construction ou de revêtement de mur ou de sol et des peintures et vernis sur leurs emissions de pollutants volatils"* was taken into consideration. This decree has four different classes of emission values that range from the best class A+, to the lower one that is C; what is more as it can be seen from Table 3 the legislation does not take into consideration all the values of TVOC, but it chooses to focus on 11 substances, among which it has not been considered in the sampling formaldehyde and acetaldehyde and 1,2,4-trimethylbenzene, 1,4-dichlorobenzene, 2-butoxyethanol since these substances requires another type of sampling. These differences among the substances considered in the decree derive from the fact that the UNI EN ISO 16000-9 standard for the determination of emissions of Volatile Organic Compounds from construction products and finishing products by emission test chamber method, does not defines a clear list of substances to be considered for analysis but leave this choice to the laboratories carrying out the analysis.

However comparing the values derived from the sampling of ABS, PLA and PET with the values defined in the decree it can be seen that the level of emissions reached allows to reach the emission class A + and therefore the substances emitted when the 3D printer is in function do not seem to exceed threshold values that make them harmful for human health.

Table 3. Comparison between the VOC emissions of ABS PLA and PET and the French legislation

	Classes defined by the French legislation				***ABS***		***PLA***		***PET***	
UM mg/m³		***B***	***A***	***A+***	***Value***	***Class***	***Value***	***Class***	***Value***	***Class***
Formaldehyde	>0.120	<0.120	<0.060	<0.060	-		-		-	
Acetaldehyde	>0.400	<0.400	<0.300	<0.200	-		-		-	
Toluene	>0.600	<0.600	<0.450	<0.300	0.016		0.026		0.011	
Tetrachlorethylene	>0.500	<0.500	<0.350	<0.250	0.000		0.001		0.000	
Xylenes	>0.400	<0.400	<0.300	<0.200	0.006		0.006		0.002	
1,2,4-trimethylbenzene	>2.000	<2.000	<1.500	<1.000	-		-		-	
1,4-dichlorobenzene	>0.120	<0.120	<0.090	<0.060	-	A+	-	A+	-	A+
Ethylbenzene	>1.500	<1.500	<1.000	<0.750	0.012		0.005		0.000	
2-butoxyethanol	>2.000	<2.000	<1.500	<1.000	-		-		-	
Styrene	>0.500	<0.500	<0.350	<0.250	0.069		0.021		0.006	
TVOC	>2.000	<2.000	<1.500	<1.000	0.391		0.255		0.151	

4.2 Materials' fingersprint

Finally, it has been tried to identify for each material its "fingerprint", that is the substances which compose the same, making an assessment of its harmfulness. Figure 1a shows the presence of VOC substances on PLA, indicating only those substances present in the material for a percentage greater than or equal to 5% of the total. In the PLA fingerprint the most present substances are acetone (22.3%), followed by N-Hexane (13.1%), and Toluene (12%). Among the substances that are present in PLA material there are three which are potentially harmful for human health: Toluene (12.0%), Styrene (9.6%) and n-Hexane (13,1%). All the three substances are classified as HP10 and therefore as substances that might cause fetal malformations. Subsequently Figure1b shows the presence of VOC substances on ABS and its relative fingerprint; the most present substances are Styrene (25.4%), Cyclohexane (18.5%), and Acetone (16.1%). Among all these, two of them are potentially dangerous, that is Toluene (6.0%) and Styrene (25.4%), and as in the case of PLA both of them are classified as HP10 substances. Finally Figure 1c shows the presence of VOC substances on PET material; the most present ones are Acetone (40%) and Ethanol (29.1%). However there is also a presence of Toluene (4.9%), that is considered a teratogenic substance

(HP10) potentially dangerous for human health. Nevertheless considering the three materials taken, PET seems to be the one with a more healthy fingerprint in terms of the presence of dangerous substances.

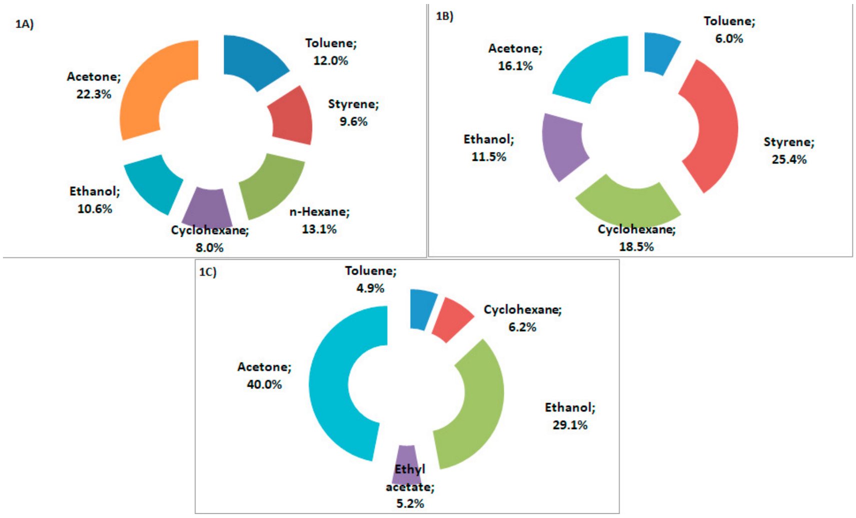

Fig. 1. (a) PLA fingerprint; (b) ABS fingerprint; (c) PET fingerprint

5. Discussion and conclusions

Desktop 3D printers use a heated nozzle to melt a solid thermoplastic filament. During this process, filament polymers and additives may react with oxygen, resulting in particulate emissions from by-products formed during heating [17]. The greater the difference between the extruder (ABS, 230°C; PLA, 215°C; PET 215°C) and filament melting temperatures (ABS, 105°C; PLA, 150°C; PET 150°C), the more vapour can be generated and condense to form UFP by gas-to-particle conversion via nucleation and/or condensation processes. For ABS, the temperature difference is 125°C and for PLA it is only 65°C. Thus, particle emissions from ABS are expected to be higher than PLA [3]. Our results show that this is true but the difference between VOC emission of PLA (0.314) and ABS (0.391) is very low. These results are in line with what has been previously found in literature and indicate that ABS is more toxic than PLA, but that the PLA under certain conditions is not free from harmful emissions to health issues, especially if melted at temperatures over 200 °C [2, 20, 22].What is more adding PET to the comparison, this is the material which emitted less substances (0.151). If we take into consideration the material fingerprint on Figure 1, which defines the percentage of substances present in each type of material when it is melted during 3D printing processes, it can be seen that some harmful substances for human health are present in materials, in detail these are teratogenic substances (HP10), that is substances that can cause fetal malformations. However these substances do not exceed the thresholds defined by the French decrees that regulate them. Therefore there is a presence in the analyzed materials of potentially harmful substances for human health, but at the same time these substances seem to be present in percentages much lower than those defined by the regulations as potentially harmful. Most research on the health effects of air pollution has focused on respiratory and cardiovascular effects occurring following inhalation. Other health-damaging routes of exposure to air pollution include dermal absorption and ocular exposure. For example, acute exposure to airborne pollutants can result in eye or skin irritation [6]. However, Italy has not defined a tolerance thresholds for these substances and therefore there should be the need to create a proper legislation on this issue. Nevertheless in order to have a clear definition of the harmfulness of 3D printing materials more investigations in the field should be needed. Some advice can be given to make the emissions of 3D printers in operation less harmful, such as the use of printers in ventilated places, even better if they are equipped with a primary air exchange system with a power of at least 3 volumes of the room per hour (e.g. a room of 100 m^3 should be equipped with at least one ventilator and a corresponding ventilation hole allows at least 300 m^3 / h of treated air). In another way, if using closed chamber printers, it would be important for the room to be equipped with active carbon filtering systems, selected according to the type of printing material; in fact the different materials do not emit all the same type of substances and therefore filters have been created that are able to absorb the VOCs according to the type of plastic used.

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