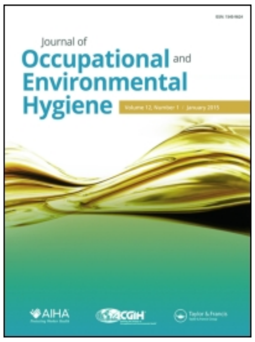

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Szymon Wojtyła, Piotr Klama & Tomasz Baran

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CASE STUDY

Is 3D printing safe? Analysis of the thermal treatment of thermoplastics: ABS, PLA, PET, and nylon

Reported By
Szymon Wojtyła [a], Piotr Klama[b], and Tomasz Baran [a,c]

[a]SajTom Light Future Ltd., Czaniec, Poland; [b]3DKreator Ltd., Cracow, Poland; [c]Department of Chemistry, University of Milan, Milan, Italy

ABSTRACT

The fast development of low-cost desktop three-dimensional (3D) printers has made those devices widely accessible for goods manufacturing at home. However, is it safe? Users may belittle the effects or influences of pollutants (organic compounds and ultrafine particles) generated by the devices in question. Within the scope of this study, the authors attempt to investigate thermal decomposition of the following commonly used, commercially available thermoplastic filaments: acrylonitrile-butadiene-styrene (ABS), polylactic acid (PLA), polyethylene terephthalate (PET), and nylon. Thermogravimetric analysis has shown the detailed thermal patterns of their behavior upon increasing temperature in neutral atmosphere, while GC analysis of organic vapors emitted during the process of heating thermoplastics have made it possible to obtain crucial pieces of information about the toxicity of 3D printing process. The conducted study has shown that ABS is significantly more toxic than PLA. The emission of volatile organic compounds (VOC) has been in the range of 0.50 μmol/h. Styrene has accounted for more than 30% of total VOC emitted from ABS, while for PLA, methyl methacrylate has been detected as the predominant compound (44% of total VOCs emission). Moreover, the authors have summarized available or applicable methods that can eliminate formed pollutants and protect the users of 3D printers. This article summarizes theoretical knowledge on thermal degradation of polymers used for 3D printers and shows results of authors' investigation, as well as presents forward-looking solutions that may increase the safety of utilization of 3D printers.

KEYWORDS
3D printer; acrylonitrile-butadiene-styrene (ABS); nylon; polylactic acid (PLA); polyethylene terephthalate (PET); VOC emission

Introduction

Three-dimensional (3D) printing is gaining popularity especially due to the fact that this is a rapid prototyping and small scale manufacturing technology. Printers have numerous applications in various industrial sectors, including electronics, medicine and medical science, consumer products, aerospace and defense, automotive industry, entertainment, and education. The discussed technology, also known as additive manufacturing, makes it faster and easier to produce complex objects with intricate designs. Soon, it will be affordable enough to have every single home equipped with it. Nevertheless, is 3D printing safe? 3D printers utilized in houses or offices may raise concerns with regard to possible health effects, especially due to toxic emissions.

Fused deposition modeling (FDM) is the most common 3D printing method, mainly due to easy handling and cost-efficiency. In FDM devices, a wire of thermoplastic material is heated in the extrusion nozzle head at various temperatures, depending on the material used. Most FDM 3D printers use acrylonitrile-butadiene-styrene (ABS), polylactic acid (PLA), nylon, polycarbonate (PC), acrylonitrile-styrene-acrylate (ASA), high impact polystyrene (HIPS), polyethylene terephthalate (PET), methyl methacrylate-acrylonitrile-butadiene-styrene (MABS) or thermoplastic copolyester (TPC) as filler materials.[1] ABS is a cost-effective engineering polymer that is easy to machine and fabricate, it has good impact resistance, resistance to chemicals, excellent machinability, high aesthetic qualities, as well as decent strength and stiffness.[2] PLA is a synthetic, aliphatic polyester—a compostable, biodegradable thermoplastic obtained from renewable sources.[3] PLA is thermally unstable and shows a fast loss of molecular weight in the course of thermal treatment. PLA tends to be slightly more brittle than other plastics. Nylon is a particularly strong, durable, and versatile 3D printing material.[4] It is characterized by low friction coefficient and high melting

CONTACT Tomasz Baran tommaso.baran@gmail.com Department of Chemistry, University of Milan, Golgi 19, 20133 Milan, Italy.
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temperature. PET (polyethylene terephthalate) is widely used in the process of plastic bottles production. In its original state, PET filament is a colorless and crystal clear material. It changes its transparency upon heating and cooling down. PET is fairly hard.

It is known that both volatile organic compounds (VOC) and ultrafine particles are emitted during thermal processing of many thermoplastic materials.[5–8] Rutkowski and Levin suggested that the carbon monoxide and hydrogen cyanide are the principal ABS thermooxidative degradation products that are of toxicologic importance.[8] However, 3D printers operation temperature is significantly lower than pyrolysis temperature at which CO and HCN are formed. It has been highlighted, that the concentrations of gaseous products differ depending on the material, cartridge type, and manufacturer.[9] Styrene corresponds to more than 50% of total VOCs emitted from ABS, while methylmethacrylate is the main pollutant released from PLA (about 40–60% of total VOC).[6,10] Kim and co-workers found that VOCs were emitted when the ABS was used, but not in the case of PLA.[9] In general, ABS was classified as a high emitter and PLA as a low emitter.[6] According to the literature, thermal decomposition of thermoplastics may result in the formation of multiple compounds, such as: styrene, hexanal, acetophenone, ethylbenzene, benzenemethanol, pinene, octanal, toluene, nonanal, pentanol, butanol, propylene glycol, and acetic acid—depending on materials utilized.[6]

The goal of this work is to analyze the thermal degradation of polymer filaments used for 3D printers. The study aims to determine VOCs emission resulting from the operation of a commercially available thermoplastics filaments: ABS, PLA, PET, and nylon. By using thermogravimetric analysis in the broad temperature range and thermal decomposition of material (*ex-vivo* 3D printer) combined with gas chromatographic analysis, the authors have identified potential hazards associated with the use of these materials in the printing process. Finally, the authors summarize available or applicable methods that can eliminate the formed pollutants and protect the users of 3D printers.

Methods

Commercially available polymer filaments were studied: ABS, PLA, PET, and nylon. Samples have been kept in dry atmosphere in desiccator over silica gel for 24 hr prior to further testing.

Thermogravimetric Analysis (TGA). Samples of materials have been analyzed using TGA (Mettler-Toledo, TGA/DSC 2 Star System) in the temperature range of 20–550°C. Heating rate has been equal to 10°C min^{-1}. All scans have been run in flowing nitrogen atmosphere at 100 mL min^{-1}. ABS, PET, nylon, and PLA were studied using thermogravimetric analysis.

VOC Emissions Testing Procedure. Samples of materials ABS, PET, nylon, and PLA (m = 1.2 g) have been heated (200–250°C) for 10 min in gas-tight tube equipped with a rubber septum. The samples of air above the materials have been taken by means of a gas-tight syringe (10 µL) and analyzed without any additional purification using Agilent gas chromatograph (HP 5890 GC with single FID) equipped with PAG 30 m × 0.32 mm capillary GC column (Supelco). Oven program: 30°C (hold for 4 min), increase to 200°C (4°C/min); carrier: He (20 cm s^{-1}), detection: FID (260°C), injection: 10 µL (injection port temperature 260°C).

Results

This study has been focused on commercially available filament for 3D printers: acrylonitrile-butadiene-styrene (ABS)—blue material, polylactic acid (PLA)—blue material, polyethylene terephthalate (PET)—black material, and nylon—white, semitransparent material.

TGA and DTG measurements

Thermogravimetric analysis (TGA) has proved to be a suitable technique to study the thermal stability of polymeric materials. Figure 1 shows TGA and DTG curves obtained in neutral atmosphere for the ABS wire. The results show that 100% weight loss has been identified for ABS at 500°C, indicating the low thermal stability in studied temperature range in N_2 atmosphere. The

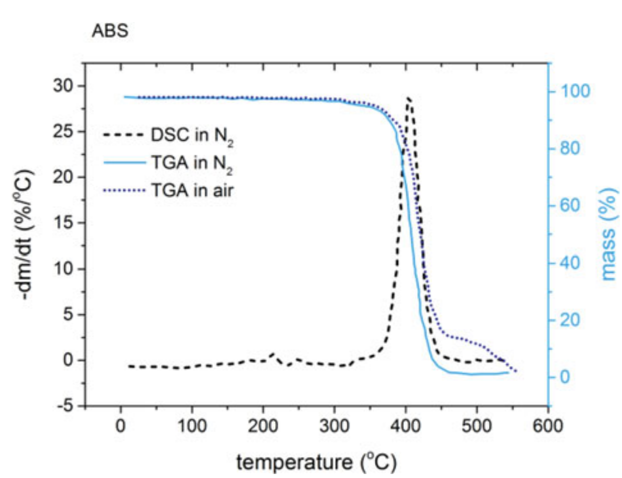

Figure 1. DTG and TGA analysis of ASB in N_2 and air atmosphere. Initial mass 0.0484 g.

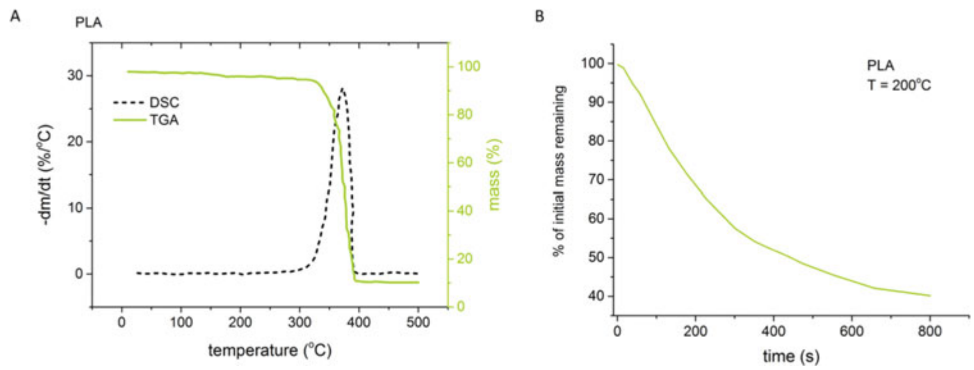

Figure 2. TGA and DTG analysis of PLA (A) and isothermal weight loss of PLA at 200°C (B). All measurements under nitrogen atmosphere. Initial mass 0.0502 g.

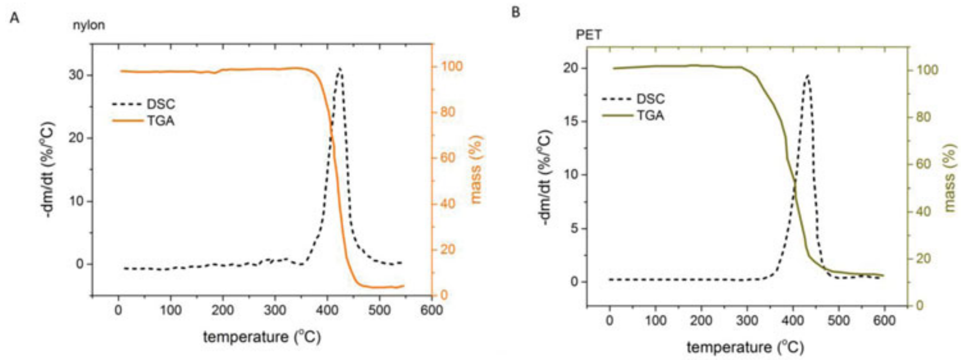

Figure 3. TGA and DTG analysis of nylon- initial mass 0.0499 g (A) and PET, initial mass 0.0510 g (B) under nitrogen atmosphere.

total thermal degradation of ABS occurs at the temperature range of approximately 380–430°C (one-step decomposition with one DTG peak at 409°C). Nevertheless, in lower temperatures (100–380°C) the loss of mass (about 4%) has also been observed as shown in Figure 1. It means that ABS releases some vapors during heating, also in the temperature typical for ABS-based 3D printing (230–250°C). Moreover, Figure 1 shows also the TGA curve registered in air atmosphere (blue dotted line). The cure under air shows two steps of degradation, one around below 450°C and the other upper than 500°C.

The total thermal decomposition of PLA under nitrogen atmosphere occurs at a lower temperature (300–400°C) than in the case of ABS, as shown in Figure 2 A. A single stage degradation process is indicated—one DTG peak at 374°C. Similar to ABS, the loss of the mass has been also observed below 300°C. The isothermal weight loss of PLA has been investigated at 200°C. The specified temperature is a typical PLA-based printing temperature. The plots of weight percent remaining vs. thermal treatment time are shown in Figure 2B. More than 13-hr heating has led to 60% weight loss and the curve has tended to reach the plateau. This fact highlights the importance of thermal degradation of polymers, typically used in 3D printers.

According to data shown in Figure 3A, nylon has a thermal behavior similar to ABS. The TGA result exhibits that nylon undergoes thermal degradation starting at 390°C with one DTG peak at 422°C and its total mass loss is higher than 99.0%. Polyethylene terephthalate (PET) has shown one DRG peak at 432°C, as presented in Figure 3B. Thermal stabilities of both nylon and PET are higher in comparison to PLA and ABS. However, from the safety point of view (i.e. the safety of 3D printer users), the correlation between temperature of printing and temperature of degradation is important. These temperatures are summarized in Table 1. Although the decomposition temperature is higher than typical printing temperature, the volatile organic compounds are emitted even below printing temperature, as demonstrated afterward. ABS, having low thermal stability and high printing temperature, may emit more VOCs than PET (low operating temperature and high thermal stability).

Table 1. Correlation between temperature of printing and temperature of degradation.

Material	Printing temperature	Decomposition temperature
ABS	230–250°C	380–430°C
PLA	200–235°C	300–400°C
Nylon	240–280°C	390–450°C
PET	160–210°C	350–480°C

Table 2. GC analysis of vapor from heated ABS and calculated amount of compounds emitted from 1.2 g of material during 1 min.

Retention time	Compound	Concentration
0.97 min	acetone	1.6E^{-4} µmol/min
5.11 min	butadien	1.4E^{-3} µmol/min
7.50 min	styrene	2.8E^{-3} µmol/min
9.33 min	iso-butanol	7.5E^{-4} µmol/min
11.85 min	ethylbenzene	2.2E^{-3} µmol/min
14.29 min	cyclohexanone	1.1E^{-3} µmol/min

Table 3. GC analysis of vapor form heated PLA and calculated amount of compounds emitted from 1.2 g of material during 1 min.

Retention time	Compound	Concentration
0.94 min	acetone	1.9E^{-4} µmol/min
2.08 min	unknown	5.0E^{-4} µmol/min
6.81 min	methyl-methacrylate	2.5E^{-3} µmol/min
9.35 min	iso-butanol	1.5E^{-3} µmol/min
14.31 min	cyclohexanone	9.8E^{-4} µmol/min

Analysis of vapors formed during thermal decomposition

In order to perform a detailed investigation of low temperature thermal decomposition of thermoplastics, samples of materials have been heated in gas-tight reactor equipped with a rubber septum. The total mass of samples was 1.2 g, corresponding to 3D printer's 10-min average filament consumption (based on data for 3D Kreator Motion model). All samples, ABS, PLA, PET, and nylon have been heated up to 240–250°C for 10 min. Vapors formed during that time have been analyzed using gas chromatography. Heating the materials in temperatures up to 250°C may lead to the release of numerous organic compounds. Their detailed analysis is provided in Table 2 (for ABS), Table 3 (for PLA), and Table 4 (for nylon and PET). Emitted compounds have varied according to the polymer used and the respective volatility of its components. Styrene, being the major component of ABS copolymer, is, together with butadiene, the main component of the emitted VOCs mixture. In the case of PLA, methyl-methacrylate is the main emitted pollutant. In case of ABS, the calculated total emission reaches 0.50 µmol per hour of printing. It means that, if printer's

Table 4. Concentration of VOCs emitted upon heating (1 min) of nylon and PET (samples 1.2 g). Data based on GC.

Nylon		PET	
Compound	Concentration	Compound	Concentration
Propylene glycol	1.59E^{-3} µmol/min	Toluene	3.6E^{-4} µmol/min
Cyclopentanone	4.1E^{-4} µmol/min	Acetaldehyde	1.3E^{-4} µmol/min
Unknown 1	1.3E^{-4} µmol/min	Acetone	0.9E^{-4} µmol/min
Unknown 2	1.7E^{-4} µmol/min	Formaldehyde	2.2E^{-4} µmol/min
		Ethylene	1.0E^{-4} µmol/min
		Benzoic acid	traces
		Unknown	Traces

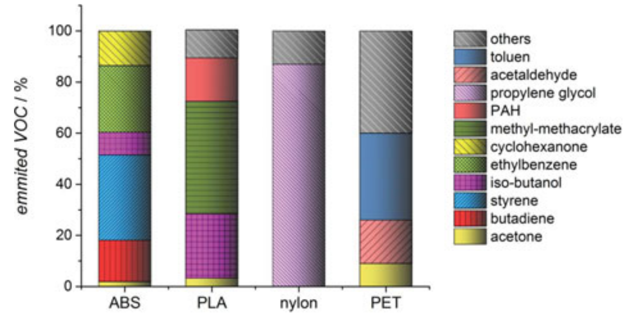

Figure 4. Emission of VOC during thermal treatment ABS, PLA, nylon, and PET. Results based on GS analysis.

dimensions are 400 × 390 × 520 mm and the volume of air inside it is about 40.56 dm^3 (≈50% of printer vol.), the concentration of produced organic pollutants reaches about 280 ppm during 1 hr of work. In turn, total emission from PLA reaches 0.34 µmol per hour of printing. It is 32% less than in the case of ABS. It means that the concentration of produced organic pollutants inside the printer of the same dimensions reaches about 191 ppm during 1 hr of work. VOC emission from all studied materials is summarized in Figure 4. Analysis of thermal degradation of nylon and PET, summarized in Figure 4 and Table 4, shown that these materials emits lower amount of VOCs than ABS and PLA: 0.14 and about 0.05 µmol per hour for nylon and PET, respectively. Lower emission may result from higher thermal stability of these polymers (see Table 1).

Control test (analysis of air from above the material without any thermal treatment) has shown the absence of VOC, thus the total amount of VOCs determined by GC is related to thermal emission from polymers. It should be highlighted that emission rates and the composition of the pollutants mixture for a given setting have been remarkably stable throughout the experiments.

Possible solutions leading to the reduction of the risk of 3D printing

In order to minimalize the negative effect of emitted particles and VOCs on user's health, it is highly recommended to install special filters inside 3D printers. Some particles (size bigger than 0.3 µm) can be removed by HEPA (high-efficiency particulate arrestance) filters. However, as reported in the literature, particles emitted during printing process are significantly smaller (10–116 nm) and thus HEPA filters seem to be ineffective.[11] Animal studies have shown that such small particles may use the olfactory system to migrate to the brain.[12]

The use of HEPA, as well as activated carbon filters does not solve the problem of air pollutants formed during 3D printing and there is the need for a new filtration system. Photocatalytic filters are one of possible solutions. Photocatalytic air treatment has the potential for degradation of organic and inorganic contaminants including volatile organic compounds from air.[13,14] A semiconductor photocatalysts, such as: titanium dioxide, zinc sulphide, tungsten oxide, copper oxides, or zinc oxide, absorb photons transferring the energy of light into excited charge carriers. They can then initiate and stimulate redox reactions occurring at the photocatalyst surface, e.g., the degradation of adsorbed organic and inorganic compounds to small safe molecules, such as H_2O and CO_2. Photocatalytic methods have a great advantage—they do not lead to the adsorption of pollutants, but to the degradation and total mineralization of pollutants. Moreover, photocatalysis has the ability to remove pollutants in very low concentrations, offering odorless and safe printing. Some photocatalytic materials and filters designed with 3D printers in mind have been already patented.[15] The first FDM 3D printer (*Accura Genius3D*) equipped with photocatalytic filtration system is commercially available since September 2016.

Conclusion

In this study, we show the thermal degradation of commonly used filaments for 3D printers. Reported decomposition temperatures mean total degradation of materials. In 3D printing process, the filament is melting at lower temperature. Unfortunately, these temperatures are high enough for partial decomposition of polymers with emission of volatile organic compounds. Within the scope of this study, the authors have shown that materials commonly used for 3D printing, such as ABS, PLA, and nylon can be a source of potentially dangerous volatile organic compounds such as: styrene, butanol, cyclohexanone, ethylbenzene, and others. In particular, heating ABS at temperature typical for 3D printing results in high VOC emission. It is an important weakness of this commonly used printing materials. It must be stated that the concentration of formed organic vapors is not dangerously high and printing in a well-ventilated, big room is not a threat to the user. However, intensive using of 3D printer in a room with weak ventilation system may lead to a significant rise of VOC concentration in the air. Due to the said fact, the development of novel type of filters and other kinds of protections dedicated to 3D printers is crucial. Presented studies have a few important limitation and difficulties, e.g., rescaling of VOC concentration to the room volume, consideration of printing rate, temperature of extruder and bed, the influence of differences between polymers from various manufactures. The results of the present study are limited in that different concentration of VOC could be found in well ventilated hall in comparison with small office. A test in an operational environment would help to clarify this point. VOC emission depends on printing rate as well as the temperature of an extruder and bed. In our study, we applied temperatures recommended by the filament manufacturer, but one can print at slightly higher temperature, thus the VOC emission would be higher. Moreover, we collect samples at one printer rate (typical for standard printing), so one might expect that the VOC concentrations may be higher with an increased printer rate or lower with a decreased rate assuming all other variables such as manufacturer, 3D printing material, room conditions, etc. remain the same. Furthermore, the slightly differences in VOC emission between various filaments made of the same polymer (e.g., various manufacturers or thickness, the presence of dyes and contaminants) might be observed. However, according to comparison of two ABS filaments from various manufacturers (data not shown), we did not find qualitative differences, while the quantitative differences were below 3%. To summarize, it should be noticed, that all above-mentioned aspects have essential influence on the safety of 3D printer using.

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ORCID

Szymon Wojtyła http://orcid.org/0000-0002-5095-3569
Tomasz Baran http://orcid.org/0000-0002-5140-3155

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