CHEMICAL ENGINEERING TRANSACTIONS

VOL. 90, 2022

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it

Guest Editors: Aleš Bernatík, Bruno Fabiano

ISBN 978-88-95608-88-4; **ISSN** 2283-9216

DOI: 10.3303/CET2290093

Time Dependence of Gas-Phase Emissions from 3D Printer Filaments

Hana Veznikova*, Michaela Skrizovska

Department of Occupational and Process Safety, Faculty of Safety Engineering, VŠB – TU Ostrava, Lumirova 13, Ostrava, Czech Republic
hana.veznikova@vsb.cz

Gas-phase emissions from 3D printers have received widespread attention with respect to their health risk. Here, we characterize the formation of gaseous emissions from polymer filaments. Analysis of gases released from different types of 3D filaments was performed on commercially available materials. The composition of gaseous mixtures was monitored, as well as the dependence of the gases on temperature and time. The thermal decomposition of material in an air stream equipment was used to formation of gaseous emissions. Experimental temperatures were determined according to the filament manufacturer's technical documentation. The analysis of the composition of gaseous products was performed on an FTIR spectrometer and the results corresponded to data from the literature. In one case, acetonitrile was detected, which was not expected to be present. Furthermore, it was found that the composition of gas-phase emissions and the time dependence of gas-phase emissions differ according to the composition of filaments. The identified dependencies allow the proper identification of health hazards when using 3D printers. In particular for newly developed filaments, it is necessary to evaluate the composition of the gaseous products of thermal decomposition of material in order to be able to take measures to ensure safety.

1. Introduction

3-D printing includes various equipment, methods and materials, and is one of the modern technologies that has the ability to transform or replace the usual technical processes. This manufacturing process is increasingly used in the industrial fields, in the design of new products in industrial and non-industrial fields, and also in households as a hobby activities. 3-D printing can also be used in crisis situations for the immediate production of various plastic products or necessary product parts.
Regardless all these products must be safe, i.e. they must comply with the requirements of the relevant EU rules. An example is the use of 3-D printers to make medical devices and their components and parts. Conformity assessment issued for these devices and their products is being addressed in the context for COVID 19. (Grow R., 2020)
3-D printers are among the so-called ‘harmonised products’ for which there is specific EU legislation in place. These regulated products are required to comply with the acceptable standards and are subjects of strict surveillance regime. Specifically, 3D printers fall under the definition of machinery within the Machinery Directive 2006/42/EC. Besides the Machinery Directive, other EU pieces of legislation may apply to 3D printers too; e.g. the Electromagnetic Compatibility Directive 2014/30/EC, and EU legislation on chemicals, WEEE 2012/19/EU, RoHS II 2011/65/EU Directive and Directive (EU) 2017/2102, and REACH 1907/2006/EU.
3-D printed products in themselves may or may not fall within the scope of specific EU legislation, such as the Medical Devices Directive 93/42/EEC1. Depending on the intended purposes of the product made on the 3-D printer, it may be included in to the regulated and non-regulated domains.
In both cases, even though this product don’t have regulatory status under the Medical Devices Directive 93/42/EEC, it has to fulfil the safety requirements of a final medical device.
Essential health and safety requirements set out in the relevant harmonized regulations are applied to the 3-D manufactured products, printing equipment and filament preparation equipment, i.e. 3-D printers and filament

Paper Received: 8 January 2022; Revised: 15 March 2022; Accepted: 16 April 2022
Please cite this article as: Věžníková H., Skřížovská M., 2022, Time dependence of gas-phase emissions from 3D printer filaments, Chemical Engineering Transactions, 90, 553-558 DOI:10.3303/CET2290093

extruders. All printing filaments do not belong among the regulated sphere products and therefore are not subjects of harmonized regulations, however no products may endanger health and safety.
The danger associated with the use of filaments lies primarily in the released emissions of hazardous substances when heated. These emissions consist of both particles and volatile organic compounds (VOCs).
Safe use of filaments is ensured in two ways. The first is to modify 3-D printers and filament extruders design and construction to meet the requirements of Article 1.5.13 of the Machinery Directive 2006/42 / EC: "Emissions of hazardous materials and substances".
For examples this article sets out the essential requirement for machinery, that must be designed and constructed in such a way that risks of inhalation, ingestion, contact with the skin, eyes and mucous membranes and penetration through the skin of hazardous materials and substances which it produces can be avoided. In addition, the machinery must be so equipped that hazardous materials and substances can be contained, evacuated, precipitated by water spraying, filtered, etc.
Manufacturers of 3-D printers and filament extruders must draw attention to the dangers of hazardous substances emissions in the instructions for use. Due to the use of a large number of materials from which filaments are made, it is not possible to specify the amount and type of emissions at this stage.
The second phase is focused on the evaluation of filament properties according to Directive 2001/95 / EC of the European Parliament and of the Council on general product safety. This directive applies to consumer products in case there are no specific provisions with the same objective in the rules of EU Law governing the safety of the products concerned.
The filament material must be evaluated in terms of emission generation of both particles and volatile organic compounds (VOCs) under conditions of 3-D printers and filament extruders processes.
The manufacturer of materials and filaments must state the safety information in the instructions for use to the extent that it allows the user to implement safety measures with the regard to the nature of generated emissions and it´s concentration.
The aim of these measures is to protect the safety and health of workers against the risks related to chemical agents at work. The limit values for hazardous chemicals and dust are set out in Council Directive 98/24/EC and other regulations issued for the implementation of this Directive.
Also, when using filament extruders, designed to create feedstocks for 3D printers, and the 3-D printers used at home, the safety of users must be ensured as is apparent from Directive 2001/95/EC of the European Parliament and of the Council on general product safety and regulations.
Therefore, filament manufacturers must obtain the information on the composition and concentration of emissions arising from the preparation of filaments and 3-D printing, to be able to market a safe product in accordance with EU legislation.
Previous research has shown that 3-D printers and filament extruders can emit large numbers of ultrafine particles and some hazardous volatile organic compounds (VOCs) during printing. Results from a screening analysis of potential exposure to these products in a typical small office environment suggest caution should be used when operating many of the printer and filament combinations in poorly ventilated spaces or without the aid of combined gas and particle filtration systems (Azimi 2016).
Given the fact that 3D printing technology is becoming more widespread in many industries (Ngo, 2018), the identification of risks in its use is of growing importance. The content of chemical compounds in heating and combustion products is an issue that must be solved with respect to its health and environmental impacts.
Reactions that take place during thermal degradation are dependent on the composition of flammable substances, oxygen concentration, temperature and many other conditions. The admixtures also greatly affect the composition of the gaseous heating products. In addition to the declared admixtures, such as metal particles or carbon nanotubes, the filaments may contain additives not listed in the technical information too. Admixtures properties and concentrations can significantly influenced gas-phase emissions. (Potter, 2021)
Therefore, the products are very diverse in terms of both quality and quantity. Toxic or harmful substances with negative impact on the workspaces and the environment can be found among these products. The focus of many research papers is to determine the toxic gaseous components or soot as particulate matter (Bølling et al. 2009). In other research works the particulate matter, carbon monoxide and polyaromatic hydrocarbons are monitored.
The two standards, ISO 13344 and ISO TS 13571, assess the toxic potency of major component of combustion gases, i.e. carbon dioxide, narcotic gases (carbon monoxide and hydrogen cyanide) and irritant gases (hydrogen chloride, hydrogen bromide, hydrogen fluoride, nitrogen oxides, sulphur dioxide, formaldehyde and acrolein). Analysis of gaseous products that contain such a wide range of chemical compounds, is rather complicated, even if used modern technology, and often requires time-consuming procedures for each component.
A broad discussion of the methods used when analysing gas mixture and comparison of toxicity is presented in the research work of Hull et al, which is mainly focused on standardised methods (Hull et al., 2007). The standard

ASTM E-800 provides comparisons between several analysing techniques, which are most often used to assess the composition of gases present or generated during a fire (ASTM 2007).
For example, the TD-GC / MS analysis method (Byrley, 2020), which was used to evaluate the emissions of ultrafine particles and flue gases during the operation of filament extruders, is a very commonly used method.
In this work, it was used the FTIR methods in a specific arrangement: Combustion flue gas analysis line (VŠB – TU Ostrava, 2021) equipped with the Nicolet iS10 FTIR spectrometer. The design of the analysis line prevents the condensation of most low-boiling substances. One of these substances is, for example, acetonitrile, a compound with a boiling point of 81 ° C, which was indicated when one type of filament was heated. The arrangement of the line allows its determination in one step together with gaseous substances and this contributes to simplifying and speeding up the analysis.

2. Materials and methods

Commonly available filaments made of various materials were selected for the measurement. These were samples of PLA (polylactic acid), ABS/PC (Acrylonitrile butadiene styrene/carbonates), PEIJet (Polyetherimide based on Ultem 1010) and ASA (Acrylonitrile-styrene-nitrile). (Vystrcilova M., 2020) Polylactic acid (PLA) and acrylonitrile-butadiene-styrene (ABS) are the primary polymer filament types used for a 3-D printing material.
Each of these materials has different properties that determine its use. The composition of gaseous products of heating is influenced not only by the type of material, but also by the technology used. One of them, the FDM (Fused deposition modelling) method uses a filament placed on a coil. After the start of the process, the filament is shifted to the print head, then melted at selected temperature and applied to the modelling board. The composition of the gaseous fumes is the result of a combination of material properties, the temperature used and also the time during which the heating takes place.
The manufacturer's recommended temperatures at which the evaluated materials are heated in 3-D printing using FDM are listed in Table 1 (materialpro3D, 2021).

Table 1: Sample identification (materialpro3D, 2021)

filament type	print temperature /°C/	pad temperature /°C/
PLA	185 – 235	40 – 60
ABS/PC	220 – 240	100 – 130
PEIJet	350 – 370	120 – 150
ASA	250 – 255	60 – 100

The composition of the gaseous fumes is the result of a combination of material properties, the temperature used and also the time during which the heating takes place.
The aim of this work was to analyse gaseous substances that are formed during thermal stress of the selected printing filament. The first step of the experiment is the preparation of gaseous fumes, and the second step is the analysis of its composition.
Preparation of gaseous fumes was carried out in the apparatus according to DIN 53436: Generation of thermal decomposition products from materials for their analytic-toxicological testing – Part 1: Decomposition apparatus and determination of test temperature. (DIN 53436-1:2015-12). A sample of 15 cm in length was placed approximately in the centre of the quartz tube. A round furnace running over a quartz tube with a sample at a rate of 1 cm·min^{-1} had a temperature such as the upper temperature limits given in Table 1 for each type of material. As an oxidation medium air was used, which was sucked into the quartz tube by means of a pump, which was placed behind the tube and filters in front of the analyser. The method according to DIN 53436 (DIN 1981) is intended for the evaluation of the toxicity of gases on the basis of experiments with animals, but also allows numerical evaluation of toxicity. In this case, it was used only as a standard method for the preparation of gaseous fumes, therefore a toxicity assessment was not carried out.
For gas analysis, an analysis line was used: Combustion flue gas analysis line (VŠB – TU Ostrava, 2021) equipped with the Nicolet iS10 FTIR spectrometer, which operates in the mid-infrared region with a range of 4000 cm^{-1} to 400 cm^{-1} with a spectral resolution of up to 1 cm^{-1}.
Gas cell with optical path length of 10 m was heated to a temperature of 165 °C. The delay between the change in concentration in the tube and the detector response was about 5 seconds for a given arrangement. Both sampling lines and filters were heated. The device allows continuous spectrum measurement, whereas the average spectrum is recorded at an interval of approximately 0,5 minutes. The spectrum measurements were controlled by software Omnic in Series mode.

3. Results and discussion

The time of analysis was 25 minutes and furnace moved with the speed of one centimetre per minute. Because the sample had a length of 15 cm only, the furnace was outside the sample at the beginning of test but the radiant heat of the oven has already affected the sample and the first gaseous substances were observed in the spectrum.

During the determination, the concentration of substances can be observed immediately using the software "Series" connected with calibration methods. The relevant substance should be known in advance. The increase in concentration of all combustion gases can be assessed immediately according to the Gram-Schmidt curve, which is a record of the overall detector response versus time (Pásztor et al., 2010). The dependence of changes in the concentration of all gaseous components in relation to time was evaluated using this function.

A sample of PLA filament was analysed at temperature of 200–220 °C. A record of the evolution of the gaseous products of heating in an oxidizing atmosphere over time is shown in Figure 1. During heating, the sample shrunk, no smoke was observed and the colour remained the same.

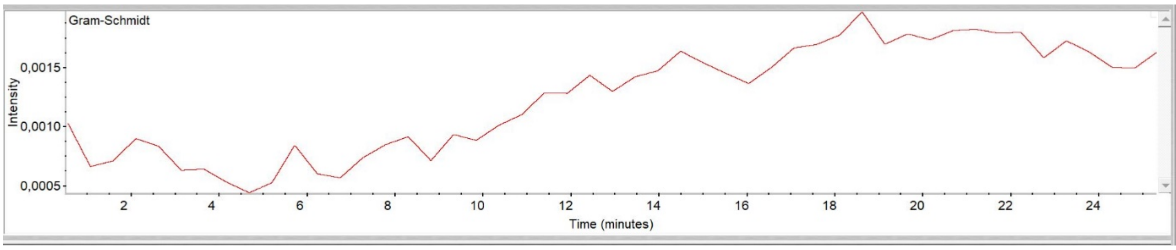

Figure 1: Time dependence of gas release during PLA filament heating at 220 °C

The maximum amount of gaseous products was formed around the 19th minute after the start of heating. Water and carbon dioxide were found in the flue gases. To evaluate the effect of temperature on the formation of flue gases, further analysis was performed at 350 ° C. Under these conditions, the formation of gaseous products changes. The maximum amount of gas is generated at the 16th minute, while traces of carbon monoxide and hydrocarbons were analysed. The total volume of gases is almost doubled when compared to previous test. During further increase of the temperature to 400 ° C, the presence of aliphatic hydrocarbons, namely methyl and methylene functional groups, were confirmed. Furthermore, the presence of carbon monoxide was confirmed and its concentration was maximal between the 22nd and 24th minute – see Figure 2.

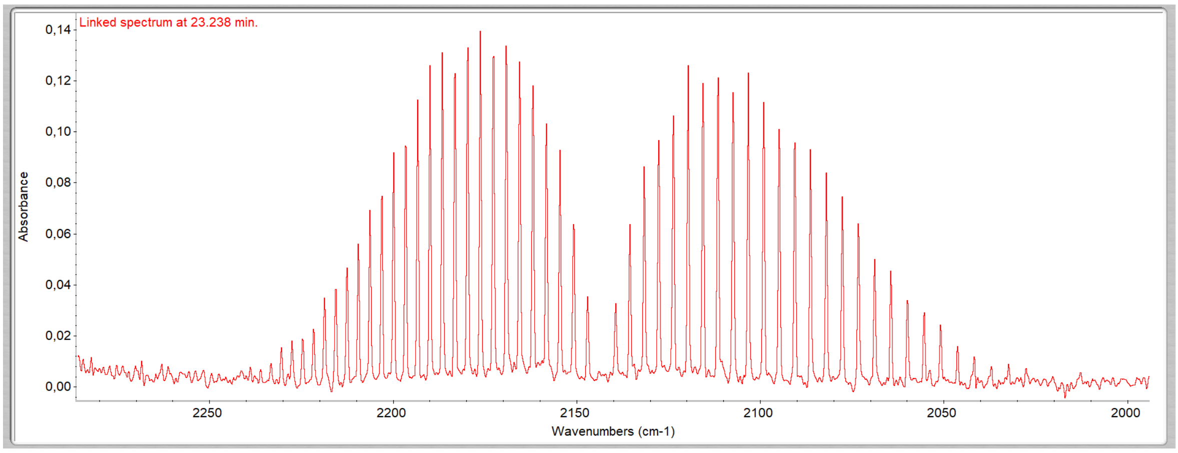

Figure 2: PLA filament spectrum of carbon monoxide, 22nd minute

The ABS / PC filament was heated to 260 °C. During heat exposure, the sample shrunk, no smoke was observed, and the sample retained its colour. The maximum increase in gaseous products occurred in the 3rd minute, then the concentration was approximately stable with a slight decrease. Water vapor and carbon dioxide were released from this material.

The PEI Jet filament was heated to 370 °C. During heat exposure, the sample did not shrink, no smoke was observed and the sample retained its colour. Small bubbles appeared inside the filament. The intensity of gas release increased evenly throughout the whole measurement process. Water vapor and carbon dioxide were released from this material.

The ASA filament was heated to 260 ° C. There was no shrinkage of the sample during heating, no smoke was observed and the colour of the sample changed somewhat. The maximum release of gases occurred in the 18th minute, and around the 21st minute there was a decrease. The gases contained water and carbon dioxide and, from the 15th minute, also carbon monoxide. At the same time, peaks were found in the spectrum around 3000 cm^{-1} and 1400 cm^{-1}, which most likely indicated the presence of acetonitrile. The presence of this compound is related to the material composition of this filament, however, its occurrence was not expected at the temperature recommended by the manufacturer for its use.

The obtained values showed that at the operating temperatures recommended by the manufacturer in the instructions for use, water vapor and carbon dioxide are released in all evaluated filaments. However, carbon monoxide is also released, which is a significant threat to worker safety. In addition, acetonitrile is formed in the ASA material.

It follows that, even if the conditions specified by the manufacturer in the operating instructions are observed, the safety of the working environment may be endangered and it is necessary to take appropriate measures to ensure safe working conditions.

4. Conclusions

EU legislation stipulates that only safe products may be placed on the market, either products fall into the regulated or unregulated sphere. With regard to the protection of the health and safety of consumers, the conditions for the safe operation of the equipment used must also be effectively ensured. Manufacturers of equipment and materials used in 3-D printing must provide sufficient information to their users to ensure safe usage. This applies not only to 3-D printers, filament extruders and 3-D products, but also to plastic filaments.

The temperatures required to print objects from plastic filaments are sufficient to thermally degrade the polymers and produce ultrafine particles and gaseous compounds, which can be dangerous for health.

The composition of the gaseous mixtures formed during the heating of the filaments was analysed as a function of time. Commercially available filaments were selected and heated to the temperatures recommended by their manufacturers. Under these conditions, mainly carbon dioxide was detected in the gaseous emissions, with the exception of the ASA filament, which produced carbon monoxide and acetonitrile as well.

It was found experimentally that the formation of gaseous products of thermal degradation occurs from the beginning of heating. Some filaments show a maximum increase in gaseous products approximately 15 minutes after the start of heating, it means that the risk of higher concentrations of hazardous substances increases with increasing time.

Safety measures must therefore be aimed at adequate ventilation of primarily small areas, to clean printers of any filament residues and formation of emissions during manufacturing of massive products.

References

Azimi, P., Zhao D., Pouzet C., Crain N.E., Stephensens B., 2016, Emissions of Ultrafine Particles and Volatile Organic Compounds from Commercially Available Desktop Three-Dimensional Printers with Multiple Filaments: A review of materials, methods, applications and challenges, Composites Part B: Engineering., 50(3)

Byrley P., Geer Wallace M.A., Boyes W.K., Rogers K., 2020, Particle and volatile organic compound emissions from a 3D printer filament extruder, Science of the Total Environment, 736, 1-10

DIN 53436-1:2015-12, Generation of thermal decomposition products from materials for their analytic-toxicological testing – Part 1: Decomposition apparatus and determination of test temperature. 2015

EU. Council Directive 98/24/EC of 7 April 1998 on the protection of the health and safety of workers from the risks related to chemical agents at work. 1998. Official Journal of the European Communities, OJ L 131, 5. 5. 98, p. 11-23. Accessed 19/12/2021. http://data.europa.eu/eli/dir/1998/24/oj

EU. Directive 2001/95/EC of the European Parliament and of the Council of 3 December 2001 on general product safety. 2001. Official Journal of the European Communities, OJ L 11, 15.1.2002, p. 4–17. Accessed 19/12/2021. http://data.europa.eu/eli/dir/2001/95/oj

GROW R., 2020, Conformity assessment procedures for 3D printing and 3D printed products to be used in a medical context for COVID-19, DocsRoom – European Commission (europa.eu), Accessed 16/12/2021. https://ec.europa.eu/docsroom/documents/40562

Ngo T.D., Kashani A., Imbalzano G., NguyenK.T.Q., Hui D., 2018, Additive manufacturing (3D printing): A review of materials, methods, applications and challenges, Composites Part B: Engineering, 143, 172-196

Potter P.M., Al-Abed S.R., Hasan F., Lomnicki S.M., 2021, Influence of polymer additives on gas-phase emissions from 3D printer filaments., Chemosphere, 279, 130543

VŠB – TU Ostrava, 2021, Veznikova H., Barcova K., Lesnak M., Combustion flue gas analysis line, Patent no. CZ 308619 B6, IPO Bulletin 1/2021, Accessed 10/12/2021. https://isdv.upv.cz/doc/vestnik/2021/vestnik_UPV_202101.pdf

Materialpro3D. 2021. Materiálový slovník. [online, accessed 10/12/2021]. https://www.materialpro3d.cz/materialovy-slovnik/

Vystrcilova M., 2020. Dangerous substances arising from 3D printing. Ostrava, Bachelor thesis. VŠB -TUO, Faculty of Safety Engineering.

Pasztor J., Šec K., Bradley M., 2010. Využití kombinace infračervené spektroskopie (FT-IR) a termogravimetrie (TGA) pro analýzu polymerů. CHEMAGAZIN. 2010, ročník XX, č. 1, s. 14-15.

Bølling A.K., Pagels J., Yttri K. E., Barregard L., Sallsten G., Schwartze P.E., Bomamn Ch. 2009. Health effect of residential wood smoke particles: the importance of combustion conditions a physiochemical particle property. Particle and Fiber Toxicology [online, Accessed 10/12/2021]. 2009, vol. 6, no. 29

Hull R.T., Paul K. T., 2007. Bench-scale assessment of combustion toxicity – A critical analysis of current protocols. Fire Safety Journal. 2007, vol. 42, s. 340-365

ASTM Fire Standards and Related Technical Material (2007). 7th edition. West Conshohocken, PA USA: 2007, ASTM International. Vol. 2. ISBN 978-0-8031-5684-5