Science of the Total Environment 805 (2022) 150181

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Real-time monitoring of the emission of volatile organic compounds from polylactide 3D printing filaments

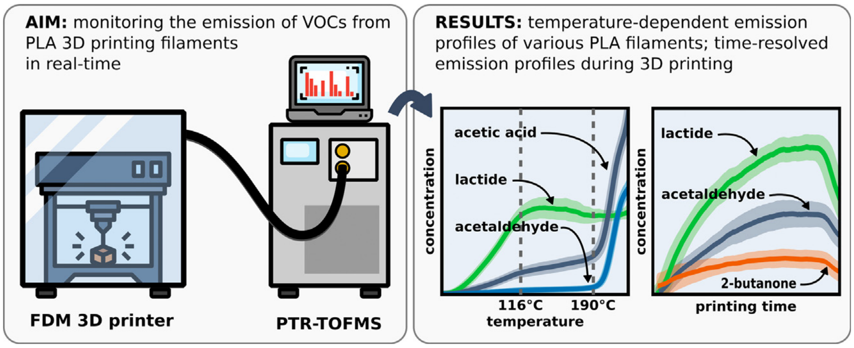
Wojciech Wojnowski *, Kaja Kalinowska, Tomasz Majchrzak, Bożena Zabiegała

Department of Analytical Chemistry, Faculty of Chemistry, Gdańsk University of Technology, 11/12 Narutowicza Street, 80-233 Gdańsk, Poland

HIGHLIGHTS

- Real-time monitoring of emission of VOCs during 3D printing is possible.
- SPME-GC–MS and PTR-MS used for qualitative and quantitative analysis, respectively.
- Approach reveals dynamic changes in emission profiles of PLA filaments.
- VOCs emission depends on temperature, type of PLA filament.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 27 July 2021
Received in revised form 1 September 2021
Accepted 2 September 2021
Available online 14 September 2021

Editor: Kevin V. Thomas

Keywords:
3D printing
Volatile organic compounds
Poly(lactic) acid
PTR-MS
Lactide
Polylactide

ABSTRACT

Establishing the emission profile of volatile organic compounds generated during fused deposition modeling 3D printing using polymer filaments is important in terms of both understanding the processes taking place during thermal degradation of thermoplastics, and assessing the user's exposure to potentially harmful volatiles. However, obtaining detailed, real-time qualitative and quantitative results poses a challenge. In this paper solid-phase microextraction-gas chromatography-time-of-flight mass spectrometry and proton transfer reaction time-of-flight mass spectrometry were used to identify and monitor the emission of volatiles during thermal degradation of polylactide filaments and during 3D printing. Filaments of two different grades and three colours were used. It was possible to obtain detailed, time- and temperature-resolved emission profiles of the main products of thermal decomposition of lactide and polylactide 3D printing filaments at concentration levels of a few μg/g. This revealed different temperature-dependent emission characteristics of particular volatiles, such as, among others, lactide, acetaldehyde, acetic acid, and 2-butanone between various polylactide 3D printing filaments. This approach can be used to monitor the emission associated with printing with various other types of polymer 3D printing materials.

1. Introduction

3D printers based on the fused deposition modeling (FDM) technology use thermoplastic polymer materials, usually in the form of solid filament spools, which melts as it is passed through a heated extruder and then solidifies upon deposition in strata to gradually form the desired object. The temperature of the extruder can be regulated to match the melting point of a particular filament, and in the case of most commercially available desktop printers can reach 280 °C. The melting of polymer filaments during printing leads to the emission of both particulate matter and volatile organic compounds (VOCs). The emission of particulate matter during 3D printing has been the focus of research in recent years [1–3], with a comprehensive meta-analysis of the body of research concerning this topic published recently [4]. However, the data regarding the qualitative and quantitative emission of VOCs during 3D printing

---

* Corresponding author.
E-mail address: wojciech.wojnowski@pg.edu.pl (W. Wojnowski).

https://doi.org/10.1016/j.scitotenv.2021.150181

is relatively scarce. Thus, despite the increasingly common and widespread household use of desktop FDM 3D printers, it remains difficult to assess the user's exposure to potentially harmful volatile chemical compounds. Still, there have been several attempts to qualitatively assess the volatiles emitted during the melting of polymer materials used in 3D printing [5,6]. In particular, it was tentatively demonstrated that emissions associated with printing using acrylonitrile butadiene styrene (ABS) are potentially more harmful to humans than those generated during printing with poly(lactic acid) (PLA) which is by far the most commonly used material for desktop printer filaments. However, the latter is by no means entirely safe for users, especially when extruded at temperatures over 200 °C [7–10].

There have also been several attempts to quantitatively characterise the emission of VOCs during 3D printing, predominantly in the form of total VOC emission measured using photoionization detectors [11,12]. In a recent study, the emission rates during printing with ABS, nylon, PLA, and polyethylene terephthalate (PET) have been examined using thermogravimetric analysis coupled to gas chromatography (TG-GC) [13]. It was shown that styrene accounts for more than 30% of total VOC emitted from ABS, while for PLA, methyl methacrylate has been identified as the predominant compound. However, in a different study conducted in the same year, it was reported that isopropyl alcohol is, in fact, the predominant VOC emitted during printing using PLA [14]. There are huge discrepancies in the reported composition of the mixture of volatiles emitted during 3D printing (e.g. the primary emitted VOC in the case of PLA was elsewhere reported to be toluene [15]) and in the estimated emission rates. It would however be reasonable to expect that substrates of the filament materials (lactide in the case of PLA) will also be the predominant volatiles emitted during printing since their boiling points are lower than the extrusion nozzle temperatures [16]. These discrepancies might result from issues with sampling, and the solution could be the use of a direct analysis method.

It was previously reported that the composition of the gaseous mixture emitted from 3D printing filaments depends on the manufacture and, to a lesser degree, on the added pigment [17], although it was alternatively proposed that the filament colour is a major parameter affecting the emission rates [16]. Another important factor that seems to affect the amount of VOCs generated during 3D printing is the extrusion nozzle temperature, with a direct relationship between the temperature and emission rates [16,17]. However, it is difficult to directly observe the effect of parameters such as the time it takes the nozzle to reach the designated printing temperature on the emission rates using sorbent tubes sampling. For this reason, direct injection mass spectrometry (DI-MS) techniques are often used for real-time, direct monitoring of the emission of volatiles as an alternative to GC-based methods. DI-MS techniques involving soft, chemical ionization in particular are useful for on-line determination of individual components of a complex gaseous mixture, as avoiding fragmentation enables assigning particular MS peaks to corresponding chemical compounds [18]. The most commonly used of these chemical ionization DI-MS techniques are atmospheric pressure chemical ionization MS (APCI-MS), elected ion flow tube mass spectrometry (SIFT-MS), and proton transfer reaction mass spectrometry (PTR-MS) [19]. In the latter, volatiles, usually VOCs, are ionized through reaction with hydronium ions (although other precursor ions are also sometimes used). The generated ions can, in theory, be then quantified based on the kinetic reaction rate and the detector response signals for the product and the hydronium ion [20]. The ionization is contingent on the proton affinity: the majority of common VOCs react with H_3O^+ ions, while main components of ambient air do not, which makes PTR-MS well-suited for direct monitoring of emissions in the atmospheric environment, for instance within an enclosure housing a working 3D printer. A carrier gas is not needed, as the analytes are carried into the system in the stream of ambient air, thus avoiding dilution.

While PTR-MS seems particularly useful for determining the emission profiles of volatiles during the heating of PLA 3D-printing filaments, it has certain limitations. For instance, it was previously reported that 3D printing with PLA filaments might lead to the emission of relatively small amounts of formaldehyde [16,17]. Since its proton affinity is not much higher than that of water, and since its characteristic m/z of 31 might also be affected by the interference of in the presence of ionized oxygen, among other interferences [21], its determination was not attempted in this work. It should also be noted that in PTR-MS concentration is estimated based on reaction kinetics which in turn depend to a degree on temperature, and so the concentration of particular chemical compounds can be determined to within ±30% of the actual value [22]. Perhaps most importantly, the use of PTR-TOFMS enables real-time qualitative monitoring of volatiles which can be tentatively identified owing to good resolution of the mass spectrometer based on the m/z value of the molecular ion and the isotopic ratio. However, the volatile products of PLA degradation consist mostly of oxygenated volatile organic compounds (OVOCs) which can have the same molecular formula which hinders their identification. When facing the analysis of possible structural isomers using PTR-MS, qualitative determination can be achieved through the complementary use of GC–MS [23].

We propose an approach in which proton transfer reaction time-of-flight mass spectrometry (PTR-TOFMS) is used for real-time, quantitative monitoring of the composition of the gaseous mixture generated during the heating of thermoplastic PLA filaments, and with respect to the duration of 3D printing using the same material. The emission profiles of VOCs were obtained for filaments of different colours and grades. The qualitative determination of the monitored compounds was confirmed using gas chromatography-time-of-flight mass spectrometry (GC-TOFMS).

2. Materials and methods

2.1. Samples and reagents

All reagents and analytical standards were obtained from Sigma-Aldrich (Merck KGaA, Darmstadt, Germany). The 1.75 mm 3D-printing filaments of two grades (economy, henceforth referred to as "ecoline" (Print-Me, Gorzów Wielkopolski, Poland), and premium (Nebula Filaments, Stare Bystre, Poland)), each in three colour variants (black, yellow, and "natural" – without added colourants) were obtained from online vendors in Poland. Prior to the experiments, the filaments were stored at room temperature in factory vacuum-sealed packaging. In the case of both filament grades, the printing temperature recommended by the manufacturer was a range from 190 °C to 230 °C. According to the information provided by the manufacturers, the "ecoline" product line is intended for beginners due to the low price and is recommended for home use, while the premium product line is supposed to offer a superior printing experience. The difference in price between the two product lines was only approx. 15%.

2.2. Determination of the VOCs emission profile from PLA filaments as a function of temperature

During 3D printing, only a relatively short fragment of the filament is passed through a nozzle heated to a set temperature at any given time. However, in order to assess the relationship between the nozzle temperature and the emission of volatiles, it is necessary to establish the emission profile of PLA in relation to temperature. To this end, each filament (approx. 15 mg – for particular masses of each sample see Table S1 in supplementary materials) were weighed on an analytical scale and placed in a 20 mL glass headspace analysis vial which was subsequently sealed with a screw cap with a silicon septum lined with PTFE. The vial was then placed in a dedicated aluminium heater block and heated to 235 °C (5 °C more than the maximum recommended printing temperature for the used filaments). The heating took approx. 15 min. The temperature within the vial was controlled using a thermocouple placed in an empty reference vial (see Fig. 1(a)). The heating block was initially heated to 60 °C and the headspace was sampled from the moment the vial was placed in the block. During heating, it was dynamically introduced into the PTR-MS in a stream of air which was first passed through a VOC filter (Supelpure HC, Supleco, Bellefonte, PA, USA). The approx. 25 cm PTFE capillaries connecting the vial to the heated transfer line (Fig. 1(a)3) were replaced after each measurement, flushed with tetrahydrofuran to remove any residue which might have collected within, purged with synthetic air, and conditioned overnight at 90 °C. The temperature of the PTR-MS transfer line was maintained at 70 °C.

The volatiles were sampled at 50 $cm^3{\cdot}min^{-1}$ and diluted with synthetic air (1:20) controlled using a mass flow controller integrated with the PTR-MS device. The relatively high flow rate (1000 $cm^3{\cdot}min^{-1}$) was optimized to avoid detector saturation. The PTR-MS was the PTR TOF 1000 Ultra (Ionicon GmbH, Innsbruck, Austria). The E/N was set to 120 Td by maintaining the drift tube voltage of 610 V. The mass spectra were averaged every 1 s. The concentration of the monitored volatiles was determined based on the kinetics of the proton transfer reaction between the analytes and hydronium ions, and on the reaction rate coefficient $k = 2.0{\cdot}10^{-9}$ $cm^3{\cdot}s^{-1}$. Air density at 70 °C (the temperature of the transfer line and the drift tube) was assumed for the calculation of the emission rates. The mass spectra were processed using PTR-MS Viewer v. 3.3.9.1 (Ionicon GmbH, Innsbruck, Austria). Each experiment was done in triplicate. The baseline was established during a measurement without the sample in a vial.

2.3. Determination of the VOCs emission profile from PLA filaments during 3D printing

The experimental setup for the monitoring of the emission of volatiles during 3D printing with PLA (see Fig. 1b) was based on one that was previously used to monitor the emission of BTEX compounds during 3D printing using ABS filaments [10]. Briefly, the instrument configuration mirrored the one described in Section 2.2, with the following exceptions: the flow rate was set to 100 $cm^3{\cdot}min^{-1}$ (undiluted), and the mass spectra were averaged every 3 s. A consumer-grade FDM 3D printer (Prusa i3 MK2S, Prusa Research a.s., Prague, Czech Republic) with a newly-replaced 0.4 mm nozzle was placed in a 0.13 m^3 enclosure. The temperature of the heated bed was set to 60 °C, and the nozzle temperature to 220 °C. Two low-poly Pikachu figurines (thingiverse.com/thing:376601) scaled uniformly to 40 mm in the z-axis were printed using PLA filaments which were fed through an air-tight interface. Each print took approx. 45 min. The air within the enclosure was mixed using three standard 120 mm fans. The gas phase was sampled through an approx. 25 cm 1/16″ PTFE capillary with the inlet mounted above the extruder, and the outlet connected to the PTR-MS transfer line. After each print, the capillaries were replaced and conditioned following the procedure described in Section 2.2. During printing, the temperature within the enclosure increased from approx. 24 °C to approx. 28 °C. After each print, the enclosure was opened and vented until the concentration of acetone and acetaldehyde (two of the predominant volatiles) within returned to baseline, and the printer has cooled down. The printed figurines were weighed using an analytical scale in order to calculate the emission rate per 1 g of filament. Each measurement was done in triplicate. The baseline was established by monitoring the emission during an entire print cycle without the PLA filament and with a clean nozzle.

2.4. Qualitative determination of volatiles in PLA filaments using SPME-GC-TOFMS

Solid-phase mircroextraction-gas chromatography-time-of-flight mass spectrometry (SPME-GC-TOFMS) was used for complementary qualitative identification of VOCs generated during thermal degradation of PLA. Prior to SPME, 15 mg of lactide and samples of PLA filaments were placed in 20 mL headspace vials, heated to 220 °C for 15 min, and subsequently cooled. A CAR/PDMS SPME fibre (1 cm, 85 μm, StableFlex, Supelco Inc., Bellefonte, USA) was then inserted into the vials, and the extraction took 30 min at room temperature. After extraction, the fibre was inserted into the GC injector operated in split mode (1:50) where desorption of the analytes (4 min at 250 °C with a continuous flow) was performed.

The analytical setup was comprised of the Agilent 7890A gas chromatograph (Agilent Technologies, Santa Clara, USA) coupled with the Pegasus 4D TOFMS mass spectrometer (LECO Corp., Saint Joseph, USA). The 30 m × 0.25 mm × 0.25 μm Equity 1 (non-polar stationary phase—PDMS) column (Supelco Inc., Bellefonte, USA) was used. During GC analysis, the temperature was initially set to 30 °C and then ramped to 55 °C at the rate of 3 °C/min, then the ramp was set to 18 °C/min to 250 °C and held at 250 °C for 2.84 min. The total time of a single analysis was 22 min. Helium at a flow rate of 1 $cm^3{\cdot}min^{-1}$ was used as carrier gas. The transfer line was heated to 250 °C. The temperature of the ion source was set to 250 °C, the detector voltage was 1745 V, and the acquisition rate was set to 10 spectra per second. The compounds were identified by comparison with the NIST Mass Spectral Library v. 2.0 (2011) and using standard solutions.

3. Results and discussion

3.1. Emission of VOCs during thermal degradation of PLA filaments

PLA can undergo multiple radical and non-radical decomposition reactions during thermal degradation, which makes a precise description of the process difficult. However, a significant increase of certain signals can be observed in the mass spectra when gradually heating filaments to 235 °C. Online PTR-MS analysis reveals two different temperature-

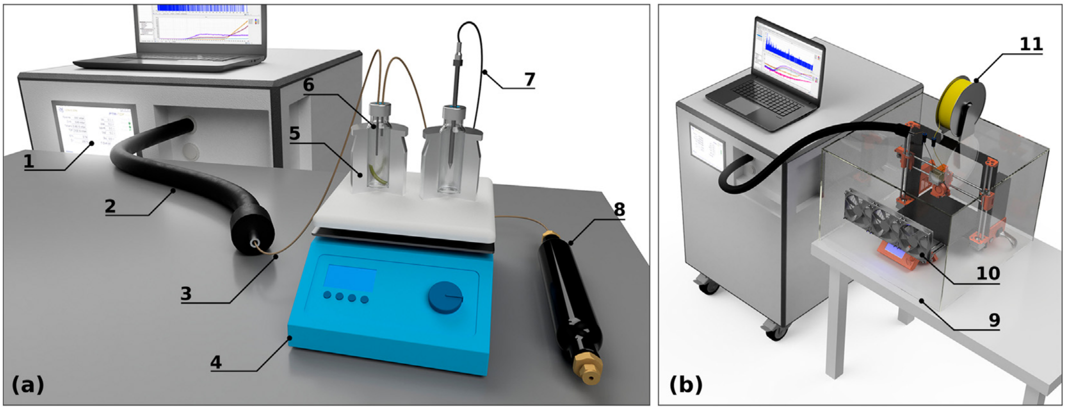


Fig. 1. The experimental setup for the determination of the VOCs emission profile of PLA filaments in relation to temperature (a), and real-time monitoring of the emission during 3D printing (b). The setup was comprised of: PTR-TOFMS (1); heated transfer line with a PEEK capillary (2); a PTFE capillary (3); laboratory heater (4); aluminium heater blocks (a cross-section is shown) (5); 20 mL glass headspace vials (6); thermocouple (7); VOCs filter (8); enclosure with an FDM 3D printer (9); three 120 mm fans; spool of PLA filament fed through a sealed port in the enclosure.

dependent characteristics of concentration changes (see Fig. 2). The emission of compounds with *m/z* of 55, 73, 75, and 145 increases markedly at approx. 120 °C and then mostly plateaus. These and other ions are denoted by adding the 'm' suffix to the protonated mass in the text and the figures. These signals can be associated with protonated lactide (m145) and two of the products of its decomposition (2-butanone and propionic acid for m73 and m75, respectively). The identification of these and further compounds, listed in Table 1, was confirmed using SPME-GC-TOFMS. Note that Table 1 contains the neutral nominal masses, while the protonated molecules detected using PTR-MS are the products of proton transfer reaction from hydronium ions (m + 1). This rapid increase of their concentration coincides with the melting point of lactide. Another, less marked increase in emission of these compounds can be seen upon reaching the recommended printing temperature of the PLA filaments (190 °C–230 °C), at which point the concentration of m55 and m73 continues to grow. This is not, however, the case with m145, which suggests that these compounds are also formed during the decomposition of PLA and its oligomers, or that compounds generated during its decomposition instantly undergo further decomposition and fragmentation at this temperature. The ratio between concentration of lactide, 2-butanone, propionic acid, and the unknown ion m55 ($(C_3H_3O)^+$) is consistent with previously reported data concerning the thermal decomposition of polylactide [24].

The remaining monitored volatiles (see Fig. 2 for emission profile and Table 1 for identification) have different temperature-dependent emission characteristics. Their concentration remains relatively low until the printing temperature is reached, at which point it increases markedly, suggesting that these compounds are either the primary products of PLA thermal decomposition or are formed in a secondary reaction [24,25], as opposed to e.g. being desorbed from the filament. The latter seems more likely since in the case of these *m/z* values groups differing in mass by e.g. 14, 28, or 44, might be formed by elimination of groups such as -CH_2, -CO, or -CO_2 [9,24]. This is supported by the results obtained using SPME-GC-TOFMS (Table 1). Some molecules, such as m127, might be the products of dehydratation of lactide. In other cases, since in PTR-MS ionization is achieved through proton transfer from H_3O^+ ions, the addition of water clusters to protonated molecules might also occur, as was the case with m163 in Fig. 3 – likely a water cluster with lactide. In order to confirm that some of the monitored molecules are products of decomposition of lactide, the emission profiling of its standard was also performed following the procedure outlined in Section 2.2.

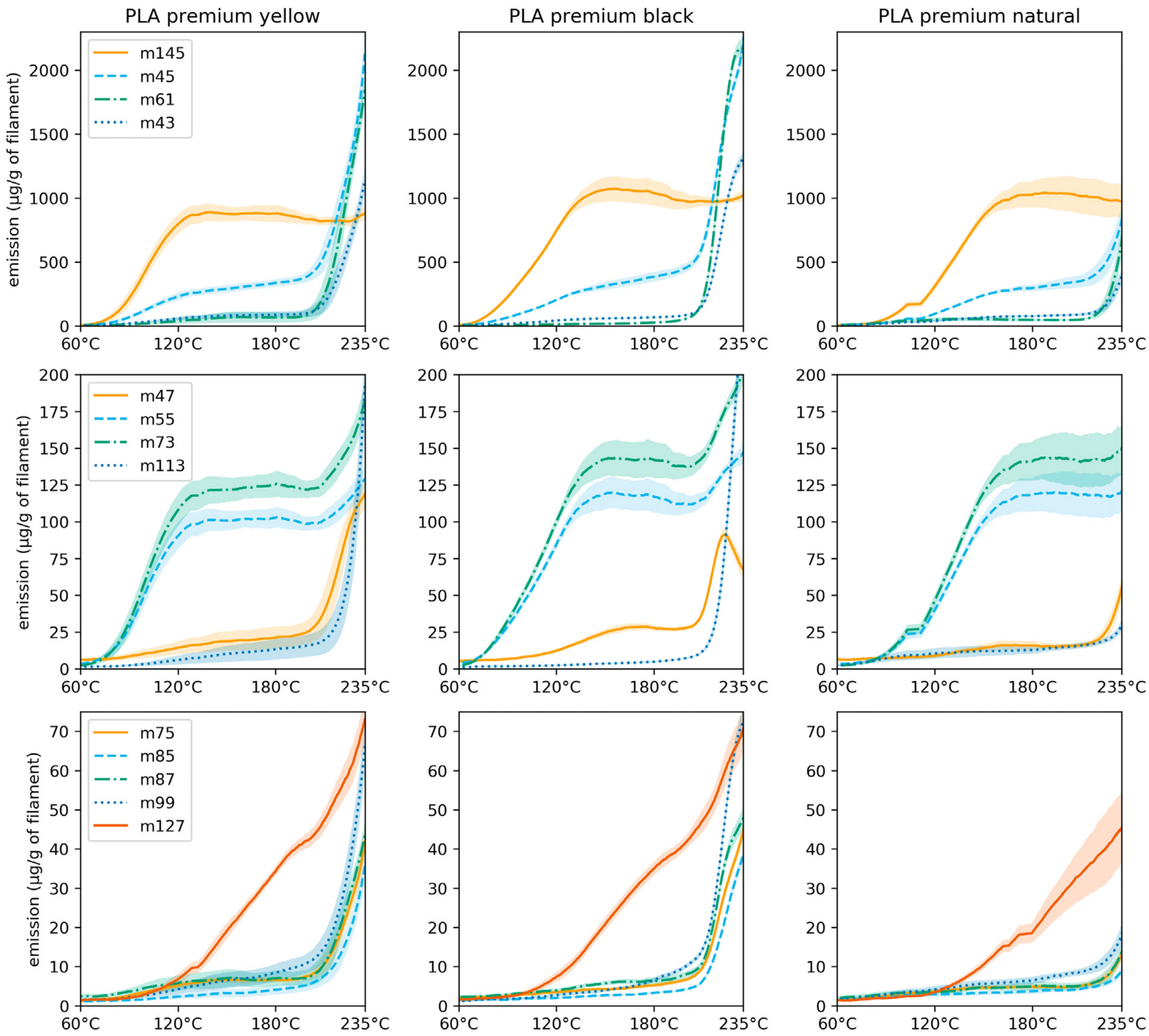


Fig. 2. Emission of most abundant VOCs (threshold: 10 cps) during the heating of PLA filaments as a function of temperature. Each column represents a different filament, and the subplots in each column were separated based on the emission rate for the sake of clarity. Lines denote the average value, and the shaded areas denote SD ($n = 3$).

Table 1

Results of qualitative determination of VOCs emitted from samples of PLA filaments and lactide heated to 220 °C performed using SPME-GC-TOFMS. The given mass is the molecular mass, corresponding to protonated ions (m + 1) used elsewhere in the text. The '+' symbols indicate that the compound was detected.

				PLA						
Compound	Formula	Nominal mass [Da]	RT [s]	Lactide	Premium natural	Premium black	Premium yellow	Ecoline natural	Ecoline black	Ecoline yellow
Lactide[a]	$C_6H_8O_4$	144	799.9	+	+	+	+	+	+	+
2,5-Furandione,3,4-dimethyl	$C_6H_6O_3$	126	736.9	+	−	−	−	+	−	−
2,5-Furandione,3-methyl	$C_5H_4O_3$	112	629.1	+	+	+	−	+	−	−
2,5-Furandione	$C_4H_2O_3$	98	465.1	+	−	+	−	+	−	−
Toluene[a]	C_7H_8	92	381.2	+	−	−	−	−	−	−
2,3-Butanedione	$C_4H_6O_2$	84	345.2	−	+	−	−	+	−	+
Propionic acid	$C_3H_6O_2$	74	284.3	+	+	+	+	+	+	+
2-Butanone	C_4H_8O	72	173.3	+	+	+	+	+	+	+
Acetic acid[a]	$C_2H_4O_2$	60	214.8	+	+	+	+	+	+	+
Formic acid	CH_2O_2	46	144.4	+	+	+	+	+	+	+
Acetaldehyde[a]	C_2H_4O	44	118.6	+	+	+	+	+	+	+

[a] Identified based on mass spectra library and standard.

A mass spectrum of most abundant volatiles (>5 cps on average) generated when heating lactide to 235 °C is shown in Fig. 3. The abundance of these volatiles in the sample's headspace increased markedly after the melting point of 116 °C was reached. The mass spectrum of lactide also revealed the presence of toluene ($(C_7H_8)H^+$, m93) which was confirmed using SPME-GC-TOFMS (see chromatogram in Fig. S1, supplementary material). It is unlikely that toluene is a product of thermal degradation of lactide, and it was not detected in any of the PLA samples using both PTR-MS and SPME-GC-TOFMS (Table 1 and Fig. 2). Instead, it was most probably present in the lactide standard, since toluene can be used during its synthesis and purification [26,27]. This might also be the source of toluene previously detected in PLA filaments [28], provided lactide was used as the substrate in their production (as opposed to synthesis from lactic acid).

As shown in Fig. 2, the emission profile of filaments with added colouring (black and yellow) is overall quite similar. In the case of the 'natural' filament, the rapid increase of emission occurred at a higher temperature (>220 °C). Since in practice during FDM 3D printing the nozzle temperature would seldom be set to above 220 °C, the addition of pigments and colourants to the filament might thus result in higher user exposure.

Similarly, only small differences between the emission profiles of the "ecoline" and "premium" grade filaments were observed, as shown in Fig. 4. The emission of particular compounds differed by, at most, a factor of two (in the case of acetic acid, m61). While the differences in filament grade might affect the printing properties and the quality of the end product, they seem to be less relevant than colour when assessing the user's exposure.

3.2. Emission of VOCs during 3D printing with PLA filaments determined using PTR-TOFMS

The results of the monitoring of VOCs emission from filaments heated gradually in small-volume headspace vials discussed in the previous section are useful for determining the emission profile of particular materials in relation to temperature. However, even when expressed in relation to the weight of the filament sample, they represent perhaps the most extreme emission scenario and are thus useful in assessing the potential risk associated with printing using particular materials. In practice, during 3D printing, only a short segment of the filament is melted in the nozzle and is then rapidly cooled using fans mounted on the printer head. As shown in Fig. 5, such conditions result in much lower immission within the enclosure compared to the headspace vial. While the enclosure was equipped with fans to facilitate the mixing of air within, the air exchange time was approx. 1300 s, as opposed to the approx. 24 s in the case of the headspace vial. This approximates well the actual use of a desktop printer, either within a dedicated enclosure or without one.

The most abundant OVOCs released during printing with all six filaments were lactide (m145), acetaldehyde (m45), acetic acid (m61), 2-butanone (m73), and the $(C_3H_3O)^+$ fragment (m55). Since the printer's nozzle rapidly reached the printing temperature of 220 °C, there was no initial lag phase in the emission profile, and the concentration of volatiles within the enclosure steadily increased until the end of printing. With the exception of the $(C_3H_3O)^+$ ion, the concentration of which in the case of the "premium" filament seems to be inversely correlated with the concentration of lactide, the

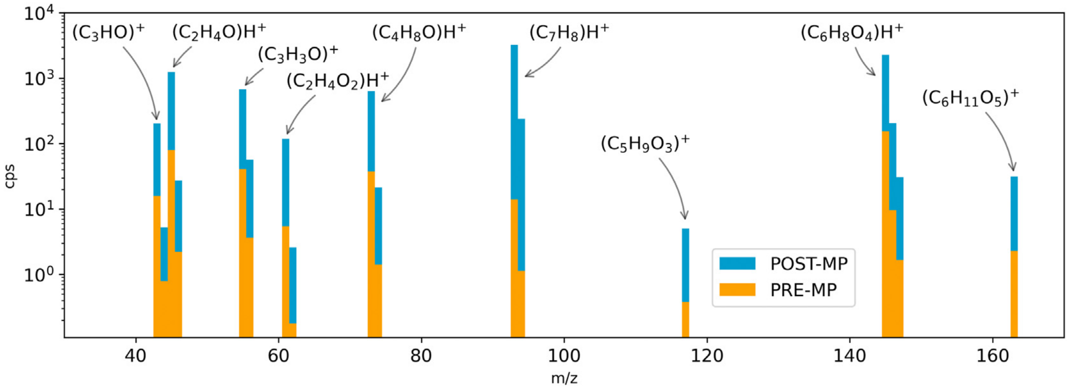


Fig. 3. Mass spectrum of the headspace of a lactide sample obtained using PTR-MS. The bins show spectra averaged before (PRE-MP) and after (POST-MP) reaching the melting point of 116 °C. Note the logarithmic scale.

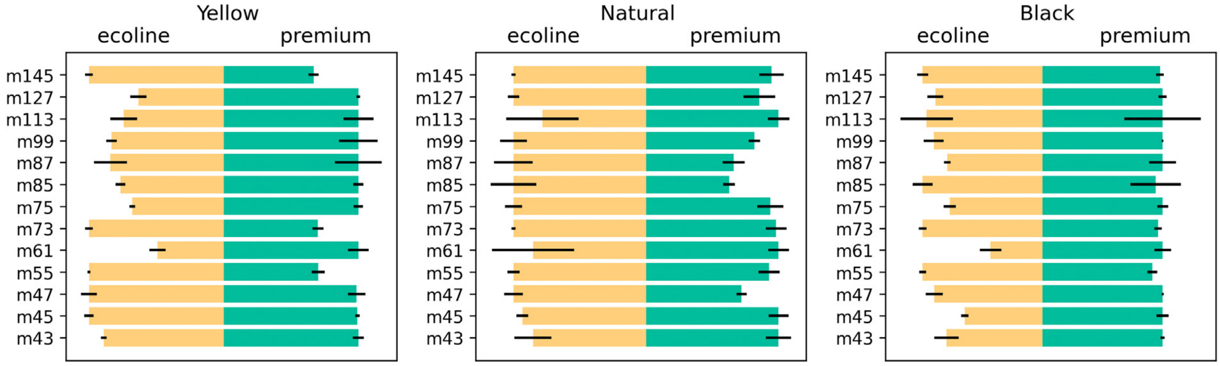


Fig. 4. Relative differences between the emission profiles of filaments of different grades at 200 °C. Black error bars denote SD ($n = 3$).

emission profiles of the filaments are not very dissimilar. In both filament grades the use of the “natural” variant, i.e. without added colourants, resulted in emission rates of lactide lower by approx. 20%. One notable outlier is the emission of acetaldehyde from the black “ecoline” filament which was nearly four times higher than in the case of other filaments. This is significant since acetaldehyde is considered a potential occupational carcinogen. However, its maximum concentration (~0.3 mg·m^{-3}) within the 0.13 m^3 enclosure remained below the threshold limit value for occupational exposure of 45 mg·m^{-3} [29].

The reasons for different emission rates of lactide between the different colour variants are not clear. In a previous study the emission of a monomer of ABS, styrene, was highest in the case of black filaments and lowest in the case of yellow filaments, with an intermediate emission in the case of the “natural” variant [10]. Possibly the admixture of colourants lowers the melting temperature of the filament. As shown in Fig. 2, the emission of lactide at its melting point is much lower in the case of the “natural” filament, than in the case of the black and yellow filaments. However, the exact composition of the filaments is a trade secret of the manufacturers, and further research, e.g. involving laboratory-extruded filaments with controlled composition, is needed to isolate and assess the impact of admixtures on the emission profile of different filaments.

4. Conclusions

In this work, a novel approach for monitoring the emission of VOCs from PLA filaments during their thermal degradation and 3D printing has been described. The use of proton transfer reaction mass spectrometry enabled direct sampling of the volatiles generated during the heating of PLA and real-time quantitative determination of these compounds. It also enabled obtaining detailed emission profiles of volatiles both in relation to temperature and to the duration of 3D printing. The emission characteristic changed after the melting point of lactide was reached, and then again after reaching the melting point of PLA filaments. The VOCs were identified using SPME-GC-TOFMS. The most abundant volatiles emitted during 3D printing were lactide, acetaldehyde, unknown $(C_3H_3O)^+$ ion, acetic acid, and 2-butanone. Of these, acetaldehyde is classified as a potential carcinogen, and so a threat to 3D printer operators exposed to it. However, the immission of

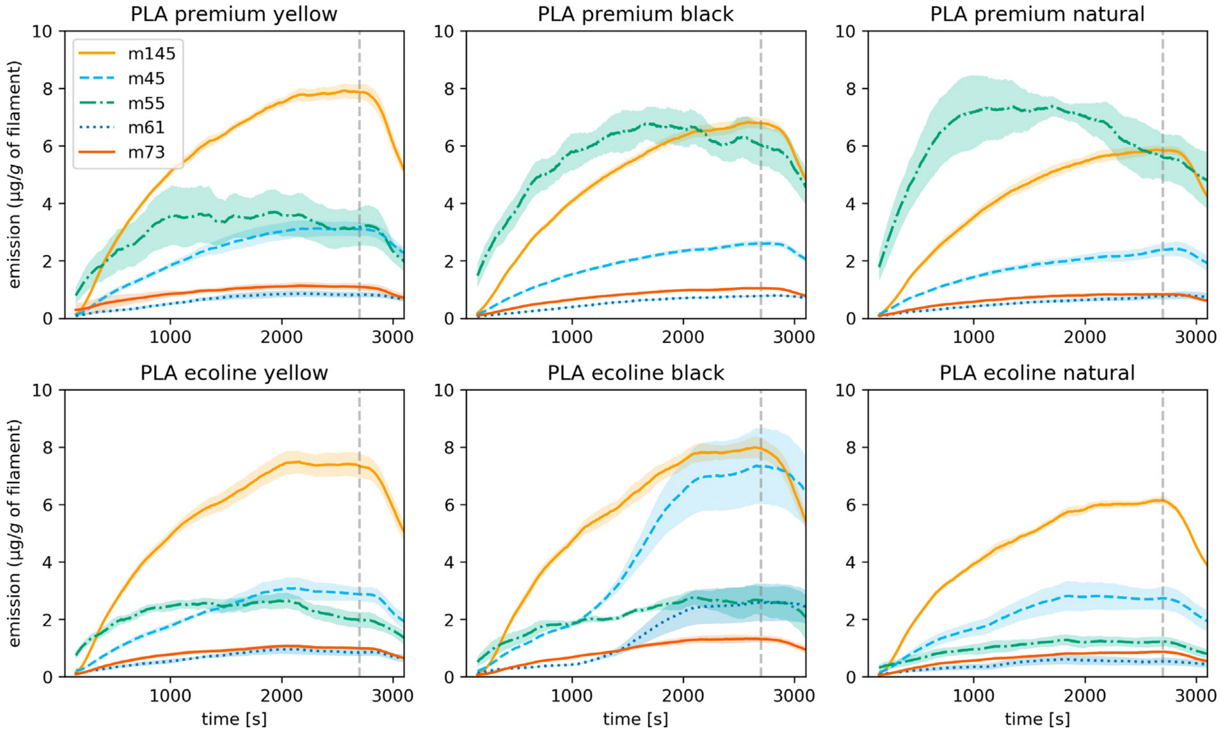


Fig. 5. Emission of main VOCs (threshold: 10 cps) during 3D printing with six different PLA filaments. The dashed vertical line indicates the end of printing. Plotlines denote the average value, and the shaded areas denote SD ($n = 3$).

acetaldehyde within an enclosure housing the 3D printer after over 40 min of printing was found to be below the threshold limit value outlined by the ACGIH. The emission profiles of various PLA filaments differed based on the grade of the product and also based on the added colourants. In the marketing materials, manufacturers refer to the print quality achievable with particular product lines, rather than to the potential user's exposure to volatiles, in contrast to e.g. manufacturers of resins for stereolithography (SLA), who market some of their products as safe in this regard.

The proposed approach can be used to broaden the understanding of the chemical processes taking place during the thermal degradation of polymers. In the particular case of FDM 3D printing, and in view of its prolific use, this translates to the assessment of the user's exposure to potentially harmful substances. A complete assessment of such exposure would involve, among others, the determination of pollutants adsorbed on the particulate matter emitted during printing, and of the condensed phase in general. However, the complementary use of SPME-GC-TOFMS for qualitative analysis and PTR-TOFMS for the real-time quantitative determination of VOCs released during printing provides a comprehensive understanding of the emission of VOCs during printing.

CRediT authorship contribution statement

Wojciech Wojnowski: Conceptualization, Methodology, Investigation, Data curation, Writing – original draft, Visualization, Funding acquisition. **Kaja Kalinowska:** Methodology, Investigation, Data curation, Writing – original draft. **Tomasz Majchrzak:** Methodology, Investigation, Writing – review & editing. **Bożena Zabiegała:** Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was funded by the National Science Centre (Poland), grant number 2018/31/N/ST4/00809.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2021.150181.

References

Stephens, B., Azimi, P., El Orch, Z., Ramos, T., 2013. Ultrafine particle emissions from desktop 3D printers. Atmos. Environ. 79, 334–339. https://doi.org/10.1016/J.ATMOSENV.2013.06.050.

Zhang, Q., Wong, J.P.S., Davis, A.Y., Black, M.S., Weber, R.J., 2017. Characterization of particle emissions from consumer fused deposition modeling 3D printers. Aerosol Sci. Technol. 51, 1275–1286. https://doi.org/10.1080/02786826.2017.1342029.

Ryan, T., Hubbard, T., 2016. 3 D printing hazards. Am. Soc. Saf. Eng., 56–62. www.asse.org.

Byrley, P., George, B.J., Boyes, W.K., Rogers, K., 2019. Particle emissions from fused deposition modeling 3D printers: evaluation and meta-analysis. Sci. Total Environ. 655, 395–407. https://doi.org/10.1016/j.scitotenv.2018.11.070.

Contos, D.A., Holdren, M.W., Smith, D.L., Brooke, R.C., Rhodes, V.L., Rainey, M.L., 1995. Sampling and analysis of volatile organic compounds evolved during thermal processing of acrylonitrile butadiene styrene composite resins. J. Air Waste Manage. Assoc. 45, 686–694. https://doi.org/10.1080/10473289.1995.10467396.

Unwin, J., Coldwell, M.R., Keen, C., McAlinden, J.J., 2012. Airborne emissions of carcinogens and respiratory sensitizers during thermal processing of plastics. Ann. Occup. Hyg. 57, 399–406. https://doi.org/10.1093/annhyg/mes078.

Liu, X., Khor, S., Petinakis, E., Yu, L., Simon, G., Dean, K., Bateman, S., 2010. Effects of hydrophilic fillers on the thermal degradation of poly(lactic acid). Thermochim. Acta 509, 147–151. https://doi.org/10.1016/j.tca.2010.06.015.

Schaper, M.M., Thompson, R.D., Detwiler-Okabayashi, K.A., 1994. Respiratory responses of mice exposed to thermal decomposition products from polymers heated at and above workplace processing temperatures. Am. Ind. Hyg. Assoc. J. 55, 924–934. https://doi.org/10.1080/15428119491018420.

Kopinke, F.-D., Remmler, M., Mackenzie, K., Möder, M., Wachsen, O., 1996. Thermal decomposition of biodegradable polyesters—II. Poly(lactic acid). Polym. Degrad. Stab. 53, 329–342. https://doi.org/10.1016/0141-3910(96)00102-4.

Wojnowski, W., Kalinowska, K., Gębicki, J., Zabiegała, B., 2020. Monitoring the BTEX volatiles during 3D printing with acrylonitrile butadiene styrene (ABS) using electronic nose and proton transfer reaction mass spectrometry. Sensors 20, 5531. https://doi.org/10.3390/s20195531.

Zontek, T.L., Ogle, B.R., Jankovic, J.T., Hollenbeck, S.M., 2017. An exposure assessment of desktop 3D printing. J. Chem. Heal. Saf. 24, 15–25. https://doi.org/10.1016/J.JCHAS.2016.05.008.

Floyd, E.L., Wang, J., Regens, J.L., 2017. Fume emissions from a low-cost 3-D printer with various filaments. J. Occup. Environ. Hyg. 14, 523–533. https://doi.org/10.1080/15459624.2017.1302587.

Wojtyła, S., Klama, P., Baran, T., 2017. Is 3D printing safe? Analysis of the thermal treatment of thermoplastics: ABS, PLA, PET, and nylon. J. Occup. Environ. Hyg. 14, D80–D85. https://doi.org/10.1080/15459624.2017.1285489.

Stefaniak, A.B., Lebouf, R.F., Yi, J., Ham, J., Nurkewicz, T., Schwegler-Berry, D.E., Chen, B.T., Wells, J.R., Duling, M.G., Lawrence, R.B., Martin, S.B., Johnson, A.R., Virji, M.A., 2017. Characterization of chemical contaminants generated by a desktop fused deposition modeling 3-dimensional printer. J. Occup. Environ. Hyg. 14, 540–550. https://doi.org/10.1080/15459624.2017.1302589.

Kim, Y., Yoon, C., Ham, S., Park, J., Kim, S., Kwon, O., Tsai, P.-J., 2015. Emissions of nanoparticles and gaseous material from 3D printer operation. Environ. Sci. Technol. 49, 12044–12053. https://doi.org/10.1021/acs.est.5b02805.

Davis, A.Y., Zhang, Q., Wong, J.P.S., Weber, R.J., Black, M.S., 2019. Characterization of volatile organic compound emissions from consumer level material extrusion 3D printers. Build. Environ. 160, 106209. https://doi.org/10.1016/j.buildenv.2019.106209.

Weber, R.J., Zhang, Q., Wong, J.P.S., Davis, A., Black, M., 2016. Fine particulate and chemical emissions from desktop 3D printers. Int. Conf. Digit. Print. Technol. 121–123.

Majchrzak, T., Wojnowski, W., Wasik, A., 2021. Revealing dynamic changes of the volatile profile of food samples using PTR–MS. Food Chem. 364, 130404. https://doi.org/10.1016/J.FOODCHEM.2021.130404.

Ellis, A.M., Mayhew, C.A., 2014. Proton Transfer Reaction Mass Spectrometry. John Wiley & Sons Ltd, Chichester, UK https://doi.org/10.1002/9781118682883.

Blake, R.S., Monks, P.S., Ellis, A.M., 2009. Proton-transfer reaction mass spectrometry. Chem. Rev. 109, 861–896. https://doi.org/10.1021/cr800364q.

Schripp, T., Fauck, C., Salthammer, T., 2010. Interferences in the determination of formaldehyde via PTR-MS: What do we learn from m/z 31? Int. J. Mass Spectrom. 289, 170–172. https://doi.org/10.1016/j.ijms.2009.11.001.

Holzinger, R., Joe Acton, W.F., Bloss, W.W., Breitenlechner, M., Crilley, L.L., Dusanter, S., Gonin, M., Gros, V., Keutsch, F.F., Kiendler-Scharr, A., Kramer, L.L., Krechmer, J.J., Languille, B., Locoge, N., Lopez-Hilfiker, F., Materi, D., Moreno, S., Nemitz, E., Quéléver, L.L., Sarda Esteve, R., Sauvage, S., Schallhart, S., Sommariva, R., Tillmann, R., Wedel, S., Worton, D.D., Xu, K., Zaytsev, A., 2019. Validity and limitations of simple reaction kinetics to calculate concentrations of organic compounds from ion counts in PTR-MS. Atmos. Meas. Tech. 12, 6193–6208. https://doi.org/10.5194/AMT-12-6193-2019.

Majchrzak, T., Wojnowski, W., Lubinska-Szczygeł, M., Różańska, A., Namieśnik, J., Dymerski, T., 2018. PTR-MS and GC-MS as complementary techniques for analysis of volatiles: a tutorial review. Anal. Chim. Acta 1035, 1–13. https://doi.org/10.1016/j.aca.2018.06.056.

Plage, B., Schulten, H.R., 1990. Thermal degradation and mass-spectrometric fragmentation processes of polyesters studied by time/temperature-resolved pyrolysis-field ionization mass spectrometry. Macromolecules 23, 2642–2648. https://doi.org/10.1021/ma00212a008.

Aguilera, C., Lüderwald, I., 1978. Strukturuntersuchung von Polyestern durch direkten Abbau im massenspektrometer, 5. Polyester aus Terephthalsäure und/oder Bernsteinsäure und Hydrochinon. Die Makromol. Chemie. 179, 2817–2827. https://doi.org/10.1002/macp.1978.021791201.

Ehsani, M., Khodabakhshi, K., Asgari, M., 2014. Lactide synthesis optimization: investigation of the temperature, catalyst and pressure effects. E-Polymers. 14, 353–361. https://doi.org/10.1515/epoly-2014-0055.

Process for the preparation of L-lactide of high chemical yield and optical purity US8895760B2, 2013

Azimi, P., Zhao, D., Pouzet, C., Crain, N.E., Stephens, B., 2016. Emissions of ultrafine particles and volatile organic compounds from commercially available desktop three-dimensional printers with multiple filaments. Environ. Sci. Technol. 50, 1260–1268. https://doi.org/10.1021/acs.est.5b04983.

CDC Immediately Dangerous to Life or Health Concentrations (IDLH): Acetaldehyde - NIOSH Publications and Products, (n.d.). https://www.cdc.gov/niosh/idlh/75070.html (accessed June 29, 2021).