**Characterization of particle emission from Thermoplastic additive manufacturing**

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# Abstract

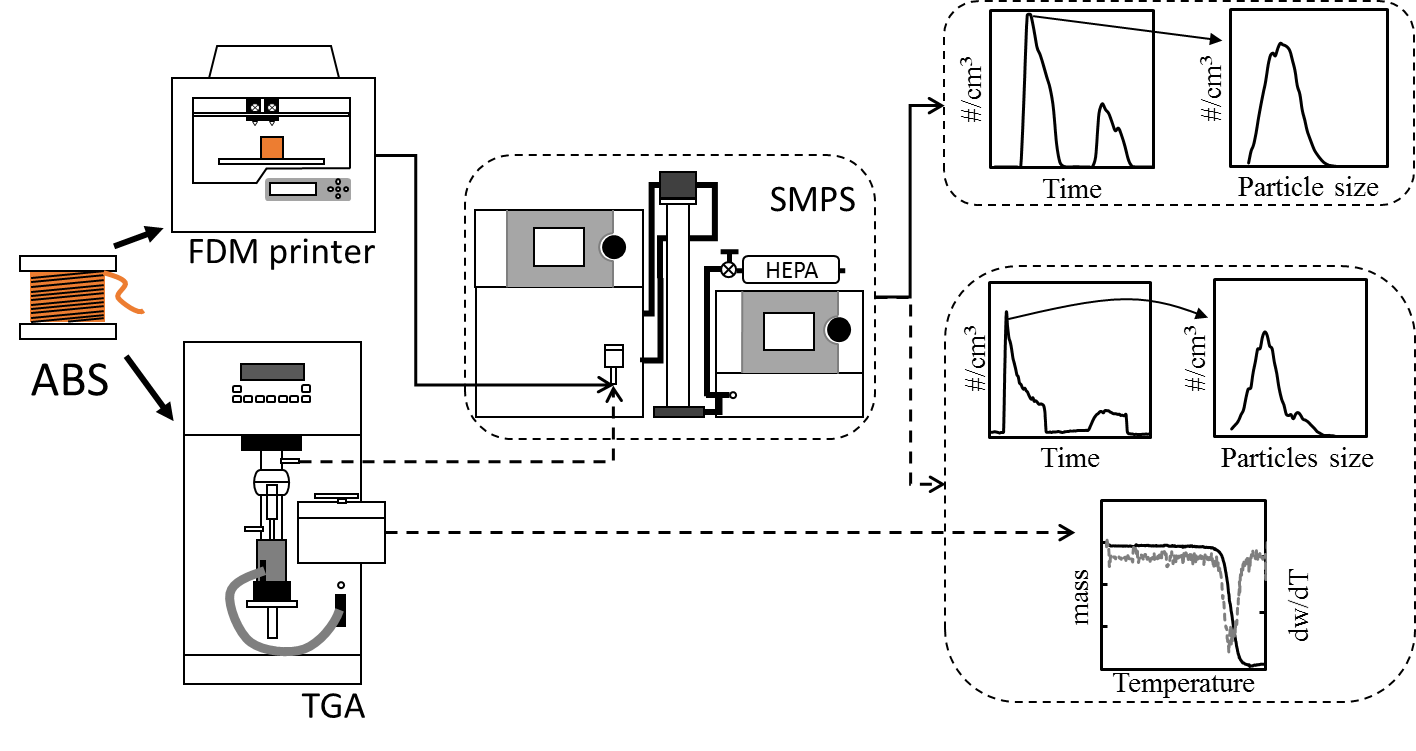
Particle emission from fused-deposition modelling (FDM) desktop 3D printer has raised concerns regarding indoor personal health due to the increased accessibility of printers. This study characterises the size, number and morphology of the emitted particles to understand particle formation processes and propose guidelines for their abatement. The effects of extruder temperature, layer height, filament colour and shape of printing object on particle characteristics emitted from a desktop 3D printer have been investigated. For first time, a novel thermogravimetric analysis (TGA) method is developed to emulate printing process, which offers an insight into particle formation during extruder heating, standing-by and during the printing process.

Printing temperature and printing layer height demonstrate a major effect on the ultra-fine particles (UFP) emitted, while ABS filament colour shows a minor effect on the nanoparticle emissions. Local temperature and concentration of volatile organic material emitted from the filament play an important role on the number of particles formed, while printing duration and air change rate (ACH) affect particle size, morphology and emission rate. The results provide guidelines to develop printing settings that will lead to lower UFP emissions for improved indoor air quality. The developed TGA method demonstrates the qualitative behaviour of particle emissions from a material under heating, which is approximately proportional to an FDM printers’ particle emissions; facilitating increased repeatability, time and cost efficiency for printing material assessment.

**Keywords:** additive manufacturing, 3D-printer, fuse-deposition modelling (FDM), acrylonitrile butadiene styrene (ABS), ultra-fine particle (UFP), emissions

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**Graphical abstract**



# Highlights

* UFP concentrations directly depends on printing temperature and filament feed rate.
* Particle emissions are directly proportional to filament thermal decomposition.
* TGA method can be used as a qualitative indicator of particle emissions from FDM printers.
* TGA demonstrates the effect of filament temperature on particle emissions.

# Introduction

In recent years rapid prototyping, otherwise known as additive manufacturing (AM), using 3D printers has been the method of choice for various applications such as aerospace, military, health and research & development [1], [2]. Its popularity is due mainly to the cost and time efficiency of prototyping a three-dimensional representation of small-scale modelling [3]. The price of 3D printers has been substantially reduced compared to their predecessors [4], [5], which has led to a significant number of 3D printers being owned in the private sector. Fused deposition modelling (FDM) 3D printers utilize a heated nozzle to melt solid thermoplastic filament and deposit melted plastic layer by layer to form a solid three-dimensional object. The most common filament materials are acrylonitrile butadiene styrene (ABS) and polylactic acid (PLA) [4]–[8]. ABS is known to have better mechanical strength in comparison to PLA, and therefore ABS has gained more popularity when the prototype needs to resist substantial amounts of force [5].

During the extruding process, the plastic filament is heated, injected through the nozzle and deposited on the bed plate to form the desired part. When materials (in this specific case: thermoplastic) are heated, solid particles can be formed and volatile and semi-volatile components released, which can be adsorbed/condensed onto the surface of solid particles and/or nucleate, leading to the formation of new particles (nucleation) [4], [7]. However, most 3D printer users are not aware of exposure to these ultrafine particles as there are a limited number of studies related to the particle emissions from desktop 3D printers. Indoor 3D printer usage is another indoor activity that contributes to significant indoor-generated particles [9], [10] apart from activities related to cooking [11]. These studies agree that a significant amount of nanoparticles up to magnitude of 1012 #/min (corresponding to approx. 105 #/cm3)[4], [6]–[8] in the size range of 5 to 50 nm can be emitted. The cornerstone study by Oberdörster et al. [12], mathematically evaluates the deposition fraction of nanoparticles in the human respiratory tract [13]. They obtained 30% deposition of 5 nm particles and 50% deposition of 20 nm particles in the alveolar region [12], [13]. Additional studies demonstrate the genotoxic activity of particles emitted from combustion sources on human lymphocytes [14], as well as alveolar exposure to particles causing inflammation leading to cardiovascular repercussions [15], [16]. The clinical relevance of the deposition rates predicted for nanoparticles [17] are in the size range of those emitted from 3D printers. Additionally, the change in concentration of indoor particles could affect blood pressure and heart rate in a study on indoor air filtration [18]. However, there are only a limited number of 3D printing studies that examine the different parameters which influence particle emissions, these are summarised in the supporting information section (Figure S1).

The effect of thermoplastic material type on 3D printing particle emissions have been investigated. A study on the effects of filament materials was carried out on a Prusa i3 Fused Deposit Material (FDM) 3D printer using various type of filaments; PLA from corn starch, wood, copper, bamboo & Flex PLA, styrene-free co-polyester (CP), carbon-fibre filled CP, nylon & Ninja-Flex [4]. The results report that wood & bamboo filaments emitted particle at the rate as high as 2.78×1012 and 2.65×1012 #/min, respectively. A test protocol namely, Blue angel method (BAM) [19] developed for characterizing laser printer emissions was used to conduct tests on six commercially available FDM 3D printers, using 3 filaments (ABS, PLA and nylon) [7]. The filament compound was found to vary for each company which affected printing performances. PLA filament emitted less SVCs (semi-volatile compound) which resulted in lower NPF (new particle formation) and lowered growth rate. Filament colour, brand, material and printer brand [8] are also factors that have be found to affect particle emissions. Different brands of PLA and ABS filaments have also shown a significant effect on particle emission characteristics. The particle yield of 3D printing using ABS has been shown to be between 3 to 1000 times more than the PLA filament equivalent [7], [8]. Higher particle emissions have been observed when printing using ABS filament, found to be caused by the higher extrusion temperature in comparison to PLA [5], [8], [20] which leads to more SVCs generated due to nucleation. For instance, particle emission rate from printing ABS is usually in 1010 #/min range while printing PLA may have emission rate of 108 #/min range [5], [21]. For a specific printing material, higher extrusion temperatures also led to higher peak of particles number for all filament materials. Elevated temperatures can increase the concentration and thus partial vapour pressure of organic material [4] which enhances volatile organic components condensation and/or particle nucleation.

Printer settings may also influence particle emissions. Bed plate temperature has been reported to influence ultra-fine particle (UFP) concentration [8], where UFPs are defined as diameter <100 nm. Additionally, at 100oC, ABS can emit vapour that condenses on existing particles in the vicinity and increases existing particle size and mass [7]. On the other hand, extrusion speed (or feed rate) has been shown to exhibit moderate effects on particle number and total particle concentration due mainly to the combined effects from nozzle thermal decomposition and rate of material fraction [20]. P. Azimi et.al [8] designed a test shape to evaluate the performance of AM, by combining a range of shapes thought to dynamically influence printer emissions. However, they concluded that changing the printing shape from a NIST (National Institute of Standards and Technology) test part into a cube resulted in an insignificant change of UFP emission magnitude. Instead UFP emission rates highly depend on printing duration. Q. Zhang et al. [7] estimated Particles Emission Rates (PERs) as a function of print time and total particle (TP). They found nanosized particles at the start of filament melting temperature independent from the mechanical part moving inside the printer. Printing malfunctions e.g. a clogged nozzle, could also cause a significant increase in particles number due to longer exposure time of filament material to the hot nozzle that enhanced filament thermal decomposition and increased particles vaporization. Ultra-fine particles or nanoparticles dominate over 90% of particle number distribution [7]. It was proposed that forcing air cooling onto the extruder nozzle could affect particle formation and its dynamics. In addition, more than 60% of total particle surface area emission was accounted for between a particle sizes of 50-200 nm. The relationship of total particle number and total particle mass was linear. The author suggested that particle yield could be determined by TP divided by printing time (yield = TP/t) or TP/object mass, but this parameter may pose some uncertainties due to different filament feed rate for different printing object.

There is scarce research literature, which aims to characterise particle emissions in terms of morphology, nanostructure and composition as well as to identify volatile organic components emitted from the printing process. Some authors have employed nanofiber-based air filter to sample particles [22], while [6], [23] have attempted to use transmission electron microscopy (TEM) in order to gain an insight the particles’ morphology, using similar methods to the previously developed for particles from combustion sources [24]. Obtaining particles to analyse with TEM can be a challenge due to small particle size and lack of carbon core resulting in inconclusive results from TEM [6]. Zontek et al. (2017) [23] successfully obtained TEM images of particles from a desktop 3D printer revealing that some of the particles from FDM printers also produce agglomerated particles similar to that of particles from diesel engine exhaust gas [25]. Volatile organic compound (VOC) emissions from FDM printers have also received attention from researchers [6], [26]–[28] due the potential health risks posed upon inhalation. ABS filament has been proven to emit more SVCs than PLA filament, which contributes to a significantly greater number of particle emissions. Overall, VOC emissions shows similar trends to particle emissions in term of concentration in given volume (i.e. room) [26].

This study aims to comprehensively understand the formation process of particle emissions derived from an FDM printer by means of particle characterization of the particle size, morphology and nanostructure. For the first time, a thermal gravimetric method has been created to gain novel knowledge on the relationship of thermal decomposition of the thermoplastic filament and particle emissions. The understanding of how particle formation is generated during the working cycle of the 3D printer operation process (i.e. pre-printing preparation, warm-up, printing phases) will increase knowledge towards particle formation prevention. This new understanding will offer direction to thermoplastic AM health and safety protocols in the workplace or during private use. Specific objectives are defined as: (i) to measure and characterize particle emission from FDM 3D printer using ABS filament, (ii) to study the parameters that affect particle emissions such as extruder temperature, layer height, printing speed and filament colour, and (iii) to understand how printing material thermal properties affects particle emission during the working cycle of printing.

# Materials and Methods

## Instruments

An FDM printer is used in this study, with 2 printing nozzles and a heated bed plate of 24.6 cm × 15.2 cm × 15.5 cm. The printer is equipped with an extruder fan and an active cooling fan. The extruder fan keeps the motor cool and disperses heat from the heat sink, while the active cooling fan cools the filament as it extrudes. A cover was positioned in the top of the printer to enable a closed space setup to minimise interactions within the laboratory. White ABS filament is used to maintain consistency of experimental results. Orange ABS filament is used for comparative study on the effect of colour on nanoparticle emissions. Printing settings are presented in table 1.

Table 1. Printing parameters.

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| **Parameter** | **Value** |
| Printing temperature | 220, 230 and 240°C |
| Build plate temperature | 110°C |
| Layer height | 0.1, 0.2 and 0.3 mm |
| Infill printing speed | 90 and 112.5 mm/s |
| Infill density/pattern | 100%/Lines |
| Number of shells | 2 |
| Shell printing speed | 40 and 50 mm/s |
| Gantry travel speed (not printing) | 150 mm/s |
| Filament diameter | 1.75 mm |

A Scanning Mobility Particle Sizer (SMPS) setup with Electrostatic Classifier (EC) model 3080 equipped with a Differential Mobility Analyser (DMA) 3081 and a Condensation Particle Counter (CPC) 3775 is employed to measure the particle size distribution (PSD). The measured particle size ranges from 7.77 to 273.8 nm and the scan up and scan down times were 45 s and 10 s, respectively. Setup operational parameters are shown in supporting information, see Table S1. Dilution system is not utilised. The sample probe is installed through an entry point at the top right corner of the printer, and the probe end is mounted in the side at the middle centre of the printing chamber.

A Thermogravimetric (TG) analyser, Perkin Elmer model Pyris 1, is used to evaluate thermal characteristic of filaments as well as particle emissions during the filament heating at several isothermal conditions within the TG analyser in order to gain the insight of how particles are formed by the 3D printing process. The temperature precision of the TG furnace is ±5°C and the microbalance precision is 0.001%.

Transmission electron microscopy was used to examine particles collected on TAAB™ carbon filmed copper grids from 3D printing of cube shape with extruder temperature of 230°C and 0.2 mm layer height.

## 3D printing test procedure

Test conditions for 3D printing are as shown in the supporting information section (Figure S2) where printing shape, extrusion temperature and printing layer height are varied. For the study of printing temperature on UFP emission characteristics a printing layer height of 0.2 mm, a bed plate temperature of 110°C and a flat shape were chosen as controlled parameters. In addition the effect of different sampling positions of the SMPS probe in the printing chamber area have been also studied.

The test shape for printing is classified into 2 forms: a flat square (referred as ‘flat’) (25 mm × 25 mm × 5 mm) and a cube (referred as ‘cube’) (25 mm × 25 mm × 25 mm) with designated printing configurations (e.g. printing temperature, bed plate temperature, layer height, %infill, rate, etc.). The test procedure is divided in the following steps:

1. After turning on the printer, allow the printer to heat up both nozzles to working temperature.
2. Clean up the nozzle using ethanol and ensure minimum residual filament material is left in the nozzle.
3. Blow/ventilate printing chamber with compressed air to flush out residual particles
4. Close printer cover during printing and measurement.
5. Start data logging particle size distribution for the background particle level
6. Emitted particle concentration during printing sampling is measured for pre-printing, during printing and post printing.

## Thermogravimetric analysis (TGA) procedure

The TGA method can be divided into 2 tests for different purposes; ramp-up test and isothermal test. The ramp test is designed to characterise the properties of the ABS filament. Isothermal tests are designed to understand particle emissions at different temperatures to emulate particle formation and growing mechanisms from real FDM printer.

During the ramp-up test, heating ramps of 3°C/min were used as shown in the supporting information (Figure S3). A heating rate of 3°C/min is selected here based on compromise between time duration requires for TGA and accuracy of kinetic reaction. Prior to the test, the sample was maintained in an ambient air atmosphere at 40°C for 10 minutes in order to minimise the effect of ambient temperature fluctuations and buoyancy effect [29]. Then the temperature was increased until the filament mass completely decomposed according to the designated heating programme. The sheath flow rate (40 mL/min) and balance flow rates (60 mL/min) were controlled constant during all experiments.

For the isothermal test, a new methodology was developed in order to relate thermogravimetric characteristics of the material to particle emissions from real printing process. The outlet flow of the TG chamber was coupled to the inlet of the SMPS to measure particle size distributions during the isothermal heating programmes (Figure S3). Isothermal temperature (230-250°C) was chosen based on the actual printing temperature (with ±10°C step). Isothermal programme at 350°C was selected to observe particle emission of ABS filament at temperature beyond ABS’s decomposition temperature onset [30].

In order to gain an insight of the relation between the effects of consecutive printing on total particle concentration a cyclic heating controlled test is designed to mimic printing behaviour. The TGA heating programme is designed to emulate this situation by heating up quickly from 31°Cto 250°C at the heating rate of 50°C /minute. Then the furnace temperature is kept isothermal at 250°C for 30 minutes to mimic ‘during-printing’ process. After that, cooling down of sample is performed at approximately 50°C /minute to 31°C and remain at this temperature for 30 minutes before repeating the same heating process again. Note that all these tests are conducted in N2 atmosphere.

## Data analysis methods

Three experimental tests have been performed to confirm the reproducibility of the results for the evaluation of 3D printing temperature, filament colour, layer height, printing speed as well as for the TGA experiment. Average results are presented throughout the manuscript. The average particle size distribution at the time at which maximum particle concentration levels are reached (peak) and the confidence interval calculated at 95% confidence level are presented.

Particle emission rate (ER) estimation (eq. 1) is proposed by Stephen et al. [5] which has been used by other researchers [4], [8], [9], [21] in the same field. Where V is the considered chamber volume in m3, C(tn+1) is total particle concentration (#/cm3) at time a step later, C(tn) is total particle concentration (#/cm3) at time (tn), tn is time step of particles measurement, LUFP is the particles loss rate constant (lpm) and  is the background particle concentration inside the chamber before printing. LUFP is the estimation from log-linear regression based on particle decay which has similar calculation to that of air change rate (ACH) calculation [31]. LUFP is direct proportional to ACH.

 (1)

The total number of particles emission (Esum) (in #) [21] is expressed in eq. 2, where Et is average particles emission rate during printing process (#/min) and toperation is total time of printer operation (minute).

 (2)

The value of total number of particles by eq. 2 is not normalised. Results between printing samples with different mass will be incomparable. Therefore, the authors [8], [21] propose a normalised total particles emission number with respect to mass or ‘yield’ (Em) (in #/g) of filament used during printing process as shown in eq. 3.

 (3)

Where mobject is the mass of printed object in gram (g).

# Results and discussion

## Effect of 3D printing working cycle and sampling position on nanoparticle emissions

### a) Flat-shape printing sample

Figure 1 (left) illustrates total particle concentration of printing flat shape. The results reveal that the highest number of particles is observed during the first specimen is being printed, while there is a substantial reduction of total particle concentration for the second and third specimens printing process as shown in Figure 1 (left). This phenomena has been reported by most authors [5]–[8], [32]. As the filament is continuously heated by the extruder, this leads to an increase in the concentration and thus partial pressure of volatile printing material in a clean environment (i.e. low local particle concentration before the first printing). The emitted vaporised VOC cools down and then the local conditions in terms of particle pressure and temperature are closer to the saturation region for the printing species. As there is limited availability of particle surface for the volatile species to be adsorbed, those are transformed into ultrafine particle (UFP) by nucleation process.

Total particle concentration and geometric particle mean size are reduced over printing time for each specimen. The increase in the average particle size is due to (i) a reduction in the number of small particles due to a decrease in the number of particle formation from emitted vapour, particle deposition in the printing chamber walls due to Brownian movement majorly affecting to small size particles and particle to particle collisions as well as to (ii) an increase in the number of large size particles due to particle to particle collisions [7] and surface growth by condensation/adsorption of newly emitted material volatile.

As printing progressed, the total particle number begins to decline, and particle mean size sharply increases (up to 33 nm). During printing of the flat shape, average emission rate of 1.01x1010 particle per minute (#/min) and maximum emission rate of 5.16x1010 #/min are observed. When the printing process ends, a noticeable fast decay of total particle concentration and size can be observed as total particle concentration returns to the background level. A printing time of 16 minutes is required to finish printing the flat shape specimen which is considered to be of short duration for 3D printing. Thus, when printing small part sizes, the particle concentration does not reach steady-state particle concentration and size levels.

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| **Figure 1.** Evolution total particle emissions (left) and particle size distribution (right) from printing flat shape as printing progresses. | |

Figure 1 (right) illustrates particle size distribution (PSD) from printing the flat shape, which indicates that particles emitted from the printing process noticeably change their size towards larger sizes whilst the number of particles decline as printing progresses. The results reveal that the printing process produces ultrafine particle (UFP) [33] as the primary mode of particle emissions throughout the duration of printing. This type of semi-volatile material is identified in a previous work [7] as being generated by the continuous heating of extruder nozzle. Meanwhile, the number of particles in accumulation mode gradually increases its concentration through particle agglomeration [7], [34], aggregation and/or surface growth; whilst the number of UFP is reduced, which partially contributes to the shift in particle size towards larger particle size. In addition, particle deposition due to Brownian motion also affect to the decrease in the number of small size particles leading to lower total particle concentration levels and larger average particle size. This particle loss causes a noticeable reduction in the total particle number concentration.

Figure S4 in the supporting information demonstrates the effect of sampling in the printing chamber area. The probe is positioned on the right side and left side of the printing chamber at two different heights to observe the change. The results reveal that the particle growth inside the printing chamber is uniform and symmetric which is confirmed by the size distribution profiles that remain relatively same size between positions of each sampling attempt. Sampling closer to the time of the particle formation peak indicates larger mean particle diameter (30 nm approx.) in comparison to particles sampled near the end of printing (20 nm approx.) regardless of sampling position. The uniformity and symmetry of particles distributed in the printing chamber is due to the extruder cooling fan and the movement of the extruder itself which assist particle homogeneity. In addition, the extruder also releases added heat into printing chamber which increases printing chamber temperature and affected natural air change rate (ACH) of the chamber.

### b) Cube-shape printing sample

Figure 2 (left) depicts total particle concentration and emission rate from printing the cube shape which indicate similar trends as discussed with printing flat shape. The printing duration of cube shape was significant longer (55 minutes) which allowed total particle concentration to reach steady-state approximately 15 minutes after printing started. According to Figure 2 (left), total particle concentration suddenly increases and reaches the peak around 4×105 #/cm3 and then drastically decreases to approximately 2×105 #/cm3 (for the first printing specimen) after 20 minutes, approximately. After 20 minutes of printing onward, total particle concentration becomes virtually constant and remains steady-state throughout printing process until the end of printing. The second and third printing specimen exhibit very similar total particle concentration pattern, but also show a noticeable smaller UFP peak concentration and lower total particle concentration during steady-state. This phenomenon is attributed to the saturation of particles inside the printing chamber and the collisions between existing particles with newly formed particles decreasing the total particle number concentration.

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| **Figure 2.** Evolution total particle emissions (left) and particle size distribution (right) from printing 3D shapeas printing progresses. | |

Figure 2 (right) demonstrates the shift of particle size distribution towards larger diameter as the printing process progresses for the second specimen (referred to printing process at t = 72, t = 87 and t = 100 minute). The results support the hypothesis on the particle agglomeration process as previously discussed. The chart indicates a similar trend of particle size distribution over printing time for the flat shape however, with a longer printing duration for the cube shape, more agglomeration and deposition are expected and thus allows particles to reach their mean size (33 nm, approx.) during steady-state. Therefore, the PSD peak of printing cube specimen is shifted towards a larger particle size than that of printing flat specimen. It can be concluded that steady-state particle emissions from the 3D printer will be reached after approximately 17 minutes at given printing settings.

The TEM images in Figure 3 illustrate the agglomeration of particles from printing ABS filament. A TEM grid has been left inside the printer chamber for a period of time comparable to the duration of the printer to exclude the possibility of influence from ambient/background particles in the TEM analysis. Particles were not found on the grids during the TEM analysis. TEM analysis demonstrates chain-like particle clusters, but without any crystal structures, therefore the nanostructure is significantly different to carbonaceous particles emitted from combustion sources [25]. Primary particle diameter (dp0) measurements reveal primary particle diameter ranges from 20 nm up to 100 nm, while the size of measured agglomerated particles is extended up to approximately 400 nm. This initially supports our hypothesis that agglomeration is a mechanism that contributes to the increase of particle size. However, due to very small number and low resolution of TEM images obtained, further statistical analysis was unachievable.

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| **Figure 3.** TEM image of particles collected from printing ABS filament. | |

## Effect of 3D printing temperature and filament colour on nanoparticle emissions

### a) 3D printing temperature

Printing at each extruder temperature was repeated three times to confirm reproducibility of the results, to ensure that the result are not affected by the saturation of particles from previous printing cycles. Figure 4 confirms the relationship between printing temperature and UFP emissions seen in previous studies [4], [6], [7]. The elevated temperature was reported to increase vapour pressure of volatile organic compound (VOC) and more semi-volatile compounds (SVC) were emitted, thus particles formation through nucleation are promoted. Overall, number of UFP emitted from printing process is highly sensitive to the change of designated extruder temperature as particle number increases more than two orders of magnitude between the results from 220°C and 240°C as shown in Figure 4.

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| **Figure 4.** Overview effect of printing temperature on particle emissions. | |

### b) Filament colour at 230°C

Figure 5 demonstrates no statistically significant differences in particle size, but more noticeable changes in number of total particle concentration profiles and emission rate between particles emitted from printing flat parts using white and orange ABS filaments. Differences in terms of filament material thermal and physical properties between various filament colour have been also identified in other publications [21]. However, the average geometric mean particle size at steady-state of both filament colours are practically the same (approx. 36 nm) as for their size profiles over time.

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| **Figure 5.** Overview effect of filament colour on particle emissions. | |

The effect of colour on particle emission has been investigated in previous studies [8], [32] which reported that filament colour affected UFP emission concentration. Yi et al. [32] hypothesise that filament colour could affect UFP emission due to different additive used to dye the filament. However, filament brand was identified by other researchers [7] to have a major effect on the different filament UFP emission characteristic and filament colour only has minor effect on UFP emissions.

## Effect of 3D printing settings on nanoparticle emissions

### a) Layer height

Figure 6 reveals the effect of changing printing layer height on particle emissions. In general, particle size distributions present a similar shape for all layer heights being more than 95% of particles by number UFP. Printing with a 0.2 mm layer height shows the largest average geometric particle diameter, while printing layer height of 0.1 and 0.3 mm exhibit similar values. In printing aspect, increasing printing layer height can be projected as increasing the filament feed rate e.g. the corresponding feed rates of layer height of 0.1, 0.2 and 0.3 mm are 10.84, 17.74 and 27.11 gfilament/h, respectively. Therefore, increasing layer height results in reduced printing duration [35]. The results demonstrate direct relationship between filament feed rate to particles emission rate as higher feed rate means increased availability of fresh filament material to be decomposed enhancing particle formation, particularly comparing 0.1 mm layer height to 0.2 and 0.3. This result disagrees with explanation in previous work by Deng et al. [20] that increasing feed rate would lead to more heat dissipation of filament (due to higher thermal conductivity or heat transfer), thus limited thermal decomposition of filament volatile component.

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| **Figure 6.** Overview effect of printing layer height on particle emissions. | |

In terms of the total number of particles emitted during printing process, layer height of 0.2 mm demonstrates the maximum total particle (in #/g) number among all other layer height. Increasing printing layer height to 0.3 mm produces a similar level of particle emissions (in #/g), while reducing printing layer height to 0.1 mm generates the least number of particles among other layer height. Therefore, with given printing speed (90 mm/s for infill and 40 mm/s for shell), layer height of 0.1 mm minimises the thermal decomposition and the release of material fraction of the filament. The results reveal that reducing printing duration by increasing feed rate through increasing layer height is not an effective approach for particles emission reduction. On the other hand, reducing layer height (to 0.1 mm) can drastically reduce total particle emission at the cost of longer printing duration.

### b) 3D printing speed

The effect of different FDM printing speed illustrates observable changes on particle emission characteristics as shown in Figure 7. The analysis indicates a 17% increase in average filament feed rate when printing speed is 25% faster than default values (90 mm/s for infill and 40 mm/s for shell). Increasing printing speed by 25% contributes to considerably lower total particle concentration. There is also a noticeable increase in geometric mean particle size in comparison to standard printing speed at the start of the printing process. These phenomena are supported by the average particle size distribution profiles which are marginally shifted towards larger particle size. The cumulative particle number in UFP mode also shows a slightly decrease from 94.49% to 93.62% which confirms that more particles are formed in accumulation mode. Increasing printing speed results in increment of filament feed rate. The results agree with results in previous work done by Deng et al. [20], which depicted the lower particle count when feed rate was larger. In this case, feed rate increases as printing speed is increased and printing layer height remains the same (0.2 mm for all printing speed) following the same methodology as Deng et al. [20]. According to the result, an increase in printing speed, within the conditions studied here, causes larger heat dissipation from extruder nozzle which leads to reduction of filament thermal decomposition; therefore, lower particles are emitted. The experiments were performed at constant 0.2 mm layer height leading to already a significant amount of available fresh filament material to be decomposed as well as the faster movement of the extruder itself contribute to the thermal effect become dominant over the higher availability of filament material.

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| **Figure 7.** Overview effect of printing speed on particle emissions. | |

## Understanding 3D printing nanoparticle emissions through material thermal analysis

### a) Thermogravimetric analysis of ABS

Thermogravimetric analysis of the 3D printing thermoplastic filaments has been performed to understand the effect of temperature on the release of volatile material from the filament. An initial heating ramp for the filament material has been performed to choose the range of temperatures which will be studied in the isothermal analysis as well as to observe the effect of printing temperatures on material devolatilisation. It is well known that high heating ramp rates shift the removal of volatile material to higher temperatures [36], [37]. This is a consequence of the shorter available time for the oxidation process to take place at high heating ramp values and therefore, the oxidation temperature continues to increase. This is a typical feature of any kinetic-controlled reaction under non-isothermal conditions (the higher the temperature ramp, the higher the temperatures required to complete the reaction). Indeed, some methods have been proposed in the literature to analyse the kinetics of a reaction based on the displacement of the MMLRT (Maximum Mass Loss Rate Temperature) under different temperature ramps [38]. As described in the TGA procedure section a heating rate of 3°C/min is chosen.

Figure S5 in the supporting information illustrates the thermal analysis for the ABS filament. The devolatilization profile is within the range for pyrolysis results from ABS reported by other researchers [30], [39]. The inflection point of ABS filaments is approximately 470°C, which are much higher than the 3D printing operation temperatures. Three temperatures close to the 3D printing operation temperatures are chosen (230, 240 and 250°C) and 350°C which produces a more significant release of material volatile.

### b) Particle emissions at different volatilization temperatures for ABS

Ambient particle size distributions inside the TGA furnace are shown in the supporting information (Figure S6). The mean size of particle is approximately 24 nm and average total particle concentration of 2.63x103 #/cm3. This ambient particle size distribution represents the background particle emission in order to determine the particle concentration exclusively due to the devolatilization process of the thermoplastic material.

Figure 8 demonstrates the TG-SMPS analysis of ABS filament using our new proposed isothermal heating programme at 230, 240, 250 and 350°C which have different particle size distribution trend from the measurement from actual printing process in real 3D printer. The particle size distribution profiles shown in Figure 8 illustrate PSD at 11, 24 and 39 minutes after start printing which referred as “Peak UFP”, “Transition” and “End of printing”, respectively.

The profiles of particles emitted from TGA evolves from “Peak UFP” to “Transition” and “End of Printing” similarly to the effect seen in real 3D printing tests due to coagulation, aggregation and deposition mechanisms. This trend occurs for temperatures close to working printing temperatures (230, 240 and 250°C), while particle size distribution at higher temperature (350°C) remain similar size at approximately 40 nm through heating process, most likely due to the continuous supplied of volatile material. In general, higher temperature of TG furnace results in significant high particle concentration and large average particle diameter due to constant release of high amount of volatile compound that transforms into new particle formation (NPF) [7] by condensation which enhances further particles collision, which is also consistent to the results seen in 3D printing process.

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| **Figure 8.** Particle size distribution of filament during TGA at different temperatures. | |

Figure 9 (right) shows cumulate particle distribution in various TGA heating programme temperatures, in which more than 90% of total particles in number are UFP (<100 nm diameter). According to results, printing temperature range (230 to 250°C), the cumulate particle size distribution in UFP size range increases with temperature. For instance, approximately 95.1%, 97.4% and 98.8% of total number of particles are classified in UFP at 230, 240 and 250°C, respectively. However, the cumulative curve of TGA at 350°C noticeably shifts towards large particle diameter due to the high availability of volatile material and particles to growth already formed ones, while approximately 95.2% of particle number is present as UFP.

Overall, all weight loss curves indicate a sharp decrease at the start of heating programme which is consistent with the high peak of total particle concentration and decrease in mean particle size as shown in Figure 9 (left) being consistently to 3D printing process. The similarity between the particle concentration and size trends found in couple TG-SMPS analysis in comparison to particles released in the real 3D printing process (e.g. Figure 2) should be noted, even though there are differences on how filament material is introduced to the heat source and air change rate. In TGA, the specific amount of sample is presented, and particles are emitted as heat is applied. Only limited amount of material can be vaporised and transforms into particle at given temperature. Meanwhile, in real printing case using 3D printer, continuously feeding of filament pass-through extruder and provides limited duration of exposure of material to heat source (extruder) which limits heat dissipation to filament. In addition, the different of air change rate (ACH) between testing material in TG furnace (ACHTG = 127.6 h-1) and real 3D printing chamber (ACH3D = 1.0 h-1) can affect NPF. Those differences result in noticeable lower total particles concentration (as shown in Figure 9, left) and lower coagulation rate for the case of particles emitted from the TG method in comparison to 3D printing. The results indicate that despite the differences in the heating duration of the filament and experimental conditions, the TGA method can be used as a qualitative indicator of particle emissions from FDM printers. It is considered that the key linkage between the two methods confirms the research hypothesis that particle emissions from 3D printing are majorly governed by the vaporisation process of the filament material which is highly dependent on the thermal properties of the material. Further, the volatile material undergoes nucleation, adsorption/condensation, coagulation and deposition processes which depend on the availability of volatile material, particle concentration and size, temperature, air change rate to determine particle evolution.

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| **Figure 9.** Overview effect of filament thermal analysis on particle emissions. | |

### c) Cyclic heating: Attempt to emulate and understand consecutive printing cycle for ABS filament

This section aims to simulate the situation when printing multiple samples with short interval in between, and with printer cover closed to gain an insight of the relation between the effects of consecutive printing on reducing the of total particle concentration as seen in Figure 1 and 2.

Generally, 98.54% of total particles are classified as UFP as shown in Figure 10. The overview of total particle concentration profile demonstrates similar trend to total particle concentrations from real printing process of both proposed sample shapes (flat and cube) in Figure 1 and 2. The peak in total particle concentration in zone A (Figure 10, top right) is consistent to the significant sample weight reduction in the TGA (Figure 10, bottom right). Meanwhile, insignificant ABS filament sample weight loss can be observed in zone C, which results in significantly less total particle concentration in comparison to heating process in zone A. Similar PSD profile to results with TGA (previously discussed in Figure 8) is also obtained in cyclic heating test.

Note that weight loss is solely contributed by vaporisation of filler content in polymer (ABS). The compositional analysis of ABS is out of the scope of this study, thus Auto-Stepwise [29] method was not introduced. A perceptible weight gain can be seen for all testing conditions which is the effect of reduced buoyancy force [40] upon the crucible pan as the furnace temperature increases.

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| **Figure 10.** Particle size distribution, total particle concentration and geometric mean size, cumulative particles number, and TGA of ABS filament of cyclic heating using single sample. | |

# Conclusions

In this study, the AM of thermoplastic material using a desktop 3D printer was shown to produce UFP emissions, with a size range that has demonstrated clinical impact on the human respiratory tract [17]. A new method which combines the measurement of real time particle size distributions with TGA of the printing filament has been successfully developed to understand particle formation. Extrusion and TGA heating temperatures were performed to characterise the particle emissions in terms of number, size and morphology. It can be concluded that the total particle concentration reaches steady-state if sufficient printing duration is left, in this case the printer takes approximately 17 minutes. Maximum particle emission rate of 5.16x1010 #/min is observed with average emission rate of 1.01x1010 #/min for short duration printing (flat shape). Particles images from TEM reveal different primary particle shape and structure from typical combustion particulate matter, however; they still exhibit similar agglomerate-like cluster. Overall, printing temperature has the most significant effect on particle emission rate. It has been demonstrated that carefully selection of printing temperature, layer height and speed can readily reduce UFP emission.

The developed TGA method provides information on the behaviour of particulate emissions of the filament materials under heating. It could be employed, for instance, as a qualitative indication of the materials’ propensity to form particles without the time and cost implications associated with repeated 3D printing. Whilst manufacturing variables are crucial parameters to explore, TGA provides a methodology for the qualitative assessment of materials against printing temperatures as well as contributing to the understanding of particle formation mechanisms. Further investigation is required to systematically compare the quantitative results of TGA with 3D printing chamber experiments, including the evaluation of the applicability of the TGA method to other types of filament. Further investigation is required to evaluate the application of the developed TGA method to other type of filaments and to other sources of particle emissions.

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