Indoor Air Concentration from Selective Laser Sintering 3D Printer using Virgin Polyamide Nylon (PA12) Powder: A Pilot Study

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Abstract: Environmental emissions from additive manufacturing (AM) have attracted much attention recently. The capability in fabricating complex part make AM famous in developing prototype and product in various industries, especially in aerospace, medical, automotive, and manufacturing industries. However, the study on emission and exposure mainly focusses on the desktop type such as fused deposition modelling. This study investigates the emission and indoor concentration from powder bed fusion of selective laser sintering (SLS) technologies. Prior to the investigation, virgin PA12 has undergone characterization in terms of morphology, size and thermal analysis. Calibration block using virgin polyamide nylon (PA12) is selected to be printed in this study. Parameters such particulate matter size 2.5 µm (PM 2.5), total volatile organic compound (TVOC), carbon dioxide (CO^2), formaldehyde, temperature and relative humidity (RH) are set to be monitored through real-time sampling of 8 hours based on Industry Code of Practice on Indoor Air Quality 2010 by Department Occupational Safety and Health (DOSH) Malaysia. Four phases of the printing process involve are background data, preprinting, during printing and post-printing. Based on the study it was found that PM 2.5 and CO^2 exceed the acceptable limit recommended by DOSH Malaysia during the preparation of powder (preprinting) at 1218 ppm and 1070 µg/m^3 respectively. Meanwhile TVOC concentration was influenced by the sintered powder temperature and recorded at 0.5 ppm. Temperature, relative humidity and formaldehyde were maintained throughout the SLS process. Mitigation strategies using mechanical ventilation and personal protective equipment (PPE) are recommended to be used to reduce the potential of occupational hazard to the operators.

Keywords: Additive manufacturing, selective laser sintering, indoor air quality, occupational exposure, and 3D printing

1. Introduction

Additive manufacturing (AM) has been widely applied in various type of industries, including automotive, constructions, biomedical, and aerospace. It is estimated that by 2025, AM could generate and impact the global economy of 200 billion – 600 billion USD [1]. The capability of AM in fabricating a wide range of structures and complex geometries make AM stands out as one of the promising technology presently. The process of joining materials to make objects from three-dimensional data (3D) are using various kind of materials including metals, polymers, ceramic, composite or biological materials [2]. Several AM technologies exist, depending on material and process category. Table 1 below summarizes AM process technologies that present worldwide.

Table 1: AM process, technologies and materials [3], [4].

Process	Technology	Materials
Material extrusion	FDM	Thermoplastics
Material jetting	MJM	Photopolymers, thermoset plastic or wax
Binder jetting	3DP	Plastic and metal powder, with binding agents
Sheet lamination	LOM	Paper with adhesives
Vat photopolymerization	SLA	Liquid photopolymer, ceramic
Powder bed fusion	SLA, SLM, EBM	Polymer or metal powders
Direct energy deposition	LMD, LENS	Metal powders

Notes: FDM (fused deposition modelling), MJM (material jetting machine), 3DP (3D Printing), LOM (laminated object manufacturing), SLA (stereolithography), SLM (selective laser melting), EBM 9electron beam melting), LMD (laser metal deposition), LENS (laser engineered net shaping).

In the last three decades, AM technologies have been progressively developed. The potential to reduce cost, waste, and ability to produce complex design and customization makes AM more preferable in industry and consumer. Therefore, AM has drawn high interest from industries, research and academic communities [5]. The interest from industries and consumer increase the question on occupational exposure of AM to the operators and indoor air quality. The industrial processing of thermoplastics where above 180 °c to 280 °c could lead to various exposure of chemical and aerosol emission [6]. Meanwhile, Jianwei Gu et al. in their study revealed that 3D printing emission likely consists of semi-volatile substances where can be found in particles and gas phases during operation of 3D printing [7]. Other electronic devices also may be exposed to variety of chemical and aerosol emission [8]–[10]. The impact of occupational exposure and poor indoor air quality has been identified as a major contribution of occupational diseases and sick building syndrome [11]–[13].

Polymers powder are the most common material used in SLS. Polyamide (PA) like nylons (PA12) is semi-crystalline polymers were reported to have high strength, fatigue resistance, high thermal stability and excellent surface resolution [14]. During SLS printing process, only powder which heated by the scanning action will crystallize to become the final product, and others remain and turn to recycled powder as presented in Figure 1. SLS is using a laser as a power source to sinter the material, which is in powder forms such as nylon 11, nylon 12 also known as polyamide 11 (PA11), and polyamide 12 (PA12). The powder is then sintered on a platform layer by layer and stick together to turn into a solid object. In contrast to other approaches, this technology does not require any supporting object to print any kind of designed product [15], [16].

Respirable and inhalable dust (PM1, 2,5 and 10 µm), volatile organic compound and other chemical compound are exposed to the environment and harmful to the operator and indoor air quality. Justin et al. [18] have address the impact of SLS present a higher potential for physical hazard and exposure of ultrafine particles (UFP) from FDM 3D printer. Health impact from AM process has been discussed by several researchers. The popularity of fused deposition modelling (FDM), and low cost of the process make FDM among top 3D printer that leads in environmental emission study of AM [19]–[25]. Nevertheless, the study on SLS emission still limited due to its high cost of operation especially machine and powder. To date, Pal Graff et al., [26] have conducted a pilot study on occupational exposure on SLS 3D printer, using metal powder. The operator of the machine exposes direct exposure from powder handling, thus process control, personal protective equipment nor using less hazardous material might reduce the cause. This paper investigates airborne emission of respirable dust, and another environmental emission from SLS 3D printer using polyamide (PA12) nylon powder.
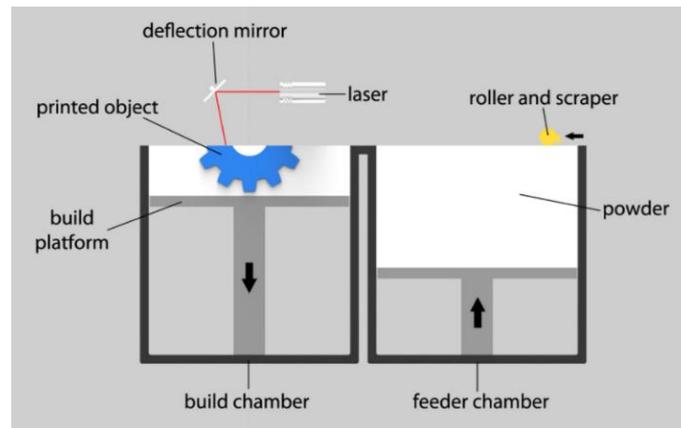
Figure 1:Typical SLS chamber[14]

2. Methodology

The polyamide nylon (PA12) virgin powder is collected from well-known SLS powder supplier. The powder was purchased (RM 400/kg) with bulk density of 0.4 g/cm^3, density of part 0.95 g/cm^3, melting point 183°C and the powder is in white color. Before airborne investigation begins, polyamide nylon (PA12) powder was undergone characterization to understand on morphology, composition, sizer and thermal analysis [27]. Prior to the investigation, polyamide nylon was characterized in term of its morphology, particle size analysis, and thermogravimetric analysis. The environmental emission monitoring from selective laser sintering (SLS) are divided into four phases, where:

A: Background data
B: Pre-processing (powder preparation and powder mixing)
C: Processing (SLS printing)
D: Post processing (powder cake break)

2.1 Characterization

Thermogravimetric analysis (TGA) is used to measure the weight changes in a material as a function of temperature or time under the controlled atmosphere. TGA also used to determine the material decomposition and thermal stability. In this work, thermal analysis properties of polyamide nylons (PA12) were analyzed using a Thermal Gravimetric Analyzer Linseis Model. Thermal analysis was conducted at room temperature until 600ºC with heating rate 10 ℃ / min. Scanning Electron Microscopy (SEM) is used to observe images of surface morphology of the powder[22-23]. It has a magnification range of 5,000-50, 0000 and operates at 2.0 kV – 5.0 kV of accelerating voltage. Particle Size Analysis (PSA) is used to observe the tabulation size of the powder. PA12 nylon sample was collected and undergo size analysis. The tabulation size of PA12 powder before SLS 3D printing process were analysed to measured particulate matter exposed during powder preparation phase [30].

2.2 Experimental setup

Selective laser sintering (SLS) 3D printer is manufactured by Farsoon model SS402P located at SLS Laboratory FTKMP of Universiti Teknikal Malaysia Melaka (2°16'40.4"N 102°16'32.4"E). The SLS machine has an external dimension size of 2660mm x 1540mm x 2150mm and weight of 3000 kg. The maximum build product in the SLS chamber is 400mm x 400mm x 450mm. CO^2 is used as a laser with 100W power while scanning speed is 12.7m/s. The laser wavelength is 0.3mm and 0.1mm thickness of powder layer for every rotating roller. Calibration block from the manufacturer [7], [31] with dimension 143mm x 143 mm x 23 mm was set to be print in this study as depicted in Figure 2. The laboratory is set to be 20 °C and relative humidity to be maintained around 60% [32]. The sampling strategies such as a number of sampling point, sample position, sampling period and sampling technique accordingly to Industry Code of Practice on Indoor Air Quality 2010, Department of Occupational Safety and Health (DOSH) Malaysia [33]. Total time for the measurement is 8 hours (480 minutes) for calibration block printing. The environmental emission monitor the ing from SLS is divided into four phases, where a) background data; b) pre-processing (powder mixing), c) processing (SLS printing), and d) post processing (powder cake break).Real time monitoring were used to measure respirable particulate matter (PM2.5), total volatile organic compound (TVOC), carbon dioxide (CO^2), temperature and relative humidity

along the process. Table 2 presents equipment's involves in measuring airborne and environmental emission of SLS 3D printing process.
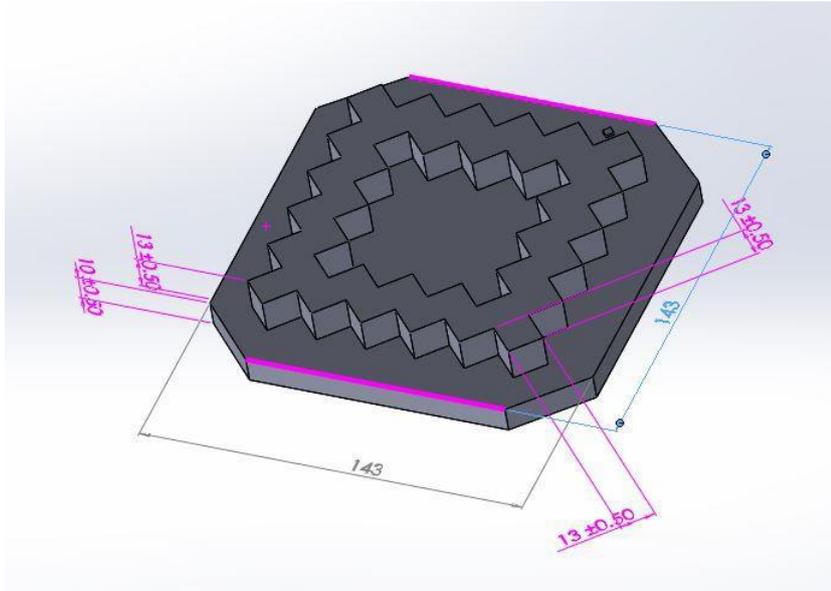
Figure 2: Calibration block layout by the manufacturer (in mm)

Table 2: Equipment's involves in emission monitoring

Parameter	Equipment's/ brand
Respirable particulate (PM2.5)	Dustrak (DRX Aerosol monitor model 8533, USA, TSI Inc)
Total volatile organic compound (TVOC)	ppbRAE monitor (ppbRAE 3000, USA, RAE System Inc)
Carbon dioxide (CO_2)	Environmental Monitor (EVM 7, USA 3M)
Formaldehyde	Formaldemeter htV-m (PPM Technology, UK)
Temperature (°C)	Environmental Monitor (EVM 7, USA 3M)
Relative humidity (RH)	Environmental Monitor (EVM 7, USA 3M)

The sampling strategies such as a number of sampling point, sample position, sampling period and sampling technique are according to the Industry Code of Practice on indoor air quality 2010. The interval times for data measurement were 5 minutes. There are two rooms involve in this project with a dimension of 6 m length x 4 m width x 3 m height where 24 m² involves as depicted in Figure 3.

Legends:
A- 3D Printer
B- Cooling fan
C- Powder cleaning machine
D- Mixing machine
E- Sand blasting machine
S1- Sampling point 1
S2- Sampling point 2
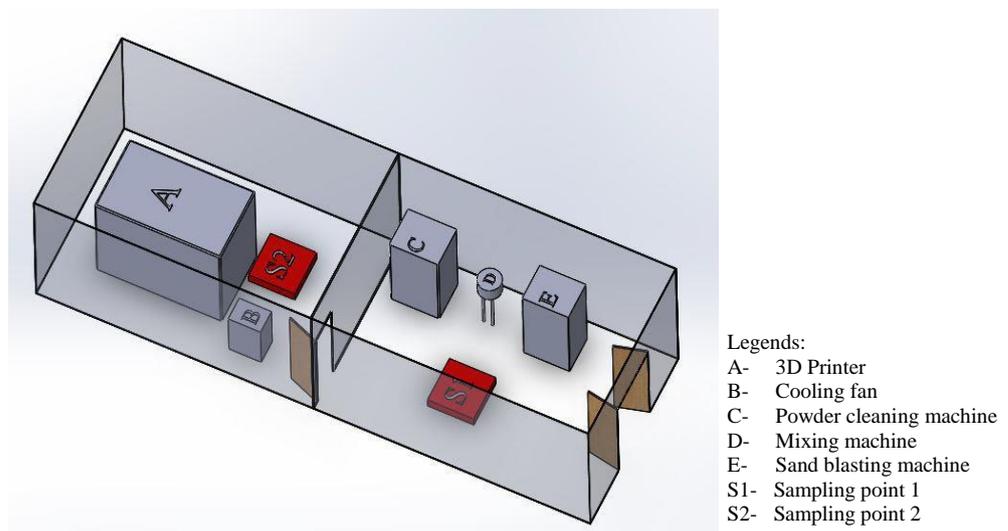
Figure 3: Sampling points and SLS laboratory arrangement

2.3 SLS Printing Process

Selective laser sintering is categorized as a powder bed fusion AM process. SLS printing process divided into three main parts:1) preparation of powder/material, 2) SLS printing process and 3) post-processing. Preparation and post-processing identified as the main source of dust contribution in the laboratory [34]. Figure 4 enlighten the whole process of SLS printing process. Background data were monitored for 30 minutes before the powder preparation start. Figure 4 (a)-(d) illustrates the activity involves in the pre-printing process (30-140 minutes). The powder was weighted accordingly to the SLS machine recommendation. Figure 4(d) shows that the SLS machine is operated at 140-360 minutes. Figure 4 (f)-(h) present the post-printing task (360-480 minutes). The total time taken for this monitoring is 8 hours [33].
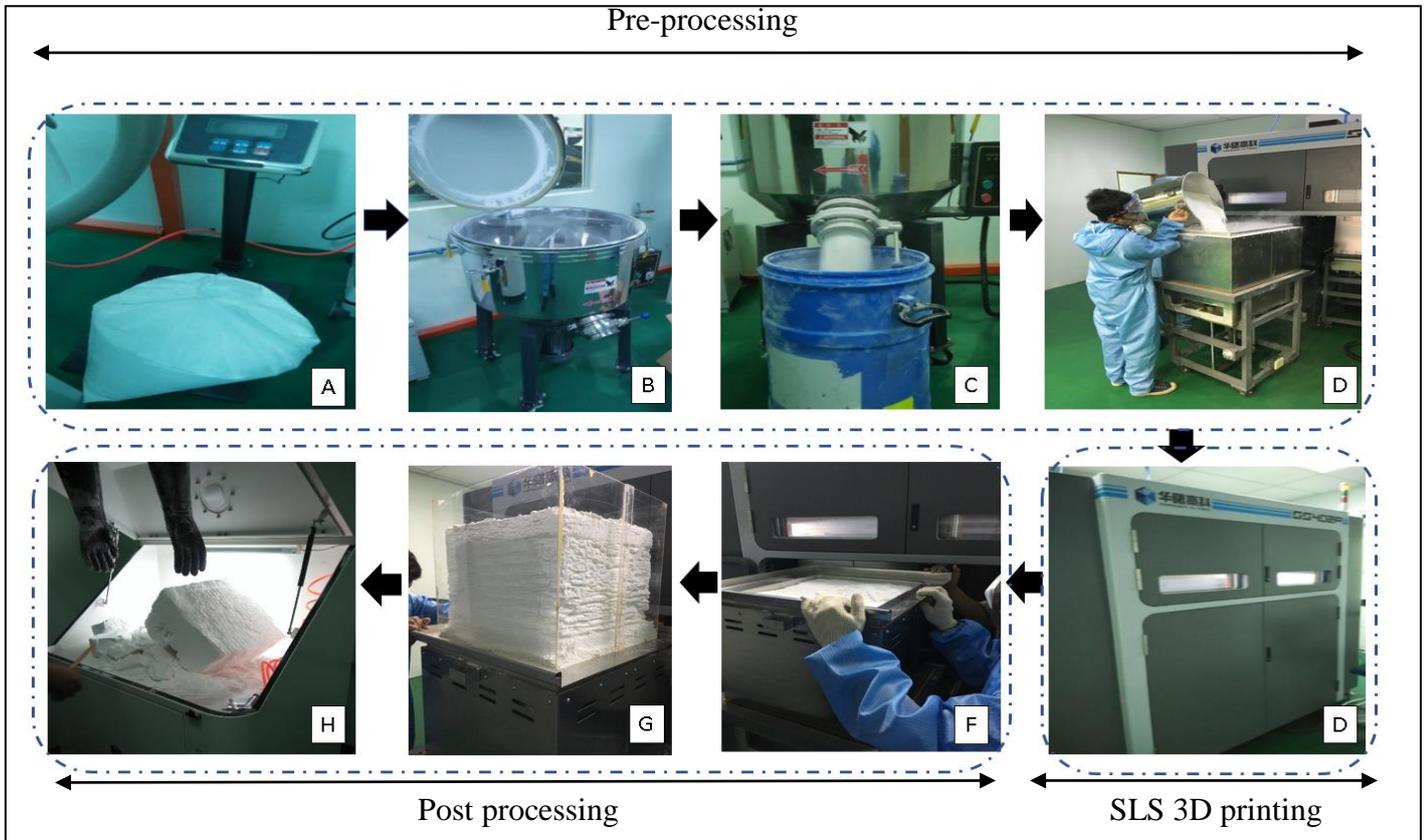
Figure 4: SLS 3D printing process

3.   Results and Discussion

Several analyses were done to investigate the characteristics of the virgin polyamide nylon (PA12). Scanning electron microscopy (SEM), particle size analysis (PSA), thermogravimetric (TGA) and derivative thermo-gravimetric (DTG) analysis presented in this study. Indoor concentration during four phases of SLS printing process was also presented.

3.1   Morphology, Size Tabulation and Thermogravimetric

Figure 5 shows the SEM images of virgin PA12 nylon powder. As shown, the PA12 powder relatively uniform sphere shapes. The regular shapes and particles sizes of PA12 powder obey Gausian distribution, conducive to the powder flowability. This behaviour will make is easy for the powder to spread in the SLS chamber [35]. The spherical structure and size also confirmed by the particle size analysis (PSA), with size distribution around 60µm as depicted in Figure 6 (a). Meanwhile, Figure 6 (b) illustrates TGA and DTG of the virgin PA12 powder. Remarkably, TGA curve shows several steps of mass loss: (i) at temperature around 300ºC, a low level of water absorption which is about 10% was observed, (ii) at around 300ºC to 400ºC with another 10% loss, (iii) at around 400ºC to 480ºC, corresponds to the most important mass loss during thermal decomposition and (iv) final mass loss at 550ºC. These results are in line with those obtained by Dotchev and Yusof [36], Dadbakhsh et al.[28] and Way et al. [37]. It was shown that the powder may be spreading continuously during SLS printing process as the process takes place at a temperature around 200ºC [36]–[38]. Therefore, dust exposure during powder handling could appear during and after the sintering process.
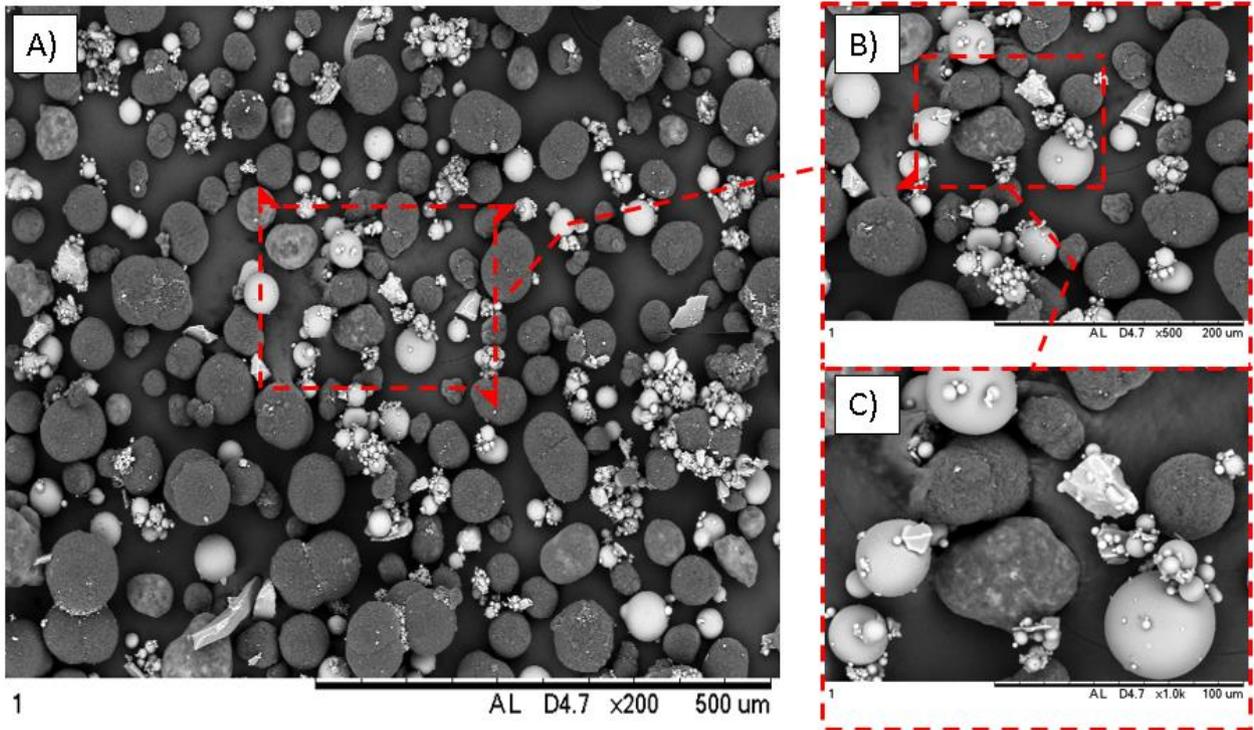
Figure 5: SEM images a) 200x resolution, b)500x resolution, c)1000x resolution
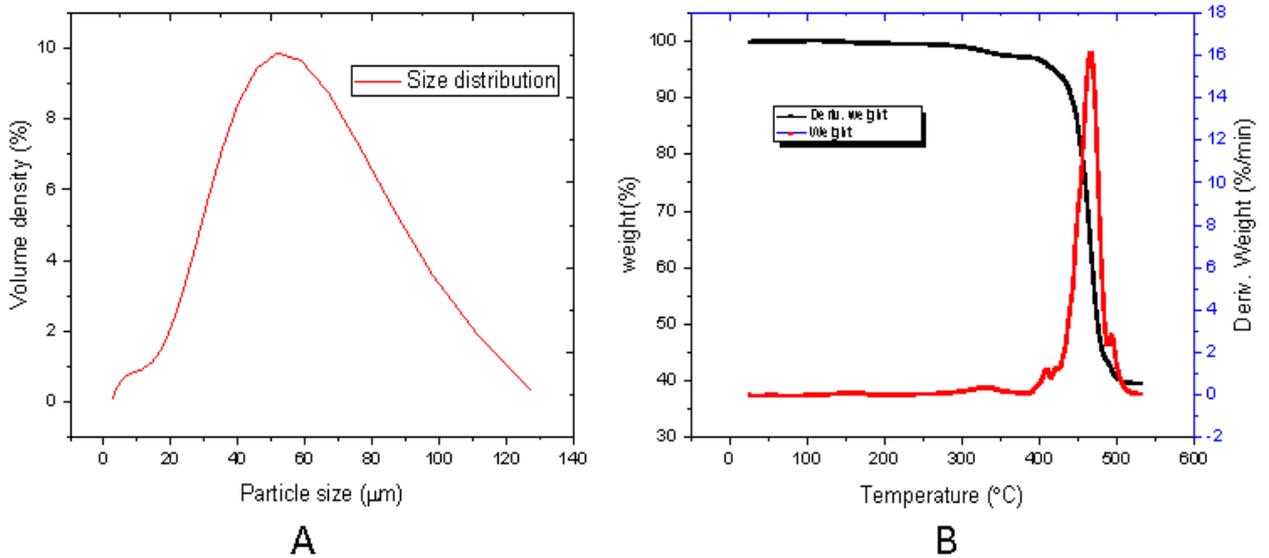
Figure 6: PSA and TGA analysis of PA12 SLS powder

3.2 Indoor air emission

The concentration of PM 2.5 and carbon dioxide (CO_2) are depicted in Figure 7. As expected, the concentration of PM 2.5 and CO_2 relatively maintain before any SLS process started. At 30 minutes, preparation of the powder where powder weight, mixture and transferring process to the SLS chamber. The generation of the respirable dust measured to be at peak along the process, at averaged 1070 µg/m^3 (SD=253.07). Meanwhile, CO_2 shows the highest value at minutes 95 at 1218 ppm. The trend tremendously decreases when the SLS printing process starts. The SLS chamber is fully closed, and the generation in the chamber is controlled. Post printing phases illustrate the increment of CO_2 at minutes 400, where shows 833 ppm. The respirable dust shows maintain the same trend with during printing process. The generation of respirable dust (PM2.5) are exposed significantly while operator handling the powder (preparation of powder) during the pre-processing task is agreed by Pal Graff et al., (2016) [26]. The release of CO_2 during powder handling may influence by the low efficiency of ventilation and air change rate in the laboratory. The roles of electronic

devices and mixing process increase the contribution of CO_2 [8], [32]. Table 3 indicates the indoor temperature, RH, TVOC and formaldehyde monitoring during this experiment. The temperature of the SLS laboratory shows the highest value during SLS printing process. This relatively influences by the heat generated from the laser sintering process [32]. The air conditioning supply to the room decreases the level of RH in the laboratory, where the trend shows decrease value and keep maintain around 50-60% of RH. Total volatile organic compound (TVOC) hit the highest peak at post printing period where 0.5 ppm. The TVOC emissions influenced by the powder cake that has been sintered, and this remarkably indicates the sintered powder during post-printing process will contribute to the increment of TVOC [7], [39]–[42]. Formaldehyde does not show any significant changes during the whole SLS process. The generation of PM2.5 and CO_2 during powder preparation exceed the recommended limit by DOSH Malaysia (PM 2.5 <0.15 mg/m3 and CO_2< 1000 ppm) [33][43]. In this SLS process, the respirable dust and particulate matter from SLS process shows significant exposure where tend to penetrate into human respiratory system [44].
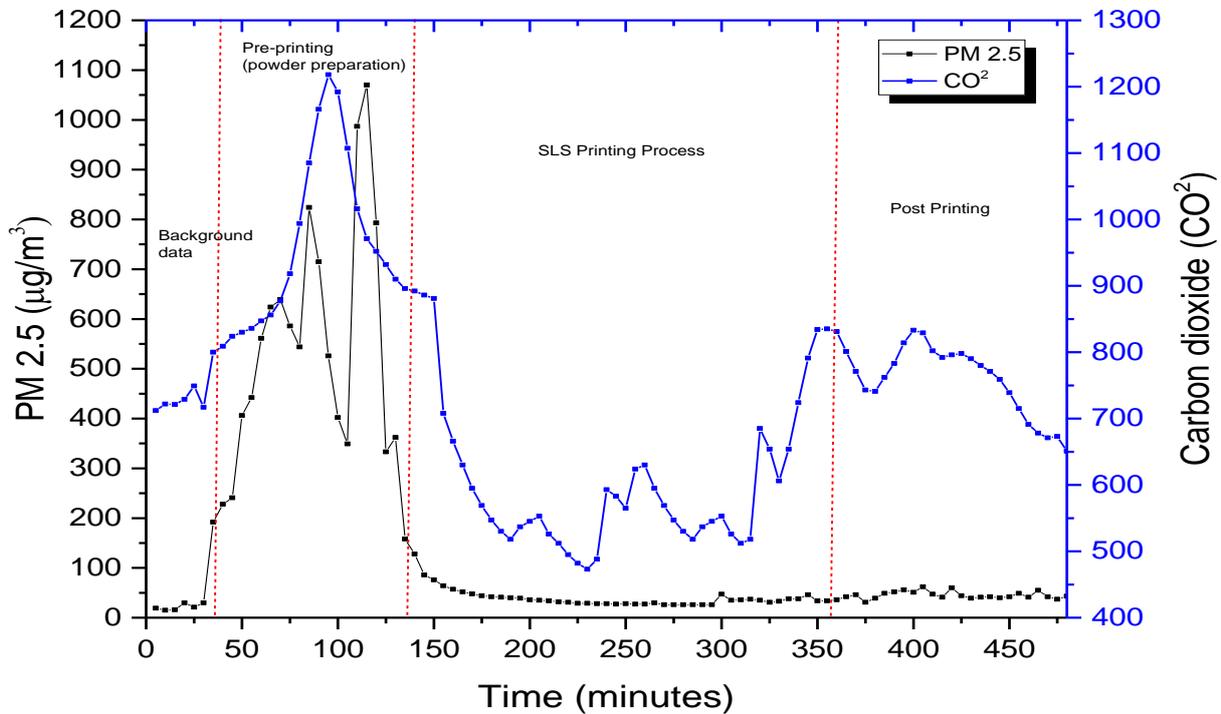
Figure 7: PM2.5 and carbon dioxide concentration during SLS printing process.

Table 3: Indoor temperature, relative humidity, TVOC and formaldehyde

	Process	Background data 0-30 minutes	Pre-printing (powder preparation) 30-140 minutes	SLS 3D Printing 140-360 minutes	Post printing 360-480 minutes
Temperature (°C)	Avg	27.50	24.20	28.10	23.89
	Min	27.50	22.50	24.00	22.40
	Max	27.60	26.90	32.20	28.80
	Std.Dev	0.04	1.78	2.54	1.192
Relative humidity (RH%)	Avg	60.93	57.07	51.19	53.70
	Min	57.91	53.10	42.56	51.50
	Max	64.40	59.30	56.80	58.10
	Std.Dev	2.45	1.59	3.93	1.62
Total Volatile Organic Compound (ppm)	Avg	0.037	0.38	0.237	0.356
	Min	0.30	0.30	0.10	0.20
	Max	0.40	0.44	0.40	0.50
	Std.Dev	0.051	0.043	0.086	0.119
Formaldehyde (ppm)	Avg	0.025	0.04	0.026	0.037
	Min	0.02	0.02	0.02	0.02
	Max	0.04	0.05	0.04	0.05
	Std.Dev	0.008	0.0094	0.006	0.01

4. Conclusion

The monitoring of environmental concentration in this SLS process relates to the occupational hazard of SLS faced by operators. The main goal of the current study was to determine the concentration of indoor environment during SLS printing process using virgin polyamide nylon (PA12) powder. Contribution of dust and chemical compound significantly exceed recommended value where must be below than 1000 ppm (CO^2) and 0.15 mg/m^3 (respirable dust). Mitigation strategies and personal protective equipment are necessary in order to decrease occupational hazard to the operators. CO^2 and PM 2.5 show the highest value during powder preparation process. This research serves as a base for future studies in promoting a better strategy to reduce the occupational hazard of AM process. These findings provide the following insights for future studies on the comparative study on indoor concentration and relationship towards emission using a different ratio of virgin powder and recycle powder.

Acknowledgement

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