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Control of Particulate Material Emission during 3D Printing

3D 프린터 가동 시 발생하는 입자상물질 제어

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서울대학교 보건대학원

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ABSTRACT

Control of Particulate Material Emission during 3D Printing

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Objective The three dimensional (3D) printer based on fused deposition modeling (FDM) technology is the most popular, due to inexpensive and easy handling. In spite of increasing popularity of 3D printers, people may overlook the possibility of the effect of 3D printing on health by 3D printing. According to recent studies, pollutants such as nanoparticles (<100 nm) and hazardous volatile organic compounds (VOCs) are emitted during 3D printing. Various thermoplastics can be used as feed materials, whereas previous studies evaluated the emitted pollutants using only PLA and ABS filament. Further, there is no specific attempt to prevent or reduce the pollutants emitted during 3D printing. This study aims to evaluate the

particle emission characteristics under the two different temperature conditions for extruder and heating bed with seven different filament materials and attempts to design filter based control methods reducing the particles emitted during 3D printing.

Methods The total number concentrations of airborne particles were measured before, during, and after 3D printing using scanning mobility particle sizer (SMPS) and optical particle sizer (OPS) in an exposure chamber. Polycarbonate filters (PC) were used for the field emission scanning electron microscope (FE-SEM) for morphological properties. The 3D printer was operated under the manufacturer recommended set and consistent temperature set with various thermoplastic materials (acrylonitrile-butadiene-styrene (ABS), poly lactic acid (PLA), polyvinyl alcohol (PVA), high impact polystyrene (HIPS), nylon and laywood). The temporal particle emission rate (#/min) was calculated by equations considering the particle concentration (#/cc). Emission rate based on time (#/min) and mass of filament used (#/g) were also estimated by equations. The eight different control methods based on filters were devised to reduce particle emission from 3D printing and conducted in identical procedure as mentioned above.

Results The FDM 3D printer with all the thermoplastic filaments examined in this study (ABS, PLA, PVA, laywood, HIPS and nylon) emit nanoparticles dominantly under both the condition of manufacturer recommended set and consistent temperature set during 3D printing.

The highest nanoparticle emission rates under the condition of manufacturer recommended set were $3.26 \times 10^{11} \#/min$ and $1.72 \times 10^{12}\ \#/g$ with HIPS filaments, whereas the lowest nanoparticle emission rates were $3.18 \times 10^{8}\ \#/min$

and 1.32×10^9 $\#/g$ with PLA filament. Accordingly, extruder temperature was higher, in adjusting consistent temperature set, nanoparticles were emitted at least one order of magnitude more than the condition of manufacturer recommended set for all filament materials. The emission rate of all materials examined under the condition of consistent temperature set were over 6.67×10^{10} $\#/min$.

In the experiments for control method, sealing tape was applied to confirm the effectiveness of enclosure. It showed a substantial effect, 74.38% of removal efficiency for ABS2 filament under the manufacturer recommended set. Then various kinds of filters were attached to the ventilation hole for removing nanoparticles. The highest removal efficiency of nanoparticles was 99.95% with HEPA filter and over 90% with other filters using ABS2 filament, except the combination of the electret and antibacterial filter which showed 76.04%, similar to no use of filter. To verify the removal efficiency in the highest concentration under the manufacturer recommended set, the HIPS filament was used as the supplying filament, and, it was the most effective method which had enclosure and attached HEPA filter on the ventilation outlet hole. The most effective method showed 99.95% of removal efficiency, regardless of nanoparticles emitted, about 20 times higher (10,776 #/cc for ABS2 vs 209,451 #/cc for HIPS).

Conclusion In this study, the particles emitted during 3D printing for all seven filament materials were primarily nanoparticles. The emission of nanoparticles was high at the high temperature of the filament extruder. The enclosure could reduce more than 70% of nanoparticle emission during 3D printing. Nanoparticle emission could be reduced more than 99.95% in case HEPA filter was attached to the

ventilation outlet hole after enclosure in the 3D printer.

Therefore, it is necessary to use the 3D printer with as low extruder temperature as possible and supply the filaments which emit less particles to cut off at the source in 3D printing. And also an enclosed type of 3D printer with a ventilation fan should be used to which is attached the filter specialized to remove nanoparticles.

Keywords: FDM, 3D printing, nanoparticle, filter, control

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1. Introduction

The three dimensional (3D) printer applies an additive manufacturing (AM) process, which is joining materials to fabricate 3D objects from computer-assisted design (CAD) data, usually layer by layer (ASTM, 2012, Wong et al. 2012). In comparison to traditional manufacturing, AM has many advantages such as reduction of material cost and process simplification (Kwak et al. 2013). From those advantages, the 3D printer market continues to grow rapidly and 3D printers are used in various fields such as aerospace, product design, medical services and education (Berman B. 2012, Shulman et al. 2012).

The 3D printer applied fused deposition modeling (FDM) technology is the most commonly used among the commercially available 3D printers, due to low cost and easy handling. In the FDM process, a thermoplastic filament is supplied into a heated extruder where it is melted, and then a thin layer is deposited on the heating bed continuously (Eweiruaku S. 2015). Although poly lactic acid (PLA) and acrylonitrile-butadiene-styrene (ABS) are used dominantly as filament materials, the other polymers such as nylon, high-impact polystyrene (HIPS), poly vinyl alcohol (PVA) and polycarbonate (PC) also have increased consumption (Azimi et al. 2016).

In spite of increasing popularity of 3D printers, people may overlook the possibility of the effect of 3D printing on health. According to recent studies, nanoparticles (<100 nm) and hazardous volatile organic compounds (VOCs) are emitted during 3D printing (Stephens et al. 2013, Kim et al. 2015, Azimi et al. 2016, Steinle et al. 2016).

As hazardous VOCs, Aldehydes and styrene were measured. Aldehydes

include formaldehyde which is classified as a carcinogen to humans by the International Agency for Research on Cancer (IARC classification 1) and acetaldehyde which is classified as a possible human carcinogen by IARC (IARC classification 2B). Styrene is also classified as a possible human carcinogen by IARC (IARC classification 2B). It is well known that nanoparticles have a potential effect on human health including adverse inflammatory response (Oberdörster et al. 2000, Brown et al. 2001, Warheit et al. 2008).

After the first study by Stephens et al. (2013) measured emission of nanoparticles during 3D printing, several studies repeated nanoparticle emission and other pollutants. (Afshar-Mohajer et al. 2015, Kim et al. 2015, Short et al. 2015 Zhou et al. 2015, Azimi et al. 2016, Oskui et al. 2016, Steinle Patrick. 2016). Although various thermoplastics can be used as feed materials, those studies focused on evaluating and characterizing the emitted pollutants using only PLA and ABS filaments. Only one recent study by Azimi et al (2016) conducted research into emitted pollutants during 3D printing with a combination of various 3D printers and filaments. Further, there is no specific attempt to prevent or reduce the pollutants emitted during 3D printing, although the result of studies showed the pollutants were emitted definitely.

Therefore, this study advances those previous studies by evaluating the particle emission characteristics in two different temperature conditions for extruder and heating bed with seven different filament materials and tries to design filter based control methods to reduce the particles emitted during 3D printing.

2. Materials and Methods

This study consisted of three sections. The first two sections are the same in evaluating the characteristics of particle emissions according to the type of filament materials. But one is under manufacturer recommended set such as different extruder and heating bed temperature for each filament material. The other is under consistent temperature set which has the same temperature condition of extruder and heating bed for every filament material. Finally, the control methods were adjusted to reduce particle emissions using various types of filters.

2.1. Subjects

All tests were carried out using a commercially available FDM 3D printer (3DISON multi 2, Rokit, Korea) capable of processing various thermoplastic filaments. The printer consisted of two extruders with a nozzle (diameter: 0.4 mm) and heating bed for stable printing of objects. All tests were conducted using only one extruder on the right side. The printer was released as an enclosed type (although it was not airtight) with door and ventilation fan at the top left back side without any filter. Most 3D printers on the market do not have any enclosure. So, the door (28.5 ㎝ × 36 ㎝) and filament supplying roller (45㎝ × 28.5 ㎝) were removed for the evaluation and comparison of particulate emission among the filament materials.

2.1.1. Set of manufacturer recommended

To evaluate particulate emission of the filament materials, seven different filaments: (1) ABS1, (2) ABS2, (3) PLA, (4) HIPS, (5) nylon, (6) PVA and (7) laywood were used. The filaments were weighed before and after each experiment for calculating the emission rate based on used weight. The specific gravity of all filaments was also estimated by weighing and calculating the unit length of 1.75 mm diameter filaments.

Under the manufacturer recommended set, the temperature of extruder and heating bed was different according to type of filament materials except HIPS and nylon filaments. To confirm whether particles were emitted or not when operating without filament materials, two types of experiments were executed under the manufacturer recommended set of ABS2. The only difference between the two types of experiment was whether glue was spread on to the heating bed or not. Table 1 summarizes the characteristics of filaments and operating conditions under the condition of manufacturer recommend set.

Table 1. Summary of the characteristics of filaments and operating conditions under the condition of manufacturer recommend set

	Filament					Operating condition			
	Material	Color	Specific gravity[1] (g/㎤)	Mass (g)	Length (㎝)[2]	Extruder temp (℃)	Heating bed temp (℃)	Bed prep	Operation duration[3] (min)
Manufacturer recommended set	ABS1	Light gray	1.04	11.70 ± 0.06	467.9 ± 2.3	230	120	tape + glue	78
	ABS2	Dark gray	1.00	11.71 ± 0.10	487.9 ± 4.2	240	110	tape + glue	73
	PLA	Red	1.21	14.73 ± 0.05	507.9 ± 1.8	220	60	tape	65
	PVA	Yellow-brown	1.33	13.67 ± 0.11	427.2 ± 3.6	190	60	tape	64
	Laywood	Brown	1.16	13.71 ± 0.08	489.8 ± 2.9	215	60	tape	64
	HIPS[4]	White	1.00	11.58 ± 0.08	482.5 ± 3.1	265	90	tape	70
	Nylon[5]	Semitransparent	1.08	12.27 ± 0.15	471.8 ± 5.9	265	90	tape + glue	70
Operating without filament material	-	-	-	-	-	240	110	tape + glue	73
	-	-	-	-	-	240	110	tape	73

[1] Specific gravity : weighing and calculating the unit length of 1.75 mm diameter filaments
[2] Length : estimated by weight and specific gravity
[3] Operation duration : including preheat time
[4] HIPS : manufacturer recommended set and consistent temperature set are the same operating conditions
[5] Nylon : manufacturer recommended set and consistent temperature set are the same operating conditions

2.1.2. Set of consistent temperature

The only difference between the manufacturer recommended set and the consistent temperature set was the condition of extruder and heating bed temperature for each filament material. In the condition of consistent temperature set, the extruder temperature and heating bed temperature were fixed at 265 ℃ and 90 ℃ respectively for every filament material. The temperature of the extruder and heating bed were set according to the stability of 3D printing for all the filament materials examined in this study. The experiments using HIPS and nylon filaments were not repeated under consistent temperature set, because HIPS and nylon filaments had the same temperature condition between manufacturer recommended set and consistent temperature set as 265 ℃ for extruder and 90 ℃ for heating bed. Table 2 shows the experiment condition under the consistent temperature set.

Table 2. Summary of the characteristics of filaments and operating conditions under the condition of consistent temperature set

	Filament					Operation condition			
	Material	Color	Specific gravity[1] (g/㎤)	Mass (g)	Length (㎝)[2]	Extruder temp (℃)	Heating bed temp (℃)	Bed prep	Operation duration[3] (min)
Consistent temperature set	ABS1	Light gray	1.04	11.82	472.8	265	90	tape + glue	69
	ABS2	Dark gray	1.00	11.95	497.9	265	90	tape + glue	69
	PLA	Red	1.21	14.54	501.4	265	90	tape	69
	PVA	yellow-brown	1.33	13.90	434.4	265	90	tape	69
	Laywood	Brown	1.16	13.79	492.5	265	90	tape	70

[1] Specific gravity : weighing and calculating the unit length of 1.75 mm diameter filaments
[2] Length : estimated by weight and specific gravity
[3] Operation duration : including preheat time

2.1.3. Set of control method adjusted

The two types of filaments including ABS and HIPS were selected to evaluate the removal efficiency using the control methods. The ABS filament is one of the most popular filament materials for 3D printing and measured a high number concentration during 3D printing in both in our experiments and other researches (Stephens et al. 2013, Kim et al. 2015, Zhou et al. 2015, Azimi et al. 2016, Steinle Patrick. 2016). All eight control methods were conducted with ABS2 filament under the set of manufacturer recommended. The HIPS filament had estimated the highest emission rate under the set of manufacturer recommended in our experiments. So one of the methods, which was verified to be the most effective to remove particles during 3D printing with ABS2 filament, was examined with HIPS filament.

Table 3. Summary of the control method adjusted experiments

	Sort	Enclosure	Suction fan operation[1)]	Ventilation fan operation[2)]	Filter
Control method adjusted	CTR1	yes	X	O	-
	CTR2	no	O	X	ACF[3)]
	CTR3	yes	X	O	ACF
	CTR4	yes	O	O	ACF
	CTR5	yes	X	O	Combination of electret and antibacterial filter
	CTR6	yes	X	O	Membrane coated polyethylene L227 filter
	CTR7	yes	X	O	Nano membrane
	CTR8	yes	X	O	HEPA

[1)] Suction fan operation : attaching at the front of extruder horizontally
[2)] Ventilation fan operation : equipped top left of back side of 3D printer
[3)] ACF : activated carbon filter

Table 3 summarizes the condition of control method such as enclosure, suction fan operation, ventilation fan operation and type of filter adjusted experiments. The CTR1 method was conducted to compare the differences of particle emissions with or without enclosure. An airtight sealing was added just to the enclosed 3D printer to which was attached a door and filament supplying roller like form originally released. Activated carbon fiber (ACF) filter were used at the CTR2, CTR3 and CTR4 methods. A suction fan (4 × 4 cm) to which was attached an ACF filter (4 × 4 cm) at the front of the extruder horizontally was installed for the CTR2 method. CTR2 method was only conducted under the condition of open type, unlike any other adjusted enclosure of control methods. The CTR3 method was the same as CTR1 but the ACF filter (10 × 10 cm) was covered at the rectangular ventilation outlet (6 × 6 cm). The CTR4 method was a combination of the CTR2 and CTR3 methods. The fan was equipped at the front of the extruder horizontally with ACF filter, and the ventilation outlet hole was covered with ACF filter (10 × 10 cm) for CTR4 method. The result of CTR2, CTR3 and CTR4 methods were reflected in the other methods. The only difference among CTR5 to CTR8 was the kind of filter covering ventilation outlet hole. The combination of electret and antibacterial filter (diameter: 12 cm) was used for CTR5 methods. The polyethylene filter (10 × 10 cm), nano membrane filter (10 × 10 cm) and HEPA filter (10 × 10 cm) were substituted for CTR6, CTR7 and CTR8 methods, respectively.

2.2. Experimental procedures

2.2.1. Experimental set up

Figure 1 shows a schematic diagram of the test chamber. All measurements were conducted in a non-static chamber in volume of 2.5 m^3, which could supply a constant air flow into the chamber with a fan. The chamber consisted of two parts which had dimensions of (2 m × 1 m × 1 m) for mixing and (1 m × 0.5 m × 0.5 m) for sampling, and a rectangular funnel shaped link between the two sections. The HEPA filter and activated charcoal filter (ACF) were installed in front of the mixing chamber for supplying purified air. There is another HEPA filter located between the sampling chamber and the fan for purifying discharged air after sampling. The fan operated to achieve a steady supply of air flow of 0.1 m/s into the sampling chamber through the time of the whole experiment. The constant velocity of air flow was confirmed prior to the experiments with an anemometer (Multi-channel anemometer model 1560, Kanomax Inc., USA) in nine spots of the plane where the sampling port was located.

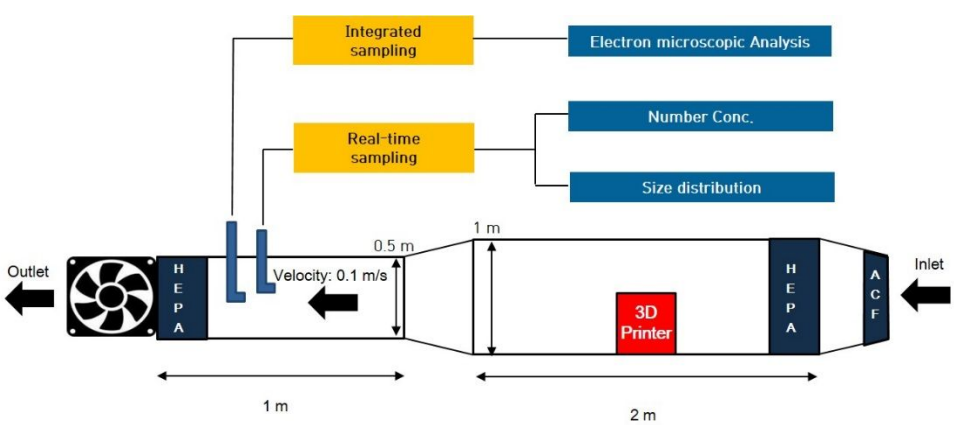


Figure 1. Schematic diagram of test chamber.

The 3D printer is placed in the center of the mixing chamber with the back toward the air inlet to minimize the influence of incoming air flow. The 3D printer heating bed was prepared for fabricating by attaching adhesive strengthening tape, or, in a few cases, spreading a thin layer of glue stick additionally, following the manufacturer guidelines. In all the tests, a cylinder shape CAD data (Thing 824739, www.thingiverse.com) was fabricated with size-expanded as a (diameter: 35 ㎜, height: 23 ㎜) for extending the operation time using software (Creator K V9.6.1) which was provided by the manufacturer. The CAD data was chosen to confirm the uniformity of particle number concentrations and emission rate during 3D printing because each layer has the same surface area. Figure 2 shows the cylinder shape objects fabricated by 3D printer with multiple filaments.

Figure 2. The cylinder shape objects fabricated by 3D printer with multiple filaments.

The measurement was conducted using both real time monitoring and integrated sampling. There were two sampling ports located 2.3 m and 2.4 m from

the 3D printer each for the real time monitoring and integrated sampling. Two identical stainless steel sampling ports (diameter: 7 mm) are L-shaped. The inlet axis of ports was installed parallel to the air streamline but at different heights so as not to disturb each other.

2.2.2. Measurement and sample analysis

Each experiment was divided into three phases according to the state of 3D printing. The phase descriptions are as follows:

1) Before the operation phase

   To remove contaminants in the chamber, the fan was operated at least 30 minutes with the same condition of the experiments at 0.1 m/s. After stabilizing the particulate concentration level, the sampling was started for 30 – 35 minutes to obtain a background particulate concentration level.

2) During the operation phase

   This phase contains preheating period to reach a preset temperature of extruder and heating bed before printing the object. The preheating period lasted 3-17 minutes depending on the preset temperature of the printer by feedstock filament. After preheating, the 3D printer was operated to fabricate a cylinder, layer by layer. It took 61 minutes to finish the whole printing process for every filament material.

3) After the operation phase

   This phase was initiated just after the printing process was completed. As the chamber fan of the exposure chamber was operated continuously, the pollutants of particles from 3D printing would be removed by time and then the number concentration level would be attained similar to background particulate concentration level which measured the first phase.

Real-time monitoring and analysis

To measure the particle number concentration and size distribution in real time, a scanning mobility particle sizer (SMPS, Nanoscan, Model 3910, TSI Inc., Shoreview, MN, USA) and an optical particle spectrometer (OPS, Model 3330, TSI Inc., Shoreview, MN, USA) were used in intervals of 1 minute. The detectable size ranges of the instruments were from 10 to 420 nm for SMPS, and 300-10,000 nm for OPS, respectively.

The number concentration and size distribution data which were measured by SMPS and OPS were used to estimate the emission rate for each filament during 3D printing. There were two methods that were used to estimate the emission rate. The first method which estimated time-varying emission rates was derived from Azimi et al. (2016). There are several assumptions in applying the method that may lead to inaccuracies in estimation of emission rate. It is ignored size-resolved particle dynamics, coagulation and constant particle loss rates.

The sum of time-varying emission rates used to calculate the emission rate during 3D printing based on time (per minute), mass of filament used (per gram). (Equation 1 and Equation 2)

$$E_t = \frac{E_{Sum}}{t_{operation}} \cdots\cdots\cdots\cdots Equation\ 1$$

$$E_m = \frac{E_{Sum}}{m_{object}} \cdots\cdots\cdots\cdots Equation\ 2$$

Where E_t is the emission rate during 3D printing based on time (per minute), E_{Sum} is the sum of time-varying emission rate during 3D printing, $t_{operation}$ is the total operation time of the 3D printer (minute), E_m is the emission rate during 3D printing based on mass of filament used (per gram) and m_{object} is the mass of filament used (gram).

The other method derived from our previous study (Kim et al., 2015) was also adjusted to calculate the emission rate during 3D printing. It is assumed that the particles are mixed well in the mixing chamber and the cross sectional area of the sampling chamber is under the same number concentration. The total number of particles emitted during 3D printing was calculated as below.

$$N_{total} = (GM_{during} - GM_{before}) \times Q_{chamber} \times t_{operation} \cdots\cdots\cdots Equation\ 3$$

Where N_{total} is the total number of particles emitted during 3D printing, GM_{during} is the geometric mean (GM) concentration of before 3D printing as a background concentration, $Q_{chamber}$ is the total flow rate of the air passed through the chamber inside and $t_{operation}$ is the total operation time of the 3D printer (minute). The total number of particles emitted during 3D printing is used to calculate the emission rate based on time (per minute) and mass of filament used (per gram).

Integrated sampling and analysis

A polycarbonate (PC) membrane filter (diameter; 37 mm, pore size; 0.4 μm, SKC Inc., USA) was used to identify the particle size, morphology and chemical

composition analyzing field emission scanning electron microscope with energy dispersive X-ray spectroscopy (FE-SEM/EDX) analysis. Samples were collected using 3-piece cassettes and air was drawn in these cassettes at 2 L/min using a high volume pump (Aircheck XR5000, SKC Inc, USA). After sampling, all the samples were kept in a desiccator (Temp. 20±1 ℃, RH 50±5%).

3. Results

3.1. Experiments under the condition of manufacturer recommended set

3.1.1. Particle number concentration

The number concentration of particles measured by OPS (300 – 10000 nm) was nearly not detected during printing. (The highest difference of GM number concentration between "before operation" and "during operation" was only 11 #/cc with PVA filament and the values for other filaments were 0 – 1 #/cc). The number concentration for all filament materials measured by SMPS (10-420 nm) increased rapidly just after printing started (not including the preheat period) and sustained for 5 to 15 minutes then decreased to a lower level, although still higher than background concentration level. After the peak concentration, some filaments (ABS1, ABS2, HIPS, PVA) were decreased rapidly and the other (PLA, nylon, laywood) filaments were decreased gradually. There was hardly any difference of concentration throughout the whole experiment period in the condition of operating without supplying a filament, regardless of spreading glue stick on the heating bed.

Table 4 summarizes the number concentration and the range of concentration for operating with various filament materials and without filament material under the manufacturer recommended set. The GM (GSD) number concentration was divided up to the order of magnitude into 3 groups: (1) HIPS and nylon (217,925 (1.27) #/cc and 212,654 #/cc, respectively), (2) ABS1 and ABS2 (20,618 #/cc and 14,131 #/cc, respectively), (3) PLA, PVA and laywood (1,468 #/cc, 1,591 #/cc, and 1,365 #/cc, respectively).

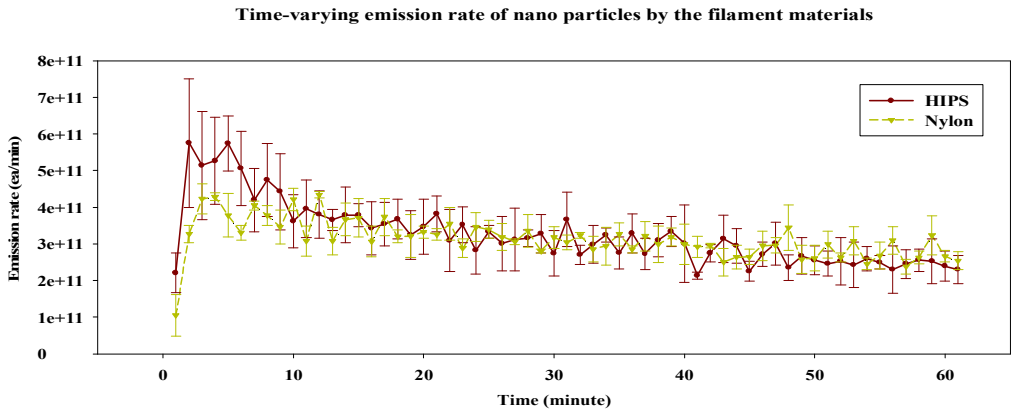
Table 4. Summary of the number concentration and the range of concentration for operating with various filament materials and without filament material under the manufacturer recommended set

Sort	Filament		Nanoparticles (< 100 nm), #/cc			SMPS (10-420 nm), #/cc		
			Before operation	During operation	After operation	Before operation	During operation	After operation
Group 1	HIPS	GM (GSD)	621 (1.09)	210,036 (1.27)	1,910 (4.95)	988 (1.07)	217,925 (1.27)	2,631 (4.25)
		Range	500 - 744	88,761 – 364,331	648-165,826	856-1157	97,016-382,124	1,099-170,370
	Nylon	GM (GSD)	677 (1.10)	203,368 (1.27)	2,085 (4.83)	978 (1.06)	212,654 (1.27)	2,632 (4.38)
		Range	554 - 853	42,647 – 26,5643	755-16,7339	881-1,112	44,091-281,894	1,072-174,532
Group 2	ABS 1	GM (GSD)	664 (1.06)	18,107 (1.65)	1,205 (2.13)	1,093 (1.05)	20,618 (1.56)	1,792 (1.90)
		Range	587 - 767	2,359 – 54,354	752-14,565	962-1,185	3,595-54,969	1,246-16,197
	ABS 2	GM (GSD)	777 (1.06)	11,553 (1.56)	1,140 (1.83)	1,094 (1.05)	14,131 (1.46)	1,558 (1.74)
		Range	698 - 847	4,360 – 34,450	762-8,454	983-1,207	5,435-36,328	1,091-10,897
Group 3	PLA	GM (GSD)	843 (1.05)	1,050 (1.09)	811 (1.05)	1,232 (1.04)	1,468 (1.07)	1,191 (1.05)
		Range	780 - 937	912 – 1,326	713-895	1,117-1,314	1,309-1,796	1,096-1,286
	PVA	GM (GSD)	706 (1.06)	1,034 (1.16)	683 (1.16)	1,068 (1.06)	1,591 (1.15)	1,085 (1.14)
		Range	637 - 833	753 – 1,485	574-1,024	941-1,174	1,072-2,175	954-1,613
	Laywood	GM (GSD)	777 (1.05)	1,006 (1.09)	880 (1.09)	1,061 (1.05)	1,365 (1.07)	1,234 (1.07)
		Range	709 - 844	720 – 1,204	737-1,070	923-1,176	1,109-1,563	1,086-1,415
Glue spread	Operating without filament material	GM (GSD)	490 (1.06)	508 (1.07)	455 (1.07)	588 (1.05)	622 (1.06)	574 (1.05)
		Range	435 - 550	446 - 573	389 - 515	540-653	530-708	500-630
No glue spread		GM (GSD)	931 (1.05)	925 (1.06)	867 (1.05)	1,131 (1.04)	1,107 (1.05)	1,061 (1.05)
		Range	837 – 1,012	791 – 1,086	768-981	1,039-1,221	977-1,254	919-1,161

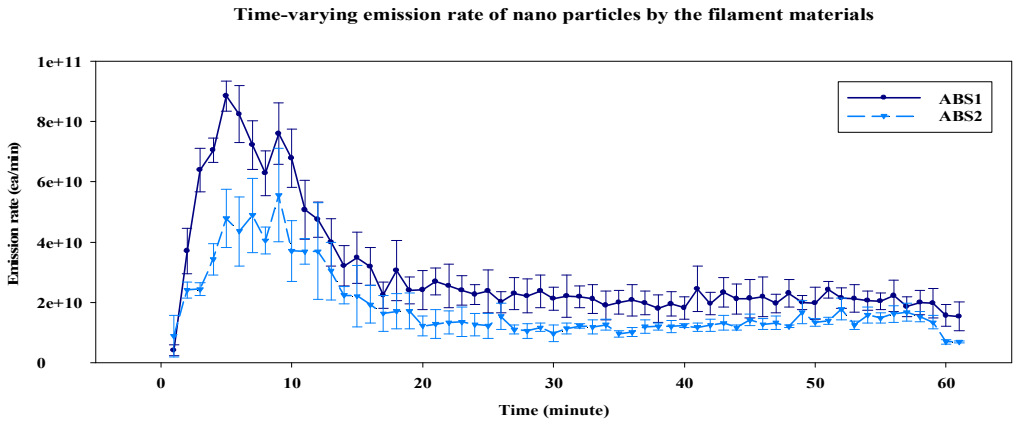
Group 1 and group 2 included over 80% of nanoparticles. Group 3 was contained below 80% of nanoparticles. But 115.5 nm particle size bin (the border of nano size) measured by SMPS had a considerable portion of the remaining nanoparticles (If 115.5 nm particle size bin was applied to calculate the percent of nanoparticles, Group 3 also exceed 80%). For these reasons, it is assumed that nanoparticles were emitted dominantly during 3D printing, irrespective of filament materials. So nanoparticles were focused to apply estimation of emission rate during 3D printing.

3.1.2. Emission rate

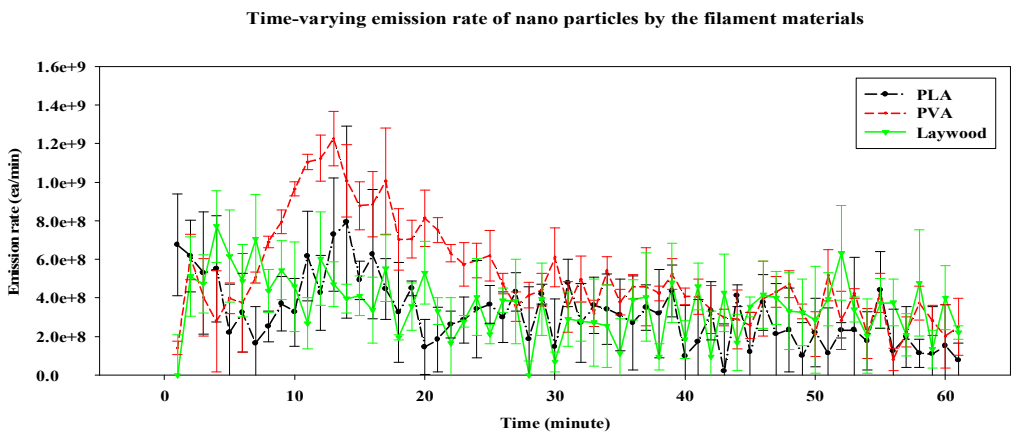
Figure 3. shows the time-varying emission rate of nanoparticles by the various filament materials under the condition of manufacturer recommended. The time-varying emission rate was also divided into three groups, the same as mentioned above. Group 1 estimated the highest emission rates based on time as ranging $2.13 \times 10^{11} - 5.75 \times 10^{11}$ #/min for HIPS and $1.05 \times 10^{11} - 4.34 \times 10^{11}$ #/min for nylon followed by group 2 ($4.10 \times 10^{09} - 8.85 \times 10^{10}$ #/min for ABS1 and $6.91 \times 10^{09} - 5.56 \times 10^{10}$ #/min for ABS2) and group 3 ($7.97 \times 10^{7} - 1.23 \times 10^{9}$ #/min for PVA, $6.83 \times 10^{7} - 7.71 \times 10^{8}$ #/min for laywood and $1.98 \times 10^{7} - 7.92 \times 10^{8}$ #/min for PLA, respectively). There were 2 data points among 61 data points which estimated a negative emission rate based on time for laywood filament. The 2 negative data points, which were likely due to the method suggested by Azimi et al. (2016) that it is affected by the concentration of previous interval time and background concentration, were excluded from analysis.



(a)



(b)



(c)

Figure 3. (a) Time-varying emission rate of nanoparticles by group 1 which is classified as the high emission rate, (b) time-varying emission rate of nanoparticles by group 2 which is classified as the middle emission rate and (3) time-varying emission rate of nanoparticles by group 3 which is classified as the low emission rate under the condition of manufacturer recommended set.

Table 5 shows the emission rate under the manufacturer recommended set during 3D printing based on time and mass of filament used. The time of the extruder operating (not including preheating period) was measured to calculate the emission rate of nanoparticles during 3D printing based on time. It took 61 minutes for all the experiment to be executed. The mass of filament used during 3D printing was calculated as the filament weighed before and after the experiment.

Table 5. The emission rates with various filament materials under the manufacturer recommended set during 3D printing

	Method 1[1)]				Method 2[2)]			
Filament	Nanoparticle (<100 nm)		SMPS (10-420 nm)		Nanoparticle (<100 nm)		SMPS (10-420 nm)	
	#/min	#/g	#/min	#/g	#/min	#/g	#/min	#/g
ABS 1	3.00.E+10	1.57.E+11	3.28.E+10	1.71.E+11	2.62.E+10	1.36.E+11	2.93.E+10	1.53.E+11
ABS 2	1.83.E+10	9.54.E+10	2.14.E+10	1.11.E+11	1.62.E+10	8.42.E+10	1.96.E+10	1.02.E+11
PLA	3.18.E+08	1.32.E+09	3.61.E+08	1.49.E+09	3.12.E+08	1.29.E+09	3.54.E+08	1.47.E+09
PVA	5.10.E+08	2.28.E+09	8.12.E+08	3.62.E+09	4.92.E+08	2.20.E+09	7.85.E+08	3.50.E+09
laywood	3.53.E+08	1.57.E+09	4.65.E+08	2.07.E+09	3.43.E+08	1.53.E+09	4.56.E+08	2.03.E+09
HIPS	3.26.E+11	1.72.E+12	3.37.E+11	1.78.E+12	3.14.E+11	1.65.E+12	3.25.E+11	1.71.E+12
nylon	3.13.E+11	1.56.E+12	3.27.E+11	1.63.E+12	3.04.E+11	1.51.E+12	3.18.E+11	1.58.E+12

[1)] Method 1 : Emission rate estimation method derived from Azimi et al. (2016)
[2)] Method 2 : Emission rate estimation method derived from Kim et al. (2015)

First, method 1 derived from Azimi et al. (2016) was applied to estimate the emission rate of nanoparticles during 3D printing. The filament which calculated the highest values of nanoparticle emission rate based on time and mass was HIPS. The values were $3.26 \times 10^{11}\ \#/min$ and $1.72 \times 10^{12}\ \#/g$ respectively. Whereas the lowest values were $3.18 \times 10^{8}\ \#/min$ and $1.32 \times 10^{9}\ \#/g$ with PLA filament. The emission rate of nanoparticles for the HIPS filament was 3 order of magnitude higher than the PLA filament supplied as a feed material.

The other, method 2, which suggested in our previous study (Kim et al., 2015) to estimate emission rate of particles during 3D printing was adjusted. The highest values of emission rate based on time and mass were $3.14 \times 10^{11}\ \#/min$ and $1.65 \times 10^{12}\ \#/g$ for HIPS filament. The lowest values were $3.12 \times 10^{8} \#/min$ and $1.29 \times 10^{9}\ \#/g$ with PLA filament. It was confirmed that both values of emission rate which were estimated by the method of Azimi et al. (2016) and Kim et al. (2015) have similar numerical value.

3.1.3. Morphology and chemical compositions

Figure 4. displays the FE-SEM/EDX images collected on PC filters during 3D printing with multiple filaments. These images demonstrate that particle shape is spherical, irrespective of filament materials. About 100 to 300 nm sized independent particles were shown in all the samples. Also aggregation of particles showed all the samples except nylon (Figure 4 (g)) only. The aggregation tendency could divided into three: (1) a couple of 100 to 200 sized particles aggregated (Figure 4 (c) – PLA), (2) a lot of nanoparticles (<100 nm) aggregated (Figure 4 (a) - ABS1, Figure 4 (e) - laywood), (3) multiple size particles aggregated (Figure 4 (b) - ABS2, Figure 4 (f) - HIPS, Figure 4 (d) - PVA). Especially, PVA (Figure 4 (d)) sample contains about 1 ㎛ particle which is 5 to 30 times larger than the other filament material samples shown. The result of energy dispersive spectroscopy (EDS) implied that the composition of all filament materials are carbon and oxygen.

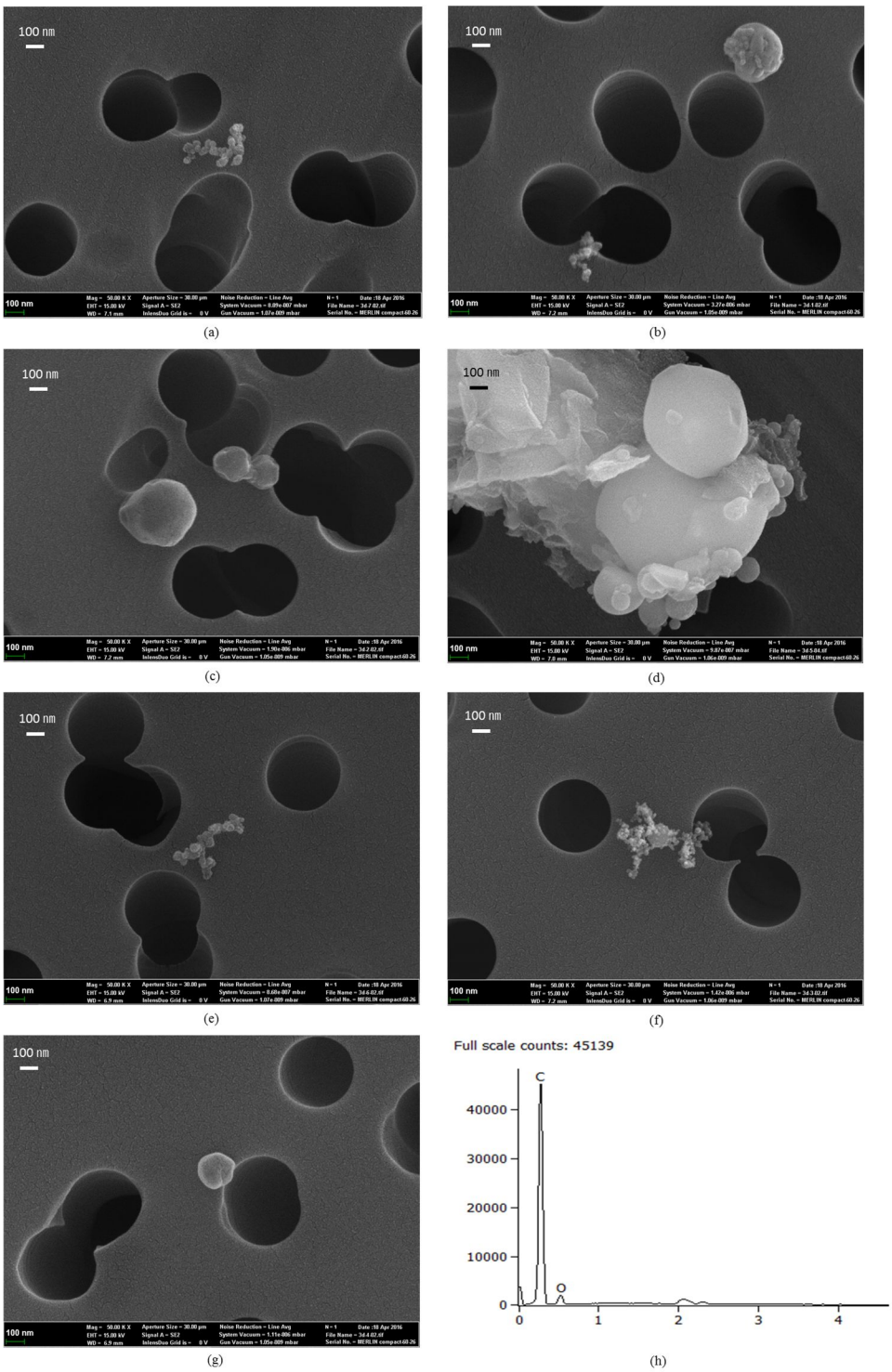


Figure 4. FE-SEM/EDX images of particles emitted during 3D printing under the recommended operating conditions. (a) ABS1, (b) ABS2, (c) PLA (d) PVA (e) laywood, (f) HIPS, (g) nylon and (h) components of ABS2.

3.2. Experiments under the condition of consistent temperature set

The HIPS and nylon filaments had the same condition of extruder and heating bed temperature (265 ℃ for nozzle and 60 ℃ for heating bed temperature) regardless of manufacturer recommended set or consistent temperature set. So the experiments using HIPS and nylon filaments were not repeated under consistent temperature set.

3.2.1. Particle number concentration

Under the consistent temperature set of 3D printer, the number concentration of particles measured by OPS (300-10,000 nm) was nearly not detected during printing, except PVA filament whose difference of GM number concentration between "before operation" and "during operation" was 863 #/cc.

Figure 5. shows the corrected time-varying number concentration as GM concentration of "before operation" was subtracted from the "during operation" measured by SMPS. In the very early stage, the pattern of number concentration for all filament materials in consistent temperature set measured by SMPS (10-420 nm) similar to the condition of manufacturer recommended set which increased sharply. But what is different is that the peak of number concentration sustained or decreased slowly until printing was completed, except ABS filament which decreased rapidly to a quarter of the highest number concentration from ~380,000 #/cc to ~90,000 #/cc.

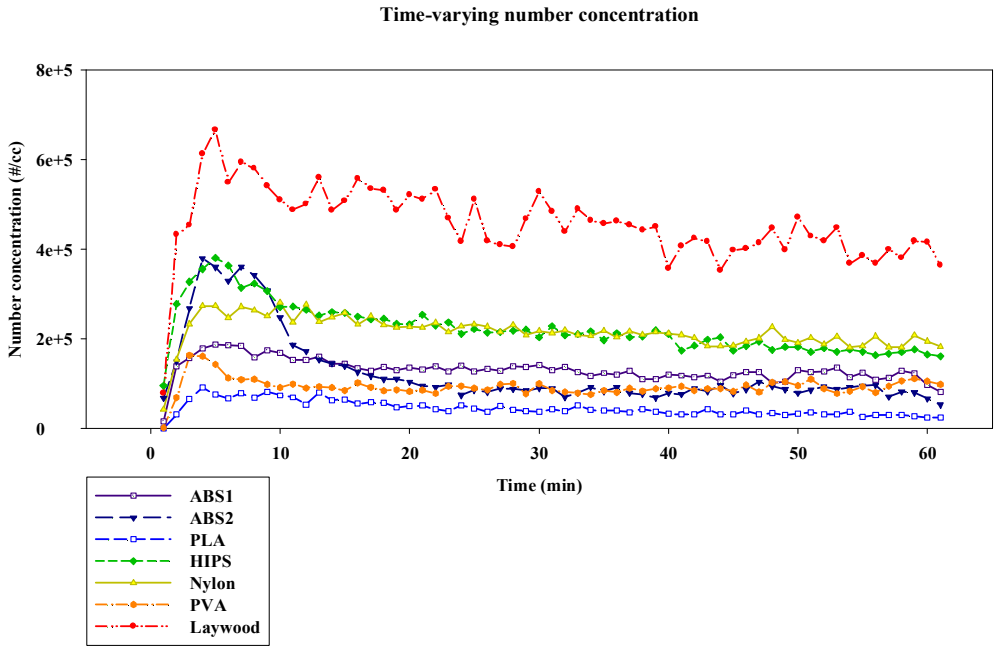


Figure 5. The corrected time-varying number concentration as GM concentration of "before operation" was subtracted from the "during operation" measured by SMPS.

Table 6 summarizes the number concentration and range of concentration under the consistent temperature set. The GM number concentration of each filament under the consistent temperature set was at least one order of magnitude higher than the GM number concentration under the manufacturer recommended set. Especially, GM number concentration for laywood under the condition of manufacturer recommended was one of the lowest value. But, it is the highest that the GM number concentration measured by SMPS (10-420 nm) for laywood under the condition of consistent temperature as 447,478 #/cc followed by HIPS (217,925 #/cc), nylon (212,654 #/cc), ABS1 (127,833 #/cc), ABS2 (109,840 #/cc), PVA (90,052 #/cc) and PLA (41,766 #/cc), respectively. The percent of nanoparticles during operation for all filaments exceeded 90% except

PVA filament. Multiple sized particle from nano size to ~1 um was measured during operation with PVA filament.

Table 6. The number concentration and range of concentration under the consistent temperature set

Filament		Nanoparticles (< 100 nm), #/cc			Total (10-420 nm), #/cc		
		Before operation	During operation	After operation	Before operation	During operation	After operation
ABS 1	GM	370	119,545	987	680	127,833	1,585
	Range	287 - 452	15,319-180,881	354-79,743	587-803	17,052-187,749	719-87,854
ABS 2	GM	652	101,064	1,460	846	109,840	1,772
	Range	519-780	50,647-363,466	684-55,054	716-995	54,268-380,221	964-58,267
PLA	GM	596	40,387	1,113	920	41,766	1,667
	Range	399-851	725-88,659	555-24,650	671-1,291	1,015-92,278	910-27,839
PVA	GM	942	52,366	1,637	1,433	90,052	2,567
	Range	677-1,191	1613-136,881	542-120,502	994-1,756	3,287-165,137	942-148,471
Laywood	GM	806	434,517	3,056	1,128	447,478	3,826
	Range	507-983	72,718-622,946	961-356,355	910-1,316	80,156-667,837	1,291-361,712

3.2.2. Emission rate

Table 7 shows the emission rate of nanoparticles under the consistent temperature set during 3D printing based on time and mass of filament used. In the condition of method 1 derived from Azimi et al. (2016) applied, the filament which estimated the highest values of nanoparticle emission rate based on time and mass was laywood filament. The values were $6.73 \times 10^{11}\ \#/min$ and $2.93 \times 10^{12}\ \#/g$ respectively, whereas the lowest values were $6.67 \times 10^{10}\ \#/min$ and $2.80 \times 10^{11}\ \#/g$ with PLA filament. The method 2 which suggested our previous study (Kim et al., 2015) to estimate emission rate of particles during 3D printing was adjusted. The highest values of emission rate based on time and mass were $6.51 \times 10^{11}\ \#/min$ and $2.83 \times 10^{12}\ \#/g$ for laywood filament. The lowest values were $5.97 \times 10^{10} \#/min$ and $2.50 \times 10^{11}\ \#/g$ for PLA filament. The emission rates estimated from both method 1 and method 2 were similar numerical value like the condition under the manufacturer recommended set.

Table 7. The emission rate of nanoparticles under the consistent temperature set

	Method 1[1)]				Method 2[2)]			
Filament	Nanoparticle (<100 nm)		SMPS (10-420 nm)		Nanoparticle (<100 nm)		SMPS (10-420 nm)	
	#/min	#/g	#/min	#/g	#/min	#/g	#/min	#/g
ABS 1	1.86.E+11	9.61.E+11	1.98.E+11	1.02.E+12	1.79.E+11	9.23.E+11	1.91.E+11	9.84.E+11
ABS 2	1.77.E+11	9.02.E+11	1.89.E+11	9.65.E+11	1.51.E+11	7.69.E+11	1.63.E+11	8.35.E+11
PLA	6.67.E+10	2.80.E+11	6.82.E+10	2.86.E+11	5.97.E+10	2.50.E+11	6.13.E+10	2.57.E+11
PVA	8.48.E+10	3.72.E+11	1.42.E+11	6.22.E+11	7.71.E+10	3.39.E+11	1.33.E+11	5.83.E+11
laywood	6.73.E+11	2.93.E+12	6.93.E+11	3.01.E+12	6.51.E+11	2.83.E+12	6.70.E+11	2.91.E+12

[1)] Method 1 : Emission rate estimation method derived from Azimi et al. (2016)
[2)] Method 2 : Emission rate estimation method derived from Kim et al. (2015)

Figure 6. shows the range of time-varying nanoparticles emission rates for all materials under both the manufacturer recommended set and the consistent temperature set. Compared to the condition of manufacturer recommended, the range of time-varying nanoparticles emission rates under the consistent temperature set positioned higher although the few lowest outlying values which occurred just after printing showed up below. The highest median of nanoparticles emission rate with the consistent temperature set was measured with laywood as $6.62 \times 10^{11}\ ea/min$ followed by HIPS ($3.10 \times 10^{11}\ ea/min$), nylon ($3.08 \times 10^{11}\ ea/min$), ABS1 ($1.86 \times 10^{11}\ ea/min$), ABS2 ($1.28 \times 10^{11}\ ea/min$), PVA ($7.76 \times 10^{10}\ ea/min$) and PLA ($5.58 \times 10^{10}\ ea/min$), respectively.

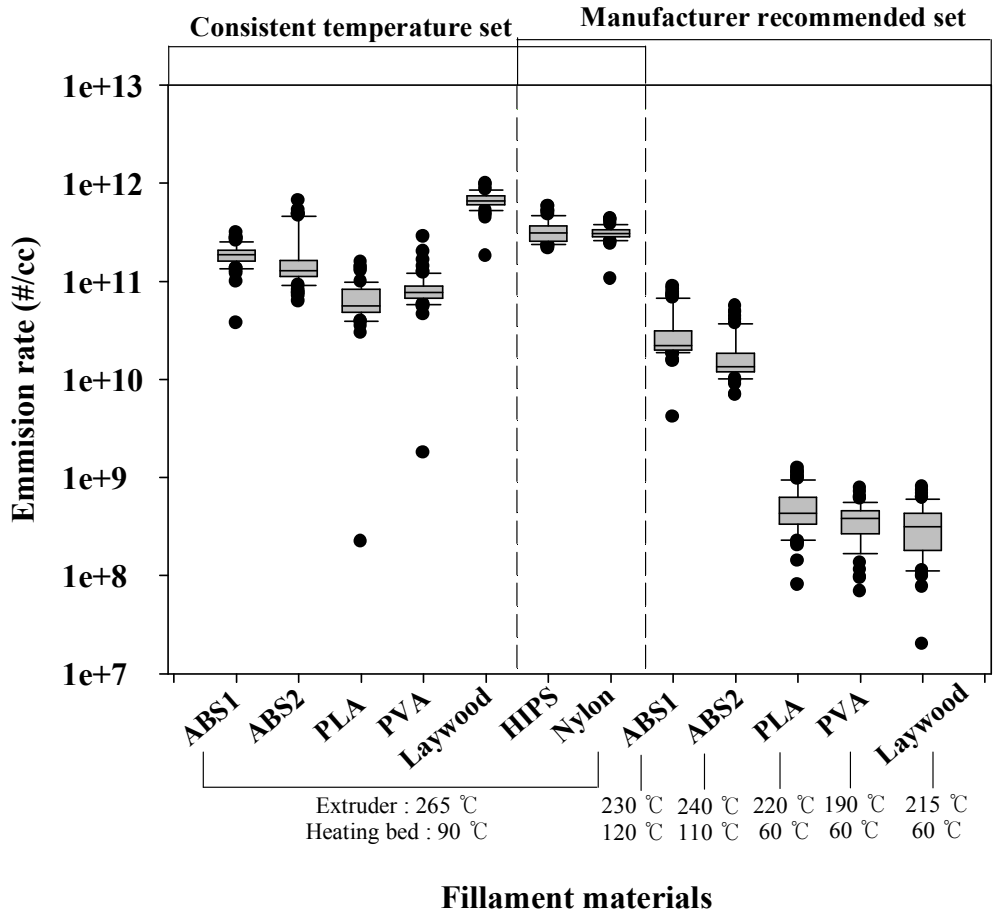


Figure 6. The range of time-varying nanoparticles emission rates for all materials under both the manufacturer recommended set and the consistent temperature set.

3.2.3. Morphology and chemical compositions of the particles

Figure 7 show the FE-SEM/EDX images collected on PC filters during 3D printing with multiple filaments under the consistent temperature set. In common with the sample in the condition of manufacturer recommended set, all the sample images show that particle shape is spherical, containing carbon and oxygen. Also aggregated nanoparticles was observed in the all samples, although ABS 2 sample contains 300 to 500 nm independent particles as well.

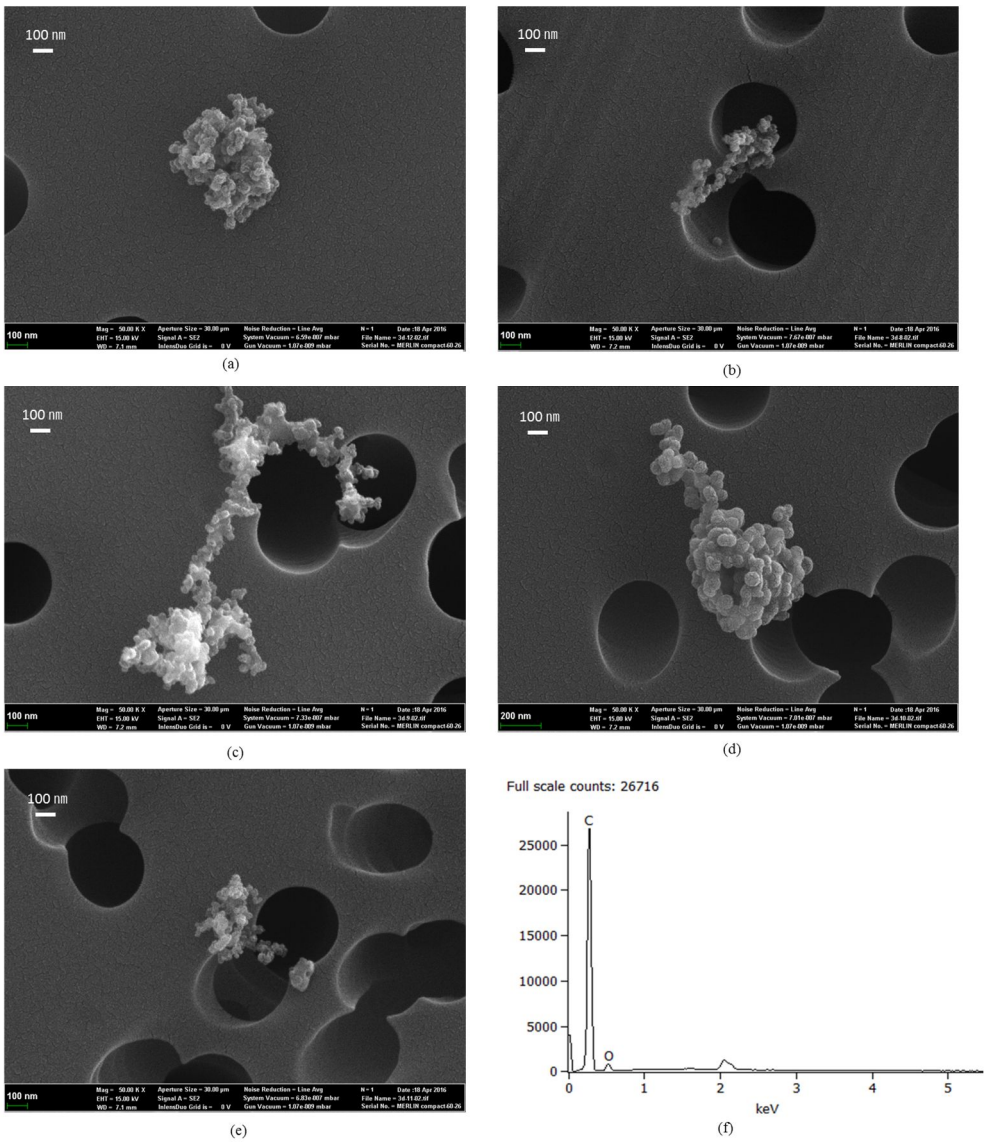


Figure 7. FE-SEM/EDX images collected on PC filters during 3D printing with multiple filaments under the consistent temperature set. (a) ABS1, (b) ABS2, (c) PLA (d) PVA (e) laywood and (f) components of ABS2.

3.3. Control methods

The ABS2 and HIPS filaments were selected for control methods under the condition of manufacturer recommended set. The feed material for all control methods (CTR1 to CTR8) was ABS2. The HIPS was used as a representative filament of emitting the most nanoparticles under the condition of manufacture recommended set during 3D printing. One of the most effective methods was executed with HIPS filament.

3.3.1. Particle concentration

The number concentration of nanoparticles was corrected so that the concentration of "before operation was subtracted from the concentration of "during operation" to compare with various filament materials. From that correction, the number concentration of nanoparticles during 3D printing were 10,776 #/cc with ABS2 filament and 209,415 #/cc with HIPS as a criteria for control methods.

Table 8. Summary of nanoparticle number concentration and the range of concentration for control methods applied operation with ABS2 filament under the condition of manufacturer recommended.

Sort		Nanoparticles (< 100 ㎚)		
		Before operation	During operation	After operation
ABS 2	GM (GSD)	777 (1.06)	11,553 (1.56)	1,140 (1.83)
	Range	698-847	4,360-34,450	762-8,454
CTR1	GM (GSD)	589 (1.08)	3,350 (1.45)	734 (1.54)
	Range	471-667	1,466-10,100	537-2,806
CTR2	GM (GSD)	673 (1.07)	15,642 (1.34)	1,235 (2.16)
	Range	606-785	6,195-20,805	814-14,669
CTR3	GM (GSD)	1,136 (1.06)	1,747 (1.19)	1,342 (1.11)
	Range	1,032-1,344	1,451-2,591	1,153-1,707
CTR4	GM (GSD)	661 (1.09)	1,663 (1.21)	740 (1.31)
	Range	518-765	748-2,335	476-1,568
CTR5	GM (GSD)	553 (1.06)	3,135 (1.55)	607 (1.59)
	Range	495-616	1,355-8,809	433-2,154
CTR6	GM (GSD)	315 (1.08)	1,081 (2.09)	358 (1.30)
	Range	280-366	432-6,069	275-647
CTR7	GM (GSD)	611 (1.05)	1,079 (1.57)	685 (1.15)
	Range	530-669	704-3,341	537-923
CTR8	GM (GSD)	798 (1.05)	803 (1.05)	809 (1.06)
	Range	690-862	720-882	685-896
HIPS	GM (GSD)	621 (1.09)	210,036 (1.27)	1,910 (4.95)
	Range	500-744	88,761-364,331	648-165,826
CTR8 with HIPS	GM (GSD)	712 (1.06)	820 (1.08)	727 (1.08)
	Range	579-780	655-1,086	620-878

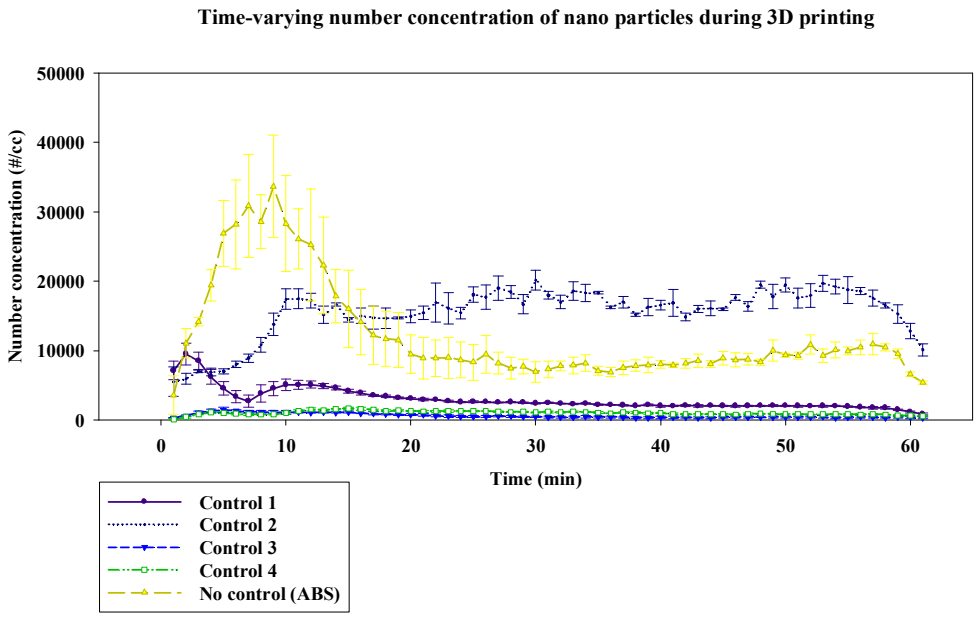
Table 8 summarizes the nanoparticle number concentration and the range of concentration for control methods applied operation with ABS2 filament under the condition of manufacturer recommended. The experiments applied the CTR1 method which added airtight sealing in the condition of the 3D printer released as enclosed type were conducted to compare difference of particle emission with or

without enclosure. The corrected number concentration of nanoparticles was 2,760 #/cc with CTR1 method during 3D printing. The ACF filter was used in the CTR2, CTR3 and CTR4 methods. The experiments for the CTR2 method were executed without enclosure and with the suction fan to which was attached the ACF filter at the front of extruder horizontally. The corrected number concentration of nanoparticles during 3D printing with the CTR2 method was 14,969 #/cc which was higher than 10,776 #/cc without any control method. The CTR3 method was the same as CTR1 but the ACF filter was covered at the ventilation outlet hole. The corrected number concentration of nanoparticles was 611 #/cc with CTR3 method during 3D printing. The CTR4 method was a combination of CTR2 and CTR3 methods. The suction fan at the front of extruder with ACF filter and ventilation outlet hole covered with ACF filter was equipped for CTR4 method. The number concentration of nanoparticles during 3D printing with CTR4 method was 1,002 #/cc.

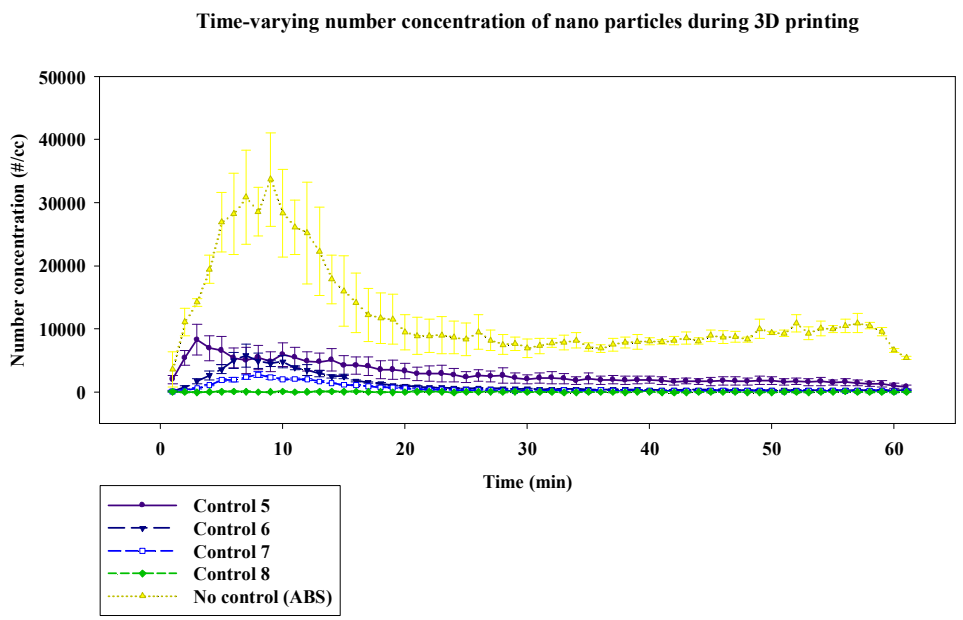
The other four methods (from CTR5 to CTR8 method) were adjusted changing the filter which covered the ventilation outlet hole likewise CTR 3, as a result above. The combination of electret and antibacterial filter was used for CTR5 method. The corrected number concentration of nanoparticles was 2,582 #/cc with the CTR5 method during 3D printing. It is nearly the same value as the CTR1 method when adjusted. The polyethylene filter was used for CTR6 method. The corrected number concentration of nanoparticles was 766 #/cc with CTR6 method during 3D printing. The nano membrane filter was applied for CTR7 method. The number concentration of nanoparticles was 468 #/cc with CTR7 during 3D printing. The HEPA filter was adjusted for the CTR8 method. The

corrected number concentration of nanoparticles was 5 #/cc with CTR8 during 3D printing.

The HIPS filament was used as feed material with CTR8 method which verified the most effective method to remove nanoparticles during 3D printing. The number concentration of nanoparticles was 109 #/cc with HIPS filament during 3D printing.



(a)



(b)

Figure 8. Time-varying number concentration of nanoparticles during 3D printing with all the control methods. (a) CTR1 which simply enclosed and CTR2 – CTR4 which used ACF filter as comparisons and (b) CTR5 – CTR8 which used various filter comparisons.

Figure 8 (a) and (b) display the time-varying number concentration of nanoparticles during 3D printing with all the control methods. The experiments applied CTR1 method showed 9,509 #/cc which is the highest time-varying number concentration at the beginning of 3D printer operation. Then the time-varying number concentration was lowered by 2,729 #/cc in 5 minutes and rallied to about 5,000 #/cc at 10 minutes which is the similar time the highest time-varying number concentration showed as 33,672 #/cc without any control method. After the rally, time-varying number concentration gradually lowered until the end of 3D printer operation. The time-varying number concentration of nanoparticles with CTR2 method was lower than the operation with ABS2 filament without any control method until early 15 minutes. But after this 15 minute, the time-varying number concentration of nanoparticles was sustained 2 times higher than the operation with ABS2 filament without any control method until 3D printing finished. Compare to CTR1 and CTR2, time-varying number concentration of nanoparticles with CTR3 and CTR4 was quite low. The highest time-varying number concentrations of nanoparticles with CTR3 and CTR4 method was 1,453 #/cc and 1,672 #/cc, respectively.

The patterns and values of time-varying number concentration of nanoparticles with CTR5 method was similar to CTR1 method adjusted. The highest time-varying number concentration of nanoparticles with CTR5 was 8,255 #/cc in the very beginning of 3D printer operation. The CTR6 and CTR7 method adjusting time-varying number concentration of nanoparticles had similar patterns except that the values with CTR6 method were about 2 times higher for 20 minutes in the beginning of 3D printer operation. The highest time-varying number

concentrations of nanoparticles were 5,753 #/cc and 2,730 #/cc with CTR6 and CTR7, respectively. The time-varying number concentration of nanoparticles with the CTR8 method show no change during the entire 3D printing. All the data points within ±80 #/cc. Considering Figure 8 (b), it is easy to identify that the CTR8 method is the most effective to remove nanoparticles emitted during 3D printing in all the adjusted method.

3.3.2. Removal efficiency

Table 9 summarizes the removal efficiency of nanoparticles with all the control methods adjusted supplying ABS2 filaments. The removal efficiency was 74.38% with CTR1 method which applied sealing tape to make the enclosed type of 3D printer. Compared to operating without any methods, the number concentration of nanoparticles increased as much as 38.91% with the CTR2 method with the ACF filter attached suction fan equipped at the front of the extruder horizontally in the open state. It was estimated that the suction fan could not draw enough of the emitted particles, rather scattered the particles. The removal efficiency was 94.34 % and 90.71% with CTR3 with the ACF filter covered at the ventilation outlet hole in the enclosed state and CTR4 method with suction fan equipped at the front of extruder and ventilation outlet hole installed ACF filter, respectively. The CTR3 method was the most effective to remove nanoparticles of the four methods (CTR1 to CTR4 method).

Table 9. Summary of the removal efficiency of nanoparticles with all the control methods adjusted after supplying the ABS2 filament

	CTR1	CTR2	CTR3	CTR4	CTR5	CTR6	CTR7	CTR8
Removal efficiency (%)	74.38	-38.91	94.34	90.71	76.04	92.89	95.66	99.95

As a result of the experiments which applied CTR1 to CTR4 methods, the other four methods from CTR5 to CTR8 were executed because only the filter which covered the ventilation outlet hole changed. The removal efficiency was 76.04% with the CTR5 method which had enclosure and attached combination of electret and antibacterial filter. It is similar to the removal efficiency of the CTR1

method which enclosed the 3D printer without any filter. The removal efficiency was 92.89% and 95.66 % with CTR 6 method which had enclosure and attached polyethylene filter and CTR 7 method which had enclosure and attached nano membrane filter. The most effective method was CTR8 method adjusted to remove nanoparticles emitted from 3D printing. The removal efficiency was 99.95% with the CTR8 method which had enclosure and an attached HEPA filter on the ventilation outlet hole.

The HIPS filament was used to verify the removal efficiency of CTR8 method applied in the highest concentration under the condition of manufacturer recommended set. The removal efficiency was 99.95% with the CTR8 method, regardless of nanoparticles being emitted about 20 times higher (10,776 #/cc for ABS2 vs 209,451 #/cc for HIPS).

4. Discussion

In this study, the particle emission characteristics were evaluated during 3D printing with multiple filament materials, and then control methods were devised using a filter to remove the particles emitted.

The FDM 3D printer with all the thermoplastic examined in this study (ABS, PLA, PVA, laywood, HIPS and nylon) emit nanoparticle dominantly under the both condition of manufacturer recommended and consistent temperature. It is well known that nanoparticles can be hazardous due to their characteristics including size and surface properties. Compared to large-sized particles with the same composition, nanoparticles produce greater adverse inflammatory response (Oberdörster et al. 2000, Brown et al. 2001, Warheit et al. 2008).

One of the characteristics of our emission chamber is a high air exchange rate (AER) at 36 per hour. So temporal time-varying size distribution and number concentration may be reflected immediately by real-time sampling instruments. The cylinder shape, which has the same surface for all layers of the object, was selected to confirm the uniformity of particle emission during 3D printing. Under the condition of manufacturer recommended, the number concentration of nanoparticles for all filament materials increased sharply just after printing was initiated and maintained for 5-15 minutes then decreased to a lower level, although still higher than the background level. It is similar to the result of the other studies although they chose complex objects (Azimi et al. 2016, Steinle P. 2016). From those results, the peak particle emission in the early period was the same phenomenon during 3D printing regardless of the shape of the object. But, the peak

concentration was sustained or decreased gradually until the finish under the condition of consistent temperature, except ABS2 filament.

To estimate the emission rate during 3D printing, two methods which are derived from Azimi et al. (2016) and Kim et al. (2015) were applied. Both values of emission rate were similar. The advantage of the method derived from Azimi et al. (2016) reflected the temporal time-varying emission rate during 3D printing. So it may be more accurate than the method of Kim et al (2015). But the method of Kim et al. (2015) to calculate the emission rate is quite simple, using the approximate emission rate during 3D printing.

The few studies of the nanoparticles emitted during 3D printing that have been conducted (Stephens et al. 2013, Kim et al. 2015, Zhou et al. 2015, Azimi et al. 2016, Steinle Patrick. 2016). All selected ABS and PLA filament as a feed material. Their result of emission rate based on time with ABS filament were $2.4 \times 10^8\ \#/min$ as the lowest (Steinle P. 2016) and $1.9 \times 10^{11}\ \#/min$ as the highest (Stephens et al., 2013). Our result of emission rate under the condition of manufacturer recommended was in the middle of them at $3.00 \times 10^{10}\ \#/min$ with ABS1 and $1.83 \times 10^{10}\ \#/min$ with ABS2 which was similar to the other studies $1.61 \times 10^{10}\ \#/min$ from Kim et al (2015). and $2 - 9 \times 10^{10}\ \#/min$ from Azimi et al (2016). Our result of emission rate based on time in the condition of manufacturer recommended with PLA filament was also positioned in the middle of the other studies at $3.18 \times 10^8\ \#/min$ with a similar level at $4.27 \times 10^8\ \#/min$ from Kim et al (2015). and $1.00 \times 10^8\ \#/min$ from Azimi et al (2016). There was only one previous study examined with multiple filaments

except for ABS and PLA. (Azimi et al. 2016) The emission rate based on time using HIPS, nylon, laywood were$3.26 \times 10^{11}\ \#/min$, $3.13 \times 10^{11}\ \#/min$ and $3.53 \times 10^{8}\ \#/min$, respectively. Compared to the result of the previous study, it is at least one order of magnitude higher. ($4.00 \times 10^{9}\ \#/min$ for HIPS, $2.00 \times 10^{8}\ \#/min$ for nylon and $8.00 \times 10^{7}\ \#/min$ for laywood, respectively). These results were distinct from using ABS and PLA filaments.

As the result of our experiments, ABS, HIPS and nylon emitted nanoparticles over $10^{10}\ \#/min$ which is called 'high emitter' which criteria set forth He et al. (2007) under the condition of manufacturer recommended. According to higher extruder temperature applied in the consistent temperature set, nanoparticles were emitted at least one order of magnitude more than the condition of manufacturer recommended for every filament material examined in this study. Especially, the emission rate using laywood was increased as high as $6.73 \times 10^{11}\ \#/min$ despite having one of the lowest values at $3.53 \times 10^{8}\ \#/min$ under the condition of manufacturer recommended. So all materials examined in this study can be classified as 'high emitter' under the condition of common temperature. It may be important that the extruder and heating bed temperatures were set as low as reasonably practical to reduce the amount of nanoparticles emitted in 3D printing.

Figure 4 and Figure 7 show the image of particles and composition emitted during 3D printing. According to higher extruder temperature applied to the consistent temperature set, aggregated spherical nanoparticles were shown dominantly in every filament material. Those nanoparticles consisted of carbon and oxygen. The chemical composition of nanoparticles emitted from 3D printing may

correspond to the filament materials as raw thermoplastics.

Our study is the first attempt to devise the control methods to prevent or reduce the nanoparticles emitted during 3D printing. Several studies of nanoparticles emitted from 3D printing have been conducted. Those were focused on the evaluation and characteristics of nanoparticles from 3D printing mainly. (Stephens et al. 2013, Kim et al. 2015, Zhou et al. 2015, Azimi et al. 2016, Steinle Patrick. 2016) Our experiments considered not only evaluations and comparisons of nanoparticles emitted up to filament materials, but also design and application for controlling nanoparticles. First sealing tape was applied to confirm the effectiveness of enclosure. It showed substantial effect with 74.38% of removal efficiency with an ABS2 filament. Then various kinds of filters were attached at the ventilation outlet hole for removing nanoparticles. The highest removal efficiency of nanoparticles was 99.95% with HEPA filter and over 90% with other filters using ABS2 filament, except the combination of electret and antibacterial filters which showed 76.04%, similar to not using any filter. To verify the removal efficiency in the highest concentration, the HIPS filament was used as the supplying filament with the CTR8 method which had enclosure and an attached HEPA filter on the ventilation outlet hole. The CTR8 method shown 99.95% of removal efficiency, regardless of nanoparticles emitted about 20 times higher (10,776 #/cc for ABS2 vs 209,451 #/cc for HIPS).

As a result of this study, it is important to use the 3D printer with low extruder temperature, as low as reasonably practical and feed the filaments which emit fewer particles to eliminate the source in 3D printing. And the type of enclosure that should be used is equipped enclosure for open type with ventilation fan which

has the filter installed specializing in removing nanoparticles. However, the first priority for preventing or reducing the pollutants emitted from 3D printers is to established standards or guidelines. In spite of increasing popularity of 3D printers, there is hardly any standard or guideline for users' health and safety. It is necessary to reflect the studies of pollutants emitted from 3D printers and then establish standards or guidelines for the environment, health and safety. Subsequently, the manufacturers of 3D printers and filaments should recognize the pollutants emitted from 3D printers and then accelerate research to invent safe filaments and technology or find the proper conditions not to emit pollutants.

Limitations

The limitation of this study was out of consideration for gaseous materials emitted in 3D printing. The hazardous gaseous materials such as styrene and aldehydes, which are suspected to affect human health, were measured during 3D printing in the other studies (Kim et al. 2015, Azimi et al. 2016). It is necessary to evaluate gaseous materials emitted during 3D printing with multiple filament materials and devise the control method to prevent both gaseous and particulate materials in future studies.

Another limitation is lack of control methods for open type 3D printers. Despite the CTR3 method that equipped filter attached to a suction fan without enclosure applied in this study, the number concentration was higher than without any control method. The effective control method for open type 3D printers should be considered in future studies.

5. Conclusions

The particles emitted during 3D printing under the two different presets, manufacturer recommended and consistent temperature set, up to seven filament materials were characterized in the extruder and heating bed temperatures. And then eight control methods were examined to effectively remove particles emitted during 3D printing.

- Under both the condition of manufacturer recommended and consistent temperature, the particles emitted during 3D printing for all seven filament materials were primarily nano-sized particles. Those nanoparticles, which consist of carbon and oxygen, were spherical shape and aggregated with each other.

- ABS, HIPS and nylon can be classified as "high emitter" which is over 10^{10} $\#/min$ under the condition of manufacturer recommended. According to higher extruder temperature applied to the consistent temperature set, nanoparticles were emitted at least one order of magnitude more than the condition of manufacturer recommended applied for all filament materials. So all materials can be classified as 'high emitter' under the condition of consistent temperature set.

- The enclosure is effective to decrease the concentration of particles emitted during 3D printing. When the proper filter was adjusted at the ventilation outlet hole of the 3D printer, the nanoparticles were removed almost perfectly. The HEPA filter was the most effective filter (removal efficiency: 99.95% for ABS2 and HIPS under the manufacturer recommended set) to remove nanoparticles

during 3D printing.

Therefore, it is necessary to use the 3D printer with as low extruder temperature as possible and supply the filaments which emit fewer particles to be eliminated at the source of 3D printing. In case of using high emitter as a feed material, an enclosed type of 3D printer with a ventilation fan to which is attached the filter specialized in removing nanoparticles should be used. However, the first priority is that the standards or guidelines should be considered to prevent or reduce pollutants emitted from 3D printers. It is important to reflect the studies of pollutants emitted from 3D printers and then establish standards or guidelines for the environment, health and safety.

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국문초록

3D 프린터 가동 시 발생하는 입자상물질 제어

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Ⅰ. 연구목적

FDM 방식 3D 프린터는 저렴한 비용과 조작의 간편함으로 인해 대중들에게 빠르게 보급되고 있다. 하지만 사용자들은 3D 프린터 가동에 의한 건강 영향을 간과하고 있다. 최근 연구에 따르면 3D 프린터 가동되면서 유해인자 발생이 확인되었다. 기존 연구는 3D 프린터가 다양한 열가소성 플라스틱이 재료로 사용될 수 있음에도 불구하고 오직 PLA와 ABS 필라멘트에 국한되어 연구가 진행 되었다. 또한 유해물질이 발생하는 것을 확인하였음에도 불구하고 구체적인 해결방안에 대한 연구는 아직 진행되지 않았다. 그렇기에 이번 연구를 통해 7종의 필라멘트를 압출기와 가열판 온도에 따른 2가지 조건으로 3D 프린터 가동 중에 발생하는 입자상 물질 특성을 파악하였으며, 필터 기반의 제어장치를 고안하여 3D 프린터 사용시 발생하는 입자상 물질을 제어를

시도하였다.

Ⅱ. 연구방법

3D 프린터 가동 전, 중, 후에 따른 총 입자 수 농도는 SMPS와 OPS를 통해 노출 챔버에서 진행되었다. PC 필터를 통해 포집한 샘플은 형태학적 특성과 정성적 성분 파악을 위해 FE-SEM/EDX을 사용하여 분석하였다. 3D 프린터는 2종류의 ABS와 PLA, PVA, HIPS, nylon, laywood 필라멘트를 압출기와 가열판 온도에 따른 2가지 온도 조건(재료별 제조사 권장 온도 조건, 동일 온도 조건)에서 시행되었다. 시간에 따른 입자 발생률은 입자 수 농도를 통해 계산식을 통해 산출하였다. 입자상 물질을 제거하기 위한 필터기반의 8종의 제어 방법을 고안 및 적용하여 위와 동일한 절차로 실험을 진행하였다.

Ⅲ. 연구결과 및 고찰

3D 프린터 가동 시, 실험에 사용된 모든 재료 7종에서 나노 입자가 지배적으로 발생하였으며, 재료별 제조사 권장 온도 실험조건에서 HIPS가 가장 높게 $3.26 \times 10^{11}\ \#/min$이 발생하였으며, PLA는 $3.18 \times 10^{8}\ \#/min$로 가장 낮게 발생하였다. 동일 온도 실험조건에서 나노 입자 발생률은 laywood가 $6.73 \times 10^{11}\ \#/min$ 으로 가장 높으며, PLA는 $6.67 \times 10^{10}\ \#/min$으로 가장 낮은 발생률을 보였다.

전자현미경을 통해 재료별 제조사 권장 온도 실험조건과 동일 온도 실험조건에서 실험한 모든 재료에 대한 나노 입자는 전부 구형이며 탄소와 산소로 구성되어있음을 확인하였다.

제어 방법 실험은 ABS 필라멘트를 제조사 권장 온도로 총 8가지 방법에 대하여 진행하였다. 우선 단순 밀폐에 의해 74.38% 나노 입자 제거 효율을 확인하였으며, 밀폐 상태에서 다양한 필터를 환기구에 부착함을 통해 최고 99.95% (HEPA 필터) 제거 효율을 확인하였으며 대부분 필터에서 90% 이상의 제거효율을 확인하였다. 다만 항균•정전필터는 필터를 부착 하지 않은 상태와 큰 차이가 없었다. 가장 높은 나노 입자 제거 효율을 보인 HEPA 필터를 대상으로 재료별 제조사 권장 온도 실험조건에서 ABS 필라멘트보다 약 20배 높은 농도로 나노 입자를 발생시키는 HIPS 필라멘트를 사용하여 실험을 진행한 결과 역시 동일하게 99.95%의 제거효율을 확인하였다.

Ⅳ. 결론

본 연구에서 7종의 열가소성 플라스틱 필라멘트를 사용하여 3D 프린터를 가동 시 나노 입자가 지배적으로 발생하였으며, 재료별 제조사 권장 온도 실험조건 보다 압출기 온도가 높은 동일 온도 실험조건에서 모든 재료가 더 높은 나노 입자 발생률을 보였다.

제조사 권장 온도 기준으로 ABS2 필라멘트를 제어 방법을 적용할 시 단순 밀폐만으로도 70% 이상의 제거 효율을 보이며, 환기구에 HEPA 필터를 부착할 시 최고 99.95%의 제거 효율을 확인하였다.

3D 프린터 가동을 통해 나노 입자 노출을 줄이려면 우선 압출기 온도를 가능한 낮추며, 나노 입자가 적게 발생하는 재료 사용을 통해 발생원 자체적으로 낮추는 것이 필요하다. 또한 나노 입자 노출을 줄이려면

개방 형태보다는 밀폐 형태가 좋으며, 밀폐 형태의 3D 프린터에 환기구 설치와 함께 나노 입자 제거에 특화된 필터를 부착하면 더 높은 제거효율을 통해 나노 입자 노출을 최소화 할 수 있다.

주요어: FDM, 3D 프린터, 나노입자, 필터, 제어방법

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