A STUDY ON RECYCLING OF WASTE POLYAMIDE 12 POWDER INTO 3D PRINTING FILAMENTS

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Abstract:

Over decades, 3D printing technology develops dramatically and is one of modern processing nowadays. 3DTech Company provides 3D printing products by using Multi Jet Fusion (MJF) technique. In this technique, nylon polyamide 12 (PA12) powders are used as main material due to its high-quality properties. In this thesis, researches in safety handling with fine powder in laboratory and recycling of waste powders were conducted. The aims of the thesis are safety handling with fine powder in lab, research in degradation properties of waste powder, and recycling waste powder into filaments. Waste PA12 powders are microparticles, thus safety working with this fine powder in lab is highly concerned because of its inhalation affects and explosion characteristic. However, after processing, a huge amount of unmolten powder turns into waste. Besides, a research in degradation of unmolten powders are declared in this thesis. During MJF, unmolten powders suffer for a certain time in very close to melting point. For this reason, viscosity of PA12 powder decreases due to increasing in molecular weight. Additionally, MJF works in oxygen environment, thus oxidation occurs during printing. In this thesis, moisture absorption characteristic of waste PA12 was conducted by a hot-air drying oven and Melt Flow Rate of waste PA12 powder was tested in Arcada lab. In order to enhance quality properties of waste PA12 powder, the topic Development of filaments using selective laser sintering waste powder is mentioned in this thesis. The authors used Tungsten carbide (WC) as added reinforcement material and they applied a filament-making machine to fabricate filaments from waste powders. The authors also declaired that the recycled filaments are appropriated for Fused Depositon Modeling (FDM) method with suitable required properties. Regarding with recycled filaments were made, the waste PA12 powders can be recycled by adding reinforcement material and processed into filaments by using a filament-making machine.

Keywords:	Waste PA12 powder, MJF, degradation, oxidation, recycling, filaments, 3DTech Company, FDM.
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ABBREVIATION

MJF	Multi Jet Fusion
DSC	Differential Scanning Calorimetry
FDM	Fused Deposition Modeling
LEL	Lower Explosive Limit
LFL	Lower Flammable Limit
MEC	Minimum Explosible Concentration
MFI	Melt Flow Index
MFR	Melt Flow Rate
MVR	Melt-volume Flow Rate
MIE	Minimum ignition energy
M_n	Molecular number
M_w	Molecular weight
PA12	Polyamide 12
PPE	Personal Protective Equipment
SLS	Selective Laser Sintering
Tg	glass transition temperature
T_m	Melting Temperature
WC	Tungsten carbide

FOREWORD

I would like to convey my gratefulness to my supervisor Maiju Virtanen, Laura Villela Pacheco for their professional reccommendations, guidance, and support through this thesis.

I would also like to thank my professor Steward Makkonen-Craig who introduced me to this interesting project and company 3DTech Company who offered this work with fused PA12 powder.

Lastly, I would like to thank you my son and family for their support and encouragement.

Helsinki, 2019

Dung Ha

1 INTRODUCTION

1.1 Background

Over the past ten years, technology has developed in leaps and bound. One cannot deny is 3D printing has been one of state-of-the-art manufacturing techniques recently. It is not only a modern fabricating but it also an eco-friendly way of process.

Nylon Polyamide 12 (PA12) is known as an extremely tough but flexible material in 3D printing. It also gives high adhesion between layers [1]. Since Nylon PA12 is an extraordinary material, giving high weight in recycling Nylon PA12 powder is deserved. Nevertheless, PA12 has some disadvantages such as degradation after processing, and its water absorption characteristic [2]. Thus, paying high attention in its drawback while manufacturing is also a helpful way to archive more experiences.

However, the heart of the matter is how to deal with waste materials from 3D printing technology. In Powder Bed Fusion family, there is approximately 60 % of unmolten powders collected after fabricating [3]. Therefore, a study on waste PA12 is conducted in this thesis to define an approach of recycling of waste PA12 powders. Besides, Nylon PA is famous for its chemically resistant and wide range of application [2]. Hence, recycling PA12 also leads to economical target.

Nowadays, various manufacturing methods are applied to reuse un-fused material. In this thesis, recycling discarded powder into 3D printing filaments with focusing on the percentages of added reinforcing material is studied. Additionally, this research is based on laboratory work condition, therefore safety handling with powder and suitable laboratory machining are discussed through this thesis.

1.2 Aims of thesis

The aims of thesis are researching in handling and recyclability of waste Nylon PA12 powder from 3D printing Multi Jet Fusion (MJF) manufacturing. By conducting this project, waste PA12 powder was determined an eco-friendly issue. Additionally, this thesis can give suggestions in working and manufacturing with powders in laboratory environment.

Objectives:

1. Study on safety handling with powders in laboratory

The experiments with fine powder are conducted in Arcada laboratory, therefore safety handling with fine powder including inhalation problem and explosion problem is going to discuss through this thesis.

2. Study on degradation of waste PA12 powder and test its moisture absorption and Melt Flow Rate (MFR)

Waste powder is discussed about its changed properties because of degradation during exposing in MJF process. Besides, some tests on MFR by a Melt Flow Index and its moisture absorption by an air-drier were conducted and reported in this thesis.

3. Study on recycling of waste powders into filaments

In this thesis, waste powder is suggested to go through recycling by applying a filament-making machine. (Kumar, 2017) This waste powder is supposed to mixed with a reinforcement material to obtain better quality [4].

2 LITERATURE REVIEW

2.1 Additive manufacturing

2.1.1 3D printing

3D printers create three-dimensional things by a technical is named “additive manufacturing”. A printing process allows people to make objects in shapes they admire. Basically, 3D printer works under control of computers and follows instructions from an electronic design file. Additive manufacturing is known as a precise and multipurpose method. Besides, digital media plays an important role in bringing virtual world to physical one because it is easy to edit and alter. Figure 1 describes Addictive manufacturing steps in general.

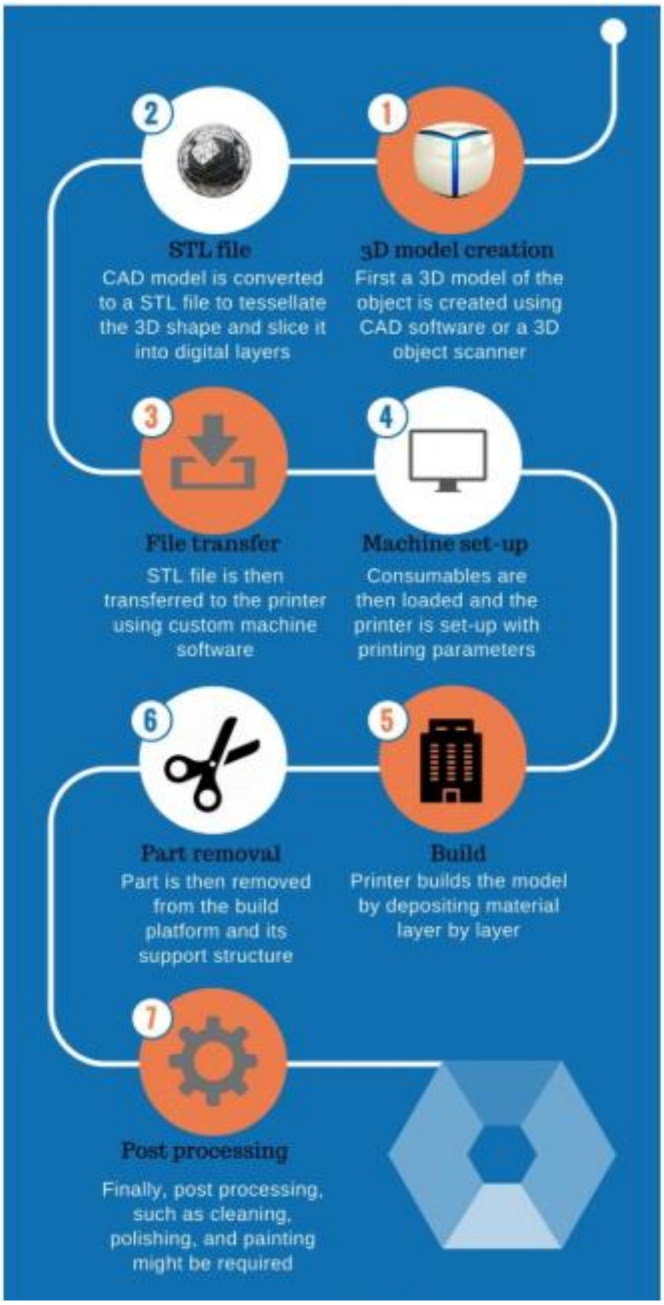


Figure 1. Additive manufacturing processing steps [5].

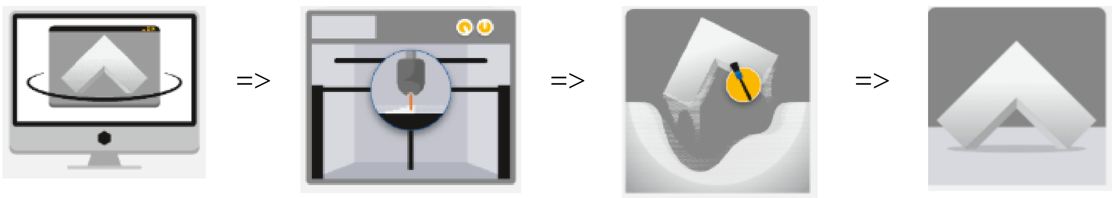
Next, "faxing" [6, p. 17] is also one of the amazing characteristics that 3D printer can do. On the other words, physical things switch from bits to atoms and atoms to bits [6]. The raw materials for additive manufacturing are various such as plastic, metals, ceramics, edible semi-solid foodstuff, lesser extent concrete or glass.

Generally, 3D printing is divided into 2 main technologies [6]:

- The first one is deposition method. In this method, raw single or mixed materials are deposited layer by layer onto the print bed. And then, a real object is shaped with three-dimension. This method includes Polyjet Printing, Laser Engineer Net Shaping (LENS), and Laminated Object Manufacturing (LOM).
- The second method introduces the selective binding process. In this method, raw materials are fused into layers. Stereolithography (SL) and Laser Sintering (LS) are well-known techniques in this group.

2.1.2 Introduction to Powder Bed Fusion family

Selective Laser Sintering (SLS) and Multi Jet Fusion (MJF) fabricating belong to Powder Bed Fusion family. Principally, a part of product is shaped by thermally fusing through layer-by-layer from bed fusion. SLS and MJF are almost similar in working methods. They use the same material applications - thermoplastic polymers. Yet, there is only one different characteristic between them is heat source. SLS sinters powders out of CO_2 laser while MJF builds up part by fusing agent [7].
This manufacturing basis divides into 3 phases including preheating, building, and cooling down. Particularly, in building phase has 3 repeated process steps - material coating, energy input and consolidation. This process will form a final product from layers of melted solid nylon powder. This step raises the powder temperature above its glass transition point. Figure 2 explains Schematic of Powder Bed Fusion processing.



Model is designed in computer by a specific software. => Powders are sintered layer by layer => Left-over powders are removed => Final product

Figure 2. Schematic of Powder Bed Fusion processing [8].

In Powder Bed Fusion family, Polyamide 12 powder is the most popular choice due to its self-supporting characteristic. Thus, support structures are unnecessary requirements in this kind of Addictive manufacturing. Final products come in very high freedom design such as visual art, high accuracy final product, and parts with good mechanical resistant [7].

Description of schematic of MJF is showed in Figure 3 [7].

Step 1: The building platform is first covered by a thin layer of nylon.

In this step, the heat reaches just below the melting temperature of the polymer (below 170 ^{0}C) and a recoating blade spreads an enough super thin layer.

Step 2: Built up

At this point, the temperature raises just above 170 ^{0}C. Gradually, layer by layer, a solid part is built by scanning entire cross section of the component by UV curing light.

Step 3: The build platform moves downwards, and the surface is recoated. Next, the whole part is formed completely by repeating the process.

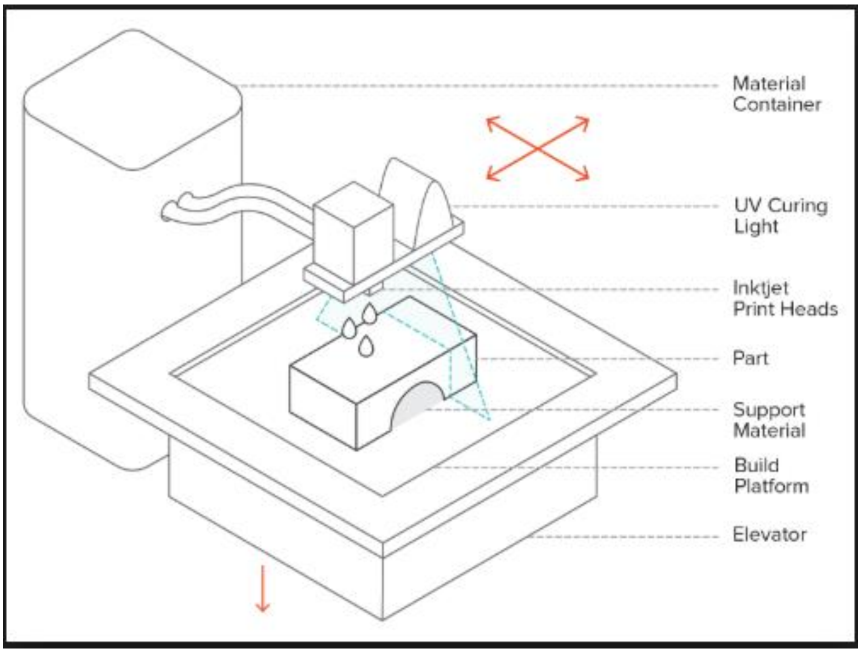


Figure 3. Schematic of an MJF printer [7].

2.1.3 Material

2.1.3.1 Nylon Polyamide 12

The most common used material in MJF is Polyamide 12 (PA 12) or Nylon 12 [7]. Nylon 12 is a polymer. It is made from Laurolactam monomers and each monomer has 12 carbons. The formula of Nylon 12 is $[(CH_2)_{11}C(O)NH]_n$. [9] and showed in Figure 4.

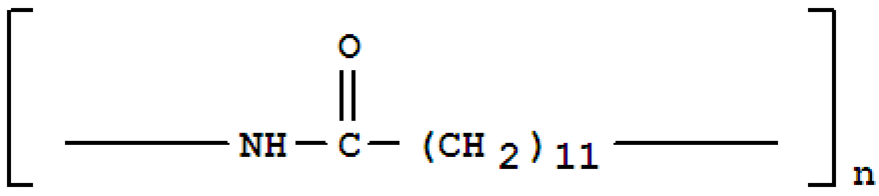


Figure 4. Chemical formula of Nylon 12 [10].

PA12 is an engineering thermoplastic - strong but flexible material. PA12 is also chemical resistant, good mechanical properties, and insensitive stress cracking. It is water resistant but not waterproof [11]. It absorbs moistures, so storage it in an air-tight bag and drying before process is required.

It is a solid material for Powder Bed Fusion technique and goes in form of fine powder. They are white, very fine, and granular powders but they have amazing manner of being self-supporting for final products. This powder-based will give design freedom for instant concept models, visual arts, or medical applications [2].

To improve the mechanical and thermal characteristic of final parts, PA12 powder can be adjusted with different additive materials for example carbon fibers, glass fiber, or aluminum [7].

2.1.3.2 PA12 powders are used in 3DTech Company

3DTech Company fabricates their products out of PA12 powders – VESTOSINT 3D Z2773 PA12 what are supplied by VESTOSINT Company [12].
The particle size of the powder is about 55 – 60 µm. In some specific requirements, it can be 30 µm or 90 µm. [13]. Its technical general properties are defined in Table 1 (a) and (b).

Table 1. Technical property (a) and General property of PA12 (b) [13].

Property	Test method	Unit	Value
Tensile Strength, Max Load⁴ – XY	ASTM D638	MPa/psi	48/6960
Tensile Strength, Max Load⁴ – Z	ASTM D638	MPa/psi	48/6960
Tensile Modulus⁴ – XY	ASTM D638	MPa/ksi	1700/245
Tensile Modulus⁴ – Z	ASTM D638	MPa/ksi	1800/260
Elongation at Break⁴ – XY	ASTM D638	–	20
Elongation at Break⁴ – Z	ASTM D638	%	15

(a)

Property	Test method	Unit	Value
Bulk density	ISO 1183	g/cm3	460
Particle size, d10 Particle size, d50 Particle size, d90	ISO 8130/13	µm µm µm	26 57 83
Relative solution viscosity (m-Kresol, acid measured)	ISO 307	–	1.59
DSC Melting point 1st heating, 20 K/min	ISO 11357	°C	187

(b)

2.1.3.3 Waste PA12 powder

The waste PA12 powders were collected from MJF - 3DTech Company. They are mixed powders from different bed printer positions and unknown storing day. The powders have light yellow-brown and shows in Figure 5.

Figure 5. Colors of virgin (left) and waste powders (right)from 3DTech Company.

Waste PA12 powders were collected by manually, and then stored in 3 plastic boxes. All powder boxes were sealed with tapes and stored in Arcada laboratory. Figure 6 shows storage condition in Arcada lab.

Figure 6. Sealed powder boxes in Arcada lab.

2.2 Safety handling with fine powder

Because PA12 powder in this research belongs to microparticle group and based on Material Safety Data Sheet of PA12 powder [14], explosion of fine powder and health effects of fine powder through inhalation are got high attention in this thesis.

2.2.1 Dust explosion

Dust explosions happen when combustible dust cloud of any flammable material formed up in the air. Basically, this explosion occurs in two main conditions are the explosive concentrations and a source of ignition.

Besides, a dust explosion involves five necessary elements at a time. They are known as "Dust Explosion Pentagon" graphic and is described in Figure 7.

Figure 7. Dust Explosion Pentagon [16].

The first three elements are needed for a fire. They are in group "fire triangle" [17]: Combustible dust (fuel), Ignition source (heat, sparks from electric or mechanical sources), and Oxygen in air (oxidizer).

An additional two factors must be present for a combustible dust explosion are Spreading of dust particles in adequate quantity and concentration and Confinement of the dust cloud.

Conversely, if one of the above five components is missing, an explosion cannot occur.

Ignition of dust cloud

The main ignition of a dust cloud is a hot surface, or/and a spark form electric or mechanical reasons. The results of Minimum Ignition Energy (MIE) and Ignition Temperature were conducted and reported only for comparison purposes and must not for explosion safety design [15]. They are showed in Table 2.

Table 2. MIE and Lower Explosive limit [15].

Material	Ignition Temp (°C)	Min Ignition Energy (mJ)	Lower Explosive Limit (g/m³)	Pmax (bar)	Kst (bar m/sec)
Aluminium	560	<1	60	11.2	515
Magnesium	760	>1000	30	17.5	508
Zinc	250	300	250	6.7	125
Cellulose Acetate	520		30	9.8	180
Methyl Cellulose					
Methylacrylamide	500	100	30	8.7	97
Phenloic Resin	460			9.3	73
Polyamide	460	>1000	125	6.9	38
Polystyrene	450	100	400	5.4	14
Urea	520	100	125	9.7	119
Cocoa (dust)			60	7.6	75
Coffee	470	>1000	60	9.0	90
Cornstarch	400	10	30	8.2	107

- The Minimum ignition energy (MIE) forecasts the ease and severity of ignition of a dust cloud.
- The minimum explosible concentration (MEC) which determines the minimum amount of dust in air required to extend an explosion. The MEC includes the Lower Flammable Limit (LFL) or Lower Explosive Limit (LEL) for gases and vapors in air.

Explosive concentrations

Explosive violence sometimes does not happen with all mixture of flammable dust and air due to their explosive concentrations. In case of the concentration of the dust and air is above or below the range of concentration, the mixture cannot explode. Additionally, the finer particle size of material the easier condition to get explode.

The lower explosive limits of many popular materials have been determined. They are various from 10 g/m^3 to 500 g/m^3. Generally, for most applied purposes, 30 g/m^3 is considered as the lower explosive limit [15]. However, the upper explosive limits are not well conducted because of insignificant duplication under laboratory environment experiments.

Table 3 defines dust deflagration index (K_{st}) stating the comparison of severity between those dusts. The larger the value of K_{st}, the more dangerous the explosion.

Table 3. Value examples of different types of dusts [15].

Examples of K_{st} Values for Different Types of Dusts

Dust explosion class*	K_{st} (bar.m/s)*	Characteristic*	Typical material**
St 0	0	No explosion	Silica
St 1	>0 and = 200	Weak explosion	Powdered milk, charcoal, sulfur, sugar and zinc
St 2	>200 and = 300	Strong explosion	Cellulose, wood flour, and poly methyl acrylate
St 3	>300	Very strong explosion	Anthraquinone, aluminum, and magnesium

The actual class is sample specific and will depend on varying characteristics of the material such as particle size or moisture.
* OSHA CPL 03-00-008 - Combustible Dust National Emphasis Program.
** NFPA 68, Standard on Explosion Prevention by Deflagration Venting.

2.2.2 Health effects through inhalation

Fine particles can go into the lungs through inhalation system and give negative health effects. In the workplace, exposure to fine particles should be avoided. The smaller particles present the bigger risks. As they can go deep into the lungs; they can offer a chance of chemical absorption into the blood along with physical interaction with respirator system [18]. Figure 8 explains the traveling of fine particles in human respirator system through conducting zone, transitional and respiratory zone.

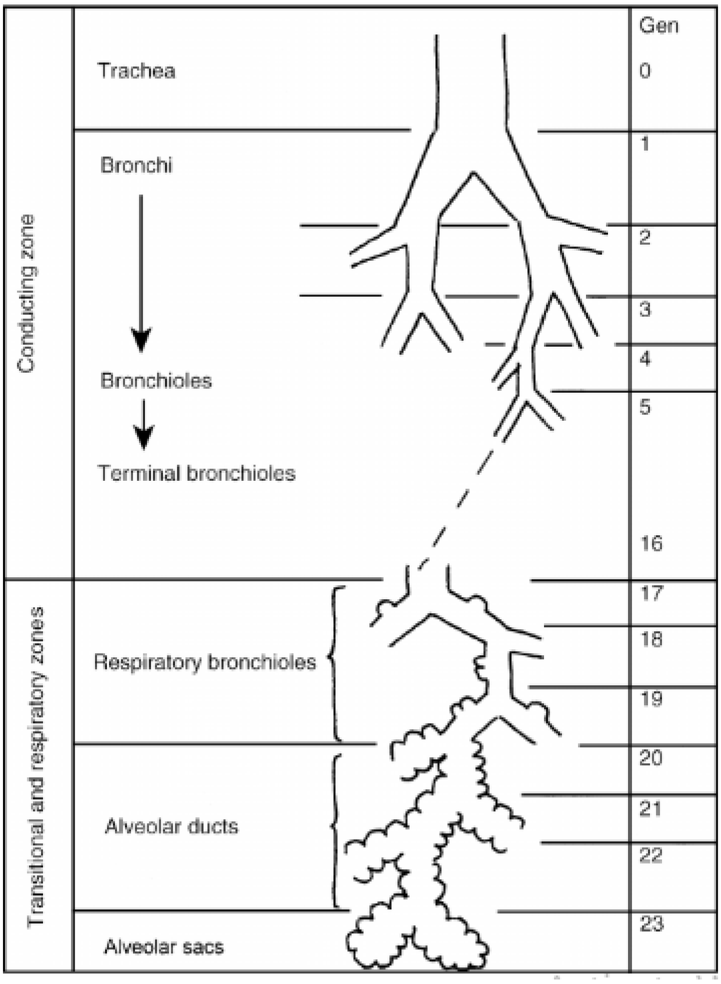


Figure 8. Human tracheobronchial tree [18].

2.3 Degradation of waste powder

2.3.1 Chemical degradation of waste PA12

In Powder Bed Fusion, final product is created by depositing layers in building flatform. Powders surrounding product are removed after cooling down process. This unused material is also named as part-cake powders. The remaining powders are collected separately and can be used for further purposes. However, other applications from the part-cake powders should be get highly considerations. Because it changed characteristics in physical and chemical properties. These different structure between part-cake powders and virgin powders occurs due to thermal processing such as heat from flat, processing time, cooling time within manufacturing [19].

During building processing, the bed heaters are kept around 170 ^{0}C for a certain time. It means the unmolten powders simultaneously undergo that temperature for that certain time. This temperature is above glass transition temperature T_g (40 – 60 ^{0}C) but just close to melting temperature T_m (170 -180 ^{0}C) [20]. This reason could explain that crystallization occurs while processing, where temperature reaches to maximum temperature of crystallization T_c [21].

Figure 9 illustrates Melt and Crystallization enthalpy of HP – MJF.

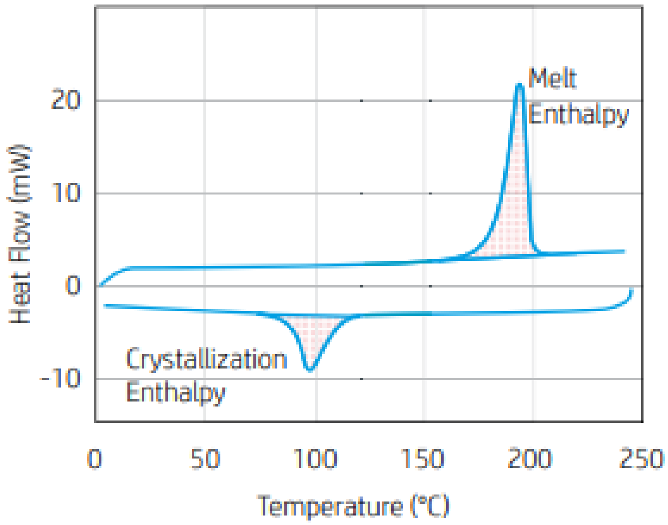


Figure 9. Melt and Crystallization Enthalpy of HP- MJF [22].

In Powder Bed Fusion method, melting and crystallization can occur throughout the process and require further completely cooling at the end of printing [23]. The maintained temperature of the building phase and cooling phase affects in polymer properties by crystallization state. And it continues increasing during cooling phase. (Pham, 2017) An investigation by Pham *et al*, (2017*)* showed that polar amide groups (-NHCO-) crystalline with some amorphous regions [23].

Moreover, the polymer chains enhance their mobility at the temperatures above T_g, the polar amide groups attract other polymer chains. Their mobility leads to lower strength but higher flexibility. Besides, they also grow the molecular weight (M_w) and molecular number (M_n) of the molecular chains. This attraction of polymer chains is explained by giving rise between hydrogen bonding -C-O- and -H-N- of molecular chain. On the other words, the rising of M_w and M_n leads to vary in PA12 melt characteristic. Additionally, the M_w is inversely proportional to the viscous. Therefore, the increasing M_w the decreasing viscosity. The decreasing in viscosity can be tested by Melt Flow Rate metrics at a given temperature [21].

HP Company (2017) conducted an experiment in degradation of Vestosint 3D-Z773 PA12 powder. The powder was aged in oven with constant temperature of 165 ^{o}C. It then was tested with Melt Flow Index ISO 1133 at above 40 – 50 ^{0}C of melting point of PA12 i.e 227 – 237 ^{0}C, weight load varies from 1.2 to 5 kg [12]. The Melt Flow Rate - Suggest Metric from HP company is 4 – 40 cc/10 min for 5 kg mass [22].

The result showed MFR drops from 60 to 20 g/10min after around 6 hours. It is described in Figure 10.

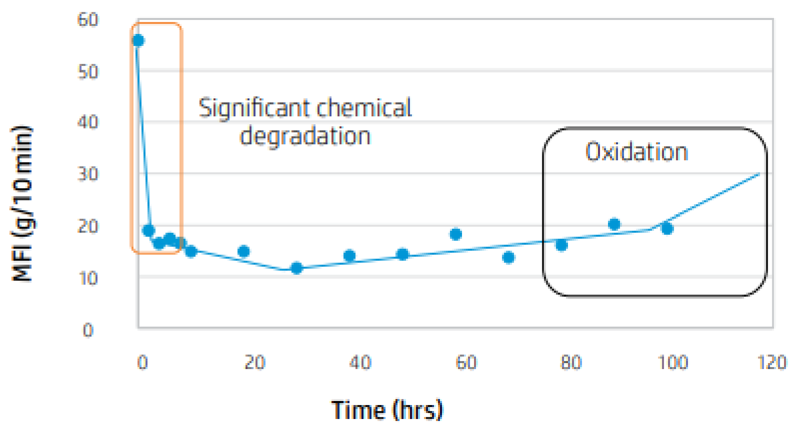


Figure 10. MFR of PA 12 oven aging [12].

It is probable to sort the powder quality from the build time. The powder is below 20 hours of building time and/or the maximum of 200 mm of building height can be considered that the powders are not very damaged. It then could be collected as good quality used powders with high potential of reuse. The MFR results of this powder group are vary from 18 – 50 g/10min. Conversely, if the building time is more than 40 hours and/or above 200 mm building height, the powders can be assumed as bad quality used powders and then collected separately. This powder group shows MFR value below 18 g/10min [19].

2.3.2 Oxidation of waste PA12

In Powder Bed Fusion family, SLS works in nitrogen environment while MJF from HP company works with air. Consequently, air environment leads the material to oxidate.

During processing in HP's Multi Jet Fusion technology, PA12 powder is exposed to about 165 ˚C in the bed temperature. Experiment from HP Company (HP Company, 2018) in oven condition indicates that it takes 80 hours for the material to start to oxidate. However, duration of printing a full print bucket takes only 15 hours in real, hence oxidation does not happen in a constant temperature of 165 ˚C.

Occasionally, it is clearly to see some areas of brown powder underneath of printed parts or between parts showing in Figure 11. The printed parts areas are hotter than the white powder location. Hence, if there is not enough space between printed parts, the white powder gets trapped between them, and so gets even hotter than 165 ˚C. It probably reaches up to 185 ˚C.

Figure 11. Oxidation in an HP MJF printed bucket [12].

For that reason, the hotter the white powder temperature is, the quicker the oxidation occurs. The processing time and temperature oxidation are very sensitive. Then, if the powder is for example at 185 ˚C, it would take only 8 hours in heat before the material begins to turn from white to yellow or brown [22]. This is defined in Figure 12.

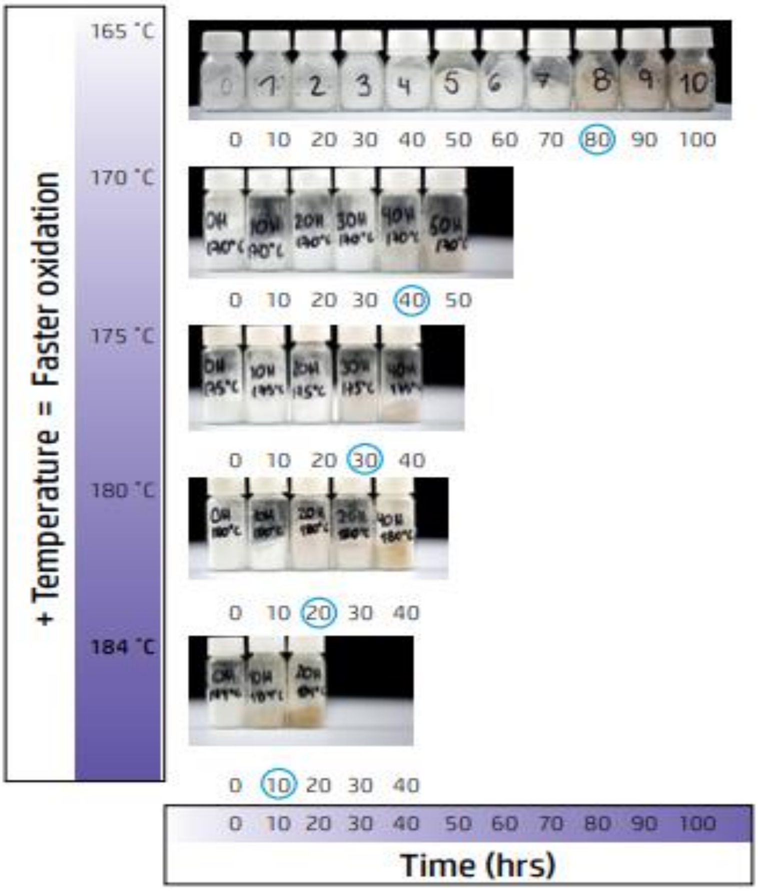


Figure 12. Effects of time and temperature on PA powder oxidation [22].

2.4 Recycling waste powder

2.4.1 Possibility of recycling of used PA12 powder

In the fusing processing, the powder is consolidated because of the heat from bed heaters surrounding the building platform. The unmolten powder undergoes a major thermal cycle and spends many hours at temperature above the T_g and very close to T_m. Then it is cooled down in room temperature. This leads to decrease in viscosity of the material. Recycling and reusing waste powder are necessary due to high cost of purchasing material and needed to minimize amount of waste.

Although there are many requirements to produce components by recycling or reuse waste powder as much as possible, it is not achievable currently to reuse 100% of used powder from Powder Bed Fusion family [21].

The percentage of virgin powder is mixed with used powder so called refresh rate in order to improve quality of used powders. An experiment was conducted by WAY Yusoff, D.T Pham, K.Dotchev [19] to declared the refresh rate powder can change shrinkage and rough surface of the finish products that is commonly called as “orange peel”. This experiment also showed selection of refresh rate in order to reduce the consumption of virgin material through relationship of refresh rate and MFR values [24]. Table 4 gives their relation data.

Table 4. Relation of refresh rate and MFR [24]

Description of Recycled PA2200	Powder grades MFR (g/10min)
3 times recycled	13
2 times recycled	17
20% once used powder mixed with 80% 2 times recycled powder	20
40% once used powder mixed with 60% 2 times recycled powder	23
48% 2 times recycled powder mixed with 52% fresh powder	25
100 % Once used powder	27
Once used powder mixed with 65% fresh powder	33

The higher number of recycled powders times increased the viscosity because of badly deteriorated. Nevertheless, the melt viscosity is improved and less degradation when fresh powder was blended in different ratios. As a result of improving MFR, the “orange peel” also developed dramatically between MFR 17 g/10min, 25 g/10min, and 27 g/10 min and showed in Figure 13.

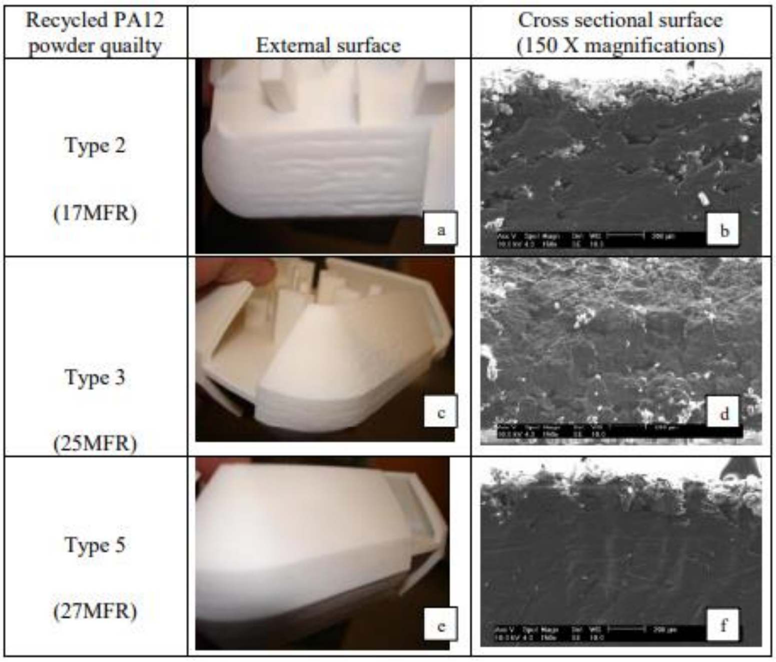


Figure 13. The influence of MFR to finished surfaces and their microstructure [24].

HP Company (HP, 2018) provides the recommended mix ratio of 80 % used and 20 % fresh. This ratio has been tested and it maintains good material quality. HP 3D High Reusability PA12 has been designed to avoid the molecular growth during the material is exposed under bed heater temperature with time.

Figure 14 describes the increasing the percentage of fresh powder can extend reusability and whiteness of the material. Besides, avoiding reuse yellow powders close contact with print parts because the very high temperature makes powders become oxidate and reduces quality.

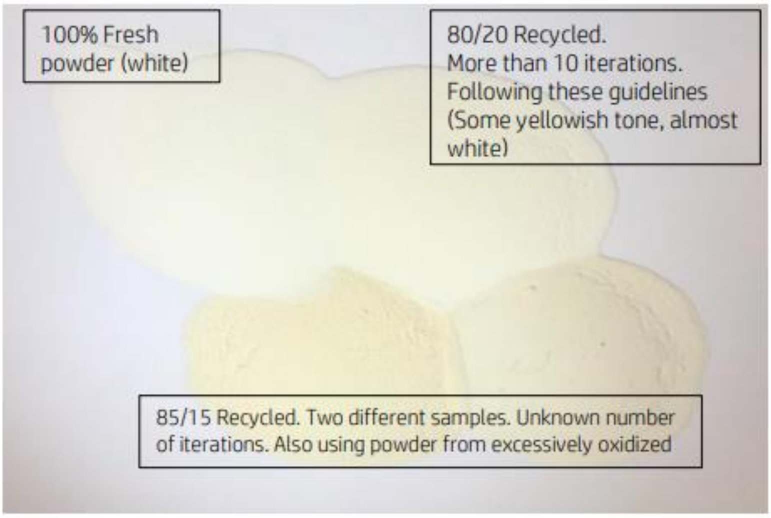


Figure 14. HP 3D high reusability PA12 [22]

The other way of recycling material for fusion printing, HP Company invented closed chain processing. Inside this closed chain work, used powder are collected directly from previous print, they then sieved and mixed with fresh powder for next print. This processing is described in Figure 15.

Figure 15. HP Jet Fusion 3D open platform [25].

2.4.2 Recycling of waste PA12 powder into 3D printing filaments

There are several tests conducted on the degradation of polymer powders and its effect on final properties. (Kumar, 2017) Used powders are mixed with 30 – 50 % of fresh powders and can be processed a few more times before powders sorted into waste [4].

HP Company mentioned that the yellow color is very important on fusing lamp calibration, for that reason always make sure mixed powder is white enough. Moreover, though over time the powder continues to yellow, this sign alone does not indicate material property degradation [12]. Therefore, in order to maintain white color of mixed powder, the darker yellow or brown powder turn into waste.

The mentioned waste powders above are high-value and are not like low value plastic wastes such as bottles, bags. Bed Fusion waste powder has its own advantage of already being in powder form and clean unlike other general polymer wastes. Consequently, recycling those waste powder into filaments are strongly cost-effective and environment friendly [12].

In order to obtain filaments, Sanjay Kumar and Aleksander Czekanski (Kumar, 2017) mixed waste PA 12 from SLS with tungsten carbide (WC) and processed by a single screw extruder. WC is added to enhance mechanical properties of filaments. The percentages of WC vary from 12.5 % to 50 % and adjusted by 12.5 % for each mixed. They were 100 % waste PA, 87.5 % PA + 12.5 % WC, 75 % PA + 25 % WC, 62.5 % PA + 37.5 % WC, and 50 % PA + 50 % WC. (Kumar, 2017) Differential Scanning Calorimetry (DSC) and Melt Flow Rate (MFR) tests were performed to define and valuate properties of each mixtures [4].

3 METHODOLOGY

3.1 Mitigating hazards with fine powders in laboratory

3.1.1 Handling

- Avoid generate dust powders into the air
- Always keep materials closed in a container while transporting
- Powder material must be sealed and grounded in store condition

- Do not use sparking tools
- Engineering controls for example working with suitable laboratory exhaust and containment systems (vented enclosure and/or powder-handling enclosures) helps reducing and preventing to spread of powder within work place.
- Everyday housekeeping should be established

3.1.2 Personal Protective Equipment

Personal Protective Equipment (PPE) is compulsory. Figure 16 describes PPE using in lab while working with fine powders.

- Safety goggles: adjustable-fitting protective eyewear with side shields and over coverage
- Lab coat
- Glove: nitrile gloves should be worn and change as frequent as possible
- Dust mask or respirator are compulsory while working with and without enclosure
- Washing hands before and after working and contact with powder
- Long pants, long sleeves shirts, closed-toe shoes are required
- Eating, drinking and chewing are not permitted in lab area

Over coverage goggles　　Dust mask　　Respirator

Figure 16. Personal Protective Equipment [26].

3.1.3 Cleaning methods

- All surfaces of supporting equipment need to be cleaned after immediately after spilling, after each use, or at the end of the workday. PA12 are micromaterials (~ 60 µm) [13], thus wet-wiped (wet paper towels), compressed air [17], and HEPA vacuum cleaner are safety and necessary ways of cleaning to minimize dust accumulations (showing in figure 17). Dry-sweep are not allowed for cleaning powders in lab.

- PPE including safety goggles, lab coat, and respirator is required for spill clean-up with wet-wiped methods. Dust masks and gloves are recommended to change as frequently as needed [26].

Compressed air gun cleaner

HEPA vacuum cleaner

Figure 17. Laboratory dust powder cleaners [27].

3.2 Degradation of waste PA12 powder

Drying tests were conducted to measure moisture absorption of waste PA12 powder and MFR tests were conducted to get its viscosity values.

3.2.1 Moisture absorption test

This experiment was conducted by a drying oven Memmert (TAMRO-APTA 90-544011) in Arcada lab. In this test, the differences in mass before and after drying were calculated in order to get the mass of lost water. Moisture absorption characteristic might show degradation of waste powders.

Temperature in this test was set based on PA12 drying temperature. It is around 80 – 85 ^{0}C [28].

Waste PA12 powders was spread on 3 trays (2 metals trays and 1 plastic trays) with around 630 g of powders for each tray.

3 trays of powder were dried in the oven at the same time. The tests were conducted with 2 conditions of drying time. First, 3 trays were dried in 4 hours. The differences of the mass were calculated every hour to measure percentage of lost water. The second test is overnight-drying. In this test, the differences in mass were calculated just once [28].

Figure 18 described 3 trays of waste powder in Memmert air-drying oven.

Figure 18. Procedure of drying powder in hot-air oven Memmert (TAMRO-APTA 90-544011), Arcada 2019.

3.2.2 Melt Flow Rate test

MFR test was conducted following standard ISO 1133:2005 showing in Figure 19.

8-10 g of powders were taken for each test and was input to barrel. The extrusion plastometer was heated to 235 °C with load of 2.16 kg. The cut off interval time was tested in 2 conditions at 15 sec and at 5 sec.

MFR is expressed in grams per 10 min, and given by the equation [29]:

$$\mathrm{MFR}(T, m_{nom}) = \frac{600m}{t}$$

Where:

T: test temperature (°C)

m_{nom}: nominal load (kg)

m: average mass of the cut offs (g)

t: cut-off time-interval (sec)

600: factor used to convert grams per second into grams per 10 min (600 s)

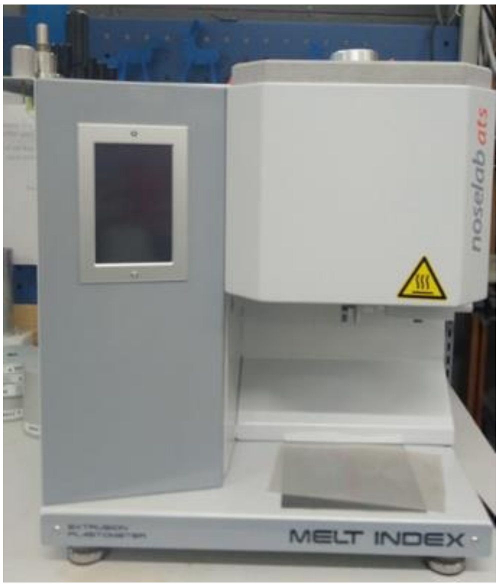


Figure 19. Melt Flow Index ISO 1133:2005, Arcada 2019.

3.3 Recycling waste PA12 powder into filaments

3.3.1 Material reinforcement

Tungsten carbide (WC) is a chemical compound obtaining equal parts of tungsten and carbon atoms. Tungsten carbide is a fine gray powder with average size of 5 µm [30].

WC is selected above all because of its hardness and strength. Those characteristics support the flow of polymer chains and increase the strength.

WC is added to enhance mechanical properties of filaments. The percentages of WC vary from 12.5 % to 50 % and adjusted by 12.5 % for each mixed. They were 100 % waste PA, 87.5 % PA + 12.5 % WC, 75 % PA + 25 % WC, 62.5 % PA + 37.5 % WC, and 50 % PA + 50 % WC.

3.3.2 Making filaments

A filament-making machine [31] by a single screw extruder was used to produce filaments from the powder mixtures. In this experiment, Filastruder filament-making machine was applied by Sanjay Kumar and A. Czekanski (2017).

Filament-making machine with nozzle diameter 1.75mm is an extruder suitable for making filament at home or testing in lab.

For making filaments from mixed waste PA12 and WC, the temperature was set at 180 ^oC and kept constantly. Then, the powder mixture is gradually feed into hopper [4].

Figure 20. Filament processing by Filastruder [4].

4 RESULTS

4.1 Drying waste PA12 tests

Table 5 and 6 give results of drying waste PA12 within 4 hours and overnight. The differences in mass before and after drying were calculated. They give almost the same values of lost water around 0.1 %, while the moisture absorption of virgin PA12 powder is 1 – 2 % [14]. Thus, degradation in properties of waste PA12 happened during MJF and its effects on moisture absorption characteristic of PA12.

Table 5. Drying waste powder results of 4-hour-test.

Time	Temperature (^{0}C)	Tray 1 (g)	Tray 2 (g)	Tray 3 (g)
10:05	80	1866.9	1050.4	1907.4
11:05	80	1865.7	1049.3	1905.7
12:05	85	1865.2	1048.8	1905.6
13:05	85	1864.6	1048.7	1905.4
14:05	85	1865	1048.6	1905.5
Differences in mass after 4 hours		**1.9**	**1.8**	**1.9**
Differences in percentage (%)		**0.1017%**	**0.1713%**	**0.0996%**

Table 6. Drying waste powder results of overnight test.

Time	Temperature (^{0}C)	Tray 1 (g)	Tray 2 (g)	Tray 3 (g)
Mon 14/1 10:00	80	1877.4	1046.8	1864.9
Tues 15/1 9:30	80	1875.1	1044.6	1863
Differences in mass overnight		**2.3**	**2.2**	**1.9**
Differences in percentage (%)		**0.1225%**	**0.2101%**	**0.1018%**

4.2 Melt Flow Rate test with waste PA12

Figure 21 gives result of extruded waste PA12 powder. They came in caramel color and with around 6.8 g in mass. The melt flow was too fast; therefore, the result was collected in around 10 cm per cutting and they are stick with each other.

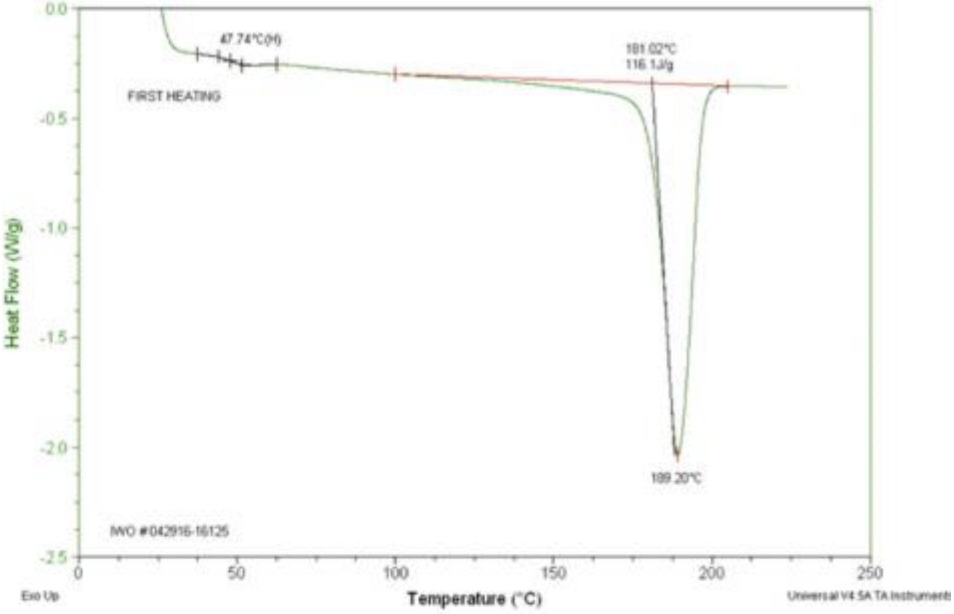
By applying the same the same temperature of 235 ^{0}C as mentioned in a procedure 3.2.1 above and based on metric of MFR test of PA12 powder [22], Figure 21 defined that MJF processing affected on its glass transition temperature.

Figure 21. Extruded material by Melt Flow Index, Arcada 2019.

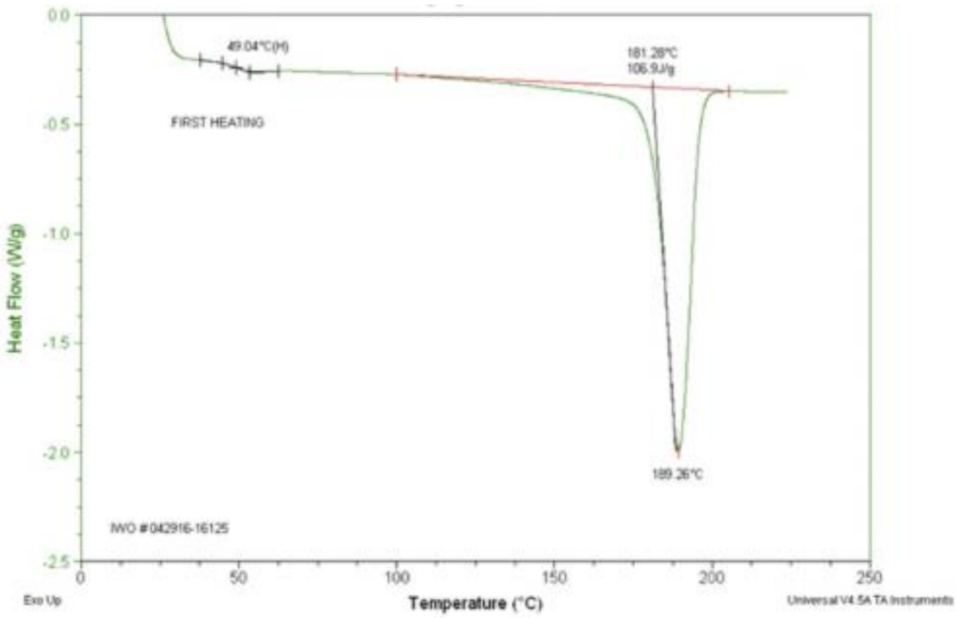
4.3 Powder mixtures and filaments tests

4.3.1 Differential Scanning Calorimetry

DSC was done with all powder mixtures by Sanjay Kumar and A. Czekanski (Kumar, 2017) to know the glass transition temperature, melting point and heat of reaction for both powder mixtures and processed materials. About 10 mg of each samples was heated from 25 to 230 ^{0}C at a rate of 10 ^{0}C/min and then cooled at the same rate.
Figure 22 and 23 show DSC results of waste PA and 87.5 % PA + 12.5 % WC during heating and cooling time.
Experiment was done (Kumar, 2017) to compare between 100 % waste PA during heating and 87.5 % PA + 12.5 % WC during the same heating. Results showed in the group of 12.5% WC, glass transition temperature increases from 47.74 to 49.04 ^{0}C. Therefore, chain flexibility decreases with an increase in WC [4].
During DSC, Figure 22 showed thermal cycles of fusion processing have increased molecular weights of PA12 powder and changed their crystallization points. 100 % waste PA12 powder has around 138 ^{0}C but 87.5 % PA + 12.5 % WC is 144 ^{0}C. Their melting points from around 187 to 189 ^{0}C [4].



(a)



(b)

Figure 22. DSC of waste PA (a) and 87.5 % PA+12.5 % WC (b) during heating [4].

Figure 23 shows the test with 100 % waste PA and 87.5 % PA+12.5 % WC during cooling, values in melting point do not change with temperature of 189 ^{0}C. Besides, the crystallization temperature increases from 144 to 146 ^{0}C.

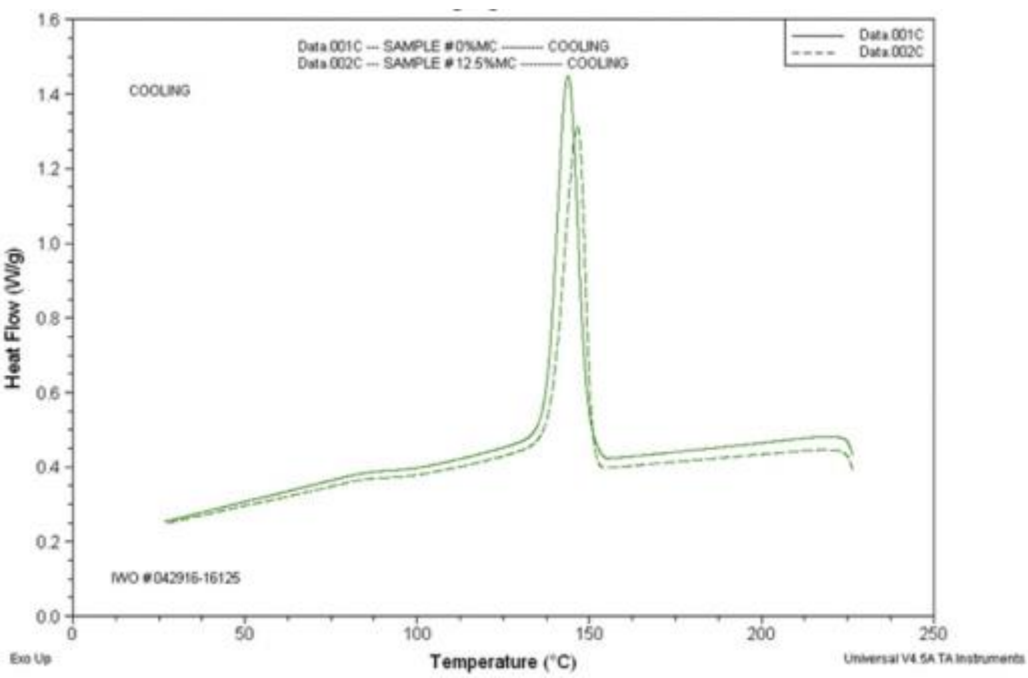


Figure 23. DCS of waste PA and 87.5 % PA + 12.5 % WC (broken lines in figure) during cooling [4].

4.3.2 Melt Flow Rate

MFR test was conducted by Sanjay Kumar and A. Czekanski (2017) at an applied load of 5 kg and at a temperature of 235 ^{0}C. The results from Table 7 show increasing values in MFR with increasing in amount of WC mixed. However, researchers reported that MFR was considered to decrease with an increase of amount WC added. Consequently, melt-volume flow rate (MVR) was calculated. Results from table 7 show decreasing values in MVR with increasing in amount of WC.

Tables 7 provides results of MFI and MVR of 100 % waste PA and all powder mixtures.

Table 7. MFI and MVR of all powder mixtures [4].

Material	Density (g/cm^3)	MFI (g/10min)	MVR (cm^3/10min)
100%PA	0.93	46.3	49.77
87.5%PA + 12.5%WC	2.77	62.1	22.42
75%PA + 25%WC	4.61	65.8	14.27
62.5%PA + 37.5%WC	6.44	66.9	10.39
50%PA + 50%WC	8.28	83.8	10.12

4.3.3 Filaments tensile test

The tensile test of the origin filament and recycled filaments are conducted (Kumar, 2017) by tensile testing ASTM D3822 and showed in Figure 24 [4].

The total length of testing filament is 17.6 cm with 76 mm for the gage length and 50 mm on both sides of the filament are tightened under a grip. The extension rate was selected is 10mm/min [4].

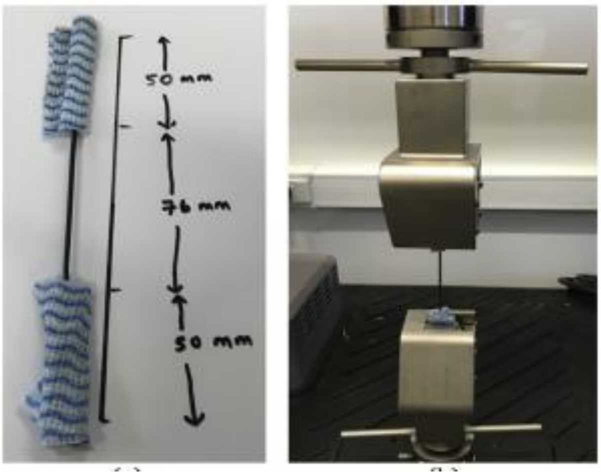


Figure 24. Filaments tensile tests with tensile testing ASTM D3822 [4].

Table 8 gives results in mechanical properties of all types of recycled filaments.

Table 8. Mechanical properties of filaments tested by ASTM D3822 [4].

Filament Composition	Youngs' Modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
100%PA	700	25	Did not break
87.5%PA + 12.5%WC	800	30	700
75%PA + 25%WC	920	40	400
62.5%PA + 37.5%WC	1170	45	300
50%PA + 50%WC	1300	60	260

5 DISCUSSION

Moisture absorption

Table 5 and 6 give almost the same values of lost water around 0.1 % (based on differences in mass collecting in 4-hour-drying test and overnight-drying test), while the moisture absorption of virgin PA12 powder is 1 – 2 % [14]. The changes in chemical properties of PA12 happening during MJF effect on its moisture absorption.

Melt Flow Rate of waste PA12

By applying the same the same temperature of 235 ^{0}C and based on metric of MFR test of PA12 powder [22], Figure 21 defined that MJF processing affected on its glass transition temperature. Therefore, the waste powders melt, burned and flowed too fast. For that reasons, WC was added in Sanjay Kumar, Aleksander Czekansk's project (2017) to enhance its glass transtion temperature [4].

Powder mixtures and filaments

Differential Scanning Calorimetry

During DSC, thermal cycles of fusion processing have increased molecular weights of PA12 powder and changed their crystallization points. 100 % waste PA12 powder has crystallization around 138 ^{0}C while 87.5 % PA + 12.5 % WC shows 144 ^{0}C. Besides, a comparison between 100 % waste PA during heating and 87.5 % PA + 12.5 % WC during the same heating showed that in the group of 12.5% WC, glass transition temperature increases from 47.74 to 49.04 ^{0}C. Therefore, chain flexibility decreases with an increasing in WC. This is a good property for FDM because it leads to a decrease in the shrinkage of FDM final parts [4].

Figure 23 shows the test with 100 % waste PA and 87.5 % PA+12.5 % WC during cooling, values in melting point do not change with temperature of 189 ^{0}C. Besides, the crystallization temperature increases from 144 to 146 ^{0}C. As a result of higher crystallization temperature, the gap between melting and crystallization points decrease. This smaller gap helps decrease shrinkage and distortion effects [4] .

Melt Flow Rate

All powder mixtures MFR tests were done (Kumar, 2017). The results show increasing values in MFR with increasing in amount of WC mixed. The increasing of MFR proves that filament is not clogged into nozzle. However, the maximum percentage of WC was not chosen in this case because of its effects on the ductility of final parts [4].

Researchers reported that MFR was considered to decrease with an increase of amount WC added. Consequently, melt-volume flow rate (MVR) was calculated. Table 7 gives value from 0 % added to 50 % added of WC that MVR decreases with an increase in WC percentages. As a reason of decreasing MVR and increasing in WC percentage, the material will flow well through nozzles and the space filled up by material depositions will be smaller and narrower [4].

However, transferring a high-strength filament into a high-strength 3D product may not be possible. Thus, development of filaments needs to be considered alongside with the selection of an FDM system [4].

Tensile test of filaments

Results from Table 8 show that the more percentage of WC added, the values of tensile strength and modulus increasing.

While Tensile strength, Young's modulus, and elongation at break of ABS filament are 39 MPa, 1924 MPa, 2 % respectively; (Kumar, 2017) the collected data form experiment of Sanjay Kumar and Aleksander Czekanski give higher in tensile strength, elongation at break and comparable in Young’s modulus. It states that recycled filaments have potentials to fulfill conditions for manufacturing high-strength ductile filaments [4].

Testing filaments by Fused Deposition Modeling

A sample of PA+37.5 % WC was chosen by researchers to apply in Fused Deposition Modeling (FDM) MakerBot Replicator 2.0 because it has higher MFR (Kumar, 2017). At the end of the process, there is no clogging inside nozzle reported [4] and showed in Figure 25.

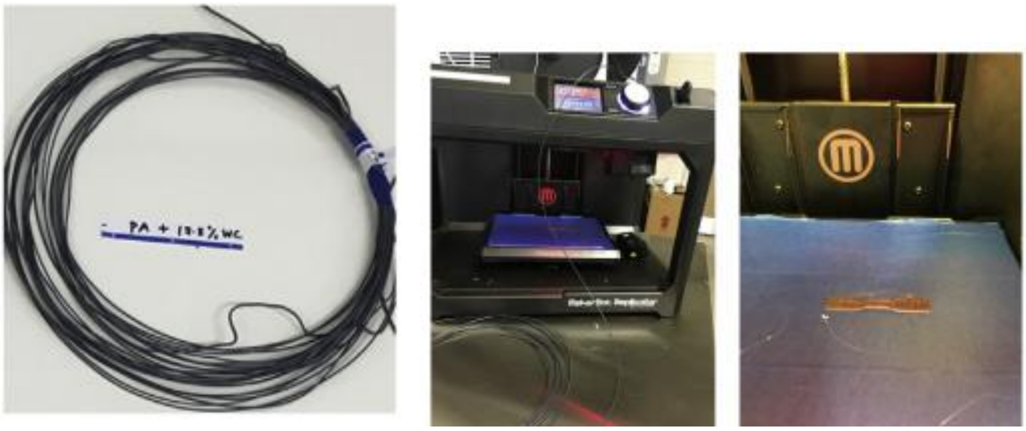


Figure 25. Filament testing with FDM [4].

6 CONCLUSION

Waste PA12 powders are microparticles, thus safety working with this fine powder in lab is highly concerned because of its inhalation affects and explosion characteristic. Safety handling in lab and Personal Protective Equipment are compulsory requirements for working with waste PA12 powders.

During MJF, unmolten powders suffer for a certain time in very close to melting point. This leads to chemical degradation and oxidation of unmolten PA12 powder. Particularly, the time and heat of printing bed close to melting point increase molecular weight of PA12 powder, thus viscosity of PA12 powder decreases. Additionally, MJF works in oxygen environment, thus oxidation occurs during printing. This can be seen that the white color of the powder turns into yellow and brown.

In order to enhance quality properties of waste PA12 powder, Sanjay Kumar and Aleksander Czekanski (2017) used Tungsten carbide (WC) as added reinforcement material. Results from their experiments showed that the higher percentage of added WC the higher Melt Flow Rate got. A filament-making machine was applied to fabricate filaments from different ratios of mixture powders. The recycled filaments gave good values in tensile strength and modulus. Besides, the filaments work well with FDM MakerBot Replicator 2.0 and no clogging inside nozzle was noticed [4].

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APPENDICES

Appendix 1

ARCADA

Rating	Criteria
Likely	Risk occurs daily or weekly
Possible	Risk occurs monthly or annually
Unlikely	Risk occurs once in a decade or less frequently

The criteria for the probability of the risk

Rating	Criteria
Very harmful	Severe long-term injuries or death, major financial loss, major damage to property that cannot be repaired
Harmful	Short-term injuries requiring medical attention, financial loss, damage that can be repaired
Slightly harmful	Minor injuries without medical attention, minor damage repaired easily

The criteria for the severity of consequences of the risk

Probability	Severity of consequences		
	Slightly harmful	Harmful	Very Harmful
Unlikely	Insignificant risk (1)	Low risk (2)	Medium risk (3)
Possible	Low risk (2)	Medium risk (3)	High risk (4)
Likely	Medium risk (3)	High risk (4)	Extreme risk (5)

Consequence/probability risk matrix

JAN-MAGNUS JANSSONS PLATS 1, FIN-00560 HELSINGFORS, TEL +358 (0)20 769 9699 FAX +358 (0)20 769 9622 www.arcada.fi

Appendix 2

Material Safety Data Sheet

Grade	**VESTOSINT® 1111 natural**
Version	5
Release Date	2002/7/19
Revision Date	2014/7/12

DAICEL EVONIK

IDENTIFICATION OF THE SUBSTANCE/PREPARATION AND THE COMPANY/UNDERTAKING

Trade Name	VESTOSINT®		
Grade Name	1111 natural		
Company	DAICEL-EVONIK Ltd.		
Head Office	〒163-0913	2-3-1 Nishi-shinjuku, Shinjuku-ku, Tokyo, Japan	
Dealing Department	Tokyo Office	Sales department	Tel.03-5324-6331 Fax.03-5324-6336
	Osaka Office	Sales department	Tel.06-6342-6712 Fax.06-6342-6718
Emergency address and tel.No.	Tokyo Office	Sales department	Tel.03-5324-6331
	Aboshi Plant	Quality Assurance Dept.	Tel.079-273-3872
Preparation of MSDS	Aboshi Plant	Quality Assurance Dept.	
	〒671-1281	1239 shinzaike,Aboshi-ku,Himeji,hyogo,Japan	
			Tel.079-273-3872 Fax.079-274-3927

HAZARDS IDENTIFICATION

GHS Classification — Not classified or Not applicable

Other Hazards

Risk of skin burns caused by hot melt.
Dust can form explosive mixtures with air.

Precautionary Statement

Avoid breathing dust/gas.
In case of inadequate ventilation wear respiratory protection.
IF INHALED: If breathing is difficult, remove to fresh air and keep at rest in a position comfortable for breathing.
Wear protective gloves.
IF ON SKIN: Wash with plenty of soap and water.
Avoid release to the environment.
Dust can form explosive mixtures with air.
Risk of skin burns caused by hot melt.

COMPOSITION/INFORMATION ON INGREDIENTS

Substance /Nature — Chemical Substance

Chemical Nature — Coating powder on the base : Nylon-12

Information on ingredients

Component	CAS No.	METI	Contents.(%)
Nylon-12	25038-74-8	Listed	95-100
Stabilizers, Others		Listed	0-5

Other information

This sheet only describes safety-relevant data. For specific data, see Product information sheet. The base material of the polymer are registered in Japanese METI.

FIRST AID MEASURES

Description of first aid measures	Pay attention to self-protection. Remove victims from hazardous area. Keep warm, position comfortably, an d cover well. Do not leave affected persons unattended.
Inhalation	In case of symptoms of irritation caused by vapor in thermal processing : provide fresh air, seek medical advice if necessary. Following inhalation of product dust : See that there is fresh air.
Skin contact	Cool melted product on skin with plenty of water. Do not remove solidified product. In case of burns by molten product medical treatment is necessary.
Eye contact	Rinse with plenty of water.

FIRE-FIGHTING MEASURES

Suitable extinguishing media	Water splay, form, CO_2, dry powder
Special hazards arising from the substance or mixture	Maybe released in case of fire : Carbon monoxide, carbon dioxide, nitric oxides, organic products of decomposition. Under certain fire conditions, trace of other toxic product may occur.
Special protective equipment for fire-fighters	Ware suitable protective clothing.

. ACCIDENTAL RELEASE MEASURES

Personal precautions, protective equipment and emergency procedures	In case of product dust is released : Dust mask
Environmental precautions	Should not be released into the environment.
Methods and material for containment and cleaning up	Sweep up or vacuum up spillage and collect in suitable container for disposal. Avoid dust formulation.

. HANDLING AND STORAGE

Handling	
Precautions for safe handling	Avoid dust formulation. Provide for appropriate exhaust ventilation and dust collection at machinery. In case of thermal processing, provide for extraction of vapors or adequate ventilation.
Advice on protection against fire and explosion	Normal measures for preventive fire protection. If dusts are formed; Take precautionary measures against static charges, keep away from sources of ignition.
Storage	
Conditions for safe storage, including any incompatibilities.	Keep in a dry, cool place.

EXPOSURE CONTROLS / PERSONAL PROTECTION

Engineering measure	In case of thermal processing, provide for extraction of the vapor or adequate ventilation. In case of dust being formed, provide for adequate extraction.
Control parameters	No data available.
Personal protective equipment	
Respiratory protection	The wearing of a dust mask is sufficient in the event of dust occurring, operation e.g. during conveyance of the granulate or filter cleaning operation. Do not inhale vapors from hot product. Should vapors inadvertently manage to permeate into the surrounding air during thermal processing, then gas masks fitted with filters designed to combat organic vapors (e.g.A2) or breathing apparatus with an or breathing apparatus with an independent air supply are to be worn.
Hand protection	The wearing of protective gloves is not required if the granulate in question is handled at room temperature. Any areas of skin covered with dust must be washed immediately with soap and water as the powder draws out natural moisture from the skin. Use barrier cream regularly. Protective heat insulating gloves are to be used during thermal processing.
Eye protection	Safety glasses
Hygiene protection	Do not wear contaminated clothing. Wash hands before breaks and at the end of work day. Smoking, eating and drinking should be prohibited in the application areas.

Appendix 3

Powder Processing Risk assessment

Risk	Risk group	Risk sources.	Worst consequences	Risk level	Risk control
Inhalation hazard from powder	P	Working without proper PPE such as full-face mask.	Breathing powder into body	5	Always wear PPE Use full-face mask
Dust explosion while working with powder	P, E, A	Working with careless, do not keep working area clean. Broken containers.	Dust explosion	5	Keep working surface cleaned (no dust) Keep extruder surface cleaned event no heat working. Always wear PPE
Slippery hazard while working with pellets	P	Working with careless, do not keep working area	Slippery accident	2	Clean floor and shoes immediately

		clean. Broken containers.			Always wear PPE
Getting burned while working with drier, press heat machine, extruder	P	Do not keep safety distance. Touch to hot surface of drier, heat mold, heat extruder, extruder dices, extruding materials. Working without proper PPE.	Self-burned from hot surface and from hot fume.	3	Always wear PPE Use full-face mask Do not touch to heating extruder Keep feeding zone always cool Use a scissors to hold hot extruding materials Need assistant while working with heat press
Fume while working with Press heat machine, extruder	P, E	Fume created while working. Working without proper PPE.	Breathing fume into my body	5	Always wear PPE Use full-face mask Always activate ventilation Keep control in temperature and pressure Need assistant while working with heat press
Flash flakes from pelletizing, grinding, tensile testing	P	Working without PPE such as mask and goggles. Working without careful such as using hands to push or pull materials into grinder and pelletizer. Flakes flash from tensile testing.	Flakes flash to eyes, skin	3	Always wear PPE Do not push and pull materials Vacuum machine after work
Fingers cut while working with grinder and pelletizer	p	Working without PPE. Working without careful such as using hands to push or pull materials.	Fingers are cut	4	Always wear PPE Do not push and pull materials Set 0rpm unit for pelletiz-

		Do not set pelletizer at 0rpm unit			er

Appendix 4

PA12 Powder Safety Metrics

Dust Characteristic Test	Standard Test Method	Acronym	Unit	Minimum Acceptance Criteria
Minimum Ignition Energy "dust cloud" w/inductance	EN13821 or ASTM E2019	MIE	mJ	> = 10 mJ
Minimum ignition temperature "dust cloud"	EN50281-2-1 or ASTM 1491	MIT	°C	> = 360°C
Layer Ignition temperature (dust layer)	EN50281-2-1 or ASTM E2021 (till 400°C even if melted before)	LIT	°C	> = 400°C
Auto ignition temp	VDI 2263 ASTM D1929	AIT	°C	> = 400°C