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Manufacture of Polymer Powders for the Industrial SFF System by Using SLS Process

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Abstract: Polyamide 12 were studied as the laser sintering materials for the three-dimensional duplicator equipment of selective laser sintering process. Though polymer powders had a similar chemical structure, there were some differences in thermal properties, particle size and distribution, and shape. These variations had a close relation with the processibility of laser sintering. As far as the particle shape approached a spherical shape, the processibility was improved. The particle size distribution played an important role in the precision of fabrication. The polymer powders with uniform size and higher bulk density were successfully prepared by controlling several finely-controlled steps, such as dissolution, nucleation, propagation and crystallization, in wet process. Several additives were added to improve the thermal, rheological, and flow properties further.

Keywords: **s**elective laser sintering, polyamide, **c**rystallization, powder, bulk density

1. INTRODUCTION

Recently, the life cycle of products has become shorter and shorter in the marketplace because of various and changeable customer's demands. Since it is almost impossible for conventional methods of product development based mainly on machining to meet with the requirements, researches into the reduction of time and cost for product development are in full swing in which diverse product models and frequent change in product design are indispensable. A solid freeform fabrication (SFF) system, known as rapid prototyping (RP) technology, used since the late 1980s, has taken its place in CAD/CAM and has been expected to cope with the dynamic manufacturing environment. RP is a material additive process, in which a 3-D computer model is sliced and reassembled in real space, layer-by-layer.[1-2]

However, these processes have reached material limitations of the prototype for the practical application even if many researchers have sought to improve the material properties of the prototype since the late 1980s.

Nanocomposites are defined as composite materials where the reinforcement has at least one dimension in the range of 1-100 nm. There are many types of nanocomposites, depending on which matrix and nanofillers are used. Mixing of nanoparticles with polymers to form composite materials has been practiced for decades [3].

Selective laser sintering (SLS) is SFF technique. Recently, SLS technology was developed, as one of the new rapid prototyping, tooling and manufacturing techniques. The SLS involves two independent technologies that are materials and manufacturing.

In manufacturing, rapid tooling is a progress from rapid prototyping. It is possible to build prototype products directly from the CAD model resulting in saving time for the market needs.

In materials, polymer for laser sintering was needed in order to fabricate the articles with the three-dimensional equipment of SLS process. The laser sintering materials have been investigated widely. For example, polypropylene, polyethylene and polyamide were used for this purpose. Especially, polyamide-12 (PA-12) proved useful in fabrication by laser sintering process.

Polyamides are common multipurpose synthetic polymers used in a wide range of industrial settings and consumer products. They can be classified into two main families: aliphatic and aromatic polyamides. These materials have excellent mechanical properties [4, 5], thermal properties [6-8], and chemical resistance [9, 10]. In these respects, aromatic polyamides are superior to aliphatic polyamides. For this reason, there have recently been several detailed studies of aromatic polyamides [11-14]. However, chemically resistant polyamides are insoluble in conventional solvents but soluble in strong acids such as sulfuric acid and hydrochloric acid. These characteristics make it difficult to mold polyamide materials in secondary processes. Recently, polymer particles with a narrow particle size distribution have received much attention for possible new applications, such as spacers for display, medical carriers, and chromatographic media [15-20].

Particle size, melting point, fusion enthalpy and softening temperature of polyamide powder for good suitability are known as 50~150㎛, 185~189℃, 127±17J/g and 138~143℃, respectively.

In this study, polymer powders for industrial SFF system were prepared by the precursor, polyamide-12, at different composition of solvent and additives. In addition, their characteristics, such as particle size, surface state and composition, were also investigated, which can give useful information about the applications of polymer powder for industrial SFF system. Therefore, this study is of interest in various field of research related to rapid prototyping system.

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2. EXPERIMENTAL

2.1. Materials

Polyamide is suitable for selective laser sintering process. Polyamides are classified according to a number of carbons, such as polyamide-4, 5, 6, 11, 12, 6/6, etc. The physical, thermal, and mechanical properties of the selected polyamides are summarized in Table 1. [21]

Table.1 Details of the selected polyamides

Property	PA 6	PA 11	PA 12
CH2/CONH ratio	5	10	11
Specific gravity	1.15	1.05	1.01
Average crystallite size (A◦)	233	204	126
Tensile strength (MPa)	55.4	40.7	47
Elongation to break (%)	378	420	446
Flexural modulus (MPa)	59	12	37
Notched Impact strength (kg/m)	4.92	5.90	10.82
Shore D hardness	74	66	76
Glass transition temperature (◦C)	50	46	46
Melting temperature, (◦C)	222	179	177
Degradation temperature	440	440	455

The as-received polyamide was polyamide-12 with pellet form from the EMS-Grivory Co.

The various additives were used for the control of polymer properties. Inorganic oxide (TiO_2) from the Ishihara Co. in Japan was used as nucleating agent and particle size stabilizer. The ethanol from Samchun-chemical Co. in Korea was used for the reaction solvent.

2.2. Instrumental analysis

For the ostensible structural analysis confirmation of the polymer powder, the scanning electron microscope (SEM) was used. The laser diffraction size analysis was used for the determination of the grain size and distribution of the powder.

2.3. Manufacture of polymer powder by high pressure wet process

The core material (TiO_2; 0~20 g) and polymer pellet (polyamide-12; 200g) were added into 1.5 liter of solvent mixture (ethanol; 80~100% + pure water; 0~20%) under vigorous stirring in order to produce the polyamide solution.

Reactor had 2 impellers (impeller; paddle type, d=7cm and h=1.5cm, 150rpm) in order to maintain the proper force to stir. After adding the materials, it took 2 hour to reach 150℃ in order to dissolve completely (dissolution step), then it was maintained for 1 hour. The internal temperature of reactor was lowered to 123℃ after that and stayed for 1 hour as a nucleation step. And then, the reactor internal temperature was further lowered to 118℃ and stayed for another 1 hour as a growth step. Finally, a crystallization step at 110℃ was carried out for 1 hour. These reaction steps were shown in Fig. 1. Also, the internal pressure changes were shown in Fig. 2. The completed products were transferred from the high pressure reactor to other reactor with the aid of heater and vacuum pump. Polymer and solvent were separated by filtration. Finally, we could obtain the polymer powder after adding additives and further drying.

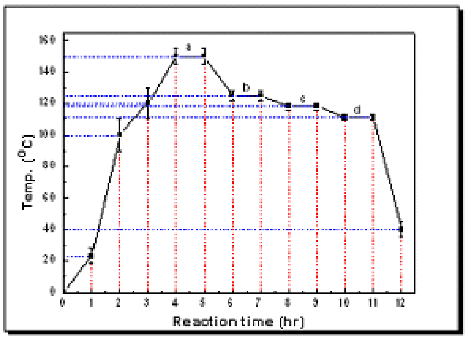

Fig. 1. Temperature control versus reaction time (a: dissolution step, b: nucleation step, c: growth step, d: crystallization step)

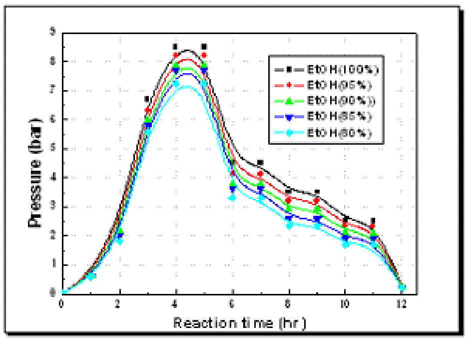

Fig. 2. Pressure coefficient versus reaction time

2.4 Sintering fabrication characteristics of polymer powder from high pressure wet process

The laser equipment and material used in this study were a three-dimensional equipment of SLS process and PA-12 powder obtained by high pressure wet process, respectively. We prepared polymer powders with uniform size and higher bulk density by several finely controlled steps, such as dissolution, nucleation, growth and crystallization, in high pressure wet process. Thermal property and morphology of powders and proper role of additives account for most of the improvement in the laser sintering process. Sintering study shows that PA-12 with low melting temperature is the suitable semi-crystalline polymer. Several additives played important roles in improving the thermal, rheological, and flow properties further.

The selective laser sintering process was employed to apply the polyamide-12 powder to the SFF system. Kim et al. [22] has developed the selective laser sintering process to increase the efficiency. The selective laser

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Table 2. Characteristic of PA-12 powder obtained from high pressure wet process

	Feed				Product			
	Composition of solvent (%)		PA-12 (g)	TiO_2 (g)	Bulk Density (g/l)	Size distribution (%) (>32>50>100)	Size average (㎛)	Morphology (Aspect ratio)
	Ethanol	DI-water						
Test 1	100	0	200	0	420	2.6/13.4/47.5	96.7	0.3~0.5
Test 2	90	10	200	0	482	45/53.7/100	49.3	0.7~0.9
Test 3	90	10	200	5	546	2.2/56.2/100	53.2	0.7~0.9
Test 4	90	10	200	10	578	2.1/57.4/100	54.6	0.7~0.9
Test 5	90	10	200	15	627	2.4/57.9/100	55.8	0.6~0.9

system which can scan divided two regions individually should be employed to develop SFF system capable of large size fabrication. The laser scanner affects the precision and efficiency of the SLS machine intensively.
As illustrated in Fig. 3, the developed dual laser sintering system consisted of a laminating module that supplied and transfered the powder, a heating module to preheat the powder, a nitrogen supply module to create a nitrogen atmosphere, the dual laser module that supplied the laser to a large area, laser units, and a control module to control the entire system.

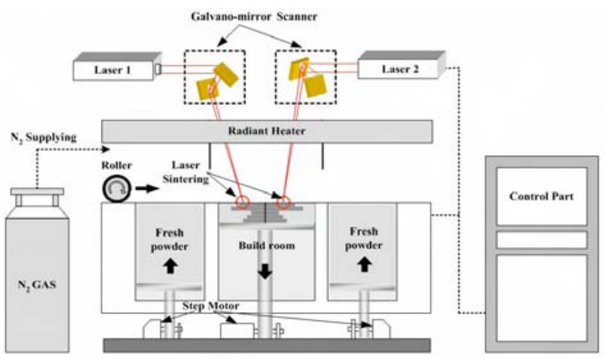

Fig. 3. Schematic diagram of SFF system

The powder was deposited layer by layer and a structure was constructed through laser sintering. For this reason, controls in the z axis to deposit powder and powder transfer in the x-axis using a roller are closely related to the precision of a 3-D structure. The layer depositing cycle started by moving the powder up to the feeding room, followed by spreading a powder layer using a roller in the building room. The roller mechanism had several specially designed features that influenced the roughness of the powder surface and the porosity of each powder, including the linear speed of the roller, the rotational speed of the roller, the feed ratio, the roller roughness, and the layer thickness.
Laser sintering using polyamide powder in the SLS process required a build room temperature of 150□ or greater to preheat the powder. This system utilized a radiant heating system to preheat the polymer powder in the build room and the feed room. In the preheat system, precise control of temperature should be required because the overshot temperature may cause curling or over-melting of the prototype. The nitrogen supply module was used to produce a nitrogen atmosphere in the work room and for the scanner lens. The nitrogen atmosphere controlled soot from micro explosions that could occur during laser sintering within the system and prevented the powder from blowing and sticking to the scanner lens. The module kept over 95% nitrogen circumstance in the work room during operation. Fig. 4 showed the fabricated articles prepared by laser sintering of PA powders.

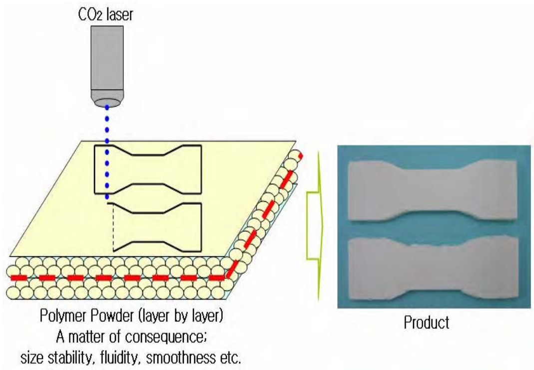

Fig. 4. Fabricated articles prepared by laser sintering of PA powders.

3. RESULT AND DISCUSSION

3.1 Characteristics of PA-12 powder by high pressure wet process

The polymer composite powder was fabricated into prototype material by selective laser sintering process. So, it was possible to manufacture the product having excellence in both size uniformity and mechanical property. The resin/solvent ratio, quantity of additives and composition of solvent were important factors.

Table 2 showed the characteristics of PA-12 powder obtained from high pressure wet process. The average size of pure PA-12 powders was 49.3㎛, while that of TiO_2-added PA-12 powders was 54.6㎛, demonstrating that PA-12 powders were easily crystallized during the process of the nucleation. The bulk density of PA-12 powders obtained with no TiO_2, 10g TiO_2 added, and 15g TiO_2 added were about 482, 587 and 627g/l, respectively, which demonstrated that the bulk density increased as the amount of TiO_2 increased. However, morphology (aspect ratio) of PA-12 powders with 15g TiO_2 was worse than that with 10g TiO_2.

Moreover, the effects of the composition of solvent on the bulk density and morphology were very severe in the

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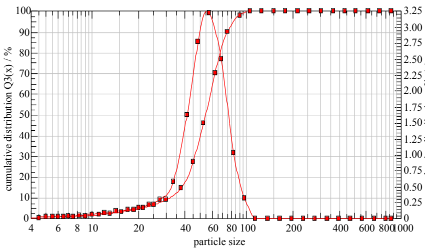
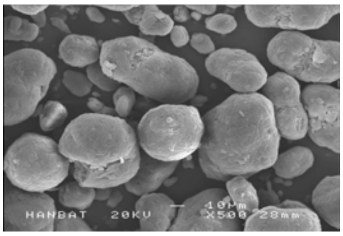
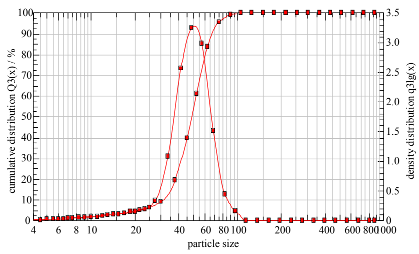
high pressure wet process. As seen in Table 2, DI-water plays an important role in making good properties. Polarity was increased between polymer resin and mixed solvent if DI-water was added into the solvent. So, powder had higher bulk density and good morphology because polarity in the cooling step caused higher cohesiveness.

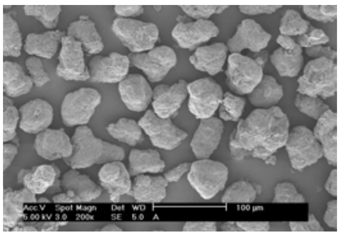
As shown in Fig. 5, the addition of TiO_2 nucleating agent caused the variation of morphology and particle size of PA-12 powder greatly.



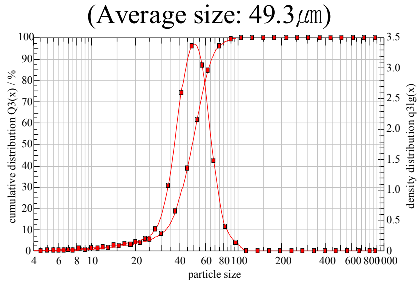


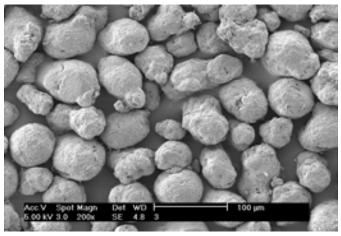
(A) 3D Systems powder
(Average size: 58.03μm)





(B) PA-12 powder without TiO_2
(Average size: 49.3μm)





(C) TiO_2-added (5.0 wt %) PA-12 powder
(Average size: 54.6μm)

Fig.5 SEM micrographs and size distributions of (A) 3D Systems powder, (B) PA-12 powder, and (C) TiO_2-added (5.0 wt%) PA-12 powder.

4. CONCLUSIONS

The investigation of manufacturing polymer powders was carried out in terms of nucleating by TiO_2 as well as the interaction of ingredients including PA-12. The high pressure wet process gave higher bulk density and narrow size distribution. The addition of TiO_2 resulted in the easy crystallization during the process of the nucleation and also the increase in the bulk density. The polarity differences between polymer and solvent showed a big influence on the powder characteristics such as the surface morphology and size distribution which were essential in the selective laser sintering process. Several additives such as flood stabilizer, electrification prevention agent, and size stabilizer were used successfully in order to improve powder properties.

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