Preparing Biodegradable PLA for Powder-Based Rapid Prototyping

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Abstract. Polylactide (PLA) is an environmental-friendly thermoplastic polymer, produced from monomers that can be derived from renewable agricultural sources such as corn and sugarcane. It has received enormous attention in plastic industry due to its degradability and mechanical properties, which are comparable to those of other commodity thermoplastics. PLA has been researched at AIT as one of alternative materials for powder-based rapid prototyping. Since PLA is typically commercially available in a pellet form, it must be transformed to powder before being used in the RP process. Presented in this paper is another technique for preparing PLA powder from its pellets. Rather than typical mechanical crushing method with the assistance of dry ice, PLA solution was prepared by dissolving the pellets in Dichloromethane before being sprayed into water medium mixed with poly(vinyl alcohol) surfactant that was added to facilitate the dispersion of the PLA solution droplets. The powder precipitant was then filtered and dried. Design of experiment was conducted to determine the optimum condition for producing the PLA powder. Pressure and the position of a spray gun's tip relative to the medium surface were the two factors investigated in this study. The results illustrate that the most suitable condition was achieved when the spray gun was operated at 1 bar with its tip submersed 20 mm below medium's surface.

Keywords: Poly(lactic acid), Polylactide, PLA, Biodegradable.

1. INTRODUCTION

Commodity thermoplastics have been widely used in various applications, including in RP applications. Most of them are produced from fossil fuels such as oil, coal, and natural gas, which are non-renewable. After being released from their functions, these commodity plastics are difficult to be destroyed, take a long time to deteriorate and some of them also release toxics to environment, as a result, waste disposal becomes a major problem (Davis and Song, 2006). Therefore, alternative materials that are environmental friendly have been campaigned to replace the traditional plastic materials.

Polylactide or PLA has been recognized as a biodegradable material since it was introduced a couple decades ago. PLA is an environmental-friendly thermoplastic polymer, produced from monomers that can be derived from renewable agricultural sources, especially corn which are widely available in USA (Vink et al, 2003) and cassava (Ghofar et al, 2005). Moreover bio-waste, such as molasses and whey, can be used as carbonate feedstock to produce PLA (Sorrentino et al, 2007). Wastewater can also be used in the process (Khardenavis et al, 2006). Because its initial substances are bio-products, PLA can be decomposed by microorganisms without leaving any residue or giving rise to toxic byproducts (Avella et al, 2005). PLA is also considered as greenhouse gas reducer. CO_2, given off when PLA is decomposed, is absorbed from the atmosphere by agricultural sources (Gupta et al, 2007). It has received enormous attention in plastic industry due to its degradability and mechanical properties, which are comparable to those of other commodity thermoplastics (Mobley, 1994). It has been used for packaging, textile, storage container products and etc.

PLA has been researched at AIT as one of alternative materials for Selective Vacuum Manufacturing (SVM), a new RP technique currently being developed. This technique employs a combination of sand casting and powder sintering processes. A layer can be built by filling loose powder material or natural rubber into a layer cavity (Risdiyono et al, 2006). Unfortunately, PLA is commercially available in a pellet form, which is too large. Thus, a process of preparing PLA powder is required. The particle sizes of materials used in powder-based RP systems, typically, are in micron. For instance, 100~150 μm for Ni-alloy powder, 100~200 μm for Fe powder and 63~100 μm for Cu powder are used in SLS (Tolochko et al, 2003), while 3~5 μm for Hydroxyapatide powder and 90~100 μm for Maltodextrin are used in 3D printing (Chamnanklang et al, 2007). Typical mechanical crushing is not suitable for producing PLA powder due to its tacky nature. Kunioka et al (2006) used dry ice before crushing the pellets to avoid this problem. The obtained

particle size was 214.2 μm which was still larger than the existing powder. Zhou et al (2007) introduced another preparing technique for producing PLLA-composite powder for applying to SLS. PLLA (L-isomeric form of PLA) pellets were transformed to microspheres by using oil-in-water emulsion and solvent evaporation procedure. Liquid solution was poured into the water, and stirred overnight to obtain fine particle sizes between 5-30 μm.

Presented in this paper is a new technique for preparing loose PLA powder. In this study, PLA pellets were transformed to liquid solution and then sprayed into the medium instead of being stirred overnight. The study focused on how to achieve PLA powder that can be used in SVM, and other powder-based RP techniques. Design of experiment was conducted to determine the optimum condition for producing the PLA powder with particle size distribution in the aforementioned range with good flow ability.

2. METHODOLOGY

2.1 Proposed Technique for Preparing PLA powder

After several initial attempts, a conclusion was reached for achieving loose PLA powder from its pellets. This PLA powder preparation process includes five steps as shown in Figure 1. First, PLA pellets are dissolved in dichloromethane solvent to form liquid solution. Time for completely dissolving PLA is dependent on the proportion of PLA pellets and dichloromethane. In the second step, water medium is prepared. Poly(vinyl alcohol) surfactant is added to facilitate the dispersion of the PLA solution droplets. Then the solution is sprayed into the water. The powder is filtered out and dried in the ambient condition. Stuck powder is then crumbled gently on a sieve to obtain PLA loose powder.

In each of the experiments, PLA solution was prepared by dissolving 1 g of PLA pellets in 10 mL of dichloromethane. The complete solution was obtained in 1 hour. 5 g of poly(vinyl alcohol) is filled in 5 L of the water. The sprayed solution was rested in the medium for one hour before filtering.

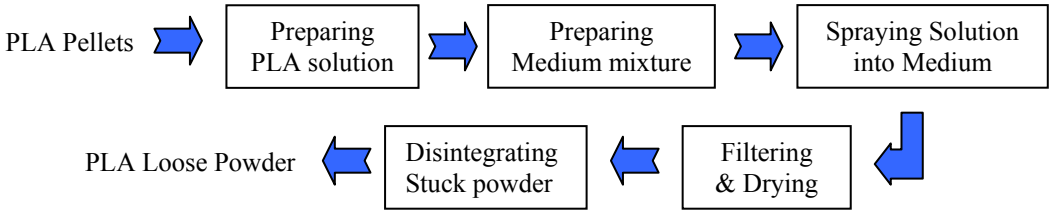


Figure 1. Steps for preparing PLA powder

2.2 Design of Experiment

After the steps for the proposed preparation technique was stabilized, design of experiment was conducted to determine the optimum condition for producing the PLA powder. The preliminary study had showed that pressure has significant effect on the powder size while the position of a spray gun's tip relative to the medium surface relates to the stickiness of stuck powder. Therefore, these two factors were investigated further to find an appropriate condition for producing loose PLA powder. Both factors were varied in three levels each, and the nine conditions are listed in Table 1.

2.3 Examination of Powder's quality

Quality PLA powder is evaluated from its flow ability, particle size and possibility of becoming loose powder. In the experiment, physical characteristic of the powder, obtained after spraying and after drying process, were observed to evaluate the possibility of becoming loose powder. Loose power obtained after disintegrating step should be small in order to produce good surface quality on a prototype. Mastersizer 2000 was used to measure particle size distributions (PSD) of loose powder, obtained from all conditions. Flow ability was measured at the end of the experiment but only on the condition that satisfied.

Table 1. Treatment conditions for 3^2 designs (2 factors each at 3 levels)

	Pressure (bar)		
Position of a spray gun's tip (mm)	1	2	3
+ 100	A	B	C
-20	D	E	F
- 100	G	H	I

Table 2. Average particle size and physical characteristic of PLA powder

Treatment condition	Average particle size (μm)		Physical characteristics of powder	
	Entire sample	Top 5 %volume	After spraying process	After drying process
A	415.71	540.64	Stuck together	Still stuck together (Difficult to be crumbled)
B	175.55	102.96	Stuck together	Still stuck together (Difficult to be crumbled)
C	288.70	86.53	Spreaded over the medium	Stuck together but able to be crumbled manually
D	159.44	103.06	Spreaded over the medium	Stuck together but able to be crumbled manually
E	143.25	118.14	Spreaded over the medium	Stuck together but able to be crumbled manually
F	73.71	39.13	Stuck together	Still stuck together (Difficult to be crumbled)
G	141.80	102.52	Spreaded over the medium	Stuck together but able to be crumbled manually
H	186.96	135.64	Spreaded over the medium	Stuck together but able to be crumbled manually
I	58.16	44.93	Stuck together	Still stuck together (Difficult to be crumbled)

Table 3. Flow ability of the powder under condition coding D, E, G and H

Condition	D	E	G	H
Flow ability ($mg.s^{-1}$)	3.2967	3.2933	3.2233	3.3767

3. RESULTS AND DISCUSSIONS

From observation during the experiment, it was found that both pressure and position of the spray gun's tip influenced the physical characteristic of powder after spraying step. When the pressure was high and the tip of the nozzle was submersed into the water, the powder tended to stick with each other on the medium. This might be because the container confined the movement of the sprayed solution, and a lot of generated bubbles obstructed the interaction between the sprayed solution and poly(vinyl alcohol). Similar results were obtained also when the pressure was low but the spray gun's tip was set above the water surface because there was time for solution droplets to accumulate before reaching the water surface. As reported in Table 2, the powder that stuck together on the water after spraying was difficult to disintegrate while the powder that spreaded over the water was much easier to disintegrate. Therefore, conditions A, B, F, and I were not suitable because loose powder was rubbed off from dried patches of stuck powder even though some of them gave small size particles.

Samples obtained from all conditions were measured for particle size distributions. The results were reported as the average particle sizes of the samples. For each condition, top five percent volume were extracted from the sample and used to recalculate another average particle size value. The different between the two average values indicates the particle size variation in the sample and should be small. From the illustration in Figure 2, pressure has direct effect on the particle size. The higher the pressure is, the smaller the particle size will be. However, there is no clear indication of the influence of the position of the tip on the size of particles. Among the remaining five conditions, condition C gave the smallest average size particles, but broad range of particle sizes was found. That might be due to time allowance for droplet accumulation. Conditions D and G which ran at low pressure of 1 bar, provided smallest particle size among the suitable four conditions but condition D was much easier to setup the position of the spray gun's tip.

Flow ability was checked to ensure that the powder could flow through the nozzle of the SVM machine. Powder was filtered through a sieve with 1,600 meshes per square inch to screen big chunk of powder before feeding through the nozzle. As shown in Table 3, there was no significant difference among them in term of flow ability. Therefore, the conditions of the pressure and of the position of the spray gun's tip in condition D gave the most suitable results. Figure 3 shows the conditions of powder obtained from condition D before and after passing through a sieve and a model made from this powder.

Scanning electron microscope (SEM) was utilized to investigate further the surface properties and topology of the PLA powder, obtained from condition D. The microstructure results, as illustrated in Figure 4, show the shape of the particles were quite round, which are suitable for applying in RP because these micro-beads can be packed closely and effectively to minimize void space in the created prototype. The result also shows that the micro-beads are highly porous that has negative effect on material density. The bulk density of the PLA powder was determined to be 0.045 $g.cm^{-3}$ which is much less than the bulk density of pellet, 0.848 $g.cm^{-3}$. Therefore, the sharp decrease in density of the powder compared to that of the original PLA pellets is due to its highly porous nature as presented in SEM results. However, leaving formed powder in the medium longer can improve this problem i.e. the degree of porosity decreases.

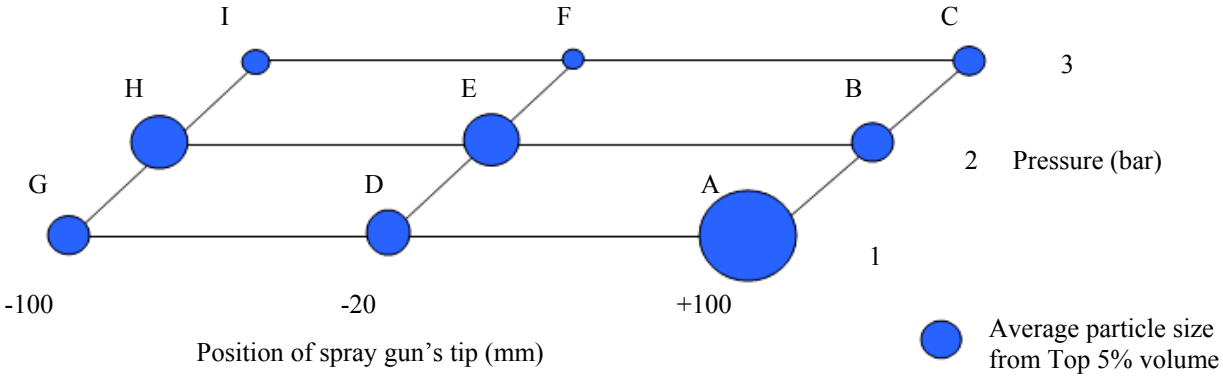
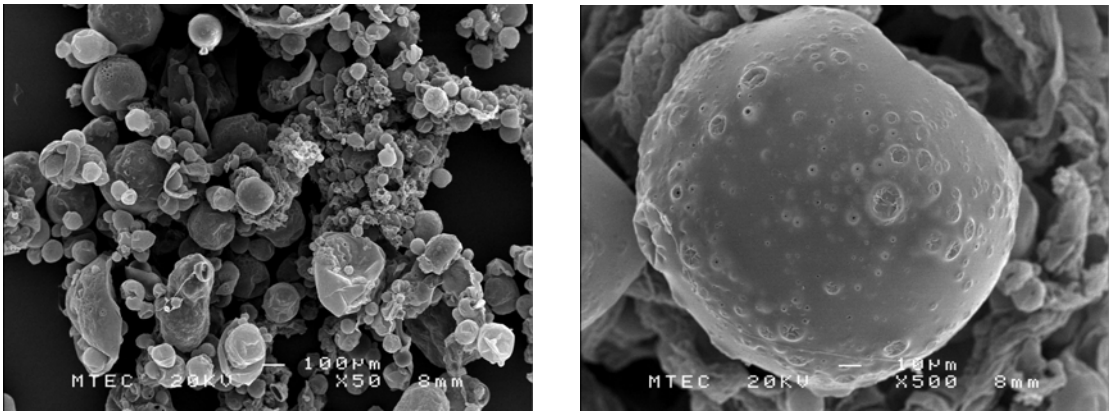


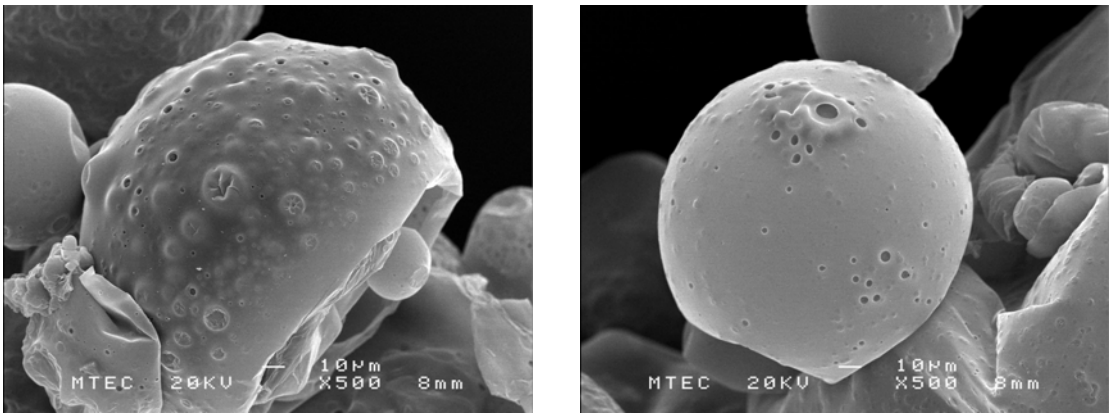
Figure 2. Effect of pressure and position of spray gun's tip on the average particle size

(a) Loose powder after disintegrating (b) After filtering through a sieve (c) A prototype

Figure 3. Loose powder obtained from condition D



(a) Magnification 50x (b) Magnification 500x



(c) Magnification 500x (d) Magnification 500x

Figure 4 SEM micrograph of PLA powder obtained from condition D

4. CONCLUSIONS

Micron-sized powder prepared from PLA pellets is investigated that can be used in powder-based RP system. Due to the commercially available PLA, which are manufactured in pellet form so their particle size can not be directly used for RP process. A new technique for preparing PLA powder from the pellets was developed as mentioned. Two controlled parameters i.e. pressure and the position of the spray gun's tip, were studied in order to determine the most suitable condition for preparing PLA powder. Within condition operated at 1 bar and fixed the spray gun's tip at 20 mm below the medium's surface, the suitable properties of PLA powder, i.e. small particle size and ability of flow, were achieved though the post-process, i.e. crumbling and disintegrating process, were required to obtain the loose powder. As a SEM results, micro-beads of the powder are such porous that the density is very low compared to the density of the original pellets. This will influence the flow ability of the powder therefore leaving formed powder in the medium can improve this drawback. However, time for decreasing this porous problem has to be investigated further. Finally, due to the characteristics of the presented prototype, which its surface was quite rough and the shrinkage problem also appeared so the properties of the PLA powder need to be studied also in order to improve the quality of the prototype.

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