

연속적인 SAS(supercritical antisolvent) 공정을 이용한 L-PLA의 재결정

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Crystallization of L-PLA using the continuous supercritical antisolvent precipitation process

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Introduction

It is important to produce the uniform particle in many field, such as pharmaceuticals, foods, polymers and materials. The most commonly used method was jet milling. But it is difficult to obtain uniform particle size and particle size distribution(PSD) is very large. As an alternative to traditional milling techniques, the supercritical fluid technology such as SAS(supercritical antisolvent), RESS(rapid expansion of supercritical solutions), and PGSS(particles from gas saturated solutions) have been attracting much attention. One of advantages of using this technology is ability to generate fine droplets with a high surface area and thereby to increase mass transfer between a droplet and drying medium. In RESS process, a solid is dissolved in a supercritical fluid that is expanded adiabatically through a capillary nozzle to gaseous state creating high supersaturation and thereby causing rapid nucleation and precipitation of the desired product as fine particles. In PGSS process, the supercritical fluid solubilized in a molten substance is expanded in a nozzle and the desired substance is solidified by cooling effect during expansion. In SAS process, supercritical antisolvent is added to liquid solution and induces the fast precipitation of the solute if this is insoluble in the antisolvent.

In this study, we chose the continuous SAS precipitation process to produce the submicron particles of the poly(L-lactic acid)(L-PLA). Methylene chloride(CH₂Cl₂) was selected as a solvent for L-PLA and carbon dioxide was used as an antisolvent.

Materials and apparatus

1. materials

Carbon dioxide(purity 99.9%) was obtained from Sinyang. L-PLA(m.w 220,000) was supplied by supercritical fluid lab. Methylene chloride(99.9%, Biotech grade solvent) was provided by sigma-aldrich chemicals(Korea).

2. Apparatus

The schematic of SAS apparatus is shown in figure 1. It consists of antisolvent supplying system, solution feeding system, precipitation vessel, filter, a back pressure regulator, and gas vent system.

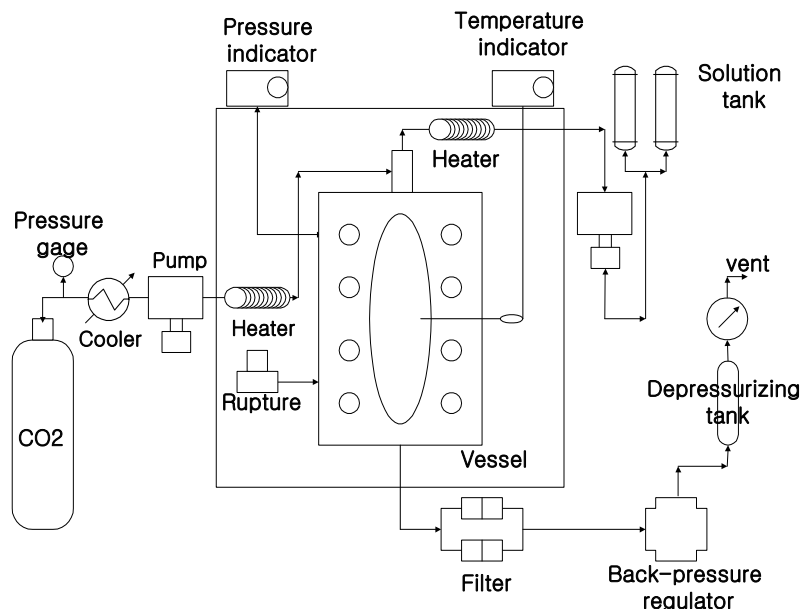


Figure 1. Apparatus of continuous supercritical antisolvent process

3. Experimental methods

The precipitation vessel was filled with supercritical CO₂ until desired pressure was reached and heated up to desired operating temperature. After flow rate of CO₂ was maintained constant at a flow rate of designated value, liquid solution composed of methylene chloride and L-PLA was pumped into precipitation vessel through the nozzle(1/4"). The experiment ends when the liquid solution in solution tank was injected completely into the precipitation vessel. However, supercritical CO₂ continues to flow into the vessel to remove the residual content of liquid solubilized in the supercritical antisolvent for several minutes. To obtain the processed particle, the valve between precipitator and filter was closed and then the filter was gradually depressurized by using the back pressure regulator. The liquid solution used during process was obtained through the depressureizing tank and CO₂ was vented passing through rotameter and dry gas meter.

Results and discussions

In table 1, the experimental conditions and results were summarized. The object of this study was to investigate effect of the various process parameters such as temperature, pressure, concentration of liquid solution and injection rate of solution on particle size and morphology of L-PLA. The SEM(scanning electron microscope) was used to observe the morphology of recrystallized particles. The mean size of processed particles was measured by using a laser diffraction particle size analyzer.

Figure 2 is showing the effect of temperature on particle size and morphology. The temperature did not affect heavily the shape of particle while the particle

size decreased slightly with increasing the temperature. But contradictory results have been obtained by different authors about the influence of temperature[2, 3].

As shown in figure 3, particle size was relatively insensitive to solute concentration in the liquid. A marked particle size decrease was observed with the concentration increase of L-PLA in Methylene chloride in contrast with results of the other author[1]. From this results, we could find out that increase of the concentration positively effect on the size of primary particles by increasing the nucleation and negatively influence the further growth of the secondary ones. Only spherical particles were measured in this study but other author discovered particles of long fiber shape at L-PLA concentrations higher than 4%[2].

Temperature [°C]	Pressure [bar]	Concentration [wt%]	Flow rate of CO ₂ [l/min]	Injection rate of solution [ml/min]
40	80	0.3	4.79	0.2
40	80	1	4.95	0.2
40	80	2	5.15	0.2
40	80	1	5.25	1
40	80	1	4.72	2
45	80	1	5.12	0.2
50	80	1	5.4	0.2

Table 1. Experimental conditions and particle size

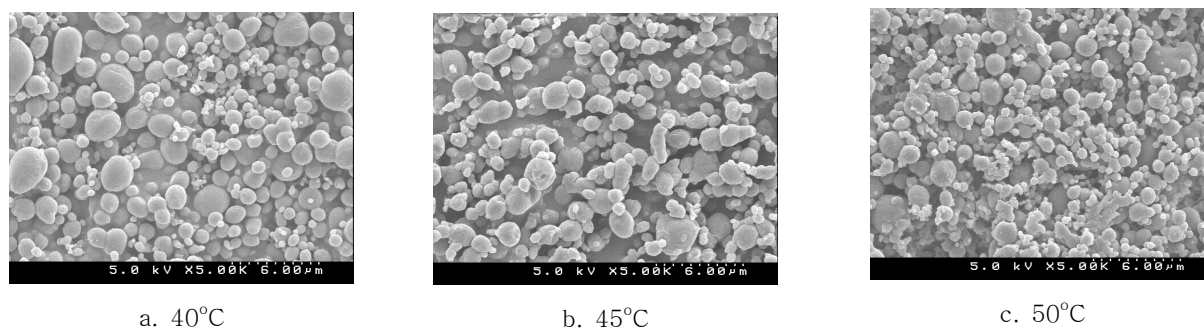


Figure 2. SEM photographs of L-PLA particles at 80bar, 1wt%, 0.2ml/min injection rate.

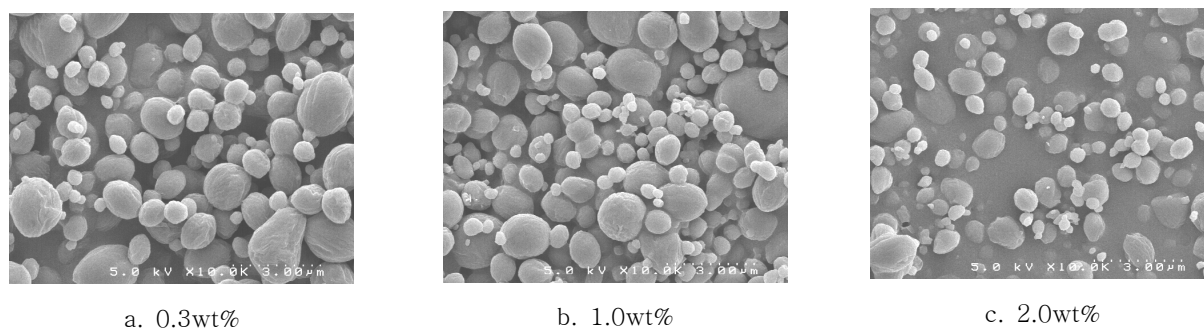


Figure 3. SEM photographs of L-PLA particles at 40°C, 80bar, 0.2ml/min injection rate.

Injection rate of solution is shown in figure 4. The particles was gradually deformed from spherical to strange shape with increasing the injection rate of solution. This is explained by rate of supersaturation. It is proportional to the expansion rate of the solution. Therefore, the rapid injection of solution causes a lower supersaturation rate, resulting in a slower rate of particle nucleation.

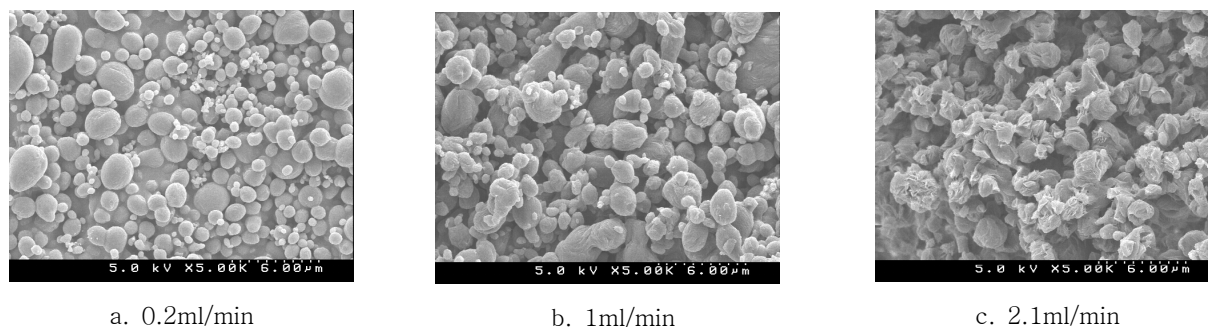


Figure 4. SEM photographs of L-PLA particles at 40°C, 80bar, 1.0wt%.

Conclusions

We investigated the effect of the various process parameters such as temperature, pressure, concentration and flow rate of liquid solution and injection rate of carbon dioxide on particle size and morphology of L-PLA. The effect of pressure on particle size or shape was not showed regular tendency while the other process parameters effected on the particle size or morphology. In case of temperature and concentration of initial solution, particle size was reduced by increasing the temperature and concentration respectively. While injection rate of solution influenced on particle morphology.

References

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