Manufacturing a Porous Structure According to the Process Parameters of Functional 3D Porous Polymer Printing Technology Based on a Chemical Blowing Agent

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Abstract. In this paper, we propose a new porous polymer printing technology based on CBA(chemical blowing agent), and describe the optimization process according to the process parameters. By mixing polypropylene (PP) and CBA, a hybrid CBA filament was manufactured; the diameter of the filament ranged between 1.60 mm and 1.75 mm. A porous polymer structure was manufactured based on the traditional fused deposition modelling (FDM) method. The process parameters of the three-dimensional (3D) porous polymer printing (PPP) process included nozzle temperature, printing speed, and CBA density. Porosity increase with an increase in nozzle temperature and CBA density. On the contrary, porosity increase with a decrease in the printing speed. For porous structures, it has excellent mechanical properties. We manufactured a simple shape in 3D using 3D PPP technology. In the future, we will study the excellent mechanical properties of 3D PPP technology and apply them to various safety fields.

1. Introduction

Recently, interest in 3D printing technology is rapidly increasing in the field of future manufacturing technologies. Three-dimensional printing technology is being applied to various fields, such as the medical field and tissue engineering, because of various benefits [1-2]. We have been conducting research on a new porous polymer printing (PPP) technology applications based on the 3D printing technology [3-4]. The porous polymer has excellent mechanical properties compared to conventional polymers [5-6]. These characteristics of the porous polymers are utilized in various fields such as functional materials, inner buffer, etc. [7-8].

In this study, we produced chemical blowing agent (CBA) hybrid filament by combining polymers and CBA, and we suggested a 3D PPP technology based on CBA for a process that is uncomplicated,
and reduces time and expense. In addition to this technology, we manufactured a simple 3D structure and experimentally confirmed the variation in porosity according to the process parameters.

2. Background

2.1. CBA-based 3D PPP process

Three-dimensional PPP refers to the layering process which simplifying processes, and forming porosity. In other words, it refers to the technology of stacking and manufacturing products with one process in a single piece of equipment by the thermos-chemical foaming process of thermoplastic polymer material. This process has the advantage of being relatively simple, is less time-consuming, and inexpensive. Figure 1 shows the overall process of the CBA-based 3D PPP. The CBA hybrid filament is mixed with a polymer and a CBA is manufactured; next, the structure is stacked as the pores were formed by the thermal decomposition reaction of the CBA.

![Figure 1. The overall process of CBA-based 3D PPP (porous polymer printing).](image)

2.2. Blowing Agent

Blowing agents are largely classified into physical blowing agents (PBAs) and CBA. PBAs supply gas by applying a physical force to the molten polymer and changing the physical state. Generally, it is used for gases such as nitrogen, dichlorotetrafluoroethane, and n-pentane [9]. On the other hand, CBAs generally supply the gas by changing the chemical condition through a thermal decomposition reaction. The CBA is easy to introduce into polymers and has the advantage of facilitating the process in general equipment [10]. The endothermic CBA absorbs heat continuously during disassembly, but the exothermic CBA releases heat during disassembly [11]. Figure 2 shows the chemical reaction equation of CBA. The CBA used in the experiment is a yellow powder with a formula $H_4N_4C_2O_2$, and the porous structure is formed by releasing the gases $N_2$ and $CO_2$ during disassembly.

![Figure 2. Thermal deposition reaction of ADC [12-13].](image)

3. Experiment
3.1. Polypropylene

Compared to other polymers, PP is relatively inexpensive and has excellent mechanical properties at room temperature [14]. The polymer used in this experiment is Homo PP H930D produced by SK Global Chemical. The characteristics are indicated in Table 1.

Table 1. The characteristics of polypropylene.

|                     | Melt index [g 10 min\(^{-1}\)] | Vicat temperature [°C] | Heat distiortion temperature [°C] |
|---------------------|---------------------------------|------------------------|-----------------------------------|
| Polypropylene       | 3.5                             | 158                    | 112                               |

3.2. Chemical Blowing Agent

The CBA used in experiment is ADC(H\(_4\)N\(_4\)C\(_2\)O\(_2\)) of Cellcom-AC series produced by Kumyang. The properties of this agent are indicated in Table 2.

Table 2. The properties of chemical blowing agent.

|                     | Particle diameter [µm] | Thermal decomposition temperature [°C] | Amount of gas [ml g\(^{-1}\)] |
|---------------------|-----------------------|---------------------------------------|-----------------------------|
| CBA                 | 3–20                  | 200–205                               | 280–300                     |

3.3. Experiment equipment

The following are descriptions of the equipment used in this experiment. We used the extrusion equipment called “Filabot Wee”, which can manufacture the CBA hybrid filament for 3D PPP at a regular thickness by combining polymers and CBA. Also, we used the 3D printing equipment from the FDM scheme which was called “Willybot MS”; it is possible to melt the CBA hybrid filament at the nozzle temperature and to produce a 3D product based on the input data.

3.4. Manufacturing of the CBA hybrid filament

Figure 3 shows the CBA hybrid filament manufacturing process. For the density of CBA to be 5 wt.%, we mixed the prepared ingredients of PP pellet and CBA powder. Manufacturing the CBA hybrid filament made of polymers and CBA by extruder is shown in Figure 3 (a). The thickness of the CBA hybrid filament is manufactured regularly as 1.60–1.75 mm; therefore, the pre-existing FDM equipment can be used, as shown in Figure 3 (b) and (c). At this point, the temperature setting is 160 °C, because the CBA should not cause a thermal decomposition reaction and the PP only needs to melt for manufacturing the CBA hybrid filament.

![Figure 3. CBA hybrid filament manufacturing process.](image)

3.5. Formation of porous structure

3D printing is performed using the fabricated CBA hybrid filament, and using the heater temperature of the nozzle, the thermal decomposition reaction of CBA is used to form a porous structure. At this
point, the heater temperature of the nozzle must be at a temperature greater than 200–205 °C sufficient enough for the thermal decomposition reaction of the CBA.

3.6. Conditions of experiment
We conducted experiments on variations of the pore according to the printing speed at the nozzle temperature near the foaming temperature of the CBA. Likewise, we conducted experiments on variations of the pore depending on the temperature change of the nozzle at a constant printing speed. The conditions of the experiment are shown in Table 3 and Table 4.

Table 3. An experimental condition about printing speed.

| CBA density [wt%] | Nozzle temperature [°C] | Printing speed [mm min⁻¹] |
|-------------------|-------------------------|--------------------------|
| 5                 | 220                     | 150                      |
| 5                 | 220                     | 300                      |
| 5                 | 220                     | 450                      |
| 5                 | 220                     | 600                      |
| 5                 | 220                     | 750                      |
| 5                 | 220                     | 900                      |
| 5                 | 220                     | 1050                     |

Table 4. An experimental condition about nozzle temperature.

| CBA density [wt%] | Printing speed [mm min⁻¹] | Nozzle temperature [°C] |
|-------------------|---------------------------|-------------------------|
| 5                 | 600                       | 190                     |
| 5                 | 600                       | 200                     |
| 5                 | 600                       | 210                     |
| 5                 | 600                       | 220                     |
| 5                 | 600                       | 230                     |
| 5                 | 600                       | 240                     |
| 5                 | 600                       | 250                     |

4. Results and Discussions
The process parameters affecting the formation of the porous structures in the 3D PPP include CBA density, nozzle temperature, and printing speed. The porosity graph showed in a ratio of the weight difference between the weight of the foamed polymer and the unfoamed polymer.

4.1. Printing speed
Figure 4 shows the result of changes in printing speed in the same conditions as the CBA density and nozzle temperature. Figure 4 (a)–(c) is white, indicating that thermal decomposition reaction of CBA was completely conducted. Figure 4 (d)–(g) is yellow, indicating that as the printing speed increases, the CBA is totally extruded before the thermal decomposition reaction is triggered by the temperature of the nozzle. As the printing rate decrease, we can see layers forming more porosity. In addition, the graph in Figure 5 shows changes in the porosity.
4.2. Nozzle temperature

Figure 6 shows the result of changes in nozzle temperature under the same condition as CBA density and printing speed. The temperature at which the blowing agent causes thermal decomposition reaction is 200–205 °C. Figure 6 (a) shows that the temperature is below the temperature that causes the thermal decomposition reaction, and therefore, does not form a porous structure. Figure 6 (b)–(e) is yellow, indicating that the temperature is low enough to produce sufficient thermal conduction for the CBA hybrid filament. Figure 6 (f) and (g) is white, which is the color of the PP, indicating that sufficient heat conduction has occurred in the CBA hybrid filament. As opposed to the printing rate, the higher the nozzle temperature, the more porosity is created and laminated. Similarly, the graph in Figure 7 shows the variation of porosity.
Figure 6. An inner cross section observed with an optical microscope at a nozzle temperature of (a) 190 °C, (b) 200 °C, (c) 210 °C, (d) 220 °C, (e) 230 °C, (f) 240 °C, and (g) 250 °C.

Figure 7. The porosity graph of the nozzle temperature.

4.3. Simple 3D structure
Figure 8 is a simple 3D shape manufactured using the 3D PPP technology. In the experiment, we set the temperature of the nozzle at 250 °C and the printing speed at 600 mm/min. In addition, the internal cross section of the simple 3D shape is shown in Figure 9. Most of the pores were created in varying sizes, and we were able to ascertain that the pores were formed within the pores.

Figure 8. The simple 3D shape manufactured by 3D PPP.
Figure 9. An internal cross section of the structure formed by 3D PPP.

5. Conclusions
In this study, based on the results of according to the printing speed and the nozzle temperature in the process parameter of the CBA-based 3D PPP, and a basic study was conducted on the porous structure of PPP. Overall, the size of the pores ranged from 10 to 300 µm. At the slight temperature difference about 10 to 20 degrees Celsius, the size of the pores was largely unrelated to the process parameter. But, if the temperature difference is very large, the size of pores will be affected by something such as the shrinkage of the polymer, cooling time and etc. At the same nozzle temperature, the slower the printing speed, the greater the porosity. At the same printing speed, the higher the nozzle temperature, the greater the porosity. In this process, compared to unformed PP, formed PP is lightweight because it forms a porous structure. The porous structure is suitable for mechanical shock mitigation because deformation will occur. In the future, we intend to use 3D PPP to conduct research on mechanical properties and, their application to various fields.

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