Laser Sintering Fabrication of Highly Porous Models Utilizing Water Leachable Filler -Experimental Investigation into Process Parameters-

Toshiki NIINO, Shunsuke OIZUMI and Hiroyuki OTSUKI
The Institute of Industrial Science, The University of Tokyo, JAPAN
Komaba 4-6-1 Meguro Tokyo, 153-8505 Japan
niino@ieee.org

ABSTRACT

The authors are developing a laser sintering process to fabricate highly porous models with such high porosities as 90% and more. In the process, water-soluble filler is mixed with designated plastic powder and leached out after laser sintering process is finished to generate pores where the grains used to exist. Previously, the authors reported successful application of this technology on a tissue engineering scaffold. However, relationship between process parameters and obtained results has not been clarified. This paper reports experimental investigation into effects of optimizing process parameters such as mixture, grain size of the filler on resultant porosity, pore size and process resolution

INTRODUCTION

A great amount of effort has been intensively invested into establishment of regenerative medicine in a couple of decades[1]. As a result, the remedy for skins had been successfully commercialized, and reconstruction of more three-dimensional bones and cartilage has become possible so far as in experimental animal tests[2]. Comparing to these tissues, on the other hand, reconstruction of soft tissues is much more difficult since metabolic rates of the most of these organs or tissues are often so high that cell culturing up to a thickness of more than some hundred microns causes necrosis at the bottom because of insufficient oxygen supply. In order to supply oxygen and nutrition to every cell, a scaffold equipped with flow channel network had been proposed[3, 4], and we are developing a fabrication technology for such scaffold as an application of laser sintering freeform fabrication (Fig. 1). In that process, water soluble filler is mixed with biodegradable plastic powder and leached out after sintering is finished to enhance porosity (Fig. 2). Formerly, we succeeded in fabricating a scaffold of polycaprolactone (PCL in the following description) as shown in Fig. 3. Owing to this porogen leaching process, the scaffold has a very high porosity of 90%. In the scaffold, there are flow channels of which minimum diameter is less than 1mm, and they are repeat branching and joining to form a network that consists of a stack of tetrahedrons (Fig. 4, 5). Using this scaffold, cells originated from liver cancer were successfully cultured up to a cell density of one sixth of human liver. These results are reported at the SFF symposium in 2006 [5].

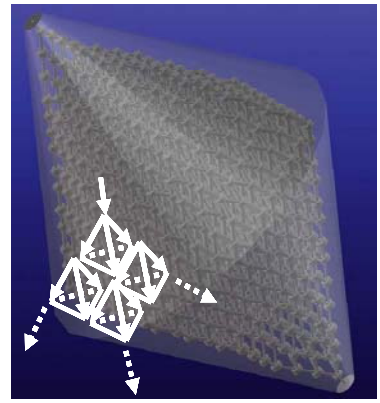


Fig. 1 Schematic of flow channel network

The first prototype produced a certain result, but relationship between the process parameters and the various results or performances of the scaffold was not investigated comprehensively. Potential application of highly porous model is not only scaffold but also other sacrificial applications such as model of investment casting. In order to prepare for such applications, we have carried out various experiments to answer the following questions.

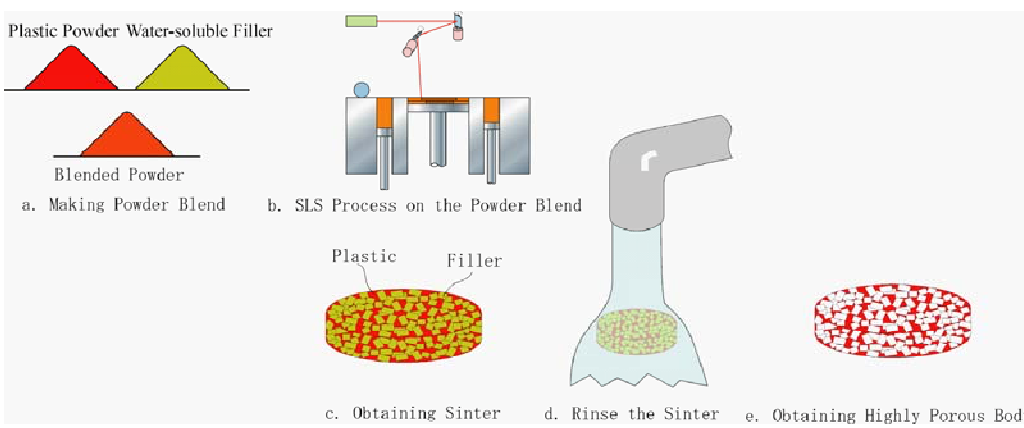


Fig. 2 Process For Fabricate Porous Object

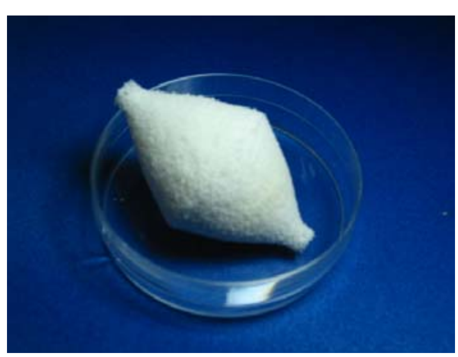


Fig. 3 Photo for Scaffold

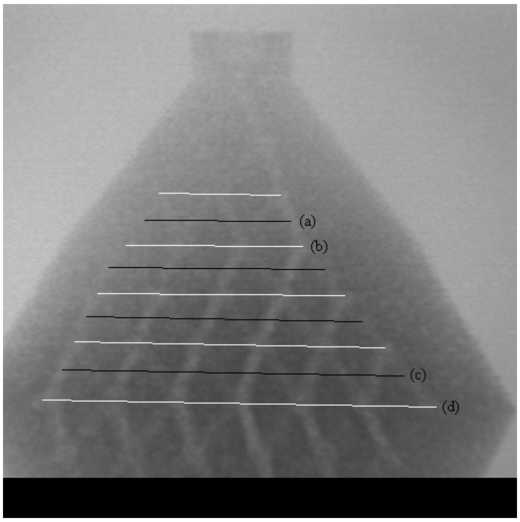


Fig. 4 X-ray photo for a scaffold

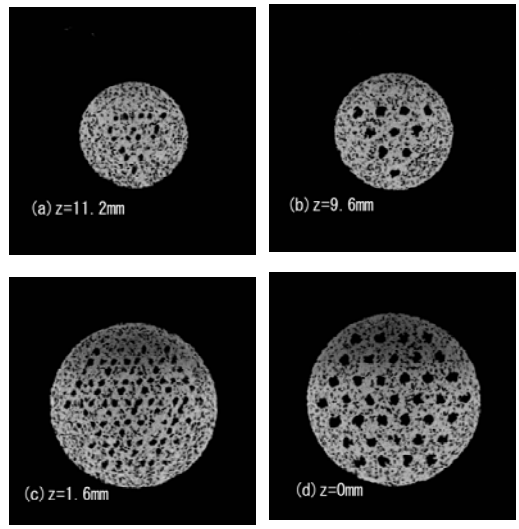


Fig.5 CT reconstructed cross section

- Does strong laser power decrease porosity?
- How porosity changes as mixture of filler is changed?
- What is the highest porosity that can be obtained?
- How can we control size of pores?
- How use of filler affect on accuracy in fabricating models?
- How does use of filler facilitate fabrication of new material?

PARAMETERS

It is required to decide a number of process parameters to complete laser sintering freeform fabrication. Since the number is so large that it is not practical to vary all the parameters and examine the results to be obtained, we selected laser power, mixing rate, grain size and plastic material as parameters to be varied and examined the effect of the variation. Other parameters that are referred in technical paper frequently are fixed as following:

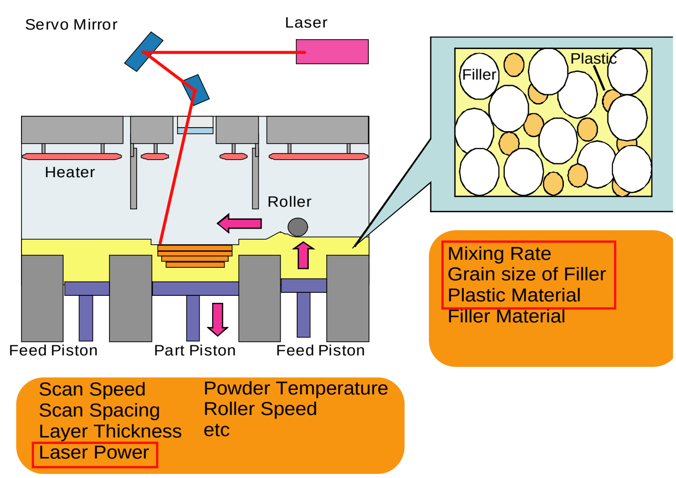


Fig. 6 Process parameters discussed in this paper

Scan Speed: 3.8m/s

Plastic Powder Grain Size: 50-60μm

Scan Spacing: 0.1mm
Layer Thickness: 0.3mm

LASER POWER

Typical fill rate of unprocessed powder having been coated layer-by-layer, i.e. cake, is in the range between 40% and 50%, thus porosity is from 50% to 60%. Normally, laser sintering increases the fill rate up to more than 90% in case when commercialized polyamide 12 (DuraForm PA distributed by 3D Systems. We call this PA12 or DF in the following description) is SLS processed. If controlling of porosity by adjusting laser power is possible, it is the most convenient way to obtain desired fill rate/porosity.

Fig. 7 shows measured relationship between porosity and laser power. In this diagram, we cannot find strong relationship between the two parameters when relatively large amount of filler is introduced. Reason for this weak relationship between laser power and porosity can be explained as following.

When laser power is supplied on the surface of powder without filler, the powder is melted and loose strength of supporting pores between grains, and the surface of the powder or its melt lowers resultantly. Then on the following powder coating, greater amount of powder is supplied than on the not sintered surface (Fig. 8 right), since the surface is lowered,. Since higher laser power increase fluidity of the melt more, fill rate of sinter is increased when higher laser power is applied. On the other hand, when large amount of filler of which grain size is larger than plastic powder is introduced, the filler plays dominating role in formation of the bulk keeping rooms between powder grains instead of plastic powder, and the plastic powder stays in the rooms rarely effecting on

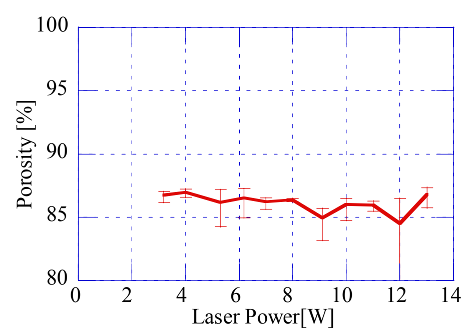
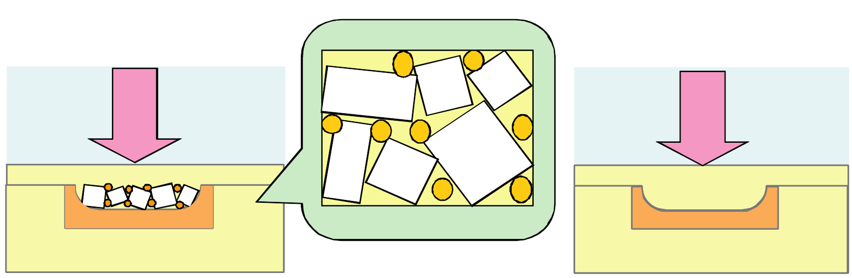


Fig. 7 Relationship between porosity and laser power. Sodium chloride was used as filler. Filler is sieved between 100 and 150mm and introduced into polycaprolactone powder by a factor of two in volume.



With high content filler without filler

Fig. 8 Explanation for weak relationship between laser power and porosity mechanical structure of the powder stack. Therefore, Laser irradiation that can melt only plastic powder does not lower the powder surface. Resultantly, additional powder is not supplied on the next powder coating, and fill rate is not increased even if higher laser power is irradiated. What will happen when filler with the same or smaller grain size in comparison with that of plastic powder will be explained in the later section.

FILLER CONTENT

We can easily guess that amount of introduced filler affects on porosity very much. In reality, porosity increases as introduced filler is increased as shown in Fig. 8. The porosity reached the highest value of 93% when filler was introduced seven times as much as that of plastic in volume, and higher filler contents lowers mechanical strength of the sinter so much that the sinter could not withstand following break-out process. Explanation for the reason why the porosities were not improved so much although a large amount of filler such as seven times of plastic powder was introduced, is following.

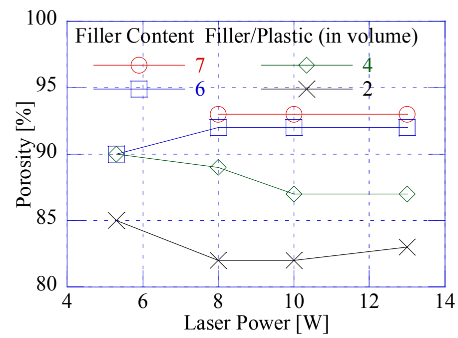


Fig. 8 Relationship between porosity and laser power with various filler content. Sodium chloride granule sieved in the range between 100μm and 150μm was used as filler.

As mentioned in the previous section, when filler with large grain size is introduced at high rate, each grain of plastic powder exists in a gap between filler grains. Therefore, fill rate of plastic in the sinter to be obtained should have very strong relationship with amount of plastic in the mixed powder. In the experiments of which results are shown in Fig. 8, we tested four filler contents, and the corresponding rate of plastic powder to filler, c_{pf}, are 50%, 25%, 17% and 14%. Filling rate of plastic powder to total bulk volume, c_{p}, can be obtained by equation,

$$c_{\mathrm{p}} = c_{\mathrm{pf}} \times c_{\mathrm{f}} \tag{1}$$

where c_{f} is content of filler to bulk volume and was measured as 49%. Since bulk volume is not changed by sintering when high content filler is introduced as mentioned in the previous section,

$$f = f_p \cong c_{\mathrm{p}} \tag{2}$$

where f and f_{p} are fill rates of final sinter. Here, f_p is introduced to show this is fill rate of plastic explicitly. Porosity, p, is obtained by subtracting f from 1, therefore

$$p = 1 - c_{\mathrm{pf}} \times c_{\mathrm{f}} \tag{3}$$

Fig. 9 shows porosities obtained by theorem explanation above and their measured value. As displayed here, these two series of data agree very well to support the explanation mentioned above.

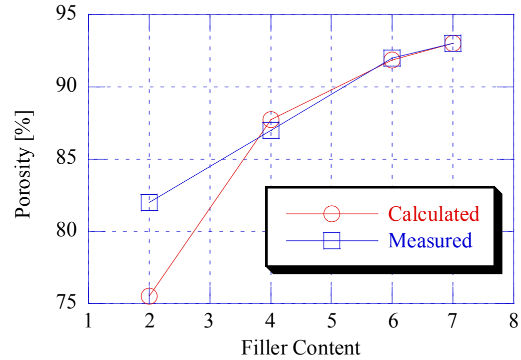


Fig. 9 Relationship between porosity and filler content. Plastic powder is polycaprolactone with average grain size of 50μm. Sodium chloride granule sieved from100-150μm was used as filler. Applied laser power is 10W.

GRAIN SIZE

Two rangess of filler size, from 100 to 150μm and from 150 to 250μm, were tested. In Fig. 10, no significant relationship between grain size of the filler and porosity was observed. When grain size of filler is comparable to plastic powder, filler is wrapped by molten plastic, and insufficient leach occurs. This was proved by electric conductivity measurement on a water in which well rinsed and ground sinter was immersed.

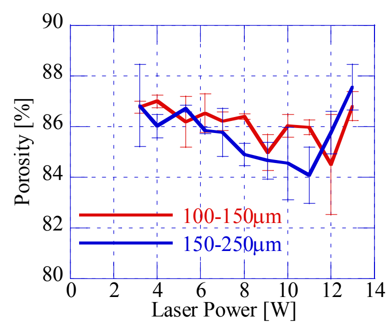


Fig. 10 Relationship between porosity and laser power under two filler grain size conditions.

Fig. 11 show optical micrographs of sinter surface and filler under condition for two ranges of filler grain sizes, from 40-63μm and from 100 to 150μm. In the photos for sinter surfaces, we can find dark shadows that seems to be a open pore, and shiny filler grains in the photos of fillers. We can also find some similarities in dimension and shape between the dark shadow and the shiny part. This indicates that pores are generated by leaching fillers

Fig. 11 Closed up pictures for sinters' surfaces and filler grains.

and we can control their size and shape by adjusting those of filler grains.

DISCUSSION ON PROCESS ACCURACY

During the research on scaffold prototyping, we often experienced lowered accuracy or process resolution. To quantify this, we fabricated flat plates with thickness of 2mm and measured expansion from the original thickness. Diagrams in Fig. 12 show relationship between the expansion and temperature on the powder surface of part bed. As shown here, use of sodium chloride as filler causes excessive sintering on the bottom side of the being processed part. As a cause of this degradation, we noticed difference in transmittance of CO_2 laser, which is typically employed in plastic laser sintering systems as heat source. As displayed in Fig. 13, salt powder transmits the laser much more than PCL. Therefore, to give sufficient energy to the top layer to sinter it results in excessive sintering of the layers that has been coated previously.

We also tested PA12 as binder plastic. As shown in Fig. 14, PA12 and its filler added version absorb the laser more than PCL and its filled version, respectively. Expansion of the flat plates fabricated out of PA12 and salt filled PA12 is also tested under various powder temperature conditions, and reduced expansion was obtained as shown in Fig. 15. We should not simply conclude that reduction of expansion owes only to the

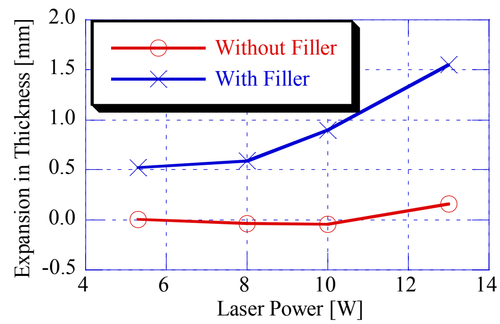


Fig.12 Relationship between expansion in thickness. Polycaprolactone and Sodium Chloride powder were used as plastic and filler, respectively. Grain size of the filler is from 100 to 150μm. Content of filler in volume is 200% of plastic.

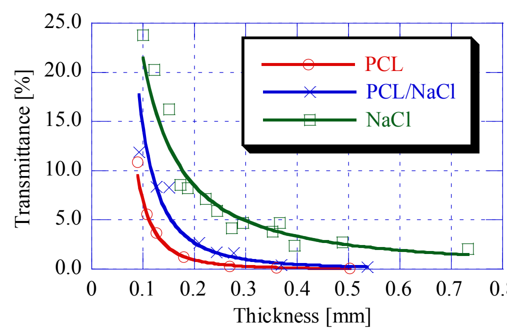


Fig.13 Relationship between infra red transmittance and powder thickness. Material parameters are the same as for Fig.12.

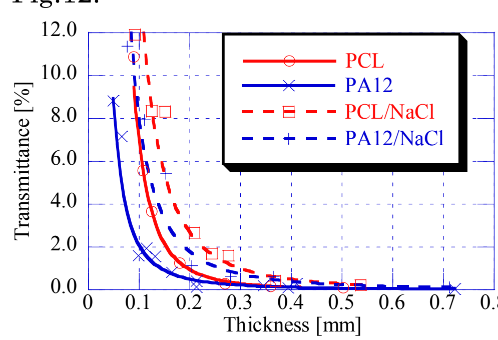


Fig. 14 Relationship between infra red transmittance and powder thickness. PCL, PA12 and their filled version were tested. Filler content is 200% of plastic for applicable case.

better absorbance of DF, which is one of the best synthesized and tuned powders for laser sintering process, but the result does not disagree with our hypothesis.

As an advantage of introducing filler, it facilitates fabrication of a part from new unknown powder. If filler is not used, laser sintering process of PA12 fails because of strong curl distortion when powder temperature is lower than 155°C. Contrarily, such a curl as can cause failure in powder recoating did not occur, if filler is introduced. When we fabricate highly porous object, we often use special plastic of which property is not well optimized for laser sintering. Therefore, this advantage fits the purpose of using leachable filler.

GENERAL DISCUSSIONS

In this paper, several parameters were varied, and effects on porosity of doing so were examined. All the results except relationship with laser power were not far from what could be expected before having made experiments. The highest value of porosity depends on the highest filler content that does not lower the mechanical strength of the sinter so much as it does not withstand break-out operation. Since irradiating high laser power increases strength of sinter, this independency of porosity on laser power suits our purpose of obtaining highly porous sinter. Geometrical accuracy or resolution of the process is another very important aspect not only in scaffold fabrication but also in other potential applications obviously. Since excessive laser irradiation can cause excessive sintering, which results in degraded accuracy or resolution, we need some trading-off between high porosity and high accuracy. One of the ways to narrow the gap between the two aspects is to find a filler material that can absorb laser as well as plastic powder. Besides laser absorbance, there might be many material properties that affects on the quality of highly porous sinter such as specific heat, latent heat, viscosity and surface tension between filler and molten plastic. We should test all of them, but optional materials with adequate properties that we can examine by means of experiment are quite limited. Thus, it is impossible to test all-inclusively, but we can or have to reach some agreeable and compromising optimization.

SUMMARY

We investigated relationships between various parameters of process for fabricating highly porous objects by using water soluble filler. Porosity can be improved by increasing filler content up to 93%, but filler introduction at very high rate lowers strength and has some limitation. Laser power rarely affects on porosity when high content filler is used. Pore size can be controlled by changing grain size of filler. Grain

size of filler must be larger than of plastic powder, or filler is trapped in the sinter staying unleachable. Use of filler lowers process accuracy, but facilitates process of new not-well-known powder by expanding process window at the same time.

References

[1] Wai-Yee Yeong, *et al*; Rapid prototyping in tissue engineering: challenges and potential ; TRENDS in Biotechnology Vol.22No.12 December2004

[2] Suman Das Scott F. Hollister *et al*; Freeform fabrication of Nylon-6 tissue engineering scaffolds, Rapid Prototyping Journal Vol.9,Number1,2003,pp.43-49

[3] Y. Sakai, *et al*; A novel poly-L-lactic acid scaffold that possesses a macroporous structure and a branching/joining three-dimensional flow channel network: its fabrication and application to perfusion culture of human hepatoma Hep G2 cells ; Materials Science and Engineering C 24 (2004) 379–386

[4] Kim SS, Utsunomiya H, Koski JA, Wu BM, Cima MJ, Sohn J, Mukai K, Griffith LG, Vacanti JP : Survival and function of hepatocytes on a novel three-dimensional synthetic biodegradable polymer scaffold with an intrinsic network of channels. Ann Surg 228: 8-13 (1998)

[5] T. NIINO, Y. SAKAI, H. HUANG and H. NARUKE: SLS Fabrication of Highly Porous Model Including Fine Flow Channel Network Aiming at Regeneration of Highly Metabolic Organs, Proc. Solid Freeform Fabrication Symposium 2006, 160-170, (2006)