Transparentization of SLS Processed SMMA Copolymer Parts by Infiltrating a Thermosetting Epoxy Resin with Tuned Refractive Index

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Abstract

Selective laser sintering is quite advantageous to build complicated tubular structures such as intake manifolds of automotive engines because of its ability of building undercut structures without using support ribs. On the other hands, inevitable opacity of the parts obtained from the process is lowering its advantage when we need to observe inside of the parts. A technology that can transparentize SLS processed parts by infiltrating curable resin with tuned refractive index was introduced by the authors in 2004, and in this paper, several modifications are added on material, process parameters and their control accuracies to improve clarity of obtained parts. As a result of these modifications, haze of the processed part was reduced by a factor of 40% reaching the lowest value of 20% through a plate with thickness of 5mm.

Introduction

In most solid freeform fabrication methods, troublesomeness of not automated post processes such as removing supports and finishing surfaces lowers their convenience and even defines an upper limit on building precision and fineness. In case of powder based solid freeform fabrication technologies, it is difficult to remove not sintered powder from narrow holes, but as for ease of building undercut structure, this type of fabrication processes are very convenient since they do not need any supporting ribs that should be removed manually. Owing to this advantage, selective laser sintering (SLS) process is often adopted to prototyping for fluid dynamic estimation of intake manifolds of inner combustion engines that contain very complicated undercut structures.

In addition to availability of complicated geometry, SLS process provides possibility of building models from variety of thermoplastic materials such as plastics, metals and ceramics as an advantage of heat based solid freeform processes. Due to this advantage, SLS can build models from PA12 engineering plastic giving its objective models the best toughness against both of impact and temperature among various plastic compatible freeform fabrication processes.

Contrarily to these advantages of flexibility in geometry and material, commercialized SLS machines possess several drawbacks in building precision and density. Since powder dimension and laser spot diameter of commercialized machines are 60μm and 500μm, respectively, building fineness and precision, which are strongly dominated by these two parameters, are lower than those of microstereolithography which have recently debuted to the market. Exner and his colleagues succeeded in very precise freeform generation by SLS using very thin laser beam and very fine powder[1] approaching MEMS compatible level stereolithography [2][3]. However, the model still contained some ten percents of pores. Inevitable porosity of SLS processed parts also brings problems. Opacity of SLS processed parts is one of such problems.

As mentioned above, simplicity when building complicated flow structure is one of significant advantage of powder based SLS process. However, we cannot observe in the model since it is always opaque even if it is processed from transparent material such as poly methyl methacrylate (PMMA). If we can transparentize SLS processed part by a simple postprocess, it provides industry and researchers with very strong tools. For example, estimation of fluid dynamic component still requires real experiments using real models although most prototyping before mass production is replaced by CAD simulation in automotive industries, and for that purpose, SLS processed transparent model must be very useful.

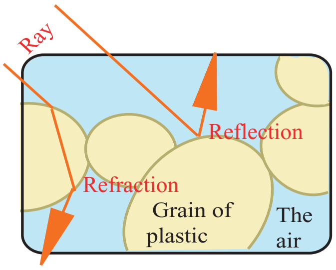
To meet these requirements, we had introduced and tested a method that can transparentize SLS processed parts by infiltrating them with UV curable resin of which refractive index is tuned to that of the powder material[4]. As a result, we confirmed transparentization phenomenon itself, but obtained clarity is not enough to observe inside a tube with thickness with some millimeters. To improve clarity of the parts, we changed powder and infiltrant materials from polystyrene (PS) to styrene methyl methacrylate copolymer (SMMA) and from UV curable epoxy to thermosetting epoxy. In addition, tuning accuracy of refractive index of the infiltrant was improved. Furthermore, relationship between clarity and process parameter of SLS process is also investigated. This paper discusses problems of previous process and describes modification given to the process and its result.

TRANSPARENTIZATION METHOD

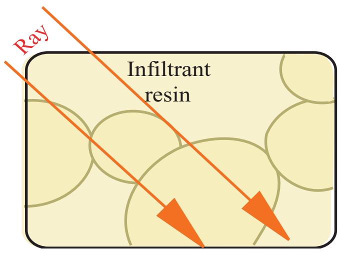
Before explanation of the transparentization method, the reason why SLS-processed parts are always opaque is explained. Figure 1a depicts behavior of a ray of light which incidents into a part obtained by SLS out of originally transparent powder. Any SLS processed part is inevitably porous, as shown in this figure, and it contains many boundaries between plastic and the air. Since the refractive index of plastic is greater than that of the air, the part is full of index boundaries. When every ray of light meets such a boundary, it refracts or reflects in most cases. Since the position and orientation of the boundary is random, the bend of every light path is random again. Resultantly, the light beam is scattered all while it passes through the part. These are reason for opacity. Therefore, there are two ways to prevent these phenomena. One is to use smaller powder than wavelength of visible light to prevent optical interaction between index boundary and the light. And the other is to unify the refractive indices in the part to eliminate index boundaries.

Currently, particle diameter of powder found in commercialized SLS is more than 10μm and it is much greater than wavelength of visible light. Thus, the way by unification of refractive index is selected. More concretely, the part is infiltrated with a liquid resin that can be cured afterward and of which index after cured is tuned to that of the original powder to unify the refractive indices in the part as shown in Figure 1b. Currently, similar technique is utilized to transparentize acrylonitrile butadiene styrene (ABS) or glass filled epoxy composite. In transparentization of ABS, refractive index of styrene acrylonitrile (SAN) copolymer is tuned to that of butadiene by adjusting proportion of styrene and acrylonitrile[5, 6]. In the case of the composite, refractive index of epoxy resin as matrix is tuned to that of the glass filler[7].

In addition, technique of liquid resin infiltration into SLS parts has been widely used to improve strength of SLS processed parts.



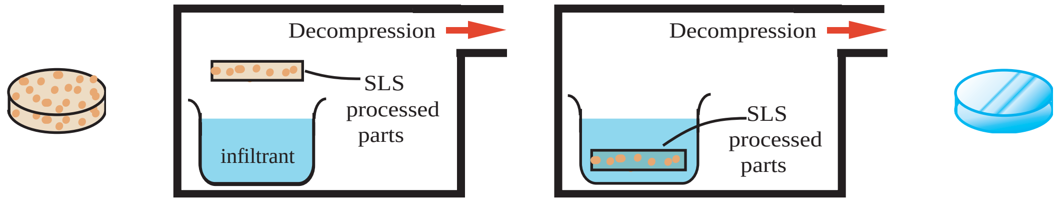
a. The path of ray inside of SLS processed parts



b. The path of ray inside of SLS processed parts infiltrated with resin whose refractive index is close to SLS resin

Figure 1: Paths of Rays inside Porous part and Transparentized Part

Figure 2 shows transparentizing process of SLS processed parts. Firstly, the original parts are loaded into vacuum chamber to remove the air from pores of the part (b), then the parts are dipped into the resin with tuned refractive index, and the pores are filled with the resin instead(c). The parts are unloaded out of the chamber and the infiltrant is cured.



a. SLS processed parts

b. Decompression of chamber in which SLS processed parts are put

c. Resin infiltration into SLS processed parts under decompression

d. Cure of infiltrant

Figure 2 : Transparentization Process of SLS processed parts

PROBLEMS IN THE PREVIOUS WORK

In the previous work, we used polystyrene for powder since CastForm PS is commercially available and its building parameter is well known. As infiltrant, we adopted UV curable epoxy since it can be cured very quickly. In these material selections, we made mistakes. One is combination of polystyrene and epoxy. While refractive index of CastForm PS is 1.588, that of typical epoxy varies between 1.49 and 1.57. To equalize the index of epoxy to that of the powder, we had to select very special resin containing many additives. As a result, we could not find not colored resin but red or yellow colored one as shown in Figure 3. The second problem is in curing process using ultraviolet light. It is difficult to expose the light over a wide area uniformly. And its failure results in varying color and transparency as found in Figure 4. In addition to non-uniformity of exposure on the plane that makes right angle with light axis, attenuation along to the axis also causes excessive and insufficient exposure in the models resulting in failure of transparentization.

Figure 3 : A Part processed out of CastForm PS after infiltration with UV curable epoxy. This treatment could lowered the haze of the test piece of 5mm in thickness to 55% at minimum.

Figure 4: Result of not uniform UV exposure. Clarity and color vary a lot if the exposure is not uniform.

Experimentals

Materials and Test Pieces

As a powder, we selected SMMA. Since refractive index of this copolymer has linear relationship with proportion of its two compositions, we can obtain any index between those of PS and poly methyl methacrylate (PMMA). In this fashion, we prepared SMMA spheres with refractive index of 1.553 which is in the range of typical epoxy resin. With regard to infiltrant, we prepared two epoxy resins of which refractive indices after curing are 1.5486 and 1.5580, respectively. Index of their mixture has again linear relationship with the mixing proportion. Since the powders index is situated between those of the two epoxies, we can tune the index of the mixture to that of powder.

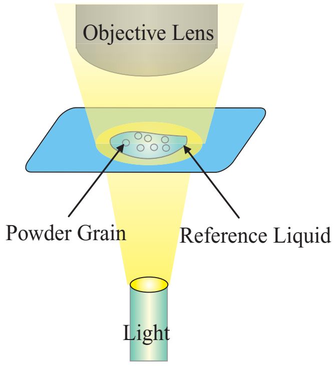


Figure 5: Measurement of Powders' Refractive Index

Abbé refractometer (ATAGO NAR-2T) was employed to measure refractive indices of resins and its cured state with precision of 0.0002. Since index of powder cannot be measured directly with this equipment, it is measured using reference liquid of which index is known. Measurement procedure is as following,

1. A single grain of the powder is immersed in the liquid and observed with microscope as shown in Figure 5.
2. If the indices of the powder and the liquid are the same, we observe nothing.
3. If powder's index is higher, a spherical grain works as a convex lens. Thus, the grain looks bright in the middle and dark near the edge when the microscope focuses in front of the grain(Table I), and we test another reference liquid with higher index. If powder's index is lower, on the other hand, the grain works as a concave lens. Thus, the grain looks dark in the middle and bright near the edge contrarily, in the same focus condition. In this case, we try reference liquid with lower refractive index.
4. Repeat the process 3 until the grain becomes invisible.

Dimensions of a test piece are shown in Figure 6. The test piece is 30mm and 30mm

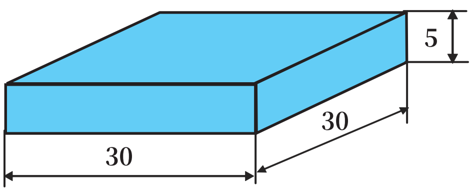
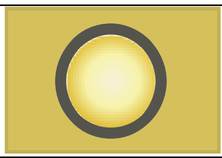
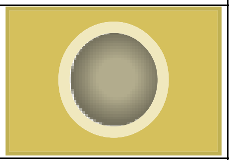
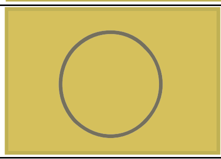
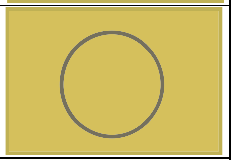
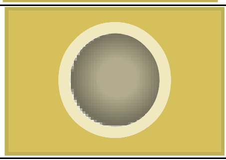
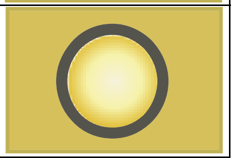


Figure 6: Built Sample

Figure 7: Dimensions of Test Piece

Table I: Relationship refractive indices and grain appearance in reference liquid

Focal Condition	$n_p > n_{ref}$	$n_p < n_{ref}$
Front Focus		
Exact Focus		
Rear Focus		

n_p: Refractive Index of Powder
n_{ref}: Refractive Index of Reference Liquid

in width and depth, respectively. Its height is 5mm, and its haze is estimated, in later discussion, along this axis through this thickness.

Relationship between Clarity and Refractive index

Table II shows summarizes relationship between clarity and deference in refractive indices of powder and infiltrant. Clarity is estimated by haze value (ISO 14782:99). Exact agreement in refractive index brings the lowest haze of 21% making it possible to read characters just below the transparentized part. Although the series of haze measurements shown in Table II indicate that very small difference in refraction index such as 0.0002 can lower clarity, it is very difficult to find the difference in photographs. However, we can find the difference much more easily when the parts are apart from the background picture/character as displayed in Table III. Even in this case, however, the part looks still clear when the difference of refraction indices is smaller than 0.0002, and we confirmed that it is possible to recognize a character of 2pt at the smallest.

Table II: Relationship between difference in refraction index and haze

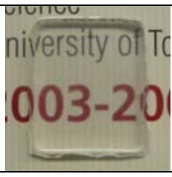
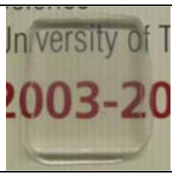
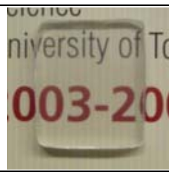
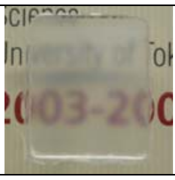
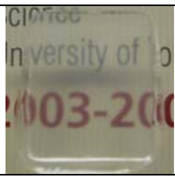
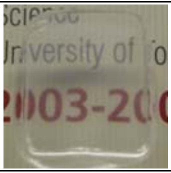
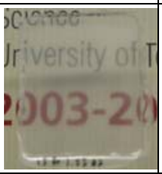
Index Difference	0.0004	0.0002	0.0000	0.0002	0.0004
Photo					
Haze [%]	50.5	23.6	21.3	33.3	35.0

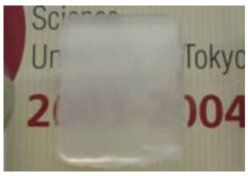
Table III: Effect of transparentization. Every part is apart from background picture by 20mm.

Index Difference	0.0004	0.0002	0.0000	0.0002	0.0004
Photo					
Haze [%]	50.5	23.6	21.3	33.3	35.0
Min.Char . size to be recognized	18pt	3pt	2pt	4pt	4pt

Curing Process

Temperature and duration in curing infiltrant are very important parameter that has a great influence of clarity. As shown in Table IV, curing at higher temperature during shorter time increases opacity of the part. It would be surmised that this increase of haze derives from infiltrant's swelling into powder grains and resulting slow

Table IV: Relationship between haze and curing temperature and duration. Every part is apart from background picture by 20mm.

Temperature	25 C°	35 C°	45 C°
Duration	120hours	48hours	48hours
Photo			
Haze [%]	33.3	70.2	78.7

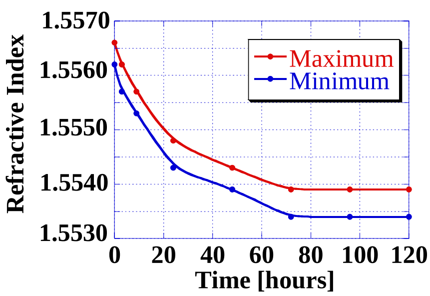


Figure 8: Variety of index of immersed grain

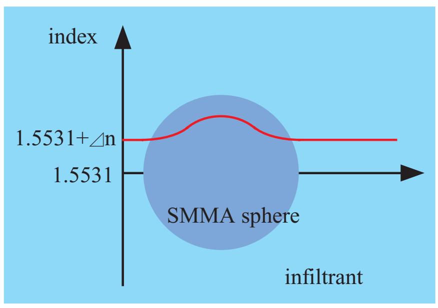


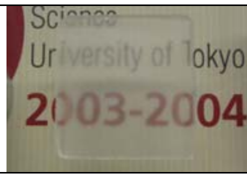
Figure 9: Varying index in a grain

decrease of their refractive index as shown in Figure 8. Assuming that index of a powder decreases uniformly, there would be a resin that could offer good transparency even if the resin were cured in short term at high temperature. Since we could not find such refractive index of resin, however, we infer that infiltrant swells into a grain so slowly that variety of refractive index occurs in a single particle of powder as illustrated in Figure 9.

Part Building Process

Part building parameters also play a very important role that affects final clarity. As shown in Table V, higher laser power increases haze of parts after transparentization. Since lower power decreases strength of original parts, trading off that maximizing transparency keeping a certain strength that is required to withstand breakout operation have to be made.

Table IV: Relationship between haze and laser power when original parts are built. Every part is apart from background picture by 20mm.

Laser Power	15W	20W	30W
Photo			
Haze [%]	35.0	37.0	42.4

Outlooks

Transparency obtained in this research is good enough for prototyping of fluid dynamic parts and devices. For example, inner diameter and wall thickness of plastic intake manifolds of automotive engines are typically around 20mm and 5mm, respectively, and through this thickness of the air and the processed parts, we can see with a resolution above 2pt. However, strength of processed parts remains as weak as that of the parts from stereolithography process since original SMMA sinter is very weak, and processed parts owed its strength to infiltrated epoxy resin. In addition, long curing time is very troublesome when being applied to industry. To avoid these problems, we are planning to employ transparent PA that is much stronger and tougher, and less swelling than SMMA to realize the toughest and clearest solid freeform fabrication.

CONCLUSIONS

A technology that can transparentize SLS processed parts by infiltrating curable resin with tuned refractive index is investigated. The original principle was introduced previously. In this paper, modification is made on material and process to improve the performance. Selecting SMMA and thermosetting epoxy resin as powder and infiltrant, respectively, lowered haze of an SLS processed part which is 5mm in thickness to 21% at the minimum making it possible to recognize and read very small character of 2pts through the parts. Transparentization tests incorporated with precise refractive index measurement indicated that index control precision of 0.0002 is required to reduce haze below 30%. It is confirmed that we should cure the infiltrant so slowly as the infiltrant resin swells into powder grains completely and their refractive index is settled. Ease of breaking the parts out of cake and obtained transparency are in tradeoff relationship, and we need to optimize build parameters such as laser power and scanning speed considering various conditions such as shape of the model and required transparency. To utilize this technology in industry, we still need progress in original powder material.

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