Reaction Heat Effects on Initial Linear Shrinkage and Deformation in Stereolithography

著者	Narahara Hiroyuki, Tanaka Fumiki, Kishinami Takeshi, Igarashi Satoru, Saito Katsumasa
journal or publication title	Rapid Prototyping Journal
volume	5
number	3
page range	120-128
year	1999
URL	http://hdl.handle.net/10228/00006914

doi: info:doi/10.1108/13552549910278946

Reaction Heat Effects on Initial Linear Shrinkage and Deformation in Stereolithography

Hiroyuki NARAHARA
Fumiki TANAKA
Takeshi KISHINAMI
Satoru IGARASHI and
Katsumasa SAITO

The authors

Hiroyuki NARAHARA is with the Department of Mechanical Systems Engineering at the Kyushu Institute of Technology, Iizuka, Fukuoka, Japan.
Fumiki TANAKA, Takeshi KISHINAMI and Satoru IGARASHI are all with the Division of Systems and Information Engineering at the Hokkaido University, Sapporo, Hokkaido, Japan.
Katsumasa SAITO is at the Gunma Polytechnic College, Takasaki, Gunma, Japan.

KEYWORDS:

Stereolithography, Deformation, Linear Shrinkage, Reaction Heat

ABSTRACT

In the industrial use of Stereolithography, precision is always a problem. The basic phenomenon of solidification shrinkage has not been sufficiently investigated. This study aims at clarifying the initial linear shrinkage of cured resin in a minute volume. An experimental equipment has been developed which measures the time history of the single strand in situ in a stereolithography machine. An analysis model on the time history of a minute volume linear shrinkage was shown using the measured shrinkage of a cured line segment. The relation between the time history of the linear shrinkage and temperature was measured and the shrinkage in the minute volume after irradiation was found to result due to temperature variation. Deformation and linear shrinkage were measured with two scanning orders to control the thermal distribution in layer forming. The effects of thermal distribution were also observed in one layer forming.

INTRODUCTION

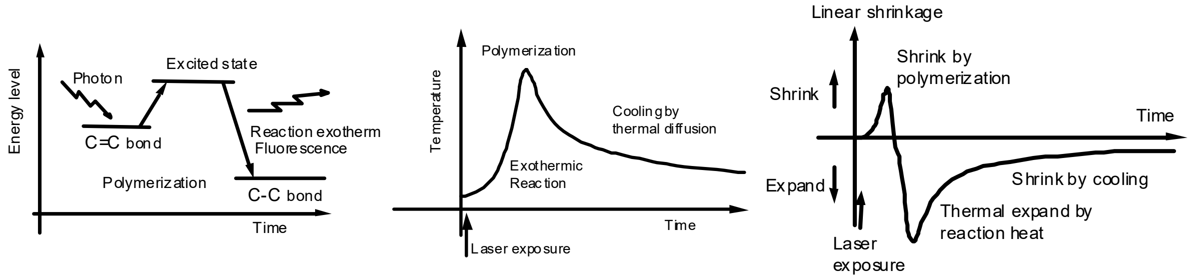
Stereolithography is a method which makes use of the phase change of material from liquid phase monomer to solid phase polymer. This phase change is the result of the polymerization by the UV-laser beam irradiation. As the laser beam can select infinitesimal volume to solidify, details of the solid shape can be expressed, which is one of the advantages of complex shape fabrication.

Disadvantages, on the other hand, include poor shape stability and surface roughness than removal processing or machining because it uses an additive method based on the material phase change in a free space (Narahara, 1997) for example. Especially the deformation of the stereolithography part poses as a significant problem in improving accuracy (Ullett, 1994). Researches have not been conducted sufficiently to establish the basic theory of solid forming (Narahara, 1996)(Narahara, 1993).

Although the development of equipments, which continuously measure the linear shrinkage and shrinkage force of the single strand produced by laser scanning, has been reported (Chartoff, 1995)(Guess, 1995) and several kinds of resins for stereolithography have been measured, it is not yet known how physical properties interact with each other within a minute volume during the solidification of the photopolymer by the laser beam scanned.

New information on the basic solid forming mechanism will contribute to new material designs, new draw patterns and simulation kernel for process analysis. To find a guide on material designs and optimum fabrication methods with computer simulation (Flach, 1994)(Kishinami, 1997), it is important to clarify the mechanism of resin dynamics in the initial exposure hardening.

In this paper, a basic solidification model on mechanical properties is discussed. Our newly developed experimental equipment to measure linear shrinkage in situ, which aims to analyze the relation between the laser scanning and linear shrinkage of a single strand, is described. Also discussed is the procedure developed to extract minute volume linear shrinkage from the measured data. This paper will also describe the results of a single strand test converted by this extracting procedure and aim to clarify the relation between the minute volume linear shrinkage and resin temperature at initial stage. The results of a three lines strand test, which aim to clarify the effects of different temperature distributions in layer forming, are also shown. Finally, the effects of the reaction heat on deformation are discussed.



(a) Schematic representation of absorption of photon and heat release in polymerization

(b) Schematic representation of exothermic change in photopolymerization

(c) Sketch of a linear shrinkage change in photopolymerization

Figure 1 Sketch of time history of linear shrinkage in minute volume for explanation

BASIC MODEL OF LINEAR SHRINKAGE AT INITIAL STAGE

The term "linear shrinkage" is normally used to evaluate the changes in the length of the material whose size is initially defined. Similarly, to discuss the phenomenon of the single strand, we define "the rate of shrinkage in appearance" as "linear shrinkage". The term "initial", which also appears in the title, indicates the curing stage just after laser irradiation.

The problem dealt here is the hardening reaction of the green material of photopolymer just after laser beam irradiation. The problem of extra hardened shrinkage induced by additional exposure, for example, the exposure at the time of lamination or that at post curing, etc, will not be discussed in this paper.

Figure 1 (a) shows the absorption and reaction exothermal relation at laser exposure known in polymer chemistry. When photopolymer absorbs ultraviolet ray, it is activated and the potential energy becomes high. After resin is polymerized, it changes to a stable basic state. The energetic difference of the excess energy for change to the stable state is released as reaction exotherm and fluorescence light.

It is illustrated as a time history of temperature before and after photopolymerization (Figure 1 (b)). When polymerization starts with laser exposure, polymerization shrinkage occurs proportionally to the reaction extent of functional groups. Temperature rises with the heat release of polymerization. At the same time, the resin swells by thermal expansion. As the functional group decreases with the progress of reaction or as the irradiation is reduced, the heat flux decreases. After temperature rise stops, temperature decreases by the cooling of thermal diffusion. The slow variation of shrinkage caused by thermal shrinkage, or by the cooling of heat diffusion, must be observed (Figure 1 (c)).

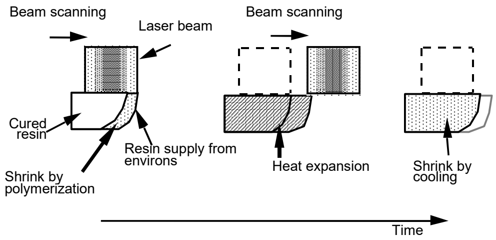


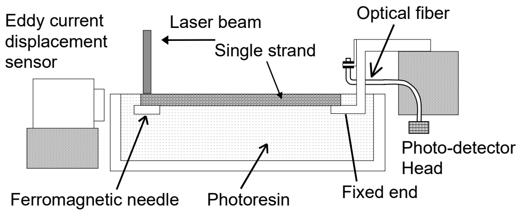
Figure 2 Sketch of single strand formation irradiated by laser scanning

For the reason mentioned above, when light passes by a minute volume of resin, the phenomenon described below will occur.

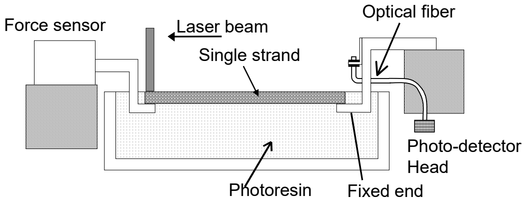
Schematically indicated by Figure 2, when UV light is irradiated to a minute volume of resin, shrinkage starts with the polymerization reaction, and resin is supplied from the environs at the same time. However, while light is passing, this resin supplied also hardens. Volume increases as the heat expansion with temperature rise that is generated by the polymerization reaction heat. When the heat release ends, the resin is cooled by the heat diffusion, and thermal shrinkage occurs. Such polymerization shrinkage → heat expansion → shrinkage by cooling, repetition of expansion and shrinkage occurs in every part of the hardened green structure. This temperature change and thermal expansion are anticipated to affect parts deformation.

Consequently, we will focus the objectives of this paper on the following topics:

- Develop the analysis method for the minute volume linear shrinkage.
- Clarify experimentally that the temperature distribution is the cause of the linear shrinkage variation.
- Show experimentally that the temperature distribution of layers and deformation are closely related.



(a) Linear shrinkage measurement



(b) Force measurement

Figure 3 Experimental arrangements for single strand measurements

EXPERIMENTAL SETUP OF INITIAL LINEAR SHRINKAGE AND SHRINKAGE FORCE MEASUREMENT OF SINGLE STRAND

The principle of the experimental arrangement for linear shrinkage and force measurement is indicated on Figure 3. When the laser beam starts from a fixed end and reaches a free end, the single strand of cured resin combines the fixed end and free one. A non-contact eddy current sensor is used to measure the displacement of a ferromagnetic needle that connects the free end of a single strand. The force sensor obtains the shrinkage force of a single strand with both restricted ends.

For tracing the beam position and measuring time, an optical fiber which connects photo detector heads is used to detect the laser traverse during laser scanning. A time lags exist between the time history origins of sensors, because sensors have different spatial positions. For the time correspondence, the origins of temperature and linear shrinkage histories are compensated with laser scanning speed.

For measuring the resin temperature, a thermocouple is placed in the course of the laser scan path. The arrangement of the thermocouple, photo sensor, and fixed end is shown in Figure 4.

The value of linear shrinkage is obtained from the displacement divided by the set distance, which is defined as the distance between the fixed end and free end. The sectional area of a single strand is measured after the experiment. The stress value is calculated from the shrinkage force divided by the sectional area.

EXTRACTION OF MINUTE VOLUME LINEAR SHRINKAGE FROM MEASURED DATA

The objective of this section is to study the relation between the scanned laser beam and initial linear shrinkage in a very small volume. In order to discuss the curing behavior of the resin in a minute volume, discussion of only the shrinkage behavior of a single strand is not sufficient. The measured output, which corresponds to the linear shrinkage, does not agree with the minute volume behavior, as a single strand consists of a serial connection of minute volumes while the measurement data contains serial effects. It is necessary to remove the serial effects and extract the minute volume curing behavior from the measured data of a single strand. Consequently, a mathematical relation of the experiment should be formulated.

Now, we define linear shrinkage $\varepsilon_S(t)$ and $\varepsilon_P(t)$ as follows:

$\varepsilon_S(t)$: The time history of the average linear shrinkage of a single strand produced by the laser irradiation which connects fixed ends and free ends.

$\varepsilon_P(t)$: The time history of the linear shrinkage of cured resin with minute length divided by the scanning direction after laser irradiation.

The length l of a single strand is drawn from a fixed end to a free end by laser scanning (Figure 4). The time history of the linear shrinkage $\varepsilon_S(t)$ is measured by the sensor. The time when the laser beam reaches the free end is defined as 0.

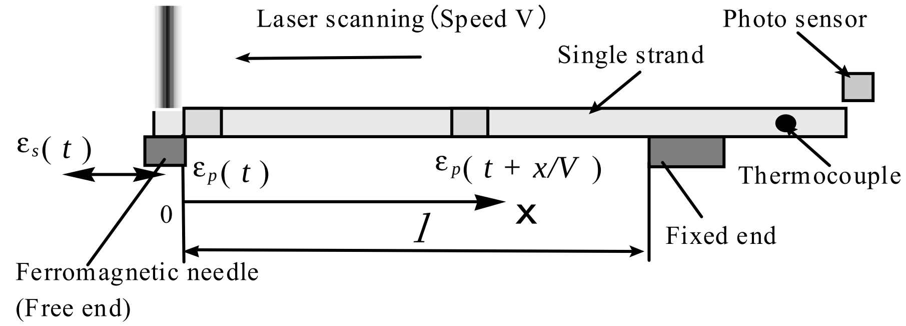


Figure 4 Definition of measured linear shrinkage and minute volume linear shrinkage

Table I Experimental conditions

Machine	Sony Co. JSC2000
Laser source	Coherent Inc. INNOVA 90-6
Wave length	UV-Ar (363.8,351.1nm)
Sampling time	0.01s
Resin (radical polymerization)	SCR300, SCR310, SCR600 (JSR Co.): All resins are urethane acrylate resin
Resin (cationic polymerization)	Epoxy A, Epoxy B : All resins are epoxy resin
Thermocouple	Chromel-Alumel thermocouple (K-type) ɸ0.127mm
Set length of single strand	25mm

The time history of the minute volume linear shrinkage is defined as $\varepsilon_P(t)$.

Considering that the laser beam scans at speed V, the minute volume linear shrinkage $\varepsilon_P(t)$ should have the same characteristics at every part of the single strand except different starting times. Therefore, the time history of the measured linear shrinkage $\varepsilon_S(t)$ is equal to the integration of the $\varepsilon_P(t)$ with a time delay that corresponds to the scanning speed V.

$$\varepsilon_s(t) = \frac{1}{l}\int_0^l \varepsilon_p(t + x/V)dx = \frac{V}{l}\int_t^{t+\frac{l}{V}} \varepsilon_p(u)du \quad (1)$$

By differentiating the integral relation, the minute volume linear shrinkage $\varepsilon_P(t)$ can be derived from the following equation:

$$\varepsilon_p(t) = -\frac{l}{V}\frac{\partial\varepsilon_s(t)}{\partial t} + \varepsilon_p(t + l/V) \quad (2)$$

Since this equation has the term $\varepsilon_P(t)$ on the right side, $\varepsilon_P(t)$ cannot be solved by this equation (2) only. An additional relation is required. After sufficient passing time, the linear shrinkage becomes uniform in the length direction. Thus, the value of the linear shrinkage of a single strand becomes identical to the linear shrinkage of a minute volume:

$$\varepsilon_s(\infty) = \varepsilon_p(\infty) \quad (3)$$

Therefore, $\varepsilon_P(t)$ is obtained by the backward substitution of strain $\varepsilon_S(t)$, which is a backward time history of measured linear shrinkage from the initial exposure up to the steady state. It means that the $\varepsilon_P(t)$ value is obtained from the time infinity, or steady state, to zero from this equation.

Using the sampled data $\varepsilon_S(t)$ from time t=0 to ta, $\varepsilon_P(t)$ can be solved as equations (5), where, Δt is the sampling time, t_a is the final measuring time and M is the total sampling number. For obtaining better resolution and calculation results, the relation $0 < (\Delta t << l/V << t_a)$ must be satisfied.

$$t_a = M \cdot \Delta t, l/V = K \cdot \Delta t, t = N \cdot \Delta t \left(N = 0,1,2,...M\right) \quad (4)$$

$$\begin{aligned}
\varepsilon_p\left(t_a - \frac{l}{V}\right) &= -\frac{l}{V}\frac{\partial\varepsilon_S\left(t_a - \frac{l}{V}\right)}{\partial t} + \varepsilon_S(t_a) \\
\varepsilon_p((M-K)\cdot\Delta t) &= -\frac{l}{V}\frac{\partial\varepsilon_S((M-K)\cdot\Delta t)}{\partial t} + \varepsilon_S(M\cdot\Delta t) \\
&\vdots \\
\varepsilon_p((M-2K+1)\cdot\Delta t) &= -\frac{l}{V}\frac{\partial\varepsilon_S((M-2K+1)\cdot\Delta t)}{\partial t} \\
&\quad + \varepsilon_S((M-K+1)\cdot\Delta t) \\
\varepsilon_p((M-2K)\cdot\Delta t) &= -\frac{l}{V}\frac{\partial\varepsilon_S((M-2K)\cdot\Delta t)}{\partial t} \\
&\quad + \varepsilon_p((M-K)\cdot\Delta t) \\
&\vdots \\
\varepsilon_p(\Delta t) &= -\frac{l}{V}\frac{\partial\varepsilon_S(\Delta t)}{\partial t} + \varepsilon_p((K+1)\cdot\Delta t) \\
\varepsilon_p(0) &= -\frac{l}{V}\frac{\partial\varepsilon_S(0)}{\partial t} + \varepsilon_p(K\cdot\Delta t)
\end{aligned} \quad (5)$$

Thus, the time history of minute volume linear shrinkage $\varepsilon_P(t)$ can be obtained from the measured data. Note that the differential value of $\varepsilon_S(t)$ should be calculated using the smoothed $\varepsilon_S(t)$ that is not affected by the measuring noise.

MEASUREMENT OF LINEAR SHRINKAGE AND REACTION HEAT OF SINGLE STRAND

Experimental Results of Single Strand Measurements

The experimental conditions are indicated in Table I. The relation between the time histories of linear shrinkage and temperature of a single strand was investigated.

Different laser powers and scanning speeds conditions are experimented, and the relation between linear shrinkage and stress after the largest expansion of a single strand is drawn. As shown in Figure 5, it is understood that these conditions move on almost the same curve. This means that the relation is not influenced by fabrication conditions with this experimental arrangement. In other words, a characteristic of the resin is observed with this experiment.

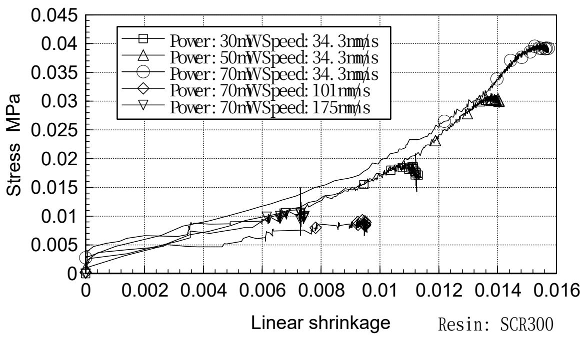


Figure 5 Relation of linear shrinkage-stress curves with different irradiation conditions

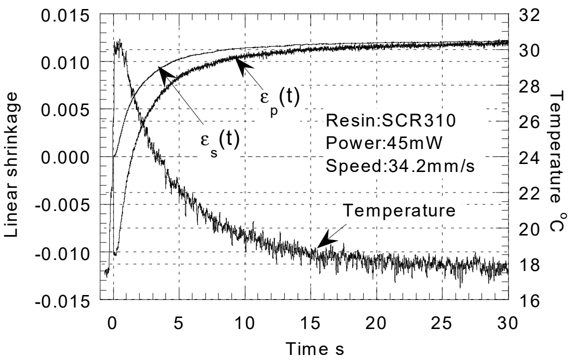


Figure 6 Time history of linear shrinkage and temperature

The time history of the minute volume linear shrinkage, which is calculated from the measured linear shrinkage, is indicated in Figure 6. The vertical axis defines a shrinkage as a positive value and an expansion as a negative one. The time history of each curve is adjusted to the origin of the minute volume, which is compensated from the detection time of the photo sensor located near the fixed end side. The representative curve of a minute volume linear shrinkage in a single strand starts to grow just after the laser exposure and shrink afterward. It can be seen that the minute volume linear shrinkage $\varepsilon_P(t)$ shows a larger variation than $\varepsilon_S(t)$.

Experimental Result between Linear Shrinkage and Resin Temperature

The experimental relation of the time history between the linear shrinkage and temperature is indicated in Figure 7. The horizontal axis is solidified resin temperature and vertical axis is minute volume linear shrinkage $\varepsilon_P(t)$. After the rise in temperature, the temperature falls and the linear shrinkage decreases linearly, which means that the proportional relation of the temperature variation has dominant effects on the shrinkage variation. It is understood that the variation of the time history of the linear shrinkage after exposure is caused by heat. In other words, the principal variation of the initial linear shrinkage is the result of thermal strain.

MEASUREMENT OF THE EFFECTS OF SCAN ORDERS

The effects of thermal strain on parts deformation were investigated. The laser-scanning path is applied in two scanning orders to control the temperature distribution in layer forming. First, parts deformation was tested with stereolithography parts, and then the linear shrinkage test of 3 lines strand was performed to find whether thermal strain effects exist even in one layer forming.

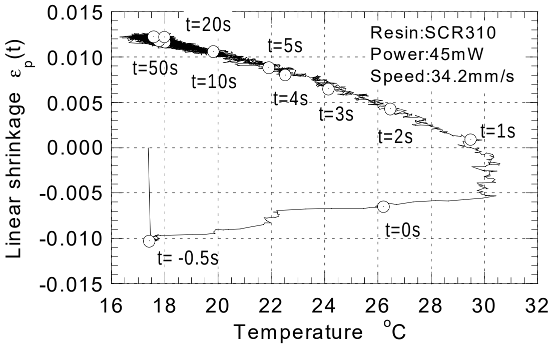


Figure 7 Relation of temperature and linear shrinkage $\varepsilon_P(t)$

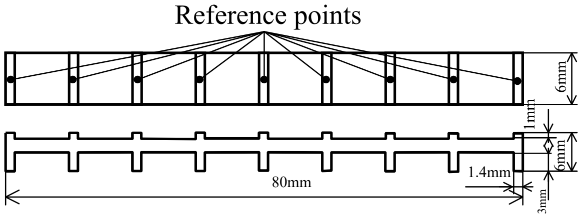
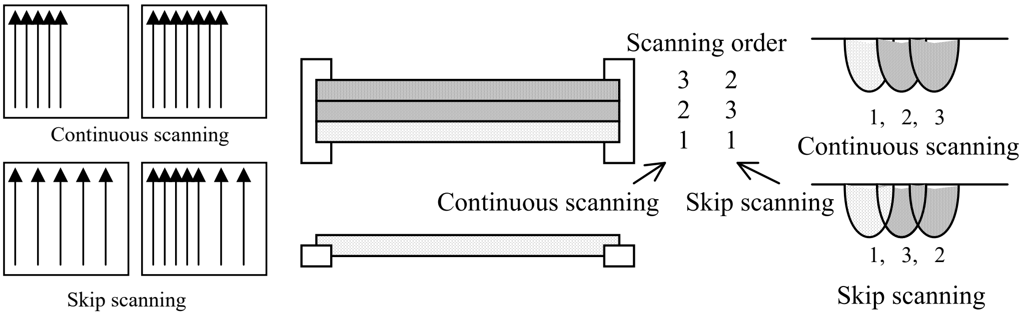


Figure 8 Sample shape for scan orders experiment

Measurements of Deformation with Different Scanning Orders

Parts deformation was measured with the different scan types. The size of the sample shape used for the experiments is shown in Figure 8. The plate with several support pillars is used. The curvature ρ, which is the reciprocal 1/r of the curvature radius r, of the plate is defined as the evaluation value of the deformation. It is measured immediately after fabrication and is calculated from the measured points by the minimum square method. In the calculation of the curvature, the positive value is defined as the case where the circular center exists in the upper part of the model. In addition, the negative value is defined as the case existing in the lower part of the model. The reference points of the model are also shown in Figure 8.

The Figure 9(a) shows the difference between the two scanning orders. In continuous scanning, as shown above, the laser beam is scanned from



(a) Draw pattern (b) Scanning order for 3 strand (c) Sectional view

Figure 9 Scanning orders of continuous scanning and skip scanning

side by side continuously. In skip scanning on the other hand, as shown below, the laser beam is first scanned with single line spaces in between, and then scanned to fill these spaces.

Figure 10 shows the experimental results of parts deformation. The vertical axis shows the curvature. The left side of each pair in Figure 10 is the continuous scanning. Skip scanning showed the tendency for smaller deformation.

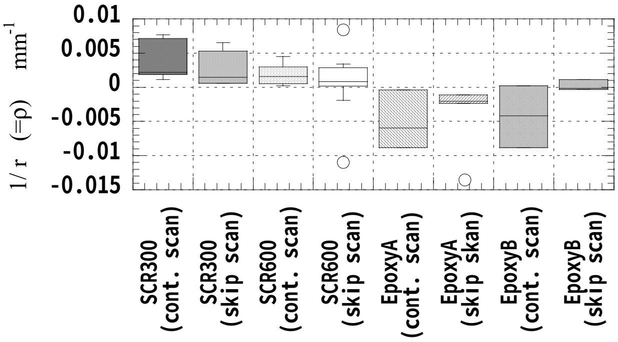


Figure 10 Deformation results of three lines scanning experiment

Measurements of Linear Shrinkage with Different Scanning Orders

This experiment was performed to study the effects of the thermal strain in one layer forming. The influence over the shrinkage and stress of a single strand is measured by the scanning order. In the case of continuous scanning, three strands are drawn overlapping from side by side and the second line is drawn immediately after the first scanning. However, in the case of skip scanning, first two strands are drawn immediately without overlapping and the third strand is drawn with fifteen seconds interval in the middle of the strands. This time delay corresponds to the time delay of one layer drawing for parts building by skip scanning. A scanning order and the difference of three strands irradiation experiments are shown in Figure 9(b)(c).

Figure 11 shows the experimental results. In the three lines scanning experiment, a smaller shrinkage and stress are observed when the skip scanning is applied. The experimental results show that the skip scanning also has the effects of linear shrinkage reduction in the case of layer forming.

DISCUSSION

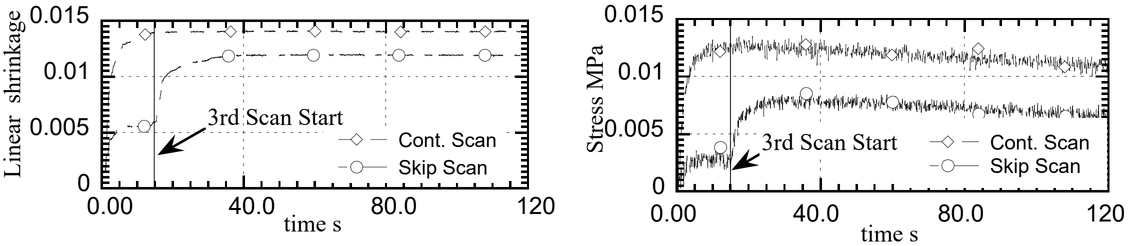
With the single strand experiment, it has been clarified that the time history of the shrinkage after irradiation is caused by temperature change. From the initial linear shrinkage measurement, the variation of linear shrinkage is proportional to the temperature decrease. The results of the skip scanning show a smaller deformation and smaller linear shrinkage can be obtained by the scan order experiments.

Next the effects of the support structure of the sample shape shown in Figure 8 on the deformation were considered. From our experiments, this support structure restricts the horizontal movement of the plate in a sample shape during the build process. After the sample shape is removed from the base plate, horizontal restriction is released and the shape changes to the stable state, which results in deformation. The layout of this restriction structure, which is the identical to the support structure, may serve as one deformation reduction methods. The effects of different support structures on deformation should also be studied in future.

The experimental results of the skip scanning show that the smaller value can be explained as follows: Considering the time history of the linear shrinkage when a new layer is formed, a brief sketch of the thermal strain in layer forming is shown as Figure 12.

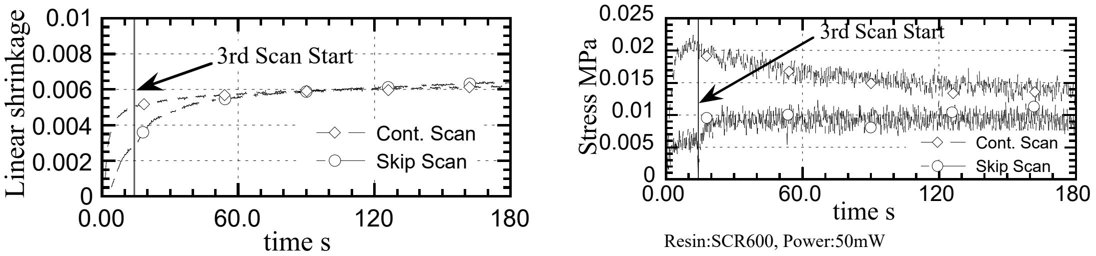
In case of continuous scanning, as the time difference of the neighbors is short, the temperature pattern and the shrinkage pattern will be equidirectional to the surrounding patterns. consequently, there is little restriction from the surrounding. On the other hand, in the case of skip scanning, due to the long time difference, the surrounding will not be equidirectional and it will restrict the thermal expansion of the middle strand. A smaller linear shrinkage was thus observed.

It suggests that the temperature distribution of layer surfaces resulting from reaction heat by laser beam scanning is one cause of shape



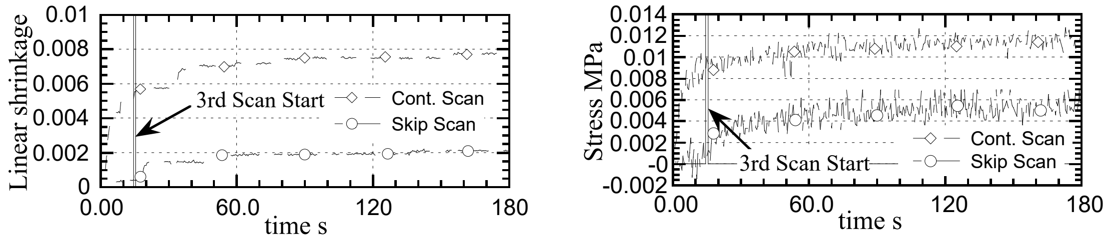
Resin:SCR300, Power:50mW
ScanSpeed:686mm/s, Length of Cured Resin:15mm

Resin:SCR300, Power:50mW
ScanSpeed:686mm/s, Length of Cured Resin:15mm



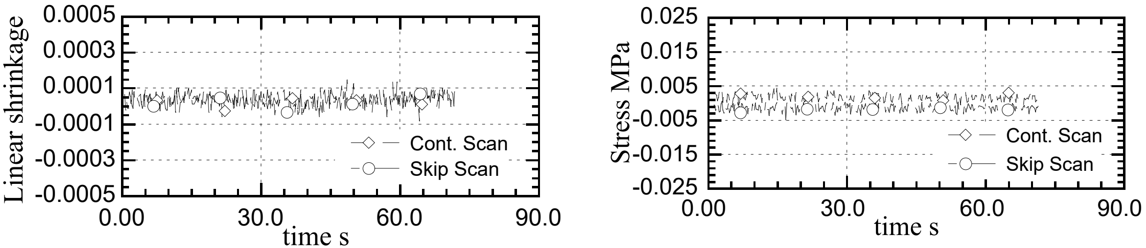
Resin:SCR600,Power:50mW
ScanSpeed:686mm/s, Length of Cured Resin:15mm

Resin:SCR600, Power:50mW
ScanSpeed:686mm/s, Length of Cured Resin:15mm



Resin:Epoxy A, Power:50mW
ScanSpeed:175mm/s, Length of Cured Resin:15mm

Resin:Epoxy A, Power:50mW
ScanSpeed:175mm/s, Length of Cured Resin:15mm



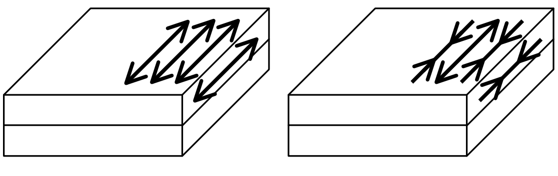
Resin:Epoxy B, Power:50mW
ScanSpeed:175mm/s, Length of Cured Resin:15mm

Resin:Epoxy B, Power:50mW
ScanSpeed:175mm/s, Length of Cured Resin:15mm

Figure 11 Time histories of linear shrinkage of three lines scanning experiment

deformation. By skip scanning, changes in the shrinkage of adjacent lines restrict the heat expansion of the middle line in the initial stage of exposure. Consequently, parts deformation has been indicated to be smaller and the linear shrinkage of three strands has also been observed to be smaller.

Our experimental results can be explained more clearly by the hypothesis that reaction does not progress if light is not irradiated. In the case of the urethane system resin whose basic reaction is radical polymerization, reaction does not progress if light is not irradiated. For epoxy resin whose basic reaction is cationic polymerization, the above assumption will be insufficient since reaction does not stop after irradiation. This phenomenon should be examined in further detail.



Continuous scanning Skip scanning

Figure 12 Sketch of strain distributions in building of new layer

The skip scanning showed the tendency of smaller deformation in the parts deformation experiment. However, different results were observed depending on the type of resin used, suggesting that further analysis and experiment of the interaction phenomenon among layers are necessary. It can be concluded that a more detailed analysis is necessary in the future.

CONCLUSIONS

This study aims at clarifying the initial linear shrinkage of cured resin in a minute volume. An experimental equipment was developed for measuring the time history of the single strand in situ in a stereolithography machine. The following results were obtained from this study:

1. The analysis method of an initial linear shrinkage of minute volume in a single strand was developed.
2. The variation of shrinkage of a single strand was observed with the variation of the resin temperature. The increase in the linear shrinkage of a single strand is more or less proportional to the drop in temperature.
3. After skip scanning, parts deformation was found to be smaller, and lower linear shrinkage was observed in three lines strand experiments.
4. The temperature distribution of the layer surfaces by laser scanning is one cause of shape deformation.

ACKNOWLEDGEMENTS

The authors wish to acknowledge graduate student, Kenji Kondo who cooperated in this research. This research has been partially funded by the Grant-in-Aid for Scientific Research (No. 09750144) from the Japanese government of the Ministry of Education, Science, Sports, and Culture.

REFERENCES

Chartoff, R. P. and Du, J. (1995), "Photopolymerization Reaction Rates by Reflectance Real Time Infrared Spectroscopy: Application to Stereolithography Resins", Proceedings of the Solid Freeform Fabrication Symposium, University of Texas at Austin, Texas, Austin, pp.298-304.

Flach, L. and Chartoff, R. P. (1994), "Stereolithography Process Modeling: Shrinkage Prediction", Proc. of the Fifth International Conference on Rapid Prototyping, Dayton, Ohio, pp.181-189.

Guess, T. R. and Chambers, R. S. (1995), "In-Situ Property Measurement on Laser-Drawn Strands of SL 5170 Epoxy and SL 5149 Acrylate", Proceedings of the Solid Freeform Fabrication Symposium, University of Texas at Austin, Texas, Austin, pp.134-141.

Kishinami, T., Tanaka, F. and Narahara, H. (1997), "Distortion Mechanism of Stereolithography Parts", Proc. of the 8th International Conference on Production Engineering -Rapid Product Development- (held on August 18-20, Sapporo Japan), Chapman & Hall, UK, pp.83-92.

Narahara, H., Igarashi, S. and Saito, K. (1997), "A New Stereolithography Process for Improved Performance and Surface Roughness", Proc. of the 8th International Conference on Production Engineering -Rapid Product Development- (held on August 18-20, Sapporo Japan), Chapman & Hall, UK, pp.93-102.

Narahara, H. and Saito, K. (1996), "Shape Analysis of Solidified Photopolymer for the Three Dimensional Photofabrication", International Journal of JSPE, Vol. 30, No 4, pp.311-316.

Narahara, H. and Saito, K. (1993), "Characterization of Solidified Resin Created by Three Dimensional Photofabrication", Proc. of the Fourth International Conference on Rapid Prototyping, Dayton, Ohio, pp.271-281.

Ullett, J. S., Chartoff, R. P., Lightman, A. J., Murphy, J. P. and Li, J. (1994), "Reducing Warpage in Stereolithography Through Novel Draw Styles", Proc. of the Fifth International Conference on Rapid Prototyping, Dayton, Ohio, pp.109-125.