REACTION HEAT EFFECT ON INITIAL LINEAR SHRINKAGE OF STEREOLITHOGRAPHY RESINS

Hiroyuki NARAHARA*, Fumiki TANAKA**, Takeshi KISHINAMI**, Satoru IGARASHI** and Katsumasa SAITO***

* Department of Mechanical Systems Engineering,
Kyushu Institute of Technology,
680-4 Kawazu, Iizuka City, Fukuoka 820, JAPAN.
** Hokkaido University, 060 kita-13, Nishi-8, Kita-ku, Sapporo 060.
***Gunma Polytechnic college, 918 Yamana, Takasaki city, Gunma 370-12.

ABSTRACT

In the industrial use of the Stereolithography, the precision is always a problem. Basic phenomenon of the solidification shrink has not sufficiently investigated. This study aims at clarifying the initial linear shrinkage of cured resin in a minute volume. Experimental equipment has been developed which measures the time history of the single strand in situ in a stereolithography machine. Analysis model about the time history of a minute volume linear shrinkage has been shown using with the measured shrinkage of a cured line segment. The relation between the time history of the linear shrinkage and the temperature was measured and the shrinkage in the minute volume after irradiation has been caused by the temperature variation.

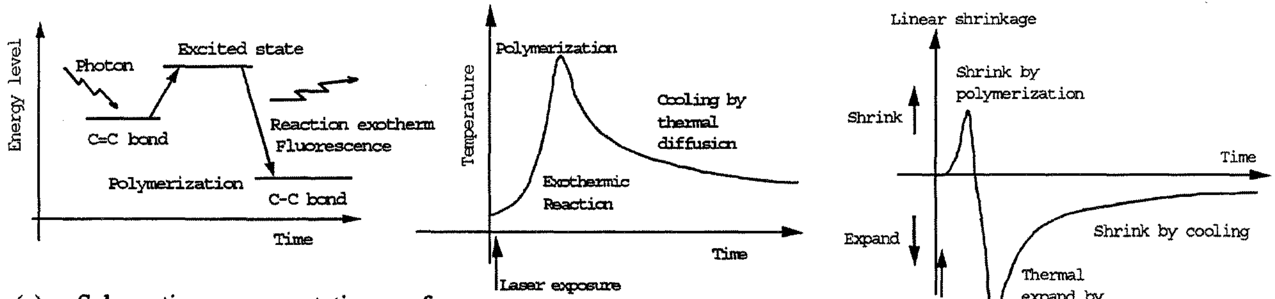
1. INTRODUCTION

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

On the other hand, it is pointed out that the problem is its worse shape stability and surface roughness than the removal processing, or machining, for example, since it uses additive method based on the material phase change in a free space [1]. Especially deformation of stereolithography part is the significant problem to improve accuracy [2]. Researches have not been studied sufficiently to establish the basic theory of solid forming [3][4]. It is not known well how physical properties interact each other within a minute volume during scanned laser beam solidifies photopolymer. For finding a guide of material design and an optimum fabrication method with computer simulation [5][6], it is important to clarify a mechanism of resin dynamics at the initial exposure hardening.

In order to observe this material change continuously, development of the equipment to measure linear shrinkage and shrinkage force at hardening by laser scanning has been reported [7][8]. Several kinds of resins for stereolithography have been measured.

In this paper, a basic solidification model about mechanical property is shown. Procedure to extract a minute volume linear shrinkage from measured data is explained and experimental setup is also shown. Finally, appropriateness of the basic model is described by



(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 the time history of linear shrinkage in a minute volume for explanation

comparing with experimental results.

2. BASIC MODEL OF LINEAR SHRINKAGE AT INITIAL STAGE

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

When photopolymer absorbs ultraviolet ray, it is activated and the potential energy becomes high. After resin is polymerized, it transits to stable basic state. The energetic difference of excess energy to shift to stable state is released as polymerization heat (Figure 1).

It is illustrated as a time history of temperature before and after photopolymerization. After polymerization starts with laser exposure, polymerization shrinkage occurs as proportion to the reaction extent of functional groups. Temperature rises with heat release of polymerization. At the same time, resin swells by the thermal expand. As the functional group decreases with the progress of reaction, or as the irradiation is reduced, the flux of heat decreases. Slow variation of shrinkage caused by the thermal shrink, or cooling result by heat diffusion, must be observed.

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 minute volume of resin, shrink starts with polymerization reaction, and resin is supplied from environs at the same time. However, during light is in passing, this supplied resin also hardens. Volume increases as the heat expansion with a temperature rise that is generated by the polymerization reaction heat. When a heat release ends, resin is cooled by the heat diffusion, and a shrink occurs by the thermal shrink. Such polymerization shrink → heat expansion → shrink by cooling, the repetition of expansion and shrink will occur in an every part of a hardening green parts. It is anticipated that this heating and cooling variation will influence on the time history of shrinkage.

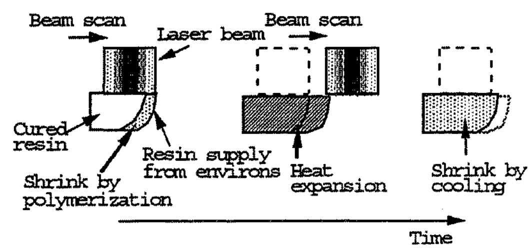


Figure 2. Sketch of a single strand formation irradiated by laser scanning

3. EXPERIMENTAL SETUP OF LINEAR SHRINKAGE AND SHRINKAGE FORCE MEASUREMENTS OF SINGLE STRANDS

Principle of the experimental equipment is indicated on Figure 3. After laser beam starts from a fixed end, it reaches a free end and the single strand of cured resin combines the fixed end and the free one. A non-contact eddy current sensor is used to measure a displacement of a ferromagnetic needle that connects the free end of a single strand. For tracing the beam position and the measuring time, a photo sensor is used to detect the laser traverse during laser scanning. The time lags exist between the time history origins of sensors, because sensors have different spatial positions. For the time correspondence, origins of time histories, temperature and linear shrinkage histories, for example, are compensated with laser scanning speed. Shrinkage force is obtained by force sensor from a single strand with both restricted ends.

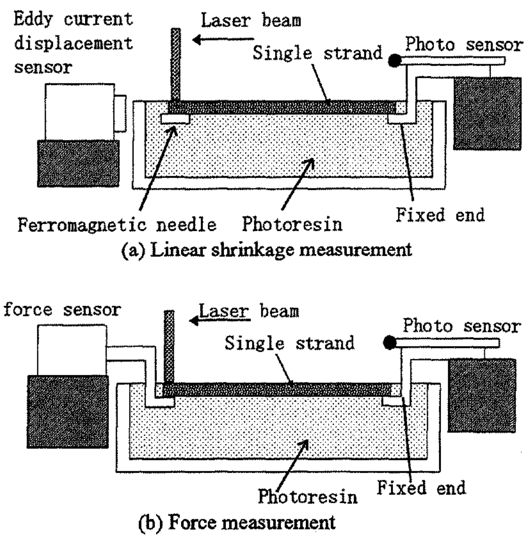


Figure 3. Experimental arrangements for single strand measurements

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

4. MEASURING METHOD AND EXPERIMENTAL CONDITION

4.1. MEASUREMENT OF LINEAR SHRINKAGE AND REACTION HEAT OF SINGLE STRANDS

Analytic method about a time history of the minute volume in a single strand is described.

Now, the length l of a single strand is drawn from a fixed end to a free end by laser scanning (Figure 4). Time history of the strain $\varepsilon_S(t)$ is measured by sensor. The time when the laser beam reaches the free end is defined as 0. Strain of minute volume is defined as $\varepsilon_P(t)$.

Consider the laser beam scans at speed V. In any part of a single strand, the minute

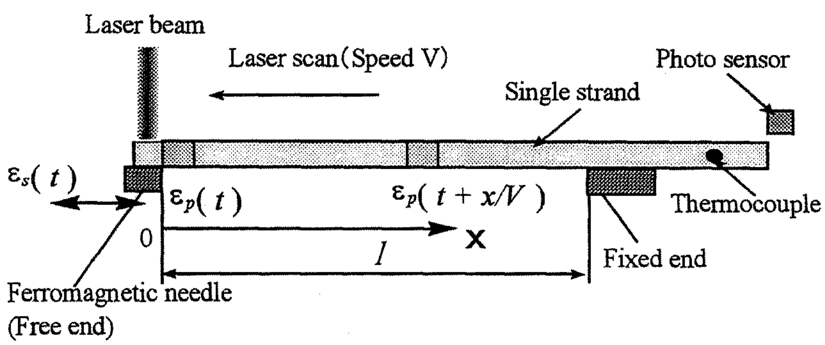


Figure 4. Definition of measured linear shrinkage and minute volume linear shrinkage

volume linear shrinkage $\varepsilon_P(t)$ should be the same but have the different irradiation start time. Therefore, the time history of a measured linear shrinkage $\varepsilon_S(t)$ of a single strand is equal to the integration of the minute volume linear shrinkage $\varepsilon_P(t)$ with the time delay that corresponds to the scan speed V.

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

The minute volume linear shrinkage $\varepsilon_P(t)$ is derived as following equation:

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

If the time has passed sufficiently, linear shrinkage will be uniform in a length direction. Thus, linear shrinkage value of a single strand coincides with linear shrinkage value of its minute volume:

$$\varepsilon_s(\infty) = \varepsilon_p(\infty) \tag{3}$$

Therefore, $\varepsilon_P(t)$ is obtained by backward substitution of strain $\varepsilon_S(t)$, which is a time history of linear shrinkage measured by displacement sensor from initial exposure to steady state.

An experimental condition is indicated on Table 1. Relation between the time histories of linear shrinkage and temperature of a single strand has experimented.

4.2. MEASUREMENTS OF THE EFFECTS OF SCAN ORDERS

By the difference of scan order, an influence over the shrinkage and the stress of a single strand is measured. When three lines are drawn, the case to scan a line from side by side continuously is defined as the continuous scan. The case to scan the middle line after scanning two sides lines is defined as the skip scan. A scan order and the difference of the three lines irradiation experiments are shown in Figure 5. In the case of skip scan, the second line is drawn immediately after the first scan. But the third line is scanned for about tens or twenties seconds later of the second scan which corresponds to the time lag of the case of parts building.

The measurements of model deformation are also tested with the different scan types mentioned above. The size of the sample shape used for the experiments is shown in Figure 6. 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 by the minimum square method from

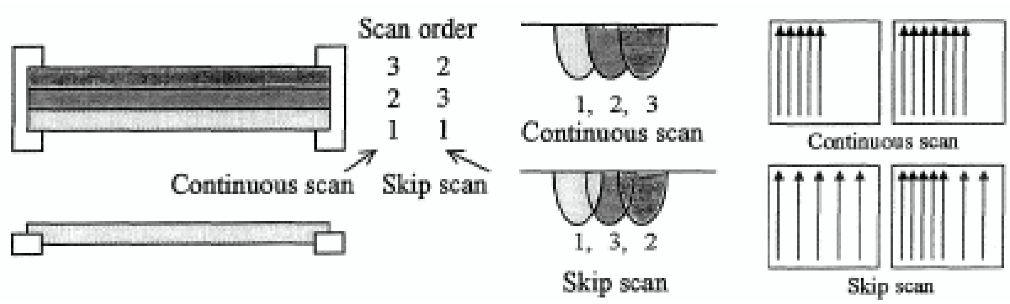


Figure 5. Scan orders of continuous scan and skip scan

the measured points. 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. Also, the negative value is defined as the case to exist in the lower part of the model. The reference points of the model are also shown in Figure 6.

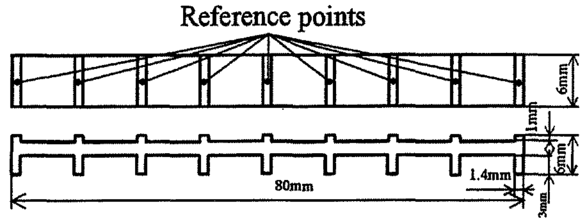


Figure 6. Sample Shape for scan orders experiment

5. EXPERIMENTAL RESULTS

Different laser powers and scanning speeds conditions are experimented, and the relation between linear shrinkage and stress after the largest expand of a single strand is drawn. As shown in Figure 7, it is understood that they move on almost the same curve. This result means that the relation is not influenced by fabrication conditions with this experimental arrangement. In other words, a characteristic of each resin is observed with this experiment.

Time history of the minute volume linear shrinkage calculated from the measured linear shrinkage is indicated on Figure 8. A vertical axis defines positive value as a shrink and negative one as an expansion. The value 0 of the horizontal axis is the origin about the time history of linear shrinkage, which is calculated from the detection time of the light sensor near the fixed end side. The representative curve of a minute volume linear shrinkage in a single strand changes to grow just after the irradiation and then to shrink afterward.

A measured result of a time history of linear shrinkage and temperature is indicated on Figure 9. Followed by the temperature fall after the rise of temperature, the single strand shrinks linearly. It is understood that the variation of the time history of the linear shrinkage after exposure is caused by heat.

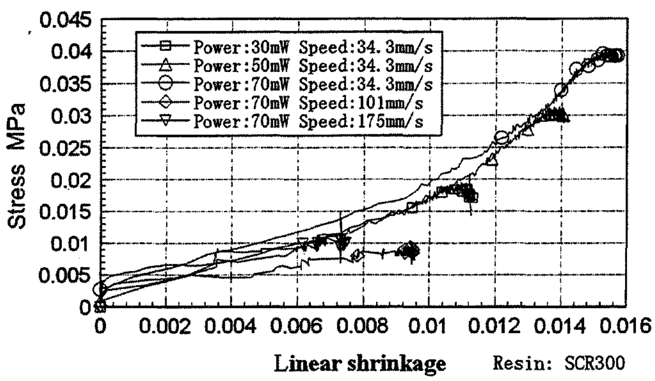


Figure 7. Relation of linear shrinkage-stress curves with different irradiation conditions.

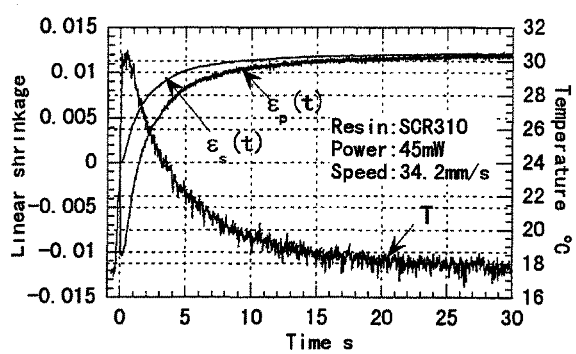


Figure 8. Time history of linear shrinkage and temperature.

Table 1 Experimental condition

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
Thermocouple	Chromel-Alumel thermocouple (K-type) ϕ 0.127mm
Set length of single strand	25mm

In the three lines scanning experiment, a smaller shrinkage and a stress have been observed when the skip scan is applied (Figure 10). It has been shown by the experiment that the skip scan has an effect of the linear shrinkage reduction in case of a layer forming.

In the case of model deformation experiment, the skip scan showed the tendency of the

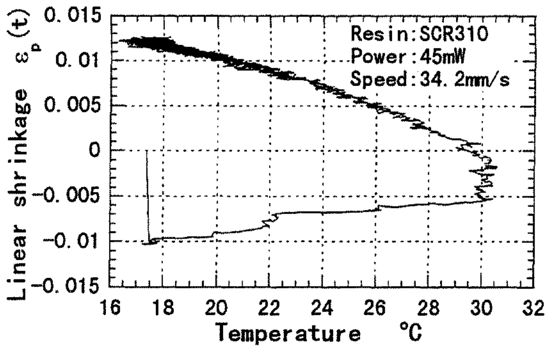


Figure 9. Relation of temperature and linear shrinkage $\varepsilon_P(t)$

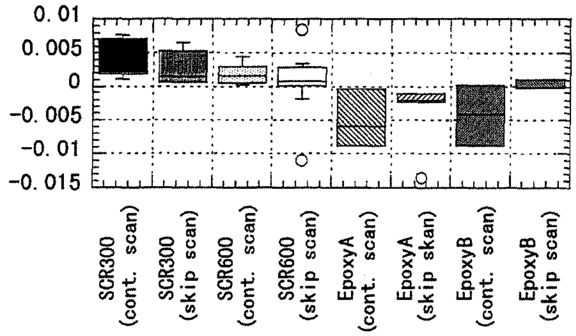


Figure 11. Deformation results of three lines scan experiment.

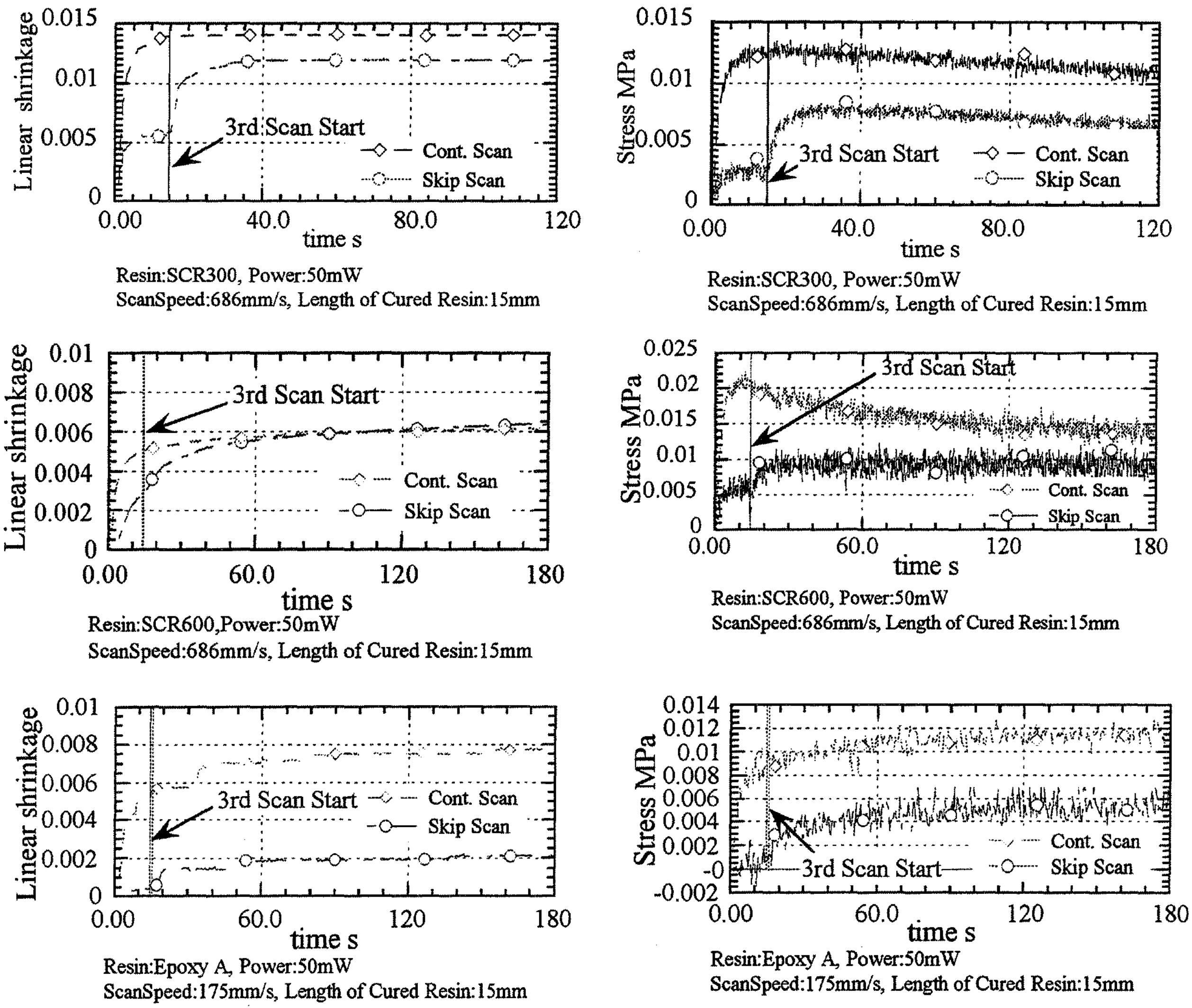


Figure 10-1. Time histories of linear shrinkage of three lines scan experiment.

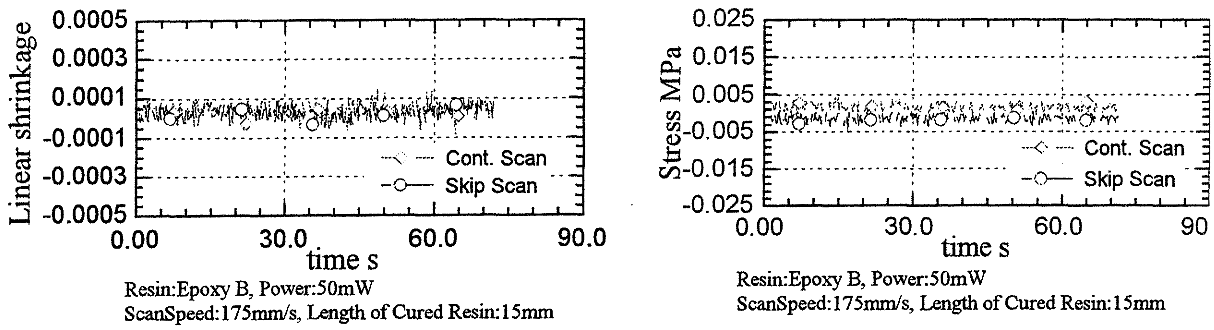


Figure 10-2. Time histories of linear shrinkage of three lines scan experiment.

smaller deformation (Figure 11).

6. DISCUSSIONS

With the single strand experiment, it has been clarified that time history of the shrinkage after irradiation is caused by the temperature change. The result that the skip scan shows the smaller shrinkage and the smaller deformation is obtained by the scan order experiments.

The experimental results that the skip scan showed the smaller value can be explained as follows: Consider the time history of the linear shrinkage when a new layer is formed as shown in Figure 12.

In case of continuous scan, because the time difference between each scan is short, there are few differences between the hardening temperature patterns around. Therefore, the shrinkage pattern of a strand resembles the ones around and little restriction from the surrounding occurs.

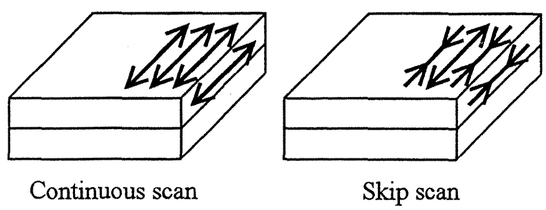


Figure 12. Sketch of strain distributions at building a new layer.

On the other hand, in the case of the skip scan, because the time difference to harden the middle among the single strands is long, the cooling progresses during the period and the single strand shrinks more. Then, the surrounding restricts the thermal expansion of the middle strand. Therefore, the linear shrinkage will be observed smaller.

In the case of the urethane system resin, whose basic reaction is radical polymerization, reaction does not progress if light is not irradiated. Method of this experiment is nothing but to observe the variation of the linear shrinkage and the stress that are caused by heating and by cooling. In the case of the epoxy resin whose basic reaction is cationic polymerization, this supposition will not be the case, since reaction does not stop after irradiation. This phenomenon in detail should be examined further.

The skip scan showed the tendency of the smaller deformation in the case of model deformation experiment. However, depending on the kind of the resin, a different result was observed in some case. As for this point, it is suggested that further analysis and experiment of the interaction among layers is necessary. It concludes that the more detailed future analysis is necessary.

7. CONCLUSIONS

This study aims at clarifying the initial linear shrinkage of cured resin in a minute volume. Experimental equipment has been developed which measures the time history of the single strand in situ in a stereolithography machine. The following results are obtained from this study:

1. The analysis method of an initial linear shrinkage of minute volume in a single strand is proposed.
2. It has been observed that a change of linear shrinkage after irradiation has been caused by the heat change, that is the results of the heating by exothermal and the cooling by heat diffusion, when the relation of the linear shrinkage and the temperature has been examined based on this method.
3. It is indicated that temperature distribution of layer surfaces that is the result of reaction heat by laser beam scanning can be one cause of shape deformation. By skip scanning, changes of shrink of adjacent lines restrict the heat expansion of middle line at initial stage of exposure. As a result, lower linear shrinkage has been observed to a single strand and model deformation has been also indicated to be small.

REFERENCES

1) H. Narahara, S. Igarashi and K. Saito: 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, (1997) (in printing).
2) J. S. Ullett, R. P. Chartoff, A. J. Lightman, J. P. Murphy and J. Li: Reducing Warpage in Stereolithography Through Novel Draw Styles, Proc. of the Fifth International Conference on Rapid Prototyping, Dayton, Ohio, (1994) 109-125.
3) H. Narahara and K. Saito: Shape Analysis of Solidified Photopolymer for the Three Dimensional Photofabrication, International Journal of JSPE, 30, 4, (1996) 311-316.
4) H. Narahara and K. Saito: Characterization of Solidified Resin Created by Three Dimensional Photofabrication, Proc. of the Fourth International Conference on Rapid Prototyping, Dayton, Ohio, (1993) 271-281.
5) L. Flach and R. P. Chartoff: Stereolithography Process Modeling: Shrinkage Prediction, Proc. of the Fifth International Conference on Rapid Prototyping, Dayton, Ohio, (1994) 181-189.
6) T. Kishinami, F. Tanaka and H. Narahara: 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, (1997) (in printing).
7) R. P. Chartoff and J. Du: 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, (1995) 298-304.
8) T. R. Guess and R. S. Chambers: 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, (1997) 134-141.