MATERIAL AND PROCESS PARAMETERS THAT AFFECT ACCURACY IN STEREOLITHOGRAPHY

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ABSTRACT

Experimental real time linear shrinkage rate measurements simulating stereolithography are used in an analysis of shrinkage during line drawing in stereolithography. While the amount of shrinkage depends on the polymerization kinetics, shrinkage kinetics and overall degree of cure, it also depends on the length of time to draw a line of plastic. A line drawn slowly will exhibit less apparent shrinkage than one drawn very quickly because much of the shrinkage is compensated for as the line is drawn. The data also indicates that a typical stereolithography resin in the green state may shrink to only 65% of its maximum, thus retaining considerable potential for shrinkage during post-cure. This information can be used to predict the amount of shrinkage to be expected under certain exposure conditions and to formulate overall strategies to reduce shrinkage and subsequent warpage that causes shape distortion.

INTRODUCTION

In order to better understand the shrinkage-related problems associated with stereolithography, and to minimize their effect, it is essential to understand the relationship between the polymerization kinetics, shrinkage kinetics, total shrinkage, and the laser scan rate. These variables directly affect the amount of shrinkage that will occur in a line of plastic drawn by the stereolithography apparatus (SLA) and ultimately in the warpage and shape distortion of the final part. In this paper we discuss the results of a series of real time shrinkage rate measurements (in an apparatus that simulates stereolithography) and use the rate data in an analysis of the shrinkage that occurs when a single strand of material is formed. The analysis indicates that the rate of shrinkage rather than shrinkage itself is the key parameter for controlling shrinkage-related dimensional effects.

EXPERIMENTAL

Real time shrinkage measurements were performed on "full line" exposures of three photopolymers: Ciba XB5081-1, UD experimental formulas 60.1 and 61.1. The so-called "full line" exposure is performed by exposing an approximately 7 mm long by 0.2 mm wide line to a focused Argon-Ion UV laser beam. The apparatus and procedures for making these measurements have been described elsewhere [1,2]. The current experiments were designed to

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compare the shrinkage rates as well as the shrinkage occurring under both short term and long term laser illumination. This was accomplished by exposing a line of polymer to a single 40 m sec pulse (short term exposure) and subsequently a series of successive 40 m sec pulses until maximum shrinkage was achieved.

Real time shrinkage measurements were made, in duplicate, for the three polymers. The laser power was varied for each so that a cure depth (C.D.) of 0.85 mm was obtained. The energy densities 76.9, 65.2, and 66.5 mJ/cm^2 were used to obtain a uniform specified cure depth for XB5081-1, 60.1, and 61.1, respectively. The total shrinkage was noted five minutes after the first exposure. Each sample was then exposed again the standard amount and the additional shrinkage noted after five minutes. This procedure was repeated to obtain the desired number of exposures. Each material was subjected to five consecutive exposures with a five minute pause between each. XB5081-1 was tested using eight consecutive exposures.

DISCUSSION OF EXPERIMENTAL RESULTS

The real time shrinkage data for the six samples (three polymers in duplicate) that were exposed once are shown in Figure 1. Resins 60.1 and 61.1 show a shorter induction time, steeper slope, and higher shrinkage than XB5081-1.

The data of Figure 2 indicate that 60.1 and 61.1 complete a greater percentage of their ultimate shrinkage after the first exposure than does the XB5081-1. Table I tabulates the percentage of maximum shrinkage that has occurred after each individual exposure. The change in shrinkage due to additional exposures became very small after the fifth exposure for 60.1 and 61.1. However, for XB5081-1 the change in shrinkage with continued exposures does not decrease significantly until the eighth exposure. Therefore, the maximum shrinkage for 60.1 and 61.1 was taken as that which had occurred after the fifth exposure, while for XB5081-1 it was taken as that which had occurred after the eighth exposure.

Additional data on the density changes for the three photopolymers measured after long term cure under Hg vapor lamp exposure indicates that approximately 15-25% of the total shrinkage that occurs is missed by the real time shrinkage apparatus. This is the amount that occurs before gelation and does not affect the dimensions of a line actually drawn by a laser. Further density characterization of full line specimens after long term laser exposure is now being carried out to determine more exactly the amount of initial shrinkage not detected in the real time shrinkage measurements.

SHRINKAGE ANALYSIS

The amount of shrinkage observed when a line of plastic is drawn by the SLA is determined by the polymerization kinetics, the shrinkage kinetics, and the laser scan rate. A detailed analysis is required in order to determine the inter-relationships between the appropriate variables. There are two shrinkage components that must be considered. These are: (1) cure related shrinkage arising due to a change in chemical bond distances in the unpolymerized monomer relative to the polymer, and (2) thermal expansion/contraction due to temperature changes in the resin on polymerization. The latter is assumed negligible as discussed elsewhere [2]. The analysis incorporates the experimental shrinkage rate data described previously.

The basis for the analysis is that any shrinkage that occurs before completing the laser scan for a particular line of plastic will be compensated for at least partially by the fact that the laser still scans a line of the correct length. The actual shrinkage that will be observed should be based on the amount of shrinkage that will occur at each point along the line **at the time the line is completed**. At that time the line is the correct length (due to a scan of the correct length) and any change in length is a result of polymerization and shrinkage occurring after completion of exposure.

If L is the desired length of a line of plastic drawn by the SLA, then the overall linear shrinkage (fraction) due to cure for the line of plastic will be given by:

$$F_c = \frac{1}{L}\int_0^L f_r(x)dx \tag{1}$$

where $f_r(x)$ is the residual shrinkage (fraction) at position x along the line, i.e. the amount of shrinkage that will occur at that point after completion of the line as indicated in Figure 3.

The residual shrinkage, $f_r(x)$, can be obtained from experimentally determined shrinkage vs. time data, or can be estimated from model-based predictions of the degree of cure along the line of plastic. If t_s is the time taken for the laser to scan from position x to the end of the line L, and $f_{ts}(x)$ the fractional shrinkage that has occurred up to time t_s at position x, then the residual shrinkage is just

$$f_r(x) = f_\infty - f_{ts}(x) \tag{2}$$

where f_∞ is the maximum fractional shrinkage that occurs at $t \rightarrow \infty$ (see Figure 4).

Using the fact that

$$f_\infty = f(t) \qquad \text{as } t \rightarrow \infty \tag{3}$$

and

$$f_{ts}(x) = f(t) \quad \text{at} \quad t = \frac{L-x}{s} \tag{4}$$

where s is the laser scan (draw) rate and f(t) the shrinkage vs. time curve, eqn. (2) can be transformed to a time integral as follows:

$$F_c = f_\infty - \frac{s}{L}\int_0^{L/s} f(t)dt \tag{5}$$

In this expression L/s is just the time required for the laser to scan (draw) the line of plastic of length L, so eqn. (5) can be written as:

$$F_c = f_\infty - \frac{1}{t_{scan}} \int_0^{t_{scan}} f(t)dt \qquad (6)$$

where t_{scan} is the scan time (= L/s).

SCAN RATES, SCAN TIMES AND SHRINKAGE

Modification of the scan (draw) rate typically requires that laser power be adjusted in order to maintain the same actinic exposure levels. This is necessary if use is to be made of a single shrinkage curve valid at a particular exposure level only. In all further discussions thus, when reference is made to scan rate adjustment, it should be understood that this is accompanied by appropriate laser power level adjustments.

A computer program was developed to investigate the relationship between the shrinkage and laser scan rate (for a line of plastic of constant length), and between shrinkage and line length (for a constant scan rate). The shrinkage data used for the investigation are those shown in Figure 1 for Cibatool XB5081-1 stereolithography resin and the faster curing experimental formulation F61.1. The program utilizes eqn. (6) to estimate the shrinkage that will occur when drawing a line of plastic of a specified length at a specified scan rate. Results were computed for two test cases. In the first, the scan rate was varied for a line of plastic of length 10 cm, and in the second, the line length was varied for a scan rate of 10 cm sec^{-1}. Typical operating laser scan rates for XB5081-1 are in the range 10-200 cm sec^{-1}. Results for the two tests can be found in Figures 5 and 6. As can be seen the shrinkage increases with increasing scan rate and decreasing line length. In both cases the maximum shrinkage value of f_∞ is attained when the scan is completed during the shrinkage induction time, i.e. before any measurable shrinkage occurs. Note that the shrinkage does not depend independently on the two parameters, scan rate and line length, but on the single parameter t_{scan} (as revealed by eqn. (6)) which is a combination of the two parameters (eqn. (4)).

A number of interesting facts are revealed when considering the results of this analysis for a single shrinkage data set:

1. F_c will always be equal to or less than f_∞.
2. If the scan is very rapid or the line of plastic is very short ($t_{scan} \rightarrow 0$), then $F_c \rightarrow f_\infty$.
3. If the scan is very slow or the line of plastic is very long ($t_{scan} \rightarrow \infty$), then $F_c \rightarrow 0$.
4. f_∞ is constant for a particular set of shrinkage data.
5. The integral part of eqn. (6) is simply the cumulative shrinkage that occurs during the laser scan and as such is subtracted from the maximum shrinkage that could occur.

6. Inspection of eqn. (6) reveals that for any particular shrinkage curve (resin, exposure combination), the measured shrinkage that occurs during the drawing of a line of plastic depends on the scan time only, i.e. on the combination of line length and scan rate, and not on the individual parameters.

It is an important consideration that experimentally measured shrinkage data, such as that in Figure 1, represent the composite effect of polymerization kinetics and shrinkage kinetics relative to the conversion.

When comparing results for different resins which exhibit different shrinkage rates and different final amounts of shrinkage, f_{∞}, some interesting observations can be made. The F61.1 resin shrinks considerably faster than the XB5081-1 and exhibits a higher final shrinkage. Figures 5 and 6, however, reveal that the shrinkage expected to occur when drawing a line of plastic is less for the faster curing and higher shrinking resin for certain scan rates and line lengths. This is a result of the compensating effect of shrinkage that occurs during the drawing process.

In lieu of a measured shrinkage curve, the mathematical process models developed for stereolithography [3], together with a kinetic shrinkage model such as that proposed by Bowman and Peppas [4], would allow estimation of the shrinkage that might be expected to occur when drawing a line of plastic. Eqn. (6) would still be required to compute the overall shrinkage. A procedure for using such an "a priori" approach will be discussed in a future report.

CONCLUSIONS

The conclusions that can be drawn from the above experiments and analysis is the following:

1. A significant amount of shrinkage occurs during cure prior to gelation that is not measured in linear shrinkage experiments that simulate stereolithography. This amounts to around 20% (or more) of total volume shrinkage and does not impact the stereolithography process. Thus volume shrinkage data will overestimate the actual SLA shrinkage.

2. The amount of shrinkage, warpage, and dimensional inaccuracies for stereolithography produced parts may be reduced by using very low scan rates (and low laser power) or, alternatively, developing a resin that shrinks rapidly compared to typical scan rates. The former of these two conclusions appears contrary to the concept of a rapid prototype technique, but should be considered when, for example, a high precision part is required. Selection of an optimum scan rate would be based on a compromise between the dimensional accuracy required and the speed of prototype production. The second conclusion is one that has influence on resin formulation. A fast curing, fast shrinking resin would be desirable for stereolithography use. A resin with a greater final shrinkage (f_{∞}) could be tolerated if the shrinkage occurred rapidly compared to the scan rate.

3. During the SLA part drawing process hatch vectors should not be attached until shrinkage is largely completed, i.e. for a fixed length vector, the scan rate should be adjusted to minimize F_c (use low scan rates).

4. Another aspect of the shrinkage/warpage problem that might be addressed by implementation of a fast curing, fast shrinking resin is residual post cure shrinkage. Resins such as F60.1 and F61.1 that shrink and cure more fully during the initial laser exposure will lead to less residual shrinkage and warpage during post cure.

NOMENCLATURE

$f(t)$	shrinkage function (fractional linear shrinkage vs. time)
$f_r(x)$	residual shrinkage at position x
$f_{ts}(x)$	shrinkage at position x at time t_s
f_∞	maximum shrinkage expected ($t \rightarrow \infty$)
F_c	overall fractional shrinkage in a line of plastic
L	length of line of plastic (cm)
s	laser scan rate (cm sec^{-1})
t_s	time for laser to scan from position x to L (sec)
t_{scan}	total laser scan time, L/s (sec)
x	position along line of plastic (cm)

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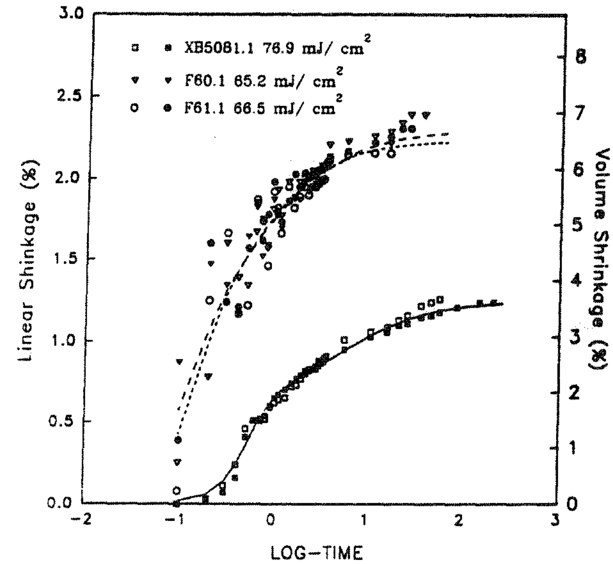
TABLE 1

SHRINKAGE AFTER MULTIPLE 0.040 SECOND EXPOSURES (DATA ARE NORMALIZED BY THE MAXIMUM SHRINKAGE FOR EACH POLYMER)

Exposure	XB5081-1 (%)	60.1 (%)	61.1 (%)
1	64.4	89.5	88.8
2	81.4	93.6	94.6
3	86.6	96.3	97.7
4	90.7	99.5	98.8
5	94.3	100	100
6	97.4	---	---
7	99.4	---	---
8	100	---	---
Ultimate Volumetric Shrinkage	6.0	6.4	7.5

Full Line Exposure

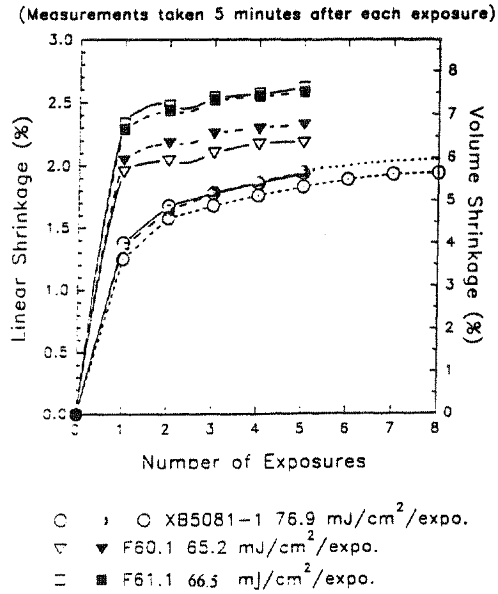
(0.04 sec. exposure, C.D.=0.86)



Real Time Shrinkage Data for XB5081-1, 60.1, and 61.1.

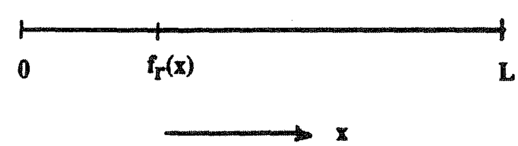
Figure 1

Shrinkage
After Multiple 0.04 Second Exposures
(Measurements taken 5 minutes after each exposure)



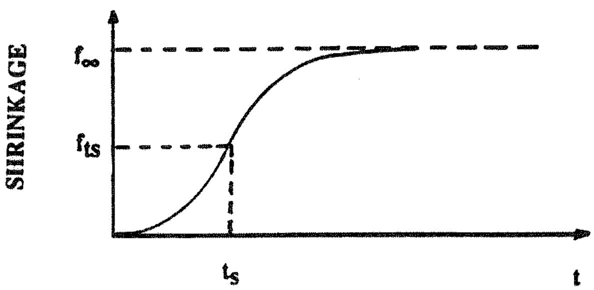
Multiple 0.040 Second Exposures in the Real Time Shrinkage Apparatus.

Figure 2



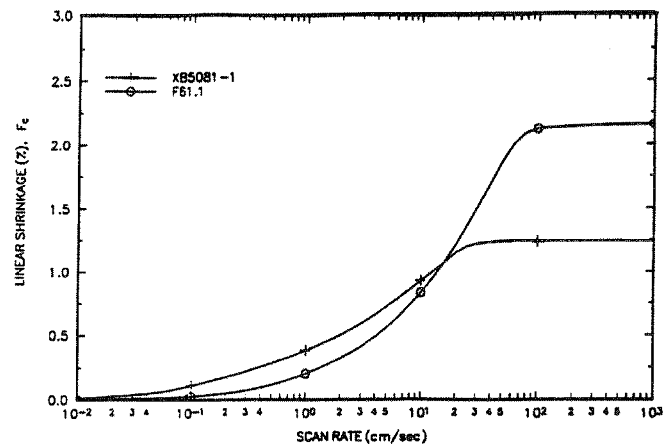
RESIDUAL FRACTIONAL SHRINKAGE ALONG LINE OF PLASTIC

Figure 3



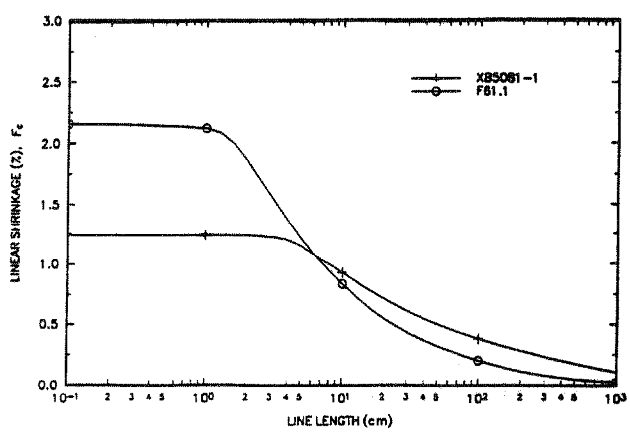
SHRINKAGE VS. TIME CURVE INDICATING VARIABLES USED TO CALCULATE RESIDUAL SHRINKAGE

Figure 4



Shrinkage vs. scan rate for a 10 cm line of plastic.
(Actinic exposure level constant.)
(Computer generated curves.)

Figure 5



Shrinkage vs. length of line of plastic when drawn at a fixed scan rate of 10 cm sec^{-1}.
(Computer generated curves.)

Figure 6