A SIMPLE POLYMER SHRINKAGE MODEL APPLIED TO STEREOLITHOGRAPHY

Lawrance Flach
Department of Chemical and Materials Engineering

Richard P. Chartoff
Rapid Prototype Development Laboratory
and
Center for Basic and Applied Polymer Research

University of Dayton
300 College Park Avenue
Dayton, OH 45469-0246

ABSTRACT

A simple polymer shrinkage model has been successfully applied to the stereolithography process. The shrinkage model, which computes specific volume changes from the degree of conversion of monomer to polymer, incorporates a lag between conversion and shrinkage. An overall process model used to simulate the stereolithography process was modified by inclusion of the shrinkage model. Use of the modified stereolithography process model allows prediction of the shrinkage that might be expected to occur when fabricating a strand of plastic. By varying the lag between conversion and shrinkage it is shown that faster shrinking resins should exhibit lower overall shrinkage than slower shrinking resins. This is a direct result of the fact that less shrinkage occurs after the strand has been scanned for the faster shrinking resins.

INTRODUCTION

The photopolymerization that occurs during stereolithography is accompanied by shrinkage. It is this shrinkage that is responsible for dimensional inaccuracies and warpage in parts produced by the process. The exact amount of shrinkage observed in a strand of plastic manufactured by a stereolithography apparatus (SLA) depends on a number of factors. These factors include the degree of cure achieved during exposure, the polymerization kinetics, the shrinkage kinetics, and also the rate at which the strand is scanned by the laser.

As part of a continuing effort to better understand the complexities of the stereolithography process, we have analysed the shrinkage phenomenon and its relationship to the laser scan rate. In addition, we have modified the general stereolithography process model to include a prediction of the shrinkage that might be expected to occur when using the SLA to fabricate a strand of plastic.

BACKGROUND

An analysis of shrinkage in stereolithography and its relationship to the laser scan rate has been presented elsewhere [1]. It is, however, pertinent to review some of this material at this stage.

The basis for the analysis is that the observed shrinkage is determined by 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 that occurs 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

$$F_c = \frac{1}{L}\int_0^L f_r(y)\,dy \qquad (1)$$

where $f_r(y)$ is the **residual** shrinkage (fraction) at position y along the line, i.e. the amount of shrinkage that will occur at that point after completion of the line.

The residual shrinkage, $f_r(y)$, 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. (The latter approach was adopted here.) If t_s is the time taken for the laser to scan from position y to the end of the line L, and $f_{ts}(y)$ the fractional shrinkage that has occurred up to time t_s at position y, then the residual shrinkage is just

$$f_r(y) = f_\infty(y) - f_{ts}(y) \qquad (2)$$

where $f_\infty(y)$ is the maximum fractional shrinkage that will occur at position y as $t \rightarrow \infty$.

The shrinkage that accompanies the polymerization of diacrylates tends to lag behind the conversion [2,3,4]. The model used for shrinkage should allow for this lag. Bowman and Peppas [3] have presented a method that satisfies this requirement. The method results in a 1st order lag between conversion and specific volume change, and details are as follows:

$$v_\infty = v_m(1-\epsilon_v x) \qquad (3)$$

and

$$\frac{dv}{dt} = \frac{1}{\tau}(v_\infty - v) \qquad (4)$$

Eqn. (3) computes the maximum specific volume change based on conversion, i.e. the specific volume that would be reached as $t \rightarrow \infty$ based on conversion x, and eqn. (4) determines the dynamics of the specific volume change from its present value to v_∞. The contraction factor, ε_v in eqn.(3), can be determined from the specific volumes of the monomer and polymer or from shrinkage data. The lag parameter, τ in eqn.(4), determines the extent of the lag between conversion and shrinkage. Bowman and Peppas change the value of τ as the polymerization proceeds. This allows τ to increase as conversion increases. Initially, at low conversion, shrinkage may occur almost simultaneously with conversion, whereas once vitrification has occurred, there may be a considerable lag between polymerization and shrinkage. Figure 1 illustrates how the model predicts the specific volume change and resultant shrinkage would respond to an instantaneous change in conversion. Results for three different values of the lag parameter are shown.

SHRINKAGE AND THE PROCESS MODEL

The stereolithography process model previously developed [5,6] has the capability of calculating conversion of monomer to polymer as a function of time for a rectangular region around the exposed resin. Conversion information is available at the nodes of a 3-dimensional grid.

In order to estimate the amount of shrinkage that we might expect in a strand of plastic manufactured by the SLA, the following sequence of calculations can be performed:

- Calculate the average conversion, $x_{AV}(y)$, for cross-sections perpendicular to the direction of laser travel at the time the scan is complete. This is necessary because conversion varies somewhat with depth and distance from the scan axis. Any 2-dimensional numerical integration technique can be used to perform this averaging.

- Determine the specific volume, $v_\infty(y)$, that corresponds to $x_{AV}(y)$ from eqn.(3)

$$v_\infty(y) = v_m(1-\epsilon_v x_{AV}(y)) \tag{5}$$

- Convert to a fractional linear shrinkage

$$f_\infty(y) = 1-\left(\frac{v_\infty(y)}{v_m}\right)^{\frac{1}{3}} \tag{6}$$

- Calculate the average specific volume, $v_{AV}(y)$, for cross-sections perpendicular to the direction of laser travel from specific volumes calculated from eqn.(4).

- Convert to a fractional linear shrinkage

$$f(y) = 1-\left(\frac{v_{AV}(y)}{v_m}\right)^{\frac{1}{3}} \tag{7}$$

- Determine the residual shrinkage using the results from eqns. (6) and (7)

$$f_r(y) = f_\infty(y) - f(y) \tag{8}$$

- Perform integration along the strand of plastic to obtain an estimate of the overall linear shrinkage

$$F_c = \frac{1}{L}\int_0^L f_r(y)\, dy \tag{9}$$

The entire procedure outline above was incorporated into the stereolithography process model. Calculated shrinkage information was included with the other data output by the computer code used to numerically solve the model equations.

RESULTS AND DISCUSSION

In order to verify operation of the shrinkage component of the process model, a number of process simulations were performed. All model parameters were unchanged from those of the previously documented test simulation [5,6], the details of which are not presented here. The results from the shrinkage component of the model are presented below. Tests were performed with shrinkage parameters as follows:

$v_m = 0.885\ \text{cm}^3\ \text{g}^{-1}$

$\varepsilon_v = 0.0738$

$\tau = 0.1$, 0.2 and 0.3 seconds.

The specific volume and contraction factor parameter values selected were appropriate for the HDDA test simulation performed. The shrinkage lag parameter values, although believed to be of the correct order of magnitude, were selected to illustrate the effect of changing that parameter value.

Plots of average conversion and average specific volume versus y (position along strand of plastic) are shown in Figures 2 and 3. These are time progressions, each curve being the profile at a particular time. As expected the conversion increases to some maximum value as time progresses (the reaction is diffusion limited) and the conversion is accompanied by a decrease in the specific volume of the material. The data shown in Figure 3 were generated using a shrinkage lag parameter of 0.2 seconds. Figure 4 shows the conversion and shrinkage dynamics at the mid-point of the strand of material. The laser passes over this point in the strand at $t = 0.5$ seconds, half way through the total scan which is of 1.0 second duration. This plot clearly illustrates the lag between the conversion and shrinkage at that point in the strand.

A series of simulations were performed with different shrinkage relaxation times (time constants). For three different values of τ, the overall linear shrinkage in the line of plastic, F_c, was calculated. The results are summarized below.

τ (sec)	% Shrinkage, F_c
0.1	0.078
0.2	0.180
0.3	0.279

The faster shrinking resins (those with the lower τ values) exhibit less overall shrinkage than the slower shrinking resins (those with the higher τ values). This supports the notion that a faster shrinking resin should result in lower overall shrinkage, with less distortion and warpage in the final part.

Figure 5 illustrates the effect of changing the shrinkage lag parameter τ on shrinkage dynamics at the mid-point of the strand of plastic. Higher values of τ result in increased lag between conversion and shrinkage. Residual shrinkage values also increase due to the fact that less shrinkage has occurred at the time the scan is complete. The remainder of the shrinkage occurs after completion of the scan and contributes to the observed linear shrinkage. The change in residual shrinkage with τ is clearly illustrated in Figure 6 where plots of residual shrinkage vs. position along the strand are shown. At higher τ values more of the shrinkage occurs after completion of the scan and as a result contributes to a higher observed linear shrinkage. The overall linear shrinkage values shown above (F_c), obtained from eqn. (9), are the average values of the residual shrinkage along the strand. The residual shrinkage tends to drop towards the end of the strand due to lower conversion of monomer to polymer. This is an "end effect" and becomes fairly insignificant for longer strands of plastic.

CONCLUSIONS

A shrinkage model has been incorporated into the general stereolithography process model. The ultimate amount of shrinkage is determined by the extent of conversion of monomer to polymer. The model allows the shrinkage to lag behind conversion in a 1st order manner.

Successful operation of the stereolithography process model with the shrinkage modification has been verified by performing various simulations. One of the tests performed involved varying the shrinkage lag parameter, and the results obtained confirmed the notion that faster shrinking resins should result in lower overall shrinkage values.

NOMENCLATURE

$f_r(y)$	residual fractional linear shrinkage at position y
$f_{ts}(y)$	fractional linear shrinkage at position y at time t_s
$f_\infty(y)$	maximum fractional linear shrinkage at poistion y ($t \rightarrow \infty$)
F_c	overall fractional linear shrinkage due to cure
L	length of strand of plastic (cm)
t	time (sec)
t_s	time for laser to scan from position y to L (sec)

v	specific volume ($cm^3\ g^{-1}$)
v_{AV}	cross-section average specific volume ($cm^3\ g^{-1}$)
v_m	specific volume of monomer ($cm^3\ g^{-1}$)
v_p	specific volume fully polymerized ($cm^3\ g^{-1}$)
v_∞	specific volume at conversion x as $t \rightarrow \infty$ ($cm^3\ g^{-1}$)
x	fractional conversion of monomer to polymer
x_{AV}	cross-section average fractional conversion of monomer to polymer
y	spatial coordinate in direction of laser motion (cm)
ε_v	contraction factor = $(v_m - v_p)/v_m$
τ	relaxation time, 1st order lag constant (sec).

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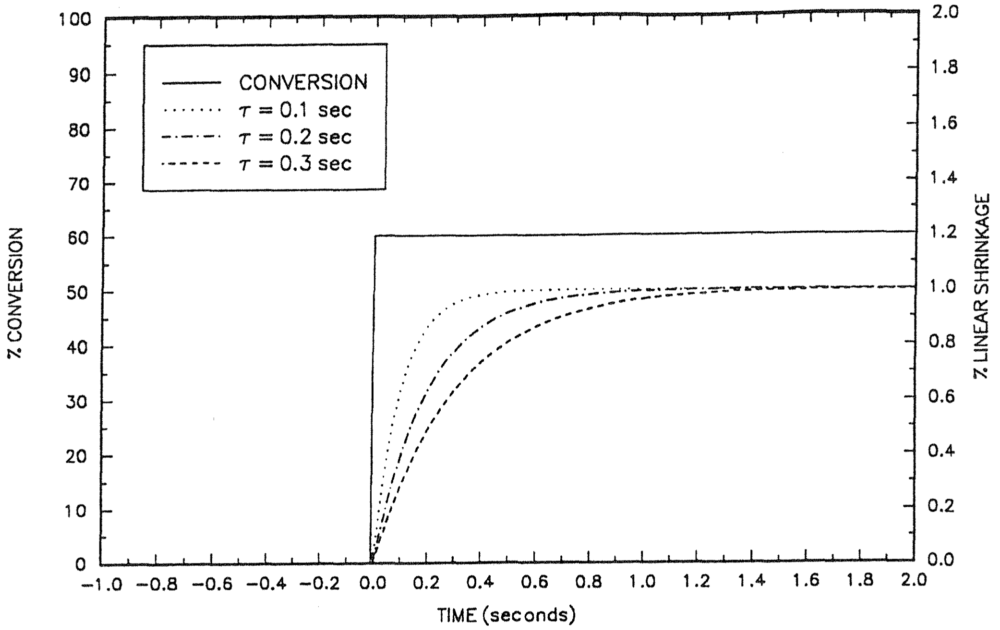

Figure 1: Plot of conversion and shrinkage vs. time. Model predictions for an instantaneous change in conversion for 3 different shrinkage lag parameter values. Ultimate amount of shrinkage determined by shrinkage factor.

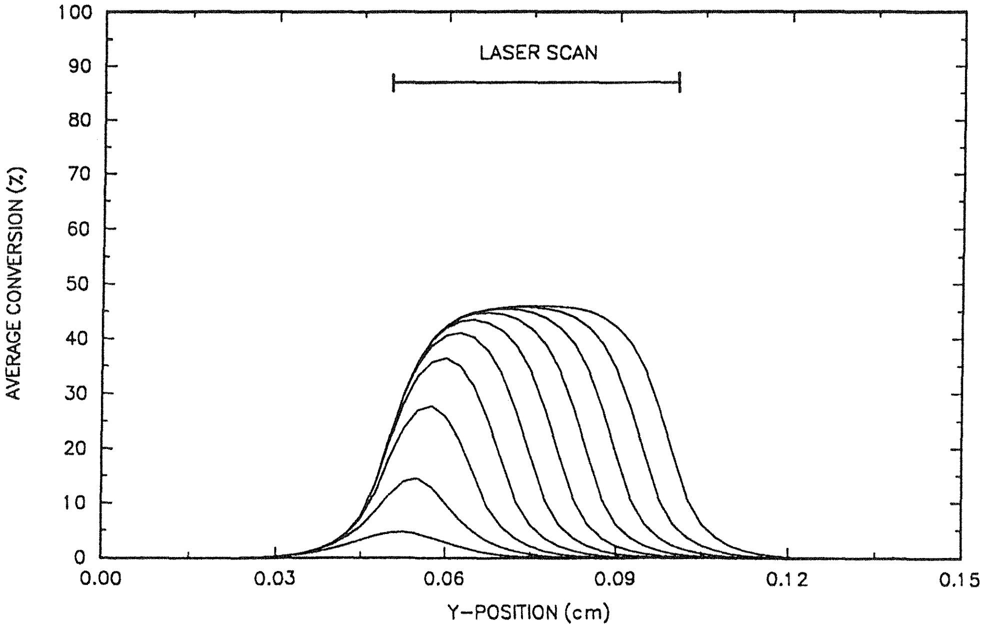

Figure 2: Average conversion vs. position along a strand of plastic. Each curve represents the conversion profile at a particular time. Laser scan duration = 1.0 sec. Plot time increment 0.1 sec.

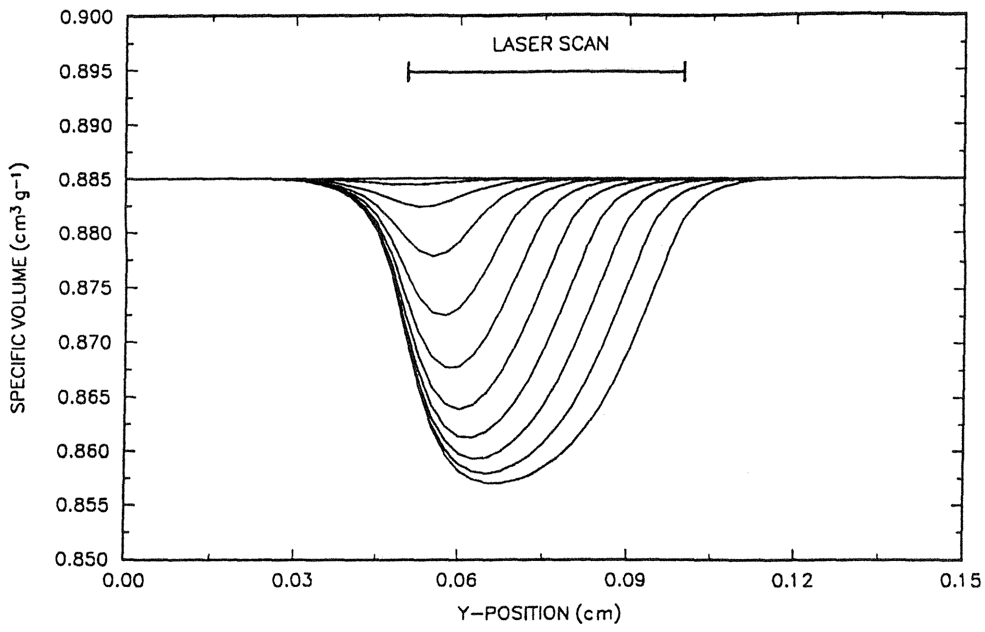

Figure 3: Average specific volume vs. position along a strand of plastic. Each plot represents the specific volume profile at a particular time. Laser scan duration = 1.0 sec. Plot time increment = 0.1 sec. Shrinkage lag parameter $\tau = 0.2$ sec. Data are complementary to Figure 2.

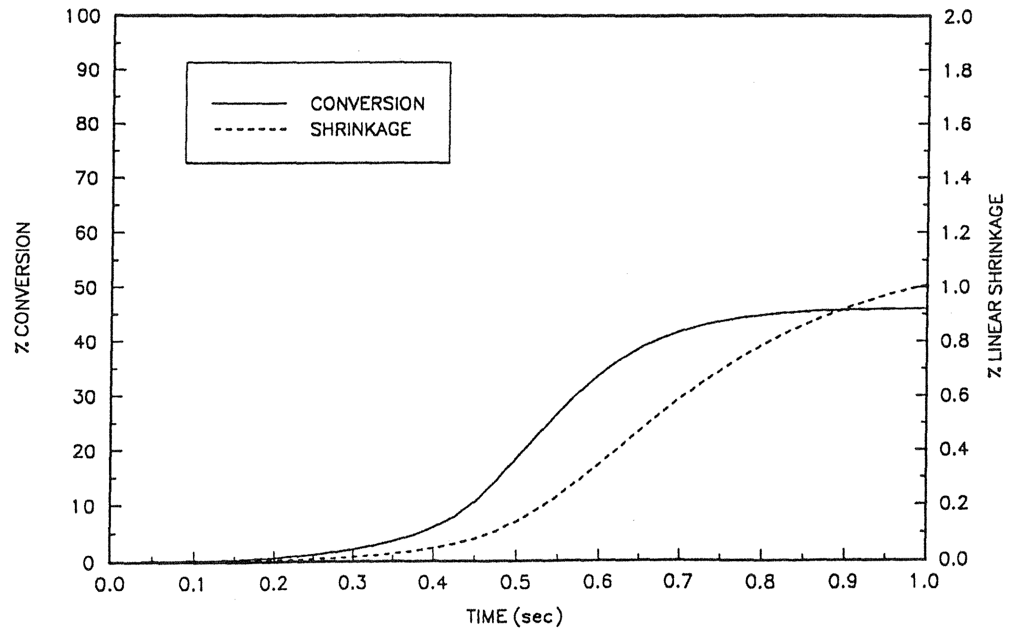

Figure 4: Conversion and shrinkage vs. time at the mid-point of a strand of plastic. Laser passes this point at t = 0.5 sec. Total laser scan time = 1.0 sec. Shrinkage lag parameter $\tau = 0.2$ sec.

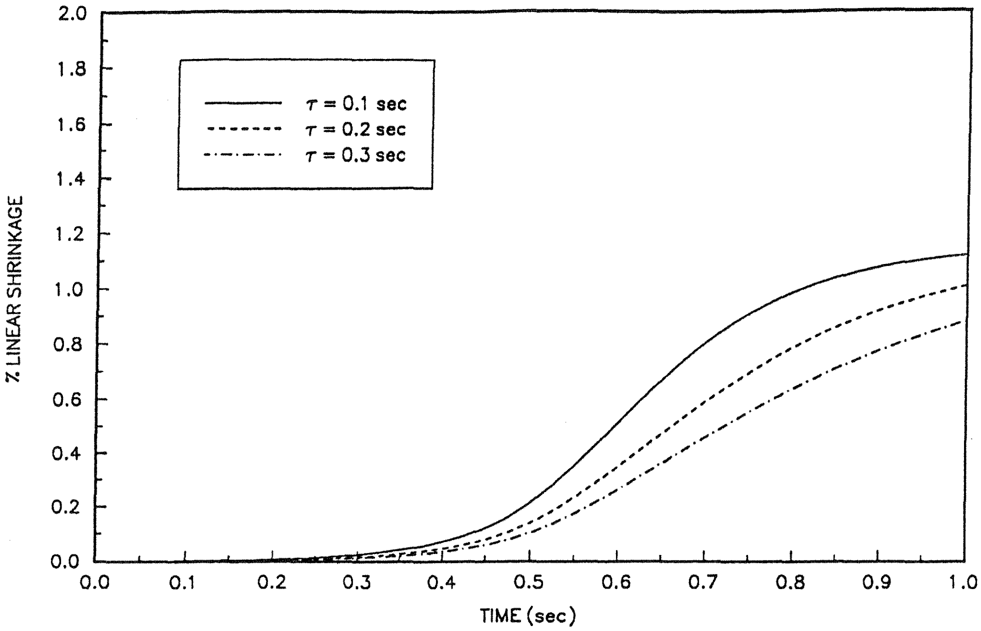

Figure 5: Linear shrinkage vs. time at the mid-point of a strand of plastic for 3 different shrinkage lag parameters. Laser passes this point at t = 0.5 sec. Total laser scan time = 1.0 sec.

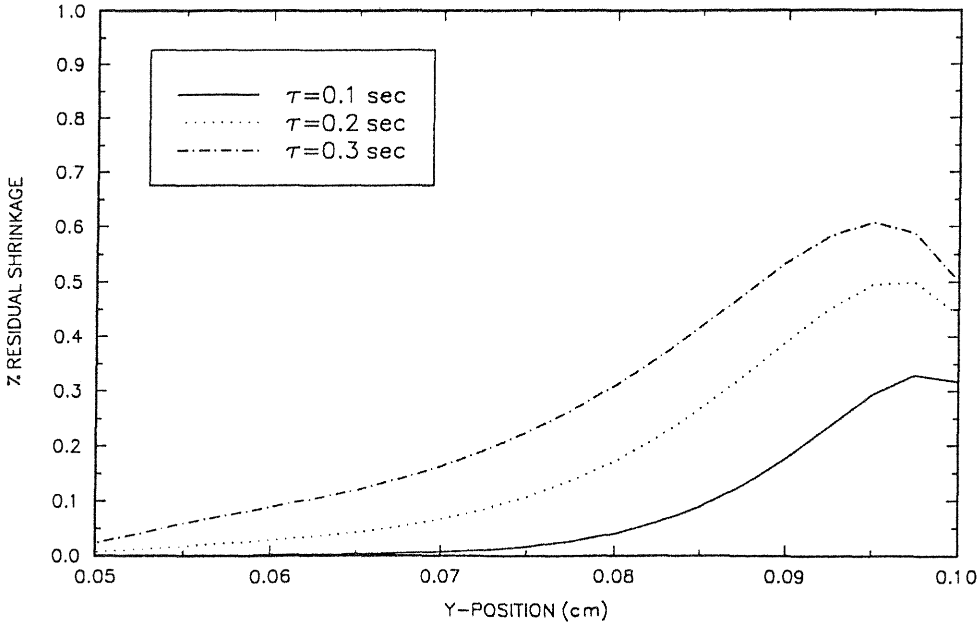

Figure 6: Residual shrinkage vs. position along a strand of plastic for 3 different shrinkage lag parameters. Residual shrinkage calculated from conversion and shrinkage profiles at the end of the laser scan.