LINEAR SHRINKAGE OF STEREOLITHOGRAPHY RESINS

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ABSTRACT

The linear shrinkage of an acrylate and an epoxy based stereolithography resin was measured during cure. A helium-cadmium (He-Cd) laser cured strands of resin as is done in the stereolithography process using two exposures. The exposure time was held constant while the delay time between exposures was varied. It was found for both resins that the final cure depth and linear shrinkage were a function of delay time.

INTRODUCTION

Dimensional accuracy is a key issue for rapid prototyping processes. The dynamics of photo-polymer cure during the stereolithography build process cause final part accuracy to be a function of resin type and build parameters such as cure depth and draw style [1]. As a result, modeling of the stereolithography build process is a complicated task. One must consider how the individual strands and layers polymerize with respect to adjacent strands and layers. In an effort to further the understanding of how process variables affect cure shrinkage, a series of linear shrinkage measurements was made on both an acrylate and an epoxy resin.

A helium-cadmium (He-Cd) laser cured polymer strands using two exposures as is commonly done during stereolithography build when the laser scans first in the x direction and then in the y. That is, most draw styles use a set of orthogonal vectors to fill in the boundary of a layer. Parallel vectors are usually spaced close together so as to minimize the amount of under-cured resin in the layer and thus minimize the amount of post-cure necessary. As a result of the close vector spacing, most of the resin in a layer is scanned twice by the laser with the time between exposures being a function of layer size and geometry, draw style, and cure depth used. The time delay between exposures was varied from 1 second to 10 minutes in the experiments discussed below. Both cure depth and strand shrinkage were found to be a function of delay time.

EXPERIMENTAL

Shrinkage Experiments - Apparatus

The linear shrinkage apparatus devised by Weissman and discussed in [2,3] was modified in order to improve its sensitivity during the first second of cure. The original mechanism used two micro balances in series. The modified apparatus uses only 1 balance as illustrated in Figure 1. It should be noted that while more shrinkage early in a cure was measurable with the modified apparatus, shrinkage rates over the first few seconds of cure were nearly the same for the old and new setups. The final linear shrinkage values were identical for the old and new apparatus which is to be expected.

The major components of the apparatus are: a HeCd laser for curing photosensitive resins, a mini-vat, a micro-balance, a HeNe probe beam with associated optics, and a video camera. The photosensitive resin is placed in a small vat which is temperature controlled and contains a shelf upon which one end of the drawn strand overlaps and becomes attached. The other end of a strand overlaps and attaches to the sensing arm of the micro-balance. The HeCd laser is directed through a mirror and a focusing lens onto the resin surface. Laser exposure is controlled by a shutter.

When the shutter is open, laser exposure on the resin surface causes a strand of polymer to form extending between the vat shelf and the balance arm. A miniature mirror is mounted at the fulcrum of the balance. The helium-neon (He-Ne) probe laser bounces off the mirror and onto a meter stick. As the strand shrinks it pulls the balance sensing arm which causes the mirror to rotate moving the probe beam along the meter stick. Although the actual movement of the balance arm is rotational, it can be approximated as linear since the rotations are small (typically less than 1 degree). The shrinkage of the specimen is, therefore, monitored as linear motion of the incident He-Ne laser along the stick. One centimeter of probe beam deflection correlates to 5.2 μm change in specimen length.

A 8-mm video camera is used to film the movement of the probe beam along the meter stick. A stop watch (graduated in tenths of a second) and the shutter driver are also in the camera's field of vision. When the trigger on the driver is pressed, a light corresponding to the opening and closing of the shutter appears in the camera's field of vision. This indicates the start of the experiment and allows a corresponding start time from the stop-watch to be noted. After the experiment has been recorded, the tape is played back to obtain the necessary data.

Shrinkage Experiments - Procedures

The humidity in the test enclosure which housed the mini-vat was monitored with an Abbeon relative humidity indicator. At the end of an experiment session, the mini-vat was cleaned of resin. Fresh resin was used every day.

Calibration: The apparatus is calibrated by moving the balance sensing arm a known distance and measuring the corresponding deflection of the probe beam. A knife edge is mounted on a precision controlled translation table. The translation table is moved in 10 μm increments and the probe beam position on the meter stick is noted. Three calibration curves are generated. The slopes of the curves are averaged to give a calibration factor. The measurement error due to variance in the calibration curves can range from 4 to 7 percent. Calibration was checked each day the apparatus was used.

Power density measurement: The HeCd laser power density at the vat surface was measured using a Spiricon laser beam analyzer. A CCD camera with a 1.6 X magnification was used to record the beam spot image in order to calculate the area of exposure. The output of the HeCd laser (λ = 325 nm) has a Gaussian profile. The beam is passed through a cylindrical lens to expose a "line" of resin. Actually, the exposed line is elliptical in shape having an aspect ratio (major axis divided by minor axis) of about 8. The area of the full ellipse was calculated to be 0.0241 cm^2. The measured power at the vat was 16 mW for all experiments.

RESULTS AND DISCUSSION

Overview

Two commercial photo-polymer resins, XB5149 and XB5170 (both from Ciba-Geigy), were tested using the linear shrinkage apparatus. Initial experiments were conducted to find the exposure level for each resin necessary to obtain strands approximately 10 mils in depth after two equal exposures. With the HeCd laser operating at 16 mW an exposure time of 10 ms for the XB5149 resin and a time of 30 ms for the XB5170 resin produced strands about 10 mils in depth after two exposures. However, it was found that the time delay between exposures affected the final cure depth.

Experiments conducted on the XB5149 resin are summarized in Table 1 and 2. Three sets of shrinkage data were measured. Delay times of 1 second, 5 minutes, and 10 minutes were used between two 10 ms exposures. It was observed that during the long delays, strand shrinkage would peak and then decline indicating expansion of strands. The maximum shrinkage measured after two exposures was found to be a function of delay time. Additional experiments were made that focused on the change in cure depth between the first and second exposure.

Fewer shrinkage experiments were performed using the XB5170 resin. The results of these experiments are summarized in Table 3. One set of tests was done with a 1 second delay and another with a 5 minute delay between two 30 ms exposures. Expansion of strands during the 5 minute delay was not observed with this resin as it was with the acrylate. However, maximum strand shrinkage in this case also was found to depend on delay time.

XB5149 Resin

Preliminary trials with the XB5149 acrylate resin indicated that after the first 10 ms exposure from the HeCd laser, strand shrinkage leveled off and then decreased before the second 10 ms exposure at 300 seconds elapsed time. Figure 2 shows averaged data for two trials. The shrinkage reaches an initial maximum of 0.35 % at an elapsed time of 20 seconds. After an elapsed time of about 40 seconds the measured shrinkage values decline indicating the strand is expanding. The shrinkage values continue to decline until the strand is exposed a second time (at 300 seconds elapsed time). After the second exposure the shrinkage increases rapidly. A maximum value of about 0.82 % was recorded at an elapsed time of about 430 seconds. At greater times the shrinkage declines indicating the strand is once again expanding. Results are summarized in Table 2.

A second set of data was taken for the XB5149 resin lengthening the delay between exposures from 5 to 10 minutes. In these trials the strands expanded enough between exposures so that the measured shrinkage returns to zero. Figure 3 shows shrinkage versus time data for the average of 3 trials. After about 20 seconds elapsed time the measured shrinkage reaches a plateau. A decrease in shrinkage or expansion starts between 30 and 40 seconds elapsed time. A zero shrinkage level was reached in each of three trials at an elapsed time between 350 and 485 seconds. After the second exposure at 600 seconds the shrinkage increases rapidly to a maximum value of about 0.81% at an elapsed time of 645 seconds. At longer times the shrinkage decreases until it reaches a steady state value of 0.44% after 1830 seconds.

A third set of shrinkage experiments was done with the XB5149 resin using a delay time of 1 second between exposures. Figure 4 shows the averaged data from three trials. For the same total exposure level a much greater maximum shrinkage value was recorded than for previous trials. As shown in Table 1, the average maximum linear shrinkage was 1.34 % which is over 60 % greater than the maximums recorded for the trials with 5 and 10 minute delay times. At an elapsed time of 10 seconds the strands have shrunk to 80 % of the maximum value. At an elapsed time of 40 seconds, the shrinkage has reached over 90 % of the maximum. The maximum shrinkage is reached after about 90 seconds elapsed time. At longer times up to 5 minutes no expansion of the strands was observed.

Additional experiments were done with the XB5149 resin to measure the effects of delay time between exposures on the strand cure depth. Strands were drawn using different exposure conditions, left in the vat for 5 minutes, removed and dried, and measured using an optical microscope. Results are summarized in Table 2. The first set of strands (Case 1 in Table 2) was exposed only once for 10 ms. The average cure depth measured was 0.222 mm (8.7 mil) with a standard deviation of 0.014 mm. For the Case 2 trials the strands were exposed twice for 10 ms with a 1 second delay between exposures. The average cure depth was found to be 0.306 mm (12 mil) with a standard deviation of 0.004 mm. In the next set of trials the delay time was lengthened to 5 minutes and the exposure time was held constant at 10 ms. The average cure depth measured was 0.244 mm (9.6 mil) with a standard deviation of 0.007 mm. Thus, lengthening the delay between exposures from 1 second to 5 minutes resulted in a final cure depth smaller by 20 %. The final case used a 5 minute delay between exposures like the previous case. However, the laser exposure time was increased from 10 to 20 ms for the second exposure. The average cure depth measured was 0.302 mm (11.9 mil) with a standard deviation of 0.02. The results indicate that for long delay times between first and second exposure, such as might occur with a large wide part, the effective cure depth may be less than what was originally desired.

XB5170 Resin

Four trials were made using a 300 second delay between two 30 ms exposures. The averaged results from those trials are shown graphically in Figure 5 and summarized in Table 3. The average maximum shrinkage value recorded was 1.24 % (standard deviation = 0.0147). At an elapsed time of 10 seconds the linear shrinkage measured was 0.6 %. After an elapsed time of 40 seconds the shrinkage has increased to 0.96 % or 79 % of the maximum value. The maximum value was attained somewhere between 100 and 140 seconds. The measured shrinkage did not change after the strand was exposed a second time at an elapsed time of 300 seconds. However, the strand cure depth did increase after the second exposure. The cure depth increased from 0.200 mm (7.9 mil) with a single 30 ms exposure to 0.26 mm (10.2 mil) after two 30 ms exposures.

A second set of trials was done with the XB5170 resin using a 1 second delay between two 30 ms exposures. The average maximum shrinkage was 1.55 % with a standard deviation of 0.186. Results are shown graphically in Figure 6 and summarized in Table 3. After 10 seconds elapsed time the average shrinkage measured was 0.91 % or about 59 % of the maximum value. At an elapsed time of 40 seconds the shrinkage was 1.4 % or about 90 % of the maximum value. The maximum was reached between 73 seconds and 118 seconds elapsed time. The variation in data for these trials was greater than what has typically been observed with this apparatus. The source of the variation is not known, however, the relative humidity was higher than normal during the time that these trials were made. Nevertheless, changing the delay time from 300 seconds to 1 second resulted in an increase in maximum linear shrinkage from 1.24 % to 1.55 %. The average cure depth measured was 0.244 mm (standard deviation = 0.002 mm). Thus, the final cure depth was less than that measured for the trials with a 300 second delay.

Resin Comparison

Contrary to the small in-plane shrinkage values (< 1 % in x or y direction) observed in three dimensional parts built in an SLA using the XB5170 resin, the linear shrinkage of XB5170 single strands is similar if not greater than the linear shrinkage of XB5149 single strands for comparable cure depths. Two 10 ms exposures spaced with a 1 second delay resulted in 1.34 % linear shrinkage in XB5149 strands and an average cure depth of 0.306 mm. Two 30 ms exposures spaced with a 1 second delay resulted in 1.55 % linear shrinkage in XB5170 strands and an average cure depth of 0.244 mm. Of course, the extent of cure in the XB5170 strands should be much greater than in the XB5149 strands. Evidence of a greater degree of crosslinking in the XB5170 strands could be seen in the data from experiments with long (300 s) delay times. A long delay between exposures resulted in significant swelling in XB5149 stands. Whereas XB5170 strands continued to shrink during a 5 minute delay. No swelling or expansion was observed in the XB5170 strands after the maximum shrinkage value was reached which was prior to the second exposure. A second exposure after the 300 second delay did not result in increased shrinkage, but did result in an increase in cure depth. Experiments with the XB5170 using a single long (2 s) exposure resulted in measured linear shrinkage values of 1.67 %. The XB5149 resin was not tested using long exposures, however, a similar acrylate resin (XB5081-1) has been tested with long exposures and linear shrinkage values in excess of 2 % have been measured. Therefore, one would expect greater postcure shrinkage in the acrylate resin compared to the epoxy resin for the exposure levels used in this study.

The effect of increased delay time on the final cure depth was different in the two resins. Increasing the delay time from 1 second to 300 seconds resulted in smaller (by 20 %) final cure depth values for XB5149 strands. The opposite effect was observed with the XB5170 resin. The strands built with a 300 second delay time had greater cure depths (0.260 mm versus 0.244 mm) than the strands built with a 1 second delay. Further testing with the XB5170 resin is needed using a controlled humidity chamber in order to verify the effect of delay time on cure depth.

SUMMARY

The linear shrinkage of two photo-polymer resins was found to depend on the amount of delay time between exposures by the curing laser. For the acrylate resin, XB5149, long (e.g., 300 s) time delays resulted in swelling of the partially cured polymer strands during the delay and after the second exposure. As a result, the maximum and final linear shrinkage values measured were less than the corresponding values measured using short (1 s) delay times. Additionally, long delay times resulted in smaller final cure depths for the strands made from the acrylate resin.

No swelling was observed in strands made from the epoxy resin when long delay times were used. However, the long delay times did result in smaller maximum shrinkage values. Unlike the acrylate resin, epoxy strands made using long delay times had greater final cure depth values than strands made with short delay times.

ACKNOWLEDGMENTS

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REFERENCES

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Table 1. Summary of XB5149 Results

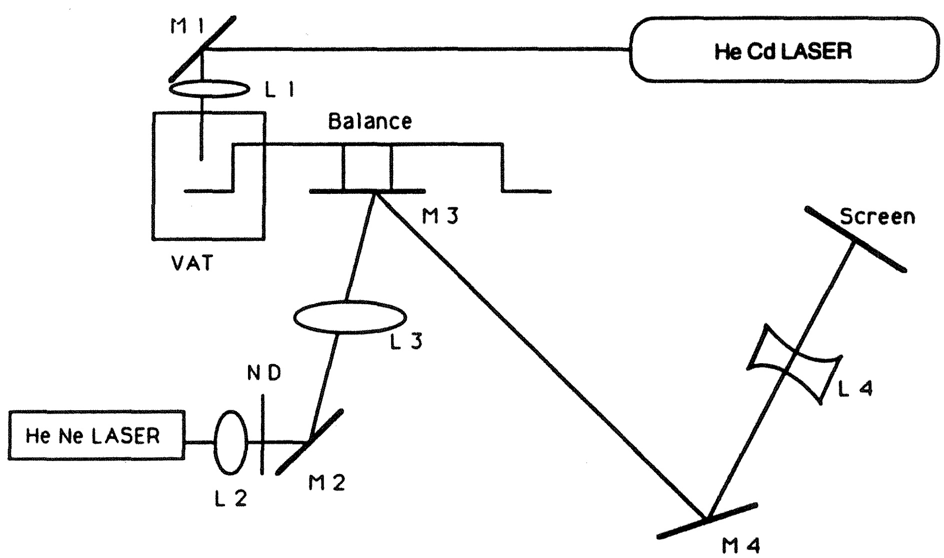
	Case 1	Case 2	Case 3
No. of trials	3	2	3
Exposure time, ms	10	10	10
Delay time, s	1	300	600
Maximum shrinkage, %	1.34	0.82	0.81
Final shrinkage, %	1.34	0.74	0.51
Final cure depth, mm	0.306	0.244	0.234

Table 2. Cure Depth Measurements for XB5149 Resin

	# of Exposures	Exposure time (ms)	Delay time (s)	Cure depth (mm)
Case 1	1	10	-	
trial 1				0.206
trial 2				0.227
trial 3				0.233
Avg.				0.222
std. dev.				0.014
Case 2	2	10, 10	1	
trial 1				0.309
trial 2				0.302
trial 3				0.307
Avg.				0.306
std. dev.				0.004
Case 3	2	10, 10	300	
trial 1				0.237
trial 2				0.249
trial 3				0.248
Avg.				0.244
std. dev.				0.007
Case 4	2	10, 20	300	
trial 1				0.322
trial 2				0.303
trial 3				0.282
Avg.				0.302
std. dev.				0.020

Table 3. Summary of XB5170 Results

	Case 1	Case 2
No. of trials	3	4
Exposure time, ms	30	30
Delay time, s	1	300
Maximum shrinkage, %	1.55	1.24
Final shrinkage, %	1.55	1.24
Final cure depth, mm	0.244	0.260



L 1 Cyliderical lens (focal length = 25 mm)
L 2 Convex lens (focal length = 90 mm)
L 3 Convex lens (focal length = 200 mm)
L 4 Concave lens (focal length = 21 mm)
M 1, M 2, M 3, M 4 Plain Mirrors
ND Neutral Density Filter (# 4)

Figure 1. Schematic of real-time linear shrinkage apparatus.

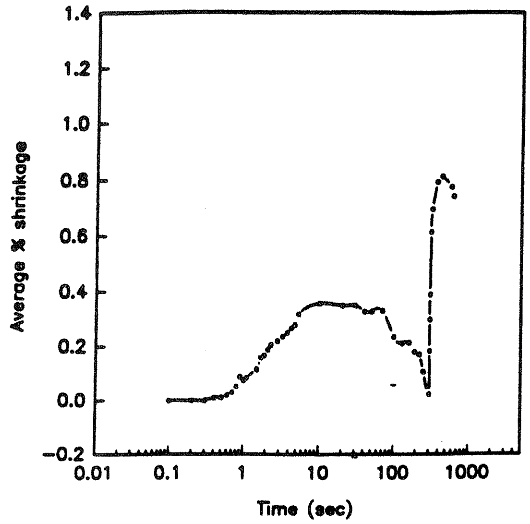


Figure 2. Shrinkage plotted versus log time for XB5149 resin, average of two trials. The first 10 ms exposure occurs at time zero. The second 10 ms exposure occurs at 300 s.

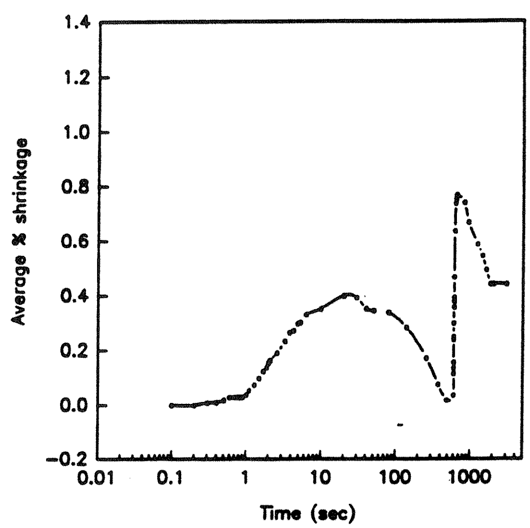


Figure 3. Shrinkage plotted versus log time for XB5149 resin, average of three trials. The first 10 ms exposure occurs at time zero. The second 10 ms exposure occurs at 600 s.

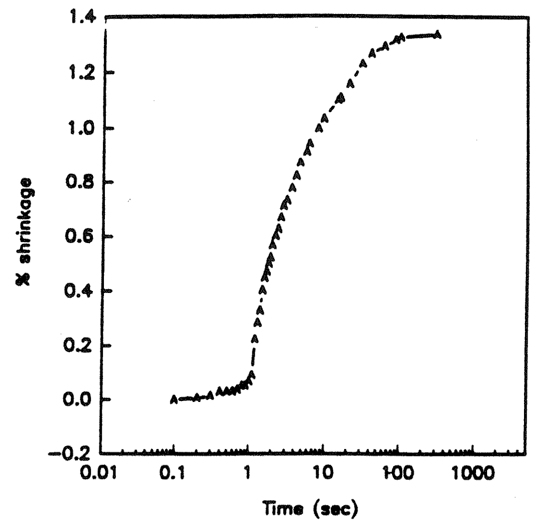


Figure 4. Shrinkage plotted versus log time for XB5149 resin, average of three trials. The first 10 ms exposure occurs at time zero. The second 10 ms exposure occurs at 1 s.

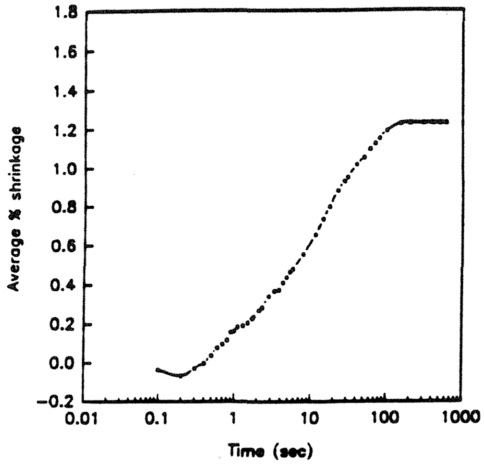


Figure 5. Shrinkage plotted versus log time for XB5170 resin, average of four trials. The first 30 ms exposure occurs at time zero. The second 30 ms exposure occurs at 300 s.

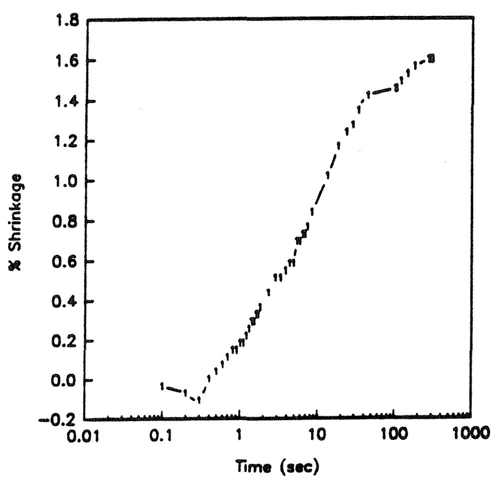


Figure 6. Shrinkage plotted versus log time for XB5170 resin. Data from trial 1 shown which is representative of the average of the three trials made. The first 30 ms exposure occurs at time zero. The second 30 ms exposure occurs at 1 s.