Post-Processing of Selective Laser Sintered Polycarbonate Parts

J. C. Nelson, N.K. Vail, M.M. Sun, and J. W. Barlow
Department of Chemical Engineering
University of Texas at Austin

Abstract

Studies were conducted to determine the effect of pressure on post-processing of polycarbonate coupons. No significant differences between coupons processed at atmospheric conditions and coupons processed in vacuum were observed. However, anisotropic shrinkage was observed in the z-direction normal to the sintering plane. This phenomena was further investigated using symmetrical polycarbonate cubes produced by Selective Laser Sintering using varied laser power varied powder layer thickness, and varied powder bed temperatures.
(Key words: post-processing, polycarbonate, densification)

Introduction

Polycarbonate parts made in the Selective Laser Sintering process do not reach full density during SLS processing. Post-processing of these parts at temperature above the glass transition (T_g) or the melting temperature (T_m) of the material, sinters the SLS part further and increases the part density. When the part approaches full density, the porous structure of the part closes which may trap air. As the pore size decreases, the pressure within the compressed pore increases and acts against the sintering forces.

The effect of pressure on pore shrinkage was modelled using an approach similar to Frenkel (1945). Frenkel described the minimum pore radius as a force balance between the initial pore conditions and the shrinking pore conditions. In our approach we consider a shrinking pore with geometry specified in Figure 1.
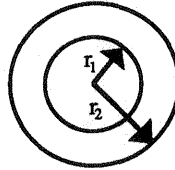

Figure 1. Shrinking pore model geometry

The pore radius, r_1, can be written as a function of the number of voids per unit volume, n, as

$$r_1 = \frac{1}{\sqrt[3]{n}} \sqrt[3]{\left(\frac{3}{4\pi}\right)\left(\frac{1-\rho}{\rho}\right)} \qquad (1)$$

Where ρ is the relative density. Differentiating r_i w.r.t. time and assuming an ideal gas relationship for the pore pressure produces an expression for the change in density of the solid.

$$\frac{d\rho}{dt} = \frac{3}{4}\sqrt[3]{\left(\frac{4\pi n\rho}{3}\right)(1-\rho)^2}\left[\frac{2\gamma - P_o\left(\frac{r_o^3}{r_i^3}-1\right)r_i}{\mu}\right] \quad (2)$$

Figure 2 illustrates the results of Eq. (2). For given material properties and pore concentration, the degree of pore shrinkage following pore closure is greatly influenced by the initial pore pressure. Namely, lower initial pore pressures result in greater pore shrinkage. These results suggest that higher density parts could result by post-sintering in vacuum oven instead of an air oven.
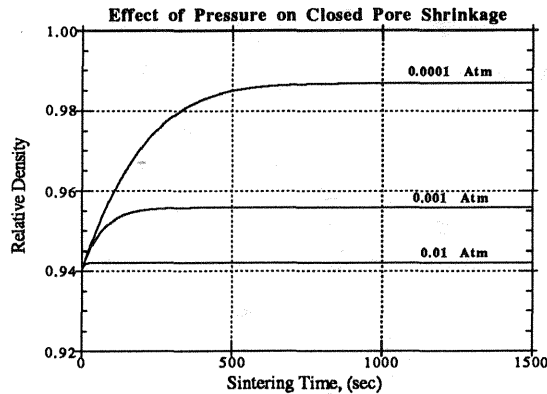

Figure 2. Pressure effect on closed pore shrinkage. Pore size is 25 μm. ($\sigma = 4.84 \times 10^{-4}$ J/m^2, $\eta = 8000$ Pa·sec, $n = 10^{12}$, $\rho^*_0 = 0.94$)

Materials and Methods

Pressure Effects on Post-processing of Polycarbonate Coupons

The vacuum chamber used for post-processing consists of a four inch diameter stainless steel tube with knife edge seals and is equipped with electrical and K-type thermocouple connections. The electrical leads are attached to a plate heater rated for 250W at 120V. The heater power leads and the thermocouple leads were connected to an Omega CN-9000 Series temperature controller. Using a line junction, the thermocouple leads were also connected to a computer controlled data acquisition system for the purposes of monitoring experimental temperature profiles. A two-stage vacuum pump was used to evacuate the chamber. Pressures of 80mTorr ($\sim 10^{-4}$ atm) were attainable with this vacuum pump. A pressure transducer placed at the chamber outlet to the vacuum pump was also attached to the data acquisition system for the purpose of monitoring experimental pressure profiles. This chamber was also used for ambient pressure experiments. Dow Corning 340 Silicone Heat Sink Compound was used to aid heat conduction between the heater and sample containers.

In one set of experiments, polycarbonate powder, contained in a one inch square aluminum container, was processed in the vacuum chamber at temperatures of 160°C,

175°C, and 190°C. Samples were kept at temperature for times of 1, 2, and 18 hours. Densities of sintered powder were measured by Archimedes principle.

In a second set of experiments, polycarbonate coupons made by SLS were obtained from BFGoodrich Corporation. These coupons measured 1/2"x5"x1/8" and were previously used for three point bending strength tests. These coupons were produced at SLS processing conditions of 10W laser power at the powder surface, 40 ips scan speed, and 130°C powder bed temperature. Each coupon was cut into four 1" pieces for the purposes of this study. Sample dimensions and densities were measured before and after post-processing. Densities were measured by Archimedes principle. Samples were dried in a vacuum oven over night at 100°C before post-processing to minimize any effect of dissolved water on density at post-processing temperatures. Samples were individually packed in the center of a 2"x3"x1" bed of alumina with particle size of 150μm.

Post-Processing of Polycarbonate Cubes

Polycarbonate cubes (3/4") made by SLS were produced on Bambi, the University of Texas research laser sintering machine. The layer thicknesses in the cubes was varied between 6 to 8 mils (150 to 200 μm), and the relative densities of the green sintered cubes ranged between 0.45 and 0.58. The sintered parts were initially packed in a bed of Alumina powder (150 μm). We later switched to granular salt (560 μm) as a packing material because it could be washed from the surface of the sintered part after post-processing. Because the salt is in granule form, the packing density is low. The packing density was increased using a binary mixture of salt and spherical glass (220 μm). The packed sample was placed in an oven which was preheated to a range temperatures between 150°C and 180°C. Samples that were rotated along one or two axes were packed with a packing material then the entire rotating apparatus was placed in a preheated oven.

Results and Discussion

The densities of polycarbonate powder samples are lower when sintered in vacuum than when sintered in air. The rate of densification is also a very sensitive function of sintering temperature relative to the polymer T_g of 150°C. Figure 3 presents the results for powder samples sintered for two hours. Similar curves resulted for powder samples sintered for one hour and for 18 hours.

Results of post-processing on the BFGoodrich polycarbonate coupons also showed the final densities to be higher when processed in air. Densities of coupons processed in vacuum increased only 33% compared to increases of 63% for coupons processed in air. These data do not support the model results discussed above. In fact, further investigation of the theory suggests the initial pore radius plays a significant role in pore shrinkage. Referring to Eq. (2) above, analysis of the effect of initial pore radius shows that pressure has a decreasing influence on pore shrinkage as the initial pore radius increases. Scanning electron micrographs of the polycarbonate coupons show pores with diameters in excess of 250μm. This is an order of magnitude larger than the pore size used in Figure 2. Figure 4 shows the results for an initial pore size of 250μm compared to the previous results of Figure 2. Shrinkage of the pore is greatly reduced by the increased initial pore size. This may explain why densities of coupons processed in vacuum were less than densities of coupons processed in air. Further, heat transfer may be effecting the results although great care was taken to try to reduce these effects. Temperatures of the alumina packing were monitored by thermocouple during the experiments. Still, lack of air in the alumina packing interstices would reduce heat transfer effectively reducing the processing temperature of the coupon causing lesser densification.
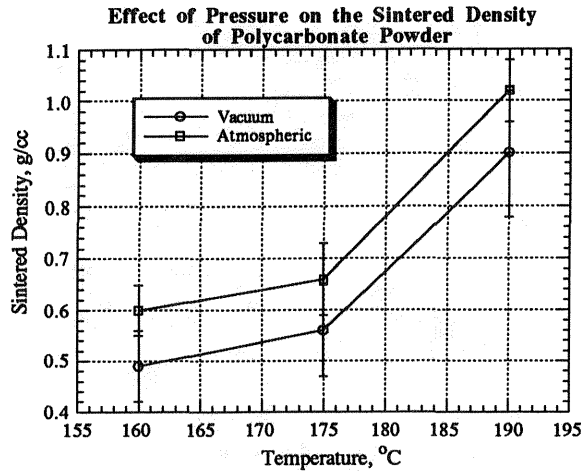
**Effect of Pressure on the Sintered Density
of Polycarbonate Powder**

Figure 3. Density of polycarbonate powder sintered for 2 hours in
vacuum and at ambient pressure.
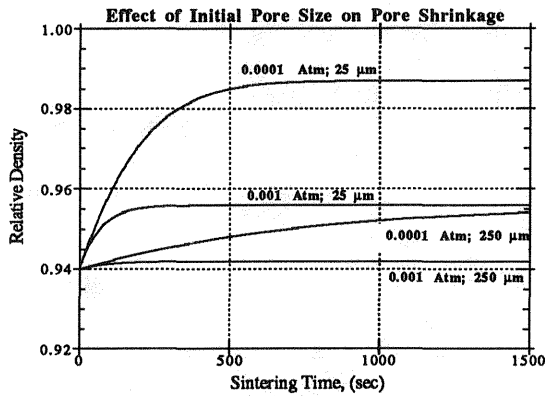
Effect of Initial Pore Size on Pore Shrinkage

Figure 4. Initial pore size effect on pore shrinkage.
$$(\gamma = 4.84 \times 10^{-4} \text{ J/m}^2; \mu = 8000 \text{ Pa·s}; \rho_o = 0.94)$$

Further analysis of the dimensional data for these coupons indicate non-isotropic shrinkage. Figure 5 shows the average shrinkage for all parts processed for two hours. Shrinkage in the z-direction is four to five greater than shrinkages in the xy-plane. Referring to Figure 6 for orientation, the z-direction is in the direction of gravity. Increased shrinkage in the z-direction suggests that gravity may have a pronounced effect during post-processing and that sintering during SLS may not be uniform in the z-direction. Further, shrinkage along direction of beam travel (y-axis) is twice the shrinkage along the direction of beam scan (x-axis) suggesting more sintering in the direction of beam travel.
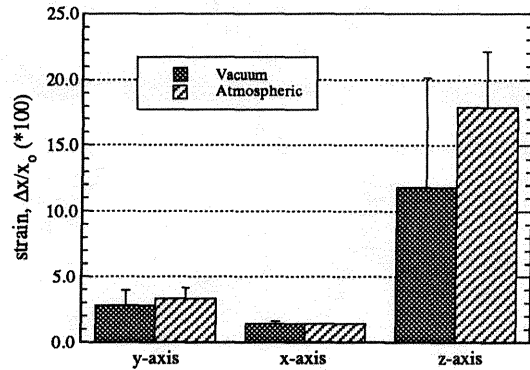
81

Figure 5. Axial shrinkages of polycarbonate coupons sintered for 2 hours under vacuum and atmospheric conditions.

Since there was little discernible difference between the SLS coupons post-processed in vacuum and atmospheric conditions, the goal of the next phase of experiments was to define post-processing parameters that could be used to sinter SLS parts to full density without distorting the shape of the part under atmospheric conditions. The first polycarbonate samples were post-processed at constant temperatures between 175°C and 180°C, just above the polymer T_g = 150°C. After the cubes were post-processed, the strain (i.e. $\Delta x/x_0$, Δx is the change in length and x_0 is the initial length) was calculated at three points along the cube's axes. Figure 7 presents the results of several runs plotted on a bar graph. The coordinate system on the graph indicates the orientation of the cube during post-processing. Below is a representation of the cube with the axes drawn, Figure 6. The sintered layers within the cubes are perpendicular to the z-axis.
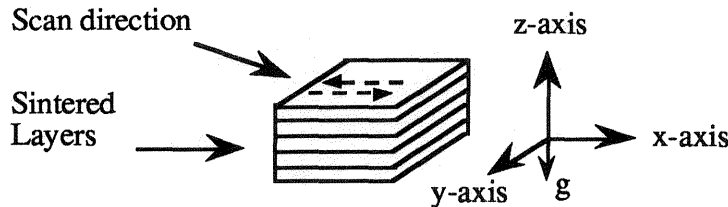

Figure 6. Coordinate system used to relate the orientation of the cube during post-processing to the scan direction during formation.

From these initial experiments, we have seen that the orientation and the initial density of the cube are important. When the xy-plane is vertical, the polymer flows downward making the base of the sample bigger than the top of the sample. But when the xy-plane is horizontal, the top and the base of the cube are more uniform. This is caused by the direction and the relative densities of the sintered layers and the pull of gravity. When the sintered layers are perpendicular to the gravitational force, the polymer flows more in a horizontal direction between the layers. This allows the cube to flatten out along the z-axis and shrink symmetrically along the x-axis and y-axis. However, when the sintered layers are parallel to the gravitational force, the layers acts as walls and the polymer flows to the base of the cube which causes non-uniform shrinkage in the horizontal plane. The shape of the cube would appear more trapezoidal if it were not packed in salt or alumina during post-processing with the xy-plane vertical.
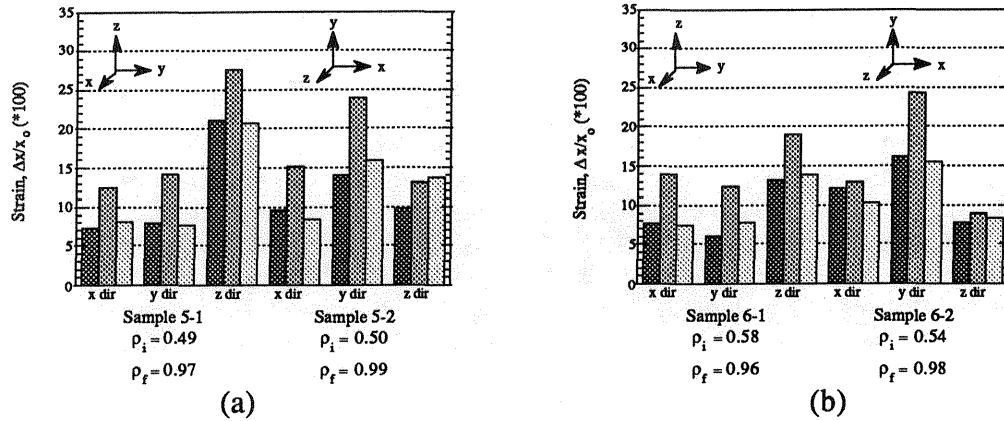
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Figure 7. Samples were post-processed for 5 hours at 175°C. Each plot presents the measurements of two cubes in different orientations.

We have also seen in these experiments at temperatures between 175°C and 180°C that the surfaces of the post-processed cubes are not flat. Measurements of the the cubes were made at three points on the cubes, at the sides and the middle of each face on the cube. The graphs of the data, show these three measurements along each axis. In most cases, the strain measured at the center of the cube's face was greater than that measured at the sides, Figure 7. This may have been caused by either the packing around the cube fixing the edges while allowing the sides to shrink inward or by thermal gradients within the cube.

Two methods are being pursued to eliminate the effects of gravity and maintain smooth surfaces during post-processing. The first is to post-process the cubes at temperatures that are only a few degrees above the glass transition temperature of the polycarbonate, T_g = 150°C. The sintering rate of polycarbonate at 155°C is 1/25 of the sintering rate at 175°C; however, the shrinkage of the cubes becomes isotropic when post-processed at a slower rate. A disadvantage of this method is the time required to sinter the SLS part to full density. For example, the polycarbonate samples shown in Figure 8, after 72 hours of post-processing at 154°C showed only six percent strain along each axis, and the relative density of cube increased from 0.53 to only 0.64.
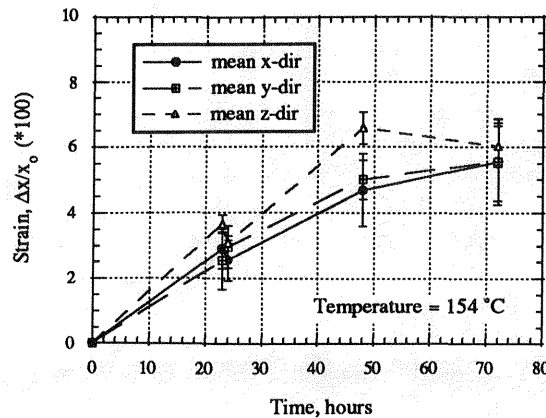

Figure 8. Polycarbonate cubes post-processed at 154°C for 24, 48, and 72 hours.

Another method to remove the effects of gravity is to rotate the SLS part during the post-processing. Currently, we are rotating the parts along one axis, and we are constructing an oven insert that will rotate the parts along two axes. Rotating the sample may eliminates the flow within the cube due to gravity. The rotational speed is also important. We have seen that at speeds greater than 2 RPMs, the centrifugal force causes the polymer to flow outward perpendicular to the axis of rotation.

The density of the SLS part before post-processing is perhaps most important. When the SLS part has a higher density, the shrinkage is more isotropic during post-processing. Currently, we are studying SLS parts made with different laser settings and layer thicknesses. We suspect that each layer may have variable density in the z-direction. That is, the top surface of a layer, which was in direct contact with the laser beam, may be more dense than the bottom of a layer which was sintered by heat conducted in from the surface and from the previous layer. Figure 9 shows the effects of part density at 175°C. Assuming the surface of each layer within the green SLS part to be close to full density, the shrinkage in the plane of the surface is consistent in both cubes. However, the shrinkage perpendicular to the surface is greater in the SLS cube with the lower initial density. Showing that the densities between the sintered layers is not uniform. Both cubes had a final relative density of 0.96.
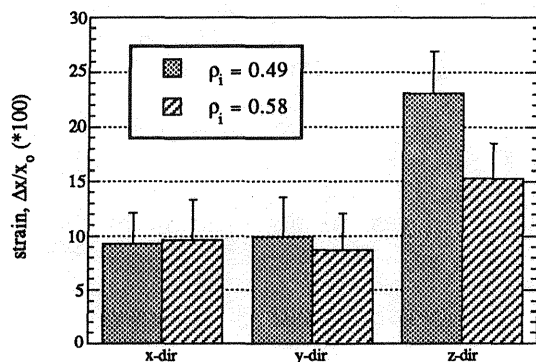

Figure 9. Effects of the density of the green SLS part during post-processing. The samples were heated for 5 hour at 175°C with the z-direction in the direction of gravity.

Conclusion

Shrinkage along the three axes of polycarbonate cubes become more uniform as the post-processing temperature approaches the T_g of the polymer. However, as the post-processing temperature is lowered through the glass transition temperature, the sintering rate is greatly reduced and any shrinkage which could be related to non-uniform sintering rates are eliminated. We are currently trying to increase the temperatures at which we post-process and still maintain the geometric proportions during post-processing by rotating the samples and by increasing the temperature of the oven gradually to prevent thermal gradients across the part.

The green density of the SLS part is also important. As the green density increases, the density across a single layer becomes more uniform and shrinkage during post-processing becomes smaller and more isotropic.

References

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