

Sintering Rates in the Selective Laser Sintering Process

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Abstract

This paper presents a procedure to determine rates of sintering as a function of temperature using an isothermal oven. The rate of height change of a powder sample in the oven at temperatures near the T_g or T_m is measured. From this information an activation energy is calculated. This activation energy is similar to activation energies calculated from viscosity versus temperature curves for polymer melts. This similarity suggests that viscous sintering models such as those by Frenkel and Scherer are appropriate. A comparison between sintering rates of polymer coated alumina powder and mixed powders of the polymer with alumina, suggest that better sintered products may result from the coated powders than from simple mixtures.

Introduction

Selective laser sintering is a process in which energy is added by the laser to a layer of powder in order to sinter the particles of that layer together in a two dimensional pattern and to sinter the top layer to the underlying layer of powder. It is important to know the optimal thickness of the layer so that the finished three-dimensional pattern has a uniform density (or void fraction). Initially this optimal thickness was found for each powder, used in the laser sintering process, by operating the SLS machine at different settings until a good part was produced.

To better understand the effects of laser sintering, a numerical model using the conduction-diffusion equation is being developed to predict the void fraction and temperature and profiles in a layer of powder. The thermal conductivity used in the model is a function of void fraction as well as temperature. But to calculate the void fraction, the rate of sintering of the powder is needed. We have developed a procedure to measure the rates of sintering of powders in an oven by measuring the change in height of the powder sample at constant temperature. The effects of the melt viscosity, the particle size and the temperature are being correlated to the rates of sintering of polymer powders.

Experimental Procedure

Rates of sintering are calculated from data collected in an oven at constant temperature. The oven is a Custom Scientific Instruments, Inc. heat distortion testing oven that has been modified for this experiment. The oven has an OMEGA CN9000 series temperature controller that can accurately maintain a temperature near the T_g or T_m of the powder sample during the measurements. A Schaevitz Engineering, Type 500HR, Linear-Variable Differential Transformer (LVDT) is fixed in place on top of the oven to measure the height change of the a rod which extends into the oven and rests of the surface of a plate. The plate sits on the powder sample (Figure 1). The voltage output from the LVDT is amplified by a Schaevitz ATA-101 (Analog Transducer Amplifier) and recorded by a MetraByte Corporation data acquisition system mounted in an IBM PC/XT. The voltage output is linear for a span of one inch, therefore the height of the powder sample can be plotted versus time if the LVDT has been calibrated. The experiment can be run for any

amount of time during which temperatures are typically kept 10 °C to 50 °C below the T_g or T_m of the polymer sample. From the experiments, we see that the majority of the sintering occurs in the first hour, but we continue to collect data for two hours before removing the sample to establish the final sintered volume.

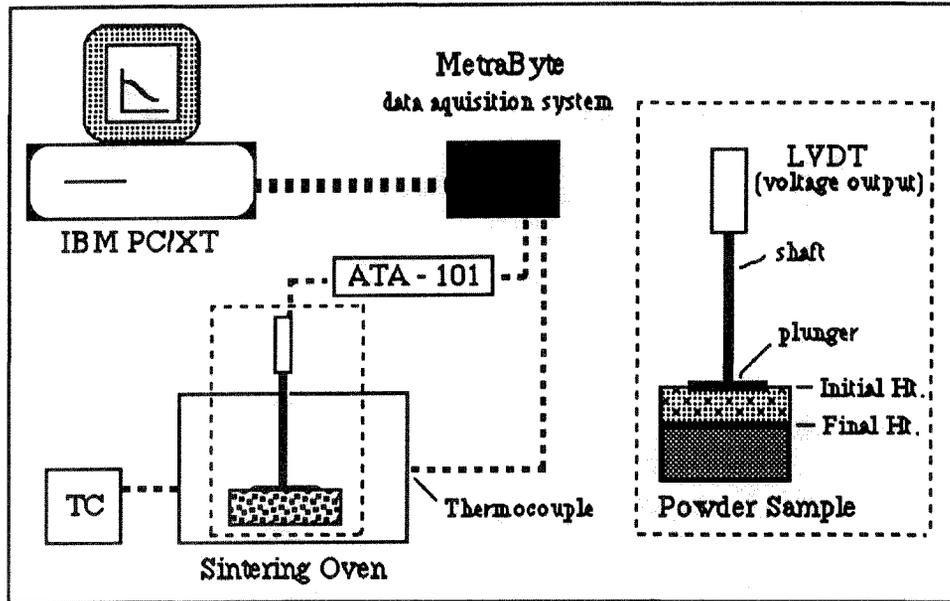


Figure 1. Experimental Apparatus

Experimental data is reported here for three powder samples (Table 1). The ABS powder is a low viscosity polymer which was used to make the first parts in our SLS machine. The PVC powder, PVC 42-3, is a material provided us by BFGoodrich. It contains a blue pigment to enhance coupling to the laser beam. The details of the composition are unknown. A miscible binary polymer blend, PCL/SAA, has also been examined. This blend is a 50/50 mixture of poly(ϵ -caprolactone) (Union Carbide PCL-700) with poly(styrene-co-alkyl alcohol) (Monsanto RJ-100). This blend may be suitable as a pattern "wax" for lost wax casting.

The weights of the rod and plunger exert a normal stress on the powder bed. To better understand the effects of stress on the powder bed in the axial direction, we measure the rate of height change as a function of stress also. In Figure 2, the two curves represent data, that has been fitted to a first order rate equation (Equation 2), for ABS powder under a normal stress of 8.312 g/cm² and 4.85 g/cm². Scherer [1] notes from similar experiments with ceramic glasses that the load increases the axial contraction rate, but counteracts the radial contraction rate. When the load is similar in magnitude to the capillary stress driving sintering, the radius remains essentially constant as the body [1]. As discussed below, the activation energy for sintering is found to decrease as the stress is increased, therefore requiring less heat to initiate sintering in the powder sample.

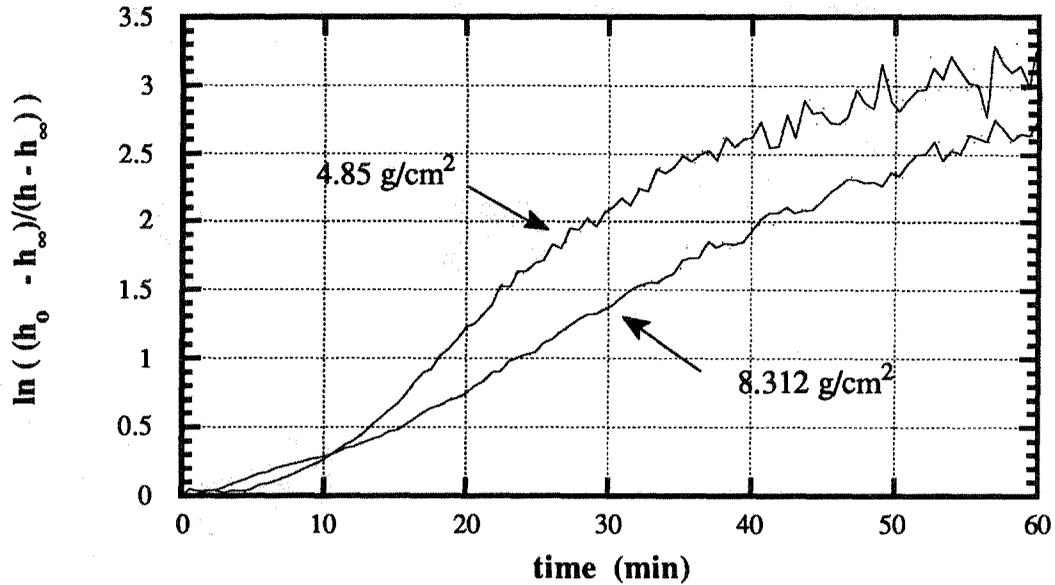


Figure 2. Data recorded from the LVDT and plotted according to a first order rate equation (Eq. 2) for two stresses at 150 °C for a ABS sample.

Results and Discussion

For purposes of simply describing the experimental rate of sintering, we reasoned that the rate of change in height of the powder bed should be proportional to the difference $(h - h_{\infty})$ between that height, h , and the final consolidated height, h_{∞} ,

$$\frac{-dh}{dt} = k (h - h_{\infty})^n, \quad (1)$$

where n is the "reaction order". Experimentally, we found that $n=1$ does the best job of fitting the experimental data. For $n=1$, equation (1) can be integrated to give

$$\ln\left(\frac{(h_0 - h_{\infty})}{(h - h_{\infty})}\right) = k t, \quad (2)$$

where h_0 is the initial bed height and k is the proportionality constant, pseudo rate constant. Figure 3 shows data from ABS samples sintered under identical conditions which was plotted according to equation (2). As indicated, the technique is fairly reproducible, and the results seem to follow equation (2) up to 30 minutes or so.

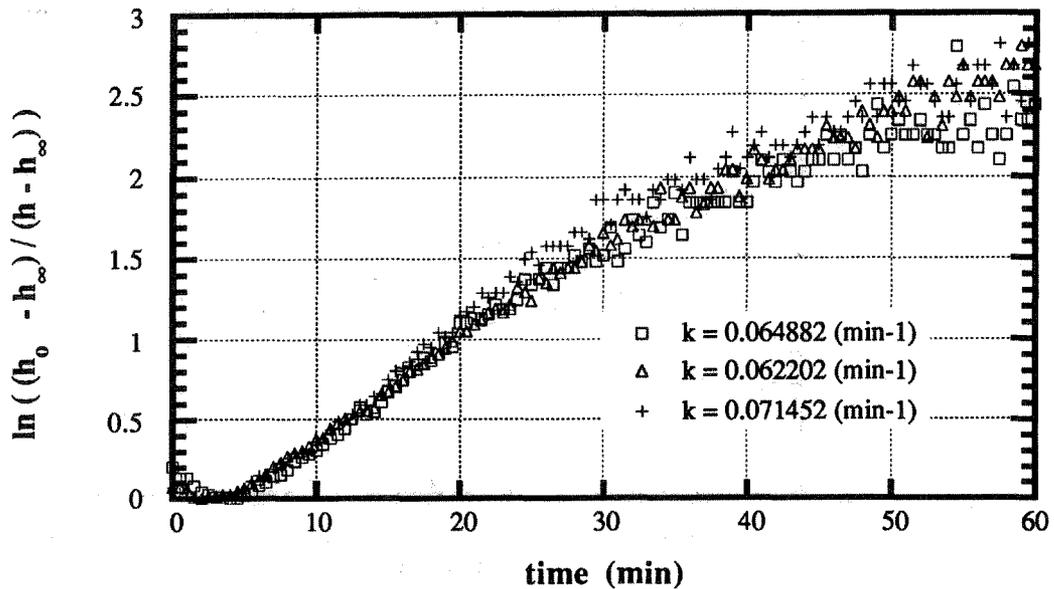


Figure 3. Three ABS experiments run at 150 °C, with an applied stress of 4.85 g/cm².

The constant of proportionality, k , in equations (1) and (2) is found to follow the Arrhenius equation,

$$k = A^* \exp\left(\frac{-E}{RT}\right) \quad (3)$$

as illustrated in Figure 4 for ABS. The activation energy, E , is found to be slightly dependent on the stress, while the stress dependence of k is primarily seen in the parameter A , see Table 1.

$$\mu = A' * \exp\left(\frac{\Delta E}{RT}\right) \quad (4)$$

Values of A' and ΔE for polymers which are similar to those used in our sintering work are taken from the literature [2] and presented in Table 1.

The comparison of E with ΔE for ABS and PVC suggests that the constant of proportionality, k , is itself inversely proportional to the viscosity of the polymer melt. There are exceptions to these findings, as implied by the PCL/SAA system, Table 1, and by PVC 42-2, not shown. These exceptions may result from experimental problems such as thermal decomposition in the case of PVC 42-2 which shows a negative activation energy.

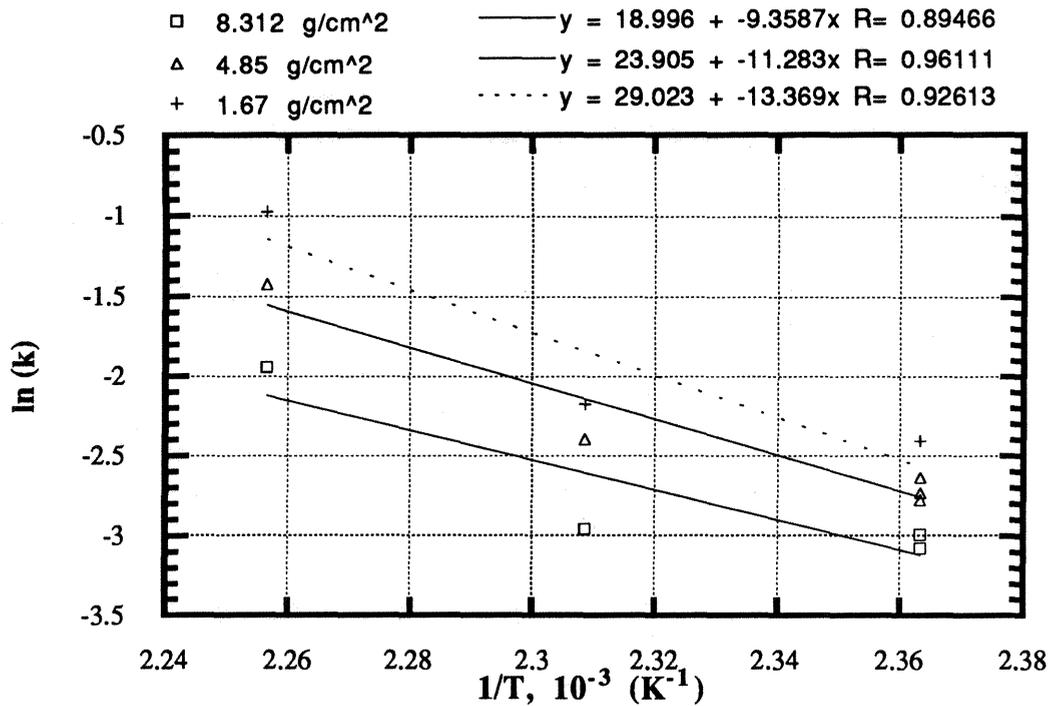


Figure 4. Activation energies for ABS

The viscous sintering models by Frenkel [4] and by Scherer [1,7] suggest that the rate of sintering is inversely proportional to viscosity, as observed. The Frenkel model describes the rate of coalescence of spherical adjacent particles:

$$\frac{y^2}{R} = \frac{2}{3} \left(\frac{\Gamma}{\mu} \right) t \tag{5}$$

valid when $y/R < 0.3$ where y is the neck radius (Figure 5), R is the radius of the particle, Γ is the surface tension, and μ is the viscosity.

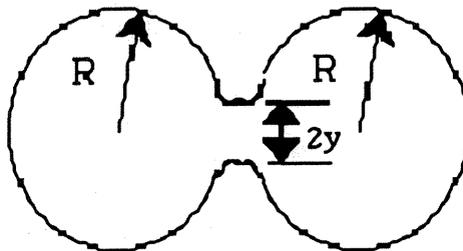


Figure 5. Schematic view of the first stage in the sintering process.

Frenkel's expression was used successfully for metals and ceramics [3], and is probably suitable for polymers at low shear rates where viscosity approaches the Newtonian plateau [5,6]. The model suggests that sintering is driven by surface tension and retarded by viscosity. The difficulty with this model is to relate neck formation to changes in porosity and dimensions.

Scherer [1,7] has developed a model that describes the rate at which a cubic array of cylinders densifies by viscous flow driven by the reduction of surface energy. The cubic array is proposed as a model for the microstructure of open-pore, low density materials. The parameters of the model structure can be deduced from Hg penetration porosimetry. The model presents a relationship between the free strain rate, or the rate at which the geometry is changing, and the surface tension σ , the viscosity μ , and the current geometry as follows:

$$\frac{\partial \epsilon}{\partial t} = - \frac{M}{\mu} \frac{(3\pi)^{1/3}}{6} \frac{2-3cx}{\sqrt[3]{x(1-cx)^2}} \quad \text{when } \rho \leq 0.94 \rho_s \quad (6)$$

$$\frac{\partial \epsilon}{\partial t} = - \frac{M}{\mu} \frac{1}{2} \left(\frac{4\pi}{3}\right)^{1/3} \left(\frac{\rho_s}{\rho} - 1\right)^{2/3} \quad \text{when } \rho > 0.94 \rho_s \quad (7)$$

where the capillary constant is

$$M \equiv \left(\frac{\sigma}{a_0}\right) \left(\frac{3}{4\pi}\right)^{1/3} \quad (8)$$

and where a_0 is the initial radius of spherical particle, $c = 8\sqrt{2}/3\pi$ and x are the geometry factors defined as the ratio of the radius of the cylinder structure to the length of the cylinder.

The void fraction can be related to the free strain and the geometry factor by:

$$\epsilon = 1 - (1 - \epsilon_0) \exp(-3\epsilon) \quad (9)$$

$$\epsilon = 1 - 3\pi x^2 + 8\sqrt{2} x^3 \quad (10)$$

This model provides an useful relation between the geometry and the temperature dependent rheological properties. By measuring the final porosity of the samples sintered by the oven sintering method, we will be able to relate the height measured to the porosity of the powder bed. Then using this model calculate the rate of sintering with respect to the change in void fraction. This rate, being temperature dependent can then be used in a model of the laser sintering process.

Material	Sintering Parameters			Viscous Flow Parameters [2]		
	Stress (g/cm ²)	E kcal/mol	A	Shear rate (sec ⁻¹)	ΔE kcal/mol	A'
ABS	8.3	18.6	3.0E+06			
	4.9	22.4	4.0E+08			
	1.7	26.6	6.7E+10			
SAN (30% AN)				20	18.3	2.5E-10
PVC 42-3	8.3	2.1	9.6E-03			
	4.9	5.6	6.4E-01			
	1.7	4.1	1.2E-01			
GEON 8750,8700A				8	4.2	3.3E-2
PCL/SAA	≈ 9	29.3	1.8E+15	high	8.9	1.2E-09

Table 1. Activation Energies (E) and (ΔE) calculated from the oven sintering method and viscosity [2] respectively.

References

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