

# Modeling of Polymer Degradation in SLS

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## Abstract

A simple computer model has been developed to predict the thermal degradation of polymer binders used in the fabrication of composite green shapes from high temperature ceramic materials. Decomposition rate kinetics of the polymer materials were determined and incorporated into the model. The polymer degradation occurring in three separate powder systems was determined as a function of applied laser energy. Agreement between model results and experimental data is quite good.

(Key Words: Polymer, Degradation, Selective Laser Sintering, Composites).

## Introduction

The development of polymer coated ceramic and metal materials has provided the capability to Selective Laser Sintering (SLS) to fabricate *green* composite shapes that can be post-processed by conventional means to yield functional objects. Already a great deal of research has been conducted to develop suitable polymer binder materials for SLS<sup>1,2</sup> as well as research that has focused on examining the performance of the developed binders in the fabrication of *green* composites via the SLS process.<sup>3,4</sup>

Still, work is continuing with polymer composite systems to maximize their performance. One problem that is evident from past studies is the occurrence of binder degradation as a result of SLS processing. Measurable amounts of binder loss have been observed in all polymer composite materials studied by these authors. Loss of polymer binder during SLS processing has the obvious consequence of reduced green strength in the fabricated object. As better binder systems are developed that require lesser amounts to yield green objects the effects of binder degradation will become more prevalent. This paper presents preliminary work to model binder degradation in an effort to predict observed results.

## Degradation Model

Polymer degradation model development follows closely the modeling of thermoplastic sintering discussed by Nelson.<sup>5</sup> The model derived from the 1-dimensional

heat transfer equation defined as

$$\begin{aligned}
 \rho C_p \frac{\partial T}{\partial t} - \frac{\partial}{\partial z} \left( k \frac{\partial T}{\partial t} \right) \\
 - k \frac{\partial T}{\partial z} = \alpha_R \langle I \rangle - h(T - T_\infty) \quad ; \quad z = 0 \quad t \leq \tau \\
 - k \frac{\partial T}{\partial z} = -h(T - T_\infty) \quad ; \quad z = 0 \quad t > \tau \\
 - k \frac{\partial T}{\partial z} = 0 \quad ; \quad z = \infty \quad t > 0
 \end{aligned} \tag{1}$$

where  $\rho$  is the bed density,  $C_p$  the heat capacity,  $T$  the temperature,  $t$  the time,  $k$  the thermal conductivity,  $\alpha_R$  the absorptivity of the material,  $\langle I \rangle$  the laser intensity,  $h$  the overall heat transfer coefficient,  $T_\infty$  the ambient temperature, and  $\tau$  the duration of the applied laser energy.

Eq. 1 was solved via a Crank-Nicholson finite difference form that is unconditionally stable with discretization errors  $O[(\Delta t)^2 + (\Delta z)^2]$ .<sup>67</sup> To complete the thermal model several of the physical parameters need to be evaluated. The bed density,  $\rho$ , is assumed to be that measured for the green parts with no changes occurring due to polymer sintering and binder loss. Previous data show part densities are very similar to measured bed densities.<sup>3</sup> The specific heat of the bed,  $C_p$ , is assumed linear with the mass fraction contribution of the constituents.<sup>8</sup>

$$\bar{C}_p = \sum_1^n x_i C_{p,i} \tag{2}$$

The effective bed thermal conductivity,  $k_{eff}$  is predicted from the Yagi-Kunii model for packed particle beds<sup>9</sup>

$$\frac{k_{eff}}{k_g} = \frac{\beta(1 - \varepsilon)}{\gamma \frac{k_g}{k_{s,eff}} + \frac{1}{\frac{1}{\varphi} + \frac{D_p h_{rs}}{k_g}}} + \varepsilon \beta \frac{D_p h_{rs}}{k_g} \tag{3}$$

where  $\varepsilon$  is the void fraction of the bed,  $\gamma \approx 1$  and  $\beta \approx 1$  for beds of spherical or cylindrical particles,  $k_g$  the thermal conductivity of the gas within the bed,  $k_{s,eff}$  the effective thermal

conductivity of the solid,  $D_p$  the average particle diameter,  $h_{rv}$  and  $h_{rs}$  the radiation heat transfer coefficients for void to void and solid to solid, respectively, and  $\varphi$  is a gas-geometry correction factor. For air, Yagi-Kunii give an empirical form of  $\varphi$  as

$$\varphi = 0.1927 e^{1.8544} \quad (4)$$

The effective solid thermal conductivity,  $k_{s,eff}$  of the composite material was estimated in two steps. The morphology of polymer coated particles used in these studies is such that it is difficult to know their exact makeup. For the purposes here it is assumed the coated particles are of a core-shell geometry thus the thermal conductivity of the coated particle,  $k_c$  is given by<sup>10</sup>

$$\frac{1}{k_c} = \left( \frac{B}{k_1^2} - \frac{2}{k_1} \right) \ln \left( \frac{B - k_1}{B - k_1 t_c / R_1} \right) + \frac{t_c}{R_1 k_2} + \left( \frac{1 - t_c / R_1}{k_1} \right) \quad (5)$$

where

$$B = 2 \left( \frac{t_c}{R_1} \right) k_2 + 2 \left( 1 - \frac{t_c}{R_1} \right) k_1 \quad (6)$$

and  $k_1$  is the thermal conductivity of the core,  $k_2$  the thermal conductivity of the coating,  $R_1$  the radius of the core particle, and  $t_c$  the thickness of the coating defined as

$$t_c = R_1 \left( \frac{1 - (1 - \phi_p)^{1/3}}{(1 - \phi_p)^{1/3}} \right) \quad (7)$$

and  $\phi_p$  is the volume fraction of the polymer coating. Some of the material systems studied were comprised of coated particles and pure powder substrate. In these cases,  $k_{s,eff}$  is determined from the rule of mixtures

$$k_{s,eff} = \sum_i \phi_i k_i \quad (8)$$

where  $\phi_i$  is the volume fraction of the  $i$ -th component. For material systems composed only of coated particles  $k_{s,eff} = k_c$ .

The laser flux,  $\alpha_R \langle I \rangle$ , was determined based on scanning geometry and is a function of laser power, laser spot size, laser scanning speed, and the distance between adjacent scan vectors. The beam is Gaussian by measurement therefore, the total applied energy to boundary condition is easily modeled as a fixed sequence of discrete pulses occurring at intervals determined from the scan speed for a total time of  $\tau$ .<sup>5</sup>

Degradation of the binder was determined at each nodal point from kinetic expressions described below. Bed properties were re-evaluated at each time step to reflect changing physical conditions.

## Materials and Methods

Two polymer composite material systems were studied. The first consisted of two batches of monodisperse silicon carbide (Norton) coated with a PMMA binder and a methylmethacrylate/*n*-butylmethacrylate (MMA/*n*BMA) copolymer binder. The preparation and evaluation of these coated powders has been described elsewhere.<sup>3</sup> The average particle size of the silicon carbide powder was  $12.6 \pm 2.9 \mu\text{m}$  (Coulter Multisizer). The second material system was a group of powders that consisted of a series of different molecular weight MMA/*n*BMA copolymer binders coated on to a spheroidized soda-lime glass (Potters Industries). The average particle size of the glass powder was  $5.0 \pm 2.5 \mu\text{m}$  (Coulter Multisizer).

Test specimens were fabricated from each of the powder materials via SLS. The silicon carbide powders were processed in an SLS<sup>TM</sup> Model 125 workstation while the glass powders were processed in the academic prototype, Bambi.<sup>11</sup> Operating conditions were maintained constant within limits of the two machines. Test specimens were fabricated using applied energy densities,  $A_N$  over the range  $0.5\text{-}3.0 \text{ cal/cm}^2$ . Two to four specimens were prepared at each scanning condition.

The fabricated specimens were fractured at the midpoint and a powder sample taken from the center of the fracture plane. The polymer content of the powder sample was determined by Thermal Gravimetric Analysis (TGA) (Perkin-Elmer Series 7). The relative mass loss of the samples were measured over the temperature range  $50\text{-}650^\circ\text{C}$  in a flowing  $\text{N}_2$  stream. The polymer content of the sample was evaluated as the difference in relative weight loss at  $600^\circ\text{C}$  and  $100^\circ\text{C}$ , respectively.

The five copolymer samples of different molecular weights used to coat the glass powder were fabricated by methods described previously.<sup>2</sup> The properties of these polymers are listed in Table 1. The degradation kinetics of these copolymers were also determined by TGA. The normalized weight losses of  $\sim 10\text{mg}$  samples of spray dried polymer powder were determined at isothermal conditions while in a stream of pure  $\text{N}_2$ . Each sample was preheated to  $175^\circ\text{C}$  for a period of five minutes before being quickly raised to a predetermined temperature at a rate of  $150^\circ\text{C}/\text{min}$ . Independent TGA traces showed no appreciable polymer weight loss during the pre-heat period. Weight loss

curves were collected over the temperature range of 290°C-350°C at 10-15°C intervals.

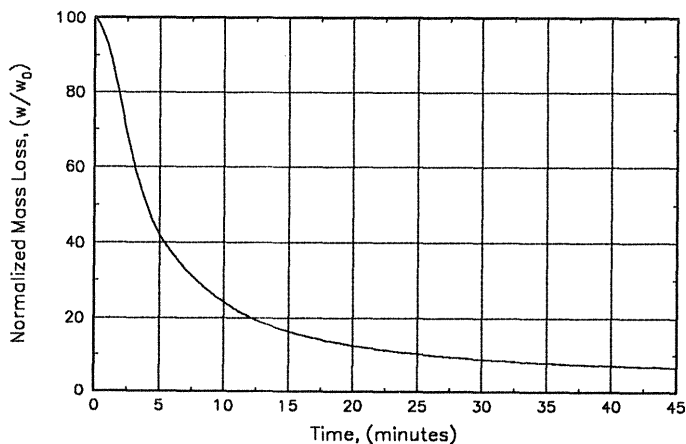
**Table 1** Properties of MMA/nBMA copolymers used to coat glass powder.

Latex	Density, (g/cm <sup>3</sup> )	T <sub>g</sub> (°C)	Melt Flow, (g/10min 200°C 75psi)
M/B -1- S	1.163	97.5	0.104
M/B -2- S	1.163	96.8	0.96
M/B -4- S	1.156	94.1	8.64
M/B -6- S	1.156	91.8	31.1
M/B -8- S	1.156	88.5	74.7

The thermal conductivities and specific heats of the ceramic powders were obtained for the solids from the literature.<sup>12,13,14,15</sup> Similar values for PMMA were also obtained from the literature.<sup>16,17</sup> The thermal conductivity of the MMA/nBMA copolymers was assumed to be that of PMMA. The specific heat of the copolymers has been determined to be<sup>18</sup>

$$C_p \left( \frac{\text{cal}}{\text{g} \cdot ^\circ\text{C}} \right) = 0.319 + 0.802 \times 10^{-3} T ; T < 90^\circ\text{C}$$

$$C_p \left( \frac{\text{cal}}{\text{g} \cdot ^\circ\text{C}} \right) = 0.341 + 1.126 \times 10^{-3} T ; T \geq 90^\circ\text{C}$$
(9)



**Figure 1** Isothermal decomposition of MMA/nBMA copolymer M/B -4-S at 330°C in N<sub>2</sub>.

## Results and Discussion

Figure 1 shows a typical weight loss trace for a MMA/nBMA copolymer. The traces of all copolymers were first-order to beyond 50% conversion over the temperature range studied. The first order degradation indicates a depolymerization mechanism similar to that of PMMA with reasonably long zip lengths and which is independent of termination reaction order.<sup>19</sup> Degradation rate kinetics were determined from the initial slopes of the relative mass loss curves according to the first-order rate-expression

$$\frac{d}{dt} \left( \frac{w}{w_0} \right) = -k_{DP} \frac{w}{w_0} \quad (10)$$

where  $w/w_0$  is the normalized mass loss of the polymer sample and  $k_{DP}$  is the degradation rate constant.

Degradation rates of all the copolymers were similar although a small dependence on molecular weight was noted. An average value of the degradation rate expression was used for prediction of polymer degradation in the model, Eq. 11. The degradation rate expression given by Inaba, *et. al.*,<sup>19</sup> was used for the PMMA coated silicon carbide sample, Eq. 12.

$$k_{DP} (s^{-1}) = 2.631 \times 10^{12} \exp \left( \frac{-21320}{T} \right), \quad T(K) \quad (11)$$

$$k_{DP} (s^{-1}) = 1.182 \times 10^{19} \exp \left( \frac{-32140}{T} \right), \quad T(K) \quad (12)$$

Figure 2 shows the polymer degradation for the PMMA coated SiC material. This material contained ~20 vol. % polymer (8.5 wt. %) and was derived from a polymer coated batch containing ~25 vol. % binder to which raw SiC had been added. The extent of binder loss is significant showing more than a 15% mass loss at the highest energy densities. In this case the model does a reasonable job of predicting the extent of binder loss. Although, the experimental data appear at a glance to be essentially linear this may be more an artifact of error in the data. On the other hand, the model predicts a more gradual development to binder loss, characteristic to the first-order rate dependence, and becomes increasingly dominant at the higher energy densities as would be expected.

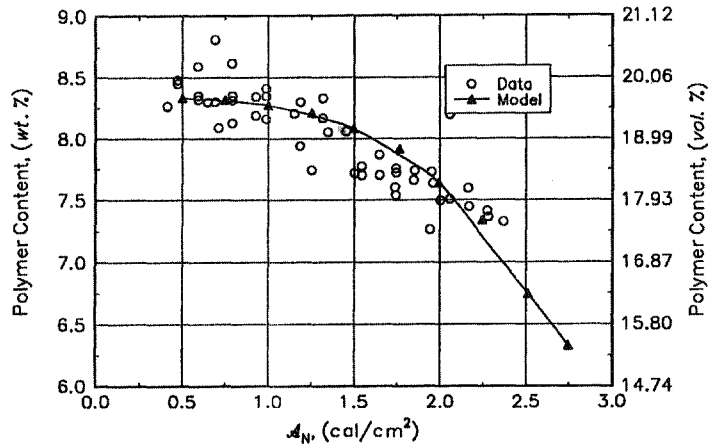


Figure 2 Comparison of predicted polymer degradation to experimental results for PMMA coated Silicon Carbide.

Figure 3 shows the extent of polymer degradation for the MMA/*n*BMA copolymer coated onto SiC. This material system has nearly the same compositional makeup as the PMMA/SiC material discussed above. The extent of degradation is much reduced for this material showing about a 6% wt. loss overall at the highest energy densities. The decreased degradation of the copolymer is consistent with the less rigorous kinetics described by Eq. 11. In this case, the model prediction is quite close to the experimental data. However, at the higher energy densities, the predicted extent of binder degradation may be too severe.

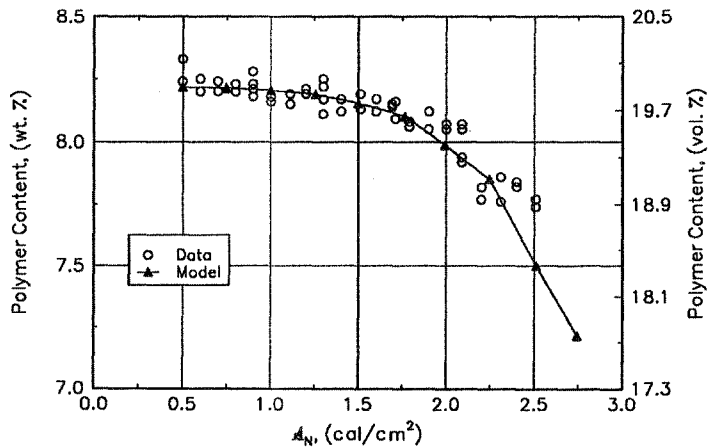
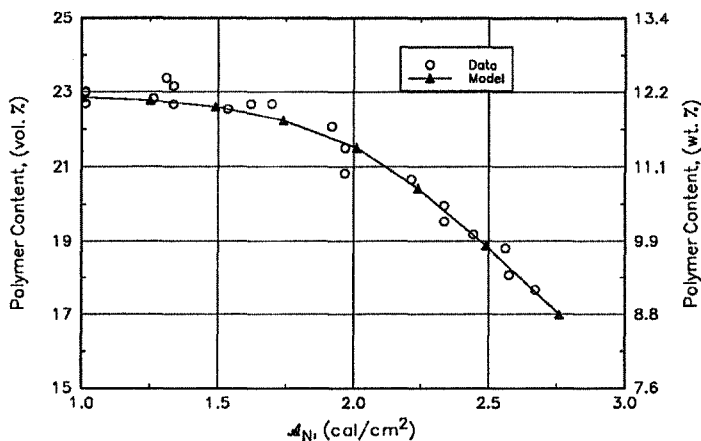


Figure 3 Comparison of predicted polymer degradation to experiment for MMA/*n*BMA copolymer coated Silicon Carbide.

Figure 4 shows the extent of binder degradation for all the copolymer glass powders described above. One set of data corresponding to the M/B -1-S coated glass powder was discarded since the polymer content of this powder was lower (~21% vol) than the remaining powders (~23 vol. %). The remaining data points represent the average of at

least three data points. This system contained only coated powders. The agreement of the model prediction with the experimental data in this case is excellent. This result offers some verification to the validity of the developed model for two reasons. First, the thermal conductivity of the glass powder much lower than for the silicon carbide powder discussed above. SiC has a thermal conductivity similar to that of most metals while that of glass characteristically lower. Second, the makeup of the material systems is altered.



**Figure 4** Comparison of predicted polymer degradation for MMA/nBMA copolymer coated A-5000 soda-lime glass.

### Conclusions and Further Work

The binder degradation model discussed briefly here appears to predict well the extent of binder degradation in the material systems studied. More work is required to verify the validity of the model by comparison to other material systems such as polymer coated metals and material systems of polymer mixed with powder substrates. With further verification of the model it will be simple to use the model to study the effects of SLS processing conditions on the extent of binder loss as possible tool for optimizing process conditions for optimal results.

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