PROCESS MODELING OF THERMAL DEBINDING

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ABSTRACT

Thermogravimetric analysis (TGA) is routinely used for characterizing binder burnout. However, the rate of binder removal from a powder compact depends not only on the intrinsic thermochemical decomposition kinetics of the binder but also the pore structure, the component geometry and the furnace cycle. In this paper, a modeling approach is presented to describe binder removal rates by accounting for the temperature distribution in a component during a furnace cycle as well the diffusion of gaseous binder decomposition products out of the pore structure. The predictions are qualitatively representative of observations made in practice. The model will provide a guide for an experimental protocol that is presented which will in turn allow for future refinements in the model.

INTRODUCTION

The last decade has witnessed a large growth in the utilization of a broad range of powdered materials in the fabrication of components for applications in transportation, microelectronic, biomedical, sporting, and tooling industries [1]. The component fabrication methods include die compaction, powder injection molding, extrusion, slip casting, tape casting, solid casting, and rapid prototyping. A common feature in these processes involves the use of organic materials, referred to as binders or lubricants in the shape forming stage. A critical requirement for the success of these manufacturing operations involves the complete removal of the binders prior to sintering [2]. Thermal debinding is the typical process variant that is used to remove the binder from a component by pyrolysis in a furnace. While fast thermal debinding cycles are desired for increased production rates, the component quality can be compromised in several ways if the debinding cycle in the furnace is too fast. For instance, incomplete debinding can increase the residual carbon content in the component and affect sintered properties and dimensions. Also, rapid removal rates can introduce component distortion in the form of slumping, blistering, cracking, and sooting. Furnace emissions and residue buildups are additional issues that may need to get addressed depending on the furnace cycle. Thus, there are upper and lower limits for useful thermal debinding rates. The overall goal of the present research program is to be able to quantitatively identify these limits [3].
Thermal debinding rates depend on a number of material and process variables [4, 5, 6]. Material variables include the physical and chemical properties of the binder as well as the particulate phase. Process variables include furnace atmosphere, heating rate, dwell temperature, and dwell times. As shown in Figure 1, this complicated situation can be effectively be addressed by first understanding the influence of pore structure (particle size, solid volume fraction, thermal properties, binder saturation, surface effects) on the intrinsic thermal degradation chemistry of the binder (temperature-dependent reaction rates, composition of degradation products, atmosphere effects). Such a treatment can then be scaled to account for changes in component geometry.

The present paper outlines a modeling approach to quantitatively identify optimal thermal debinding rates. The theoretical considerations will help identify an experimental strategy to evaluate and refine the model by systematically examines the effects of critical material and process variables.

THE MODEL

The weight loss of a binder as a function of temperature is typically represented by a sigmoidal function as seen in Figure 2. Here the thermal decomposition of polypropylene in air and nitrogen was measured on a thermogravimetric analyzer (TGA) at a heating rate of 5 °C/minute. The dependence on the instantaneous residual fraction of binder on temperature and atmosphere can be noted. The data can be represented as a temperature-dependent rate expression as shown in Equation 1.

\[
\frac{dW}{dt} = A \exp(- \frac{E}{RT})W^n
\]

where, \(W\) is the weight fraction binder present at any instant, \(t\) is the debinding time, \(T\) is the debinding temperature, \(R\) is the universal gas constant, \(A\) is the frequency factor for pyrolysis, \(E\) is the activation energy for pyrolysis, and \(n\) is the reaction order. Equation 1 describes the intrinsic thermal decomposition kinetics of a given pure binder in a given atmosphere. The next step is to account for the presence of the binder within a pore structure of a component.

A classical unsteady state conduction model to capture the component effects, previously presented by Tsai, was initially used in this study [7]. Tsai’s model assumes that for a given furnace cycle, the temperature distribution in the component is determined by its thermal properties, size and shape. This temperature distribution results in a distribution of binder removal rates. A typical thermal debinding cycle involves a ramping step to a hold temperature followed by heating for a specified time at that temperature. Using such analysis, the effects of furnace cycle on the removal of polypropylene were computed for a cylinder of 1 cm radius, containing 60 vol. % alumina.

Figure 3 shows the effect of hold temperature on the removal rate of polypropylene from the porous alumina cylinder. It can be seen that the polypropylene is completely removed within 30 minutes at 400 °C. In comparison, the time for complete removal at 200 °C is nearly 100 times higher. This is qualitatively in agreement with observations in practice.

Figure 4 shows the effect of heating rate on the removal of polypropylene from the porous alumina cylinder at 300 °C. At a heating rate of 10 °C/minute, polypropylene removal is complete by 100 minutes. In contrast, the removal time at 1 °C/minute heating rate is about 350 minutes. This too is qualitatively in agreement with observations in practice.
While the above approach allows us to account for the effects of furnace cycle, the model assumes that any gaseous burnout product is instantaneously removed from the component. Thus, diffusion effects on debinding rates are ignored in the above approach. An alternative model developed by German incorporates diffusion effects on binder removal rates [8]. In the present study, German’s model was adapted to describe the removal rate in terms of the radial movement of the binder front from the surface to the center of the part and is represented in Equation 2.

\[
\frac{dr}{dt} = \frac{d_p \Delta P U \varepsilon^2}{4r(MkT)^{0.5}}
\]  

(2)

where, \( r \) is the radius of the cylinder, \( t \) is the debinding time, \( T \) is the debinding temperature, \( \varepsilon \) is the porosity in the cylinder. \( d_p \) is the particle diameter. \( k \) is the Boltzmann’s constant. \( M \) is the molecular weight of gas, \( U \) is the molecular volume of gas, and \( \Delta P \) is the pressure drop between the radial position and the surface of the cylinder. Thus, the model can be additionally used to capture the effects of particle size, solids loading, and the gaseous binder degradation product. By combining Equation 2 with the unsteady state conduction equation for a cylinder used by Tsai, one can account for both heat and mass transfer effects.

Figure 5 shows the effect of particle size on the removal of polypropylene from a porous alumina cylinder of 1 cm radius at 300 °C. It can be seen that the radial binder front recedes considerably faster for the 25 μm particle compared to the 0.5 μm particle. Figure 6 shows the effect of component size on the radial movement of the binder front for a porous alumina cylinder under the same heating conditions. In qualitative agreement with observations in practice, the component of 0.1 cm radius undergoes complete removal within 10 minutes while the component of 1 cm radius takes considerable longer.

**IMPLICATIONS OF THE SIMULATION RESULTS**

The preceding analysis presents an overall approach for computing thermal debinding rates as a function of common material and processing variables. This analysis can now be used to prescribe the upper limits on debinding rates, as dictated by requirements for defect avoidance. The hypothesis underlying the analysis is that the strength of a component should exceed the thermally-induced stress within the component.

The thermally-induced stress within the component during thermal debinding can be represented by the pressure buildup due to the formation of the gaseous binder product. Adapting the analysis of Tsai [7], the pressure buildup, as a function of material and process variables is shown in Equation 3.

\[
P = (1 + p b_1 b_2 g)^{0.5}
\]  

(3)

where, \( p \) is the parameter accounting for particle effects and is given by \( 180/(1 - \phi)^3 d_p^{-2} \), where \( \phi \) is the solids loading and \( d_p \) is the diameter of the particle; \( b_1 \) is the parameter accounting for the characteristics of the burnout gas and is given by \( (\mu/M)RT \), where \( \mu \) is the viscosity of the gas and \( M \) is the molecular weight; \( b_2 \) is the parameter accounting binder degradation: \( (-dS/dt)/(1-S)^3 \) where \( S \) is the saturation of pores and is related to the instantaneous amount of binder, as determined by TGA; and \( g \) is the parameter for component geometry is given by \( kR^2 [1 - (r/R)^2] / v \), where \( k \) is the cylinder radius, and \( r \) is the location of the gas pocket. Details of Equation 3 have been presented earlier [9].

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A microstructural model has been previously developed to describe the in situ strength evolution during thermal debinding [9]. The treatment captures several physical origins of the evolved strength, $\sigma_{SE}$, arising due to various particle characteristics as well as the presence of a wetting liquid. The component strength can be expressed by the following equation:

$$\sigma_{SE} = N_c \phi F_p / (\pi d_p^2)$$  \hspace{1cm} (4)$$

where, $N_c$ is the coordination number, $\phi$ is the solids loading, $d_p$ is the particle diameter, and $F_p$ is the interparticle force. The general nature of the above relationship has been developed to quantitatively treat processes such as agglomeration [10] and liquid phase sintering [11] and have, as such, been verified experimentally in these contexts.

Equations 3 and 4 can be combined to assign limiting values to thermal debinding rates computed by the model in this study. Refinement of these models will be achieved by experimental analysis using a combination of tools:

a) kinetics and thermochemistry of binder decomposition using a state-of-the-art thermal analyzer interfaced with an infrared spectrometer

b) in situ strength evolution using a three-point bend test in a batch temperature

c) pressure distributions using fiber optic sensors

d) in situ monitoring of distortion in a furnace using video imaging

The combination of experimental and modeling techniques described in this paper will enable a quantitative understanding of the material, process and component geometry variables affecting the microstructure prior to sintering. Such an understanding can then be linked with sintering models to relate the pre-sintered microstructure to densification and distortion following sintering. The ultimate benefits of the proposed research program will be to enable the intelligent selection of polymers, powders, and process conditions that yield desired microstructures, properties and dimensional tolerances for any given geometry. Such approaches will aid the development of new materials and process refinements, resulting in improved products obtained from hybrid powder-polymer and sintering technologies such as powder injection molding, die compaction, extrusion, rapid prototyping, slip casting, tape casting and agglomeration.

CONCLUSIONS

A modeling approach has been developed to account for binder evolution from a component as a function of various thermal debinding material and furnace cycle parameters. Predictions of the model were evaluated for the removal of polypropylene from a porous alumina cylinder. The relevant parameters used in the model can be evaluated by a combination of experimental methods. The experimental protocol identified in this paper will enable the validation and refinement of the model. The consequence of this work is to eliminate the trial-and-error associated with identifying optimal thermal debinding conditions that maximize debinding rates while avoiding component distortion.

REFERENCES


Figure 1. Schematic representation of binder burnout from a porous component.
Figure 2. Sigmoidal decomposition curves obtained from thermogravimetric analysis (TGA) of polypropylene under two different atmospheres.

Figure 3. Effect of hold temperature on binder removal from a porous alumina cylinder of 1 cm radius.
Figure 4. Effect of heating rate on binder removal from a porous alumina cylinder of 1 cm radius.

Figure 5. Effect of particle size on binder removal from a porous alumina cylinder of 1 cm radius.
Figure 6. Effect of component size on binder removal from a porous alumina cylinder.