In situ Monitoring of the Dimensional Changes and Mechanisms During Solvent Debinding

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ABSTRACT

Binder removal is an important step in the powder injection molding (PIM) process. During debinding, thermal expansion, polymer swelling, and binder extraction cause dimensional changes that may affect final component dimensions. Dimensional changes during solvent debinding have not been studied extensively because, in the past, it was difficult to measure samples during debinding without contacting them and disrupting the accuracy of the observations. In an effort to overcome this problem, a non-invasive laser dilatometer was designed for precise *in situ* monitoring of the dimensional changes of components during the solvent debinding stage of the PIM process. Through utilization of the laser dilatometer, as well as debinding rate observations, an extensive analysis of the solvent debinding process has been developed and new insight into the significant mechanisms has been made.

INTRODUCTION

Powder injection molding (PIM) is recognized as an effective process for the production of complex components for various industries [1]. Unfortunately, the PIM industry's inability to produce large, highly asymmetric components within the projected dimensional tolerances and without defects has been a major limitation [2]. Some of this variability is due to the large amounts of dimensional change that occur throughout the process. The majority of this dimensional change results from sintering, during which 25 to 30% shrinkage occurs [1]. Significant dimensional change can also occur during the solvent debinding process, which has been a widely adopted debinding process used in conjunction with a subsequent thermal debinding cycle. Consequently, the quantification of dimensional change during solvent debinding has become an important topic of research.

These studies have examined the effect of binder content, temperature, and debinding solvent on the dimensional change occurring during solvent debinding and made insights into the mechanisms acting during the process [3-9]. PIM components experience dimensional change due to swelling and thermal

expansion in a heated solvent. While the observed dimensional change is far less than the shrinkage occurring during sintering, it is significant when compared to dimensional tolerances of PIM components and can cause sufficient stress for the formation of defects such as cracking or distortion[2, 4].

Unfortunately, the main technical limitation of this research has been an inability to find a reliable method to measure the *in situ* dimensional changes [4]. All previous studies have utilized dilatometers that have used force or contact with a push rod or measuring apparatus to make *in situ* dimensional observations, which can cause local deformations, exert force resulting in creep defects, or result in disruptions to the solvent debinding mechanisms. Therefore, the objective of this study was to use a truly non-invasive, high precision laser dilatometer to record *in situ* dimensional changes during solvent debinding.

In this study the effects of four binder compositions and three debinding temperatures were analyzed. These results were then compared with mass loss observations during debinding in order to investigate the mechanisms and stresses associated with solvent debinding.

EXPERIMENTAL PROCEDURE

1. Feedstock Characteristics

The feedstock used for this study consisted of carbonyl iron powder and four different combinations of paraffin wax (PW), polypropylene (PP), and surfactants. Two different densities of PW—low density (LD) and high density (HD)—were used in this study. The binder polymer characteristics are given in Table 1. The binder compositions, shown in Table 2, were selected to emphasize the differences in dimensional change behavior due to PW density and content. The feedstock was mixed in a sigma blade mixer and granulated.   Rectangular bars, 63.5 mm $\times$ 12.7 mm $\times$ 3.175 mm, were molded using a reciprocating screw molding machine.

Table 1: Binder polymer characteristics

Binder Component	Abbreviation	Pycnometer Density (g/cm^3)	Melting Temperature (°C)
Paraffin Wax (Low Density)	PW(LD)	0.8900	52.8
Paraffin Wax (High Density)	PW(HD)	0.9173	65.6
Polypropylene	PP	0.8996	142

Table 2: Feedstock characteristics

Feedstock Identification	Binder Description	Viscosity at 140°C (Pa-s)
LD-LC	Low PW Density, 60% PW Content	106.6
HD-LC	High PW Density, 60% PW Content	111.8
LD-HC	Low PW Density, 40% PW Content	35.7
HD-HC	High PW Density, 40% PW Content	46.5

2. *In Situ* Dimensional Measurements

The molded components were debound by immersion in a heated heptane bath incorporated with a self-designed laser dilatometer. The dilatometer was used to measure the *in-situ* dimensional changes occurring during solvent debinding without specimen contact. For testing, a molded, weighed component was placed on a porous substrate so the longest dimension was monitored, as shown with a top-view in Figure 1.
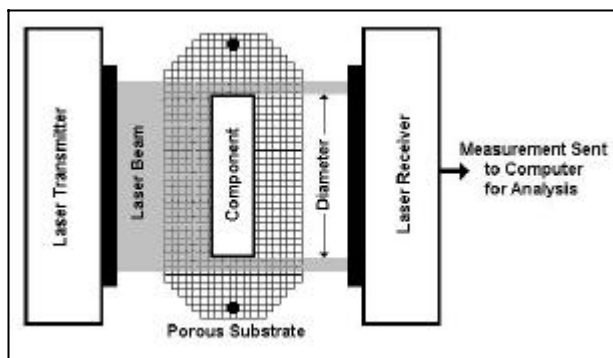

Figure 1: Schematic drawing of measurement with the laser dilatometer

The solvent, contained in a transparent debinding tank, was preheated using a solvent heat circulator. Brief measurements were made in air to establish an initial sample dimension then the component was immersed, with dimension measurements continuing throughout the process. Initially, convection waves due to the temperature difference between the sample and the surrounding solvent disrupt measurements, but precise measurements are attained after about 90 seconds. During debinding, the solvent bath was covered to avoid excess solvent evaporation. After predetermined periods of time, the solvent bath was uncovered and the sample was extracted.

3. Soluble Binder Mass Loss Observations

In order to relate the dimensional change to mass loss due to solvent extraction of soluble polymers, mass loss observations during solvent debinding were performed. Molded components were initially weighed, placed on a porous substrate, and debound in a heated, stationary solvent bath. Samples were removed from the solvent at predetermined intervals of time, allowed to dry completely, and weighed again. Mass loss, by percentage, was calculated as a function of the calculated amount of PW initially present in the individual sample.

RESULTS AND DISCUSSION

Solvent debinding phenomena have been illustrated both empirically and theoretically using a variety of measurement tools. The objective of this paper, however, is to use quantitative data from non-invasive observation techniques to explain the mechanisms of solvent debinding.

1. Solvent Debinding Mechanisms

Solvent debinding is best defined as a four-stage process by which soluble polymer binder constituents are dissolved due to reaction with a heated solvent, and removed from the PIM component by capillary forces. The first stage of solvent debinding is the diffusion of the solvent into the binder, followed by the

interdiffusion of the solvent and binder. During these first two stages, the solvent diffuses into the polymer to produce a swollen gel. This polymer swelling may be all that occurs if, for instance, strong intermolecular forces or cross-linking exist between the polymer molecules. However, if the solvent-polymer interactions are sufficiently strong enough to overcome the intermolecular forces, the polymer will dissolve into a true solution in the third stage of solvent debinding. Finally, the solvent-binder solution is diffused to the surface of the component [3, 8-10].   This inward progression of debinding leaves fine pore channels behind, which increase in size with time, and produce a network of tortuous paths. These paths, which are much longer than the bulk thickness of the component, serve as conduits for the diffusing solvent-binder solution [1,11-12].

It has been shown that the rate of the solvent debinding process is controlled by two distinctly different mechanisms throughout the solvent debinding process [3,13]. The rapid initial solvent debinding rate is controlled by dissolution of the polymer into the solvent, which is limited only by the dissolution of polymers across a short binder-solvent interfacial distance [3]. As debinding progresses, the rate-limiting mechanism of debinding changes from dissolution of the binder to diffusion of the dissolved binder through the pores created within the component [13]. The inward progression of the binder-solvent interface causes the diffusion distance to increase and the debinding rate to decrease, since the dissolved soluble binder cannot be diffused as quickly. Therefore, diffusion becomes the rate-limiting step for the duration of the solvent debinding process.

2.   Dimensional Change During Solvent Debinding

The solvent debinding process results in the extraction of soluble binders from the PIM component, but it also causes length change due to thermal expansion, polymer swelling and a decrease in mass [3-9]. Initially, thermal expansion causes a rapid expansion within the PIM component as it is submerged in a heated solvent [3-8]. Following the initial thermal expansion is a gradual increase in dimension caused by the swelling of soluble and insoluble binder polymers as they interact with the debinding solvent [3,8]. During the intermediate stages of solvent debinding, the binder/solvent interface recedes deeper into the component slowing the debinding rate. Since soluble binder polymers cannot be extracted quickly, they form a swollen gel within the component, causing a transient increase in dimension [8]. During the later stages of debinding, insoluble binder polymers are exposed to the solvent and gradually swell, also increasing the component's dimensions. The magnitude of dimensional change is dictated by a variety of factors including temperature, binder content, and the molecular weight of the debinding solvent.

The *in-situ* dimensional change of PIM components during solvent debinding varies significantly. Figures 2, 3, and 4 show the dimensional change curves observed for components molded with each of the four binder systems debound in a heptane solvent heated to 40, 50, and 60°C, respectively. The mechanisms illustrated in these plots will be explained in detail, but a simple qualitative analysis exhibits the large difference in behavior of four, similar binder systems.
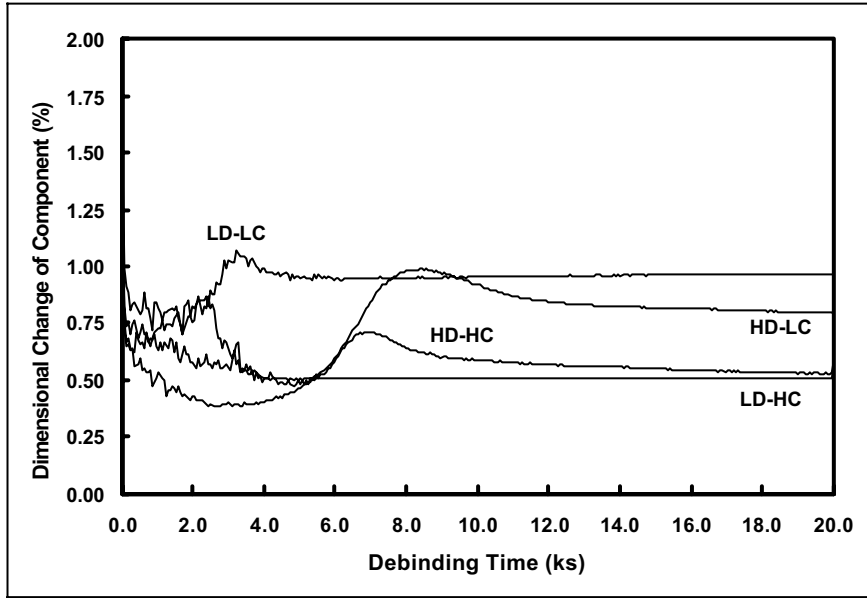
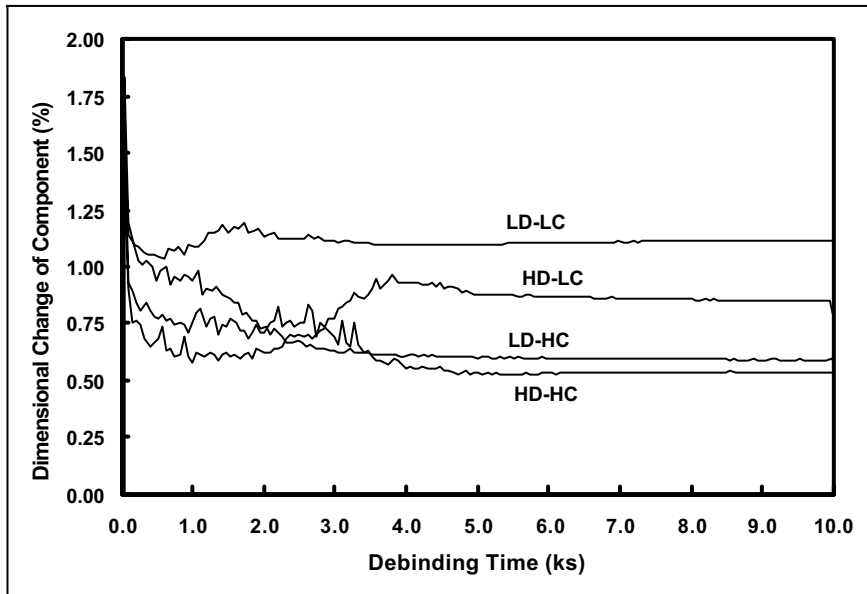**Figure 2: Effect of binder composition on length change of component debound in 40°C heptane.**

Figure 3: Effect of binder composition on length change of component debound in 50°C heptane.
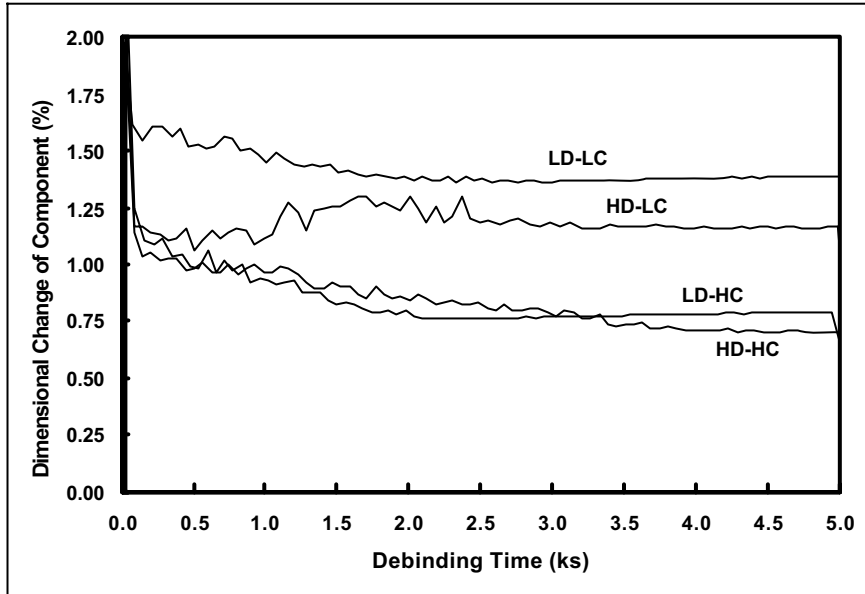
Figure 4: Effect of binder composition on length change of component debound in 60°C heptane.

3.   Effect of Temperature

Figure 5 shows the effect of solvent temperature on the dimensional change during solvent debinding of PIM components formed with the same binder system, LD-LC. Although this is a plot of only one of the four binder systems observed in this study, it can sufficiently serve as a basis for explanation of the general solvent debinding mechanisms. The plot shows the dimensional change behavior of three components, each with the same composition, when immersed in 40, 50, and 60°C heptane for 20, 10 and 5 ks, respectively. Observations were stopped once the component was extracted from the solvent. As can be seen, the final swelling of the components is directly related to the increasing solvent temperature, but a complex relationship exists between solvent temperature and the intermediate swelling depicted by the transient peak in the curves at 40 and 50°C.
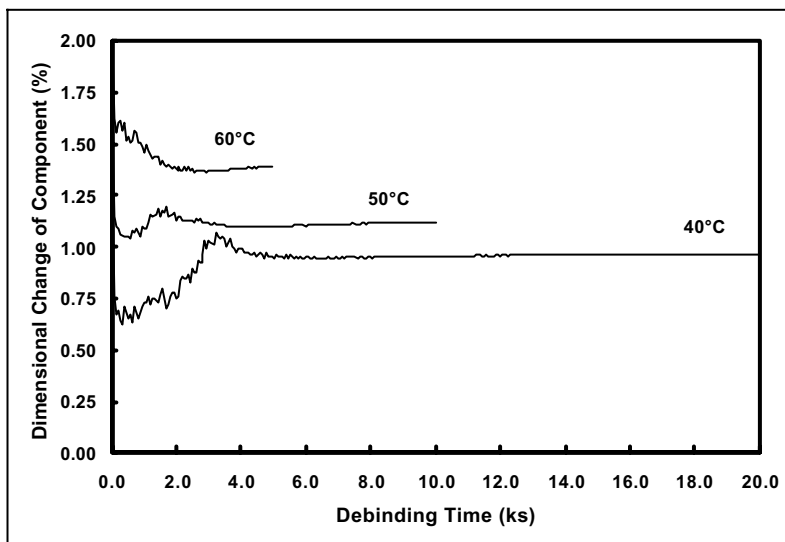

Figure 5: Effect of temperature on dimensional change of a component molded with the LD-LC binder debound in heptane at 40, 50 and 60°C for 20, 10 and 5 ks, respectively.

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At 40 and 50°C, the components exhibit a peak in the dimensional change curves. This is due to three factors: insoluble polymer swelling, thermal expansion, and temporary soluble polymer swelling. As previously described, polymer dissolution is a two-step process during which solvents diffuse into the polymer molecules to form a swollen gel, and the swollen gel dissolves to form a true solution that is extracted via capillary forces from the component [1,10]. Evidence suggests that when the rate of soluble polymer dissolution is impeded by a deep binder-solvent interface and low solvent temperature, the swelling can be significant enough to cause expansion of the entire PIM component. The effects of the soluble polymer swelling can clearly be seen, represented by the peaks of the swelling curves in Figure 5.

The peaks due to soluble polymer swelling aren't as significant at higher temperatures, though. German [1] observed that faster debinding rates are always possible at higher temperatures. In terms of dimensional change, higher solvent temperatures, and subsequently faster debinding rates, lead to a decrease in intermediate soluble polymer swelling, which could possibly lead to a decrease in swelling-induced defects. Unfortunately, high solvent temperatures also increase the probability of forming defects or distortions within the PIM component [1]. An optimal temperature must be determined for solvent debinding at which swelling-induced dimensional change and temperature-induced defects are minimized.

4.   Effect of Paraffin Wax Content

Lin and Hwang [4] observed that a decreased amount of PW actually resulted in an increased amount of time necessary to complete debinding. This was attributed to the assumption that the subsequent increase in insoluble binder resulted in greater swelling, which clogged the developing pores, thus impeding solvent extraction. It was also observed that decreased soluble binder content results in greater swelling of PIM components. The dimension and soluble binder mass change plots in Figure 6 emphasizes the observation that greater amounts of PW actually result in more rapid debinding as well as less significant dimensional change. In the component with a greater amount of PW, labeled LD-HC, there is more soluble polymer dissolved by the end of the process. This results in less late-process thermal expansion, less swelling and, therefore, less observed dimensional change.
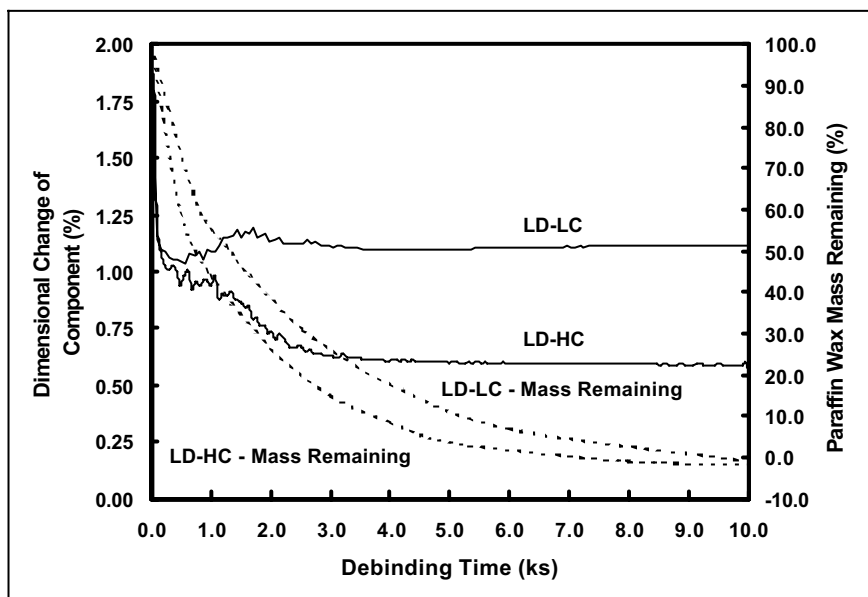

Figure 6: Effect of PW content on the length change and soluble binder mass loss of components debound in 50°C heptane.

5. Effect of Paraffin Wax Density

Although many of the process variables regarding solvent debinding have been considered in previous research, the density of the soluble binder has not, although it determines much about the debinding rate. In this study, two densities of PW were considered. Figure 7 displays the effect of density on the dimension and soluble binder mass change behavior of PIM component immersed in 50°C heptane for binders containing low soluble binder contents.
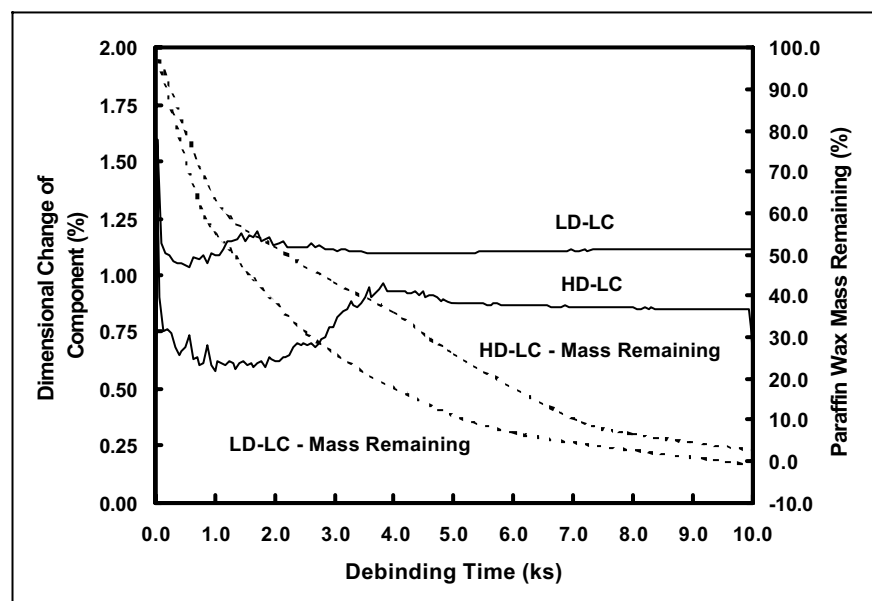

Figure 7: Effect of PW density on the length change and soluble binder mass loss of components debound in 50°C heptane.

PW density affects both intermediate and final swelling of the component. In Figure 7, the intermediate swelling in the component with the higher density PW, labeled HD-LC, exhibits a later, more dramatic swelling peak associated with the swelling of the soluble binder. Since an increase in PW density results in a decrease in dissolution rate, the binders cannot be extracted as quickly and the debinding rate is subsequently slower. Therefore, they remain within the component's interior, swell due to interaction with the solvent, and result in a significant intermediate peak in the dimensional change of the component occurring while the insoluble binders have been softened by solvent interactions.

PW also affects the final swelling of PIM compacts. As seen in Figure 7, the final swelling is lower for components with a higher PW density, yet the components have equal quantities of backbone binder. As mentioned, a higher PW density is associated with a slower debinding rate. During solvent debinding, the extraction of soluble binders exposes the insoluble backbone polymers to the heated solvent resulting in expansion due to swelling. When the solvent debinding rate is impeded by slow polymer dissolution associated with high density PW, less insoluble binder is exposed to the solvent. Therefore, final swelling decreases as soluble binder density increases.

6. Relationship Between Mass Loss and Dimensional Change

The results of this research suggest a relationship between *in-situ* mass loss and dimensional change during solvent debinding. Shivashankar and German [13] observed a transition in the rate-determining mechanism from dissolution to diffusion during solvent debinding. Close investigation of the current results show, not only a transition from dissolution- to diffusion-controlled solvent debinding, but also a strong correlation between the changes in gradient of the two curves.

As an example of this behavior, Figure 7 shows the dimensional change and mass loss due to the extraction of PW for components molded with high and low PW densities and immersed in 50°C heptane. As would be expected, higher PW density results in slower debinding. Also, as shown, the initial debinding rate is rapid in the case of both PW densitie s, exhibited by the steep initial slope of the mass loss curve. A significant change in slope appears, however, as the debinding rate becomes controlled by diffusion of the dissolved polymer molecules from the compact. This change in slope and rate-controlling mechanism occurs at the same time as a significant change in the slope of the dimensional change curve. A similar relationship can be observed in Figure 6, where slope changes in the dimension and soluble binder mass change curves occur at the same time. Therefore, it is likely that the concurrent observed changes represent a relationship between the mass loss, dimensional change, and solvent debinding mechanism.

The concurrent change in mass loss and dimension suggests that the increased distance between the binder-solvent interface and the component surface is impeding the diffusion of soluble polymer molecules. Therefore, the polymer molecules are interacting with the solvent and subsequently swelling more rapidly than they are being diffused out of the compact. Due to the swelling of these trapped soluble polymers, the dimension is increasing due to the internal stress from swelling, and the debinding rate is slowing.

Analysis of mass loss and dimensional change during later solvent debinding shows another change of slope in the mass loss curve coinciding with the diminishing dimensional change peak. The decreasing swelling peak suggests that the swollen polymer gel within the component is being diffused out of through the surface. Once these previously swollen polymers have been extracted, the debinding rate abruptly slows, due to a reduction in solid soluble binder. Further analysis of the relationship between these phenomena will yield good insight into the mechanism of the solvent debinding process, and could aid in the reduction of related component defects.

CONCLUSIONS

A non-contacting laser dilatometer was developed and is able to measure *in situ* dimensional changes of powder injection-molded components during solvent debinding. The dimensional change of components with four different binder compositions was observed along two axes in heptane at three temperatures.

The dimensional change curves for length-measured components exhibit two characteristic stages—a transient intermediate peak and final swelling. The intermediate peak is caused by the swelling of soluble polymers and increases with higher PW density and lower solvent temperature. The final swelling is caused by the swelling of insoluble backbone polymers and increases with insoluble binder content and temperature.

Results suggest a relationship between *in situ* dimensional change and solvent debinding rate. Decreases in the debinding rate are concurrent with increases in the dimension of the component, which is due to the swelling of soluble polymers. Further investigation into the parameters of PIM feedstocks and solvent debinding will result in a more precise understanding of the mechanisms acting during the process.

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