Effect of thermo-mechanical properties of PIM feedstock on compacts shape retention during debinding process[①]

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[Abstract] The removal of the binder from the powder compacts (debinding) can be a slow step and a source of problems. To improve the debinding process of powder injection molding operation, it's necessary to understand the thermal and mechanical properties of powder injection molding feedstocks and to find the major causes responsible for molding difficulties and compacts shape retention during debinding process. The effects of thermo-mechanical properties of the PIM feedstock on the compacts shape retention during debinding process were discussed and explained from practical point of view. The results indicate that the heat of fusion affects the cooling time. The binder component with high heat of fusion and high decomposed temperature is more effective as the second binder component for the compact to retain its shape during debinding.

[Key words] thermo-mechanical properties; shape retention; debinding; thermal stresses

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1 INTRODUCTION

Among critical issues in the powder injection molding process there are the control and avoidance of distortion during thermal debinding and the minimization of stresses in the compact after die filling[1]. After molding the strength of the compacts is dependent on the particles size and shape, solids loadings, and the interfacial adhesion between the powder and the binder. During thermal debinding the compact strength reaches a minimum due to softening and decomposition of the binder whereupon relaxation of the internal residual stresses relieved to some extent[2]. The release of these stresses generally results in corresponding strains. For polymer moldings, this may not be a serious problem but the objective in powder moldings is to position the particles for sintering. Small organized displacements from these positions caused by release of residual stresses may result in large domains of particles failing to make contact with their neighbors at the start of sintering. The origin of stresses developing in the component during thermal debinding can be traced to the residual stresses due to thermo-mechanical properties of the PIM feedstock, molding conditions, evolution of burnout gases, and strain due to thermal gradient[3].

The aim of this work is to study the effect of the mechanical and thermal properties of the powder injection molding feedstock on the powder injection molding compacts shape retention during debinding process. Much has been published on the stresses and its effects on distortion during debinding[1,4~11].

Kostic et al[10] found that the stress distributions are strongly influenced by control sprue solidification time and there is steep changes in pressure in molding during the course of solidification, which widens the residual stress distribution. Fox[11] has studied warpage and fracture in green parts due to residual stresses created during cooling. He concluded that the green part exhibits viscoelastic behavior during cooling and that cooling generated stresses lead to internal fractures and asymmetric cooling lead to warpage. James[1] studied the mechanical behavior of compacts at a typical temperature for molding and the initial steps of a thermal debinding. He found that the feedstock is not purely viscous at molding and initial thermal debinding temperature, but displays a combination of viscous, elastic and plastic behavior.

2 EXPERIMENTAL

The metal powder used in this study was gas atomized 17~4 ph stainless steel powder (BASF Germany). The particle size distribution of this powder is $d_{10} = 5\,\mu m$, $d_{50} = 12\,\mu m$, $d_{80} = 22\,\mu m$, and average particle size of $12\,\mu m$. Apparent density and tap density of the powder are $3.92\,g/cm^3$ and $4.70\,g/cm^3$ respectively. A binder system based on paraffin wax was used in this study. The minor components were poly ethylene vinyl acetate (EVA) and high-density polyethylene (HDPE). Stearic acid was included as a surface active agent. The binder system characteristics are shown in Table 1. The same binder was utilized for all experiments although the binder content

was selected to make different feedstocks. Four mixtures with different binder contents were prepared to investigate the effect of powder loading. The feedstocks were then produced by mixing this binder system with stainless steel powder in a LH60 Roller mixer for 2 h.

Table 1   Composition of binder systems

Component	Composition/%	t_m/ ℃	ρ/ (g·cm^{-3})
PW	65	58	0. 91
HDPE	10	139	0. 98
EVA	20	80	0. 96
SA	5	66	0. 96

TGA experiments were carried out in a nitrogen atmosphere at a rate of 10 ℃/min on a Dupont 9900 thermal analyzer. The feedstock was injection molded on an SZ-28/250 injection-molding machine after granulation on a LSJ20 plastic extruder. The thermal debinding was performed in a hydrogen atmosphere. The sintering was carried out in vacuum atmosphere at 1350 ℃ for 1 h. A statistical method was used to evaluate the compact shape retention during debinding. A number of samples were molded in each step and the distorted compacts were collected from the total number of samples in each step to calculate the percentage of distorted compacts. The standard deviation in the dimensions shrinkage measured after molding and sintering was used as the measure of distortion for the sound compacts. A disc shaped with 20 mm in diameter and 4 mm in thickness, MIM standard tensile specimen and a rectangular bar with 42 mm in length and 5 mm in both width and thickness, were the three different shapes that were used for comparison.

3   RESULTS AND DISCUSIONS

3. 1   Effect of mechanical properties

The behavior of the molded compacts during debinding makes evaluation of the mechanical properties very important. The uniformity of the feedstock is critical[12]. In general, the higher the powder loading, the less the distortion occurs during debinding (Fig. 1, first section) and the small shrinkage during sintering (Fig. 2).

From Fig. 1 it can be concluded that the higher the powder loading, the lower the distortion occurs during debinding up to 64% to 68% powder loading. An excess of binder will cause compact slumping, since the particles will settle or migrate during debinding, which is clear in the first section of Fig. 1. On the other hand, lowering binder content at which the viscosity approaches maximum value deteriorates flowability or moldability of feedstock and leads to the
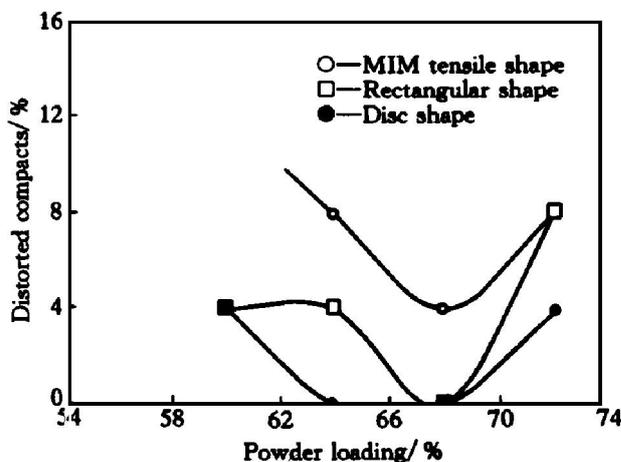

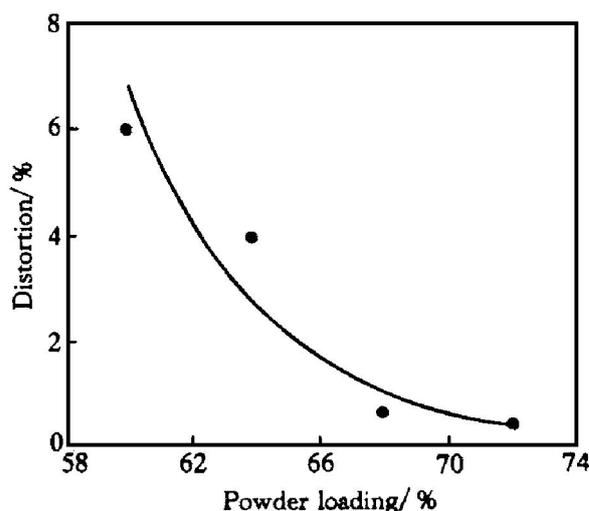**Fig. 1**   Percentage of distorted compacts at various powder loading and sample shapes

Fig. 2   Standard deviation in dimension shrinkage as measure of distortion against powder loading

occurrence of molding voids. During debinding, these voids cause cracking due to internal vapor buildup as shown in the second section of Fig. 1.

Powder-binder mixtures are viscoelastic materials that are characterized by a combination of elastic and viscous response[13]. The elastic component is similar to the stress-strain behavior of a spring (Hooke's law), while the viscous behavior is a kin to a dashpot (Newton's law)[14]. By applying a sinusoidal cycle of strain to a viscoelastic material, it is possible to record the stress. The compact stress due to the viscoelastic behavior of the powder injection molding feedstock is

$$\tau = \tau_0 \exp(-(G/\eta)t) \qquad (1)$$

where τ is compact stress, τ_0 is original stress, and t is measured time. There is a time period over which the stress τ will decay after straining.

$$\tau = \tau_0 \exp(-t/t_r) \qquad (2)$$

where t_r is relaxation time period. A short relaxation time is desirable to minimize retained stress and to avoid distortion after ejection. In the mixture, the elastic modulus influences the compact molding and distortion during debinding. Usually the modulus de-

creases as temperature increases, but the relaxation of stresses due to the difference in thermal expansion coefficients between the powder and binder can complicate the behavior. The resistance to creep is important to compact shape retention and to avoid distortion due to stress relaxation during debinding.

3. 2 Effect of thermal properties

After the molds are filled, heat is extracted from the feedstock through the die. The prediction of a given molded part's temperature history, and subsequent development of stresses, which are due to the cooling history, is very important[15]. The powder-binder mixture cools more rapidly than the common thermoplastics, allowing more opportunity for large thermal stresses[16]. The rate of cooling depends on the heat capacity of the mixture, heat of fusion and heat flow rate. The heat flow rates of the feedstock as a function of temperature and heating rate measured by Perkin-Elmer DSC-7 are plotted in Fig. 3.
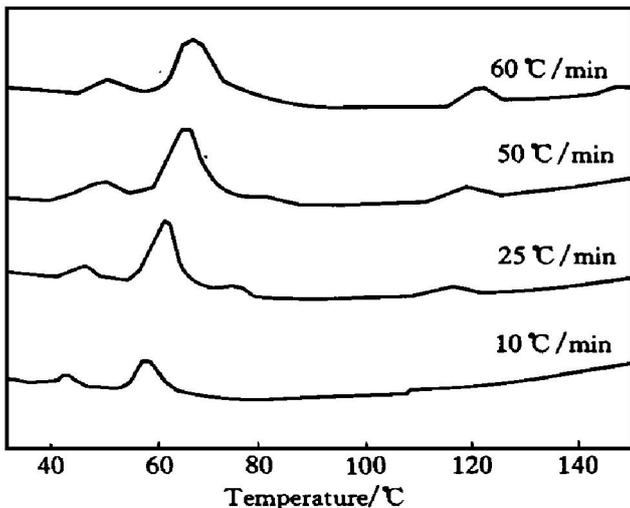

Fig. 3   Differential scanning calorimetry for feedstock at different heating rates

The heat of fusion and melting points for the feedstock as a function of heating rate calculated from the DSC curve are listed in Table 2. It shows that there are three temperature peaks in each heating rate. The first one was caused by paraffin wax and stearic acid. EVA caused the second peak and the third peak was caused by HDPE. These temperatures are slightly lower than the melting points of those binders measured independently, as given in Table 1. This indicates that all three components interacted to a certain degree but did not completely dissolve into each other. The heat of fusion and melting temperature increased with increasing heating rate. The heat of fusion of the second peak caused by EVA is the highest one, the next is the first peak caused by PW and SA and the third peak caused by HDPE is the lowest one. The heat of fusion affects the cooling

Table 2   Melting temperature (t_m) and heat of fusion (ΔH) of feedstock

Heating rate /($°C·min^{-1}$)	Peak 1		Peak 2		Peak 3	
	t_{m1} /$°C$	ΔH_1 /($J·g^{-1}$)	t_{m2} /$°C$	ΔH_2 /($J·g^{-1}$)	t_{m3} /$°C$	ΔH_3 /($J·g^{-1}$)
10	43. 1	0. 41	58. 5	3. 34		
25	45. 9	0. 44	60. 8	3. 38	115. 3	0. 37
50	48. 8	0. 42	64. 0	3. 52	117. 6	0. 36
60	50. 4	0. 48	65. 8	3. 46	118. 3	0. 45

time. It takes more time for the feedstock with a larger heat of fusion to cool to room temperature, and the feedstock with lower heat of fusion cools rapidly, allowing more opportunity for large thermal stresses[16]. This means that the EVA as the second binder component with higher heat of fusion is more effective for the compact to reduce the thermal stresses and to retain its shape during debinding.

The compact contains stresses due to the differences in thermal properties between the binder and powder, given by

$$\sigma = E_b \Delta T (\alpha_b - \alpha_p) \tag{3}$$

where σ is the stress, E_b is the elastic modulus for the binder, α_b and α_p are the thermal expansion coefficient of the binder and powder, and ΔT is the temperature change. The feedstock must exhibit a large viscosity increase on cooling, with a high final yield point, low thermal expansion coefficient, and high creep resistance. Internal stresses can be minimized by progressive binder removal.

Many different binders can be found in the literature, binders based on waxes are most common because powder injection-molding compacts formed with wax-based binders exhibit less residual stresses and better shape retention in debinding[17, 18]. Binder component with high-decomposed temperature is effective as second binder component. The thermo-gravimetric analyses (TGA) of the binder system compositions and feedstock used in this study are shown in Figs. 4 and 5.

From Fig. 4 we can find that the decomposed temperature of SA, paraffin wax, EVA and HDPE are 160, 188, 348 and 430 °C respectively. The softening point of HDPE is higher than that of SA, paraffin wax and EVA. This means that the SA in low temperature range will so easily decompose and leave a pore channels. The mixed binder showed a three-stage decomposition behavior, as shown in Fig. 5, the first stage completed at 350 °C, the second completed at 400 °C and the third completed at 500 °C. The mass loss in the first stage was caused by paraffin wax and stearic acid, which accounts for 80% of the binder. As the temperature further increased, the high temperature polymer began to decompose. EVA, which accounts for 20% of the
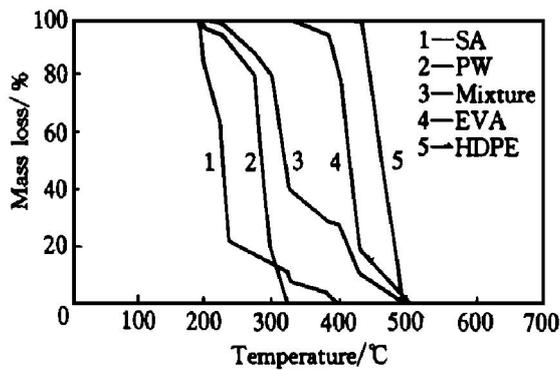
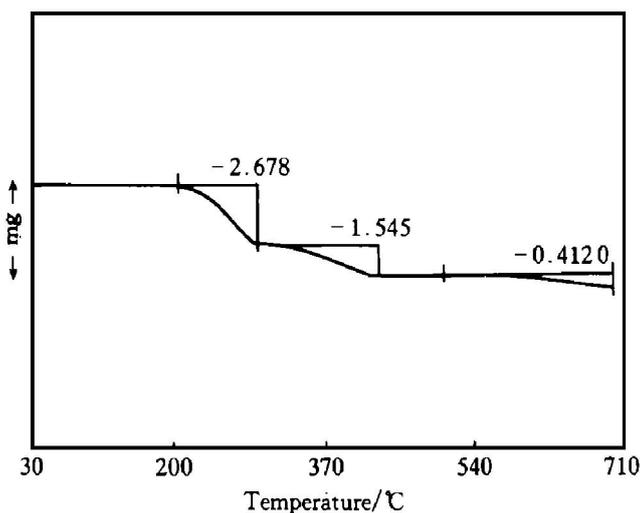**Fig. 4** Thermogravimetric analysis curves
for binder components

Fig. 5 Thermogravimetric analyses for feedstock

binder, caused the second stage decomposition and the third stage was caused by HDPE as shown in Fig. 5. This means that the decomposition temperature of HDPE is higher than that of EVA. So, the HDPE is more effective as a second component of the binder for the compact to retain its shape during debinding.

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