Study of hyperbranched polymer on POM-based binder in metal injection molding

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Abstract

Metal injection molding POM-based binder and related catalytic debinding technology have been widely applied in the MIM industry. However, the POM-based binder has a high viscosity and poor flow performance. The products are prone to produce wrinkles and cracks, which restrict their application in many materials and fields. Therefore, improving and developing POM based binder system has become the research focus of the system. In this research, hyperbranched polymer was used as a modifier of POM-based binder, and the fluidity, uniformity and thermal properties of the feedstock were analyzed. Meanwhile, the influence of the content of hyperbranched polymer on the green part, brown part and the sintered part was also studied. The results indicated that the fluidity and uniformity of the feedstock are both improved as the content of hyperbranched polymer increases and the hyperbranched polymer can improve the flexural strength and impact strength of the green part. Furthermore, the addition of the hyperbranched polymer can improve the tensile strength and dimensional accuracy of the sintered part.

1. Introduction

Metal injection molding (MIM) is a new powder metallurgy near net shape forming technology combined with powder metallurgy technology and plastic injection molding technology [1–4]. It mainly includes feedstock preparation, injection molding, binder removal and sintering processes [5–7]. The binder used in feedstock is the core of metal injection molding, and it has always been one of the research hotspots of MIM [8].

The POM-based binder uses catalytic debinding technology to depolymerize polyacetal in an acidic atmosphere [9–14]. Large-size parts can be quickly and defect-free degreased since no liquid phase is generated during the debinding process, nor are the deformation and cracking. Polyformaldehyde (POM) is a linear polymer compound containing [−CH₃−O−] chains in the main chain of molecules. It is a linear polymer with high density and high crystallization without side bases, and has excellent comprehensive properties. POM is the main component of POM-based binder, which provides fluidity and shape retention for feedstock mixed with metal powder. In recent years, many scholars have researched and developed POM-based adhesives. Duxin Li et al studied a novel catalytic debinding binder and used HNO₃ as a catalyst to investigate the effects of temperature, time and binder composition on catalytic debinding, which found that the catalytic debinding process requires a higher content of POM. The content is too low and the degreasing effect is very poor [15]. Aiping Wu discovered that EVA can improve the compatibility of the binder system while studying the catalytic debinding binder. The addition of microcrystalline wax can reduce the complex viscosity of the binder.

Xiaoming Xu et al modified the POM-based binder and successfully prepared a porous metal material with good product performance [16]. These researchs provide new theoretical guidance for the development and improvement of POM-based binder systems. However, in the actual use process of the existing POM-based binder, the main problem is that the feedstock viscosity is too high and the equipment wears severely during the injection molding process, moreover the obtained product is prone to defects such as under-injection and crack. The polymer HPN202 is a high molecular weight, highly active terminal hydroxyl hyperbranched polymer based
on an aromatic polyamide hyperbranched polymer. Due to its strengthening and toughing characteristics and high flow, it can be used as a processing aid for thermoplastics such as PP, PE, PS, POM etc to improve rheological properties. In this paper, the existing POM-based binder modified by hyperbranched polymer HPN202 was used to study the effects of adding hyperbranched polymer on feedstock, green part, brown part and sintered part.

2. Experimental procedure

2.1. Materials

In this experiment, 17–4PH gas atomized stainless steel metal powder produced by Osprey Company of the United Kingdom was used. The chemical composition and powder particle size are shown in tables 1 and 2, respectively.

The powder SEM topography is shown in figure 1. The POM-based binder component consists of polyoxymethylene (AsahiKASEI, Japan), high density polyethylene (Yanhong plastic material co. LTD, China), ethylene-vinyl acetate copolymer (Dongguan yingfei plastic import and export co. LTD, China), stearic acid (Tianjin zhiyuan chemical reagent co. LTD, China), and hyperbranched polymer HPN202 (Wuhan Hyperbranched Resin Technology Co., Ltd, China). Among them, POM quality accounts for 78%–83%; HDPE + EVA) quality accounts for 17%; SA quality accounts for 1%; hyperbranched polymer HPN202 accounts for 0% - 5%.

Table 1. Chemical composition of 17 - 4PH stainless steel powder (mass fraction, %).

| Element | Cr | Ni | Cu | Si | Mn | Nb | Mo | N  | O  | C  | P  | S  | Fe |
|---------|----|----|----|----|----|----|----|----|----|----|----|----|----|
| Wt/%    | 16.3 | 4.8 | 4.2 | 0.65 | 0.57 | 0.24 | 0.15 | 0.08 | 0.074 | 0.03 | 0.023 | 0.005 | Bal. |

Table 2. Particle size and size distribution of powder.

| Powder size/μm | D10/μm | D50/μm | D90/μm |
|----------------|--------|--------|--------|
| 22             | 4.0    | 11.9   | 27.6   |

Figure 1. Powder morphology of 17-4PH stainless steel.

2.2. Feedstock preparation and injection molding

In the POM-based binder system, the hyperbranched polymer HPN202 replaces part of POM, and the added amount of hyperbranched polymer accounts for 0 wt%, 1 wt%, 3 wt%, 5 wt% of the total mass of the binder,
The binder component and the 17–4PH stainless steel powder were kneaded in a kneader at a powder loading of 58%. Mixing at 35 rpm for 3 h at 195 °C in a kneader. After mixing, the powder-binder mixture is extruded through a single-screw extruder and crushed by a crusher to obtain a MIM feedstock. The obtained feedstock were marked as F1, F2, F3, and F4, respectively. The feedstock was completed by injection molding at the injection temperature of 195 °C and injection pressure of 90 bar. The shape of the green parts was as it is shown in figure 2.

2.3. Binder removal and sintering
In this experiment, a two-step degreasing method using catalytic debinding and thermal debinding was used. The green part was first placed in a catalytic debinding furnace, using nitric acid as a catalyst and degreased at a temperature of 120 °C for 4 h. The decomposition of polyformaldehyde is formaldehyde, and the formaldehyde gas is decomposed into H₂O and CO₂ through the combustion chamber of the catalytic degreasing furnace. Then the samples were placed in a thermal debinding furnace for thermal debinding. In order to avoid the damage of the brown part due to the low strength of the brown part during the transfer process, the brown part is pre-sintered by raising the temperature to 850 °C based on the original debinding temperature. Lastly the brown part was placed in a vacuum sintering furnace for sintering at a sintering temperature of 1350 °C for 1 h.

2.4. Test methods
The archimedes spiral mold was used to inject the four groups of feedstocks at injection temperatures of 185 °C, 195 °C, and 205 °C. Other injection parameters were all injected at a pressure of 95 bar and injection speed of 75 mm s⁻¹ (Supplementary note: high temperature can easily lead to partial component decomposition of the binder; Excessive pressure and speed may lead to defects such as flying edges and bubbles. Too low temperature, pressure and speed may lead to poor fluidity and failure to fully fill the mold cavity). Then the fluidity of the feedstock was judged by the length of the spiral. The mold is shown in figure 3 and the sample is shown in figure 4. The impact energy of the green part was tested with a JYW-83 simply supported beam impact tester to characterize the toughness with impact work. The bending strength and tensile strength of the green part was tested by Instron 3369 material mechanical testing machine; The morphology of stainless steel powder, green part and brown part was observed by Nova Nano SEM 230 and Quanta FEG 250 scanning electron microscope. TGA test was conducted on the feedstock by using a SDT-Q600 synchronous thermal analyzer, with nitrogen as
a protective atmosphere, and the temperature was raised from room temperature to 550 °C, at the heating rate of 10 °C min$^{-1}$.

3. Results and discussions

3.1. Feedstock performance analysis

3.1.1. Fluidity analysis

The above four feedstocks were injected with archimedes spiral mold at different injection temperatures, and the green part obtained has good appearance and no defects. Figure 5 shows the spiral length of the green part injected by four groups of feedstocks at different injection temperatures. Figure 6 is a green part obtained by injecting four groups of feedstock at 195 °C respectively.

It can be seen from figure 5 that at the same temperature, with the increase of the amount of hyperbranched polymer HPN202, the archimedes spiral length also increases significantly. When the content is 3 wt% (Corresponding to F3 feedstock) and 5 wt% (Corresponding to F4 feedstock), archimedes spiral length is the longest and when the hyperbranched polymer content to 5%, the modification effect of the fluidity is not so obvious. This indicates that the addition of the hyperbranched polymer can improve the fluidity of the POM-based binder. The cause is that the hyperbranched polymer has a highly branched structure, which is difficult to crystallize and has no chain entanglement as compared with the linear macromolecule. The molecular chain itself and the intermolecular entanglement make the intermolecular interaction force small, thereby lowering the viscosity and feedstock fluidity is improved [17–20]. It can also be seen from the figure that for the same feedstock, as the injection temperature increases, the fluidity of the feedstock will also increase. At the same time, we found that when the injection temperature reached 205 °C, a little pungent odor started to be produced.

![Figure 4. Archimedes spiral sample.](image)

![Figure 5. Spiral length of feedstocks at different injection temperatures.](image)
during the process; when the injection temperature was 185 °C, the fluidity of the feedstock was relatively low. Therefore, in combination with the above, 195 °C is the best injection temperature.

3.1.2. Feedstock uniformity analysis
The uneven distribution of the binder between the metal powders, the occurrence of binder enrichment areas, and the failure to uniformly coat the surface of the metal powder will reduce the loading of the feedstock and the uniformity of the green part, and the final product may occur problems such as poor density uniformity and low dimensional accuracy [21]. The image of the SEM of the green part can directly reflect the uniformity of the feedstock to a certain extent. For an ideal feedstock, the binder uniformly coats the metal powder particles without binder enrichment or powder agglomeration. Figure 7 shows the SEM fracture image of green part with different feedstocks.

It can be seen from the above figure that the F1 feedstock green part has a uniform distribution of powder and binder in most areas of the cross-sectional SEM diagram. However, a binder enrichment zone appears in a local area of a few green part samples. It is shown from the figure that of the three groups of feedstock with modifiers added to, the metal powders gaps was evenly filled with the binder, leading to the formation of a uniform feedstock. This may result from the addition of hyperbranched polymers which improves the uniformity of powder dispersion in the binder.

Another way to evaluate feedstock uniformity is to measure its pycnometer density and calculate the standard deviation [22]. Assuming that there is no loss in the feedstock ingredients during the mixing process, the components in the binder retain their original mass and volume after mixing. Then the theoretical density of the feedstock can be calculated by equation (3–1).

\[ \rho_t = \text{vol}\%_p \rho_p + \text{vol}\%_b \rho_b \]  

(3-1)

In the above formula, \( \rho_t \) is the theoretical density of feedstock, \( \text{vol}\%_p \) is the volume fraction of the powder, \( \text{vol}\%_b \) is the volume fraction of the binder, \( \rho_p \) is the theoretical density of the powder, and \( \rho_b \) is the theoretical density of the binder.

Figure 8 shows the theoretical density, actual density and density deviation of feedstock for different hyperbranched polymer HPN202 contents. Since the density of HPN202 (0.81 g cm\(^{-3}\)) is slightly lower than the other components in the binder, the theoretical density of the feedstock decreases slightly as the content of HPN202 increases. Xie et al. [23] found that the increase in the number of polymer components in the binder
promoted the uniformity of the feedstock. In this study, the density standard deviation of the feedstock F2-F4 was smaller than that of the feedstock F1, and the addition of the hyperbranched polymer improved the uniformity of the feedstock, which is consistent with this viewpoint.

### 3.1.3. Thermal performance analysis

The physical properties of the components of the binder are shown in table 3. As demonstrated from the data in the table, the temperature interval of decomposition of the binder component is obvious, so that the binder in the sample can be degreased by segmental thermal debinding. In order to further determine the optimal thermal debinding process route, the feedstock was subjected to DSC and TG test, as shown in figures 9 and 10, and thermal performance analysis was carried out to develop an optimal process curve.

Figure 9 shows the DSC curve of F1 feedstock, and figure 10 shows the TG curve of F3 feedstock. From the DSC curve, we know that a peak appeared at 130.1 °C, 168.7 °C, 399.4 °C, and 479.1 °C for the F1 feedstock, and a peak appeared for the F3 feedstock at 130.4 °C, 169.8 °C, 399.9 °C, and 480.2 °C. Obviously, the change of each peak point before and after hyperbranched polymer was very small, and there was only a slight deviation after the hyperbranched polymer was added, which indicated that the hyperbranched polymer had a good compatibility with the original POM-based binder system, and its addition had little influence on the feedstock system.

Therefore, the same injection process and debinding process can be used.

It can be seen from figure 9 that the first peak is the melting temperature of HDPE, the second peak is the POM melting temperature, and the third peak is the main decomposition temperature of the binder. It can also be seen from the TG curve that the thermal decomposition temperature of the binder ranges from 280 to 500 °C and there are two weight loss intervals. In the first stage, the weight loss interval is 280~417 °C, which is mainly the thermal decomposition weight loss of POM, HDPE and some SA and EVA. The second stage weight loss interval is 417~500 °C. It is the thermal decomposition weight loss of EVA and the balance HDPE, SA, and all binder components were removed at 500 °C.

### 3.2. Effect of hyperbranched polymer on mechanical properties of green part

#### 3.2.1. Effect on impact strength

The products prepared by metal injection molding are mostly small parts with complex three-dimensional shapes. In order to smoothly demould the product during injection and to avoid surface and internal cracks caused by external force, the green part after injection should hold relatively high strong toughness toughness. The impact strength of the four sets of green parts is shown in figure 11.
It can be easily seen from figure 11 that the impact strength of feedstock F1, F2, F3 and F4 is increasing in order, that is, as the amount of hyperbranched polymer HPN202 is increased, the impact strength of the green part is also increasing. From the change trend, when the amount of hyperbranched addition is 3 wt% (corresponding to F3 in the figure), the impact strength of the green part is the most obvious, reaching 17.33 kJ m$^{-2}$. When the hyperbranched polymer is added to 5 wt% (corresponding to F4 in the figure), the impact strength is improve, but at a slow speed. Compared with the green part without the hyperbranched
Figure 9. DSC curve of F1 feedstock and F3 feedstock.

Figure 10. TG curve of F1 feedstock and F3 feedstock.

Figure 11. Impact strength of green parts.
polymer modification, the impact strength is increased by 67.2%, and the increase is more obvious. The reason may be that the combination of the active end group of the hyperbranched polymer and the metal powder can form a three-dimensional network structure which can absorb a large amount of impact energy. The reason is also likely to be that the hyperbranched polymer has a highly branched structure which can increase molecular chain’s branched degree and reduce the entanglement of the molecular chains. Thereby, the toughness is enhanced to make the impact strength increase.

3.2.2. Effect on bending strength
In order to avoid damage caused to the product by collision during the handling and transfer process (such as edge drop, corner drop, etc), the green part should also hold relatively high strong toughness strength. At the same time, the green part’s high strength is also a prerequisite for the smooth completion of degreasing. Figure 12 shows the bending strength of the green parts prepared with different feedstocks.

It can be seen from the figure 12 that the bending strength of the green parts prepared by F2 and F3 feedstock is the highest, and the bending strength of the green parts prepared by F1 feedstock is the lowest, which means that the addition of hyperbranched polymer has an effect of enhancing the green parts. In particular, when the content of hyperbranched polymer is 1 wt% or 3 wt%, the flexural strength exceeds 18 MPa. When the content of hyperbranched polymer is 1 wt%, the flexural strength is the highest, reaching 18.9 MPa. When the content of hyperbranched polymer increases, the flexural strength decreases correspondingly. When the content is 5 wt%, the flexural strength is 17.17 MPa. However, it is still higher than the strength of the unhybridized polymer green part. From the pycnometer density analysis method in figure 8, it is known that with the addition of hyperbranched polymer, the fluidity of the feedstock is improved and it can fill the mold cavity well when injected, and the uniformity of feedstock is also improved. The binder is evenly coated with metal powder, and the small particles are filled in the large gap between the particles, the residual gap between the particles is small, and the strength of the green part is improved. In addition, the hyperbranched polymer contains a rigid group of a benzene ring, and the introduction of the rigid group of the benzene ring can also enhance the strength. The flexural strength of the above four groups is far greater than the minimum strength required for degreasing of 5 MPa, so that the subsequent degreasing can be ensured smoothly [24].

3.3. Effects of hyperbranched polymer on debinding process
3.3.1. Catalytic debinding
Catalytic debinding is mainly used to remove POM from green parts. The removal rate of POM is shown in figure 13.

It can be seen from the figure above that for the same feedstock, the removal rate of POM increases with the increase of degreasing time. At the same time, it can be seen that at the same debinding time, the POM removal rate of feedstock F4 is the worst, while that of feedstock F1 is the best. This indicates that the addition of hyperbranched polymer has a negative effect on catalytic debinding. With the increase of hyperbranched polymer content, it becomes more difficult to remove POM during the process of catalytic debinding. Especially
when the debinding time is 2 h, this effect is very evident. But when the debinding time is 8 h, this adverse effect is almost negligible. The SEM diagram of body section after 8 h of thermal debinding is shown in figure 14.

It can be seen from the figure that the original morphology of the powder particles of the four sample groups is clearly visible, and the particles retain a large number of internally interconnected pore structures and externally communicating pores between the particles. Additionally, there is almost no binder between the powder particles. It shows that after 8 h of catalytic debinding, the POM has been completely decomposed. Only a small amount of white flocculent binder is distributed in the intergranular gap, which serves as a skeleton support to ensure the strength of the degreased body until the subsequent thermal debinding stage is completely removed. Therefore, for this sample to which a hyperbranched polymer is added, the time for catalytic degreasing is recommended to be not less than 8 h. When it is less than 8 h, the POM in the sample is not removed completely. In the second step of thermal degreasing, the product is prone to cracking and other

Figure 13. Removal rate of POM in the sample.

Figure 14. SEM diagram of body section with different hyperbranched polymer after catalytic debinding of (a) 0 wt%, (b) 1 wt%, (c) 3 wt%, (d) 5 wt%.
defects, because the decomposition temperature of POM is relatively low, and the temperature of the second step of thermal degreasing is relatively high. Then, the POM is rapidly decomposed into a gas, so that the molecular pressure in the sample is too large, which may cause degreasing defects such as cracking, and affect the performance of the degreased blank.

3.3.2. Thermal debinding
Thermal debinding is widely used to remove the backbone binder components in MIM. Inappropriate debinding conditions can lead to defects such as distortion, bloating and cracking. Cracks occurred to some samples after thermal debinding. Therefore, considering the above analysis of the pyrolysis behavior of the feedstock and repeated testing, the final optimized thermal process is obtained, as shown in figure 15.

In order to prevent damage caused by low strength of the degreased during the transfer process (falling edge, corner drop, etc), the temperature is further raised to 850 °C in the late stage of thermal degreasing for pre-sintering for 1 h. The specific thermal debinding process is:

1. room temperature ~130 °C, the heating rate is 3 °C min^{-1};
2. 130 °C, heat preservation for 30 min;
3. 130~170 °C, the heating rate is 2 °C min^{-1};
4. 170 °C, holding for 30 min;
5. 170~400 °C, the heating rate is 2 °C min^{-1};
6. 400 °C, heat preservation 60 min;
7. 400~500 °C, the heating rate is 2 °C min^{-1};
8. 500 °C, heat preservation for 60 min;
9. 600~850 °C, the heating rate is 4 °C min^{-1};
10. 850 °C, heat preservation 60 min;
11. cooling with the furnace.

3.4. Effect of hyperbranched polymer on sintered part
3.4.1. Effect on tensile strength
Figure 16 shows the tensile strength of the sintered part corresponding to each group of feedstock.

It can be seen from the figure 16 that the tensile strength of sintered part prepared by F4 is the highest, and the tensile strength of the sintered part prepared by F1 feedstock is the lowest. This means the addition of the hyperbranched polymer modifier can increase the tensile strength of the sintered part. Moreover, when the content of the hyperbranched polymerranges from 0 wt% to 5 wt%, the tensile strength of the sintered

Figure 15. Thermal debinding process curve.
part has a small increase accompanied by the rise of the content. When the content of the hyperbranched polymer is 5 wt%, the tensile strength is the largest, reaching 1121.92 MPa; From the change trend, when the content of hyperbranched polymer is 3 wt% or less, the tensile strength increases at its highest speed. When the content of hyperbranched polymer is 3 wt%–5 wt%, the tensile strength increases slowly. This is because the addition of the hyperbranched polymer improves the fluidity and uniformity of the feedstock, which is more conducive to the densification of the sintering process, so the mechanical properties of the sintered part, including the tensile strength, have also been improved accordingly.

3.4.2. Effect on the dimensional accuracy of the sintered part

Figure 17(a) shows the shrinkage rate of four samples. It can be seen from the figure that the shrinkage rate in the three directions of length, width and height all is about 16%, the degree of shrinkage in each direction is relatively uniform, and the difference in shrinkage in three directions is less than 0.5%. It shows that the sample has good sintering uniformity and high dimensional accuracy.

Figure 17 (b) shows the standard deviation of one-dimensional direction shrinkage after sintering of different hyperbranched polymer content green part. With the increase of hyperbranched polymer, the standard deviation of linear shrinkage rate decreases, and the sample does not have such defect as deformation, and product accuracy is improved. In the range of 0–5 wt% hyperbranched polymer content, the standard deviation slightly decreased with the gradual increase of hyperbranched polymer content, indicating that the addition of hyperbranched polymer has a certain degree of improvement in sample size accuracy.

4. Conclusions

In this study, hyperbranched polymer was used as a modifier of POM-based binder, and the fluidity, uniformity and thermal properties of the feedstock were analyzed. Meanwhile, the influence of the content of hyperbranched polymer on the green part and the sintered part was also explored. The results show that with the increase of the amount of hyperbranched polymer, the fluidity and uniformity of the feedstock is also improved, and when the content of hyperbranched polymer is 5 wt%, the helical length is the longest, reaching 27.8 cm, indicating the fluidity is the best. The hyperbranched polymer can improve the flexural strength and impact strength of the green part. When the hyperbranched polymer content is 3 wt%, the composite mechanical properties of the green parts are the best, and the flexural strength reaches 18.11 Mpa, and the impact strength is up to 17.33 kJ m⁻². After adding the hyperbranched polymer, the tensile strength and dimensional accuracy of the sintered part can be improved.

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Figure 17. (a) Long-width and high shrinkage of four samples. (b) Standard deviation of shrinkage rate of four samples.

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