# Novel PEG-based binder system and its debinding properties for MIM①

LI Du-xin(李笃信), QU Xuan-hui(曲选辉), HUANG Bai-yun(黄伯云),
ZHONG Xiao-xian(钟孝贤), LI Song-lin(李松林), LI Yi-min(李益民)
(State Key Laboratory for Powder Metallurgy, Central South University,
Changsha 410083, P. R. China)

[Abstract] Binder system is critical to the success of metal injection molding( MIM). A novel PEG-based binder for MIM was developed, which was made of high density polyethylene (HDPE), polyethylene glycol (PEG), polymer W, stearic acid(SA) and dioctyl phthalate (DOP). The components of binder have interactions with each other, so the binder have good compatibility. The thermal decomposition process of binder exhibits three stages during debinding. The binder could be debound by pyrolysis or solvent, and could easily be removed in a short time in ethanol without defects and evironmental concern. A lot of interconnected pores formed after solvent debinding, which is helpful to the escape of pyrolysis gases during subsequent thermal debinding or presintering.

[Key words] metal injection molding; binder; debinding

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## 1 INTRODUCTION

Metal powder injection molding (MIM) is an emerging advanced net-shaping technology, which offers important advantages over the conventional powder metallurgy. This technology has attracted more and more attention and undergone rapid development in the recent years[1~4]. The binder plays a very important role in MIM process, the choice of the binder and debinding techniques is a key issue and determines the success of the whole process[5]. The binder system used in MIM can be classified as thermoplastic, thermosetting, water-based, inorganics and gellation system, all those have certain advantages and disadvantages associated with them. The thermoplastic binder systems have been widely used in MIM process because of their good mobility and moldability. The binder system is related with the debinding technique, and the debinding method and process are mainly decided by the binder, so the feature of popular MIM process lies in binder and debinding techniques. Debinding technique is very important to the quality of products. The usual debinding techniques of MIM include thermal debinding, solvent debinding, and catalytic debinding etc. Thermal debinding is the most frequently used techniques in industry. Compared with the other debinding techniques, the solvent debinding has the advantage of little deformation, high rate and easy control of carbon content. The solvent debinding will be the dominant trend in the MIM.

Polyethylene glycol(PEG) is nontoxic and has good stability and lubricity. It has been widely used

as water soluble binder system[6~11]. PEG-based binder, developed from the Solid Polymer Solution (SPS) system in 1990s, is the new solvent debinding binder. PEG-based water soluble binder exhibits good rheological properties, moldability, excellent shape retention, and can be easily removed without defects and evironmental concern, but PEG-based water soluble binder has the same drawbacks as a long hot mixing stage, a relatively small powder loading, and being limited to the less active metal powder as the other SPS system due to the system viscosity and interface adhesion of binder to powder. These drawbacks hinder its development and applications. The main objective of the present study is to develop a novel thermoplastic PEG-based binder, which can fulfill the requirements of the MIM process and overcome certain problems associated with the conventional PEG-based water soluble system. The thermal debinding and solvent debinding of the novel thermoplastic PEG-based binder is also studied in this paper.

## 2 EXPERIMENTAL

### 2.1 Material

The powder used in this study are carbonyl iron powder (98%) modified by carbonyl nickel powder (2%), whose characteristics are presented in Table 1. PEG of C P grade with molecular mass of 800~2 000 was purchased from Shanghai Gaonan Chemical Factory. Commercial molding grade high density polyethylene (HDPE) was supplied by LG Chem. Corporation. Stearic acid (SA) of C P grade was included as a surface active agent of the binder.

**Table 1**  Characteristics of carbonyl iron powder and carbonyl nickel powder

| Powder | Particle size/$\mu$m | Apparent density/($g \cdot cm^{-3}$) | Tap density/($g \cdot cm^{-3}$) | Shape | Impurity content/% | | |
|---|---|---|---|---|---|---|---|
| | | | | | C | O | N |
| Fe | 3.97 | 1.64 | 2.99 | Spherical | 1.5 | 1.5 | 0.3 |
| Ni | 2.60 | 0.75 | 1.95 | Spherical | 0.1 | 0.3 | 0.1 |

## 2.2  Experimental procedure

Binders, which were multi-polymer components systems consisting of a major fraction of PEG (binder formulations were $W_1$, $W_2$, $W_3$, $W_4$ and $W_8$ respectively), were carried out in a z-blader mixer for 1 h at 160 ℃. Feedstocks were then produced by mixing these binder and metal powders in a LH60 Roller mixer for 2 h at 145 ℃ (powder loading 55%). After the powder-binder mixtures were granulated on a LSJ20 plastic extruder, granulation was injection molded on an SJ-28/250 injection molding machine and $d$ 20 mm × 5.2 mm cylindrical pellets were formed. Two different debinding methods were used, the first method was solvent debinding, the second was a thermal debinding process. Both polymers and other components used were thermally debound at different elevated temperatures. The MIM parts during thermal debinding were embedded on alumina powder to serve as a wicking medium. The embedding powder gave more uniform heating and helped to prevent the distortion of the MIM parts. The sintering was carried out at 1 250 ℃.

## 2.3  Characterization

The thermal gravimetric analysis (TGA) of the binder was performed using a thermal analyzer DT-40 (Shimadzu, Japan) over a temperature range from 25 to 600 ℃ at a heating rate of 10~15 ℃/min. The morphologies of the fracture surfaces of binder and solvent debound samples were observed using a Scanning Electron Microscope (SEM) (JEOL JSM-5600LU, Japan). The debinding efficiency was calculated by the mass loss of the binder during debinding. PEG was determined by using Infrared Spectroscopy (NICOLET 740, USA).

## 3  RESULTS AND DISCUSSION

### 3.1  Binder formulation and properties
3.1.1  Binder formulation

One of the keys to the successful production of MIM parts is the selection of binder. The binder in the MIM process must provide some functions[12], for example, provide suitable plasticity and fluidity to feedstocks so that green parts without any defects are available for injection molding, and provide enough strength to avoid any deformation or cracking during demolding and removal, and could be effectively removed to obtain brown parts with good quality. The role of each binder component and the important binder requirements were discussed in detail in Refs.

[3, 5]. All of the requirements can not be achieved by a single component binder. Therefore the multi-component PEG-based binder system, which was composed of HDPE, PEG, SA and DOP etc, was formulated with the particular characteristics of each component in this study. HDPE, which has higher melting point and viscosity, was used as backbone polymer to provide the plasticity of the feedstocks and mechanical strength of the green parts. Moreover, HDPE remained in the debound parts was used to hold the metal particles in the desired shape during solvent debinding. PEG has lower melting point, good mobility, and can be easily removed with solvent, and also can be homogeneously mixed with the other components of the binder system, PEG was used as filler to lower the binder viscosity and the feedstocks viscosity, thereby allowing the feedstocks to be successfully molded. PEG was firstly removed during debinding to form a lot of pores, which was helpful to finally removing HDPE. Moreover, PEG acted as a lubricant to promote the injection molding of the feedstocks and demolding of the green parts. As a surface active agent, SA served as a bridge between the binder and powder to improve dispersion of powder in binder and avoid the phase separation of binder from powder during injection molding. In addition, it could also serve as a lubricant which reduces the friction between powder and machine/die wall. The physical and chemical interaction between binder and metal powder has significant effect on the homogeneity and rheological properties of feedstocks, powder loading, and strength of green parts[13, 14]. Other modifiers are also sometimes included in the binder formations to modify specific properties. To improve the compatibility of the binder, enhance the adhesion of binder to metal powder, improve the rheological properties and moldability of feedstocks, and increase the strength of green parts, polymer W was used together with PEG in the binder. In addition it could also promote the interfacial reaction between binder and metal powder.

Current investigations concerning binders consist mainly of seeking suitable binder formulations and studying the role of binders in the MIM technology. However, the selection of binder formulation still seems to be on a trial and error basis. The experimental results of the binder formulation selection showed that higher HDPE content gives the binder with higher viscosity, and the debound parts with more defects; but lower HDPE content gives the debound parts with worse shape retention. Increasing the pro-

portion of PEG/ polymer W increases the brittleness of the binder and green parts. As the proportion of PEG/ polymer W decreases, the toughness of binder and feedstocks increases. But excessive polymer W dosage leads to extremely elastic behavior, which is unfavorable to dimensional control, and goes against molding and debinding. The PEG molecule mass has significant effect on the system viscosity, mobility, green strength, and debinding[7]. The PEG with a molecule mass of 1 000 has been selected by a trial and error basis. PEG is easily oxidatively degraded at high temperatures (Fig. 1), so little antioxidant is included in the binder to inhibit the oxidation of PEG. From these observations, it can be concluded that the novel thermoplastic PEG-based binder was composed of HDPE 9~ 20, PEG 47~ 67, polymer W 21~ 41, SA 0. 9~ 10, DOP 0. 9~ 10, and little antioxidant.
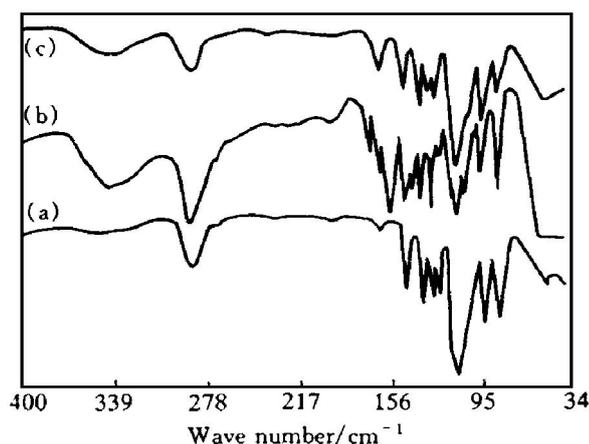


**Fig. 1**　FTIR of PEG
(a) —Ambient temperature; (b) —150 ℃;
(c) —150 ℃, adding antioxidant

### 3. 1. 2　Thermal analysis of binder

　　Binder system selection depends on melting, thermal pyrolysis range, solubility, and debinding completeness etc. Thermal analysis in this study is focused to survey the physical properties and the thermal decomposition range of the binder. Although the TG analysis does not represent the actual experimental conditions, the results are used as a guide for selecting the debinding cycle. Fig. 2 shows the TG curves of the PEG-based binder $W_8$, the thermal decomposition temperature of binder components is listed in Table 2. It is found that the TG curve of the binder is clearly divided into three sections corresponding to the decomposition temperature of components. The mass loss is about 15. 84% at 188. 6~ 321. 2 ℃, about 73. 94% at 321. 2~ 484. 3 ℃, and about 4. 40% at 484. 3~ 556. 5 ℃. At 556 ℃, there is little binder components remained, which is helpful to shape retention. Step by step thermal debinding and good shape retention are possible according to the results of TG analysis. By analyzing the TG curve of

binder, the thermal decomposition temperature of binder components, and the compositions of binder, it is found that the decomposition temperature range of the binder consisted with that of literature, but had some changes in comparison with those of pure components, and the mass loss of each stage does not completely consist with the proportion of binder composition, which illustrates that there are strong interactions between the components of the binder, and the binder has good compatibility. Examination by SEM on the binder $W_8$, has also illustrated that the binder system has good compatibility, which accords with the compatibility requirement of MIM binder.

**Table 2**　Thermal decomposition temperature of binder components[6, 11]

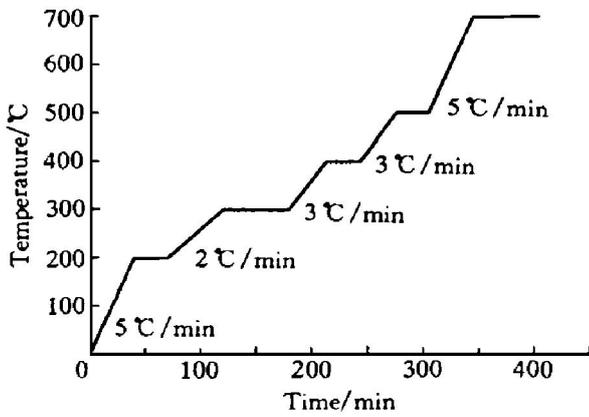| Component | $\theta_f$/ ℃ |
| --- | --- |
| HDPE | 430~ 490 |
| PEG | 336~ 421 |
| SA | 205~ 328 |
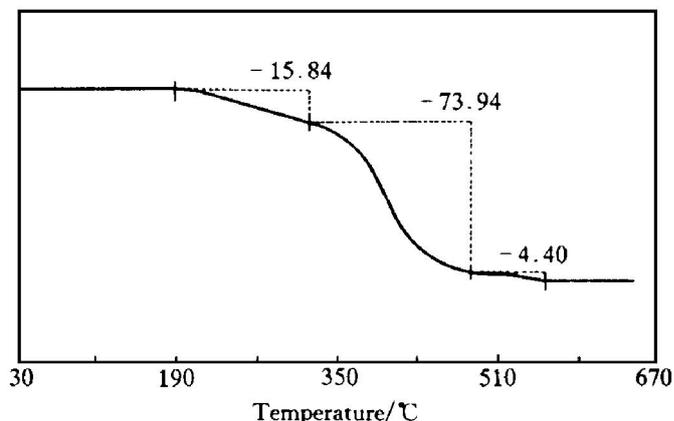


**Fig. 2**　TG curves of PEG-based binder $W_8$

### 3. 2　Debinding properties

　　Debinding is the most critical operation of the MIM process. Thermal debinding is perhaps the more frequently used techniques in industry, which is mainly used for production of small parts. Solvent debinding, which is suitable for production of large parts, is the development direction. The binder studied in this paper could be thermal debinding or solvent debinding which are favorable to selecting production techniques.

### 3. 2. 1　Thermal debinding

　　The molded parts, irrespective of initial composition, were thermally debound for several hours according to the thermal debinding process shown in Fig. 3, which was developed by considering the thermal decomposition behavior of the binder as indicated in TG. The debinding results are shown in Fig. 4, which shows that debinding rate is comparatively fast, and about 50% of the binder is removed after the second debinding stage. Owing to the different

**Fig. 3**　Thermal debinding process
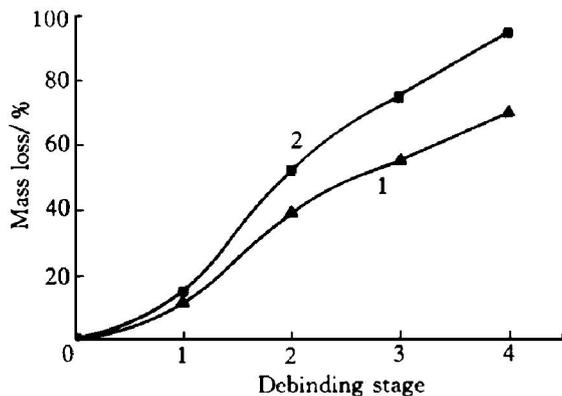


**Fig. 4**　Thermal debinding curves
1 —$W_2$; 2 —$W_3$

decomposition temperature of binder components there is little difference of debinding amount at every debinding stage for different binders formulations (curves 1 and 2 in Fig. 4). Debound parts showed good surface appearance without visible defects and good shape retention due to the difference of the decomposition temperature of HDPE and PEG and other components. Like the mass of thermoplastic binder systems, the binder system needs long thermal debinding time at high temperature, and several defects arising in the thermal debinding process like deformation and cracking could not be easily avoided because the thermal decomposition is carried out simultaneouly inside and outside, and evaporation and decomposition temperature of components is over the softening point of the binder.

3. 2. 2　Solvent debinding

　　Solvent debinding accomplishes debinding by diffusion of solvent into green parts and the dissolution of the dissoluble components. Solvent debinding can decrease the debinding time and give good compact shape retention because of low debinding temperature and diffusion of solvent from surface to interior. In terms of PEG dissolution and environmental requirement, ethanol was used as debinding solvent. The debinding results of green parts using ethanol as the debinding solvent are presented in Fig. 5. Binders

with different formulations have approximately the same debinding relationship (curves 1 and 2 in Fig. 5). The debinding amount increases initially very fast with debinding time, then slowly, most of the binder are removed after debinding for 4~6 h, so it could drastically reduce the subsequent thermal debinding time, and even the debound parts after solvent could be directly sintered. But the debinding amount of different formulation binders has little difference because of different dissolution ability of binder components in ethanol and the amount of PEG and polymer W affecting the interactions of binder components which lead to the change of dissolution ability of binder in ethanol. Increasing the debinding temperature, the debinding relationship is still approximately the same, but the debinding rate increases (curves 1 and 3 in Fig. 5) because the dissolution ability of binder increases in ethanol with increasing debinding temperature. Great care must be taken to match the vaporization of the solvent and the melting point of the binder when raising the debinding temperature to accelerate the debinding rate. Fig. 6 shows the SEM micrograph of the debound part $W_8$ after debinding time of 4 h using ethanol as solvent at room temperature. It could be found from the SEM micrograph that due to PEG having good solubility in ethanol and most PEG being
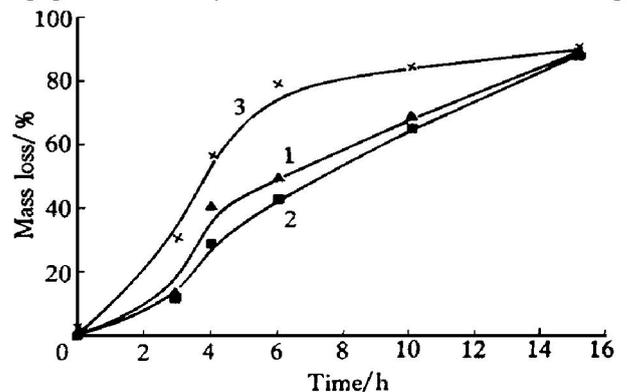


**Fig. 5**　Solvent debinding curves
1 —$W_2$, 200 ℃; 2 —$W_4$, 200 ℃; 3 —$W_2$, 400 ℃



**Fig. 6**　SEM micrograph of debound part $W_8$

removed after debinding for 4 h, a lot of interconnected large pores are formed in the debound parts, which is favorable to subsequent thermal debinding or presintering. The debound parts have sufficient strength for handling after solvent debinding due to the remaining polymer backbone which did not dissolve in ethanol. The solvent debinding which used ethanol as solvent is effective, the debound parts have no visible defects and exhibit excellent shape retention. Moreover, ethanol is safe and harmless for environment, and 94% of the ethanol used can be recovered by distillation, which is attractive for reducing cost.

## 4  CONCLUSIONS

1) A novel thermoplastic PEG-based binder, which consists of HDPE/PEG/polymer W/SA/DOP/antioxidant, is an ideal binder system for MIM. The thermal properties and SEM micrograph of the binder show that the binder system exhibiting three thermal decomposition stages has good compatibility.

2) The PEG-based binder could be efficiently removed from the green parts by thermal debinding or solvent debinding techniques. The solvent debinding which uses ethanol is desirable. Using this method, quick debinding and excellent shape retention are possible. Moreover, ethanol used in the method is safe and harmless for environment, and could be effectively recovered.

### [REFERENCES]

[1]  LI Yi-min, HUANG Bai-yun and QU Xuan-hui. Improvement of rheological and shape retention properties of wax-based MIM binder by multipolymer components [J]. Trans Nonferrous Met Soc China, 199, 9(1): 22.

[2]  FAN Jing-lian, HUANG Bai-yun, QU Xuan-hui, et al. Low temperature thermal debinding behaviors of wax-based multicomponent binder for tungsten heavy alloy [J]. Trans Nonferrous Met Soc China, 1999, 9(1): 93.

[3]  QU Xuan-hui, YAN Han-song and HUANG Bai-yun. The development of binder for metal injection molding [J]. Powder Metallurgy, (in Chinese), 1997, 15(1): 61.

[4]  LI Yi-min, HUANG Bai-yun and QU Xuan-hui. The technological progress of metal injection molding [J]. Rare Metal Materials and Engineering, (in Chinese), 1996, 25(1): 1.

[5]  LI Du-xin, LI Yi-min, QU Xuan-hui, et al. Metal injection molding binder [J]. Material Review, (in Chinese), 2000, 14(5): 36.

[6]  Anwan M Y, Davies H A, Messer P F, et al. A novel binder system for powder injection molding [J]. Adv/P/M, 1992, 6: 15.

[7]  Anwan M Y, Messer P F, Ellis B, et al. Injection molding of 316L stainless steel powder using novel binder system [J]. P/M, 1995, 38(2): 113.

[8]  Anwan M Y, Davies H A, Messer P F, et al. Preparation of feedstock for PIM by using a new binder system [J]. Adv in P/M, 1992, 6: 37.

[9]  Hens K F, Weaver T, German R M, et al. Injection molding of various metals and ceramics using an acetal binder [J]. Adv in P/M, 1992, 6: 27.

[10]  LI Song-lin, HUANG Bai-yun, QU Xuan-hui, et al. Solvent debinding of water soluble binder in PIM [J]. Trans Nonferrous Met Soc China, 1999, 9(3): 579.

[11]  Yong M T, Atre S V, German R M, et al. Wax-based and PEG-based binder systems development for metal and ceramic powders [J]. Adv in P/M and Particulate Materials, Princeton, MPIF, 1996, 5: 19-265.

[12]  German R M. Powder Injection Molding [M]. Princeton: MPIF, 1990.

[13]  Yan M J and German R M. The Interaction between the cemented carbide powder and the binder for powder injection molding feedstock [J]. Adv in P/M, 1992, 6: 179.

[14]  Lin S T and German R M. Interaction between binder and powder in injection molding of alumina [J]. J of Mater Sci, 1994, 29: 5207.

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