IMPROVEMENT OF RHEOLOGICAL AND SHAPE RETENTION PROPERTIES OF WAX-BASED MIM BINDER BY MULTI-POLYMER COMPONENTS①

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ABSTRACT The rheological and shape retention properties of wax-based binders with different polymer components were studied. The effects of different polymer components on rheological, shape retention and mechanical properties, and isotropic dimension shrinkage were investigated. The feedstock based on the PW-PP binder can not be used for injection molding due to severe separation of the binder from metal powder. The general rhelogical properties of the Fe-2Ni feedstock based on the PW-EVA binder were superior to that of the Fe-2Ni feedstock based on the PW-HDPE binder, while the shape retention properties of the PW-HDPE binder were superior to that of the PW-EVA binder. By the combination of EVA and HDPE as multi-polymer components, the PW-EVA-HDPE binder should have the best rheological and shape retention properties. The shrinkage homogeneity and mechanical properties of the feedstock based on this binder were also the best.

Key words rheological property metal injection molding (MIM) binder polymer component

1 INTRODUCTION

Metal injection molding (MIM) is an emerging net-shaping process with the capability of producing complex metal products which cannot be made by conventional powder metallurgy processes. Combining high part complexity with high production quantities, metal injection molding supplements the established processes like press/sinter, machining and investment casting. Its basic process is as follows: first, metal powders with specific particle size and range and shape are uniformly mixed with an organic binder to prepare a moldable feedstock; then, the feedstock flows and fills into a mold under heat and pressure to form green parts. Subsequent debinding and sintering finally produce parts of full or near full density[1-4].

The binder plays a very important role in MIM process. It is not only the vehicle of flowability during injection molding, but also provides shape retention during debinding. Typical wax-based binders are composed of paraffin wax and a kind of polymer component such as polyethylene, polypropylene, polystyrene. The paraffin wax with low molecular mass and low melting point plays a major role in transferring flowability during injection molding, whereas the ploymer component mainly provides shape retention during debinding besides helping provide flowability. There are often contradiction between the flowability and the shape retention. In this paper, a new kind of wax-based MIM binder of multi-polymer components was presented. The rheological and shape retention properties were compared with those of the wax-based MIM binder of mono-polymer component.

2 EXPERIMENTAL

The metal powders used in the experiment were carbonyl iron and nickel powder, the

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binders were based on paraffin wax. The minor components were poly (ethylene vinyl acetate), high density polyethylene and polypropylene respectively. Stearic acid was included as a surface active agent. The material characteristics are shown in Tables 1 and 2. Carbonyl iron powder and nickel powder were premixed in a V-type mixer in a mass ratio of 98∶2.

The composition of binders is listed in Table 3. Binders 1#, 2# and 3# were prepared individually while binder 4# was prepared by mixing binders 1# and 2# in a mass ratio of 1∶1. The feedstocks were then produced by mixing these binders with Fe/Ni premixed powders in a LH60 Roller mixer for 3 h. The corresponding codes for the above feedstocks were A, B, C and D respectively. The powder loadings of the four feedstocks are the same as 58 %(volume fraction).

An Instron 3211 capillary rheometer was used to measure the viscosities of the feedstocks. It has a diameter (D) of 1.27 mm and a length (L) of 76.2 mm, giving a ratio of L/D of 60. TGA experiments were carried out in a nitrogen atmosphere at a rate of 10 ℃/min on a Dupont 9900 thermal analyzer. The reference substance was α-Al_2O_3. MIM standard tensile specimens, recommended by MPIF[5], were injection molded using the four kinds of Fe-2Ni feedstocks on a SZ-28/250 injection molding machine after granulation on a LSJ20 plastic extruder. A schematic of the MIM standard tensile specimen is shown in Fig.1. The thermal debinding and sintering were performed in a hydrogen atmosphere. The sintering was carried out at 1 260 ℃ for 2 h. The shrinkage after debinding and sintering was measured, and the tensile properties of as-sintered samples were determined and compared.

3 RESULTS AND DISCUSSION

3.1 Rheological properties of feedstocks

In MIM processes, the rheological properties of the feedstock are key features which influence the steady flow and the uniform filling into the mold[6]. The evaluation of rheological properties of the feedstock was based on the viscosity of the feedstock and its shear sensitivity and temperature sensitivity. On the condition of the same powder loading of 58 %, the viscosities of the Fe-2Ni MIM feedstocks based on the PW-EVA, PW-HDPE, PW-PP and PW-EVA-

Table 1 Characteristics of carbonyl iron and nickel powder

Powder	Particle size /μm	Apparent density /(10^3kg·m^{-3})	Tap density /(10^3kg·m^{-3})	Shape	Impurity/ %		
					C	O	N
Fe	4.0	1.64	2.99	Spherical	1.5	1.5	0.3
Ni	2.6	0.75	1.95	Spherical	0.1	0.3	0.1

Table 2 Characteristics of components of binders

Component	Chemical structure	t_m/℃	ρ/(10^3kg·m^{-3})
PW (Paraffin wax)	C_nH_{2n+2}	58	0.91
HDPE (High density polyethylene)	$\text{-[}CH_2-CH_2\text{]}_n\text{-}$	139	0.98
PP (Polypropylene)	$\text{-[}CH_2-CH(CH_3)\text{]}_n\text{-}$	142	0.95
EVA (Poly(ethylene vinyl acetate) with 14 % vinyl acetate)	$\text{-[}[CH(COCH_3)-CH_2]_x-[CH_2-CH_2]_y\text{]}_n\text{-}$	80	0.96
SA (Stearic acid)	$CH_3[CH_2]_{16}COOH$	66	0.96

Table 3 Composition of binders (%)

Feedstock	Binder	PW	EVA	HDPE	PP	SA
A	1#	79	20	-	-	1
B	2#	79	-	20	-	1
C	3#	79	-	-	20	1
D	4#	79	10	10	-	1

HDPE binders were measured, and the viscosity data are shown in Table 4. The experiment showed that the feedstock based on the PW-PP binder was obstructed in the capillary due to severe separation of the binder from the metal powder. Thus the viscosity data for feedstock C were not obtained.

The viscosity data in Table 4 indicate the flowability of the MIM feedstocks. The lower the value of viscosity is, the easier it is for a MIM feedstock to flow. It can be found in Table 4 that at a temperature of 150 ℃ the viscosity of feedstock A is the lowest at every given shear rate, next comes feedstock D, while the viscosity of feedstock B is the highest. Therefore, the feedstock based on the PW-EVA binder is the best in these three kinds of feedstocks from the standpoint of flowability.

A MIM feedstock is generally considered to be a pseudoplastic fluid[7,8]. The viscosity data in Table 4 also indicate that viscosity generally decreases with the increase of shear rate. For a pseudoplastic fluid,

$$\tau = k\dot{\gamma}^n \quad (1)$$

where τ is the shear stress, $\dot{\gamma}$ is the shear rate, k is a constant, n is a flow behavior exponent (<1). The value of n indicates the degree of shear sensitivity. The lower the value of n, the more quickly the viscosity of the feedstock changes with shear rate. Injection molding of MIM feedstocks is conducted under pressures and temperatures. It is desirable that the viscosity of MIM feedstock should decrease quickly with increasing shear rate during injection process. This high

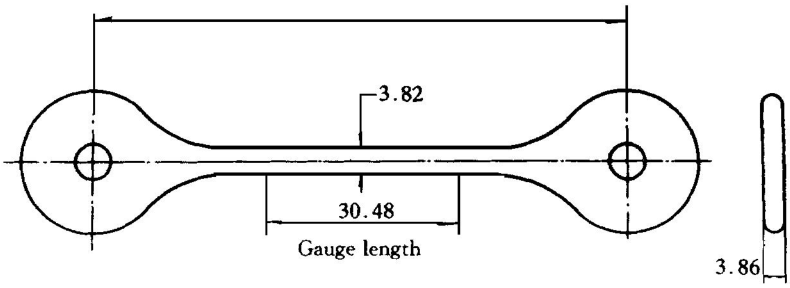

Fig.1 Schematic of MIM standard tensile bar

Table 4 Viscosity data for MIM feedstocks (Pa·s)

Feedstock	Temperature/ ℃	Newtonian shear rate/ s^{-1}					
		3.543	11.81	35.43	118.1	354.3	1 181
A	120	1 182	757	337	187	65	41
	135	998	548	246	184	53	27
	150	953	381	146	57	33	20
B	130	2 921	1 556	361	214	126	52
	140	1 670	866	423	163	90	43
	150	1 601	920	445	146	94	34
D	130	3 800	2 529	1 244	394	126	38
	140	1 273	698	363	81	48	31
	150	1 256	505	196	87	47	28

shear sensitivity is especially important in producing complex and delicate parts which are leading products in MIM industry. Plotting the logarithm of shear stress against the logarithm of shear rate for the temperature of 150 ℃ as shown in Fig. 2, values of n, namely n_A = 0.377, n_B = 0.345, n_D = 0.318 could be determined. This implies that concerning shear sensitivity feedstock D based on the PW-EVA-HDPE binder is considerd to be the best.

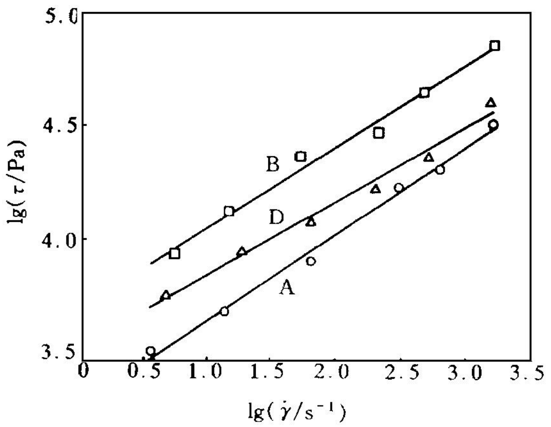

Fig.2 Correlation of shear stress and shear rate

The dependence of feedstock viscosities on temperature can be expressed by an Arrhenius equation[9],

$$\eta(T) = \eta_0 \exp(E/RT) \quad (2)$$

where E is the flow activation energy, R is the gas constant, T is temperature, η_0 is reference viscosity. The value of E expresses the influence of temperature on the viscosity of MIM feedstocks. If the value of E is low, the viscosity is not so sensitive to temperature variation, then any small fluctuation of temperature at injection molding will not result in a sudden viscosity change that can cause undue stress concentrations in the molded parts and result in cracking and distortion. On the condition of shear rate 1 181 s^{-1} which falls in the normal range of shear rate during injection molding of MIM feedstocks, by plotting the logarithm of viscosity against the reciprocal of temperature, as shown in Fig.3, the flow activation energy of feedstocks can be determined as E_A = 32.5 kJ/mol, E_B = 31.8 kJ/mol, E_D = 22.0 kJ/mol. The flow activation energy of feedstock D is the lowest which indicates that the sensitivity of the viscosity of feedstock D to temperature is the lowest. This feedstock can thus be injected into mold in a relatively wide temperature range. Feedstocks A and B with higher values of E are more sensitive to temperature fluctuation. Therefore, feedstock D based on the PW-EVA-HDPE binder is again the best from the standpoint of temperature sensitivity.

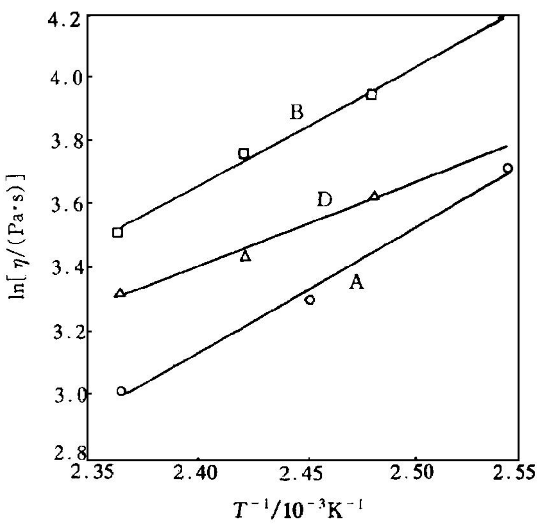

Fig.3 Correlation of viscosity and temperature

Although other properties such as melt compressibility, melt elasticity, specific heat, thermal conductivity can affect injection molding, for simplicity, it can be concluded from the above discussion that a feedstock with lower viscosity, lower flow behavior exponent and higher flow activation energy has good rheological properties and is suitable for injection molding. However, there are usually contradictions among these three requirements. From the standpoint of viscosity, feedstock A is the best and feedstock D is better than feedstock B. From the standpoint of shear sensitivity, feedstock D is the best and feedstock B is better than feedstock

A. From the standpoint of temperature sensitivity, feedstock D is the best and feedstock B is better than feedstock A.

Weir[10] proposed a moldability index for polymers which includes the effect of the above mentioned three factors,

$$\alpha_{STV} = \frac{1}{\eta_0} \frac{\left| \frac{\partial \lg \eta}{\partial \lg \gamma} \right|}{\frac{\partial \lg \eta}{\partial (1/T)}} \quad (3)$$

where η is viscosity, η_0 is reference viscosity, γ is shear rate, T is temperature, α_{STV} is a moldability index. Introducing this index α_{STV} into MIM to evaluate the general rheological properties of feedstocks, and defining α_{STV} as a general rheological index for MIM feedstocks[11], simplifying equation 3, then

$$\alpha_{STV} = \frac{1}{\eta_0} \frac{|n-1|}{E/R} \quad (4)$$

where n is the flow behavior exponent, E is the flow activation energy, R is the gas constant. The subscripts S, T, V of α_{STV} represent the effect of shear sensitivity, temperature sensitivity and viscosity respectively. The higher the value of α_{STV}, the better the general rheological properties. By taking 150 ℃ as a reference temperature and 1 181 s^{-1} as a reference shear rate, the values of α_{STV} of these three feedstocks were calculated. After multiplying the results by 10^6 to give numbers between 1 and 10, we got $(\alpha_{STV})_A = 7.8$, $(\alpha_{STV})_B = 4.0$, $(\alpha_{STV})_D = 9.3$. Feedstock D has the highest general rheological index, feedstock A intermediate, feedstock B the lowest. Therefore, it can be concluded finally that feedstock D has the best general rheological properties and is the most suitable for injection molding. Feedstock A is second to it, and feedstock B is inferior to these two.

3.2 Shape retention properties

The TGA curves of PW, EVA and binder 1# are shown in Fig. 4, and those of PW, HDPE and binder 2# are shown in Fig. 5. It is found from these two figures that PW has a pyrolytic temperature interval of 188 ~ 327 ℃. HDPE has a narrow pyrolytic temperature interval of 430 ~ 490 ℃, whereas EVA has a comparatively broad pyrolytic temperature interval of 384 ~ 559 ℃. It is known from the data of Table 1 that the softening point of EVA is 60 ℃ lower than that of HDPE and the starting pyrolytic point is 55 ℃ lower than that of HDPE, which indicates that EVA is less effective as the second component of the binder from the standpoint of shape retention properties.

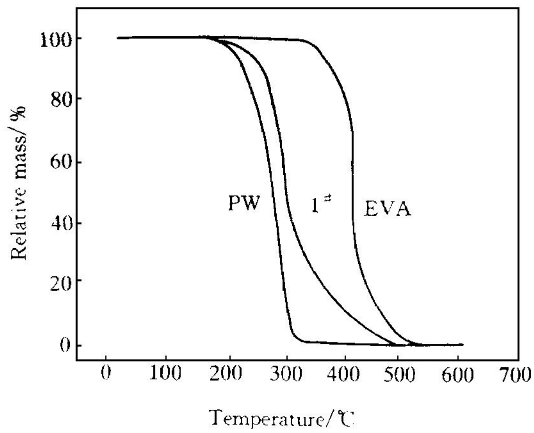

Fig.4 TGA curves of PW, EVA and binder 1#

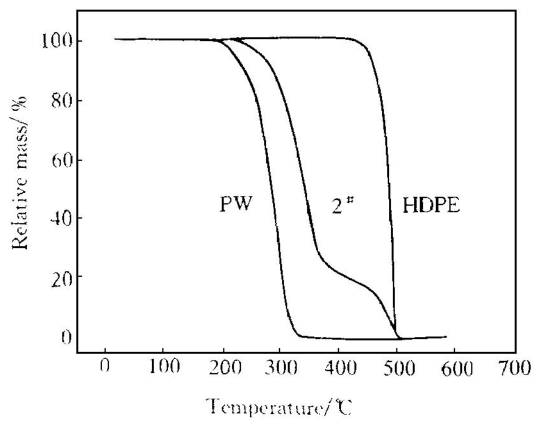

Fig.5 TGA curves of PW, HDPE and binder 2#

Furthermore, it is found that the TGA curve of binder 2# is composed of two sections.

The first section, which corresponds to the pyrolysis of PW, has a pyrolytic temperature interval of 210 ~ 360 ℃. The starting pyrolytic point is higher than that of the individual PW, and the pyrolytic temperature interval is broadened. Following a platform, comes the second section of the TGA curve of binder 2# which corresponds to the pyrolysis of HDPE, which has a pyrolytic temperature interval of 430 ~ 490 ℃. It is consistent with that of the individual HDPE. Thus, the pyrolysis of component HDPE is not affected in binder 2#. But the situation is different for the pyrolysis of binder 1#. There is no platform in its TGA curve. The pyrolytic sections of the component PW and the component EVA connect with each other. Except that there is a pyrolytic rate change at the inflection point, the individual pyrolytic sections corresponding to the pyrolysis of the components PW and EVA can not be distinguished. Therefore, it is diffcult for binder 1# to achieve the effect of step by step debinding, which is the aim for multi-component binder design, and is diffcult to fulfil the function of shape retention during debinding. Thus, it is further proved that HDPE is superior to EVA as the second component of the binder from the standpoint of shape retention properties.

Fig.6 shows the TGA curve of the PW-EVA-HDPE binder. It can be found out that the TGA curve is clearly divided into three sections. The mass loss of the first section was about 80 %, which corresponds to the pyrolysis of the component PW with a pyrolytic temperature interval of 176 ~ 338 ℃. The mass loss of the second section is 10 %, which corresponds to the pyrolysis of the component EVA with a pyrolytic temperature interval of 338 ~ 415.5 ℃. The mass loss of the last section is 10 %, which corresponds to the pyrolysis of the component HDPE with a pyrolytic temperature interval of 415.5 ~ 485 ℃. The pyrolysis of components PW, EVA and HDPE takes place successively. Following the removal of PW, the component EVA, which is less effective in shape retention, is removed before the removal of HDPE. At this monent, HDPE is still remained in the injection molded parts to hold the shape of parts. Therefore, the mass loss of the binder is divided into three steps. The shape retention properties are improved by the combination of EVA and HDPE as multi-polymer components. Fe-2Ni MIM tensile specimens prepared by the MIM feedstocks based on these three kinds of binders are debound in hydrogen. By taking out the tensile specimens and weighing them at different temperatures, the complete removal temperature points of PW, EVA and HDPE were determined to be 350, 420 and 500 ℃ respectively. These results are consistent with the TGA curves in Figs.4, 5 and 6. Therefore, it can be concluded that the shape retention properties of the feedstock based on the PW-EVA-HDPE are the best, next comes the feedstock based on the PW-HDPE binder, while the shape retention properties of the feedstock based on the PW-EVA binder are inferior to these two.

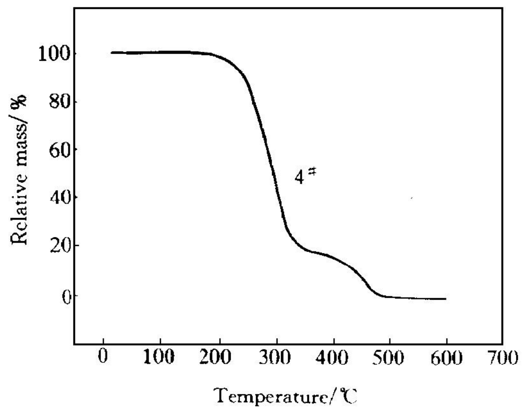

Fig.6 TGA curve of binder 4#

Based on the above results, an ideal fast debinding curve for MIM standard tensile specimens was obtained as shown in Fig.7. The whole debinding time is 220 min. The debinding rate reaches 1 mm/h. By applying this debinding curve, the debound tensile specimens are free from any defects such as crack, blister, slump, cavity and lamination. The debinding process is divided into three steps. The first step is to increase the temperature from ambient temperature to 350 ℃ at a rate of 5 ℃/min and hold for 1 h, in which most of PW is removed slowly, and connected pores throughout parts are formed gradually. After this step is finished, the connected pores through parts have been formed, while the remained binder can still connect with each other to hold the shape of the green parts. The second step is to increase the temperature from 350 ℃ to 420 ℃ at a rate of 5 ℃/min and hold for 30 min. At this stage, EVA with low softening point is removed, while HDPE which is more effective in shape retention still remains in the parts. In the last step, the temperature is increased from 420 ℃ to 500 ℃ at a rate of 5 ℃/min and hold for 30 min, in which HDPE is removed, and the whole debinding process is fulfilled. Fig.8 shows the microstructure of tensile specimens when debinding is finished at 500 ℃.

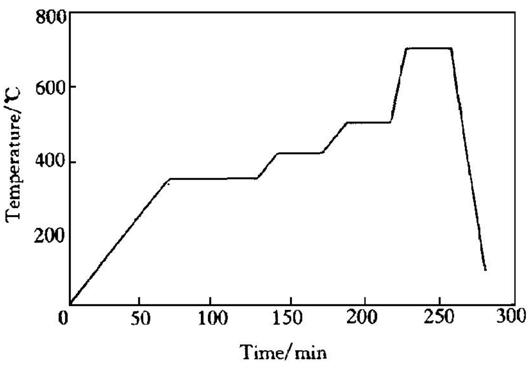

Fig.7 Ideal debinding curve

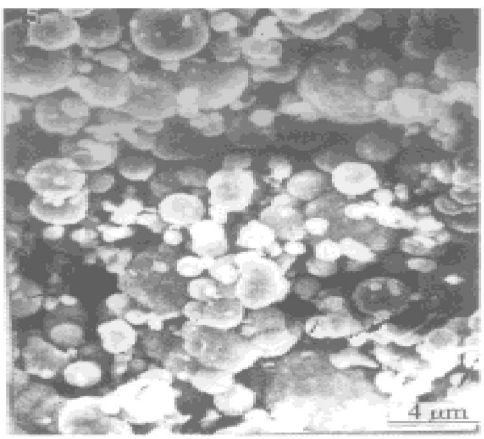

Fig.8 Microstructure of tensile specimens after debinding at 500 ℃ for 30 min

It can be seen that the binder is removed completely and a slight presintering occurs.

3.3 Shrinkage homogeneity and mechanical properties

MIM feedstocks contain a high volume percentage of binder which needs to be removed in the debinding step. The shrinkage after sintering is much greater compared to that of conventional press/sinter processes. Therefore, homogeneous shrinkage is especially important to the control of dimension tolerance for complex and delicate MIM parts. Measuring the diameter and gauge length of as-molded and as-sintered tensile specimens, the shrinkage homogeneity of parts prepared by these feedstocks is compared. The results are shown in Table 5. Because injection molding of feedstock C based on the PW-PP binder fails due to powder/binder separation, there are no data for parts based on this feedstock. It can be found that the deviations between the shrinkage rates of diameter and gauge length are 1.63, 0.85 and 0.01 for feedstocks A, B and D respectively. The use of feedstock D leads to the best shrinkage homogeneity, feedstock B intermediate, and feedstock A the worst. This result suggests that good rheological and shape retention properties are beneficial to the control of dimensional tolerance of MIM parts. Although good rheological properties and good shape retention properties may both contribute to the shrinkage homogeneity, it is supposed that shape retention properties contribute more to the shrinkage homogeneity.

Table 5 Shrinkage rates of diameter and gauge length of MIM tensile specimens (%)

Feedstock	Diameter	Gauge length	Deviation
A	16.55	14.92	1.63
B	16.40	15.55	0.85
D	15.56	15.57	0.01

The mechanical properties of as-sintered parts are shown in Table 6. It is found that the mechanical properties of MIM tensile specimens prepared using feedstock D are the best in terms of density, ultimate tensile strength and elongation. These results suggest that good rheological and shape retention properties also contribute to the mechanical properties of MIM parts to some degree.

Table 6 Mechanical properties of Fe-2Ni alloy prepared with different feedstocks

Feedstock	Density /(10^3kg·m^{-3})	Ultimate tensile strength/MPa	Elongation /%
A	7.27	270.2	18.9
B	7.41	276.2	24.7
D	7.52	298.0	24.8

4 CONCLUSION

The polymer component plays an important role in the rheological and shape retention properties of wax-based MIM binders. The feedstock based on the PW-PP binder can not be used for injection molding due to severe separation of the binder from metal powder. The general rheological properties of the Fe-2Ni feedstock based on the PW-EVA binder are superior to that of the Fe-2Ni feedstock based on the PW-HDPE binder, while the shape retention properties of the PW-EVA binder are inferior to that of the PW-HDPE binder. By the combination of EVA and HDPE as multi-polymer components, the PW-EVA-HDPE binder shows the best rheological and shape retention properties. The shrinkage homogeneity and mechanical properties of the feedstock based on the this binder are also the best.

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