RHEOLOGICAL PROPERTIES OF METAL INVECTION MOLDING BINDER AND FEEDSTOCK①

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ABSTRACT The fundamental rheological properties of metal injection molding (MIM) feedstock and binder are theoretically analysized. The viscosity of MIM binder and feedstock at different temperature and at different shear rate was measured and evaluated. The results indicated that MIM binder and feedstock possess pseudoplastic rheological behavior. The Fe-Ni MIM feedstock prepared has the lower value of flow activation energy and the higher value of strain sensitivity exponent. Its injection and filling properties are good.

Key words metal injection molding feedstock binder viscosity

1 INTRODUCTION

Metal injection molding (MIM) is a new net-shaping technology of powder metallurgy which is developed on the basis of conventional plastic injection molding[1]. Its basic process is as follows: firstly, the metal powders with particular particle size and shape and organic binder are uniformly mixed to prepare feedstock; then, the feedstock flows and fills into mold under heat and pressure to form green parts; after debinding and sintering, the parts of full or near full density are fabricated.

In this process, good rheological properties of binder and feedstock are one of the keys to get green parts with uniform density and no defect, and make debinding and sintering successfully and get high quality products. This paper analyses the fundamental rheological properties of MIM feedstock and binder firstly, then investigates the viscosity of Fe-Ni MIM feedstock and binder.

2 THEORETICAL FUNDAMENTALS OF RHEOLOGICAL PROPERTIES OF MIM FEEDSTOCK

MIM feedstock is a kind of powder/binder suspension. Generally, the binder is a multicomponent system which is mainly composed of a low melting point and low molecular weight component, a high melting point and high molecular polymer, and a few of surface active agents. The flow viscosity of binder is controlled by backbone polymer[2], The polymer melts are normally pseudoplastic fluid of which the viscosity decreases with shear rate at certain temperature. Its rheological property can be expressed by following equation:

$$\tau = k\dot{\gamma}^n \tag{1}$$

where τ is shear stress, $\dot{\gamma}$ is shear rate, k is coefficient, n is strain sensitive exponent which is less than 1. The flow property of MIM feedstock is provided by the binder at the injection molding temperature[3], so the MIM feedstock also possesses a pseudoplastic behavior which is shown in Eq 1. But the viscosity of MIM feedstock is quite higher than that of binder because of the high volume fraction of powder particles which hinder the flow of the binder. At injection molding temperature, the viscosity of MIM binder is usually demanded to be less than 10 Pa•s. The viscosity of MIM feedstock may vary from 10 Pa•s to 1 000 Pa•s with shear rate at the same temperature.

The capillary rheometer which is shown in

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Fig. 1 is used for measuring the viscosity of MIM feedstock, There are several advantage of capillary rhometer:

(1) The shear rate and flow geometry in a capillary rheometer are very similar to the conditions actually encountered in injection molding.

(2) A capillary rheometer typically covers the widest shear rate ranges.

(3) A capillary rheometer can not only be used to measure viscosity, but also provide the information on stability and homogeneity of feedstock and powder/binder seperation phenomenon.

The working principle is as follows: a fluid is forced by a piston from a reservoir through a capillary. On the condition of stable flow, the shear stress and shear rate at this temperature can be obtained by measuring the pressure drop across the capillary or the volumetric flow rate through the capillary, and the viscosity is determined. For Newtonian fluid, the shear stress and shear rate are shown in following equations[4]:

$$\tau_w = \frac{\Delta P}{2(L/R)} \quad (2)$$

$$\dot{\gamma}_a = \frac{4Q}{\pi R^3} \quad (3)$$

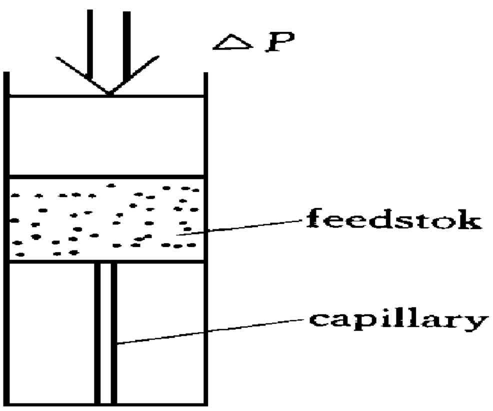

Fig. 1 Schematic figure of rheometer

where τ_w is shear stress at the capillary wall, ΔP is pressure drop across the capillary, L and R are length and radius of the column, $\dot{\gamma}_a$ is shear rate at the wall for Newtonian fluid and is effective shear rate for non-Newtonian fluid, Q is volumetric flow rate. For MIM feedstock which is non-Newtonian fluid, the Rabinowitsch correction is applied for the correction of shear rate[5, 6]:

$$\dot{\gamma}_w = \frac{\dot{\gamma}_a}{4}\left(3 + \frac{1}{n}\right) = \frac{\dot{\gamma}_a}{4}\left[3 + \frac{\mathrm{dln}\,\dot{\gamma}_a}{\mathrm{dln}\,\tau_w}\right] \quad (4)$$

where $\dot{\gamma}_w$ is shear rate at the wall. Although the shear stress at the wall of capillary rheometer has nothing to do with fluid behavior, there is an "end effect" of pressure drop across the capillary for different L/R ratio, the shear stress also need correction. Bagley[7] thought that this "end effect" could be corrected by assuming an effective capillary length, $(L + aR)$, greater than the actual capillary length. So Eq. (2) is changed as

$$\tau_w = \frac{\Delta P}{2(L/R + a)} \quad (5)$$

On the condition of fixed shear rate, ΔP are plotted against L/R for the capillary of different L/R ratio and we get a linear ΔP-L/R curve. The intercept at $\Delta P = 0$ is the value of "end effect", a. The detailed correction method was given in Reference [7]. Because this kind of correction is complicated and need a series of capillaries of different L/R ratio, the capillary of higher value of L/R is often used to neglect the end effect. So, the effective viscosity of MIM feedstock at certain temperature can be shown as follows:

$$\eta = \tau_w / \dot{\gamma}_w$$

The dependence of viscosity η on temperature can be expressed by Arrhenius equation:

$$\eta(T) = \eta_0 \exp\left[\frac{E}{R}\left(\frac{1}{T} - \frac{1}{T_0}\right)\right] \quad (6)$$

where E is flow activiation energy, R is gas constant, T_0 is reference temperature, and η_0 is viscosity at T_0.

3 EXPERIMENTAL

3.1 Raw materials

The metal powders used in experiment were carbonyl iron and nickel powders. The paraffin wax-based binders were adopted. The charateristics of the raw materials are presented in Tables 1 and 2.

3.2 Preparation of binder and feedstock

The blade mixer was used to prepare the MIM binder and feedstock. The formulation of binders prepared is shown in Table 3. Because the binders of *BP* series are easy to seperate from metal powders, and the softening point of *BE* serial binders is low, the feedstock was prepared by mixing 98% iron powders and 2% nickel powoders with binder BH_4, The volume ratio of powder/binder was 57/43 and the weight ratio was 91.83/8.17. The mixing temperature was 160 ℃ and the mixing time was 2h.

Table 1 The characteristics of carbonyl iron and nickel powders

	Particle size / μm	Apparent density / $g \cdot cm^{-3}$	Tap density / $g \cdot cm^{-3}$	Shape	Chemical elements C	O	N
Fe	3.97	1.64	2.99	sphere	1.5	1.5	0.3
Ni	2.60	0.75	1.95	sphere	0.1	0.3	0.1

Table 2 The characteristics of components of binder

Component	Chemical structure	t_m / ℃	ρ / $g \cdot cm^{-3}$
PW (Paraffin wax)	C_nH_{2n+2}	58	0.9
HDPE (High density polyethylene)	$\lbrack CH_2—CH_2 \rbrack_n$	139	0.95
PP (Polypropylene)	$\lbrack CH_2—CH(CH_3) \rbrack_n$	142	0.9
EVA	$\lbrack CH(COCH_3)—CH_2 \rbrack_x [CH_2—CH_2]_y \rbrack_n$	80	0.96
SA (Stearic acid)	$CH_3[CH_2]_{16}COOH$	66	0.96

3.3 Viscosity measurement

The viscosity of binder was measured by spheroid rotation method. The diameter of spheroid was 18.1 mm, the rotation speed was 5.48 r/s. The instrument was checked with standard silicon oil. The distilled water was refered when the viscosity was less than 0.015 Pa·s. The viscosities of PW, SA and several binders were measured. The viscosity measurement of feedstock was performed using the capillary rheometer shown in Fig 1 on the Instron material tester, The length and diameter of the capillary were 35 mm and 1.0 mm. The viscosities of feedstock with shear rate at 130 ℃ and with temperature at shear rate of $10 s^{-1}$ were measured respectively.

Table 3 The formulation of binders

Binder	Component / %	Mixing temperature / ℃	Mix time / h
BP_1	90% PW + 10% PP	160	1
BP_2	85% PW + 15% PP	160	1
BP_3	80% PW + 20% PP	160	1
BP_4	79% PW + 20% PP + 1% SA	160	1
BE_4	79% PW + 20% EVA + 1% SA	135	1
BE_5	74% PW + 25% EVA + 1% SA	135	1
BE_6	69% PW + 30% WVA + 1% SA	135	1
BH_4	79% PW + 20% HDPE + 1% SA	160	1

4 RESULTS AND DISCUSSION

4.1 The viscosities of binders

Table 4 lists the viscosities of PW, SA and several binders at $1.23 s^{-1}$ at different temperatures. The data in the table shows that PW has very low viscosity and good flowability. Besides the flowability, MIM binder should maintain the shape of parts after molding, so the polymer such as PP, EVA, HDPE etc. were added to PW. We can see from table 4 that the viscosity of a binder decreased with temperature which accorded with the rheological behavior of pseudoplastic fluid. At same temperature, the viscosity changed regularly with the formulation of binder. From BP_1, BP_2 to BP_3, the viscosity increased rapidly due to the increase of PP content. BE_4, BE_5 and BE_6 showed the same regularity. Furthermore, comparing the data of BP_3 and BP_4, it is shown that the viscosity largely decreased due to the addition of 1% SA and this trend strengthened with temperature.

Table 4 Viscosities of Binders(Pa•s)

Sample	Temperature/ ℃						
	120	130	140	150	160	170	180
PW	0.0006	0.0005	0.0005	0.0004	0.0004	0.0003	0.0003
SA	0.0009	0.0007	0.0006	0.0005	0.0004	0.0003	0.0002
BP_1	-	0.0012	0.0009	0.0007	0.0006	0.0005	0.0004
BP_2	-	0.06	0.038	0.01	0.008	0.002	0.0015
BP_3	-	0.218	0.135	0.084	0.052	0.025	0.01
BP_4	0.0183	0.088	0.025	0.002	0.001	0.001	0.0008
BE_4	-	0.803	0.638	0.48	0.342	0.266	0.173
BE_5	-	2.034	1.381	0.92	0.693	0.511	0.373
BE_6	9.019	6.502	4.832	3.754	2.976	2.354	2.002

4.2 The viscosities of Fe-Ni MIM feedstock

At first, on the condition of controlling the change of plunger speed of capillary to control the change of shear rate, the volumetric flow rate Q was measured at 130 ℃, τ_w in Eq. (2) and $\dot{\gamma}_a$ in Eq. (3) were obtained. Because L/R ratio is 35 in this test, the "end effect" was neglected and the Bagley correction was not necessary. The shear rate was corrected according to Eq. (4). The viscosities are shown in Table 5. Then Q was measured at different temperatures at fixed plunger speed of capillary. The determined viscosities are shown in Table 6.

As shown in Table 5 and 6, the viscosities of MIM feedstock increased with shear rate at same temperature and manifested pseudoplastic rheological behavior. At the same shear rate, the viscosities decreased with temperature. Therefore, the best injection molding rule in MIM process should be made on the basis of considering the function of temperature and shear stress together.

The strain sensitive exponent n in Eq. (1)

Table 5 The viscosities of Fe-Ni MIM feedstock at different shear rates (t= 130 ℃)

Shear rate/ s^{-1}	5	10	50	100
Viscosity/ Pa•s	223	239	169	144

Table 6 The viscosities of Fe-Ni MIM feedstock at different temperatures ($\dot{\gamma}$= 10 s^{-1})

Temperature / ℃	120	130	140	150	160
Viscosity / Pa•s	423	239	117	142	81

and the flow activiation energy E in Eq. (6) represent the influence of shear stress and temperature on viscosity of MIM feedstock respectively. The higher the value of n, the more slowly the viscosity of feedstock changes with shear rate and the better the rheological stability of MIM feedstock. The relation of shear stress and shear rate is shown in Fig. 2 from which the value of n can be determined. There is usually vibration of shear rate during injection molding, therefore this rhelolgical stability is advantageous to MIM. And if the value of E is low, the sensitivity of

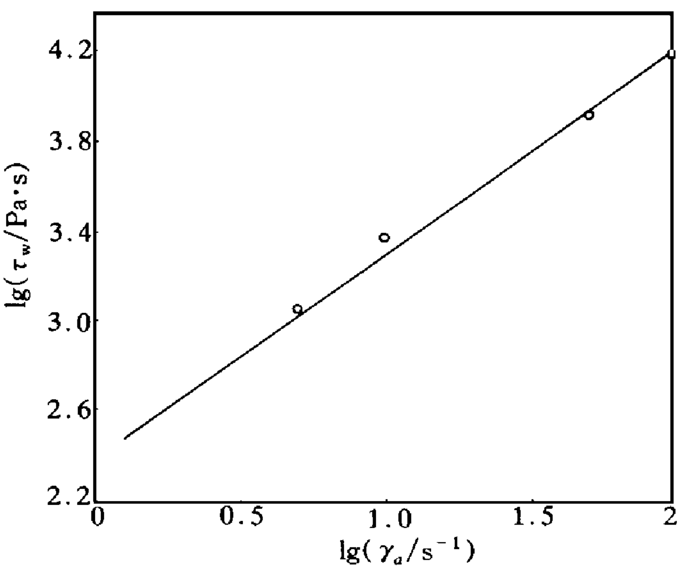

Fig. 2 The relation of shear stress and shear rate of feedstock

viscosity of feedstock to temperature is low and the vibration of temperature will not greatly affect the quality of injection molding parts. It is also advantageous to MIM. The relation of logarithm of viscosity and temperature was shown in Fig. 3 from which the value of E can be determined. $n = 0.88$, $E = 52.6$ kJ/mol. The value of n was higher and E was lower. It indicated that the injection filling property of the feedstock was good.

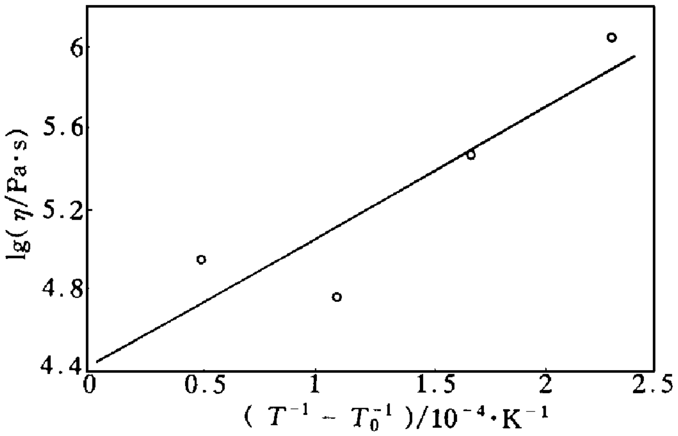

Fig. 3 The relation of viscosity of feedstock and temperature

5 CONCLUSIONS

(1) The viscosities of MIM binder decrease with temperature, and the viscosities incrase with the content of polymer.

(2) The viscosities of MIM feedstock decrease with shear rate at certain temperature which accorded with pseudoplastic rheological behavior, and the viscosities decrease with temperature at certain shear rate.

(3) The Fe-Ni MIM feedstock prepared has lower flow activiation energy and higher strain sensitive exponent which is advantageous to metal injection molding.

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