Rheological properties of metal injection molding feedstock [①]

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[Abstract] Viscosity of a polyethylene glycol-polymethyl methacrylate (PEG- PMMA) binder and PEG- PMMA/ Fe-2Ni feedstock in powder injection molding was measured and calculated. A logarithmic additivity between viscosity of the binder and that of its constituents was found. Other factors, such as temperature, powder loads, content and type of surface-active agents and those of polymers, in relation to rheological properties of feedstock were discussed as well. The results showed that with increasing viscosity of surface-active agent, polymer melt index or temperature, the feedstock viscosity decreased while higher polymer content and powder loading would lead to additional feedstock viscosity. The relationship mentioned above is expressed and effectively explained why the change rate of feedstock viscosity will slow down with the increase of shear rate.

[Key words] powder injection molding; rheology; feedstock property

[CLC number] TF 124　　　　　　　　　　　[Document code] A

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1 INTRODUCTION

Powder injection molding is a developing technology in near net shaping of powder metallurgy. Flowing feedstock made of powders and binders can fill into complex mold chambers at the pressure of injection[1~3]. Rheological property of feedstock (mainly viscosity) is an important mold-filled measurement, which is influenced by powder properties (such as morphology, granularity, loading and surface chemistry structure), binder properties (such as viscosity of its constituents), constituent proportions and process conditions (such as temperature and shear rate)[4~6]. Therefore, it's necessary to clarify influences on viscosity and rules of feedstock viscosity.

Many fitting equations were reported on the relationship among feedstock viscosity, binder viscosity and powder loading in powder injection molding[7~9]. The widely used one is $\eta = \eta_b A (1 - \Phi/\Phi_m)^{-n}$, where n approximates 2, however, such equation can't directly show feedstock viscosity as a function of shear rate. In this paper, the authors design a new feedstock system of PEG-PMMA/ Fe-2Ni[10,11] and systematically study its rheological properties.

2 EXPERIMENTAL

Feedstock was mixed[10] by metallic carbonyl iron and nickel powders and binders composed of PEG, PMMA and a small amount of surface-active agents.

Feedstock viscosity was measured by Instron 3211 capillary rheometer. As feedstock was pseudo-plastomer, the wall shear stress τ_w should be corrected by non-Newton equation:

$$\dot{\gamma}_w = \frac{\dot{\gamma}_a}{4}(3+ \frac{1}{n}) = \frac{\dot{\gamma}_a}{4}(3+ \frac{d\ln \dot{\gamma}_a}{d\ln \tau_w}) \tag{1}$$

where $\dot{\gamma}_w$ —wall shear rate; $\dot{\gamma}_a$ —apparent shear rate; n —non-Newton index, τ_w —wall shear stress.

The length to radius ratio of our capillary was $L/ R = 40$, so its inlet effect was negligible and feedstock viscosity could be calculated as follows:

$$\eta = \frac{\tau_w}{\dot{\gamma}_w} = \frac{2\Delta p R}{L \dot{\gamma}_a(3+ \frac{d\ln \dot{\gamma}_a}{d\ln \tau_w})} \tag{2}$$

where η —feedstock viscosity; Δp —capillary pressure; R —capillary radius; L —capillary length.

3 RESULTS AND DISCUSSION

3.1 Viscosity of binder and constituents

The viscosity of PEG, PMMA and binder is shown in Figs. 1~ 3 and found to rarefy during shearing. In our experiment PEG is measured at 220~ 260 ℃ and binder at 140~ 170 ℃, so it can be inferred that at the same temperature and shear rate, viscosity of the binder lies between that of PEG and PMMA. Considering that viscosity is usually expressed by Arrhenius equation as $\eta_i = \eta_{io}\exp(- E_i/ RT)$, ($E_i > 0$) and if their viscosity has logarithmic additivity, i. e.

$$\ln \eta_b = \sum_i w_i \ln \eta_i \tag{3}$$

where η_b, η_i are respectively viscosity of the binder and constituents, w_i is mass ratio of i, then the val-

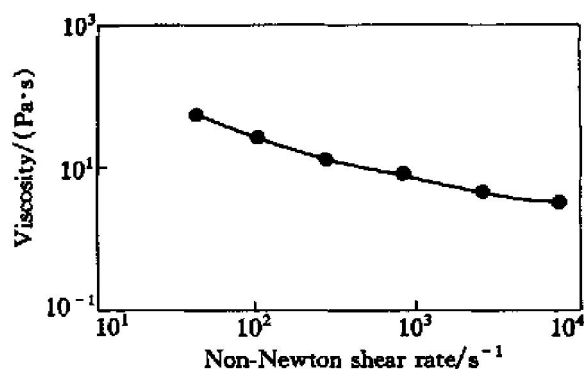ue of binder viscosity can be calculated by formula(3) and results obtained are listed in Table 1.

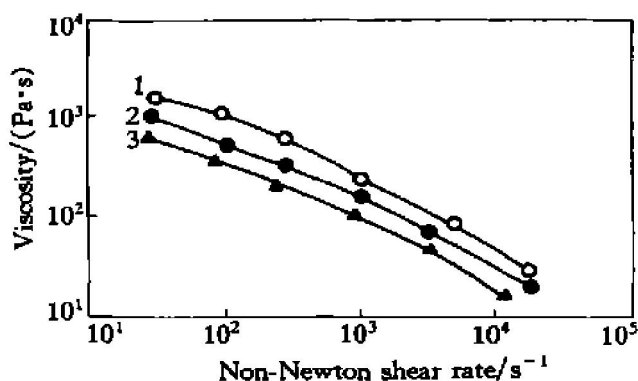**Fig. 1**   Relationship between viscosity and non-Newton shear rate (γ of PEG)

Fig. 2   Relationship between viscosity and γ of PMMA
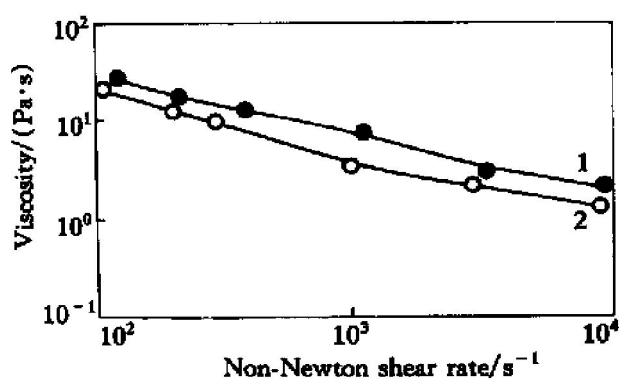1 —220 ℃; 2 —240 ℃; 3 —260 ℃

Fig. 3   Relationship between viscosity and γ of PEG-PMMA binder
1 —140 ℃; 2 —170 ℃

Table 1   Experimental and calculated viscosity of PEG-PMMA binder ($100 s^{-1}$)

Temperature/ ℃	Viscosity/ (Pa·s^{-1})	
	Calculated	Experimental
140	52. 0	36. 2
170	31. 3	21. 0

It's found in Table 1 that the value of calculation approximates that of measurement, which means that

their viscosity has additivity. Given rheological properties of its constituents, viscosity of the binder can be obtained. Such theoretical model has promising application for the design and improvement of binder and feedstock.

3. 2   Influence of surface-active agent on feedstock viscosity

Fig. 4 shows feedstock property as a function of surface-active agent (A). Without A, the feedstock viscosity is relatively high, adding 1% A the viscosity reduces a lot and keeps down at a small rate till A to 5%. However, the viscosity with 1% A is close to that with 5% A, which means only proper amount of addition A can change viscosity in a limited range.
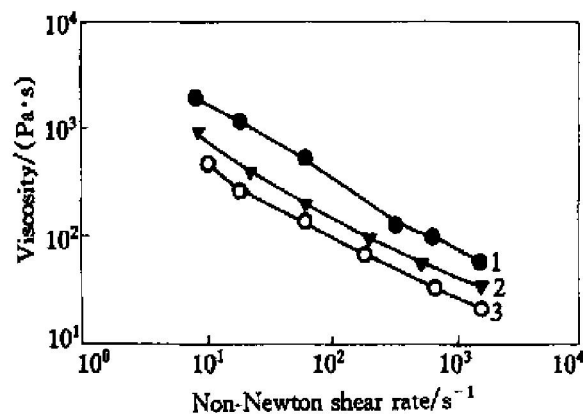

Fig. 4   Influence of surface-active agent on feedstock viscosity
1 —0% A; 2 —1% A; 3 —5% A

3. 3   Influence of polymer on feedstock viscosity

PMMA (I) and PMMA (II) with different molecular masses and melt index ratio MI(I)/MI (II) = 18 are chosen. Shear viscosity of feedstock prepared by PMMA(I) and PMMA(II) is listed in Fig. 5. It's found that feedstock made by PMMA (I) of higher MI has lower viscosity. MI is a measurement of "static" fluidity at a low shear rate in polymers while capillary determines "dynamic" fluidi-
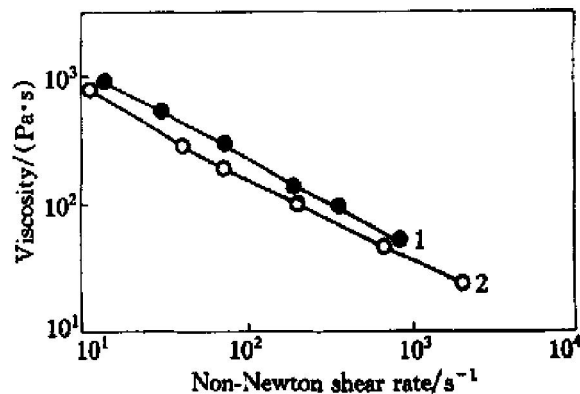

Fig. 5   Influence of polymer type on feedstock viscosity
1 —With PMMA (I); 2 —With PMMA (II)

ty ——(shear) viscosity of feedstock, which relates to shear rate and should have the same static fluidity tendency as its constituents. However, dynamic fluidity of different feedstock doesn't have a solid variation as their MI and changes with shear rate. At low γ (non-Newton shear rate), feedstock viscosity differs obviously and with increasing γ the difference becomes smaller, which indicates that feedstock viscosity is a more complex characteristic parameter than polymer melt index and results mentioned above lead to the conclusion that feedstock of good fluidity can be obtained by choosing polymers with higher MI.

Fig. 6 shows feedstock viscosity as a function of binder content in polymers. The viscosity of feedstock is low with 20% PMMA (mass fraction, as followed) in binders, then it becomes higher with 25% PMMA and it is highest with 30% PMMA. In binders, viscosity of polymer is much higher than that of low molecular or addition components. Increasing viscosity of polymers and binder can enhance that of feedstock due to the additivity of binder constituents' viscosity. Considering filled-in properties of feedstock, less polymers help to reduce its viscosity, however, the strength of green and debinding parts decreases at the same time, so the amount of addition polymer should be decided by overall consideration.
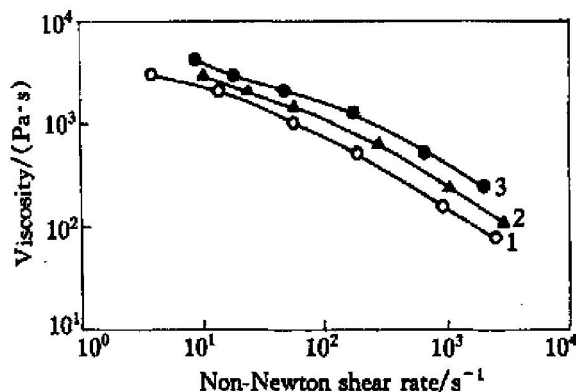

Fig. 6　Influence of polymer content on feedstock viscosity
1 —20% PMMA; 2 —25% PMMA; 3 —30% PMMA

3. 4　Relationship between feedstock viscosity and temperature

Feedstock viscosity of PEG-PMMA/Fe-2Ni is measured at 160 ℃, 170 ℃, 180 ℃ (Fig. 7). It's found that with increasing temperature, feedstock viscosity decreased showing the behavior of shear rarefaction. The viscosity greatly changed with different γ, the highest value (3 560 Pa•s) was obtained at 160 ℃ with low shear rate (4.5 s^{-1}) and it reduced to 448 Pa•s with shear rate of 100 s^{-1}. Compared with binder viscosity (less than 10 Pa•s or so), that of feedstock is much higher, which can be explained as follows: powders of Fe-2Ni have no fluidity and their viscosity can be regarded as infinite. Adding

powders can restrain binders from flowing and largely improve viscosity of the system. At higher temperature, feedstock viscosity decreases due to unbinding of molecular chaining.
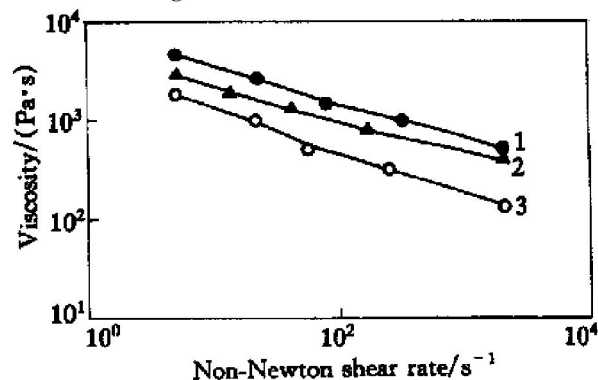

Fig. 7　Influence of temperature on feedstock viscosity
1 —160 ℃; 2 —170 ℃; 3 —180 ℃

3. 5　Relationship between feedstock viscosity and powder loading

As it shows in Fig. 8 that adding powder loads φ can enhance feedstock viscosity η. With increasing φ from 25% to 50%, η increases slowly; with φ more than 50%, η increases quickly; with φ= 56% and at low shear rate, η increases exponentially to 934 Pa•s and when γ = 100 s^{-1}, η can be more than 1 000 Pa•s. Therefore, it is concluded that the maximum of powder loading is about 55%.
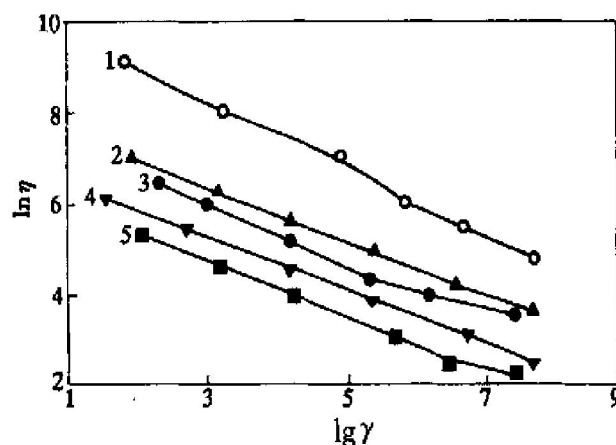

Fig. 8　Relationship between viscosity of feedstock and powder loads
1 — φ= 58; 2 — φ= 56; 3 — φ= 54; 4 — φ= 50; 5 — φ= 25

Relationship between content of particles and viscosity of particles filled polymers was induced by German[4] as η= A (1− Φ/Φ$_m$)$^{-n}$ and η changed with γ (η —feedstock viscosity, n —about 2 (constant), Φ—actual powder loads, Φ$_m$ —maximum powder loads, A —proportionality coefficient). Given a solid γ, the lineal relationship can be figured out by graphical analysis of ln η~ ln(1− Φ/Φ$_m$) as ln η= lnA − nln(1− Φ/Φ$_m$), then values of n and A can be calculated by slope and interception. Changing γ, another pair of n and A could be obtained in the same

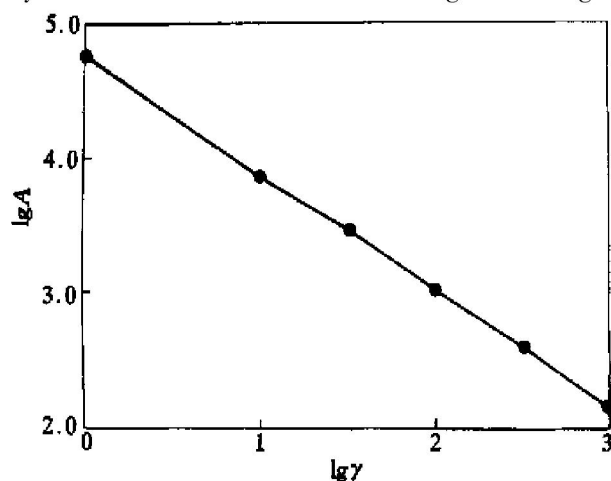way and their results are shown in Fig. 9 and Fig. 10.
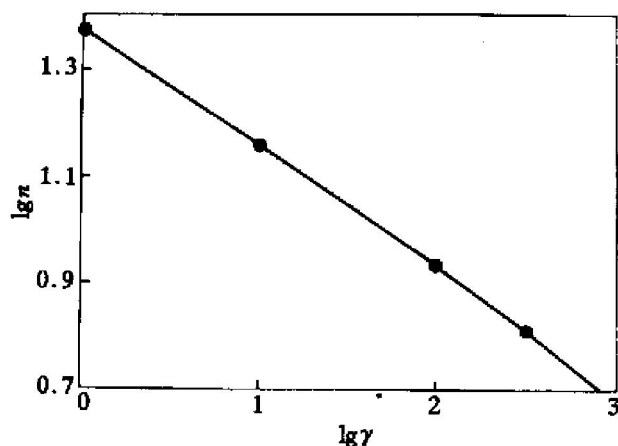

Fig. 9   Relationship between A and γ

Fig. 10   Relationship between n and γ

Thus, feedstock viscosity in the system can be expressed as:

$$\eta = 6.3 \times 10^4 \, \gamma^{-0.875} [\, 1 - \frac{\Phi}{\Phi_m}]^{-22.13 \, \gamma^{-0.187}} \quad (4)$$

It is found that A and n change with γ and considering the measurement conditions the equation is proportional with γ at $1 \sim 10^4 \, s^{-1}$. In our experiment, η decreases with increasing γ but when γ is high, η only reduced slowly, which cannot be explained by the hypothesis that n was a constant of 2. To qualify the influence of shear rate on feedstock viscosity correctly, we comes up with the expression of η as mentioned above, which is a dependable theoretical basis for the design of molds and injection process.

4 CONCLUSIONS

1) Viscosity of the binder and its constituents has logarithmic additivity, and lower viscosity of them is a prerequisite for good fluidity of feedstock.

2) Feedstock viscosity decreases with temperature, surface active agents and polymers of high fluidity while higher polymer content and powder loads can enhance its value.

3) Relationship among feedstock viscosity, powder loads and shear rate can be expressed as $\eta = 6.3 \times 10^4 \, \gamma^{-0.875} [\, 1 - \Phi/\Phi_m]^{-22.13 \, \gamma^{-0.187}}$, which effectively explains why the change rate of feedstock viscosity will slow down with the increase of shear rate.

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(Edited by HUANG Jin song)