

## Chemistry principles for thermoplastic polymer binder formula selection for powder injection molding<sup>①</sup>

LIANG Shu-quan(梁叔全)<sup>1</sup>, TANG yan(唐艳)<sup>1</sup>, HUANG Bai-yun(黄伯云)<sup>2</sup>, LI Shao-qiang(李少强)<sup>1</sup>  
 ( 1. School of Materials Science and Engineering, Central South University, Changsha 410083, China;  
 2. State Key Laboratory of Powder Metallurgy, Central South University, Changsha 410083, China)

**Abstract:** The polymer binder selection is one of the very important aspects for the powder injection molding. However, even nowadays the binder selection is still mainly performed by try and error method. Six commercial or intensive studied binder formulas were analyzed according to state diagram and chemical characteristics of ingredients in each binder formula. In addition, the interactions between the binder components and additives were also taken into account. Based on the analysis, the optimum binder formula was selected and some selection criterions were put forward for the binder and additives.

**Key words:** binder; chemistry; powder injection molding

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### 1 INTRODUCTION

The more and more materials and products have been manufactured by powder injection molding(PIM)<sup>[1-6]</sup>. PIM process includes feedstock preparation, injection molding, debinding and sintering. In PIM, the first important aspect is the binder selection for the processing time to be reduced, and the processing problem to be avoided, and the product size to be increased<sup>[7-11]</sup>. Since the research in this area usually is concerned with much more technical know-how, even today, there are very few articles to cover this topic in details<sup>[12]</sup>. Particularly, for most PIM researches, the main attention is paid to the pro-

cessing industrialization<sup>[13]</sup>. Therefore, there is a big gap between fundamental research and industrialization. The main objective of this paper is trying to put forward some selection guidelines for the polymer binders and additives, on the basis of analyzing and experimental results.

### 2 BASIC COMPONENTS IN BINDER FORMULA

#### 2.1 Typical commercial binder formulas

Table 1 lists the typical commercial binder formulas according to the developing time. A practical binder formula is composed of more than one component, and each compound has its own special function<sup>[14, 15]</sup>. In terms of the analysis on the prac-

**Table 1** Commercial binder systems for powder injection molding

No.	System	Main component (primary binder)	Secondary component (secondary binder)	Additive	Reference
F1	Wax system	Paraffin wax	Bee wax	Stearic acid	[ 16, 17]
F2	Wax-polymer	Paraffin wax	PE, PP, PAPS, EVA, PEA	Stearic acid, oleic acid	[ 18 - 21]
F3	Polymer wax	PP, PE, PS(high MW)	Paraffin wax	Phthalic acid, stearic acid	[ 17, 21]
F4	Polymer system	Polystyrene(high MW)	Resin(low MW)	Petroleum oil	[ 17, 21]
F5	Water-soluble polymer system	10% - 20% PMMA	PEG's	Unknown	[ 10]
F6	Catalyical debinding polymer system	Polyacetal	10% - 20% non-catalyical Polymer	Unknown	[ 9]

PE—Polyethylene; PP—Polypropylene; PA—Polyacetals; PS—Polystyrene; EVA—Ethylene vinyl acetate; PEA—Polyethyleneamine; PEG—Polyethylene glycol; PMMA—Poly methyl methacrylate.

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**Correspondence:** LIANG Shu-quan, Professor, PhD; Tel: + 86 731-8876690; E-mail: sqliang@mail.csu.edu.cn

tical binder formula, a general binder formulation can be considered as a system composed of primary binder, secondary binder and additives. The basic components in the binder formula are the primary binder and the second binder. The additives might be a dispersant, a stabilizer, a plasticizer or an inter-molecular lubricant, depending on the practical cases.

## 2.2 Primary binder, secondary binder and their selections

The primary and the secondary binders will form a continuous medium in which the powder particles are distributed randomly. Their basic functions include entrusting the system sufficient flow ability and binding the powder together after forming. The phase state for the binder component can be semi-crystalline, such as paraffin wax and PE, and also can be glassy like polystyrene and PMMA. These two kinds of polymers have quite different behaviors when they are heated, see Fig. 1<sup>[22]</sup>. The relative molecular mass for a polymer to be used as a binder should be located in a suitable range, that is, between  $M_1$  to  $M_2$  in Fig. 1. If the relative molecular mass is lower than  $M_1$ , the binder has very narrow melting range, which will result in some serious problem during the debinding, such as slumping higher and distortion. If the relative molecular mass of binder is too high, like over  $M_2$ , only at a higher temperature, the polymer can be transformed into the viscous liquid. This often causes the binder degradation. The transition temperature range ( $t_g - t_r$ ) from rubbery state to viscous liquid state for a binder polymer should be so wide that the binder can be removed from the green body in a wide temperature range during the debinding process.

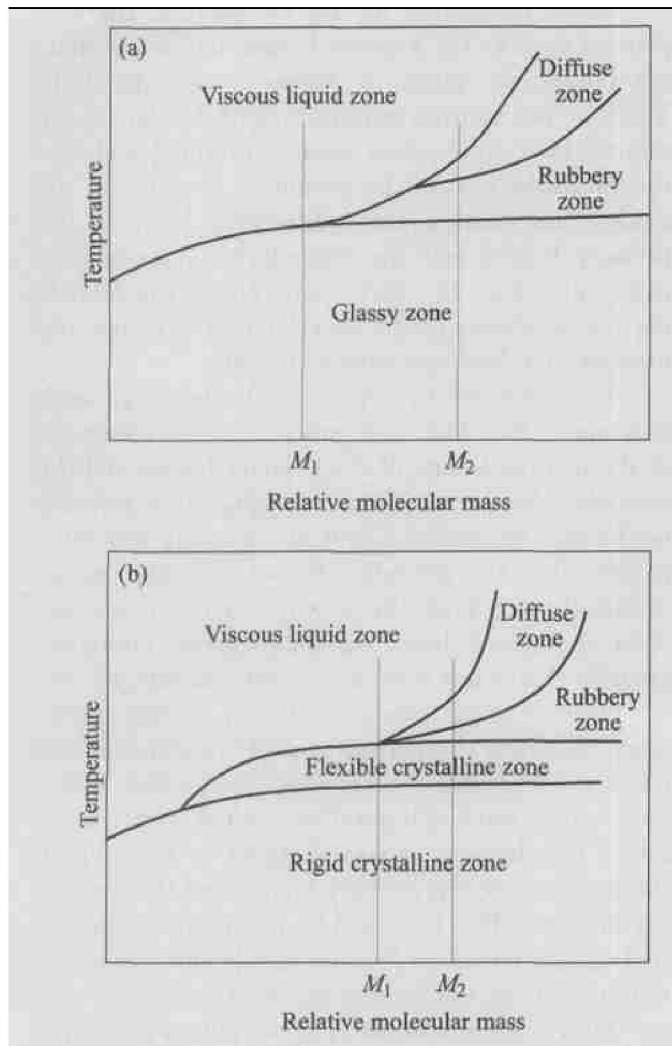
Some properties of the commercial thermoplastics used as the primary binder and the secondary binder are given in Table 2. According to Table 2, the melting points for both binders in F1 are too low. This often causes slumping and distortion of the part in the debinding process. In addition, the melting point difference between the primary binder and the secondary binder is narrow, only about 13–46 °C. Therefore, the debinding temperature should be relatively low and the process time becomes extremely long.

F2 is formed by replacing the bee wax with polymer in F1. The main problem is the mismatch of the melting points of the primary binder and the secondary binder. During debinding, the primary binder will be removed first at relatively low temperature and the secondary binder will take the responsibility to bind the powder together and entrust the green body sufficient green strength. Usually this is not easy job for the secondary binder. In order to get a better balance, F3 was developed, in which the percentages of the paraffin and polymer components were very close, like 45%–50% (mass fraction) paraffin against 40%–45% PE or PP. In fact, it was obtained by exchanging the positions of the primary binder and the secondary binder in F2. F4 could be regarded as a modified system based on F3. F5 and F6 are very new systems. They are formed based on very novel ideas. They overcome a lot of short points presented in the old binder formulas. Particularly F6, it has been applied in industry in Germany and Switzerland<sup>[7]</sup>. By examining the molecular structure, it could be found that paraffin waxes are alkenes with a chain molecular structure of  $C_nH_{2n+1}$  ( $n = 25 - 35$ ), and PE with  $[-CH_2-CH_2-]_n$ , PP with  $[-CH_2-CH(CH_3)-]_n$ , polystyrene with

**Table 2** Properties of typical primary binders and secondary binders<sup>[2, 18, 22, 23]</sup>

Name	Trade mark	$t_m$ or $t_g/$ °C	Average relative molecular mass	Density/ ( $g \cdot cm^{-3}$ )	Solubility parameter/ $MPa^{1/2}$
Paraffin	Shell 120	75( $t_m$ )	367	0.75	15.18*
	Okerin	108( $t_m$ )	500	0.70	14.20*
Bee wax		62–65( $t_m$ )	801	0.92	18.8*
High melt index PE	NA-250	130( $t_m$ )	12 500	0.93	16.3
Low melt index PE	MN711-20	120( $t_m$ )		0.914	16.3
PP	GY545M	140( $t_m$ )	31 850	0.905	16.3
PS	HF66	50( $t_g$ )	101 400	1.06	18.7
PMMA	CM-211	102( $t_g$ )		1.19	19.06*
PEG	PEG1500	45–50( $t_m$ )	1 500	1.20	21.08*
Polyacetal		175( $t_m$ )		1.42	22.6

$t_m$ —Melting point;  $t_g$ —Glass transition temperature; \* —Calculated values



**Fig. 1** Temperatures relative molecular mass diagram for amorphous(a) and crystalline(b) polymer

[ -CH<sub>2</sub>-CH(C<sub>6</sub>H<sub>5</sub>) - ]<sub>n</sub>, PMMA with [ -CH<sub>2</sub>-C(CH<sub>3</sub>)(COOCH<sub>3</sub>) - ]<sub>n</sub>, and polyacetal with [ -CH<sub>2</sub>-O - ]<sub>n</sub>. Therefore, a better binder should have a linear main chain with short branch chains, and with polar or polarizable function groups.

Another important aspect for binder selections is the solubility parameter match. The solubility parameter ( δ<sub>q</sub> ) can be calculated from the molar attraction constants ( F<sub>i</sub> ) and molar volume V<sub>i</sub> according to Eqn. (1)<sup>[24]</sup>.

$$\delta_q = \sum F_i / V_i \quad (1)$$

The representative molar attraction constant at 25 °C is listed in Table 3.

The interaction parameter( x<sub>12</sub>) can be estimated by Eqn. (2)<sup>[24]</sup> when the mixing process is endothermic:

$$x_{12} = V_1(\delta_1 - \delta_2)^2 / RT \quad (2)$$

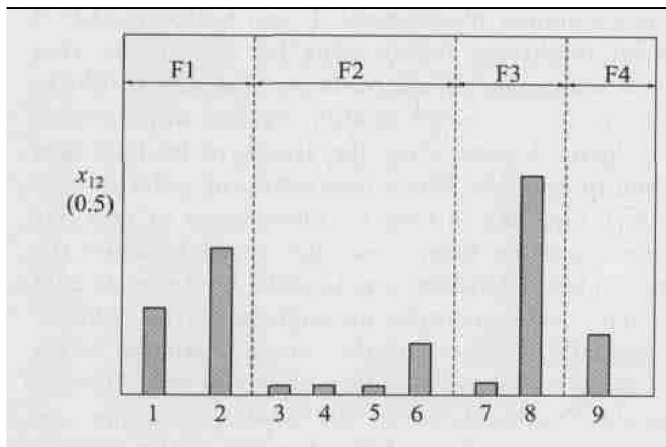
where 1 represents the primary binder; 2 represents the secondary binder; V<sub>1</sub> is the molar volume of the primary binder; R is gas constant; T is absolute

**Table 3** Representative molar attraction constant for typical atomic group in polymer ( at 25 °C )<sup>[24]</sup>

Group	Molar attraction constant F / ( MPa <sup>1/2</sup> •cm <sup>3</sup> •mol <sup>-1</sup> )		
	Small <sup>[21]</sup>	Hoy <sup>[22]</sup>	Van Krevelen <sup>[23]</sup>
-CH <sub>3</sub>	438	303	420
-CH <sub>2</sub> -	272	269	280
CH-	57	176	140
C	-190	65.5	0
-CH(CH <sub>3</sub> )-	495	476	560
-C(CH <sub>3</sub> ) <sub>2</sub> -	686	672	840
-CH=CH-	454	497	444
C=CH-	266	422	304
Phenyl	1 504	1 398	1 517
p Phenylene	1 346	1 442	1 377
-O-( ether)	143	235	256
-OH	-	462	754
-CO-( Ketones)	563	538	685
-COO-( esters)	634	668	512
-OCOO-( Carbons)	-	904	767
-CN	839	726	982
-N=C=O	-	734	-
-NH-	-	368	-
-S-( Sulfides)	460	428	460
-F	250	84.5	164
-Cl(primary)	552	420	460
-Br(primary)	696	528	614
-CF <sub>3</sub> ( n-fluorocarbons)	561	-	-
-Si-	-77	-	-

temperature.

The calculated interaction parameters for some formulas listed in Table 1 are showed in Fig. 2. According to the interaction parameters and reasons mentioned above, the best system is No. 7 in F3. However, the binder formulas with relative high interaction parameter, like over 0.5 of x<sub>12</sub> value, are also used due to their other good properties, like PS-wax system. In this case, the additives are added to subside the interaction between the binder's molecules. Even for the binder formula with relative low x<sub>12</sub> value, it was also important to add some additives to improve the other processing properties.



**Fig. 2** Interaction parameters between primary binder and secondary binder calculated according to Eqn. (2) and Table 1 and Table 2

- 1—Paraffin Shell 12—Bee wax;
- 2—Paraffin okerin 1865—Bee wax;
- 3—Paraffin Shell 120—High melt Index PE;
- 4—Paraffin wax (Shell 120)—Low melt Index PE;
- 5—Paraffin wax (Shell 120)—PP;
- 6—Paraffin wax (Shell 120)—PS;
- 7—PP—Paraffin wax (Shell 120);
- 8—PS—Paraffin wax (Shell 120);
- 9—PMMA-PEG

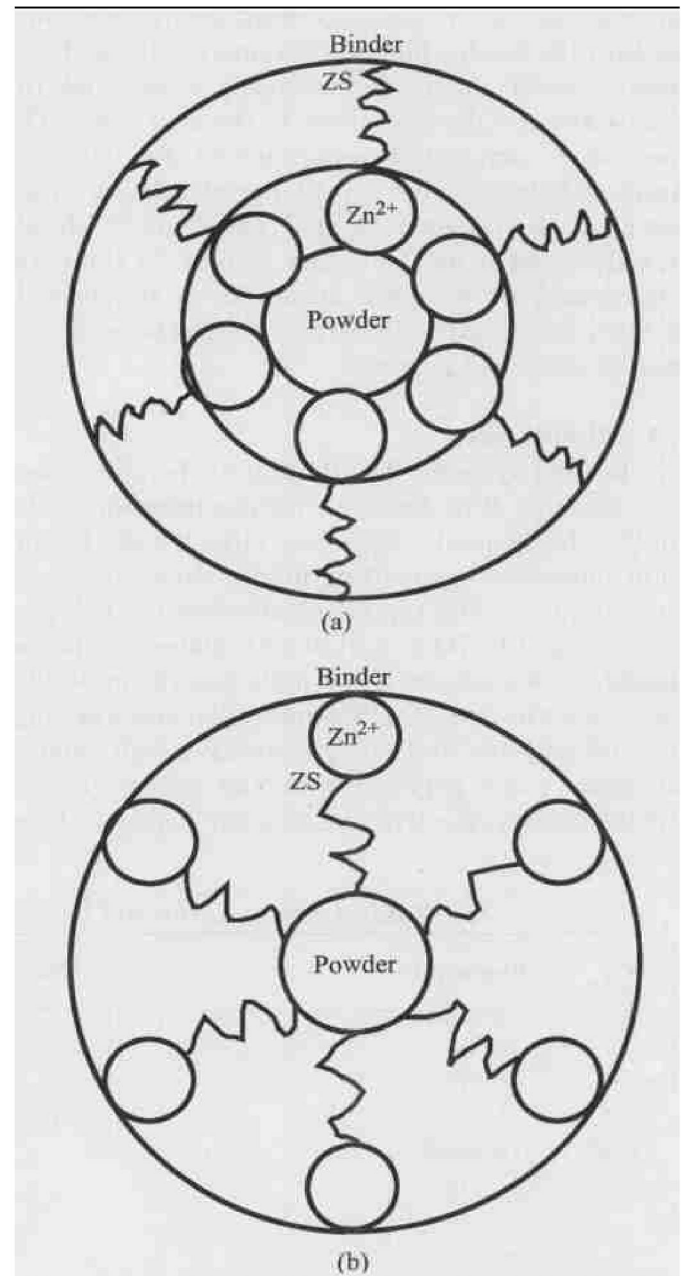
### 3 ADDITIVES AND THEIR SELECTIONS

The common additives include dispersants, which can help to distribute the powder in the media uniformly; stabilizers, which can keep the particles from agglomeration; plasticizers, which will enhance the feedstock flow ability; and inter-molecular lubricants, which can decrease the micro friction in the system.

#### 3.1 Dispersants

Dispersing processing includes wetting in which the interface of powder/ air is replaced by that of powder/ media, and dispersing in which the interface of powder/ powder is replaced by powder/ media. Since the physical interaction between the powder and the binder media is not strong enough to gain a well-dispersed system<sup>[25]</sup>, it is necessary to add dispersants. In addition, the dispersants can also increase the solid loading without decreasing the fluid ability<sup>[26]</sup>. The main mechanism of the dispersants is to form enough positions, from which the binder can react with the powder by chemical bonding or physical bonding. Another mechanism of the dispersants is electrostatic effects. For example, zinc stearate(ZS) was added to a negatively charged powder.  $Zn^{2+}$  ions (head) adsorbed to the powder surface, leaving the carbon chain (tail) to dissolve in the binder polymers. On the other hand, when a positively charged powder was mixed with ZS, the negatively charged stearate tail adsorbed on the powder surface, leaving the more

polar  $Zn^{2+}$  head to dissolve in the binder, see Fig. 3<sup>[27]</sup>. When shear forces act on the particle for both cases, the adsorbed layers will not be damaged and are helpful for dispersion processing. Organotinates, small molecular polystyrene and hydrosilylation-based compounds are common chemical-bond dispersants<sup>[28]</sup>.



**Fig. 3** Reaction of powder surface with dispersant  
 (a) —Negatively charged powder;  
 (b) —Positively charged powder

#### 3.2 Stabilizers

The main mechanism of the stabilizer is steric effect, which is produced in the molecular chains adsorbed on the powder particles<sup>[29]</sup>. Two basic requirements of steric stabilizers are strong anchoring to the surface and sufficient extension into the binder blend to prevent approaching particles. If the stabilizer

er molecules are not strong anchoring to the surface, they will be squeezed out when the two particles are approaching. In addition, if the adsorbed films have negligible extension into the binder media, these stabilizers still can't work. These are the main difference between the dispersant and the stabilizer. The copolymers with functional groups can be ideally designed as steric stabilizers, with one group adsorbing strongly to the particle and the strongly solvated group extending out into the binder blend. Obviously, the acid stabilizer should anchor to the basic sites, and the basic stabilizer should anchor to the acid sites. The most three important requirements for effective steric stabilization are<sup>[30]</sup>: 1) the stabilizing moieties (i. e. the polymer "loops" and "tails") should be well solvated by the binder media; 2) the polymer should be strongly anchored to the particle surface; 3) the particle surface should be well covered by adsorbed polymer.

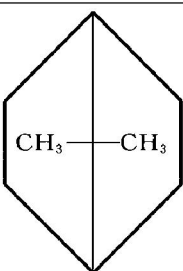
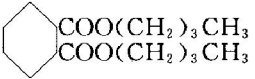
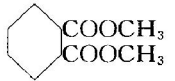
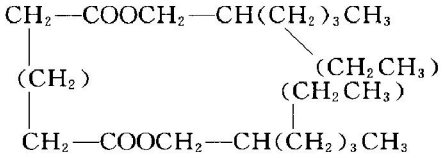
### 3.3 Plasticizers

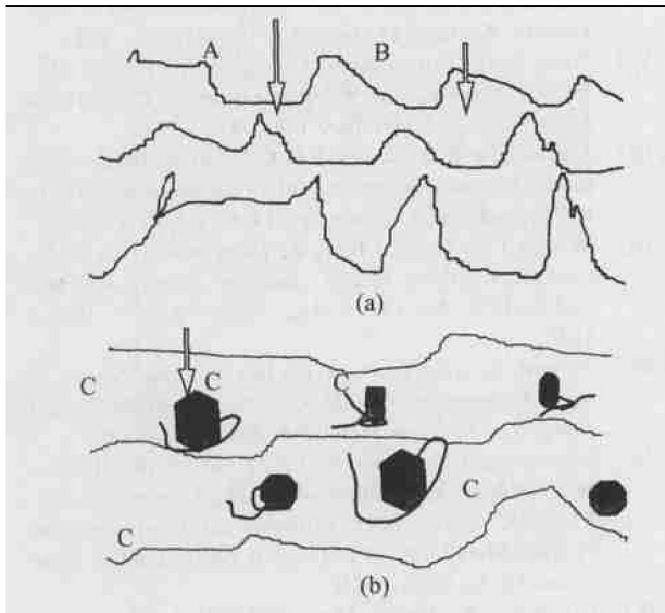
In PIM system, the addition of the plasticizers is to promote flow behavior during injection molding<sup>[31]</sup>. In general, they are either high boiling point liquids or low melting point solids such as esters camphor. The typical plasticizers for polypropylenes, and PMMA include phthalates, adipates, stearates, and oleates. For high relative molecular mass polyethylene, the low molecular mass copolymers of ethylene and vinyl acetates, small relative molecular mass

polyethylenes and polypropylenes can be used as effective plasticizers. Table 4 shows some common plasticizers. It can be found that it is an important requirement for plasticizers that their molecules should contain a ring group, like in case 1 - 3, or contain an atomic group which probably forms a loose ring-like structure by hydrogen bond or van der Waals interaction or polar dispersion force, like in case 4. These rings or ring-like atomic groups insert into the space between the molecules of binders to reduce the binder molecular contacts and generates an additional free volume. Especially, these specific atomic groups might work as a molecular pulley to reduce the intermolecular friction between the binder molecules and result in extra flow ability for the binder blends. This mechanism can be understood in terms of Fig. 4.

Fig. 5 shows the influence of dibutyl phthalate (DBP) on the viscosity of W-Ni-Fe-PS-PP-VO feedstock. It shows that due to the addition of DBP, the viscosity of the system is reduced a lot, particularly at low shear rate case. Since under low shear rate, the chain parts would be tangled the Ben ring up in DBP molecule to form a bigger size molecular pulley. The molecules of PS and PP in binder would obtain more free volume. With the increase of the shear rate, the chain parts will be untangled from the Ben ring, and the size of the plasticizer pulley is reduced. The effects of plasticizer will be depressed<sup>[31]</sup>. In addition, other factors for plasticizer selection are low volatility, no toxicity, sufficient high stability, and no corrosion.

**Table 4** Structures and basic properties of some typical plasticizers

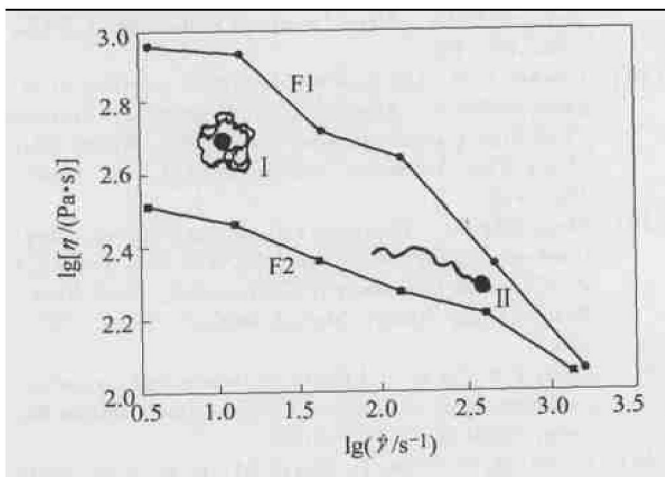
No.	Plasticizer	Molecular structures	Solubility parameter
1	Camphor		15.3
2	Dibutyl phthalate		19.2
3	Dimethyl phthalate		21.4
4	Diocetyl sebate		17.8



**Fig. 4** Plasticizing mechanism of plasticizer in blend of binders

A —Interlock sites in binder molecules;  
B —Unlocked sites in binder molecules;  
C —Plasticizer molecules

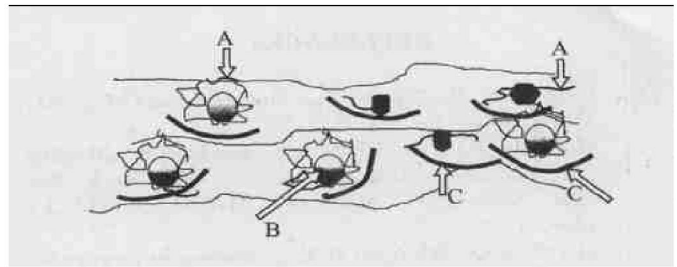
(a) —Before addition; (b) —After addition of plasticizer



**Fig. 5** Influence of DBP on viscosity of W-Ni-Fe-PS-PP-VO feedstock  
I —Interlocked; II —Stretched

### 3.4 Inter-molecular lubricants

The inter-molecular lubricants are some low relative molecular mass compounds which promote the flow of the binder formula in the melt, but have little effect on the solid state properties. In general, they have similar solubility parameters to the binder polymer and much lower viscosity at the processing temperature. The possible mechanism is to decrease the inter-molecular friction between the absorbed layer of the powder particles and the binder molecules. However, according to our research, the inter-molecular lubricants have a new mechanism<sup>[31]</sup>, that is, to improve the “pulley” effect of the plasticizer molecules.



**Fig. 6** Mechanism of inter-lubricant in powder injection molding feedstock

A —Plasticizer molecule;  
B —Powder particle with an absorbed shell;  
C —Inter-lubricant molecule

Fig. 6 shows these mechanisms of the inter-molecule lubricants in the binder formula. The molecular size should be smaller than that of the plasticizer molecule and should include some polar or polarizable function group so that they can be more affine to the plasticizer molecules and binder molecules, which are attached on the surface of the powder particles. The common inter-lubricants are high-class fatty alcohol, industrial stearic acid, wax GL-3, wax OP, wax E, and so on.

## 4 CONCLUSIONS

1) The temperature—relative molecular mass diagram is of great importance for the binder selection.

2) The binders should be a linear chain polymer with a polar or polarizable function group, and have good compatibility to the additives. An optimum binder formula in conventional binder systems could be designed in PP-wax system.

3) The dispersants molecules attach to the powder surface to improve the dispersing processing by forming a shell around the powder. A good dispersant should not be replaced by the small molecules in the binder media.

4) The stabilizers should contain a functional group, which can be strongly anchored to the particle and the moieties extend into the binder media to keep the particles from getting too close.

5) A good plasticizer should have a very close solubility parameter to the binders, and with a ring molecular structure. Its molecules work as a pulley to promote the flow of the binder melt.

6) The inter-molecular lubricants reside in the micro area around both the plasticizer molecules and the shell of the powder particles to enhance the plasticizer's pulley effect and the slide movement between the powder particles and binder molecules.

## REFERENCES

- [1] German M R. Powder Injection Molding [M]. NJ: MPIF, 1990. 1 - 20.
- [2] Mutsuddy B C, Rord R G. Ceramic Injection Molding [M]. London, Glasgow, Weiheim, New York, Tokyo, Melbourne, Madras: CHAPMAN HALL, 1995. 1 - 26.
- [3] LIANG S Q, HUANG B Y. Advances in powder injection molding[A]. SONG Jian, YIN Rui-yu. Proc of Inter Conf On Eng & Techn[C]. Vol. 2. Beijing: New World Press, 2000. 1206 - 1211.
- [4] Aparecido C G. Metallic powder injection molding using low pressure [J]. Materials Processing Technology, 2001, 118: 193 - 197.
- [5] Supati R, Loh N H, Khor K A, et al. Mixing and characterization of feedstock for powder injection molding [J]. Materials Letters, 2000, 46: 109 - 115.
- [6] Metz S A, Flemings M C. A fundamental study of hot tearing[A]. Flemings C. Symposium on Solidification and Materials Processing[C]. MA, USA: USA Publishers, Cambridge, 2001. 181 - 188.
- [7] LIANG S Q, HUANG B Y, QU X H, et al. High techniques and new concepts in metal powder injection molding[J]. High Technology Letters, 1996(12): 54 - 58.
- [8] Ebenhoch J. Ceramic injection molding with a polyacetal based binder system[A]. Press-information BASF. Advances in Powder Metallurgy and Particulate Materials [C]. MPIF, 1993. 45 - 56.
- [9] Aunette S A. Powder injection molding for metal and ceramics[A]. Press-Information BASF, K'95 Trade Press Conference[C]. Ludwigshafen, Germey, 1995. 29 - 30.
- [10] Anwar M Y, Messer P F, Ellis B, et al. Injection molding of 316 stainless steel powder using a novel binder system[J]. Powder Metallurgy, 1995, 38(2): 113 - 119.
- [11] Cooper P S, Borge G, Convery R D. Compacted product additives for the aluminium casthouse[J]. Aluminium World, 2001, 2(1): 39 - 42.
- [12] Wiech R E Jr. MIM binder systems and basic feedstock design[A]. Metal Injection Molding Seminar [C]. Florida, 1998. 19 - 34.
- [13] Loh N H, Tor S B, Khor K A. Production of metal composite part by powder injection molding[J]. Materials Processing Technology, 2001, 108: 398.
- [14] Lin S T P, German R M. The influence of powder loading and binder additive on the properties of alumina injection moulding blends[J]. Mater Sci, 1994, 29: 5367 - 5373
- [15] Loh N H, Tor S B, Khor K A. Powder injection molding-mixing study using Tagnchi method[A]. 1998 International Conference and Exhibition on Powder Metallurgy and Particulate Materials[C]. Las Vegas, NV, USA: Metal Powder Industries Federation, 1998. 559 - 570.
- [16] Wiech R B Jr. Method of Making Inelastically Compressible Ductile Particulate Material Article and Subsequent Working Thereof[P]. US 4445936, 1984.
- [17] Reed R B. Principles of Ceramics Processing[M]. Second Edition. A Wiley-Interscience Publication, John Wiley & Sons, Inc, 1995. 477 - 492.
- [18] Edirisinghe R B, Evens J R G. Systematic development of ceramic injection Molding process[J]. Material Science and Engineering, 1989, A109: 17 - 26.
- [19] Wright J K, Evans J R G, Edirisinghe M J. Degradation of polyolefin blends used for ceramic injection molding[J]. Am Ceram Soc, 1989, 72(10): 1822 - 1828.
- [20] Farrow G, Conciatori A B. Injection Moldable Ceramic Composition Containing a Polyacetal Binder and Process of Molding[P]. US 4624812. 25, 1986.
- [21] Stenvenson J E, Roser R, Ilica F, et al. Metal injection molding: mold filling and packing dynamics [A]. PM2TEC 2001: 2001 International Conference on Powder Metallurgy & Particulate Materials[C]. New Orleans LA: USA, 2001.
- [22] Brydson J A. Plastic Materials[M]. London, Boston, Durban, Singapore, Sydney, Toronto: Butterworth Scientific, 1982. 20 - 82.
- [23] Pine S H, Hendrickson J B. Organic Chemistry[M]. 4th Edition. McGraw-Hill Book Company, 1980. 830.
- [24] Fried J R. Polymer Science and Technology[M]. Englewood Cliffs, New Jersey: Prentice Hall PTR, 1995. 99 - 110.
- [25] Fowkes F M. Dispersions of ceramic powders in organic media[A]. Messing G L. Advances in Ceramics (Vol. 21): Ceramic Powder Science[C]. Westerville, Ohio: The American Ceramic Society, Inc, 1987. 411 - 419.
- [26] Mustuddy B C. Rheology and mixing of ceramic mixtures used in plastic molding[A]. Lee B I, Pope E J A. Chemical Processing of Ceramics [C]. New York, Basel, Hong Kong: Marcel Dekker, 1994. 239 - 259.
- [27] Chan T Y, Li S T. Effects of stearic acid on the injection molding of alumina[J]. American Ceramic Society, 1995(78): 2747 - 2758.
- [28] Green M, Kramer T, Paush M, et al. Chemically bonded organic dispersants[A]. Advances in Ceramics (Vol. 21): Ceramic Powder Science[C]. The American Ceramic Society, Inc., 1987. 450 - 480.
- [29] Osmond D W J, Waite F A. Dispersion Polymerization in Organic Media[M]. Barrett K E J. New York: Wiley & Sons, 1975. 9 - 44.
- [30] Johnson R E Jr, Morrison W H Jr. Ceramic powder dispersion in nonaqueous system[A]. Advances in Ceramics (Vol. 21): Ceramic Powder Science[C]. The American Ceramic Society, Inc, 1987. 323 - 345.
- [31] LIANG S Q, HUANG B Y. Rheology for Powder Injection Molding[M]. Changsha: Central South University Press, 2000. 90 - 103.

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