

P O L I M E R Y

MIESIĘCZNIK POŚWIĘCONY CHEMII, TECHNOLOGII I PRZETWÓRSTWU POLIMERÓW

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Rheological characterization of powder injection molding compounds

Summary — This review concerns the rheological research related to compounds obtained using powder injection molding (PIM) technology. PIM is a process for making metallic and ceramic items using forming method for thermoplastics. This technique allows the large-number production of relatively small (corresponding to a weight of around 100 grams) parts of complex shapes with reduced cost comparing to traditional metallurgy and increased efficiency by avoiding the use of extra processes. On the other hand, the number of process variables is very high, and their interactions are only partially understood. The knowledge of the flow properties is the key factor for successful injection molding. Its novelty consists in the polymer physics aspects of the problem, considering the compounds obtained in PIM process as polymer melts highly filled with powder particles.

Key words: powder injection molding technology, rheology, viscosity, powder, binder.

CHARAKTERYSTYKA REOLOGICZNA MIESZANEK FORMOWANYCH METODĄ WTRYSKIWANIA PROSZKÓW

Streszczenie — Artykuł stanowi przegląd literaturowy (81 pozycji) dotyczący formowania mieszanek z zastosowaniem technologii wtryskiwania proszków (PIM, z ang. *powder injection molding*). Podczas tego procesu łączy się proszek metalowy i/lub ceramiczny z tworzywem termoplastycznym jako spoiwem. Technika ta pozwala na otrzymywanie bardzo różnorodnych, stosunkowo niedużych (o masie około 100 g) elementów o złożonym kształcie, a koszt ich wytwarzania jest znacznie mniejszy niż w przypadku zastosowania typowych metod, np. metalurgicznych. Z drugiej jednak strony parametry procesu wtryskiwania mają duży, ale jeszcze nie w pełni poznany, wpływ na charakterystykę otrzymywanych elementów. Znajomość właściwości dotyczących przepływu tworzywa o wysokim stopniu napełnienia cząstkami proszku jest warunkiem uzyskania właściwej jakości wytworów i z tego powodu reologia tego rodzaju polimerów jest ostatnio przedmiotem wielu badań.

Słowa kluczowe: technologia formowania metodą wtryskiwania proszków, reologia, lepkość, proszek, spoiwo.

Powder injection molding (PIM) is a relatively new forming method for ceramics (CIM) and metals (MIM) with a significant technological and economic potential.

It was first applied to the production of ceramic parts in the twenties of last century [1]. By the late fifties, many carbide and ceramic components were shaped using this

method, but the production was very small. In the eighties, when major advantages of PIM were identified, a great progress in production was made, and since then the growth rate is as high as 50 % per year [2].

A special case, registering nowadays a significant priority, is micrometal injection molding (μ MIM) — the miniaturization of the conventional MIM, where the requirements for the materials and processing equipment are even more stringent because the dimensions are reduced to a micron scale [3].

During the production of PIM-parts [4, 5] the powder is mixed with an organic (polymeric) binder to form a homogeneous compound. In the next step, the compound is formed by injection molding into the required shape. After accomplishing its primary role — dispersion with powder into compound showing a viscosity suitable for injection molding — the binder is thermally or chemically removed (debinded) from the feedstock. Finally, the compact is sintered to obtain metallic or ceramic item of density about 96 % of theoretical one.

This method is first of all intended for the production of relatively small, high-precision parts with complex geometries. It combines the flexibility and mass production of injection moldings of thermoplastics with the efficient use of materials and techniques employed in powder metallurgy. The advantages of this method — in comparison to the conventional metallurgy — have been recently discussed *e.g.* by Petzold *et al.* [6].

The future PIM technology growth is linked to solution of already identified problems [2]. There are numerous critical points that may arise during processing as reported by Hunt *et al.* [7], Hens *et al.* [8] and Zhang *et al.* [9]. The processing requirements for μ MIM follow those established for micro injection molding of polymer melts [10, 11]. Besides, μ MIM feedstocks fail in complete mold filling [12].

Successful PIM processing always involves elements of compromise among processing conditions, powder characteristics and binder composition. While the rheology of suspensions of non-interacting spheres seems to be well established, the understanding of the rheological behavior of multiphase systems as those intended for the processing *via* PIM technology is necessarily a difficult task. The interpretation of the rheological data is further complicated by the interactions among the particles, which cause their redistribution and reorientation, and thereby influence the bulk rheological behavior [13]. Since there are number of excellent papers discussing rheological properties of composite materials [14, 15], only the aspects related specifically to highly filled polymer systems as PIM compounds will be briefly reviewed in the following paragraphs.

RHEOLOGICAL EXPERIMENTS

The use of steady-state mode of rotational rheometer, especially for highly concentrated compounds, is rather

difficult since the material trapped between the plates of the rheometer tends to hang out during the measurements [16]. Kurzbeck *et al.* [17] have thoroughly analyzed the accuracy of cone and plate rheometers' use for the measurements of materials prone to wall-slip, secondary flows and temperature changes due to dissipation energy from shear heating. Wall slip was discerned using two different geometries according to Mooney method (described and discussed *e.g.* in [18]). The secondary flows might be accounted for *via* estimation approaches, where relative torque (ratio of measured torque influenced by secondary flow and theoretical one under laminar flow) is related to Reynolds number. In case of the experimental setup described in [17] the maximum increase in torque due to secondary flows would be 0.2 %. An increase in temperature due to dissipation was calculated under adiabatic condition to be 40 K, but the measured values reached less than 1 K.

Rotational rheometers are more often used for investigation of dynamic viscoelastic properties. Though elasticity of filled thermoplastics remains a subject of considerable controversy [16], the basic dynamic viscoelastic properties provide the information about the degree of dispersion of the filler in a polymer binder and the presence of yield indicating agglomerations in the system [19]. Further, they can be used to demonstrate the effect of modification treatment as shown *e.g.* by Novak *et al.* [20]. In their work the dynamic properties were examined to establish the effect of coating on alumina powder, which is prone to destabilization in water due to its hygroscopic character. Stearic acid coated compounds exhibited structural breakdown close to the exit from the linear viscoelastic region, whereas in the case of non-coated compounds the moduli continuously decreased at higher shear stresses beyond the limit of this region. Dynamic modulus of coated compound remained almost the same after immersion in water confirming the chemical bonding of a stearate layer at the surface of the powder, preventing water absorption.

The capillary tests are currently realized as the best approach to predict the flow behavior of PIM compounds [21, 22], since they involve wide shear rates range. However, even the use of this type of instrument is complicated by several factors as the flow restrictions caused by instabilities or so called Serge-Silberberg effect, *i.e.* movement of particles from the capillary wall to the centre during flow, achieves a great magnitude and thus leads to an axial solids concentration gradient [23].

Furthermore, the data interpretation shows often lack of relevant application of corrections necessary to compensate non-Newtonian character of the materials studied in terms of both Bagley method to revise shear stresses, and Rabinowitsch approach to obtain true shear rates, *e.g.* [24]. Failure to recognize this fact can lead to errors in the reporting of the data intended to show flow behavior of PIM compounds.

RHEOLOGICAL REQUIREMENTS FOR PIM MATERIALS

Flow properties of polymer binders

Rheological effect of polymer binder must always be taken into account in connection to the filler. Minagawa and White [25] suggested that the importance of filler interactions to viscosity of a filled melt decreased as viscosity of polymer component rised. The stress contribution from a filler is approximately constant, and therefore as stress contribution from a polymer binder increases, the relative importance of filler is reduced.

Current investigations concerning binders are based mainly on the seeking tailored formulations, presented *e.g.* in [26, 27], and the role of additives [28–30]. Viscosity of a binder should be less than $0.1 \text{ Pa} \cdot \text{s}$ in order to provide PIM mixtures with viscosity below $1000 \text{ Pa} \cdot \text{s}$ [4]. Binders are usually multicomponent systems, where two parts can be generally discerned.

The first, major part, is a low-molecular weight polymer, typically wax. However, due to its low viscosity the shear forces necessary to disperse the particles and break up agglomerates may not be sufficient [13]. Hsu *et al.* [31] compared four kinds of waxes: paraffin, polyethylene wax, carnauba and acrawax serving together with PE-LD as binders for 304L stainless steel. They have shown that the latter two waxes exhibited higher viscosity and more suitable pseudoplastic flow, arising from their polar character (carnauba is alkyl acid ester and acrawax is a secondary amide) forming hydrogen bonds with a metal powder.

The other part, containing high-molecular weight polymers and additives, should provide suitable interactions with powder, and thus prevent the separation from powder during the flow. Block copolymers are often used for this purpose since they can be made of polymer blocks soluble in the dispersion medium and blocks with high affinity to powder, and thus impart steric stabilization of a compound. In [22] three types of polymer binders differing in the block copolymer used (ethylene-butyl acrylate, ethylene-vinyl acetate, ethylene-acrylic acid) were studied. As the concentration of a solid component increased to 30 vol. %, the influence of the particular binder composition on the flow properties diminished.

Polyethylene glycol (PEG) plays a similar role as copolymers. Chuankrerkkul *et al.* [32] investigated the effect of molecular weight of PEG on viscosity of compounds based on cemented carbides and three-component binder [PEG, poly(methyl methacrylate), stearic acid] and found out that replacing a quantity of higher molecular weight PEG with an equal amount of lower one did not affect the flow behaviour of the feedstock. This rather unexpected result is explained with help of a slip band model presented in the following paper of this group [33], and introduced later.

Majority of researchers concentrated on the effect of binder composition on rheological properties of feed-

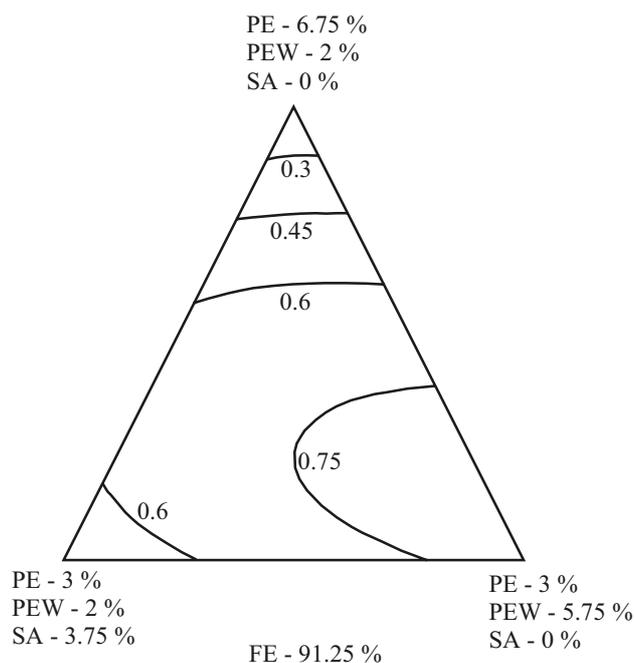


Fig. 1. Effect of four-component binder composition on the pseudoplasticity expressed by the power law index according to ref. [34]; descriptions of symbols in the text

stocks, but the roles of particular binder components and their inter-relations remain still unclear. One of the rare systematic investigations has been presented by Hsu and Lo [34]. They used McLean-Anderson statistic method [35] to study fluidity (inverse of viscosity) and pseudoplasticity (in terms of power law index) of 15 binder formulations and presented the contour maps showing how these two rheological variables varied for four-component binder composition at a constant concentration of the fourth component. As an example, Fig. 1 shows the effect of each binder component on the pseudoplasticity of the iron powder (FE) based feedstock. For higher polyethylene (PE) content ($> 4.5 \%$), an increase in PE amount and simultaneously decrease in stearic acid (SA) or polyethylene wax (PEW) amounts resulted in lowering of power law index. For low PE content ($< 4.5 \%$) binder formulations the effect was opposite.

Powders in a view of bulk process

Processing properties of PIM powders are governed by the way of their preparation as documented in Fig. 2. From the rheological point of view the most important powder characteristics are: particle size, particle size distribution and shape of particles.

Small particles increase viscosity during mixing and molding due to their high surface area, but simultaneously exhibit smaller molding defects. They have also pronounced tendency to form agglomerates resulting in further increase in viscosity; the greater the number of particles in the agglomerate, the lower the maximum

packing density and the higher viscosity [4]. Viscosity change with solids loading caused by agglomeration was intensively studied by Lewis and Nielsen [36]. The spheres (30–40 μm) were agglomerated by sintering into various clusters before mixing. Generally, more liquid is immobilized within the cluster as the number of particles in the cluster increases.

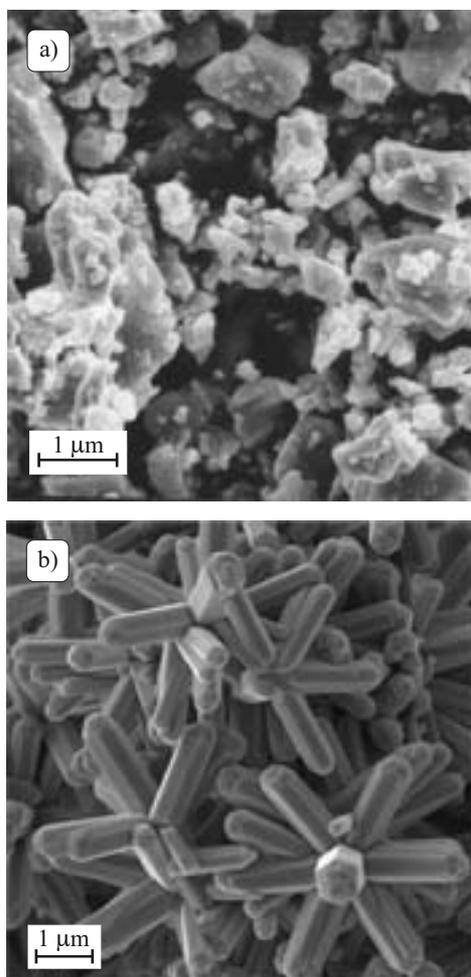


Fig. 2. Powders characteristics governed by the way of their preparation: a) mechanically milled tungsten carbide-cobalt alloy (WC-Co), b) chemically synthesized ZrO (courtesy of M. Machovsky from Polymer Centre TBU in Zlín)

In cases where high volume loading of fillers is needed — as for PIM process — the concomitant high viscosity is usually not favorable. High solids loading accompanied with small increase in viscosity can be attained using fillers having a wider particle size distribution rather than particles of similar sizes [13, 37], especially if the size ratio of one particle and the next is high. It has been shown [9] that if an infinitely wide range of particle size is available, maximum solids loading achieved will be greater than proposed theoretical value of 68 %. The negative aspect of a wide distribution of particle size is enhanced tendency to inhomogeneous microstructure.

Contreras *et al.* [38] pointed out that for irregular particles not only particle size distribution but also mean size is an important factor to set optimal solid loading; as it diminishes, maximum loading level increases. It is a result of larger interstices between coarser powder particles, where higher amount of binder is needed to fill the space among them.

Irregular particles — in contrast to spherical ones — exhibit lower packing density and higher inter-particle friction of the powder, and therefore have a negative influence on the viscosity of a filled polymer [14]. The viscosity increases and the maximum loading decreases when the length-to-diameter ratio of a particle increases [39].

The contradictory requirements for the powders suitable for production of sintered parts by PIM technology are even more stressed if other steps of the process are considered. Small particles allow faster sintering, but on the other hand increase sintering shrinkage, give slower debinding compared to larger particles, and are considerably more expensive [4]. A broad particle size distribution offers higher packing density, lower sintering shrinkage, but it causes slower debinding [40]. The disadvantages of spherical particles are slumping during debinding and lower compact strength [4]. In this view, new alloys with improved tailored properties should be developed to further advance the PIM applications [41].

Powder-binder ratio optimization

The crucial task during PIM processing is adjustment of a ratio between powder and binder, *i.e.* optimal loading level or packing fraction. The optimal loading refers to the powder concentration at which the compound exhibits good flow properties (viscosity lower than $10^3 \text{ Pa} \cdot \text{s}$) as well as homogeneity and stability in the shear rate range of 10^2 – 10^5 s^{-1} [42]. It occurs slightly below a maximum (critical) packing fraction attainable for a given system; according to Dihoru *et al.* [42] it should be set 6–14 % lower than a maximum value. Relative viscosity (ratio of the mixture viscosity and the viscosity of a binder) as a function of volume fraction of solids is often used variable to obtain maximum packing fraction for the particular powder-binder system. Powder particles stay mobile only to some filling degree. As the concentration reaches the maximum a fluid or a melt is confined among powder particles and the motion of the fluid is impossible, which results in a sharp increase in viscosity beyond all limits due to the friction among hard powder particles [4].

The value of the maximum packing fraction depends strongly not only on the materials properties, but also on the packing conditions. Nielsen [43] proposed that the value of maximum packing ranges from 0.601 to 0.637 for random packed spheres, Chong *et al.* [44] used the value 0.605 for monodispersed glass beads in PIB matrix, *etc.*

More than hundred of empirical and theoretical relations have been proposed in order to obtain the value of maximum packing fraction [4]. Often a simple empirical Maron-Pierce relation [45] is employed to calculate maximum loading level for PIM compounds [27, 46], even though the obtained values might sometimes be unrealistically high [27]. In cases, where Maron-Pierce model departs from experimental data, as shown *e.g.* by Jorge *et al.* [47] describing behavior of alumina powder and PEG/PE wax binder, its modification proposed by German and Bose [1] offers the good compatibility with experimental data, predicting the maximum loading degree value with high accuracy.

A set of most often recommended relations in the literature [4, 14] were tested in [48] and it has been found that the values predicted by the models were rather overestimated or underestimated, when compared to the experimental data. Furthermore, the predicted values of the maximum volume fraction of the same powder varied with the models used even though the maximum loading levels of PIM compounds established using these models [48] followed well the powder characteristics: the highest value of maximum loading corresponded to the powder with the broadest distribution of particle size, while the lowest value was attained for powder with high portion of small particles.

It should be mentioned that the volume fraction of particles also slightly varies due to pressurization, because of a great discrepancy between bulk moduli of the powder and binder [4]. The pressure is usually accounted for *via* pVT characteristics [49, 50] important for injection molding, and especially for predictions of the shrinkage of the final parts [51]. Except of the studies of pressure affected flow behavior of PIM compounds reported by Hausnerova *et al.* [52, 53] for the system consisting carbide powder and three-component binder (polyethylene, polyethylene based copolymer, paraffin wax), the effect of pressure is still omitted in the rheological characterization of PIM compounds.

Another rheological method to obtain critical powder volume concentration has been proposed by Barreiros and Vieira [54], which employed torque rheometry to set the optimal compositions of feedstocks based on powders having non-conventional characteristics for PIM. The optimal particle loading was evaluated as the highest value resulting from the intersections of the adjustment of linear functions of the mixing torque as a function of powder loading. The product coming from the feedstock selected by this method showed high density and flexural strength.

Recently, Dihoru *et al.* [42] demonstrated a possibility to determine optimal solid loading by use of neural network modeling. Consequently, they proposed an idea of combining the neural network with knowledge-based systems to optimize PIM process.

FLOW CHARACTERISTICS OF PIM COMPOUNDS

Flow course

As documented in the schematic diagram (Fig. 3), PIM compounds generally show high sensitivity to shear rate variations, even if a binder behaves in a Newtonian mode (plot A). Generally accepted statement that viscosity of compounds at all concentrations is higher than that of pure binder is not valid for certain materials. Instead, flow curves of low concentrated systems (up to 10 vol. %) may overlap or be even lower than that of binder (plot B) as has been shown *e.g.* for 10 vol. % of zirconia in CIM compound [55], hard-metal carbide particles in polyolefine based binder [56], or carbon black in liquid crystalline polymer matrix [57]. This flow behavior suggests that the rigid structure formed by particles increases viscosity significantly at low deformation rate, however, this structure becomes destroyed as shear rate increases, and thus it does not enhance resistance to flow, but acts rather as a lubricating agent.

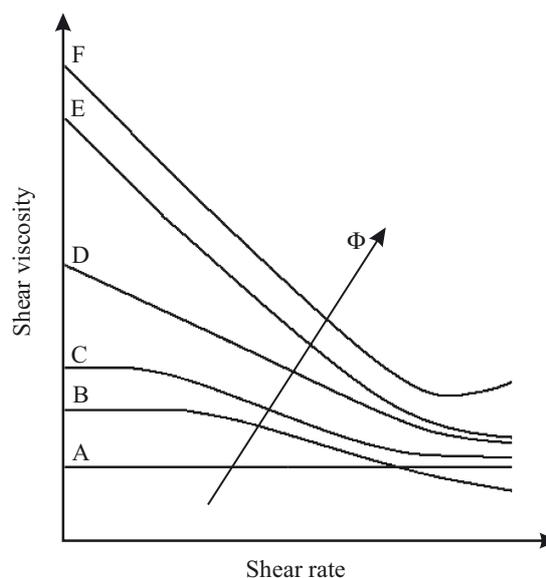


Fig. 3. Schematic flow curves of compounds obtained in PIM proces: A — newtonian binder, B — 5–10 vol. % powder loading, C, D — medium concentrated compounds, E — yield stress affected flow curve, F — dilatant flow occurring at high concentrations

As concentration of powder rises further, the Newtonian plateau becomes reduced (Fig. 3, plot C) or even disappears (Fig. 3, plot D) in the measured range of shear rates. It has been widely accepted that the change in non-Newtonian flow arises from the disruption of agglomerates formed by particles [17]. The two mechanisms of affecting viscosity can be discerned. One concept is based on the assumption that agglomerates' destruction during shearing causes decrease in the amount of suspending fluid entrapped among particles. Thus, viscosity decrease is due to the drop of an effective

volume fraction of a powder [58]. Other assumptions relate the change in viscosity to the dissipation energy rising from rotation and distortion of particle agglomerates [59].

Depending on the type of dispersed particles, especially on particle size, yield point may appear for highly concentrated compounds (Fig. 3, plot E) at low shear rate as an indication of particle network structure within the melt, which is relatively stable at lower shear rates [14, 19]. At higher shear rates, however, this structure is broken, and the viscosity is dominated by hydrodynamic interactions [60] resulting in shear thinning as particles and polymer orientate and order in the flow direction to allow inter-particle motion.

As pointed out by Kurzbeck *et al.* [17], some authors claim that yield stress might be the result of extrapolation rather than a real phenomenon [61]. Zakharenko *et al.* [62] first reported the existence of yield stress at high concentrations of carbon black in a rubber matrix due to build-up and destruction of particle structures and agglomerates.

Since fine particles exhibit larger surface area and higher inter-particle friction, they have enhanced tendency to yield. However, yield stress may also be observed for larger particles due to steric hindrances at concentrations near the maximum volume of the filler in a compound [63].

The Casson method [59] based on energy dissipation mechanism or the empirical Herschel-Bulkley model [64] are widely accepted ways of yield stress evaluation. Kurzbeck *et al.* [17] reported equal yield stress values predicted by the two mentioned ways for inorganic pigment in paraffin wax compounds, supporting Casson's idea of energy dissipation mechanism responsible for the viscosity variation with shear rate.

At still higher powder concentrations, with further rise of shear rate, the volume increases because particles cannot form layers and slide over each other [65]. Then, depending on the binder wetting characteristics, shear thinning may turn into dilatant flow, especially for irregularly shaped particles (Fig. 3, plot F). There is still considerable uncertainty about the source of such be-

havior. An increase in viscosity with shear rate may be indicative for particle disordering [65] or dilation. Jansma and Qutubuddin [66], who studied this phenomenon using different viscometers, showed that it could not be an experimental artefact due to the slip at the wall.

The mechanism proposed by Barnes [67] is that with increasing shear stress (rate) the layers formed in the pseudoplastic flow region becomes disrupted, and at a certain (critical) shear stress or rate are fully eliminated and the flow turns into dilatant. It implies that each highly concentrated suspension exhibits dilatant flow at the proper flow conditions depending on filler concentration, particle size distribution and also viscosity of a polymer component.

Finally, highly concentrated compounds (about 50 vol. % of solids and higher) may exhibit radical changes in their flow curves accompanied by distortions of the extrudate surface called melt flow instabilities [22, 56, 68, 69].

Unstable flow phenomena

Melt flow instabilities

Only a few phenomena in polymer processing have attracted such attention for more than half a century, from both theoretical and practical points of view, as melt flow instabilities.

A particular type of unstable capillary flow are pressure oscillations (spurt flow) as observed for certain polymers as high density or linear low density polyethylenes, polyisobutylene, and the most recently metallocene linear low density polyethylene [70]. The shear rate range, where this effect appears, lies below the chaotic flow range [22]. In the oscillation region the flow curve is split into two branches and the pressure pulsates between them (Fig. 4).

In the literature several interpretations of the underlying mechanisms have been offered and can be found *e.g.* in the comprehensive studies by Leonov and his co-workers [71, 72]. The basic explanations of spurt flow are following [72]:

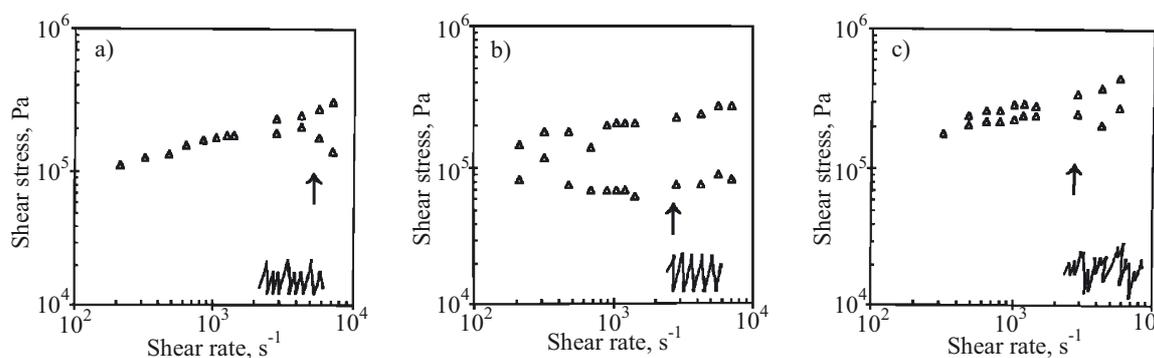


Fig. 4. Pressure oscillations affected flow curves of compounds based on multicomponent binder (paraffin, PE, PEG 6000, ethylene vinyl acetate) at 50 (a), 55 (b), or 57.5 (c) vol. % of WC-Co powder; according to ref. [56]

— fluidity loss or hardening: flow induced relaxation transition in polymers from the fluid to solid-like structure;

— compressibility of the polymer melt in the capillary reservoir;

— the occurrence of the flow instabilities is related to the “inherent constitutive instability”, assuming the real existence of the true branched flow curve in the bulk shear polymer flows;

— slip-stick at the capillary wall;

— polymer chains disentanglement at the capillary wall, with the following slippage of the neighboring chains near the wall.

Having studied the PIM compounds, Isayev and Fan [73] observed unstable flow for the system consisting of polypropylene binder filled up to 65 vol. % of silicon powder. In this case instabilities occurred in a capillary rheometer at the entire range of shear rate studied ($1\text{--}10^2\text{ s}^{-1}$). Yilmazer *et al.* [74] reported for 73 vol. % of ammonium sulphate powders in polybutadiene acrylonitrile-acrylic acid that steady flow could not be obtained under a critical shear stress. The substitution of the larger particles with the smaller ones resulted in the flow without disturbances.

In Hausnerova and coworkers papers [22, 56, 69] flow instabilities of a “pressure oscillations” type were recorded for carbide compounds containing 50 vol. % of solids and higher. However, resulting flow curves had quite different character compared to the data usually related to the oscillation effect [22] of polymer melts. For the pure polymers, the upper branch ends at a rate (stress) level, where the pressure oscillations cease. In the oscillation range the lower branch overlaps with the other one along the shear rate axis. Beyond that range, the flow follows the lower branch. For the PIM compounds studied [22] the lower branch of the flow curve extends only over the pressure oscillations region (Fig. 4.) Apart from this area the overall flow is governed by a continuous line exhibiting a weakly developed inflexion. This appears to be a novel instance of the oscillating phenomenon not reported herein.

In the work [69] it has been shown that temperature is the key factor limiting the pressure oscillations of PIM compounds affecting their onset in the opposite manner to polymer melts, almost independently on the filler concentration. At higher temperature the formation and reformation of particles mat at the capillary entrance is enhanced by lower binder viscosity, which supports the mechanism of filtration effect as a possible explanation of unstable flow occurring during capillary flow of highly filled compounds, introduced first by Yilmazer *et al.* [74], and then studied by Yaras *et al.* [75].

Wall slip

Wall slip is the phenomenon considered as typical to occur during flow of highly concentrated suspensions [44, 74–78]. Mooney method [16] is a common approach

to detect the presence of wall slip during rheological measurements. Nevertheless, Huzzard *et al.* [77] reported the experimental contradictions with Mooney assumption of the wall slip as a large velocity gradient adjacent to the capillary wall. The later approach to evaluate wall slip given by Hatzikiriakos and Dealy [79] is based on the slip velocity dependence on the wall normal stress. On the other hand, Barnes [67] supposes that slip can occur without influencing the flow properties as he relates its origin to more general wall effects. According to Cohen and Metzner [80] the ratio of capillary diameter and that of particles should be greater than 30 to neglect wall effects.

For cemented carbides in a three-component binder system [PEG, poly(methyl methacrylate), stearic acid] the existence of a criss-cross slip has been reported by Chunkrerkkul *et al.* [33]. It is a phenomenon occurring typically for clays in water, where the flow occurs on the sets of slip bands (mobile binder) formed on planes near to the planes of maximum shear stress. The slip bands are composed of aligned particles layers of a plate shape, which slip one past another, lubricated by water. The authors propose a “slip band model” resulting in equation similar to the empirical relations of Maron-Pierce [45] or German and Bose [1] relating the relative viscosity to the volume fraction of a filler. The apparent viscosity of a compound is related to the viscosity of the slowest moving molecules in the mobile part of the binder (in their case PEG) instead of to viscosity of a binder, and further, the volume fraction is replaced with the actual volume fraction taking into account the voids. Thus, the model accounts for the viscosity reduction with shear rate caused by enhanced voids formation allowing more slip bands to be mobilized.

CONCLUSIONS

Processing of materials *via* powder injection molding is clearly an interdisciplinary challenge, combining the metallurgy with plastics technology and material science of polymer resins, metals and ceramics. From the number of works devoted to the rheology of PIM in the last decade over 90 % were published in the journals devoted to powder metallurgy, the remaining ones in polymer and material science oriented journals.

The possibility to use an injection molding developed for thermoplastics to produce the metallic or ceramic items is still not widely spread information within the polymer processing society. The present state might be partly affected by the fact that majority of PIM realizations is patented, and the research groups involved do not will to publish their findings.

On the other hand, the design methodology currently developed in the PIM industry is based on the trial-and-error approach. Computer aided engineering (CAE) gives the predictions of pressure, velocity and temperature profiles throughout the flow region *via* commer-

cially available PIMSolver (Cetatech, South Korea), which is a 2.5D FEM software package developed for the simulation of the PIM process [81]. However, the essential knowledge of the treatment of the rheological data is often missing in the experimental works. Important factors, pressure for example, influencing the flow properties of these highly filled polymers are still omitted from both experimental and theoretical insights. *A priori* application of the fundamental theories on the suspensions to prediction of the flow properties of PIM compounds should be taken with an extreme caution, because it brings a number of obstacles and limitations. Therefore, the main intention of this review was concentrated on the PIM compounds with the aim to point out the important experimental findings on the background of basic rheological statements.

ACKNOWLEDGMENT

This work has been financially supported by the Grant Agency of the Czech Republic (Project No. 103/08/1307) and Ministry of Education, Youth and Sports of the Czech Republic (Project No. MSM 7088352101). It is based on the inaugural dissertation "On the Rheology of Filled Polymer Melts" defended by B. Hausnerová at the Tomas Bata University in Zlín in 2004. B. Hausnerová is the laureate of the national section "For Women in Science", being financially supported by L'Oréal during the year 2007.

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Received 18 II 2009.