Optimization of processing of powder injection molding feedstocks prone to phase separation

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Doctoral Thesis Summary

Tomas Bata University in Zlín

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Faculty of Technology

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Optimalizace procesu vstřikování práškových materiálů vykazujících fázovou separaci

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ABSTRACT

In the last decades Powder Injection Molding (PIM) became an effective technology for a mass production of precise and shape-complex metal and ceramic items. The main issue of PIM process is phase separation occurring during injection molding step. The phase separation causes defects which are detected mostly after final sintering, and thus leading to significant economic and ecological losses.

The aim of the thesis is optimization of PIM process and detection of powder/binder separation during/after injection molding step, when the process is still reversible - materials can be regranulated and used again. Direct testing of molded samples, without any additional treatments or knowing an exact composition of used binders, is provided for a broad cast of PIM feedstocks including commercially available ones. The proposed testing method combines scanning electron microscopy with energy dispersive X-ray to detect changes in powder or binder concentrations due to a phase separation, which are then analyzed with a mathematical approach to provide the single variability parameter to quantify the tendency of the particular feedstocks towards phase separation.

Further, rheological properties of PIM feedstocks were investigated with the special regard to wall slip effect, which serves as a parameter indicating phase separation during shear deformation. The results reveal the importance of the surface roughness and geometry of the processing tools for the wall slip development; therefore, these parameters should be considered for reliable testing to optimize the molding step of PIM.

Finally, the influence of processing parameters such as injection molding temperature and debinding route on the sintered surface structure of PIM parts revealing signs of phase separation was investigated by contactless scanning. The obtained qualitative data were then treated with suitable statistical approaches to quantify the quality of the resulting PIM parts.

This thesis provides the contribution to predict and reduce the phase separation of PIM feedstocks, thus positively influencing the effectivity of the PIM process.

ABSTRAKT

Technologie vstřikování práškových materiálů (tzv. PIM) patří v posledních letech mezi rychle se rozvíjející postupy pro velkoobjemovou výrobu přesných a tvarově komplexních produktů z kovu a keramiky. Defekty finálních výrobků jsou zpravidla způsobeny fázovou separací materiálu (polymerní pojivo a kovový/keramický prášek) během fáze vstřikování. Tyto vady jsou detekovány až v poslední fázi výroby (sintrace), kde je proces nevratný, což působí značné ekonomické a ekologické ztráty.

Dizertační práce se zabývá optimalizací procesu vstřikování práškových materiálů a detekcí fázové separace kovového/keramického prášku a polymerního pojiva během vstřikování, kdy je proces ještě vratný. V rámci dizertační práce byla vyvinuta nová testovací metoda za použití elektronové mikroskopie v kombinaci s prvkovou analýzou EDX. Výhoda této metody spočívá v přímém testování vstřikovaných tělísek bez nutnosti dalších úprav, a je možné ji použít i pro komerčně dostupné materiály bez znalosti složení použitého polymerního systému. Tato nová metoda byla otestována na komerčně dostupných materiálech a také na materiálech připravených na UTB ve Zlíně. EDX data byla analyticky zpracována s cílem poskytnout kvantifikaci náchylnosti jednotlivých PIM materiálů k fázové separaci prostřednictvím jednoduchého parametru, tzv. koeficientu separace.

Materiály používané v PIM technologii byly také testovány z reologického hlediska, a to se zaměřením na skluz na stěně, který při toku kanálem mění hodnoty gradientů smykových rychlostí, a tím ovlivňuje míru fázové separace. Pro testování bylo zvoleno několik typů kapilár s rozdílnou geometrií a povrchovou drsností. Výsledky ukazují na citlivost reologických dat vysoce plněných materiálů vzhledem ke zvoleným charakteristikám tokového kanálu.

Kvantifikace vlivu procesních parametrů na kvalitu povrchu finálních sintrovaných produktů byla provedena pomocí bezkontaktní profilometrie. Optimalizace vstřikovací teploty a způsobu odstranění polymerního pojiva za účelem dosažení lepší finální povrchové struktury sintrovaného výrobku se jeví jako perspektivní nástroj pro potlačení projevů fázové separace.

Tato disertační práce představuje přínos k porozumění a potlačení jevu fázové separace vysoce plněných materiálů, a tím přispívá ke zvýšení efektivity procesu vstřikování práškových materiálů.

INTRODUCTION

Metal and ceramic products bring many advantages in comparison to polymeric materials. They have usually high strength, stiffness, higher temperature resistance, and also better electric and magnetic properties in case of metals. On the other hand, they exhibit inferior processability in comparison to plastics [1-3].

Powder injection molding technology (PIM) combines advantages of metals/ceramics with processability of polymers [4]. Polymeric binders are used for shaping of metal/ceramic powders by injection molding, holding them until bonding in a sintering furnace close to a theoretical density. PIM includes four basic steps consisting of mixing, injection molding, debinding and sintering. All these steps contribute to precise final product without defects. Nowadays, the main problem of the process is a detection of defects resulting from so called phase separation in final products after sintering, when process is irreversible. Thus, current research is focused on methods capable to determine and reduce issues and defects prior sintering [1,5-7].

THEORETICAL BACKGROUND

1. Compounds for powder injection molding

Highly filled polymers used in PIM technology contain typical binder volume of 35 – 60 vol. % to form a homogeneous feedstock.

The role of binder system is to provide suitable flow properties to a feedstock during injection molding step, and holding powder particles into the required shape prior sintering. The binder system usually consists three main parts. First one is main component (low molecular polymer – paraffin, PEG, etc.) which ensures flow properties of a bulk feedstock; polar waxes improve also an adhesion between powder and binder system [1,6][6]. The backbone polymer that provides strength to the initial of sintering is the next ingredient (e.g. PE, PP, PS, PMMA). Binder systems also contain a small amount (less than 5 vol. %) of additives (dispersants, stabilizers, plasticizers and intermolecular lubricants) to enhance suitable rheological behavior [1,8].

Second component of a PIM feedstock is powder. Typical powders used in PIM technology are based on iron (alloy steels, high speed steels, stainless steels, etc.), reactive titanium powders or ceramics (Al_2O_3, ZrO_2) [1,9]. Requirements on an ideal powder representing a balance among all factors are summarized bellow [1,6,8]:

- particle size smaller than 20 μm
- tap density over 50 % of theoretical
- round shape
- no agglomeration and clean surface
- low explosion and toxicity hazard

2. Phase separation

Nowadays, the main issue of the PIM technology is the powder/binder separation during injection molding step. The phase separation causes up to 25 % imperfections such as surface defects, porosity or cracks on the final products due to non-optimized molding/flow properties [10]. These defects are usually non visible after injection molding, neither during debinding. Furthermore, these defects cannot be removed from the final products. Thus, for an efficient production it is very important to analyze and prevent phase

separation during injection molding step, because after molding the process is still reversible.

2.1. Mechanism of phase separation

The role of local shear rate gradients in a phase separation of highly filled PIM feedstocks (assuming no slip conditions) was proposed by Thornagel [11]. There is a significant shear rate gradient near the wall, and a plateau of a lower shear rate in the middle of the channel (Figure 1). The shear rate gradients cause rotation of the particles near the wall. Naturally, the rotating particles try to move to the area in the middle of the channel, where the values of the shear rate are lower. The result is the area near the wall showing a high concentration of separated binder, and powder particles are concentrated in the middle of the channel.

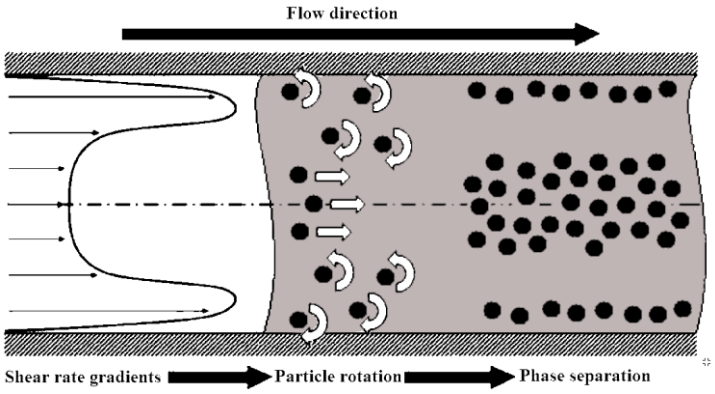

Figure 1 – Shear rate gradients as a cause of phase separation [11]

Thornagel [11] furthermore provides a flow simulation to predict phase separation. The influence of the history of the feedstock travelling through the barrel, nozzle, runner system and cavity is considered in his model.

2.2. Testing of phase separation

The phase separation is commonly tested by moldability test, i.e. filling of a spiral mold [1]. The pioneer investigation on moldability of particle filled (glass spheres) polymers was done by Kubat and Szalanczi [12]. They investigated the influence of different size of glass particles and length of spiral testing mold on a phase separation. The glass concentration after molding was determined gravimetrically on incinerated samples.

From their study it can be concluded that phase separation increases with a spiral length. The particles with large diameter (50-100 μm) were more prone to the phase separation than smaller particles (4-40 μm), because larger particles travel faster along a spiral mold.

Another approach was proposed by Jenni et al. [13], which compared spiral, square spiral and zig-zag molds for testing of moldability and associated phase separation. Jenni et al. [13] compared the balance model, representing a flow of solid, spherical particles in a Newtonian fluid, with the experimental data.

More sophisticated mold design to test phase separation (Figure 2) was developed at the Polymer Center, TBU Zlin in cooperation with Fraunhofer IFAM, Bremen (Utility Design 001704974-0001). The testing mold contains all critical elements, such as inner and outer corners, radical thickness changes, weld lines, thin gates, films and flashes.

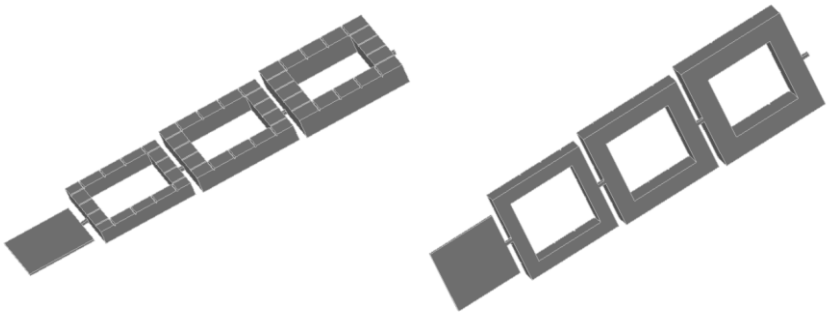

Figure 2 – New design of testing mold; top and bottom side [14]

Highly separated areas (Figure 3) were found near the gate of each element by initial testing, but more precise testing and quantification of separation was needed, thus the topic of the thesis presented was proposed.

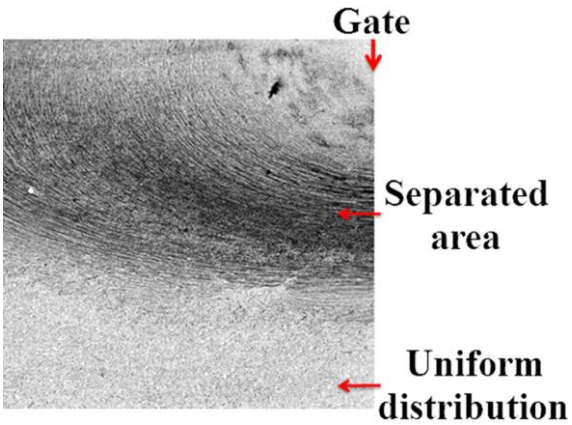

Figure 3 – SEM of powder/binder separation

2.2.1. Quantification of phase separation

Differential scanning calorimeter (DSC) was used by Jenni et al. [13,15] for local powder content monitoring from the differences in glass transition temperatures. The experiments run under various moldability conditions – flow length, nozzle and mold temperature or injection speed. Experiments obtained by DSC, showed lower powder content in the corners of the mold cavity. This was confirmed by a balance model (solid particles in Newtonian fluid), however the instabilities of the feedstock such as wall slip were not predicted by this model [13,15].

Currently, the research of phase separation phenomenon is carried out mainly using X-ray tomography [16-18]. Yang et al. [16] presented a new method of detailed quantification analysis of the different powder–binder separation characteristics of the SiC molded samples with different initial solid loadings. In their study the linear fitting equation between gray value of X-ray and actual density of sample was used (the output from an X-ray scanner is a gray-scale image where the variations in gray darkness correspond to variations in density) [19]. According to this assumption, the actual density at a specific area of molded sample can be calculated, when we know density of pure binder system and powder particles. Furthermore, the powder content in the feedstock is calculated from this actual density [16]. In their studies [17,18] the method is tested on L-shape mold with different processing parameters. As in the previous researches [11,15,16], binder rich areas were formed near gates and mold walls.

However, the analyses are complicated by several factors, the separation is accompanied by a non-homogeneity of a material caused by flow instabilities or a movement of particles from a solid wall to a center of a channel during flow. Currently, the mechanism of phase separation occurrence has still not been fully understood [20].

2.3. Flow behavior of highly filled compounds

The important parameter preventing the phase separation is homogeneity of feedstock, which affects whole PIM process. The inhomogeneity of the feedstock can be detected by pressure instabilities obtained from a capillary rheometer [21].

The other problems are resulting from processing conditions during injection molding. This step usually needs an expensive, time consuming, trial and error testing to design desired process conditions [13]. In addition, as thermoplastics, highly filled materials also exhibit moldability defects such as jetting, air traps, dead zones, flash or welding lines.

PIM compounds introduce also many obstacles and limitations because of a multi-component character of polymer binder and complex powder characteristics, mainly irregular shape and broad particle size distribution [1,6,22]. First problem during shearing of highly filled systems is agglomeration of solid particles in non-Newtonian fluid. This phenomenon has been already studied in seventies by Michele et al. [23]. They found that - upon shearing - glass solid particles can create chains or agglomerate groups in non-Newtonian fluids (Figure 4).

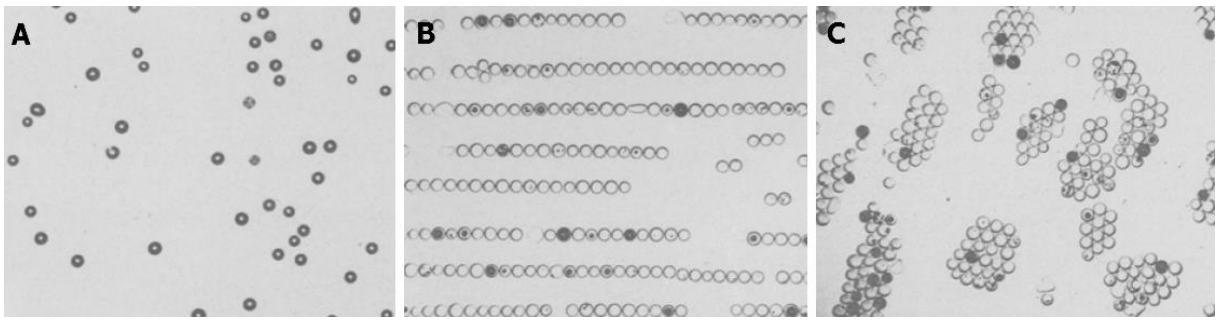

Figure 4 – Glass particles in non-Newtonian fluid
a – before shearing, b –one dimension shearing, c –circular shearing [23]

This effect has a significant relevance for rheological testing. Measurement of flow curves can derive different viscosity data if an experiment is started from low shear rates towards higher or vice versa, because agglomerated structure created at higher shear rates will not be destroyed at lower shear speeds.

Complexity of rheological behavior and thermal properties of the PIM feedstocks which affect injection molding step was tested by Ahn et al. [24]. They concluded that non-Newtonian index is more sensitive to a binder selection than to a powder. Both, powder and binder composition has the same effect on thermal conductivity and heat capacitance of the feedstocks. The injection pressure and clamping force can be minimalized better by binder systems, but controlling of the maximum shear rate is affected by both powder and binder systems.

Unstable flow behavior of highly filled polymers was also studied by Isayev et al. [25] and Hausnerova et al. [4]. Their studies demonstrate change of shear thinning behavior into a dilatant flow. The viscosity is decreasing due to

the orientation of particles with the flow at the low shear rates, but at higher shear rates the particles cannot form layers and slide over each other, thus viscosity is increasing [4,25]. These findings bring many obstacles for rheological modeling. Herschel – Bulkley or Casson models cannot describe flow curves in a whole range of shear rates, and more complicated eight parameter model has to be applied [4,26].

2.3.1. Wall slip as rheological parameter related to phase separation

The mechanism of separation proposed by Thornagel [11] supposed no slip condition during flow, however the wall slip may cause instabilities during injection molding and understanding of this phenomenon is important.

While Newtonian fluids exhibit no-slip conditions during the flow [1,27,28] through the tubes, and the solid-liquid boundaries have exactly the same velocity, highly filled suspensions exhibit flow instabilities at high stresses [29]. The theory, known as an apparent slip [30], assumes that upon shearing a narrow polymer layer of low viscosity with typical thickness of 0.1 – 10 μm is created near the wall and solid particles are migrating away from walls [31-33]. Theory of this migration was proposed by Delime and Moan [34]. They expected that the migration of solid particles is initiated by the failure of Brownian movement near the walls, which is supported by shear rate gradients which promote particles collision [32,34]. Other experiments confirm this theory especially for particles in range 20 – 100 μm [35].

2.3.2. Evaluation of slip velocity

Mooney [36,37] proposed a method for wall-slip evaluation from capillary and couette flow data to determine the slip velocity from the slope of the apparent shear rate versus reciprocal radius or gap data collected at constant apparent wall shear stress. Mooney method is based on measurement with three different capillaries having the same length-to-diameter ratio (L/D), but different diameter of the dies.

The presence of slip can be also detected from single geometry measurement such as unexpected low Newtonian plateau, sometimes with an apparent-yield stress at even lower stresses, as well as sudden breaks in the flow curve at higher shear stresses or rates [31]. Further, the flow curves of material should be independent on capillary dimensions or surface roughness when wall slip does not occur. Some studies [32,38] reports increasing slip velocity with higher

temperature, and proportionally increasing low molecular layer with increasing size of the particles.

From the previous studies it can be observed that the most significant conditions causing a slip effect are [39-44]:

- strong dependence of viscosity on a filler concentration
- large particles as a dispersed phase
- smooth flow channel walls
- small flow geometry size
- low speed rates
- electrostatic charges of wall or particles.

Very recently, slip of PIM compounds was considered by Liu et al. [45] for a micro-PIM of zirconia feedstocks with the clear conclusion that wall slip cannot be ignored in numerical simulations, because it leads to unrealistic low viscosity values, and as a consequence to a failure of flow simulation approaches applied. In the following work, Liu et al. [46] supported this finding when compared the simulations of temperature, viscosity and pressure gradient distributions during mold filling including/excluding wall slip. Therefore, the slip is the crucial flow phenomenon influencing the most severe issue of injection molding step of PIM [20].

DISCUSSION OF RESULTS

The discussion of the work performed within this thesis is divided into three sections describing different approaches to optimization of Powder Injection Molding (PIM) process in order to achieve a final structure of PIM parts without defects resulting from phase separation.

First, the development of the new non-destructive method for the quantification of the phase separation of highly filled polymers is proposed. Second, the wall slip as a rheological phenomenon affecting shear rate gradients causing phase separation during a flow of PIM feedstocks is investigated with the regard to an appropriate choice of testing methods and tools as a type of rheometer, surface roughness of dies, capillary dimensions and capillary entrance angles. Third, the surface structure of the final sintered parts as a function of processing parameters of injection molding and debinding steps of PIM is quantified via contactless surface scanning following with a statistical analysis of the results obtained.

3. Quantification of phase separation

This chapter summarizes findings published in the Paper I

As shown in the theoretical background, currently used testing methods detecting a phase separation on molded parts employ simple mold geometries such as square spiral or L-shape [13,17]. These mold shapes are not entirely suitable for the testing of highly filled polymers as they do not contain most severe critical areas causing a phase separation as rapid thickness changes, thin films or weld lines. In addition, the methods to quantify the separation presented so far are inaccurate (DSC) and time consuming (X-ray computed tomography) [13,15-18]. Both methods have not proved to be a suitable approach to detect the changes in powder concentrations for feedstocks containing multi-component binders (typical for PIM feedstocks) [13,15-18].

Therefore, a development of a new testing approach should be focused on a simple and precise method testing molded samples from a broad cast of feedstock types. In this respect, the scanning electron microscopy (SEM) seems to be useful method for the qualitative analysis of the development of the phase separation prior to debinding and sintering, where the whole process is still reversible (material still can be re-granulated and re-used). Especially, backscattered electrons detector (BSE) can be used to detect materials with

different atomic numbers [47]. Therefore, the samples prepared on a testing mold developed at TBU and IFAM were analyzed by a BSE detector to confirm its suitability. From the results, the signs of the powder/binder separation was detected at the entrance to each square element (Figure 5: dark points – carbon, bright points – iron) which complies with theoretical assumptions [11].

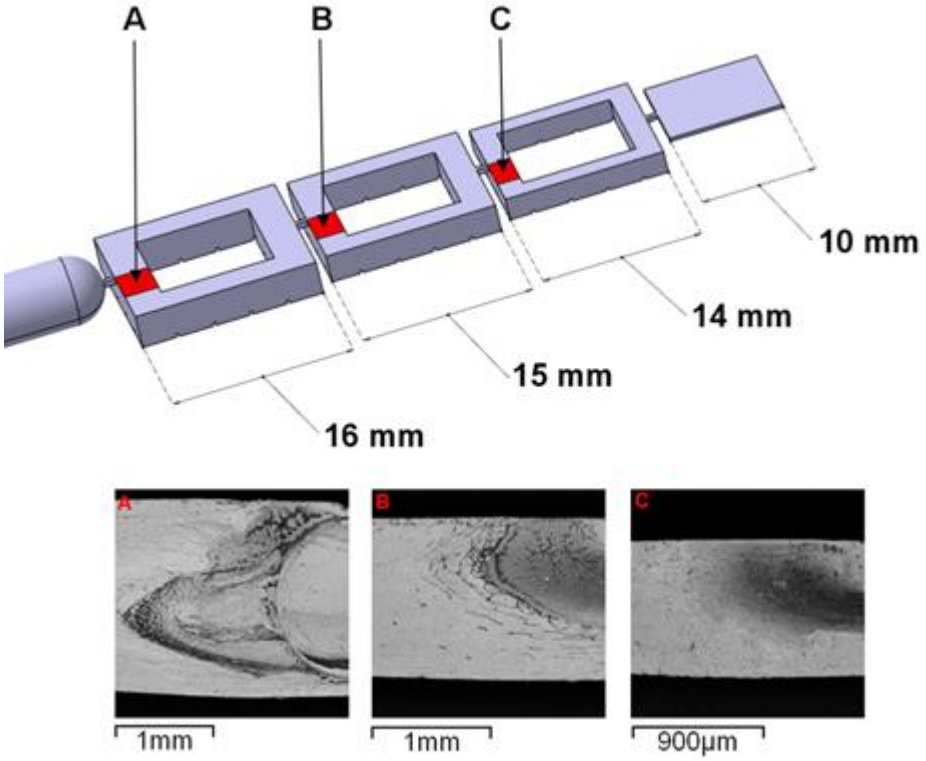

Figure 5 – Development of a flow front obtained at the positions A to C of the testing mold in separated areas

However, a qualitative analysis is not sufficient for the purpose, because it does not provide information about the degree of a phase separation which would help PIM producers to predict the structure defects as unacceptable porosity and cracks of their products. For this reason, combination of SEM with EDX analysis (Energy-dispersive X-ray spectroscopy) of the distribution of elements typical for binder (carbon) and powder (iron/oxide ceramics) was performed in order to quantify phase separation.

SEM/EDX is a semi-empirical method, which allows for a major and minor element concentration determination – in our case carbon and iron/oxide ceramics. It is capable to detect elements appearing in concentrations higher than 0.1 % with analytical accuracy commonly ± 2% [48]. This is acceptable for PIM feedstocks as they contain tens of percent of carbon and iron/oxide

ceramics [1,6]. In comparison to the DSC or X-ray methods [15,17], where the results have to be compared to the standard samples of a known composition and a powder concentration, the SEM/EDX analysis offers quantitatively significant results. This can be seen from the examples of EDX spectrum derived from unseparated and separated areas depicted in Figure 6. As can be seen in Table 1, the occurrence of elements typical for the binder (carbon) rises more than two times in the area of separation, while the occurrence of the iron as well as other alloying elements of the powder considerably decreases.

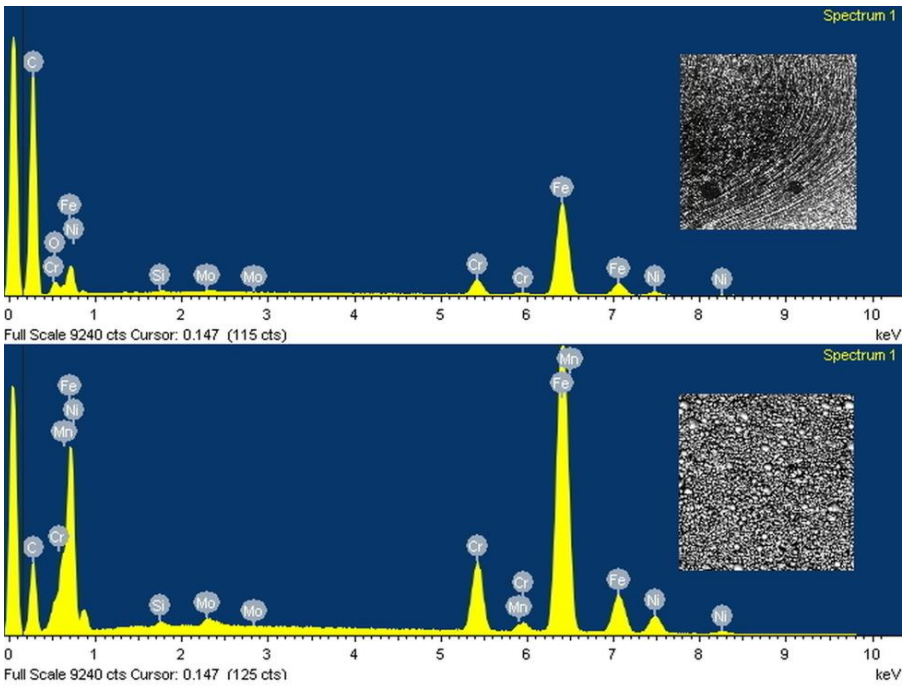

Figure 6 – EDX spectra of separated and unseparated areas in PIM feedstocks

Table 1 – Concentration of elements in separated and unseparated areas displayed in Figure 6.

Separated area		**Unseparated area**	
Element	Weight (%)	Element	Weight (%)
C	**62.61**	**C**	**24.98**
Si	0.09	Si	0.24
Cr	2.71	Cr	8.35
Mn	-	Mn	0.15
Fe	**27.43**	**Fe**	**59.73**
Ni	1.51	Ni	5.52
Mo	0.36	Mo	1.03

SEM/EDX arises a possibility to provide a quantitative EDX mapping of testing areas A to C representing individually a distribution (in weight percentage) of an element typical for powder or binder. The concentration of iron or ceramic oxide has been selected as a measure of the separation or the uniformity of the distribution of the powder particles within the binder. In the following, the EDX maps were converted to a black/white scale for a better data processing. Figure 7 demonstrates such distribution map of iron from 0 % (black color) to 100 % (white color) in positions A to C of the tested stainless steel sample. Clearly, there is an evidence of the separation, which is more pronounced with the flow front.

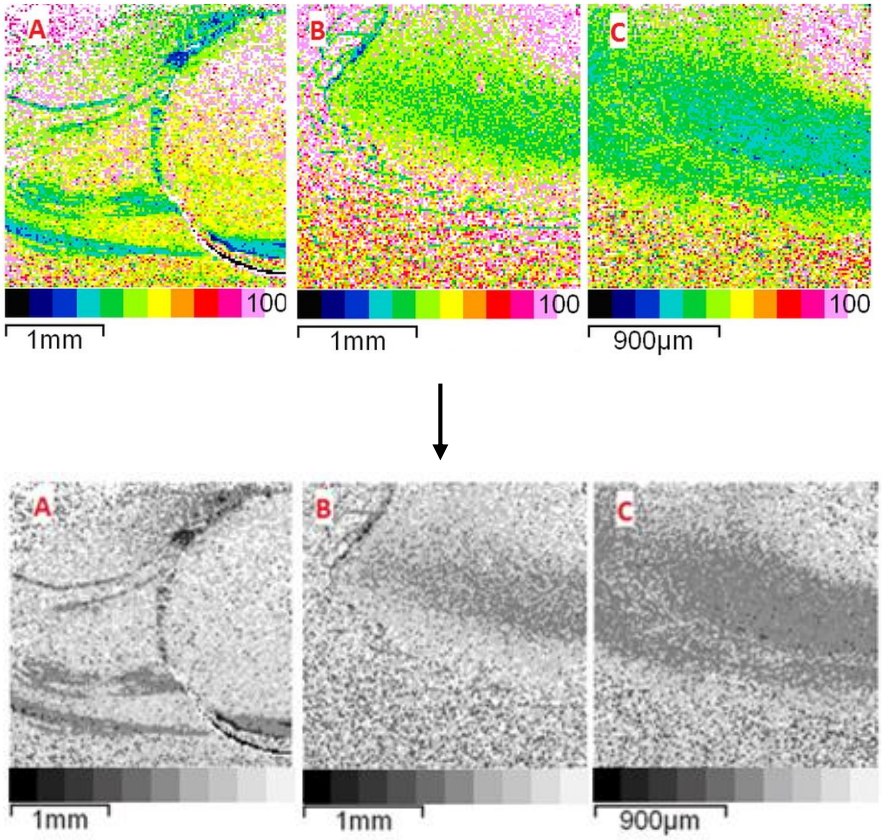

Figure 7 – EDX quantification maps of iron distribution; black/white conversion

For a purpose of a simple comparison among different feedstocks, the distributions of the elements were analyzed mathematically in order to provide a single parameter (so called variability coefficient of separation) characterizing a tendency of tested feedstocks to separation.

The rate of the phase separation represents the non-uniformity of powder and binder distribution, i.e. non-uniformity of bright and dark points on EDX maps. First, the data smoothing by averaging the value of the neighboring pixels was provided (due to tests artifacts resulting from processing). Then, if a completely bright area is assigned with 100 % and purely dark picture to 0 %, it is possible

to convert an image into a matrix. For the determination of the variability coefficients, the compute of standard deviations (σ) of pixels in averaged images was used. The phase separation expressed the deviation from the original content of powder in the feedstocks, therefore the $\bar{x}$ (mean value) in the Equation 1 is replaced by the parameter *B* representing the original content of the powder in a feedstock (measured by EDX for an exact comparison).

$$\sigma = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - B)^2} \tag{1}$$

Thus, the variability is calculated relatively to the initial (unseparated, unmolded) state of a powder concentration. Schema of a calculation of variability coefficients is depicted in Figure 8.

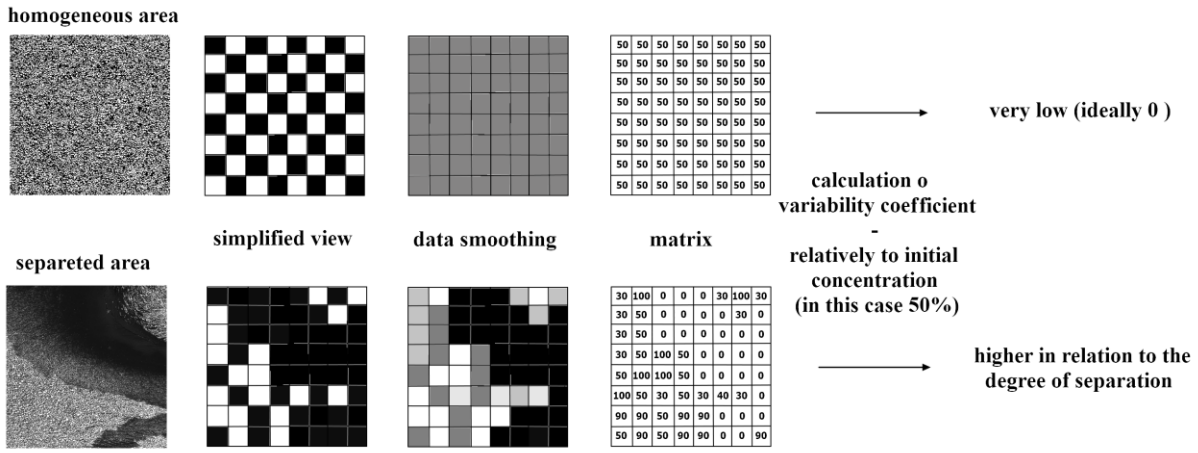

Figure 8 – Schematic demonstration of variability coefficient calculation

The testing of the developed method covered both in-house prepared and commercially available PIM feedstocks; their composition can be seen in Table 2. Commercial feedstocks C316L, P316L and E316L were based on gas atomized pre-alloyed stainless steel 316L and varied in polymer binders (abbreviated C, P and E for catalytic, partly water soluble and partly ethanol soluble binder systems, respectively). All these feedstocks had powder volumetric concentration higher than 60 %. On the other hand, ceramic powders – zirconium oxide (ZrO_2) and aluminum oxide (Al_2O_3) – were admixed to commercially available binder system Licomont EK 583 at the loading level of 50 vol.%.

Table 2 – Overview of tested feedstocks

Abbreviation of feedstock	Type of powder	Type of binder	Commercial name	Producer
C316L	Stainless steel 316L	Catalytic (Poly-acetal based)	Catamold 316LG	BASF
P316L	Stainless steel 316L	Partly water soluble (PEG based)	PolyMIM 316L D 110 E	PolyMIM GmbH
E316L	Stainless steel 316L	Partly ethanol soluble	Embemould 316L S16	eMBe GmbH
ZrO_2	Ceramic ZrO_2	LDPE+EVA+PW	-	in-house
Al_2O_3	Ceramic Al_2O_3	LDPE+EVA+PW	-	in-house

Results of the analysis (Figure 9) for Fe, Al and Zr as typical elements of tested feedstocks provide the quantification of the development of the separation at the tested positions (A, B, C) of the mold. Low and uniform variability anticipates the PIM process without defects arising from the separation. Each feedstock was also inspected in the area without separation (sample prepared by pressing; dotted lines in Figure 9). As can be seen, the samples without separation reached low and constant variability ranging from 2 to 5 % for E316L and other feedstocks, respectively.

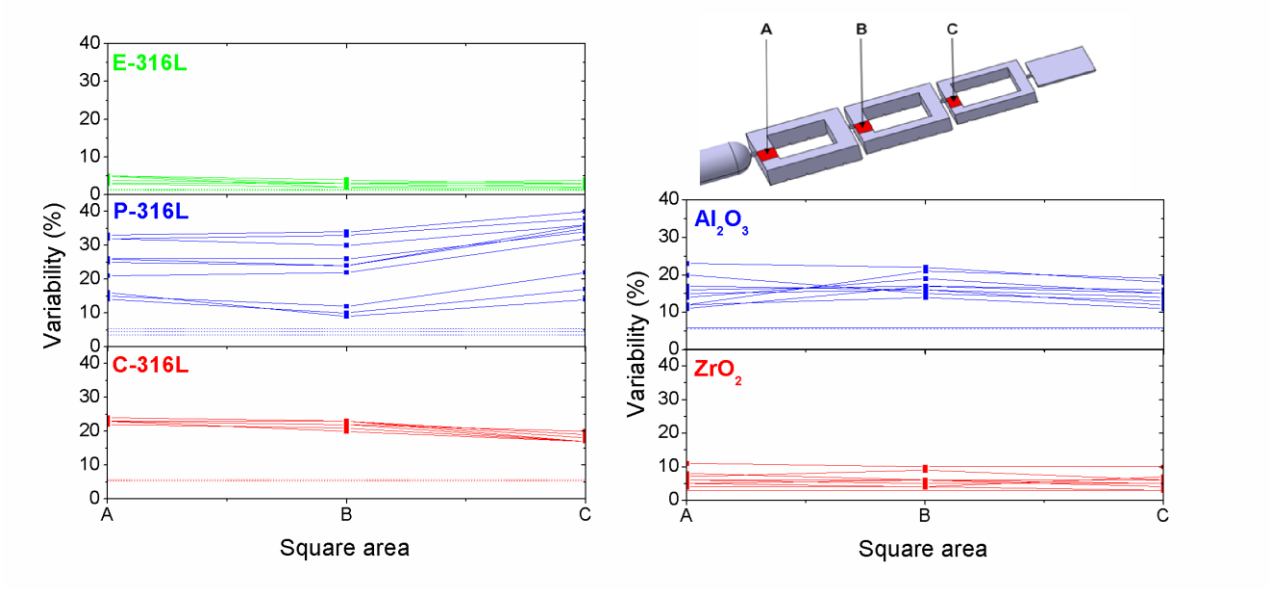

Figure 9 – Variability coefficients of tested feedstocks

at positions A to C of testing mold (each representing a set of 10 samples)

From the results obtained on the separated samples the different mechanism of the separation for tested materials is evident. The variability of the tested materials shows that C316L is faster prone to the separation, but it has a certain ability to reverse it back, while the continuous progress is attained for P316L. The reproducibility is very good for C316L (±2) in comparison to about ±10 in case of P316L feedstock. The feedstock E316L exhibited the lowest variability (with reproducibility ±2), even the values of separated E316L could be compared with values of unseparated C316L and P316L. This means very low tendency of E316L to a phase separation affected by critical geometric elements of injection molds, which is advantageous for PIM production.

In case of ceramic feedstocks, zirconia oxide feedstock exhibited a better reproducibility (4 %) in comparison with alumina oxide feedstock (7 %). In addition, the uniform and lower variability of zirconia feedstock reduced defects of PIM process.

The group of metal based feedstocks contained the same type of powder with the different binders, on the other hand, the group of ceramic feedstocks was composed of the same type of binder with two different powders. Therefore, the different tendency of PIM materials to the phase separation can be concluded. Both – powder and binder – are important for optimization of PIM feedstocks to ensure efficient manufacturing process.

The new approach to detect the phase separation of highly filled polymers prior debinding/sintering provides some advantages in comparison with exiting methods. The analysis can be done without the need for standard sample preparation of defined powder concentration. In addition, it is not necessary to know a composition of a binder, and therefore, commercially available feedstocks can be tested. Finally, the molded samples can be analyzed directly without any additional treatment.

4. Wall slip effect during the flow of PIM materials

This chapter summarizes findings published in Papers II and III

Phase separation is closely related to a wall slip effect; shear rate gradients located close to flow channel walls cause a displacement of powder particles during shearing. Nevertheless, the wall slip affects not only a phase separation, but also an overall rheological performance of PIM materials. Mooney [49] proposed rheological approach to determine the wall slip velocities already in 1931. This analysis is based on changing the surface-to-volume ratio of the

capillary dies via changing length L and radius R of the dies, but keeping their ratio constant.

For a capillary rheometer, apparent values of shear rate $\dot{\gamma}_a$ and shear stress τ_a are determined as

$$\dot{\gamma}_a = \frac{4\dot{Q}}{\pi R^3};\ \tau_a = \frac{\Delta p R}{2L} \tag{2}$$

where $\dot{Q}$ is the volumetric flow rate and Δp is the measured pressure drop.

Consequently, a true average velocity (v_{true}) is given by the difference of an average v_{av} $\left(= \dot{Q}/\pi R^2\right)$ and slip v_{slip} velocities

$$v_{true} = v_{av} - v_{slip} \tag{3}$$

Multiplying this relation by 4/R and using Eq. (6) we obtain the dependence of a slip-corrected shear rate on apparent shear rate and wall slip velocity

$$\dot{\gamma}_{a,slip-corrected} = \dot{\gamma}_a - \frac{4v_{slip}}{R} \tag{4}$$

or in other form

$$(intercept) = \frac{4\dot{Q}}{\pi R^3} - (slope)\frac{4}{R} \tag{5}$$

Geometrical interpretation of the last two relations is illustrated in Figure 10.

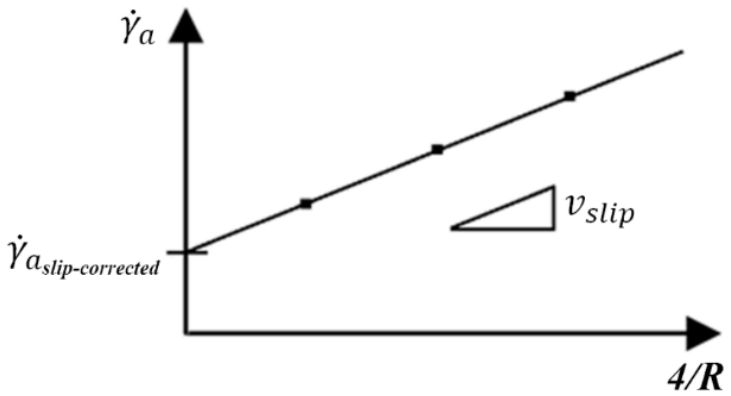

Figure 10 – Calculation of wall slip velocity using Mooney approach

As can be seen from Eq. 4 and/or Eq. 5, the viscosity of a compound exhibiting a wall slip must be corrected; otherwise, obtained shear rate values are unrealistic.

From the previous studies (described in the theoretical part of the Thesis) it can be concluded that the wall slip velocity of highly filled compounds is affected above all by:

- binder system and testing temperature through variations in a thickness of a polymer layer formatted close to walls [38,50]
- size of powder particles; small particles can approach close to a wall, and thus reduce a polymer layer thickness [51]
- mold design, material and surface roughness [52-54]

Therefore, first part of a wall slip analysis focused on online rheometer testing with adjustable die gap and different surface roughness (Table 3) in order to obtain experimental data at the conditions close to processing ones.

Table 3 – Characteristics of slit dies used

Metal powder feedstocks			**Ceramic powder feedstocks**		
Geometry (mm)	**Surface**	**Roughness S_a (µm)**	**Geometry (mm)**	**Surface**	**Roughness S_a (µm)**
10x0.5x100	smooth	0.25 ± 0.03	10x1x100	smooth	0.81 ± 0.03
	roughened	0.95 ± 0.02		roughened	9.65 ± 0.18
15x1x100	smooth	0.07 ± 0.00	10x2x100	smooth	0.82 ± 0.04
	roughened	0.77 ± 0.03		roughened	7.87 ± 0.70

At first, the purpose was to point out that wall slip is a typical rheological effect for PIM compounds, occurring for the most often employed PIM feedstocks, and thus it should be always examined when performing rheological characterization of these highly filled polymers. Therefore, both commercially available and in-house metal and ceramic feedstocks (Table 4) were tested.

Table 4 – Wall slip tested PIM feedstocks

Abbreviation of feedstock	Type of powder	Type of binder	Commercial name	Producer
P316L	Stainless steel 316L	Partly water soluble (PEG based)	PolyMIM 316L D 110 E	PolyMIM GmbH
P17-4PH	Stainless steel 17-4PH	Partly water soluble (PEG based)	PolyMIM 17-4PH D 110 E	PolyMIM GmbH
C316L	Stainless steel 316L	Catalytic (Poly-acetal based)	Catamold 316 L G	BASF
C17-4PH	Stainless steel 17-4PH	Catalytic (Poly-acetal based)	Catamold 17-4PH G	BASF
ZrO_2	Ceramic ZrO_2	LDPE+EVA+PW	-	in-house
Al_2O_3	Ceramic Al_2O_3	LDPE+EVA+PW	-	in-house

Concerning the effect of processing tools (roughness and chemical nature of materials), stainless steel was found more prone to a wall slip than aluminum [52] and the rough surface, where solid particles can move into a groove, suppresses the formation of a low molecular layer on channel walls [41]. In case of PIM compounds, we obtained the same trend during testing metal powders (316L and 17-4PH) in a catalytic binder and ZrO2 feedstocks, where the effect of surface roughness was evident – a lower viscosity is obtained for the smooth surfaces. The observed trend is also in an agreement with the simulations performed by Papanikolaou et al.[55], where parallel liquid layers formed near a smooth wall surface were disturbed in case of a roughened surface (leading to a higher viscosity).

On the other hand, there are some unexpected results, such as imperceptible influence of a surface roughness for the water soluble binder. In that case the thickness of the polymer layer formed at the channel wall, must be higher than the surface irregularities of the tested slit dies [41,56]. Figure 11 demonstrates that the values of slip velocities obtained for Al_2O_3 powder in the smooth slit die are comparable with the slip velocities of ZrO_2 feedstock in the roughened slit die. However, Al_2O_3 feedstock could not be tested at the roughened slit die due to the pressure fluctuations occurring during the flow.

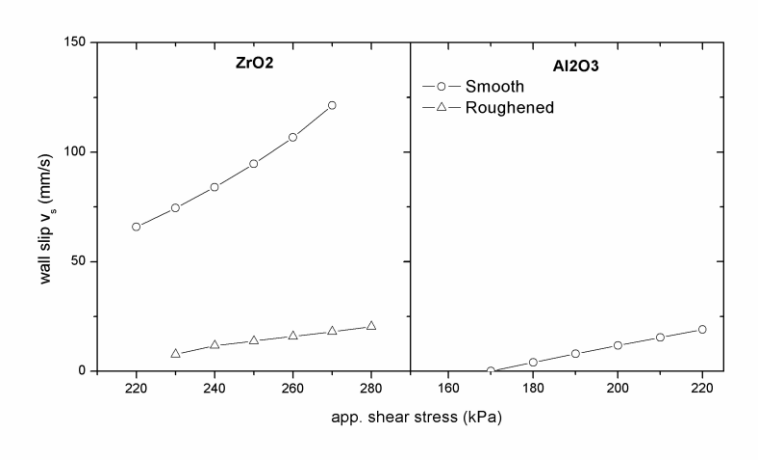

Figure 11 – Effect of surface roughness on wall slip velocity of zirconium oxide (ZrO_2) and aluminium oxide (Al_2O_3) powders in LDPE+EVA+PW binder

Another factor influencing wall slip might be a die geometry. The feedstocks based on stainless steel powders as well as ZrO_2 feedstock showed the same trend in the slip dependence on die dimension regardless of surface roughness – the smaller gap height (1 mm) supported the wall slip effect, while this was substantially reduced for 2 mm gap. However, the feedstocks with partly water-soluble binder (P316L and P17-4PH) show a stronger influence of the flow channels geometry on viscosities than that with the catalytic binder, indicating an enhanced tendency to slip. In addition, the tendency of Al_2O_3 feedstock to wall slip as a function of the die geometry and surface roughness is generally less pronounced than for ZrO_2 compound, although as it was showed recently by Hausnerova et al. [57], their surface characteristics (surface energies) were fairly similar - 44 and 47 J/m2 for ZrO_2 and Al_2O_3, respectively.

The results obtained correspond to findings on pure linear low density polyethylene in capillaries with different surface roughness [52] as well as on suspensions containing polymer matrix poly(butadiene-acrylonitrile-acrylic acid) filled with glass spheres (particles mean size 35.3 μm and 85.4 μm) [53] and poly(methyl methacrylate) solid spheres (121.2 μm) in hydroxyl-terminated polybutadiene [51], where smooth flow channels wall and small channels geometry [32,58] were found to be the most significant factors causing wall slip.

Finally, the influence of an entrance angle of a capillary die was investigated. Application of flat or conical dies (Figure 12) might change both – slip layer thickness and slip velocity.

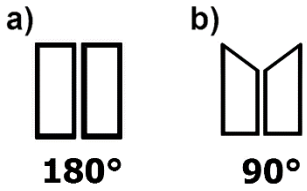

Figure 12 – Schematic representation of testing dies: a – flat, b – conical

The literature comparing flat and conical dies in connection with a wall slip is rather scarce. Liang [59] and Ardakani et al. [60] tested changes in a pressure drop with different capillary entrance angles during extrusion. They found that under a constant pressure, the shear rate increased with the capillary entrance angle. In our experiment, the dies tested are flat (180°) and conical (90°). Suitability of each die was evaluated by Mooney method with respect to compatibility of the obtained results with the general findings on a wall slip issue stated in literature.

The same metal-based feedstocks as in previous on-line rheomery testing were used, see Table 4. From the results of wall slip velocities, the strong effect of the entrance angle of the capillary is obvious (Figure 13).

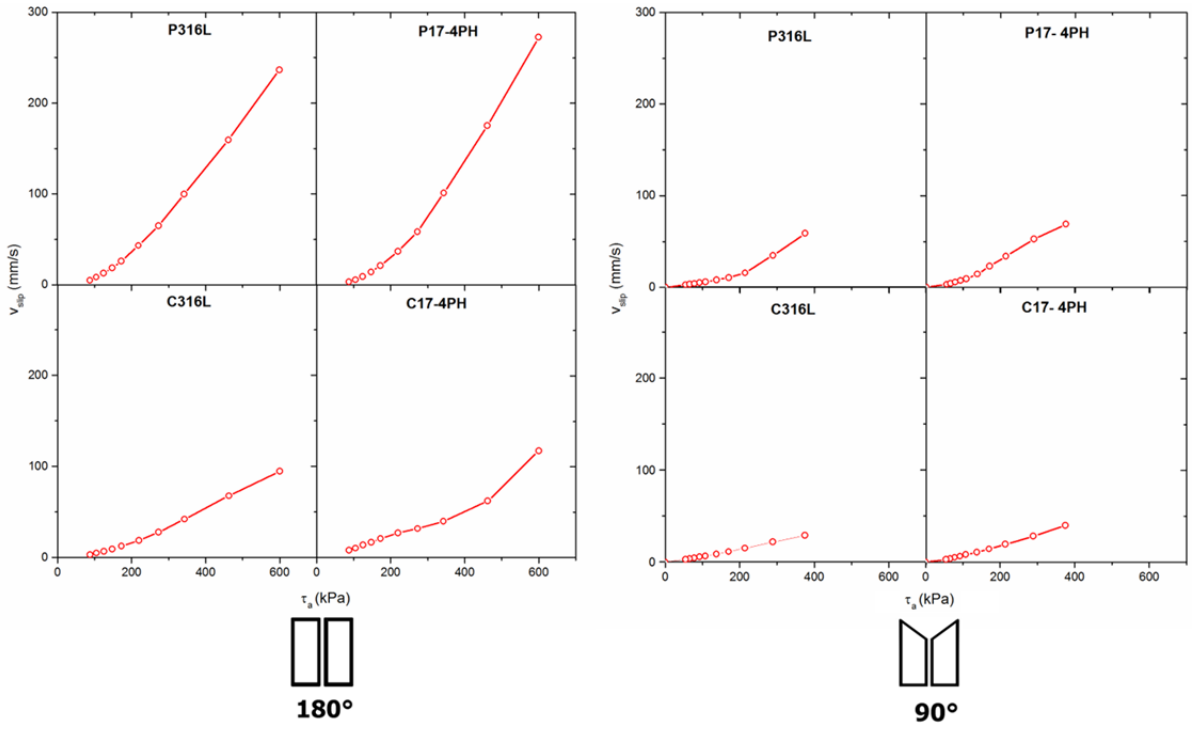

Figure 13 – Wall slip velocity as a function of apparent shear stress based on using of flat 180°and conical 90° entrance dies

According to Figure 13 both metal feedstocks (316L and 17-4PH) based on the partly water soluble binder system (P) exhibited the substantially higher slip velocity at the wall than those containing the catalytic binder system (C).

Further, the slip velocities of both binder systems with 17-4PH powder are slightly higher than those with 316L compounds. When considering rounded shape of all types of powders (gas atomized), and also their similar particle distribution, the interactions between binder and powder plays a significant role in a wall slip evaluation. This applies also for an overall improvement of the processing of PIM feedstocks, where the interactions between binder system components are critical as we recently showed in the studies dealing with the interactions among parafin, acrawax, carnauba wax and polyethylene glycol binders [61,62].

The same procedure was carried out with a conical 90° entrance die, see Figure 13. The lower (conical) entrance angle decreases the wall slip velocity. Similar observations have been done for viscoelastic materials; Liang [59] founded that the minimum pressure drop occurred about 75° entrance angle, during testing of unvulcanised rubber compound (natural rubber, styrene-butadiene rubber, sulphur, stearic acid, carbon black, etc.) on Monsanto processability tester. This result was confirmed by Ardakani et al. [60] for an extrusion of toothpaste compounds, where almost negligible pressure drop in a conical zone was obtained.

Nevertheless, the main finding of this experiment is the better linear proportionality between wall slip velocity v_{slip} and shear stress τ_a obtained with 90° entrance dies. The relation has been proposed by Yilmazer and Kalyon [50] and Soltani and Yilmazer [38] for concentrated suspensions

$$v_{slip} = a(T)\tau_a \tag{6}$$

where $a(T)$ is a temperature dependent coefficient.

As it can be seen from Figure 13, only results obtained for 90° entrance dies comply with the above linear relation (especially for the catalytic binder system). No such relation can be derived in Figure 13 for a flat 180° die. This justifies the applicability of the conical entrance dies in simulations of PIM feedstock flows. The flat 180° entrance die enhances the tendency of the feedstocks to the separation of polymer binder and powder, which is then accumulated in the dead zones (edges) above the dies. In addition, the sharp edges cause rapid changes in a shear rate, which further support separation of feedstocks (binder and powder) components [11,63,64] resulting in higher wall slip velocities.

5. Surface properties of PIM parts related to processing conditions

This chapter summarizes findings published in Papers IV a V

Nowadays, optimization of powder injection molding step is done largely by a trial and an error approach; therefore, there is a strong need for investigation of the relation between the processing conditions and the final surface properties evaluated with the help of appropriate mathematical/statistical methods.

Mixing and injection molding parameters are selected usually according to viscosity data (Figure 14), while conditions for debinding and sintering are set up based on thermal analyses of PIM feedstocks (Figure 15). It has been generally accepted that the rheological performance of PIM feedstocks is also important parameter affecting the surface quality of final PIM items.

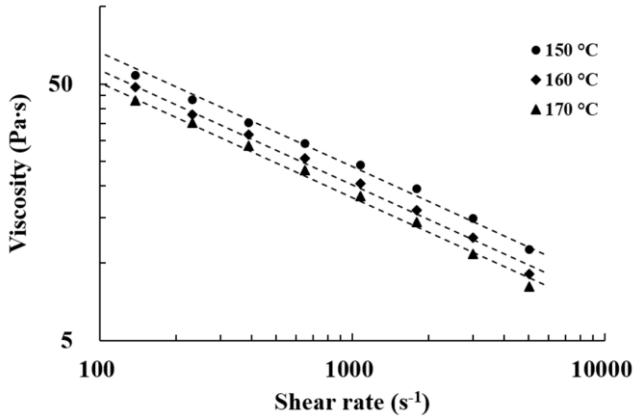

Figure 14 – Temperature dependent viscosity data of PIM feedstock (67 vol.% titanium powder)

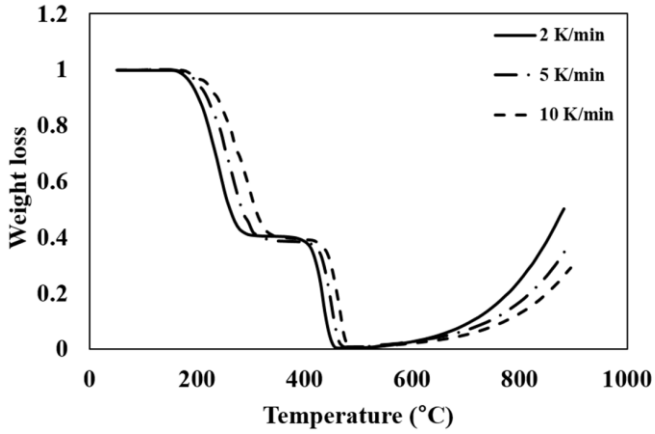

Figure 15 – Thermogravimetric analysis of PIM feedstock (67 vol.% titanium powder)

The last part of the thesis deals with optimization of processing conditions of PIM process to achieve an acceptable surface quality of final sintered parts. PIM items with high surface quality requirements as those depicted in Figure 16 were tested. They are made of aluminium oxide and contain complicated rotational areas. The internal sections of the spirals exhibited the surface cracks and defects after sintering resulting from the phase separation during the injection molding step of PIM (

Figure 17).

Figure 16 – Design of tested Al_2O_3 PIM part

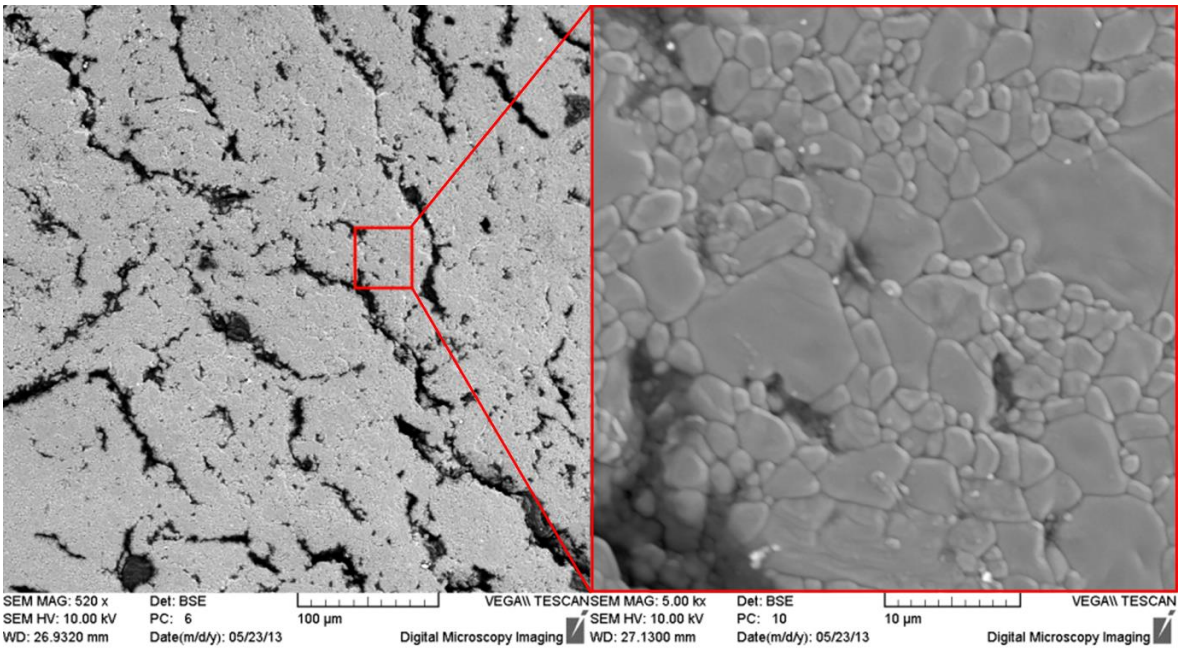

Figure 17 – Surface defects of sintered alumina oxide PIM part

The testing samples were prepared by injection molding of 60 vol.% of Al_2O_3 powder compounded with a commercial multi-component binder Licomont EK 583-G and surfactant (1 wt.% oleic acid) at various conditions. Two series of samples were selected differing in molding (nozzle) temperatures – 150 °C and 160 °C, and debinding routes, where T in the abbreviation means that the sample were debound thermally and ST stands for combined solvent/thermal debinding. In order to obtain a quantitative analysis, a contactless 3D Chromatic Length Aberration (CLA) scanner (Talysurf 300, Taylor and Hobson, UK) was used for roughness measurement. Tested surfaces were subjected to a height measurement over a rectangular area (1 x 1) mm with the scanning rate of 100 μm/s and spacing 5 μm.

Firstly, the Box-Plot diagrams of R_p, R_v and R_a showing the considerable scatter of measured data were created for samples molded at 150 and 160 °C, and then debound thermally or solvent/thermally (Figure 18).

Therefore, Kruskal-Wallis statistical approach has been employed further as it enables simple analysis of a median scatter of differently processed samples (differing in temperature and debinding route). A Zero-hypothesis expects that the particular surface roughness parameters (R_p, R_v, R_a) have the same median values in the sample groups. In the following, the Zero-hypothesis for R_a parameter of the samples molded at two different temperatures and debound thermally (150T and 160T) in the longitudinal direction is:

$$H_0: \tilde{X}_{Ra}150T_1 = \tilde{X}_{Ra}150T_2 = \tilde{X}_{Ra}150T_3 = \tilde{X}_{Ra}160T_1 = \tilde{X}_{Ra}160T_2 = \tilde{X}_{Ra}160T_3$$

The alternative hypothesis expects not equal of median:

$$H_A: NON$$

$$p = 0$$

According to this result, Zero-hypothesis H_0 is denied on the confidential level 0.95 %, i.e. we suppose that the differences in the investigated surfaces are due to the changes in the processing conditions (in this case – temperature).

The same procedure has been made for the samples molded at two different temperatures and debound by a combined solvent/thermal route (150ST and 160ST) in the longitudinal direction as well for the sample groups in transverse direction (Table 5).

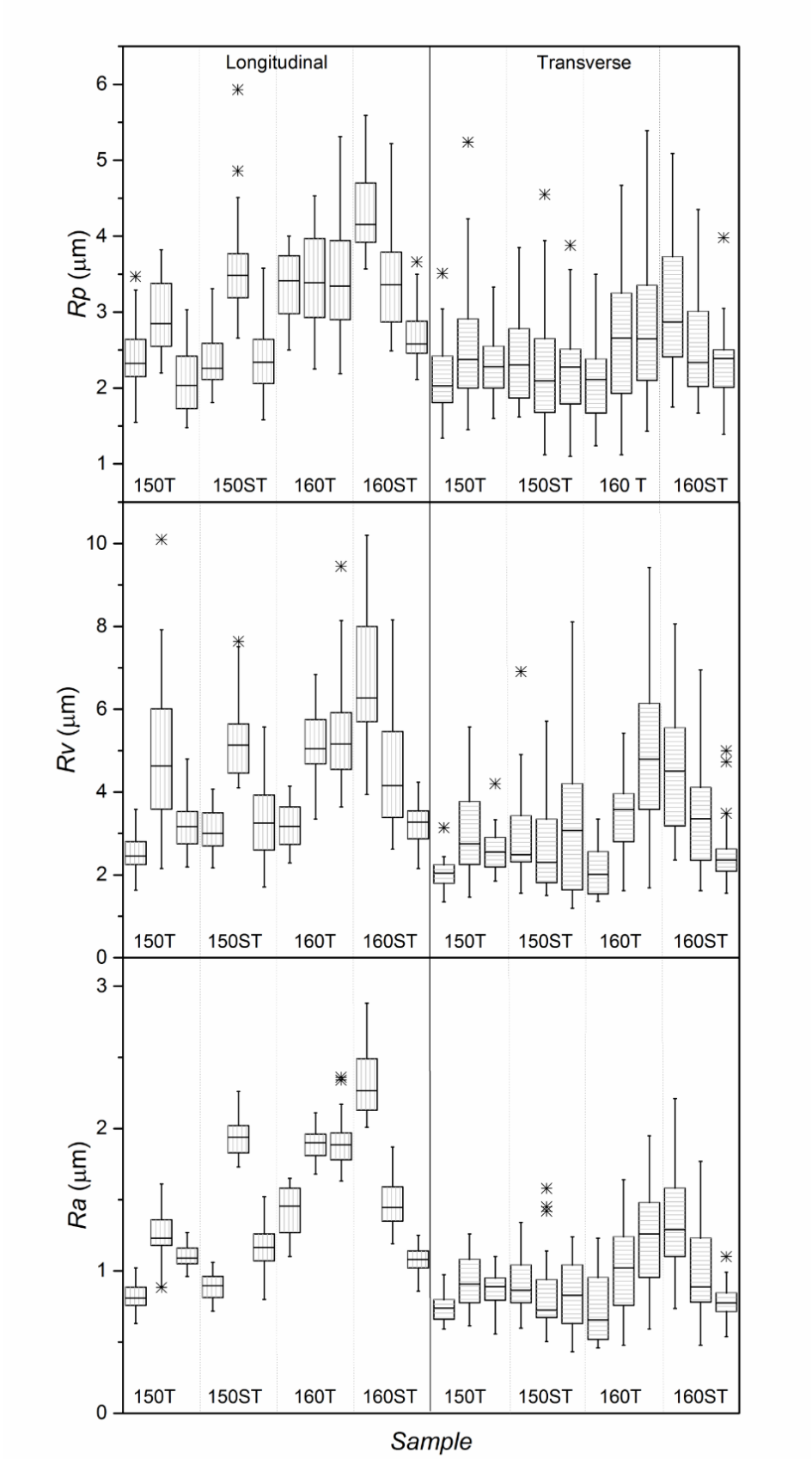

Figure 18 – Box-Plot diagrams of Rp, Rv and Ra for measured samples

Table 5 – Results of Kruskal-Wallis analysis

Testing group	***P* value**	H_0
150T/160T – Longitudinal	0 < 0.05	denied
150ST/160ST – Transverse	0 < 0.05	denied
150T/160T – Longitudinal	0 < 0.05	denied
150ST/160ST – Transverse	0 < 0.05	denied

Zero-hypothesis for all sample groups was denied. It means, Kruskal-Wallis method confirmed on the confidential level 0.95 (i.e. 5 % error) that the medians of selected samples do not vary at random, and surfaces of samples were affected by molding temperature (150 °C or 160 °C) as well by debinding route. Therefore, the surface structure of sintered parts depended on these processing conditions and according this knowledge process can be optimized in relation to surface properties.

Unfortunately, parameters R_p, R_v or R_a cannot intercept a profile shape of a surface. Thus, Abbott-Firestone curves, which describe a surface texture of an object and detect a flatness or pointedness of surface, were also derived. All measured surface profiles were quantified by a cumulative probability of values of Abbott-Firestone curves (Figure 19).

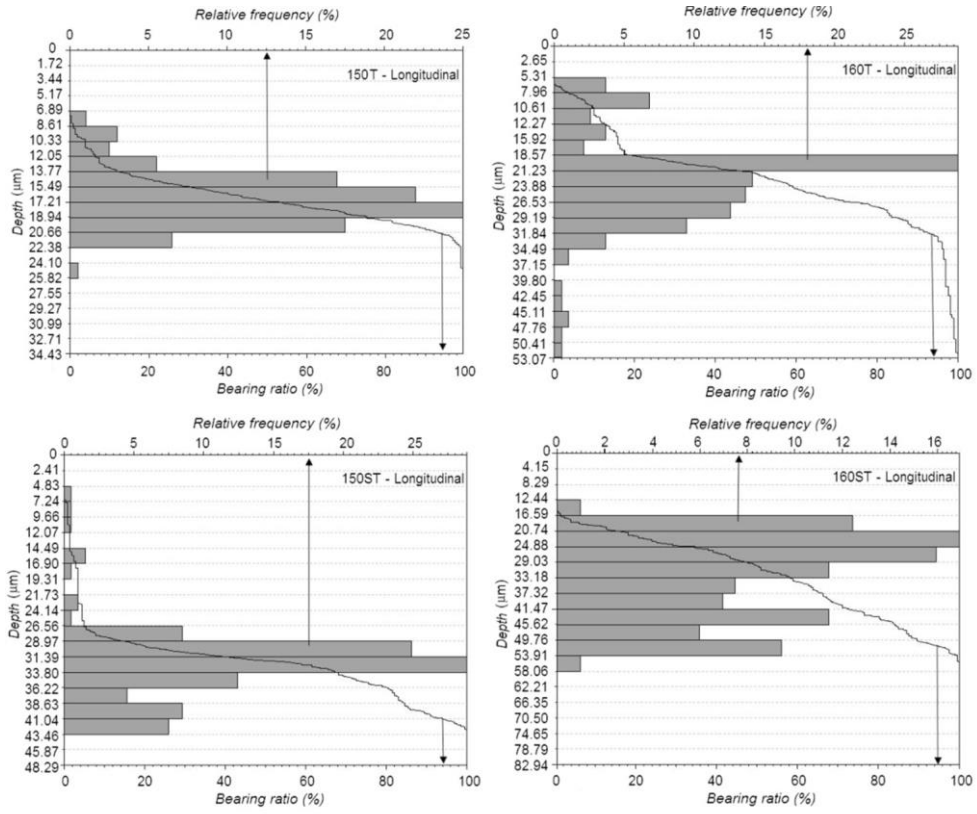

Figure 19 – Abbott-Firstone curves of tested surfaces

This analysis shows that the Abbott-Firstone curves of the surfaces molded at 150 °C decline faster than those obtained at 160 °C (for both debinding routes). A steeper curve means a low accumulation and a sharp surface profile, which should be avoided whenever a smooth surface of parts is desired. In this respect, the final conclusion is that the higher temperature of injection molding results in the more suitable surface structure of the alumina sintered items.

Overall, the obtained surface roughness data treated with suitable statistical analytical methods reveals the effect of the processing conditions during the PIM process on the final parts. Relating the surface properties of the final sintered parts to the processing parameters might provide a powerful tool to control the particular steps of PIM process.

CONCLUSION

The thesis is devoted to phase separation of highly filled materials employed in Powder Injection Molding (PIM) causing defects on final sintered parts. These defects cannot be removed from sintered parts with a post-processing treatment, and thus the separation is a source of considerable economic and environment losses. The detection of the phase separation prior debinding/sintering is an important step in optimization of PIM process.

In this regard, the non-destructive method for the quantification of the phase separation was developed by combination scanning electron microscopy and energy-dispersive X-ray spectroscopy in order to intercept inhomogeneities in distribution of chemical elements contained in PIM feedstocks. These inhomogeneities (resulting from separated binder and powder) were quantified with the help of a mathematical approach based on standard deviations of analyzed element concentrations. Then, the tendency to the phase separation is expressed as a single parameter, so called variability coefficient of separation.

From rheological point of view, the phase separation is connected to a wall slip phenomenon. Commercially available as well as in-house PIM materials were tested to a wall slip, and it was found that at certain flow conditions they all are slip-prone. Thus, a slip correction cannot be neglected when reliable rheological data are derived, especially for flow simulations of injection molding step of PIM. The research results reveal also an importance of a surface roughness of flow channels to wall slip development if surface irregularities are higher than polymer layers formed at flow channel walls. Wall slip velocities decrease with increasing surface roughness. In addition, higher tendency of PIM materials to wall slip was observed in smaller flow dies. Finally, wall slip velocities are affected not only by surface roughness and dimension of dies, but also by entrance angle of a die. In this respect, lower entrance angle of capillaries was proposed for testing of PIM materials as it provides more accurate rheological data.

Finally, final sintered structures resulting from a phase separation might be affected by process conditions. The relation of the final surface roughness to the molding and debinding conditions might provide a powerful tool to optimize PIM process. Surface properties of sintered PIM items were evaluated and treated by carefully selected statistical methods (Kruscall-Wallis and Abbot-Firstone) and it was observed that the surface profiles of the tested samples do not vary at random with the processing conditions as mold temperature or debinding route. Therefore, PIM process can be optimized to reduce and/or

eliminate phase separation by tailoring not only feedstocks compositions, but also by controlled set-up of processing conditions during injection molding and debinding step.

CONTRIBUTION TO SCIENCE AND PRACTICE

Nowadays, the phase separation of feedstock components during Powder Injection Molding (PIM) causes up to 25 % defects [10] of final sintered parts. The PhD thesis represents the contribution to eliminate this issue. In this respect, the new approach to quantify the phase separation prior sintering, when the products can be still re-granulated and employed again, was developed. In addition, the research focused on an investigation of phase separation via rheological approaches, where a wall slip phenomenon is a parameter to be tested. Concerning PIM compounds, there are - to our best knowledge - no studies considering the dimensions and surface roughness of the processing dies for the wall slip measurements of PIM materials. Also, there are no wall-slip studies performed on commercial feedstocks available. Finally, the method to relate and quantify PIM processing conditions to surface structure of final products resulting from phase separation was proposed.

The following findings can be considered as important contributions of the PhD thesis to science and practice:

- non-destructive method for quantification of phase separation enabling direct testing of molded samples developed
- integrating of wall slip to rheological characterization of PIM feedstocks - requirements for the proper rheological testing set up investigated and proposed
- processing conditions related to resulting surface quality of PIM items supported with the reliable and suitable statistical analysis.

In summary, this work conduced understanding of PIM process aimed to eliminate its most severe issue - phase separation of feedstock components occurring during injection molding step. The results presented in the thesis were published in highly respected scientific journals.

REFERENCES

[1] German R. M., Bose A., *Injection Molding of Metals and Ceramics, Metal Powder Industry*, 1997, ISBN 978-1878954619

[2] German R. M., *Metal Injection Molding*, 2011, ISBN 978-0-9819496-6-6

[3] Bilovol V. V., Kowalski L., Duszczyk J., Modeling of transient temperature fields during filling stage of powder injection moulding, *Powder Metallurgy*, 2000, 43, 228-232

[4] Hausnerova B., Marcanikova L., Filip P., Saha P., Optimization of Powder Injection Molding of Feedstock Based on Aluminum Oxide and Multicomponent Water-Soluble Polymer Binder, *Polymer engineering and science*, 2011, 51, 1376-1382

[5] Mannschatz A., Hohn S., Moritz T., Powder-binder separation in injection moulded green parts, *Journal of European Ceramic Society*, 2010, 30, 2827-2832

[6] Heaney D. F., *Handbook of metal injection molding*, 2012, ISBN 978-0-85709-066-9

[7] Huang B., Liang S., Qu X., The rheology of metal injection molding, *Journal of Materials Processing Technology*, 2003, 137, 132-137

[8] Moritz T., Lenk R., Current status of ceramic injection moulding, *Fraunhofer Institute for Ceramic Technologies and Systems*, 2010

[9] Zauner R., Micro powder injection moulding, *Microelectronic Engineering*, 2006, 83, 1442-1444

[10] Williams N., Fraunhofer IFAM: A Commitment to industry oriented research helps drive MIM product development, *PIM International*, 2009, 3, 51-56

[11] Thornagel M., MIM-Simulation: A Virtual Study on Phase Separation, *Euro PM 2009*, 2009, 135-140

[12] Kubat J., Szalanczi A., Polymer-Glass Separation in the Spiral Mold Test, *Polymer Engineering and Science*, 1974, 14, 873-877

[13] Jenni M., Schimmer L., Zauner R., Stampfl J., Morris J., Quantitative study of powder binder separation of feedstocks, *Powder Injection Moulding International*, 2008, 2, 50-55

[14] Jiranek L., Testing mold design for investigation of powder-binder separation during powder injection molding, *Master Thesis*, Tomas Bata University in Zlin, Faculty of Technology, 2010

[15] Jenni M., Zauner R., Stampfl J., Measurement Methods for Powder Binder Separation in PIM Components, *Euro PM2009*, 2009, 141-146

[16] Yang S., Zhang R., Qu X., X-ray tomographic analysis of powder-binder separation in SiC green body, *Journal of the European Ceramic Society*, 2013, 33, 2935-2941
[17] Yang S., Zhang R., Qu X., X-ray analysis of powder-binder separation during SiC injection process in L-shaped mould, *Journal of the European Ceramic Society*, 2015, 35, 61-67
[18] Yang S., Zhang R., Qu X., Optimization and evalution of metal injection molding by using X-ray tomography, *Materials Characterization*, 2015, 104, 107-115
[19] Busignies V., Leclerc B., Porion P., Evesque P., Couarraze G., Tchoreloff P., Quantitative measurement of localized density variations in cylindrical tables using X-ray microtomography, *European Journal of Pharmaceutics and Biopharmaceutics*, 2006, 64, 38-50
[20] Hausnerova B., Marcanikova L., Filip P., Saha P., Wall-slip Velocity as A Quantitative Measure Of Powder-Binder Separation During Powder Injection Moulding, *World Congress PM2010*, 2010, 557-562
[21] Adames, J.M., Characterization of polymeric binder for metal injection molding (MIM) process, *Doctoral Thesis*, Arkon, Ohio, 2007
[22] Hausnerova B., Rheological characterization of powder injection molding compounds, *Polimery-W*, 2010, 55, 3-11
[23] Michele J., Patzold R., Donis R., Alignment and aggregation effects in suspension of spheres in non-Newtonian media, *Rheologica Acta*, 1977, 16, 317-321
[24] Ahn S., Park S. J., Lee S., Atre S. V., German R. M., Effect of powder and binder on material properties and molding parameters in iron and stainless steel powder injection molding process, *Powder Technology*, 2009, 193, 162-169
[25] Isayev A. I., Xiyun F., Steady and oscillatory flows of silicon-polypropylene ceramic compounds, *Journal of Materials Science*, 1994, 29, 2931-2938
[26] Filip P., David J., Pivokonsky R., Modelling of non-monotonous flow curves using empirical constitutive equations, *Acta Technica CSAV*, 2006, 51, 349-362
[27] Shivashankar T. S., Enneti R. S., Park S. J., German R. M., Atre S. V., The effects of material attributes on powder-binder separation phenomena in powder injection molding, *Powder Technology*, 2013, 243, 79-84

[28] Mohseni M. M., Rashidi F., Axial annual flow of a Giesekus fluid with wall slip above critical shear stress, *Journal on Non-Newtonian Fluid Mechanics*, 2015, 223, 20-27
[29] Laun M. H., Capillary rheometry for polymers melts revisited, *Rheologica Acta*, 2004, 43, 509-528
[30] Lam Y. C., Wang Z. Y., Chen X., Joshi S. C., Wall slip of concentrated suspension melts in capillary flows, *Powder Technology*, 2007, 177, 162-169
[31] Denn M. M., Extrusion Instabilities and Wall Slip, *Annual Review of Fluid Mechanics*, 2001, 33, 265-287
[32] Barnes H. A., A review of the slip (wall depletion) of polymer solutions, emulsions and particle suspensions in viscometers: its cause, character, and cure, *Journal of Non-Newtonian Fluid Mechanics*, 2005, 56, 221-251
[33] Bryan M. P., Rough S. L., Wilson D. I., Investigation of static zone and wall slip through sequential ram extrusion of contrasting micro-crystalline cellulose-based pastes, *Journal of Non-Newtonian Fluid Mechanics*, 2015, 220, 57-68
[34] Delime A., Moan M., Lateral migrations of solid spheres in tube flow, *Rheologica Acta*, 1991, 30, 131-139
[35] Lam Y. C., Chen X., Tan K. W., Chai J. C., Yu S. C. M., Numerical investigation of particle migration in poiseuille flow of composite system, *Composites Science and Technology*, 2004, 64, 1001-1010
[36] Kalyon D. M., Review of factors affecting the continuous processing and manufacturability of highly filled suspensions, *Journal of Materials Processing and Manufacturing Science*, 1993, 2, 159-187
[37] Martin P. J., Wilson D. I., A critical assessment of the Jastrzebski interface conditions for capillary flow of pastes, foams and polymers, *Chemical Engineering Science*, 2005, 60, 493-502
[38] Soltani F., Yilmazer U., Slip Velocity and Slip Layer Thickness in flow of Concentrated Suspensions, *Journal of Applied Polymer Science*, 1998, 70, 515-522
[39] Kwon T. H., Ahn S. Y., Slip characterization of powder/binder mixtures and its significance in the filling process analysis of powder injection molding, *Powder Technology*, 1995, 85, 45-55
[40] Korhonem M., Mohlaschemi M., Puisto A., Illa X., Alava M. J., Apparent wall slip in non-Brownian hard-sphere suspensions, *European Physical Journal E*, 2015, 38

[41] Medhi B. J., Kumar A. A., Singh A., Apparent wall slip velocity measurement in free surface flow of concentrated suspensions, *International Journal of Multiphase Flow*, 2011, 37, 609-619
[42] Ghosh S., Ende D., Mugele F., Duits M. H. G., Apparent wall-slip of colloidal hard suspensions in microchannel flow, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 2016, 491, 50-56
[43] Yoshimura A., Prud'homme R. K., Wall slip corrections for Couette and parallel disk viscometers, *Journal of Rheology*, 1988, 32, 53-67
[44] Nickerson C. S., Kornfield J. A., A "cleat" geometry for suppressing wall slip, *Journal of Rheology*, 2005, 49, 865-874
[45] Liu L., Ma Y.H., He Z.Y., Rheological behavior of zirconia feedstock flowing through various channels considering wall-slip, *Ceramics International*, 2018, 44, 22387-22392
[46] Liu L., Gao Y.Y., Qi X.T., Qi M.X., Effect of wall slip on ZrO2 rheological behavior in micro powder injection molding, *Ceramics International*, 2018, 44, 16282-16294
[47] Postek M.T., Critical Issues in Scanning Electron Microscope Metrology, *Journal of Research of the National Institute of Standards and Technology*, 1994, 99, 641-671
[48] Hobbs A.L., Almirall J.R., Trace elemental analysis of automotive paints by laser ablation–inductively coupled plasma–mass spectrometry (LA–ICP–MS), *Analytical and Bioanalytical Chemistry*, 2003, 376, 1265-1271
[49] Mooney M., Explicit formulas for slip and fluidity, *Journal of Rheology*, 1931, 2, 210–222
[50] Yilmazer U., Kalyon D.M., Slip effects in capillary and parallel disk torsional flows of highly filled suspensions, *Journal of Rheology*, 1989, 33, 1197-1212
[51] Gulmus S.A., Yilmazer U., Effect of volume fraction and particle size on wall slip in flow of polymeric suspension, *Journal of Applied Polymer Science*, 2005, 98, 439-448
[52] Chen Y., Kalyon M., Bayramli E., Effects of Surface Roughness and the Chemical Structure of Material of Construction on Wall Slip Behavior of Linear Low Density Polyethylene in Capillary Flow, *Journal of Applied Polymer Science*, 1993, 50, 1169-1177
[53] Aral B.K., Kalyon D.M., Effects of temperature and surface roughness on time-dependent development of wall slip in steady torsional flow of concentrated suspension, *Journal of Rheology*, 1994, 38, 957-972

[54] Gulmus S.A., Yilmazer U., Effect of the surface roughness and construction material on wall slip in the flow of concentrated suspensions, *Journal of Applied Polymer Science*, 2006, 103, 3341-3347
[55] Papanikolaou M., Frank M., Drikakis D., Effects of surface roughness on shear viscosity, *Physical Review E*, 2017, 95, 1-12
[56] Lam Y.C., Wang Z.Y., Chen X., Joshi S.C., Wall slip of concentrated suspension melts in capillary flows, *Powder Technology*, 2007, 77, 162–169
[57] Hausnerova B., Bleyan D., Kasparkova V., Pata V., Surface adhesion between ceramic injection molding feedstocks and processing tools, *Ceramics International*, 2016, 42, 460–465
[58] Jeong M., Kim Y., Zhou W., Tao W.Q., Ha M.Y., Effects of surface wettability, roughness and moving wall velocity on the Couette flow in nano-channel using multi-scale hybrid method, *Computers & Fluids*, 2017, 147, 1–11
[59] Liang J.Z., Influence of Die Angles on Pressure Drop during Extrusion of Rubber Compound, *Journal of Applied Polymer Science*, 1999, 80, 1150-1154
[60] Ardakani H.A., Mitsoulis E., Hatzikiriakos S.G., Thixotropic flow of toothpaste through extrusion dies, *Journal of Non-Newtonian Fluid Mechanics*, 2011, 166, 1262-1271
[61] Bleyan D., Svoboda P., Hausnerova B., Specific interaction of low molecular weight analogues of carnauba wax and polyethylene glycol binder of ceramic injection moulding feedstocks, *Ceramics International*, 2015, 41, 3975-3982
[62] Bleyan D., Hausnerova B., Svoboda P., The development of powder injection moulding binders: A quantification of individual components` interactions, *Powder technology*, 2015, 286, 84-89
[63] He H., Li Y., Lou J., Li D., Liu Ch., Prediction of density variation on powder injection moulding-filling process by using granular modelling with interstitial power-law fluid, *Powder Technology*, 2016, 291, 52-59
[64] Liang J.Z., Chan J.S.F., Wong E.T.T., Effects of operation conditions and die angles on the pressure losses in capillary flow of polystyrene melt, *Journal of Materials Processing Technology*, 2001, 114, 118-121.

LIST OF FIGURES AND TABLES

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LIST OF SYMBOLS AND ACRONYMS

Abbreviations

BSE – Backscattered electrons
C – Catalytic binder system
DSC – Differential scanning calorimetry
E – Partly ethanol soluble binder system
EDX – Energy-dispersive X-ray spectroscopy
IFAM – Fraunhofer Institute for Manufacturing Technology and Advanced Materials
LLDPE – Linear low-density polyethylene
P – Partly water soluble binder system
PE – Polyethylene
PEG – Polyethylene glycol
PIM – Powder injection molding
PP – Polypropylene
PMMA – Polymethyl methacrylate
PS – Polystyrene
SEM – Scanning electron microscopy
TBU – Tomas Bata University

Symbols

$a(T)$ – Temperature dependent coefficient
B – Original content of the powder in a feedstock
D – Capillary diameter
L – Capillary length
ΔP – Pressure drop
$\dot{Q}$ – Volumetric flow rate
R – Pipe/Capillary radius
R_p, R_v, R_a – Roughness parameters
$\bar{x}$ – Mean value
$\tilde{x}$ – Median value
$\dot{\gamma}$ – Apparent shear rate
v_{av} – Average velocity
v_{Slip} – Slip velocity
v_{True} – Average true velocity
σ – Standard deviation

τ – Shear stress
τ_a – Apparent shear stress

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LIST OF PUBLICATIONS

Journal articles:

SANETRNIK D., HAUSNEROVA B., PATA V., On-line Rheometry Investigation of Flow/Slip Behaviour of Powder Injection Molding Feedstocks, *Polymers*, 2019, 11, 432

HAUSNEROVA B., PATA V., SANETRNIK D., Surface Properties of Powder Injection Molded Parts Related to Molding Conditions, *Manufacturing Technology*, 2018, 18, 895-899

SANETRNIK D., HAUSNEROVA B., FILIP P., HNATKOVA E., Influence of capillary die geometry on wall slip of highly filled powder injection molding compounds, *Powder Technology*, 2018, 325, 615-619

LIN D., SANETRNIK D., CHO H., CHUNG S.T, KWON Y.S., KATE K.H., HAUSNEROVA B., ATRE S.V., PARK S.J., Rheological and thermal debinding properties of blended elemental Ti-6Al-4V powder injection molding feedstocks, *Powder Technology*, 2018, 311, 357-363

HAUSNEROVA B., MUKUND B. N., SANETRNIK D., Rheological properties of gas and water atomized 17-4PH stainless steel MIM feedstocks: Effect of powder shape and size, *Powder Technology*, 2017, 312, 152-158

HNATKOVA E., SANETRNIK D., PATA V., HAUSNEROVA B., DVORAK Z., Mold Surface Analysis after Injection Molding of Highly Filled Polymeric Compounds, *Manufacturing Technology*, 2016, 16, 86-90

HUBA J., SANETRNIK D., HAUSNEROVA B., HNATKOVA E., DVORAK Z., New Application of Powder Injection Molding Product in Medical Field, *Manufacturing Technology*, 2016, 16, 94-98

HUBA J., SANETRNIK D., HNATKOVA E., HAUSNEROVA B., Mechanical Properties of New and Recycled PIM Feedstocks, *Applied Mechanics and Materials*, 2015, 732, 103-106, ISSN: 1662-7482

HAUSNEROVA B., SANETRNIK D., PONIZIL P., Surface structure analysis of injection molded highly filled polymer melts, *Polymer Composites*, 2013, 34, 1553–1558

SANETRNIK D., HAUSNEROVA B., Moldability of Highly Filled Polymers. *Chemické Listy, Special Issue*, 2013, 107, 81-82, ISSN: 1213-7103

HAUSNEROVA B., SANETRNIK D., PONIZIL P., Eliminating separation during powder injection molding, *Society of Plastics Engineers, Plastics Research Online*, 2013

Conference proceedings:

HNATKOVA E., SANETRNIK D., PATA V., HAUSNEROVA B., DVORAK Z., Mold Surface Analysis after Injection Molding of Highly Filled Polymeric Compounds, *ICTKI2016 Conference,* Litoměřice, 2016

HUBA J., SANETRNIK D., HAUSNEROVA B., HNATKOVA E., DVORAK Z., New Application of Powder Injection Molding Product in Medical Field, *ICTKI2016 Conference*, Litoměřice, 2016

HUBA J., SANETRNIK D., HAUSNEROVA B., HNATKOVA E., DVORAK Z., ZLINSKY V., New Design of Adenoid Curette Produced via Powder Injection Molding Technology, *8th International Conference on MATERIALS SCIENCE*, Rome, 2015

HNATKOVA E., SANETRNIK D., HAUSNEROVA B., Effects of SA surfactant on critical solid loading and flow properties of PIM feedstocks, *2nd International conference on rheology and modelling of materials*, Miskolc-Lillafured, 2015

HNATKOVA E., SANETRNIK D., HAUSNEROVA B., Effects of Molecular Weight on Entrance Pressure Drop in Highly Filled Systems, *2nd International conference on rheology and modelling of materials*, Miskolc-Lillafured, 2015

HAUSNEROVA B., SANETRNIK D., HNATKOVA E., Wall-slip as a phenomenon attending processing of highly powder particle filled polymer melts, *6th international Conference on Mechanics and Materials in Design*, Ponta Delgada Azores 2015

HAUSNEROVA B., SANETRNIK D., Critical Issues of Ceramic Injection Molding Feedstocks (Invited Lecture), *2015 EMN Ceramic Meeting*, Orlando 2015

HUBA J., SANETRNIK D., HNATKOVA E., HAUSNEROVA B., Mechanical properties of sintered PIM test specimens, *International Conference Plastko 2014*, Zlín, 2014

HAUSNEROVA B., SANETRNIK D., PARAVANOVA G., Slip of Highly Filled Powder Injection Molding Compounds: Effect of Flow Channel Roughness, *7th International conference Times of Polymers and Composites*, Ischia, 2014

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