

# Binder systems for powder injection molding: A review

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## Abstract

Regardless of high demands on properties of powder injection molding (PIM) compounds, there is still uncertainty in the role of the polymer binder in the process. To a great extent this is caused by the relatively low number of suitable direct methods to observe the interactions among binder components as well as binder-powder and binder-powder-processing tool reactions, because of the complexity of occurring interactions. In this paper the review of state-of-art in the field of binder development and characterization is reported with the special regard to methods to quantify their mutual relationship. Copyright © 2017 VBRI Press.

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## Introduction

The material component which allows shaping of metal and ceramic powders via injection molding is called binder. It plays a crucial role in powder injection moulding (PIM) process.

During the first step of PIM – mixing - the binder composition has to be adjusted to the powder characteristics, because successful injection molding of powdery materials requires preparing feedstock whose individual powder particles are fully lubricated with the smallest effective amount of a binder.

The next step - injection molding - is carried out on injection molding machines which are usually optimized for the processing of powdery materials (wear-resistant cylinder and screw), the screw geometry adopted to lower compression ratio (from 1.4:1 to 1.6:1) and extended compression zone compared to standard screws for thermoplastics [1]. During injection molding, binders serve as a temporary vehicle to proceed powder particles into the cavity of injection mold requiring suitable rheological properties.

In the following step of the PIM process - rebinding - a binder is chemically or thermally withdrawn from the green part. Selection of debinding method or even their combination is dictated by a binder composition. Thermal debinding, where a binder is removed in a controlled heating, is carried out under air (for ceramics), hydrogen and/or nitrogen (for metal powders) or argon (titanium alloys) atmospheres at various temperature regimes. In

solvent debinding, the molded part is placed into a solvent (water, ethylene dichloride, n-heptane, etc.) for several hours and binder is extracted, or alternatively a solvent vapor is used which initiates condensation, and subsequently liquid extraction of the binder components is carried out. A binder removal should be gradual, step-by-step [2], providing shape retention until the powder particles start bonding to each other at high temperature. To achieve this requirement, binders are multi-component systems with different decomposing temperatures.

The final stage of the PIM process - sintering - consists in densification of so called brown part, whose strength is largely reduced after debinding. Sintering produces parts with the final density generally more than 97 % of the theoretical values [3]. Sintering is performed in sintering furnaces under protective or vacuum atmospheres for metals and an air atmosphere for ceramics.

## Binder composition

In a binder composition, waxes as paraffin, carnauba, beeswax are usually combined with thermoplastics (polyethylenes, polypropylene, poly(methyl methacrylate), poly(ethylene glycol) or ethylene-based block copolymers). Due to various requirements arising from molding and debinding steps of PIM, the polymeric binder is usually designed as a multi-component system in which each component plays a specific role. It generally consists of three components: main body, backbone (non-

reactive during debinding process, keeping the shape of the part prior to sintering) and additive<sup>3</sup>.

### **Main body**

Main body is commonly based on low molecular weight components providing low viscosity to a highly concentrated feedstock. Paraffin wax (PW), a soft solid consisting of a mixture of hydrocarbons commonly with twenty to forty carbon atoms in a chain is the most widely used polymer in PIM binders due to its low melting temperature (45–65 °C) and inherently low viscosity. As debinding time increases with the chain length, one could believe that it is a suitable material for this application, but due to its nonpolar character, the shear forces necessary to disperse the particles and break up agglomerates may not be sufficient [4]. Further, as reported by Thomas-Vielma *et al.*[5] feedstocks with high content of PW are not suitable for PIM because they do not retain the shape during a polymer extraction, and sintered parts contain many defects.

In this view, more perspective waxes seems to be carnauba wax (CW) and acrawax (AW). Acrawax (N, N'-Ethylene Bis-stearamide) belongs to a group of amidic waxes with melting point of 145 °C, while carnauba wax contains mainly wax esters (85%) accompanied by small amounts of free fatty acids and alcohols, hydrocarbons and resins. The wax esters constitute C16 to C20 fatty acids linked to C30 to C34 long-chain fatty alcohols. Melting point of CW is of 82–86 °C allowing lower processing temperature than with polyolefins, thus suitable for reactive powders such as titanium alloys, low pressure injection moulding as well as  $\mu$ PIM.

Currently, the role of waxes as a main body is often overtook by oligomer of ethylene oxide - poly(ethylene glycol) (PEG). Especially for combined solvent/thermal debinding process, due to its non-toxicity and solubility in water [6-9], PEG allows an easy and fast [10] removal leaving open pores for gaseous products of a remaining backbone to diffuse out of a structure in a secondary stage of debinding.

The binder system designed with PEG was firstly reported by Cao *et al* [11]. Then, Hens and German [12] investigated the role of PEG in feedstocks with regard to enhance processability and shape retention during debinding. Since then, water-soluble binders based on PEG have been widely studied for both metal and ceramic feedstocks [13-16]. In comparison to PW, PEG is able to better sustain high shear deformation during processing as we have shown [4] for carbide powder feedstocks and two types of powder-binder mixtures. In the first one paraffin wax was used, in the other one PEG 6000/PEG 2000 served as a binder. At low shear rates, the flow was pseudoplastic. At a shear rate of about  $10^3 \text{ s}^{-1}$ , there was a critical point, where the shear stress raised up dramatically for the suspension containing the PEG mixture, and then continued at the higher level. It may be supposed that above this critical shear rate only PEG 6000 plays the role of a vehicle facilitating the flow. In the case of the paraffin compound, the capillary was blocked by

the powder as paraffin, due to its poor adhesion to the powder, separated out from the compound.

### **Backbone**

The role of backbones in feedstock is to remain in brown (debound) parts until late debinding and early sintering stage to hold the powder particles together before they can be sintered. Thermoplastic polymers, especially polyolefins polyethylenes (PE-HD, PE-LD), polypropylene (PP), but also poly(methyl methacrylate) (PMMA) and ethylene-based copolymers as ethylene vinyl acetate (EVA), ethylene acrylic acid (EAA), or ethylene butyl acrylate (EBA) are commonly used as backbones in PIM process. Huang and Hsu<sup>17</sup> demonstrated that a backbone polymer strongly affects not only the processability of a PIM compound during injection molding, but also dimensions and mechanical properties of sintered parts. Therefore, the proper selection of a backbone polymer is required to increase the dimensional accuracy and quality of sintered parts. They found out that PE-HD having higher molecular weight provides better dimensional stability to the parts, while PE-LD results in more favourable flow behaviour of feedstocks.

Meanwhile, due to their high molecular weight (over 250000 g/mol), polyolefins having relatively high viscosity and poor adhesion to polar powders always require use of additional processing aids. This can be to some extent balanced with polar polymers as PMMA or PEG. PMMA is a polymer of high-average molecular weight which is often used together with PEG, providing stiffness and strength to the mouldings<sup>18-21</sup>. Bakan *et al.*<sup>18</sup> studied a binder system composed of PMMA and PEG, and found out that reducing the content of PMMA allows higher solids contents to be molded. On the other hand, reducing the PMMA content lowers the stiffness and strength of the moldings. Furthermore, Singh *et al.*<sup>22</sup> showed that increasing the content of PMMA in a binder system containing PC and PMMA, lowers linearly the degradation temperatures.

### **Additives**

Incorporation of surface active agents is an important aspect of binder design as well. They create a thin surface transition layer between powder particles and remaining binder composed of chemical absorption bonds<sup>23</sup>, which lubricates particles allowing them sliding at particle contacts and reducing a system viscosity during mixing or moulding.

Low molecular weight surface active agents are usually more effective in reducing a feedstock viscosity than high molecular weight ones due to their lower intrinsic viscosities and higher polarities. However, interlinking strength among binder components is weak, due to the relatively short chain lengths of the low molecular weight surface active agents, and necking during plastic forming occurs easily<sup>24</sup>. Thus, a polymer having suitable functional groups in each repeating unit

can enhance the interlinking strength among binder components, in addition to improving the adhesion force with the powder surface. This requirement suits well for PEG showing low contact angles and high total surface energy<sup>25</sup>.

Stearic acid (SA), consisting of a functional group adhering to the powder surface and an oriented molecular chain extending into the binder to prevent aggregation of powder and stabilizing particles during high shearing, is often used as low molecular weight additive. This effect can be also attributed to the known amphiphilic character of this fatty acid functioning as a surface active agent<sup>25</sup>.

Li *et al.*<sup>26</sup> investigated effect of various SA contents in a feedstock based on 17-4PH stainless steel and paraffin wax-based binder, and confirmed that a tailored content of SA in a feedstock can decrease viscosity and improve dispersibility of the powder and increase the critical solid loading due to the enhancement of interactions between the powder and the binder. The FTIR analysis showed that chemical adsorption occurs between SA and powder surface after mixing, reinforcing the interacting force between the powder and the binder.

Further, experiments performed by Chan and Lin<sup>27</sup> showed that about 5 wt.% of SA is the optimal amount for improving wettability of a binder and enhancing processing properties of feedstocks. The positive effect of using 5 wt.% of SA such as an improved wettability and a better rheological stability has been confirmed also by Ren *et al.*<sup>28</sup>. On the other hand, Fan *et al.*<sup>29</sup> showed that addition of only 1 wt.% of SA leads to an easier mixing and a better feedstock fluidity, noticeably improving the compatibility of the powder and the binder. They also pointed out that at lower temperatures (<125 °C), the feedstock containing SA has improved rheological performance over the feedstock without SA, whereas at higher temperatures (>125 °C) the situation is vice versa. This work also claims that addition of SA can reduce the temperature required for injection molding, and such binders are more suitable for feedstocks based on ultrafine powders.

Oleic acid (OA) is another surfactant employed in PIM binder systems as a processing aid. Hausnerova *et al.*<sup>15</sup> studied feedstock based on aluminium oxide and multicomponent water-soluble polymer binder by examining the pressure-volume-temperature characteristic, because in high-pressure molding process the feedstock is in a pressurized melt form. The hydroscopic fine alumina powder and the binder, sensitive to destabilization in water, often result in a high viscosity, which can be reduced with dispersants and lubricating agents. In this study, only 1 wt.% of oleic acid lowered the viscosity sufficiently, enhanced the processing properties and ensured the moldability of the feedstock.

Nevertheless, the comparative study of SA, OA and 12-hydroxystearic acid (HSA) influences on the flow behavior of an alumina feedstock done by Tseng<sup>23</sup> showed that systems based on SA exhibited superior pseudoplastic flow behaviour and lowered viscosity more effectively than binders containing OA and HSA. Also, it was found

that yield stress and viscosity decreased proportionally with the increase in SA amount.

### Binder Performance during PIM Process

As it has been already mentioned a binder should ensure wetting of powder surface, and thus promote an appropriate mixing and molding of metal and ceramic powders. Simultaneously, there must be good adhesion between powder and binder preventing the feedstock from phase separation or segregation during processing via injection molding.

For a successful molding without formation of any defects, a feedstock has to satisfy tailored rheological requirements: 1) too low viscosity can lead in a feedstock separation, while too high viscosity can cause problems during mixing and mold filling, 2) low sensitivity of viscosity on temperature resulting in no fluctuations during injection molding, but once a part is cooled down in a mold cavity, there should be a rapid increase in viscosity in order to retain a shape of injected components (without large thermal contraction of a binder). Second group of requirements is related to the removal of binder, which should be easy, fast, but gradual without forming defects. There, more emphasis is devoted to low residual oxygen and carbon contents for low contamination prior sintering. Moreover, it has to be chemically inert with respect to a powder, i.e. no reactions resulting in polymerization or degradation of binder components during process can occur.

However, currently there is still lack of knowledge and research devoted to the role of the particular binder components during the process and their interactions as well as interactions with powders and processing tools. Commonly used structural analyses such as electron microscopy or X-ray diffraction serve as a basis for discussion about macroscopic properties. Some of these direct methods - such as 3D Raman spectrometry, X-ray computer tomography, or 3D transition electron microscopy provide a 3D insight into the material structure, but only in a qualitative way.

Structure control in terms of tailoring binder characteristics to a process leads to the necessity of correlating the physical properties (e.g. viscosity) to the material characteristics in a quantitative way. Rheological properties of binders are important when seeking for an optimum binder formulation or selecting a proper additive. Hausnerova *et al.*<sup>30</sup> studied the particular influence of block copolymers used as a binder component on the rheological properties of PIM feedstocks. Hsu and Lo<sup>31</sup> employed the McLean-Anderson statistic method<sup>32</sup> to carry out systematic investigation of 15 binder formulations resulting in contour maps demonstrating the influence of the particular binder components on fluidity and pseudoplasticity of PIM compounds. Ahn *et al.*<sup>33</sup> have investigated various binder systems with an objective to optimize their composition, feedstock composition, part geometry and injection molding process. Rheological

characterization as well as simulation analysis revealed that injection molding pressure-related parameters such as wall shear stress, injection pressure, and clamping force depend rather on a binder system, than on powder characteristics. For the temperature-related parameters such as melt front temperature difference and cooling time, the binder selection was also found to be more critical than the powder selection.

However, majority of researchers so far have considered the rheological behavior of binder as a bulk, and thus the roles of particular binder components and their inter-relationships still remain rather unclear.

### Analyses of binder interactions

The interactions of a binder with a powder and among binder components are often deduced from their rheological performance. Up to date, the miscibility of particular components has been investigated with the help of differential scanning calorimetry (DSC), atomic force microscopy (AFM), and Fourier transform infrared spectroscopy (FTIR). Nevertheless, studying the interactions of polymers might be a challenging task, because the interactions detected mainly present their self-interactions, which are significantly stronger.

Chen *et al.*<sup>34</sup> investigated the miscibility of both nonpolar PW and polyethylenes (PE-HD, PE-LD and PE-LLD) using DSC and AFM. By evaluating the morphology, crystallization and crystallinity, combined together with equilibrium melting temperature and melting point depression, the interaction parameters for polymer-diluent systems were defined. This data served as an evidence of a partial miscibility of paraffin in polyethylenes with PE-LLD/PW being favourable over the PW/PE-HD.

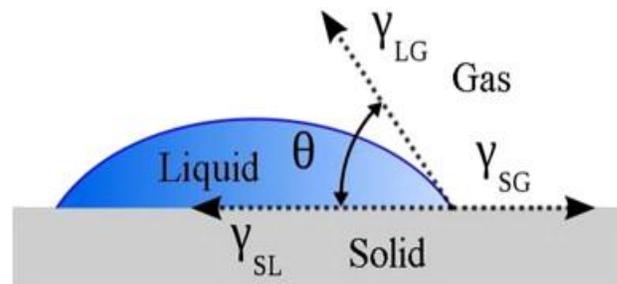
Sudhakar and Selvakumar<sup>35</sup> reported on miscibility of chitosan and PEG blend using a buffer solution. From collected FTIR spectra for polyblend films and polymers it was observed that with increasing the amount of PEG, the O–H stretch peak tends to lower peak wavenumbers, serving as an evidence of the components miscibility.

Doulabi *et al.*<sup>36</sup> studied the miscibility of PEG and chitosan by using acetate buffer solution for different blend compositions. The viscosity, density, and refractive index were measured in order to quantify the interaction parameters. The results showed that the components at 80 % or higher chitosan concentration were miscible by means of intermolecular hydrogen-bonding interaction between hydroxyl groups of polyethylene glycol fumarate with amino and hydroxyl groups of chitosan.

Hsu *et al.*<sup>37</sup> studied the effect of PW and CW on carbonyl iron based feedstock, where PE-LD served as a backbone. The rheological measurements using capillary viscometer and a statistical analysis based on the McLean-Anderson<sup>32</sup> design method showed that polar CW has stronger interactions or adsorptions with iron powder than nonpolar PW, exhibiting higher viscosity, greater pseudoplasticity and lower flow activation energy

than PW/PE-LD. The carbon contents in sintered specimens were also in favour of CW/PE-LD composition.

The adhesion properties of binders can be evaluated from the surface tension of tested materials and their contact angles, **Fig. 1**.



**Fig. 1.** Contact angle at a liquid–gas–solid interface, where  $\theta$  is degree of contact angle, and  $\gamma_{SL}$ ,  $\gamma_{LG}$ ,  $\gamma_{SG}$  are solid/liquid, liquid/gas, solid/gas interfacial tensions, respectively.

Yang *et al.*<sup>38</sup> studied the surface tensions together with the contact angles of PP, PE-HD, PS and PMMA melts. The experimental results were used to build a mathematical model representing the relationship between surface tension and temperature of polymer melts. The increase of a force between melt–solid molecules was found to be higher than that between melt–melt molecules, suggesting that internal molecules of a melt will squeeze into a melt interface layer. This study also showed that the surface tension increases gradually, and reach the steady value with increasing time, and the melt interface layer tends to extend leading to the smaller contact angle, and thus better wettability.

Michalski *et al.*<sup>39</sup> tested Van Oss (Lifshitz and electron donor–electron acceptor components of a surface free energy) and the Owens–Wendt (dispersive and nondispersive components of a surface free energy) methods to calculate of the surface free energy of PVC/EVA polymer blends. According to the obtained results, the surface free energies were found to be greatly dependent on the calculation method and on the number of standard liquids used for contact angle measurements.

Ucar *et al.*<sup>40</sup> studied surface properties of EVA, PE-HD and polyvinyl acetate blends using contact angle analysis and X-ray photoelectron spectroscopy. Tested EVA samples varied in the content of vinyl acetate in the range of 12 to 33 wt.%. Thin layers of each blend were prepared from their xylene solutions at high temperatures by a dip coating technique. Static and dynamic contact angle measurements were carried out using grade water, methylene iodide, ethylene glycol and formamide liquids. The obtained data showed that the increase of the polar hydrophilic vinyl acetate in the blend resulted in the decrease of the water equilibrium contact angles.

In the recent work of Hausnerova *et al.*<sup>25</sup> PE-LD, PEG, PW, CW, AW and SA binder components for  $\text{Al}_2\text{O}_3$  and  $\text{ZrO}_2$  feedstocks were tested. The surface energy was

determined from the measurements of contact angles of three testing liquids (deionized water, ethylene glycol and diiodomethane) using the SEE (Surface Energy Evaluation) system. Low contact angles measured for PEG in all testing liquids could be explained by the hydrophilicity of its surface. Contact angles for CW and SA exhibited very similar values in water, and crosswise for the remaining testing liquids. SA offers excellent adhering to the powder surface, fully coating the particles and preventing powder aggregation. As it has been already mentioned, the interlinking strength between binder components is weak, due to the short chain lengths of the low molecular weight surface active agent as SA, which can result in a necking during plastic forming<sup>24</sup>. In this view, and according to the contact angle analysis, it seems that CW could overtake the role of a plasticizer in PIM binders. Interestingly, AW exhibits the values of contact angle comparable with those obtained for PW, where no adhesion is expected.

Meanwhile, investigation of polymer interactions is a challenging and highly time consuming task requiring advanced knowledge, which also leads to proposal of numerical models to predict the feedstock properties<sup>41-44</sup>. Polymer-polymer miscibility guide developed by the group of Coleman *et al.*<sup>45</sup> represents one of the early predictive approaches.

Still, there is a noticeable lack of efforts in studying interactions between binder system components, although their understanding can be the key for a development of novel binder systems with advanced processing properties, making PIM feedstocks highly robust and significantly shortening overall processing time. In this respect, the substitution of polymers by their low molecular analogues can be used, where the specific interactions between polymers cannot be studied by other means. This technique allows eliminating the majority of self-interactions during cross-interaction measurements, which is not possible for polymer-polymer interactions evaluation<sup>46</sup>.

### Substitution of binder components with low molecular weight analogues

Only few studies have considered the substitution of polymers with their low molecular analogues for investigation of specific interactions between theoretically immiscible polymers. French *et al.*<sup>47</sup> employed the exothermic mixes of chemical analogue of poly(vinyl phenol) with analogues of polyacetal and poly(ethylene oxide) suggesting miscibility for the blends of poly(vinyl phenol) with both polymers. It was found that the interaction parameter corresponding to poly(vinyl phenol) and poly(ethylene oxide) analogue mixtures is in agreement with the interaction parameter reported for the polymer mixtures, which was based on the melting point depression of poly(ethylene oxide) in blends with poly(vinyl phenol). Strong hydrogen bonding between phenol and ether groups in these analogue mixtures were observed using FTIR. It was predicted that rather wide range of styrene-vinyl phenol copolymers would exhibit

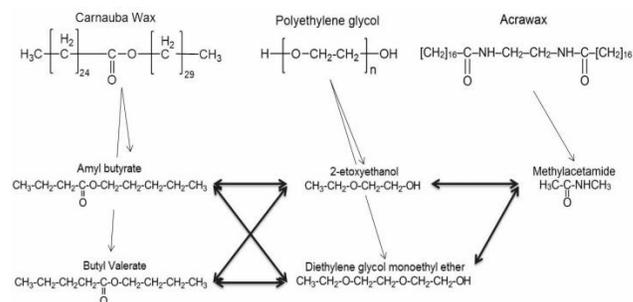
miscibility with polyacetal via the application of the binary interaction model.

Svoboda *et al.*<sup>46</sup> investigated the miscibility window in the blends of polycaprolactone and poly(styrene-co-acrylonitrile). Components were substituted by their low molecular weight analogues and corresponding to monomers of each polymer, since respective homopolymer pairs are not miscible. FTIR and calorimetric measurements were carried out for studying the interactions within the miscibility window in detail.

Landry *et al.*<sup>48</sup> investigated the miscibility between polystyrene polymers containing potential hydrogen bond donor groups and other polymers that are good hydrogen bond acceptors. The thermodynamics of mixing of low molecular weight analogues of chosen organic polymers of interest were studied using calorimetry. In blends which included both, substitute liquids and polymers, the strengths of the interactions with the acids were found to be different for esters and amides. Authors suggest that for forming miscible blends with strong, self-associating hydrogen bond donors, the preference must be set towards stronger bases, since the stronger interaction between the acid and the base helps to break up the self-associations. In this study<sup>48</sup>, differential scanning calorimetry together with infrared spectroscopy and optical transparency was used in order to investigate the miscibility of composed blends.

Combination of FTIR measurements together with other techniques is often used for studying the specific interactions, where the shift of peaks is assumed as an evidence of a partial miscibility<sup>49-51</sup>. Analogue calorimetry is used as a tool for rationalizing and extending the results of polymer-polymer miscibility<sup>52-54</sup> and number of researchers reported on successful use of both (FTIR and calorimetry) for quantifying and evaluating the specific interactions<sup>55-57</sup>.

Detailed analysis<sup>58,59</sup> of specific interactions between binder component often used in PIM - polyethylene glycol (PEG) with carnauba wax (CW) and acrawax (AW) was also performed using their low molecular weight analogues (see Scheme 1).



**Scheme 1.** Low molecular weight analogues for PIM binder components.

First, an optimum dilution level was defined at 1 % concentration as it can be seen from the example in **Fig. 2** revealing shift of carbonyl C–O stretching peak for 2ET diluted in hexane<sup>58</sup>.

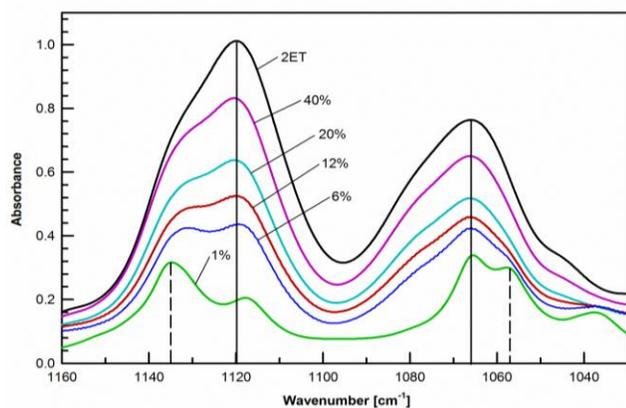


Fig. 2. Shift of FTIR peaks for C–O bonding of 40, 20, 12, 6 and 1 % of 2-ethoxyethanol (2ET) in hexane<sup>58</sup>.

At initial 40 % the development of the peak shoulder is observed, which progressively grows at 20 and 12%. At 6% concentration, already the half of 2ET molecules is isolated by hexane. For the dilution at 1% concentration the magnitude of  $1131\text{cm}^{-1}$  peak suggests that the majority of 2ET molecules are surrounded by hexane (molecules are separated), even though the small peak at  $1119\text{cm}^{-1}$  is a hint of a presence of insignificantly small amount of self-interaction pairs. Moreover, due to the asymmetry of the C–O bonding in 2ET, the second peak shift was also observed at  $1065\text{cm}^{-1}$ , with minor shoulder for 12 and 6 %, and prominent peak at  $1056\text{cm}^{-1}$  for 1% dilution. Then, the investigation of the interactions between PEG, CW and AW substitutes was carried out, and with the help of FTIR results of peak shifts in solvents the baselines were constructed (see example shown in Fig. 3), and the corrections of peak shifts calculated. The obtained results from FTIR suggested the presence of the specific interactions between the liquid pairs tested according to Scheme 1 by displaying the shift of peaks towards the lower wavenumbers, which is in agreement with other reports<sup>49-51</sup>.

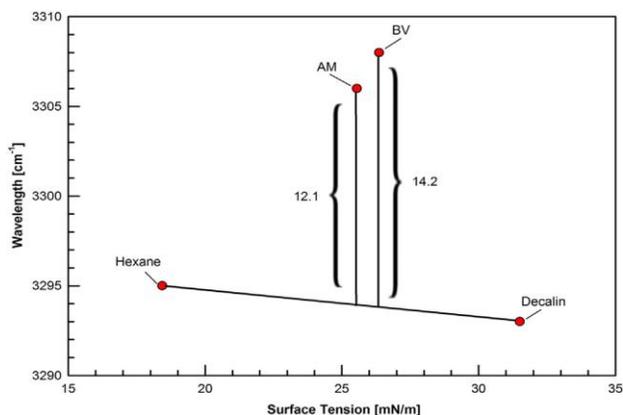


Fig. 3. Calculation of corrected peak shift from the baseline for N–H stretch bonding of 1 % methylacetamide (NMA) in hexane, decalin, butyl valerate (BV) and amyl butyrate (AM)<sup>59</sup>.

The quantitative analysis of interactions is based on the assumption<sup>60</sup> that the change of Van der Waals intermolecular interactions accompanying mixing is negligible, all contributions to the heat of mixing are due to specific acid-base interactions, as well as that all organic liquids (except for saturated hydrocarbons) make the specific self-association based on electron donor (basic) and electron acceptor (acid) sites of one molecule. Further, it is assumed that molecules are self-associated in  $X-X$  pairs consisting of two molecules by the acid-base interaction and all  $X-X$  interactions are broken in the case of high dilution, where all dissociated  $X$  molecules form new  $X-Y$  interactions and molecules  $Z$  (saturated hydrocarbons) do not have any acid-base self-associations and do not form acid-base interactions with another molecule ( $X$  or  $Y$ ).

Calorimetric measurement allows to quantify  $X-X$  and  $X-Y$  interactions. The analysis allowed determining the temperature drop - an exothermic reaction for the dilution of AW-PEG substitutes, while the dilution of CW-PEG and CW-AW substitutes exhibited endothermic reaction<sup>59</sup>. The increase in temperature during mixing is associated with strong, newly formed interactions between blended liquids.

Finally, the peak shifts from FTIR were plotted against the association energies obtained from calorimetry (Fig. 4), and a linear connection of these two independent experiments was found<sup>58,59</sup>. This is in accordance with Drago's equation<sup>61</sup>.

The observed endothermic reaction from calorimetric analysis combined with the shift of the spectral peaks in FTIR suggests a presence of specific interactions between substitutes, predicting a partial miscibility of respective polymers. The highest cross interaction suggesting strong interactions were found for PEG and acrawax binders (almost twice stronger than between PEG and carnauba wax)<sup>59</sup>. In contrast to the studies of miscibility of polymer/polymer blends, where self-interactions are significantly higher than polymer  $X$  to polymer  $Y$  interactions, with the help of low molecular substitutes, the values of  $X-Y$  interactions are calculated precisely.

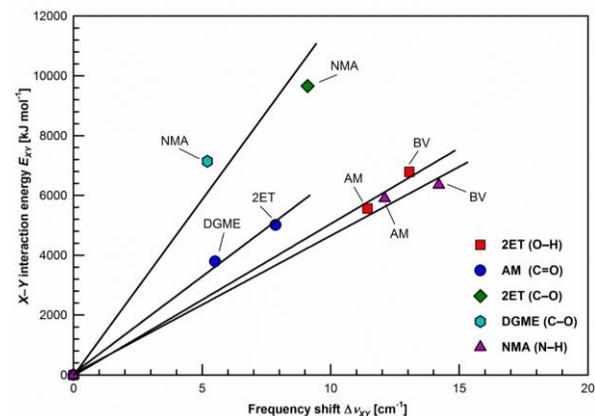


Fig. 4. Association energies vs. shift of peaks for low-molecular analogues of acrawax, carnauba wax and polyethylene glycol<sup>59</sup>.

### Interactions of binders with processing tools

In PIM, one of the main concerns for studying liquid-solid interface interactions is a wall slip phenomenon<sup>62,63</sup>. Wall slip occurs when feedstock does not adhere to mold channel walls, but instead moves in a narrow stream at the wall, and can cause a row of defects in molded parts.

Silberzan *et al.*<sup>64</sup> reported on spreading behavior of high molecular weight and low molecular weight polymers on high energy surfaces using optical microscopy and ellipsometry. The results showed that on the same kind of surfaces, low molecular weight polymers exhibited more rapid spreading rate than polymers with high molecular weight. Schonhor *et al.*<sup>65</sup> studied the kinetics of wetting of high-energy (aluminum, mica) and low-energy (teflon) surfaces by polyethylene and ethylene-vinyl acetate copolymer melts using contact angle measurements. However, the study concludes that the mechanism of wetting of liquids remains unknown, as well as no empirical rate law of wetting process could be evaluated.

Often simulations and modelling are used for broader understanding of interactions of feedstocks with the processing channels. Pearson and Petrie<sup>66</sup> suggested that the ratio of molecule size to the wall surface roughness is of a key importance. For the cases, where the molecular size is smaller than the wall roughness scale, no effective slip can occur, while for the large macromolecules, slip is more likely to occur. This is in agreement with Jabbarzadeh *et al.*<sup>67</sup>, who studied the effect of wall roughness on the wall slip using a molecular dynamics simulation. Obtained results indicated that the wall slip increases with the size of molecules and the wall roughness period, while it decreases with increasing wall roughness amplitude.

Nevertheless, the analysis of interactions between feedstock components and mold channel walls are very scarce. Contact angle analysis of four most often used treatments of steel considered for channel walls of an injection mold: hardened, hardened TiN, nitridized and heat-treated was performed by Hausnerova *et al.*<sup>25</sup>. The lowest total surface energy was obtained for nitridized and hardened TiN surfaces, where also dispersion and polar components were similar. As it can be derived from Fig. 5, significantly different behavior showed heat-treated surface with the highest value of surface energy of 55.4 J/m<sup>2</sup> compared to other measured surfaces.

However, it should be mentioned that in case of investigation of the binder/feedstock interactions with the material of the processing tools the situation is further complicated not only with the processing properties as temperature and pressure, but also with the surface structure of the tools. This aspect has not been to our best knowledge considered and included in the studies, with the only exception of work by Hausnerova *et al.*<sup>25</sup>, where the surface roughness was quantified with the help of contactless scanning analysis.

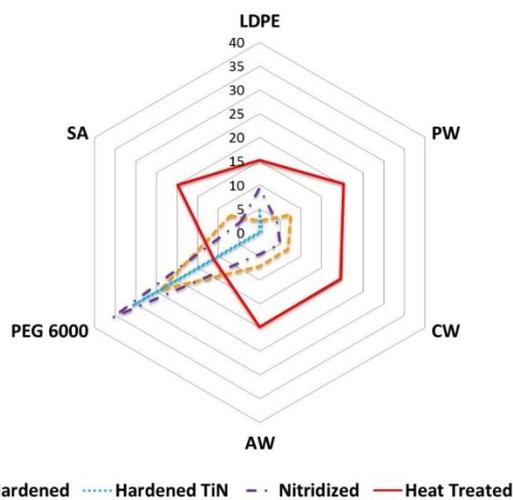


Fig. 5. The differences of surface energies between polymer binders and mold materials<sup>25</sup>.

In addition, in order to determine their suitability for injection molding step of PIM process, rheological and thermal characterization of the proposed binders should always accompany and be in accordance with FTIR, calorimetry and contact angle methods as shown very recently by Hausnerova *et al.*<sup>68</sup>.

### Conclusion

Still widely considered a new and developing technology, powder injection moulding (PIM) constitutes an attractive topic for both basic and applied research as it has some quality-determining issues to be dealt with. There have been tries devoted to the simplification of the process and reducing the conventional steps by implementing sophisticated techniques and by merging of two consequent stages, but the development of advanced binder systems may eliminate such needs.

Regardless of the current trend to employ ready-to-use (commercial) feedstocks based on a patented binder systems, complexity of demands on binder systems has always been a research challenge for composing advanced feedstocks, since the required processing properties are usually achieved by using a binder system consisting out of 3 to 5 different polymers, waxes and processing aids. This diversity of components makes it extremely difficult to study the complete and individual reaction pathways and chemical mechanisms occurring within such systems.

This paper intends to review the present state-of-art of the binder development, with the special regard to the investigation of the role of the particular binder components. Combining FTIR and calorimetry, providing the possibility to evaluate binder interactions quantitatively, together with the substitution of binder components with their low molecular weight analogues, which bring an advantage of eliminating majority of self-interactions, is proposed for a deep understanding of compositions of PIM binders.

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