



# The development of powder injection moulding binders: A quantification of individual components' interactions



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## ABSTRACT

The study of interactions between binder system components is critical for improving the processing properties of powder injection moulding (PIM) feedstocks. In this paper the interactions between acrawax (AW) and polyethylene glycol (PEG) were analysed and compared with those obtained for carnauba wax (CW). Due to the complexity of interaction mechanisms, the polymers were substituted with their basic low molecular weight analogues and analysed by FTIR and calorimetry. Self-interaction energies and association energies were determined using calorimetric analysis. Shifts of FTIR absorption peaks (C–O stretch and N–H stretch) served as evidence of the presence of interactions between the components. The calorimetric study of AW/PEG analogues showed a temperature increase during mixing, indicating the presence of strong interactions. The combined data from FTIR and calorimetry allowed a quantitative evaluation, which indicated about two times stronger interactions between AW (with C=O and N–H groups) and PEG (with C–O and –OH groups), as compared to CW (with C=O and C–O groups) and PEG analogues.

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## 1. Introduction

In recent years, powder injection moulding (PIM) has established itself as a cost-effective production technique derived from plastic injection moulding, allowing large scale production of complex parts. The binder system in PIM plays an important role, bestowing on the feedstock the required processing properties and ensuring defect-free processing throughout each production stage [1].

Suitable processing properties of a powder feedstock are usually achieved by using a binder system consisting of up to 5 different polymers and waxes, which complicates the investigation of the complete and individual reaction pathways and the chemical mechanisms occurring within such a system. The majority of binder systems is based on polyolefin backbones such as polyethylene (PE) or polypropylene (PP), and includes also polyethylene glycols (PEGs) with various molecular weights and waxes such as paraffin wax (PW).

Despite the substantial effort made in studying PE and PP binders [e.g. 2], their usage often leads to processing issues such as insufficient initial pore formation and weak internal transport mechanisms within the green parts, resulting in lower debinding rates. PEG's main role is as plasticiser [3]; besides improving the viscoelastic properties its use

is endorsed by water solubility allowing an environmentally safe debinding process [4] (in contrast to PW, which dissolves in heptane, hexane, or kerosene [5]).

At present, the binder's properties are assessed by rheological measurements and thermogravimetry [6–11]. There is a noticeable lack of research effort in the area of specific interactions among the particular binder system components. In order to improve the feedstock properties, mathematical models for predicting the feedstock properties or substituting conventional processing stages by implementing sophisticated techniques requiring the merging of two consequent stages are employed. However, even the latter approach can be justified if an outsourced and intensive study of the adhesion of binder to powder, and the interactions between binder components are performed prior to it.

Various techniques were exploited for studying the interactions in polymer blends. Chen and Wolcott [12] reported on a study of interaction parameters for polymer-diluent systems of PW and PE (HDPE, LDPE and LLDPE). The morphology, crystallization and crystallinity together with equilibrium melting temperature and melting point depression were analysed using differential scanning calorimetry and atomic force microscopy. The results showed evidence of partial miscibility of blends, with LLDPE having an advantage over HDPE and LDPE.

Doulabi et al. [13] studied the miscibility of PEG and chitosan by using an acetate buffer solution for different blend compositions. Viscosity, density, and refractive index were measured in order to quantify the interaction parameters. The results showed that the components at

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80% or higher chitosan concentration were miscible by means of the intermolecular hydrogen-bonding interaction between hydroxyl groups of polyethylene glycol fumarate with amino and hydroxyl groups of chitosan.

In our previous research, polar waxes were exploited as binder system components applicable to the PIM process [14] to substitute nonpolar PE and PW with the aim of eliminating the necessity to use processing aid, e.g., stearic acid (SA), in order to achieve the adhesion of the binder to the powder required to withstand high shear forces during injection moulding. Similarly to the most recent work by Liu et al. [15], who substituted paraffin wax with bee wax for the production of micro-injection moulding gears from zirconia, better feedstock stability has been achieved. However, with such novel binders, an understanding of core mechanisms of interactions between the individual system components would allow a precisely-balanced composition, bringing the feedstock properties to their higher limits (e.g., substantially lowering the processing temperatures in the case of substitution of PE by carnauba wax (CW) or acrawax(AW)) [14].

While quantification of the interactions of two polymers is a difficult task, in the case where both polymers are polar it becomes even more challenging. This is because the interactions between polymer (X) and polymer (Y) are significantly weaker than the self-interactions X–X and Y–Y in each polymer. To bypass this issue, polymers might be substituted with low molecular weight analogues to have an advantage of eliminating the majority of self-interactions, and replacing them with newly formed X–Y interactions. This rarely used [16,17] approach allows the substitute liquid for the X polymer to be fully surrounded by the substitute liquid for the Y polymer, resulting in precise measurements of the present interactions. Furthermore, the calorimetric analysis combined together with Fourier transform infrared spectroscopy (FTIR) measurements can provide a quantitative evaluation of specific interactions.

Some researchers have reported on the successful use of FTIR or calorimetry techniques for quantifying and evaluating interactions [18–20]. To our best knowledge, no research has yet been performed on the miscibility of PEG and polar waxes.

In our previous paper [21], we tested this approach to verify the presence of interactions between CW and PEG low molecular substitutes. Motivated by the work of Hsu et al. [22] who compared CW and AW in 56 vol.% 304L stainless steel feedstocks containing 22 vol.% of low density polyethylene (LDPE), and from the separation and aggregation of LDPE molecules from the binder during mixing, it was speculated that AW, containing strong polar amide groups and short hydrocarbon chain ends, was less compatible with LDPE than CW. The aim to quantify the interaction potential of both waxes increased.

Thus, in this work, the interactions between AW and PEG are examined and compared to those employed in our novel powder feedstock [14] based on CW/PEG in order to investigate whether the approach of low molecular weight analogues treated with combined FTIR/calorimetry is able to intercept the slight differences in behaviour viewed by other techniques currently used (rheometry and thermogravimetry).

## 2. Experimental

### 2.1. Materials

Table 1 shows the low molecular weight analogues of AW, CW and PEG used in this study. The molar mass  $M_w$ , density  $\rho$ , and the specific heat capacity  $c_p$  of analogues are shown in Table 2. As buffer solutions (solvents), hexane and decahydronaphthalene (decalin) were used. The chemicals were obtained from Sigma-Aldrich.

### 2.2. Methodology

The quantitative analysis of interactions is based on the assumption that the change of Van der Waals intermolecular interactions

**Table 1**  
Low molecular analogues of corresponding polymers.

Name	Abbreviation	Chemical structure
Acrawax	AW	$\text{CH}_3(\text{CH}_2)_{16}\text{CNHCH}_2\text{CH}_2\text{NHC}(\text{CH}_2)_{16}\text{CH}_3$
Analogue Methylacetamide	NMA	$\text{CH}_3\text{CNHCH}_3$
Carnauba wax	CW	$\text{H}_3\text{C}-(\text{CH}_2)_{30}-\text{C}(=\text{O})-\text{O}-(\text{CH}_2)_{33}\text{CH}_3$
Analogues Amyl butyrate	AM	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$
Butyl valerate	BV	$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{C}(=\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$
Polyethylene glycol	PEG	$\text{H}-\left[\text{O}-\text{CH}_2-\text{CH}_2\right]_n-\text{OH}$
Analogues 2-Ethoxyethanol	2ET	$\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OH}$
Diethylene glycol monoethyl ether	DGME	$\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$

accompanying mixing is negligible (e.g., the mixing of hexane and heptane) and 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, all X–X interactions are broken in the case of high dilution, all dissociated X molecules form new X–Y interactions, and finally, molecules Z (saturated hydrocarbons) do not have any acid–base self-associations, nor do they form acid–base interactions with another molecule (X or Y) [23].

#### 2.2.1. FTIR analysis

The X–X self-interactions and X–Y interactions between two liquids were studied using FTIR analysis. An FTIR reflection spectroscope (Nicolet 6700, Fisher Scientific, USA) equipped with a KBr glass holder accessory was used. A drop of each mixture was placed between two KBr glasses and measured in a transmission mode. The spectra with 32 scans were collected in the range of 400–4000  $\text{cm}^{-1}$  at the resolution of 1  $\text{cm}^{-1}$ . The procedure was repeated three times, and the results were averaged.

#### 2.2.2. Calorimetry

A thermocouple (type copper–constantan) was connected to National Instruments data acquisition equipment (NI USB-9211A, Data Acquisition for Thermocouples) and used for measuring the temperature change during the mixing. LabVIEW Signal Express 2.5 software was used for collecting the temperature with a precision of 0.0001 °C. A 0.5 s sampling period was applied. The thermocouple was dipped in the blend, which was placed on a hot plate in the insulated flask with

**Table 2**  
Physical properties of low molecular liquid substitutes.

Name	Molar mass $M_w$ [g/mol]	Density $\rho$ [ $\text{g}/\text{cm}^3$ ]	Heat capacity $c_p$ [J/kg K]
AW	593.02	0.97	2910
Analogue NMA	73.09	0.957	3748
CW	1000	0.97	3373
Analogues AM	158.24	0.863	1927
BV	158.24	0.868	1927
PEG	1000–20,000	1.09–1.41	2200–2460
Analogues 2ET	90.12	0.930	2414
DGME	134.17	0.999	2193

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