



# Specific interactions of low molecular weight analogues of carnauba wax and polyethylene glycol binders of ceramic injection moulding feedstocks

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## Abstract

This paper is devoted to understanding of the molecular interactions between components of Ceramic Injection Moulding (CIM) binders – carnauba wax (CW) and polyethylene glycol (PEG). Due to the complexity of interactions mechanisms the binders were substituted by their basic low-molecular analogues, which were then investigated using the combination of FTIR and calorimetry. Calorimetric analysis derived the self-interaction energies and association energies for the respective pairs. FTIR spectra were collected in the range of 400 to 4000  $\text{cm}^{-1}$  for the analogue blends, where the shift of C=O and O–H stretch bounding peaks were assumed as the evidence of the presence of the partial interactions between the components. Combining obtained data a linear relation of these two independent analyses was found. The results proved reliable quantification of interactions between CW and PEG low molecular substitutes implying the partial miscibility of the respective polar polymers.

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## 1. Introduction

In Ceramic Injection Moulding (CIM) the binder system serves important role by granting ceramic powder with suitable viscoelastic properties [1]. For the meeting of the processing requirements (especially debinding) and simultaneous exploitation of the attractive features of each component, the typical binder system is usually composed of 3 to 5 polymers, making the systems complex, where understanding of complete and individual reaction pathways or chemical mechanisms still remains a challenge [2,3].

In majority cases, polymers serving as components of binder systems include polyolefins, waxes (mainly paraffin) and polyethylene glycols. In the papers devoted to the development of the binders system [e.g. [4,5]], the interactions of a binder with a

powder and among specific binder components are often deduced from their rheological performance during mixing and injection moulding.

Though a combination of polyethylene (PE) and paraffin wax (PW) is widely used in CIM industry, it creates many issues, including insufficient initial pore formation resulting in weak internal transport mechanisms within the specimens and highly affecting debinding rates. Binder system solely composed of PE/PW may also limit the control of viscoelastic properties. A role of plasticizer in such systems is often granted to polyethylene glycol (PEG), which also serves as an endorsement for enabling initial gradual debinding process [3,6]. Furthermore, a binder system based on paraffin wax requires usage of various chemicals (heptane, hexane, or kerosene) for a solvent debinding step [7,8], which not only raises the cost of the overall process, but also – in a large scale – have a negative ecological impact. On the opposite, PEG can be easily debound in water.

The substitution of PE or PW with acrylic polymers such as poly(methyl methacrylate) (PMMA) has also been reported

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[9], however they still require a range of additional components to make the feedstock applicable. In addition, in CIM the feedstock processing temperature, being one of the key factors, highly influences the success of the overall process [10], and thus elevates the need of novel backbone binders such as carnauba wax (CW). As we have shown in the previous work [2,3], in contrast to PE, the CW (having lower melting temperature) significantly advances processing characteristics of CIM feedstocks.

There have been tries devoted to simplification of the process and reducing the conventional steps by implementing sophisticated techniques and by merging of two consequent stages [11], but the development of an advanced binder system may eliminate such needs by making the feedstock more robust, and significantly shortening the processing time. In addition to processing advantages, feedstocks based on CW/PEG are environmentally benign.

An understanding of molecular interactions between the particular components of CIM binders is complicated due to the complexity of interactions mechanisms. Chen et al. [12] investigated the miscibility of both nonpolar PW and polyethylenes (HDPE, LDPE and LLDPE) using differential scanning calorimetry (DSC) and atomic force microscopy. By evaluating the morphology, crystallisation 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 LLDPE/PW being favourable over the PW/HDPE.

Sudhakar et al. [13] reported on miscibility of chitosan and PEG blend using a buffer solution. From collected Fourier transform infrared spectroscopy (FTIR) spectra for polyblend films and polymers it was observed that by increasing the amount of PEG the O–H stretch peak tends to lower peak wavenumbers, serving as an evidence of blend components miscibility.

Hsu et al. [4] studied the effect of PW and CW on carbonyl iron based feedstock, where LDPE served as a backbone. The rheological measurements using capillary viscometer and a statistical analysis based on the McLean-Anderson 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/LDPE. The carbon contents in sintered specimens were also in favour of CW/LDPE composition.

Studying the interactions of both polar polymers (such as in the case of CW/PEG) might be a challenging task. For polymer blends, the interactions measured will mainly present their self-interactions, even there are polymer (X) to polymer (Y) interactions they are significantly weaker than the self-interactions. Due to this fact, the polymers need to be substituted with low molecular weight analogues, which bring an advantage of eliminating the majority of self-interactions and their replacing by newly formed XY interactions. The component X can be fully surrounded by component Y, therefore, the interactions can be measured precisely. Such an approach representing advanced understanding of compatibility of blend components has been reported scarcely [14,15].

Using low molecular weight analogues also gives the opportunity to measure the interactions by calorimetry, which cannot be applied to polymer blends. Consequently, combining two techniques – FTIR and calorimetry – provides the possibility to evaluate the interactions quantitatively. Only few studies reported on achieving results by using analogue calorimetry as a tool for extending and scaling the results of interactions present [16–18], while FTIR combined with other techniques is commonly used as for investigating miscibility where the shift of peaks is assumed as an evidence of a partial miscibility [19–21]. Meanwhile, to our best knowledge there has been no investigation of the miscibility between CW and PEG.

## 2. Experimental

### 2.1. Materials

Several low molecular weight analogues of PEG and CW were used in this study (Table 1). As buffer solutions (solvents) hexane and decahydronaphthalene (decalin) were chosen. The properties of used analogues and solvents, including molar mass  $M_w$ , density  $\rho$ , and the specific heat capacity  $c_p$  are shown in Table 2.

### 2.2. FTIR analysis

The FTIR measurements were carried out in order to study the peak shift for both X–X and X–Y interactions. FTIR reflection spectroscope (Nicolet 6700, Fisher Scientific, USA) equipped with KBr glasses holder accessory was used. A drop of each mixture was measured between two KBr glasses in a transmission mode. The spectra in the range 400–4000  $\text{cm}^{-1}$  with 32 scans were averaged and recorded at a resolution of 1  $\text{cm}^{-1}$ . The procedure was repeated three times and the data was averaged.

### 2.3. Calorimetry

Calorimetric measurements were performed in order to study the thermodynamics of interactions of two components. The data

Table 1  
Chemical structure of polymers, their low molecular weight analogues and solvents.

| Name   | Chemical formulas   |
|--|---|
| <b>Carnauba wax (CW)</b>                         | $\text{H}_3\text{C}(\text{CH}_2)_{30}\text{COO}(\text{CH}_2)_{33}\text{CH}_3$ |
| Analogues  |   |
| <b>Amyl butyrate (AM)</b>                        | $\text{C}_9\text{H}_{18}\text{O}_2$   |
| <b>Butyl valerate (BV)</b>                       | $\text{CH}_3(\text{CH}_2)_3\text{CO}_2(\text{CH}_2)_3\text{CH}_3$             |
| <b>Polyethylene glycol (PEG)</b>                 | $\text{C}_{2n}\text{H}_{4n+2}\text{O}_{n+1}$                                  |
| Analogues  |   |
| <b>2-ethoxyethanol (2ET)</b>                     | $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OH}$                        |
| <b>Diethyl ether (DE)</b>                        | $(\text{CH}_3\text{CH}_2)_2\text{O}$  |
| <b>Diethylene glycol monoethyl ether (DGME)</b>  | $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ |
| <b>Diethylene glycol dimethyl ether (DGDE)</b>   | $(\text{CH}_3\text{OCH}_2\text{CH}_2)_2\text{O}$                              |
| <b>Triethylene glycol monoethyl ether (TGME)</b> | $\text{CH}_3\text{CH}_2(\text{OCH}_2\text{CH}_2)_3\text{OH}$                  |
| Solvents   |   |
| <b>Hexane</b>                                    | $\text{C}_6\text{H}_{14}$   |
| <b>Decalin</b>                                   | $\text{C}_{10}\text{H}_{18}$  |

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