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Development of PEG based binders for metal injection moulding with special focus on titanium

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A thesis for the degree of Doctor of Philosophy

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New Zealand 2015
Abstract

Metal Injection Moulding (MIM) combines the benefit of polymer injection moulding with powder metallurgy, and involves the moulding of a metal/alloy powder and polymeric binder system mixture using conventional plastic injection moulding. Thus, the resulting products have the subsequent strength of metal or alloy with the shape complexity of conventional injection moulding. In a nutshell, MIM is a cost-effective and high production rate fabrication technique that provides an excellent alternate for metal and alloys, which are otherwise expensive and hard to machine. Although titanium (Ti) and its alloys MIM (Ti-MIM) technology fits the former description, it has not seen significant breakthroughs as these materials can easily be contaminated by the binders during the debinding and sintering stages. The lack of industrial confidence in the Ti-MIM is likely due to the limited understanding of binder chemistry. As the same binder systems are often used for different powders in MIM, a poor binder may still lead to acceptable properties for less reactive metals/alloys, but for Ti-MIM it can be detrimental to the final mechanical properties.

Water soluble binder systems are garnering increasing attention due to their environmentally friendly nature. Among these, binder systems based on polyethylene glycol (PEG) are most popular due to its commercial availability, high solubility in water and non-toxicity. However, PEG based binder systems are less commonly found in the MIM industry. Therefore, such systems have been given special attention in this thesis in order to fully integrate them into the current MIM industry.

In this research, extensive study of water soluble PEG based binder systems is carried out. Rheological analysis, scanning electron microscopy (SEM), differential scanning calorimetry (DSC), thermal analysis and mechanical tests have been extensively used to evaluate binder systems. This study provides a useful guideline towards the Ti-MIM practice. The main findings are summarised below.

(1) It is noted that the effect of PEG molecular weight on the rheological properties of the feedstock, as well as its water debinding behaviour, has not been well investigated. In this work, four molecular weights of PEG, i.e. 1500, 4000, 10,000 and 20,000 g/mol were selected and the PEG/polymethyl methacrylate (PMMA) based feedstocks were formulated with titanium metal powder. A systematic investigation of the rheological properties of the prepared feedstocks, and the study of the effects of shear rate and temperature on viscosity
was reported. The water debinding behaviour of each feedstock was also investigated in terms of its debinding temperature and the PEG molecular weight.

(2) Considering the role of the binder in metal injection moulding (MIM) process, it is important to have a good interaction between the metal powder and binder system in order to produce defect free green parts. Surfactants are often employed in the MIM process to enhance or create this interaction. To study the effect of different surfactants on the metal-and-binder interaction that has not been reported before, three different surfactants – stearic acid (SA), peanut oil and castor oil – were chosen to prepare PEG/PMMA based Ti feedstocks. It was found that castor oil as a surfactant results in excellent overall properties of the feedstock by enhancing metal-and-binder interaction. The reason for this higher interaction is due to the increased polar ester functional groups in castor oil that latch onto the metal powder surface via dipole-dipole attraction forces, thereby resulting in a better powder dispersion and a higher powder-binder interaction. This is a significant finding that will improve the mouldability of MIM feedstocks.

(3) Irregular hydride-dehydride (HDH) Ti powders have poor rheological properties and a high initial content of impurities, therefore giving way to spherical powders, which provide better control of the moulding operation and good mechanical properties, particularly elongation. However, spherical powders are expensive and increase the cost of the final product. For components where elongation is not the main requirement, HDH irregular powder can be utilized. However, solids loading are kept low so as to accommodate poor rheological properties. To facilitate the use of irregular Ti-HDH powder in MIM in order to improve rheological properties, a new binder system was developed. The rheological behaviour of the feedstock based on the newly developed binder system, is presented and compared with the existing binder system. Rheological properties analysis showed that by using this new binder system, a higher solids loading can be employed.

(4) Due to environmentally friendly nature, water soluble binder systems have received much attention in recent years. PEG and PMMA binder system is one such example and has been widely reported in the literature. In this thesis, a comprehensive investigation of the PEG/PMMA binder system was carried out. Feedstocks were made using a stainless steel 17-4PH powder and subsequent conventional and micro injection moulding (μMIM) processes were carried out. DSC and fracture surface analysis of moulded samples were performed for complete evaluation. It was found that despite great potential there are certain drawbacks associated with this binder system. The main problem was the formation of shrinkage voids
during solidification. It is proposed that this binder system is more suitable for μMIM process.

(5) Efforts were made to increase the workability of the PEG/PMMA binder system for conventional metal injection moulding (MIM) by adding a crystallization inhibitor, polyvinylpyrrolidone (PVP). After complete evaluation of moulded samples, it was found that by incorporating PVP into PEG/PMMA binder system, void free high quality MIM components can be produced whilst maintaining the clean nature of PEG/PMMA binder system.

(6) To minimize impurity uptake during the thermal debinding process, a low decomposition temperature binder system was developed. PEG was used as the major component, while polymer Q was used as the backbone polymer. The decomposition temperature of polymer Q is 100 °C lower than that of the PMMA: a significant achievement in Ti-MIM. Thermal debinding and rheological properties analysis further demonstrated excellent results. On the other hand, solvent debinding properties were poor. The solvent debinding properties can be improved by incorporating little amount of PMMA into the binder system.

In summary, water soluble binder systems had been investigated in this study with a special focus on a low decomposition temperature binder system for the Ti-MIM. However, it was difficult, if not impossible, to obtain excellent mechanical properties of Ti-MIM samples due to different processing constraints. Nonetheless, the binders developed in this study have great potential and can be used in the industry. This project also opens further questions for future investigations.
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# Abbreviations Index

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE</td>
<td>Blended elemental</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>CAB</td>
<td>Cellulose acetate butyrate</td>
</tr>
<tr>
<td>Co</td>
<td>Cobalt</td>
</tr>
<tr>
<td>CP</td>
<td>Commercially pure</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy dispersive X-ray spectrometry</td>
</tr>
<tr>
<td>EL</td>
<td>Elongation</td>
</tr>
<tr>
<td>ESEM</td>
<td>Environmental scanning electron microscope</td>
</tr>
<tr>
<td>EVA</td>
<td>Ethylene vinyl acetate</td>
</tr>
<tr>
<td>GA</td>
<td>Gas-atomised</td>
</tr>
<tr>
<td>H</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>HDH</td>
<td>Hydrogenation-dehydrogenation</td>
</tr>
<tr>
<td>HDPE</td>
<td>High-density polyethylene</td>
</tr>
<tr>
<td>HIP</td>
<td>Hot isostatic pressing</td>
</tr>
<tr>
<td>LDPE</td>
<td>Low-density polyethylene</td>
</tr>
<tr>
<td>MIM</td>
<td>Metal injection moulding</td>
</tr>
<tr>
<td>MS</td>
<td>Microwave sintering</td>
</tr>
<tr>
<td>NNS</td>
<td>Near-net-shaping</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>O</td>
<td>Oxygen</td>
</tr>
<tr>
<td>PA</td>
<td>Pre-alloyed</td>
</tr>
<tr>
<td>PBMA</td>
<td>Polybutyl methacrylate</td>
</tr>
<tr>
<td>PE</td>
<td>Polyethylene</td>
</tr>
<tr>
<td>PEG</td>
<td>Polyethylene glycol</td>
</tr>
<tr>
<td>PIM</td>
<td>Powder injection moulding</td>
</tr>
<tr>
<td>PM</td>
<td>Powder metallurgy</td>
</tr>
<tr>
<td>PMMA</td>
<td>Polymethyl methacrylate</td>
</tr>
<tr>
<td>POM</td>
<td>Polyoxyethylene</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>P&amp;S</td>
<td>Press-and-sinter</td>
</tr>
<tr>
<td>PS</td>
<td>Polystyrene</td>
</tr>
<tr>
<td>PVB</td>
<td>Polyvinyl butyral</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>PVP</td>
<td>Polyvinylpyrrolidone</td>
</tr>
<tr>
<td>PW</td>
<td>Paraffin wax</td>
</tr>
<tr>
<td>SA</td>
<td>Stearic acid</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SHS</td>
<td>Self-propagating high-temperature synthesis</td>
</tr>
<tr>
<td>SPS</td>
<td>Spark plasma sintering</td>
</tr>
<tr>
<td>Ti</td>
<td>Titanium</td>
</tr>
<tr>
<td>TiH$_2$</td>
<td>Titanium hydride</td>
</tr>
<tr>
<td>Ti-MIM</td>
<td>Titanium and its alloys metal injection moulding</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal gravimetric analysis</td>
</tr>
<tr>
<td>UTS</td>
<td>Ultimate tensile strength</td>
</tr>
<tr>
<td>WA</td>
<td>Water-atomised</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>Zirconium oxide</td>
</tr>
<tr>
<td>$\mu$MIM</td>
<td>Micro metal injection moulding</td>
</tr>
</tbody>
</table>
## Table of Contents

Development of PEG based binders for metal injection moulding with special focus on titanium

Abstract ................................................................................................................................................. iii

Acknowledgements .............................................................................................................................. vi

Abbreviations Index ........................................................................................................................... viii

Chapter 1 Introduction ......................................................................................................................... 1

1.1 Background .................................................................................................................................... 1

1.2 Objectives ..................................................................................................................................... 3

1.3 Thesis outline ................................................................................................................................ 4

Chapter 2 Literature review ................................................................................................................ 6

2.1 Metal injection moulding .............................................................................................................. 6

2.1.1 General powders characteristics for MIM .............................................................................. 7

2.1.2 Basics of binder systems for MIM ......................................................................................... 8

2.1.3 Feedstock preparation ............................................................................................................ 10

2.1.4 Moulding operation ............................................................................................................... 11

2.1.5 Debinding ............................................................................................................................... 12

2.1.6 Sintering ................................................................................................................................. 13

2.2 Overview of Ti-MIM ................................................................................................................... 13

2.2.1 Titanium powders ................................................................................................................ 16

2.2.2 Binder systems ....................................................................................................................... 18

2.2.3 Debinding ............................................................................................................................... 24

2.2.4 Sintering ................................................................................................................................. 26

2.2.5 Further processing ............................................................................................................... 27

2.3 Mechanical properties .............................................................................................................. 27

2.4 Final remarks .............................................................................................................................. 28

Chapter 3 Materials and experimental procedures ......................................................................... 30

3.1 Materials ..................................................................................................................................... 30

3.2 Experimental procedures .......................................................................................................... 32

3.2.1 Feedstock preparation .......................................................................................................... 32

3.2.2 Viscosity measurement ......................................................................................................... 32

3.2.3 Injection moulding ............................................................................................................... 35

3.2.4 Water debinding ................................................................................................................... 36

3.2.5 Thermal debinding and sintering ......................................................................................... 36

3.2.6 Characterization ................................................................................................................... 37
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.3.1 Feedstock formulation</td>
<td>72</td>
</tr>
<tr>
<td>7.3.2 Void nucleation</td>
<td>73</td>
</tr>
<tr>
<td>7.3.3 Discussion and proposed solutions</td>
<td>74</td>
</tr>
<tr>
<td>7.4 Summary</td>
<td>80</td>
</tr>
<tr>
<td>Chapter 8 Incorporation of PVP into PEG/PMMA based binder system to</td>
<td>81</td>
</tr>
<tr>
<td>minimize void nucleation</td>
<td></td>
</tr>
<tr>
<td>8.1 Introduction</td>
<td>81</td>
</tr>
<tr>
<td>8.2 Experimental procedures</td>
<td>83</td>
</tr>
<tr>
<td>8.3 Results and discussion</td>
<td>84</td>
</tr>
<tr>
<td>8.3.1 Inhibition of PEG crystallization</td>
<td>84</td>
</tr>
<tr>
<td>8.3.2 Shear sensitivity</td>
<td>87</td>
</tr>
<tr>
<td>8.3.3 Solvent debinding</td>
<td>88</td>
</tr>
<tr>
<td>8.3.4 Thermal degradation behaviour</td>
<td>89</td>
</tr>
<tr>
<td>8.3.5 Mechanical properties</td>
<td>90</td>
</tr>
<tr>
<td>8.4 Summary</td>
<td>93</td>
</tr>
<tr>
<td>Chapter 9 An easy-to-decompose binder for Ti metal injection moulding</td>
<td>94</td>
</tr>
<tr>
<td>9.1 Introduction</td>
<td>94</td>
</tr>
<tr>
<td>9.2 Experimental procedures</td>
<td>95</td>
</tr>
<tr>
<td>9.3 Results and discussion</td>
<td>95</td>
</tr>
<tr>
<td>9.3.1. Decomposition temperature of polymer Q.</td>
<td>95</td>
</tr>
<tr>
<td>9.3.2. Feedstock optimization</td>
<td>96</td>
</tr>
<tr>
<td>9.4 Summary</td>
<td>102</td>
</tr>
<tr>
<td>Chapter 10 Conclusions</td>
<td>103</td>
</tr>
<tr>
<td>Chapter 11 Recommendations and future work</td>
<td>105</td>
</tr>
<tr>
<td>References</td>
<td>107</td>
</tr>
</tbody>
</table>
### Chapter 1 Introduction

#### 1.1 Background

Titanium is a material of great interest. Attributes such as high strength at lower density, stiffness, good toughness, and good corrosion resistance makes it a first choice material. Various combinations of properties can be achieved by using titanium alloys. Significant weight reduction can be achieved by using titanium or its alloys in aerospace structures and other high-performance applications, which directly leads to reduction in energy costs. Moreover, the high corrosion resistance combined with good strength at lower weight make titanium and its alloys useful in chemical, petrochemical and marine environment applications [1, 2]. Among metallic biomaterials such as stainless steels and Co-Cr alloys, titanium and its alloys exhibit the most suitable characteristics for biomedical applications due to their non-toxicity, high biocompatibility, specific modulus and corrosion resistance [3]. They are currently utilised as metallic structural biomaterials for use in implants such as artificial hip joints and dental roots.

However, the applications of titanium and its alloys are still limited in these industries primarily due to its low affordability that stems from its difficult extraction process, poor cold workability, and difficulty of machining. Powder metallurgy (PM) which is a near-net-shaping technique offers a pathway to overcome this problem. Some widely used PM fabrication methods of titanium alloys include self-propagating high-temperature synthesis (SHS) [4], hot isostatic pressing (HIP) [5], spark plasma sintering (SPS) [6, 7], microwave sintering [8, 9], metal injection moulding (MIM) [10] and conventional press-and-sinter (P&S) [11]. Among these techniques, MIM can be considered an ideal candidate for titanium and its alloys processing due to its ability to process intricate shapes at low production cost per part (in large volume production). This project looks at the MIM process for the production of high quality titanium parts.

MIM, a sub group of powder injection moulding (PIM), is a combination of conventional plastic injection moulding and powder sintering. MIM has found great success in manufacturing near net shape, small to moderate size components of metals such as nickel, copper and steel. The low cost production and high material utilisation makes MIM an excellent fabrication technique for metals or alloys such as titanium and its alloys, which are expensive and difficult to machine [12, 13]. Although MIM on common engineering
materials e.g., steel has been practised since early 1970s [14], Ti-MIM is a fairly new technology; the first report of its use was published in Japan in the late 1980s [15].

Optimistic metallurgists claim that the Ti-MIM technology has been ready for industry to take up [16, 17]. However, in reality, MIM industry is still wary of its adoption. There is currently no titanium products produced by MIM on massive scale even though several demonstration titanium products have been showcased for many years. The lack of industrial confidence in Ti-MIM is because of the limited availability of commercially viable Ti-MIM feedstocks. In addition, due to its reactive nature Ti-MIM needs exhaustive care during processing in order to keep impurity levels to a minimum [18]. All the equipment involved during Ti-MIM process should only be used for its processing. Although exhaustive care during processing does have its limitation, the lack of industrial confidence in Ti-MIM is likely due to the limited understanding of binder chemistry.

MIM employs a mixture of metal powder and polymeric binder system known as a feedstock. The commonly used binder systems for MIM involve components of a plasticizer (waxes), polymers and surfactants in order to possess specific characteristics vital to the success of the MIM operation. Each binder component has an effect on overall properties of the system. German [19] outlines the criteria that a binder must meet for MIM processing. Some of these conditions are even more stringent for titanium and its alloys metal injection moulding, given that Ti is a universal solvent for many common interstitials such as H, O, C and N. Experimental studies have shown that the pick-up of nitrogen during Ti-MIM processing is usually not a problem. Hydrogen can also be ignored because sintering of titanium is done under high vacuum at high temperatures. Under these conditions the hydrogen contents are drawn out from the material. On the other hand, carbon and oxygen must be considered given carbon is present in all binders, and oxygen due to its high solubility and high affinity for titanium above 400 °C [20]. The primary component of binder systems (plasticizers) is usually removed completely by solvent extraction at low temperatures. Therefore, it does not increase the overall impurity level unless improper extraction is done. Contaminations during sintering can also be monitored by carefully controlling the sintering atmosphere. However, contaminations during thermal debinding, which arise from the thermal decomposition of backbone polymers (as most of the typical backbone polymers employed in MIM have decomposition temperature above 400 °C) still remain a big concern for product designers. Hence, a comprehensive understanding of binder system and its thermal decomposition behaviour is crucial to achieving the desired mechanical properties.
Although efforts have been made to find alternative ways to remove binder systems whilst reducing the debinding time and contaminations [13], no significant progress has been made, hence, this part has been given special focus in this thesis.

Wen et al. [21] have recently reviewed the binder systems commonly used for Ti-MIM. According to them binder systems used in Ti-MIM fall into four groups according to the debinding routes used: wax-based, polyoxymethylene (POM) based, aromatics-based, and water-soluble binder systems.

Water soluble binder systems have received increasing interest in recent years because they can be extracted in an environmentally-friendly manner. Among these binder systems, PEG is the most extensively reported polymer due to its non-toxicity, commercial availability and solubility in water [22-25]. It is a crystalline polymer (chemical structure: HO-[CH₂-CH₂-O]ₙ-H) with an open helical structure responsible for its low melting point and solubility in water. PMMA is often employed as the backbone polymer in PEG based binder systems because of their excellent compatibility. Moreover, PMMA is a clean polymer which leaves little residue upon decomposition. This is important when MIM of titanium is employed [26]. In spite of the numerous publications and great potential [22, 24, 27], the use of the PEG/PMMA system in MIM industry is rather limited, much less in Ti-MIM.

To facilitate the use of water soluble, clean binder systems in MIM industry we have extensively studied the PEG/PMMA based system and have reported some interesting new findings. In addition, we have developed a new binder system for Ti-MIM to reduce impurity uptake during processing. The MIM practitioners and customers would benefit from our studies. The specific objectives are dependent on this and summarised below.

1.2 Objectives

The specific objectives are summarised below.

(1) Extensive study of PEG/PMMA based feedstocks

Detailed study of PEG/PMMA binder system is one of the main parts of this research. Despite numerous publications about this binder system, some important information is still missing. For instance, the effect of PEG molecular weight on rheological properties has seldom been taken into account. As the main component of binder controls the flow properties of feedstock, inherent properties of PEG will have a significant effect on the overall properties of feedstocks. Thus, such studies are part of this thesis. Secondly, water
debinding performance is also studied with respect to PEG molecular weight. These studies will help establish a relationship between PEG molecular weight, rheological properties and the debinding behaviour of the feedstocks. Furthermore, during this study we found that there are certain drawbacks associated with this binder system. The main problem is the formation of shrinkage voids during solidification. We have thoroughly studied this problem and efforts have been made to rectify it, alternate solutions have also been proposed. These new findings will shed new light on the use of such binders in the MIM industry, therefore enhancing its industrial applications.

(2) Compatibility improvement of Ti-MIM feedstocks using liquid surfactant

The effects of the nature of surfactants on the rheological properties of feedstocks are largely missing, particularly in the case of Ti-MIM. Owing to the importance of the surfactant, a series of experiments were carried out to study the effects of the different types of surfactant on the properties of Ti-MIM feedstock. The objective of these experiments is to find a suitable surfactant that yields excellent properties of the feedstock. It may be noted that the results from this study can be also used for other powders’ injection moulding.

(3) Development of an easy-to-decompose binder for Ti-MIM

To minimize residue upon decomposition and impurity pick-up during debinding of Ti-MIM feedstocks, efforts have been made to design and test a new binder system based on PEG and a low decomposition temperature polymer known as polymer Q.

1.3 Thesis outline

This thesis is divided into 10 chapters. Most of the chapters are based on the published or submitted works by the author. Chapter 1 provides a general overview of this thesis. Chapter 2 is a literature review on MIM with particular emphasis on titanium and its alloys MIM. Chapter 3 presents the basic Methodology used in this project. Chapter 4 discusses the effects of PEG molecular weights on the rheological properties of feedstocks. Chapter 5 signifies the importance of surfactants for MIM feedstocks and presents results for different surfactants. Chapter 6 presents a new lubricant based binder system for feedstock preparation comprising of HDH-Ti powders, while Chapter 7 discusses the problems associated with PEG/PMMA binder system and proposes a solution to overcome those problems. Chapter 8 presents a modified PEG/PMMA binder system to improve the workability of this binder system while maintaining its clean nature. Chapter 9 discusses the development of an easy-to-decompose
polymer for Ti-MIM whilst Chapter 10 introduces some new questions and makes suggestions for future.
Chapter 2 Literature review

2.1 Metal injection moulding

Like powder metallurgy, MIM relies on shaping metal particles and subsequently sintering those particles. It is derived from plastic injection moulding and involves the moulding of a mixture of plastic/elastomer and a metal or alloy powder, using conventional plastic injection moulding. Unlike press-sinter powder metallurgy, the final product is nearly of full density. Hence MIM products are competitive with most other metal component fabrication routes, and are particularly successful in not only delivering improved tolerances compared to investment or sand casting, but also higher strength compared with die casting, and increased shape complexity compared to most other forming routes, Figure 2.1. [28].

![Diagram showing where MIM is most appropriately used in comparison with other fabrication processes](image)

Fig. 2.1 Diagram showing where MIM is most appropriately used in comparison with other fabrication processes [29].

The key steps of MIM include: (1) selecting and tailoring a powder for the process; (2) mixing metallic powder and a binder system to form a homogenous feedstock; (3) moulding to achieve the required shape and geometry; (4) removal of the binder system whilst keeping the geometry (debinding); (5) sintering to achieve the desired mechanical properties and lastly; (6) post sintering treatments to further improve properties, if required [19, 30, 31]. The steps involved in MIM are illustrated in Figure 2.2 below.
Fig. 2.2 Steps involved in a MIM operation. Taken from [19]

2.1.1 General powders characteristics for MIM

Powders shape, size and its distribution play a decisive role in determining the overall quality of MIM product by affecting its rheological properties. It is often sought to incorporate a high proportion of metal in the feedstock, which means that powders having a high packing density are desirable [32, 33]. Any non-spherical shape has an adverse effect on the feedstock viscosity because of the lower packing density and higher inter-particle friction. The fact that surface roughness and particle shape are two different things must also be kept under consideration. Surface roughness is related to the texture of the surface and greatly affects the wetting and spreading of binder [19], however it has a relatively small influence on the packing density and viscosity. Particle shape has a more profound effect on the particle packing density and inevitably, on the feedstock viscosity [34], Figure 2.3.
Fig. 2.3 Maximum solids loading for different shapes of glass particles. Redrawn from ref. [19]

Therefore spherical or near spherical shapes should be preferred, but the risk of shape distortion also increases during the debinding process. Fine powders sinter more readily than coarser powders. Therefore, they are the best choice for MIM, however the risk of impurity pick-up also increases in the sintering process due to the relatively higher surface area of fine particles [35].

High packing density MIM feedstocks can be made by mixing particles of different sizes [36, 37]. According to German [19], “at a solid loading of 66%, the viscosity can be reduced by a factor of 24 by introducing smaller particles to fill the inter-particle voids, thereby releasing previously immobilized fluid”, Figure 2.4.

Fig. 2.4 Influence of bimodal mixture composition on viscosity at constant temperature and shear rate. Redrawn from ref. [19]

2.1.2 Basics of binder systems for MIM

The binder is a temporary vehicle that helps powder particles to flow into the mould and then holds the powder particles until early sintering. A binder system usually has three components: a low molecular weight component that provides the necessary flowability
during moulding (primary component), a backbone polymer that provides the green strength (secondary component), and a surfactant which acts as a bridge between the binder and powder particles. The amount of binder system ranges from 15 vol.% to 50 vol.% of the mixture with the remainder being metal powders.

Some of the desired binder characteristics are [38-41]:

1) easily available and non-expensive; 2) long shelf life; 3) safe and environmentally acceptable; 4) non degradable due to cyclic heating; 5) soluble in common organic solvents; 6) high strength and stiffness with low thermal expansion coefficient; 7) low contact angle. The low contact angle will result in better wetting of the binder to the powder surface, which will assist the overall mixing and moulding process; 8) good adhesion with powder; 9) capillary attraction of particles; 10) chemically passive towards powder particles; 11) low viscosity at moulding temperature (preferably below 10 Pa.s); 12) low viscosity change during moulding; 13) increase in viscosity during cooling; 14) degradation temperature above moulding and mixing temperatures; 15) non-corrosive and non-toxic burnout products; 16) low residual carbon content after burnout.

Thermoplastic and thermosetting are two common types of polymers. Thermoplastic polymers are formed due to repetition of small monomer groups along the chain length without cross linking. Thermoplastic based binders are widely used in MIM industry and usually consist of a wax (as major component) and a thermoplastic as (backbone polymer). Additives, such as stearic acid, are added for lubrication, viscosity control and better wetting. Removal of such binders is normally done by thermal degradation, solvent extraction and wicking, as is explained in the later sections.

Thermosetting polymers undergo cross-linking of polymer units at high temperatures. The cross-linking will result in the formation of a three dimensional rigid structure. Resins such as, phenolic and epoxies are the most popular choice among thermosetting polymers. These are usually cured at elevated temperatures between 110 °C and 180 °C or by adding a catalyst [42]. Only the addition crosslinking reactions are of interest for MIM, as the alternative condensation crosslinking (typically of polyurethanes) usually involves vapour formation and leads to moulding defects. The cross-linking of thermosetting polymers upon heating can be helpful during debinding. However, thermosetting polymers are rarely used in MIM because of their slow hardening process that leads to a higher injection moulding time [42].
Gelatin is a relatively new technique and involves polymers which form gels upon mixing with solvents such as water and alcohol. The gel formation involves only a small portion of the polymer and once the solvent is evaporated, it leaves behind a highly viscous structure that binds the powder particles together. Subsequent debinding can be achieved via thermal degradation. The advantages of this technique are the: lower pressure and temperature requirement (therefore lower capacity equipment can be used) and faster debinding. However, the poor dimensional stability and variations in the composition of the final moulded parts are significant disadvantages of this binder system. Some commonly used binder components are summarized in the table 2.1 below.

| Table 2.1 Common binder systems for metal injection moulding [19, 43] |
|---|---|---|---|
| Binder type | Main ingredients | Polymer backbone | Additives |
| Thermoplastic | Waxes (paraffin/ microcrystalline/carnauba/natural waxes) | PE, PP, PS, PA, PVB, HDPE, LDPE, PBMA, CAB, EVA, PMMA | stearic/oleic acid, oils |
| Polyacetal | polyoxymethylene | | Proprietary |
| Thermosetting | epoxy resin | waxes | stearic acid |
| Gelation | water | methyl cellulose, agar | glycerine, boric acid |

Composition of the binder plays a significant role in determining the binder viscosity and flow behaviour, especially for mixtures with large differences in viscosities among the components. Viscosity increases as the molecular weight is increased, so a proper selection of molecular weight of each binder component is necessary.

2.1.3 Feedstock preparation

The feedstock is the terminology used for the mixture of powder and binder. Several shear mixer designs are used for MIM feedstock preparation. These include twin screw extruder, double planetary, single screw extruder, plunger extruder, twin cam extruder, shear roll compounder, and most common sigma or z-blade mixers. Some of the mixers geometries are shown in Figure 2.5.
Homogeneous mixing of feedstock is crucial to the final product quality, as any inhomogeneities such as bubbles; binder pockets; powder segregation, etc. will subsequently be carried over to the injection moulding stage. Therefore, higher shear mixers such as twin screw extruder are preferred [19].

2.1.4 Moulding operation

The design of injection moulding machines from various suppliers all have certain general design features in common which are necessary to carry out and control the injection moulding process. The most important components of injection moulding machine are the: injection unit, the clamping unit, and the tooling attached to the clamping unit. These units are generally placed horizontally. In fact, the maximum clamping force is the main characteristic by which the power and size of an injection moulding machine is defined. Moulding parameters like, injection pressure, injection speed, mould quality, and mould temperature are very important for preparing parts without defects and minimum porosity [44].

Barrel temperature is very important, if the temperature is too low, the feedstock may freeze before the mould cavity is completely filled. If the temperature is too high, it will lead to very low viscosity that causes problems such as molten feedstock dripping out of the nozzle, flashing, prolonged cooling times, etc. It should also be considered that some heat is generated in the barrel by the frictional forces between the screw and the feedstock. Typical melt temperatures for common wax-polymers systems are between 150 °C to 190 °C and the mould temperature is 25 to 55 °C. Typical melt temperatures for catalytic systems are 200 to 260 °C and the mould temperature is 100 to 150 °C [45, 46].
Due to the higher thermal conductivity of the feedstock, MIM injection speeds are typically higher than compared to pure polymers. The injection speed is typically set at the minimum injection speed required to completely fill the component's cavity without any defects. Too low an injection speed will result in surface imperfections such as flow lines and incomplete fill. Too high an injection speed will result in flash due to powder/binder separation [45, 46].

2.1.5 Debinding

After the injection moulding step binder system becomes a disposable component and hence, must be removed from the samples. During debinding operation special attention is paid to the shape retention of the moulded samples. The method of binder removal has a considerable effect on the moulded sample shape retention, uniformity of shrinkage and final product mechanical properties. Therefore, proper selection of debinding method is extremely important for good quality control, particularly in case of reactive materials such as titanium as explained in the next section. The most commonly applied debinding techniques include: vacuum debinding, thermal debinding, catalytic debinding and solvent-thermal debinding [47-51]. The pie chart in Figure 2.6 shows different debinding techniques used around the world.

Fig. 2.6 Different debinding techniques used by companies around the world. Taken from ref. [52]

The solvent debinding combined with thermal debinding is the most widely used technique in the MIM industry. It involves two steps: 1) removal of primary binder usually by solvent dissolution, 2) removal of backbone polymer and surfactant by thermal process without cracking or degrading the moulded part. Some of the important points which must be considered during solvent-thermal debinding are summarized below:

1) The dissolution rate of primary binder in solvent increases as the primary binder is liquefied. This implies temperature of the solvent must be chosen with great care.
2) The reaction of the backbone polymer with solvent should not cause any part distortion.

3) The solvent should not have high vapor pressure at debinding temperatures. Care must be taken if any of fire hazard solvents are used.

When the primary binders are removed, no diffusion bonding between powder particles takes place, as low temperatures are involved. It is the backbone binders, and interparticle friction that holds the powder particles together and maintain the shape provided by the injection moulding. The secondary binders are removed thermally at moderate to high temperatures. This is achieved by heating the parts slowly to the temperature where the secondary binder evaporates. At those temperatures interparticle diffusion is enough to hold the parts together [53].

2.1.6 Sintering

During sintering densification several material transport mechanisms may be active like surface diffusion, vapor transport, boundary diffusion and lattice diffusion, all which lead to the reduction in surface energy [54, 55]. Surface diffusion and vapor transport are surface transport mechanisms and mainly related to particle coarsening. They promote the neck growth among the particles without increasing the density of the compact as only particle surfaces are involved [55]. Density is increased by the bulk transport mechanisms which include lattice (volume) diffusion, boundary diffusion, plastic flow and viscous flow. Depending on the type of material being sintered, one or couple of these mechanisms may be active during the sintering.

The sintering parameters like temperature, atmosphere, heating and cooling rate, and holding time are established according to material type, composition and size of the part being sintered. For example the preferred sintering procedure for tool steel H11 is, sintering temperature range of 1200-1275 °C under N₂ atmosphere [56].

2.2 Overview of Ti-MIM

Titanium is always listed as a material of great promise and often called a wonder metal [16]. Attributes like low density but higher strength (compared to stainless steel), biocompatibility, high corrosion resistant and ability to withstand aggressive environments make it a perfect choice for aerospace, offshore oil, medical/surgical, chemical processing industries [57, 58].
Like all other engineering materials, titanium’s mechanical and physical properties largely depend on its chemistry (Fig. 2.7) and microstructure [59-61]. The main focus is on two alloy classes – commercially pure (CP) Ti, and α-β class alloys (Ti-6Al-4V and Ti-6Al-7Nb, particularly on Ti-6Al-4V). Ti-6Al-4V is the widely used Ti alloy and accounts for 90% of total titanium consumption. It exhibits higher strength (1100 MPa) in combination with reasonable levels of ductility (12% elongation) [33]. The two basic microstructures exhibited by conventional titanium alloys are, elongated alpha and equiaxed alpha. These exhibit good fracture toughness and creep performance on one hand, and good ductility and fatigue crack initiation on the other hand [33].

Fig. 2.7 Compositions of U.S. technical Ti-alloys mapped onto a pseudobinary β isomorphous phase diagram. Taken from ref. [29]

The most important feature of titanium—also a lingering challenge for Ti-MIM is its high affinity to interstitial elements such as oxygen, carbon etc. The great affinity to interstitial elements is combined with a strong influence on the mechanical properties, even at low contents in the range of 0.1–0.4 wt% [18]. Increasing the impurity level increases the tensile strength but decreases ductility. Among the interstitial elements, oxygen is the most important element with regard to its influence on mechanical properties, particularly elongation. Figure 2.8 gives an illustration of the effects of oxygen on mechanical properties of titanium.
Fig. 2.8 Effect of oxygen on the ductility and strength of titanium. Redrawn from ref. [29]

Owning to its affinity to interstitial elements, titanium is graded by the impurity level. The strength and grade number increase as the impurity level is increased. In the Aerospace Materials Standards; grade -1 Ti has < 1800 ppm oxygen and a tensile strength of 240 MPa and 30% elongation, grade -4 has < 4000 ppm oxygen and a tensile strength over 660 MPa and 20% elongation. The Ti6Al4V, in the annealed grade -5 condition with < 2000 ppm oxygen has a tensile strength of 950 MPa and 14% elongation [16]. The ASTM standards have listed in detail the mechanical properties requirements for CP-Ti and Ti6Al4V against different levels of impurities for surgical applications [62, 63].

Due to their high raw material and manufacturing costs, utilizations of titanium alloys have been limited to aerospace, medical/surgical implants, offshore oil drill and chemical processing industries which can afford the high costs [64, 65]. The high cost of titanium stems from three sources: high extraction cost, high alloying cost and high processing cost, Figure 2.9. The spring-back characteristics of titanium and relatively low thermal conductivity make it difficult-to-machine [66-70]. The high processing costs are related to the very high material wastage associated with conventional machined and wrought products, e.g., many aerospace applications involve removal of over 90 % of the starting material during the machining process. A fly-to-buy ratio of titanium of 1:50 is commonly employed in the aerospace industry. This means that one needs to buy 50 kg of titanium to make a 1kg flight component. In other words, 98 % of titanium is wasted during machining. Moreover, titanium scraps are difficult to recycle. In order to mitigate these problems, one useful and generally accepted approach is through the use of a near-net-shaping (NNS) process such as powder metallurgy (PM) [1, 71, 72].
Among NNS processes, MIM appears to be the ideal candidate for processing of titanium. The typical advantages are high material utilisation, low production costs in large-quantity manufacturing, and most importantly shape complexity that cannot be achieved using other manufacturing processes as explained earlier (Fig. 2.1).

Although MIM is increasingly being used to produce metal such as stainless steel parts with complex geometries, titanium powder usage is less than 1 % of the MIM market [73]. Researchers and industries are working together to increase the awareness of the potential benefits of Ti-MIM [74, 75].

Ti-MIM was first demonstrated in late 1980s [15]. Early work showed an impressive 1000 MPa tensile strength, however, only 2% elongation was achieved [15]. On this basis, early Ti-MIM reached production status for decorative applications as early as 1991 [76-78]. The earliest applications were in watch cases, sporting equipment, spectacle frames and firearm trigger guards. After the initial demonstrations, scientific studies refined processing with a primary focus on oxygen control and microstructure homogenization to improve as-sintered ductility and corrosion resistance [79, 80]. Significant work was required to isolate the processing variables and their interactions.

Although the main focus is on CP-Ti, and α-β class alloys (Ti-6Al-4V and Ti-6Al-7Nb) MIM, research efforts have been made to include alloys such as TiAl [81], TiNi [82] and Ti-4Fe-7Cr [83]. The following is a detailed outline of Ti-MIM processing with emphasis on the binder systems.

### 2.2.1 Titanium powders

Efforts to lower titanium powder cost have not been fruitful. The selection of powder is based on the desired product application e.g., decorative, mechanical or life critical, and inherently
involves different price structures depending on powder attributes [17]. The available titanium powders can be summarised into following categories as mentioned in Table 2.2.

**Table 2.2: Ti-powder classification and characteristics [36]**

<table>
<thead>
<tr>
<th>Powder Type</th>
<th>Median size μm</th>
<th>Tap density % of pycnometer</th>
<th>Oxygen wt%</th>
<th>Carbon wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sponge fines</td>
<td>38</td>
<td>48</td>
<td>0.35</td>
<td>0.05</td>
</tr>
<tr>
<td>Hydride-dehydride</td>
<td>38</td>
<td>38</td>
<td>0.25</td>
<td>0.04</td>
</tr>
<tr>
<td>Titanium hydride</td>
<td>35</td>
<td>40</td>
<td>0.20</td>
<td>0.02</td>
</tr>
<tr>
<td>Reactive</td>
<td>30</td>
<td>47</td>
<td>0.30</td>
<td>0.10</td>
</tr>
<tr>
<td>Gas atomised</td>
<td>32</td>
<td>60</td>
<td>0.15</td>
<td>0.03</td>
</tr>
<tr>
<td>Plasma atomised</td>
<td>60</td>
<td>62</td>
<td>0.15</td>
<td>0.04</td>
</tr>
<tr>
<td>Rotating electrode</td>
<td>130</td>
<td>72</td>
<td>0.15</td>
<td>0.02</td>
</tr>
</tbody>
</table>

In general, the key attributes for MIM powders are: particle size distribution, particle shape, and the level of impurities being the most important attribute (particularly oxygen and carbon levels). Final oxygen level depends on the starting level (powder purity) and changes encountered in each PIM step. Because of the difficulty in controlling impurity contents during MIM processing, it is desired to start with the impurity content as minimum as possible. Generally speaking, Ti-MIM processing adds from 0.02% to 0.1% interstitials. However, it is not a hard and fast rule and in some studies, the change in oxygen and carbon from the initial powder to the final product was in excess of 0.15 wt % oxygen and 0.10 wt % carbon [17]. Thus, starting with 0.2 wt % oxygen in the powder will roughly give final oxygen content of 0.3 wt % in the sintered product. The desire to minimise impurities also puts a limit on minimum powder size that can be used, and larger particle size is preferred in order to reduce surface area for contaminations. Unfortunately, this affects the final product density and surface finish. Moreover, large particle size leads to inferior dimensional precision and slower sintering densification. Typically, gas atomised (GA) spherical powder is used in Ti-MIM with particle size below 45 μm, Figure 2.10. Angular powders such as HDH have poor packing density and higher levels of impurities (Table 2.2). Even though angular powders are cheap, their use is rather limited in MIM industry.
2.2.2 Binder systems

As described before, the first practice of MIM on titanium and its alloys did not begin until 1988 [15]. Early attempts in developing a viable Ti injection moulding process were plagued by the limited availability of suitable powders (in terms of powder size, impurities and cost), less than optimum binders for as reactive materials as titanium, and inadequate protection of titanium during elevated temperature processing (thermal debinding and sintering).

The early choices for Ti-MIM were to use already developed binder systems for other metals PIM such as stainless steel. Therefore, the initial development of a binder for Ti-MIM was based on the knowledge of binder systems developed for other powders. However, the solubility of impurities such as oxygen, carbon, hydrogen and nitrogen in titanium at higher temperatures, (particularly oxygen, Figure 2.11), was given little attention [13]. This improper selection of binder system was one of the main reasons that led to poor mechanical properties of initial Ti-MIM practice.

Fig. 2.10 Morphology of GA- spherical Ti powder
Baril et al. [20] published a detailed study about the sources of interstitials, especially oxygen, during MIM processing. As shown in Figure 2.12, there are several sources, starting with the powder and ending with the sintering support which is commonly made from ceramics like ZrO$_2$. The ratio between these sources marginally changes with the powder particle size; the overall pickup remains nearly the same. Among these sources, the initial oxygen content of starting powder contributes the most, followed by sintering atmosphere and debinding atmosphere. However, high quality powders with oxygen content as low as 0.15 wt% and high vacuum sintering furnaces are now available. On the other hand, oxygen content arising from the binder system and its subsequent debinding is a lingering threat to successful Ti-MIM operation.
Over time the importance of proper selection of the binder system for successful Ti-MIM has been realised and has received much attention. Nonetheless, to date, there is no commercially available binder system that can be considered ideal for Ti-MIM. The control of impurity contents arising from the binder system is, therefore, considered the most challenging part of Ti-MIM and is one of the biggest hurdles in convincing product designers to use this technology.

As described before, for a successful MIM operation a binder system should possess certain characteristics. Some of these requirements are even more stringent given the solubility of interstitial elements in titanium. Binder systems for Ti-MIM can be classified into following main categories according to the techniques involved in the debinding process: wax-based, aromatics-based, and water-soluble binder systems, respectively [21].

In the early days of Ti-MIM, wax based binders were the popular choice for other metals MIM such as stainless steel. Logically, it became the firsthand choice for Ti-MIM. For instance, in the first published study by Kaneko et al. [15] wax-PBMA [poly(butyl methacrylate)]-EVA-DBP (dibutyl phthalate) was used as the binder system and mixed with Ti powders at 140 °C. The subsequent debinding was carried out in a single step by gradually increasing the temperature to 300 °C in air. However, sintered samples showed very little elongation. It was soon established that the poor properties stemmed from severe contamination from oxygen and carbon residues and believed to be the result of incomplete binder removal [85]. On the other hand significant improvement in mechanical properties was achieved by a two-step debinding process which involved solvent extraction followed by thermolysis. This two-step debinding process significantly reduced the contamination of carbon and oxygen after sintering [77]. The importance of complete removal of binder in case of Ti-MIM was thus, soon established afterwards.

The search for wax-based binders for Ti-MIM has never stopped. Guo et al. [86, 87] used a modified wax-based binder system for CP-Ti and Ti-6Al-4V alloy and demonstrated its validity. The documented results showed good control over oxygen (0.26 wt%) and carbon (0.095 wt%) of sintered samples and yielded mechanical properties comparable with the wrought alloys (UTS 835 MPa, elongation 9%).

The most commonly used wax in wax-based binder systems is paraffin wax (PW). The PWs are hydrocarbonaceous mixtures of alkanes and have chain lengths ranging from C20 to C40 and melting point ranging from 52 °C to 74 °C. They have consistent chemical structures and
therefore consistent rheological properties, which are important for easy moulding operation, consistency and reproducibility of the product quality. Moreover, PWs are more cost effective than other waxes [21].

In a wax-based binder system, the popular backbone polymers are ethylene–vinyl acetate (EVA), polypropylene (PP), polyethylene (PE), and high molecular-weight PMMA. Rhee et al. [88] claimed that EVA with low vinyl acetate content was the best MIM binder, based on a great improvement in binder performance in both injection molding and thermal debinding. In addition, EVA resulted in an improved feedstock homogeneity, and shape retention during debinding. However, there are reports which contradict this. Moreover, EVA leaves behind residue, which can be detrimental to final mechanical properties [89]. On the other hand, German claimed that a binder system containing PW, PP/PE, and stearic acid is one of the best binder systems for Ti-MIM [90].

Recently, Weil et al. [91] developed a binder formulation for a Ti-MIM process, in which an aromatic compound was used as the binder and solvent, and therefore, only a small fraction of the traditional binder materials was required as minor additives. The main advantage of aromatics such as anthracene, naphthalene, and pyrene is that they melt at relatively low temperatures and can be completely removed from the green parts by sublimation under reduced pressure at temperatures well below their melting points. Their binder formulation consisted of naphthalene, 1 vol.% stearic acid, and from 3 to 12 vol. % EVA. Their debinding cycle involved sublimation for 20-h at 80 °C. They demonstrated that complete removal of naphthalene can be achieved, if the debinding is done under a vacuum of 2.67 Pa. In the subsequent debinding step, EVA was thermally removed in the temperature range of 360 °C to 450 °C. The main benefit of aromatic binder is, as sublimation involves low surface energies in the vaporization process, the specimen volume remains constant throughout the debinding process. This means that common debinding problems such as part distortion and cracking can be avoided by using such types of binder systems. Moreover, they claimed that the sintered titanium samples showed little impurity pick-up. Although this binder system provides an excellent solution for different solvent debinding issues such swelling, cracking, there are no further reports on this binder system. The main reason of this may be due to health and environmental concerns associated with toxic aromatic compounds.

Although wax-based binder systems have been widely used in MIM, there are some environmental concerns associated with this binder system. In order to extract the wax from
the green parts, organic solvents must be involved, such as heptanes and hexanes. The use of these solvents causes toxicologic and environmental concerns. This has led to the development of water-soluble binders, which have received increasing interest in recent years [21].

Water-soluble binders can be divided into two sub-groups, based on the interaction of the binder component and water: gelation based and non-gelation based. In the case of non-gelation-based binders, feedstock formulation does not need water. Rather, water is used as an extraction medium during solvent debinding step. The commonly used water-soluble polymers in this category are, PEG and PVOH. On the contrary, the gelation-based binders involve solvents when formulating the feedstock. Water is the most common medium, but others like glycerol can also be used. Most gelation-based binders are natural polymers and the commonly used are, polysaccharides (such as cellulose, starch, and agar) and polyamino acids (such as proteins) [92].

Among the gelation-based binders, agar and its derivatives have been attracting much attention [93, 94] due to its unique viscosity and strength change with temperature [21]. Agar-based binder for injection moulding was first used in 1988 [95], and a process was developed by Fanelli et al. Further progress in this binder system revealed that a gel strengthening additive is necessary for agar-based binder systems. This additive can be sodium silicate, sodium borate, sugar or a mixture of an acid and a base [96-98]. As with wax in the wax-based binder, water in agar serves as the fluid medium and amounts to approximately 50 vol.% of the binder system. The agar molecules form a gel network with open channels providing the necessary strength to moulded parts, and allowing easy removal of the water by evaporation. The time required to completely remove agar and water during debinding is much less than that required for the wax-based binders. Although the use of gelation-based binders can be very useful in general due to the avoidance of thermal burnout at relatively high temperatures, such systems are not free from problems. Firstly, polysaccharides are costly and add significant cost to the final product. Secondly, the low gelling temperature 35 °C to 39 °C of an agaroid binder system prolongs the moulding cycle time, which adversely affects the production rate [21]. Moreover, the moulded parts have poor dimensional stability. Nevertheless, agar based binder systems have been used for Ti-MIM. Tokura et al. [94] first employed the agar based binders in Ti-MIM and investigated the solubility, thermal stability and viscosity of the feedstock. Chen et al. [99] used an agar based binder for the production of porous NiTi alloys. Metal Powder Report (MPR) [100]
reported the application of an agar-based binder in production of titanium alloy dental implants. Suzuki et al. [101] used agar-based binder system to produce CP-Ti parts by MIM. The subsequent mechanical testing showed yield strength of 539 MPa, tensile strength of 784 MPa, and elongation of 10% respectively. However, when higher molecular weight agar was used (for higher gel strength) the sintered parts showed poor elongation, i.e. 3% only. The poor elongation was caused by higher oxygen and carbon contents. Even though gelation-based systems provide the opportunity to control impurity content by minimizing the thermal debinding step, such systems are rarely used in Ti-MIM mainly due to moulding and dimensional stability issues.

Most of the non-gelation synthetic polymeric binder systems are proprietary protected [102, 103]. However, in most cases, PEG is commonly used binder component among the non-gelation based binder systems. The popularity of PEG is due to its commercial availability, performance and low cost. PEG is very similar to wax [21]. It is a nontoxic polymer and has good solubility in water even at low temperature. Depending on the molecular weight, PEG is either in the state of liquid or low-melting-point solid at room temperature. PEGs with low molecular weight can be rapidly and near-completely removed in water at 60 °C. The commonly used molecular weight of PEG in formulating MIM feedstock is usually in the range of 500 to 2000 [21].

In PEG-based binders, currently employed backbone polymers are PMMA, PVB, EVA and HDPE [24, 104-106]. Among these, the PEG/PMMA system has found wide spread recognition and numerous reports have been published in literature on this system. The main reason of this increased interest is mainly due to the thermal decomposition behaviour of PMMA. PMMA thermal decomposition can produce more than 90% of pure gaseous methyl methacrylate (MMA) monomer depending on molecular weight and leaves very little residue behind under both vacuum and inert atmospheres [26].

Research on PEG/PMMA binder system was first reported in 1992 [24] and it was observed that the green parts had excellent shape retention, remained rigid after solvent debinding, and sintering shrinkage was uniform and isotropic. Since then, there have been numerous reports published in the literature encouraging the use of PEG/PMMA binder system [107, 108].

Sidambe et al. [109] injection moulded Ti-6-Al-4V alloy parts with 69 vol.% solid loading by using PEG/PMMA/SA (ratio: 87:11:2 wt %). PEG was completely removed by distilled water at 55 °C after 5-h, and PMMA was removed at temperature lower than 440 °C by
thermal debinding under argon flow. The sintered samples showed good elongation in the range of 8.5 to 16%. The same group successfully employed this binder system for CP-Ti and the reported elongation values were 20% on average. In spite of these elongation values, no further progress was made on this system for Ti-MIM, and to date its use remains limited in Ti-MIM. Although, for Ti-MIM, PEG binder systems based on other backbone polymers such as PVB and EVA have been reported [106, 110] in literature, no mechanical properties have been documented for such system.

The debinding process for non-gelation synthetic polymers is cheap, environment friendly and easier to control compared to wax polymers. Nevertheless, care must be taken while disposing binder contaminated waste water [21].

2.2.3 Debinding

Removal of binders in case of Ti-MIM is usually done in two stages. The first stage involves the removal of primary component and most often solvent debinding is used for this purpose. Feedstocks based on other removal techniques are few and far between, and to date only one commercial feedstock [111] that employs catalytic debinding to remove primary component is available. As a primary component constitutes more than 50% of the binder system in general, and in some cases as high as ~85%, complete or near complete removal of it is very important in order to minimize contamination. In case of wax based binder systems, solvent debinding is usually performed by immersing samples in heptanes at 60 °C, but several other solvents can also be used including chlorinated hydrocarbons, and mixtures such as heptanes and ethanol. Penetration rates are in the range of 2 mm per hour. For PEG based binder systems, warm water or water-ethanol mixtures are used. However, the penetration rates are slightly lower than wax based systems. After solvent debinding, the compacts are slowly dried to avoid cracking, though it is not a compulsory step and can be done in conjunction with thermal debinding.

The removal of backbone polymer (second stage of debinding) is always carried out via thermal decomposition and temperature is slowly increased to include early stage of sintering in order to hold the particles together until final sintering. The successful option is to initially use argon to remove moisture and oxygen, and then heat up to a thermal decomposition temperature of the polymer. The decomposed gaseous by-products escape from the interconnected open pores facilitated by the previous solvent debinding. This debinding step is one of the crucial stages in order to keep impurities to a minimum level. Impurity contents
depend on the decomposed by-products, and increase with higher thermal debinding temperature. Therefore, the chemistry of backbone polymer is very important with regards to impurity control.

The current best practice is to use a wax/PEG-polymer binder with first solvent debinding followed by sweep gas thermal debinding up to a peak temperature of 450 °C to minimise the impurity pick-up. Guo et al. [87], studied the effect of debinding atmosphere on impurity control. Figure 2.13 compares the results of thermal debinding carried under vacuum with argon debinding. They used an ‘improved’ wax-based binder system. The Ti-6Al-4V samples were first debound by solvent immersion with 75 % of the binder was removed. The second stage thermal debinding was carried out at 600 °C followed by final sintering in vacuum at 1230 °C for 3-h. It was observed that flowing argon was unable to prevent oxygen pick-up. This study also shows how oxygen content is increased with an increase in the debinding temperature or with prolonged holds, as shown in Figure 2.14. The carbon content decreased during debinding, while the oxygen content continued to increase with the debinding process.

![Fig. 2.13 Correlation between carbon and oxygen content of the specimens with debinding atmosphere. Taken from ref. [87] with permission.](image-url)
2.2.4 Sintering

Sintering is the most critical production step with regard to contamination by oxygen as shown in Figure 2.12. In addition, the resulting microstructure is defined by this process and so are the mechanical properties. The key considerations for Ti-MIM sintering cycle are, peak temperature, holding time, rack material and most importantly sintering atmosphere [18].

It is not possible to avoid oxygen pick-up entirely. However, it can be kept to a minimum by using high vacuum (> $10^{-2}$Pa) during sintering. High purity argon can also be used as sintering atmosphere, but it leads to lower sintered density due to trapping of gas in the pores [18].

Selection of sintering parameters is a tough task and is always a compromise between low residual porosity and small grains [18]. Generally speaking, higher sintering temperature and longer holding time lead to higher density resulting in higher strength and ductility. On the contrary, a higher sintering temperature also leads to more oxygen contamination and hence reduced ductility. Moreover, it also leads to grain coarsening which is detrimental to strength. Pure titanium and typical alloys like Ti–6Al–4V are sintered above the beta-transus temperature in the single phase beta region, which boost grain growth. It should be kept in mind that the reduction in the grain size of titanium-based materials is not possible without a mechanical treatment. Therefore, the optimal sintering cycle depends on the starting powder characteristics, desired density, alloying approach, microstructure and final impurity level requirements. Typical sintering parameters include temperature of around 1300 °C combined with a holding time of 2-h. Lower temperature and shorter sintering time is favoured if HIP is used to reach full density [112]. Zhang et al. [113] showed it can be beneficial to sinter at
lower temperature for a longer time than to hold a higher temperature briefly. Smaller powder particle size can lower the sintering temperature, but usually result in increased oxygen pick-up. Similar studies were performed for TiNi and TiNiAl alloys by Liu et al. [114], and for Ti6Al4V by Nor et al. [115]. For optimizing the sintering parameters, statistical tools can be useful for example, Sidambe et al. [116] used Taguchi method in order to find the best combination of sintering time, temperature, heating rate and atmosphere for MIM of pure titanium and Ti–6Al–4V, for a given binder system.

As titanium reacts with most materials at high sintering temperatures, it limits the materials suitable for sintering support, and only less than five materials are suitable for racking [112]. The improper choice may cause surface distortion, increased impurity levels etc. The most suitable and successful racking materials are, zirconia (ZrO2) and yttria (Y2O3). Uematsu et al. [117] found that the zirconia substrates require a prebake at 1250 °C for 2 h in vacuum to remove impurities prior to first use. An assessment of the lining material used for handling molten metal confirmed that Y2O3 was the most promising material [118, 119]. However, these materials are expensive and to reduce cost some firms rely on plasma sprayed coatings on alumina setters [112]. The only metal that can be used as sintering support is molybdenum. However, it is susceptible to grain coarsening at high temperatures and therefore, its service time is relatively limited.

2.2.5 Further processing

Hot isostatic pressing (HIP) is the preferred final densification treatment in Ti-MIM and can be applied using an argon atmosphere. Typical parameters are 850-915 °C for 2-h at a pressure of 100-200 MPA [18]. Other post-sintering treatments for Ti-MIM components include bead blasting, coining, anodizing and polishing [119].

2.3 Mechanical properties

As explained earlier, there are a number of studies documenting the mechanical properties of Ti and its alloys processed via MIM. However, it is rather difficult to compare these studies, because different powders, binders and processing parameters were used. Some samples were even additionally applied to a hot iso-static pressing process [18]. Nonetheless, the negative effect of impurity contents has been well documented and established in literature now. For instance, Kursaka et al.[120] investigated MIM of CP-Ti. They reported that an increase of oxygen content from 0.2 to 0.4 wt% gave a linear loss of ductility from 20% to 8% while UTS increased from 560 to 720MPa. Similarly, Baril [121] evaluated the data from all studies

27
on MIM of Ti–6Al–4V with regard to oxygen equivalent and tensile properties. He concluded that to match the mechanical requirements for surgical implants impurity contents should not exceed 0.34 wt% and the porosity should be kept under 3%. German [16] presented an overview of mechanical properties for different Ti alloys MIM. According to it well balanced combinations of ultimate tensile strength (UTS) and elongation: 640MPa/20% for unalloyed titanium, 900MPa/14% for Ti6Al4V, and 830MPa/11% for Ti–6Al–7Nb respectively, can be achieved by proper processing and using adequate powders. Chen [99] reported that common Ti alloys deliver tensile strength in the 700 to 900 MPa range, but ductility varies from 1~3 % for high oxygen content to 12~15 % for the low oxygen content.

There are very few studies on the fatigue behaviour of Ti-MIM alloys. Few researchers have investigated the fatigue behaviour of Ti-MIM alloys [122-124]. Among these, Ferri et al. [122, 123] has studied the fatigue behavior of Ti6Al4V in detail. They investigated the fatigue behaviour under bending and axial load, respectively. In both cases the endurance limit defined for 10⁷ cycles was between 350 and 400MPa for the as-sintered samples. Thus, the fatigue properties of Ti-MIM alloys are better than those of the cast, but inferior to those of wrought material (for wrought Ti6Al4V a range between 450 to 800 MPa is assumed). The poor fatigue properties of Ti-MIM are attributed to coarse grains and poor surface quality compared to wrought titanium [18]. Ferri et al. [123] further investigated this and reported [125] that fatigue properties of Ti6Al4V can be improved by the addition of boron which acts as grain refiner. Furthermore, the boron addition improved the sintering process resulting in a residual porosity of only 2.3%. The final mechanical properties were: fatigue strength of 640 MPa (equivalent to high performance wrought material), UTS of 902 MPa, and elongation of 11.8% respectively, fulfilling all the requirements of the ASTM B348 grade 23. This example shows that it is worthwhile to develop specific alloys optimised for MIM processing.

2.4 Final remarks

In general, MIM process consists of four main steps: mixing, injection moulding, debinding and sintering. MIM of titanium and its alloys is a relatively novel process when compared with steel MIM and it is under continuous development. The high affinity for oxygen and carbon uptake complicates the whole production chain from powder production to sintering. In particular, the debinding stage is one of the most critical stages and introduces contamination from the binders to titanium. Therefore, the debinding step-especially the thermal debinding of backbone polymer- must be controlled more stringently to ensure the
success of Ti-MIM. The demand of green manufacturing has led to the use of environment friendly binder system for example, PEG based binder systems have received increasing interest in recent years. The PEG/PMMA binder system has proven to be promising for Ti-MIM. Nevertheless, to date, there are only few commercially available feedstocks which employ water soluble binder system.

In recent years, several review articles have been published on Ti-MIM: Prof. Randall German in 2009 [16] and in 2013 [17], Dr David Whittaker [126], Dr É. Baril [121], and Dr Thomas Ebel [18] have published comprehensive reviews of the current status of Ti-MIM including the mechanical properties of Ti-MIM alloys. In addition, Wen et al. [21] has published a detailed article on the binder systems for Ti-MIM. Therefore, it is highly recommended to read these review articles in order to start with MIM of titanium.
Chapter 3 Materials and experimental procedures

This chapter details the basic materials, equipment and experimental procedure used to prepare/test feedstocks for every chapter that follows. The specific experimental procedure and equipment are included within the chapters.

3.1 Materials

The starting metal powders include Ti powder produced by gas atomized (GA) (Ch. 4, 5 & 9) and hydrogenation-dehydrogenation (HDH thereafter) processes (Ch. 6). Water atomised stainless steel 17-4PH powder was also used in place of GA titanium powder (Ch. 7 & 8). This was mainly based on the following two reasons: (1) GA titanium powder is much expensive and not always available commercially and (2) the powder type has no effect on the intrinsic rheological properties of the studied binder systems. The chemicals used for the preparation of powder feedstock include PEG, PMMA, PBMA, polymer Q, PVP, SA, peanut oil and castor oil. The basic characteristics of the metal powders and raw chemicals are listed in Tables 3.1 and 3.2, respectively. The morphologies of metal powders are shown in Fig. 3.1. The binder systems compositions and solids loading used to prepare feedstocks are included in the individual sections of each chapter (It should be kept in mind that some feedstock compositions are propriety protected, hence, may not be completely disclosed).

However, in each case PEG is used as the primary component and provides the necessary fluidity. Stearic acid (SA), peanut oil and castor oil were used as lubricants.

<table>
<thead>
<tr>
<th>Powder type</th>
<th>Supplier</th>
<th>Mean particle size (µm)</th>
<th>O (wt. %)</th>
<th>C (wt. %)</th>
<th>N (wt. %)</th>
<th>Si (wt. %)</th>
<th>Cr (wt. %)</th>
<th>Powder Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDH-Ti</td>
<td>Beijing HoldFortune</td>
<td>&lt; 47</td>
<td>0.35</td>
<td>0.080</td>
<td>0.02 3</td>
<td>-</td>
<td>-</td>
<td>irregular</td>
</tr>
<tr>
<td>GA-Ti</td>
<td>OSAKA Titanium Technologies</td>
<td>45</td>
<td>0.122</td>
<td>0.003</td>
<td>0.00 8</td>
<td>-</td>
<td>-</td>
<td>spherical</td>
</tr>
<tr>
<td>Water atomised (WA) - stainless steel 17-4PH</td>
<td>Epson Atmix Corporation, Japan</td>
<td>6.96</td>
<td>-</td>
<td>0.038</td>
<td>-</td>
<td>0.28</td>
<td>16.41</td>
<td>spherical</td>
</tr>
</tbody>
</table>
Table 3.2 Basic characteristics of raw chemicals

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Supplier</th>
<th>Density (g/cm³)</th>
<th>Average $M_w$ (g/mol)</th>
<th>Melting / Glass transition ($T_g$) point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEG</td>
<td>Sigma Aldrich</td>
<td>1.2</td>
<td>1500; 4000; 10,000; 20,000</td>
<td>45 ~ 66</td>
</tr>
<tr>
<td>PVP</td>
<td>Sigma Aldrich</td>
<td>1.05</td>
<td>10,000; 55,000</td>
<td>110 ~ 155</td>
</tr>
<tr>
<td>PMMA</td>
<td>Chimei</td>
<td>1.19</td>
<td>45,000</td>
<td>110 ~ 115</td>
</tr>
<tr>
<td>PBMA</td>
<td>Sigma Aldrich</td>
<td>1.07</td>
<td>337,000</td>
<td>15</td>
</tr>
<tr>
<td>Polymer Q</td>
<td></td>
<td>1.26</td>
<td>150,000</td>
<td>-</td>
</tr>
<tr>
<td>SA</td>
<td>Sigma Aldrich</td>
<td>0.85</td>
<td>284.5</td>
<td>70</td>
</tr>
<tr>
<td>Peanut oil</td>
<td>In-house</td>
<td>0.92</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Castor oil</td>
<td>In-house</td>
<td>0.96</td>
<td>-</td>
<td>-18</td>
</tr>
</tbody>
</table>

Fig. 3.1 Morphologies of metal powders, a) HDH-Ti, b) GA-Ti, c) WA-17-4Ph stainless steel provided by the supplier
3.2 Experimental procedures

3.2.1 Feedstock preparation

The feedstocks preparation method is schematically shown in Figure 3.2.

In the first stage, all of the binder components were mixed in an organic solvent such as acetone (apart from PVP, acetone can dissolve all the chemicals used in this thesis) and stirred at the acetone boiling temperature until all the components were completely dissolved. The acetone amount was added according to 30ml per 5g of binder. Titanium powders were then added into the solution and mechanically stirred at 200 rpm until it became a paste as the acetone evaporated. The remaining acetone was removed by vacuum drying at 40 °C.

In the second stage, the pre-mixed feedstocks were hot mixed using a sigma blade mixer for 40 min to study the impact of solvent mixing and to further improve the homogeneity. The mixing temperature and speed were 130 °C and 40 rpm respectively. For Ch.8, feedstock preparation is explained in the experimental part of the chapter.

3.2.2 Viscosity measurement

Viscosity can be measured by a variety of techniques. For polymers, the most common technique is the melt index, in which the mass in grams of a polymer is extruded from a cylindrical die under a prescribed pressure during a period of ten minutes. However, as MIM
feedstocks exhibit different behaviour at different shear rates, a simple index is inappropriate and viscosity should be measured over a range of conditions. By far, the Capillary Rheometer is most useful testing technique in characterizing MIM feedstocks. It is design for characterizing materials at high shear rates, typically between 10 to 10,000 S\(^{-1}\) and hence, is used in these studies for complete evaluation of MIM feedstocks.

Rheological experiments were carried out on a Shimadzu capillary rheometer (CFT-500D) in temperature range of 80 °C to 140 °C. Different pressure values and die sets with different length-radius (L/R) ratios (\(D_1=1\text{mm}, L_1=10\text{mm} ; D_2=1\text{mm}, L_2=1\text{mm}\)) were used for calculations, based on the Bagley & Rabinowitsch corrections [127]. Capillary rheometers are designed to calculate viscosity based on Newtonian fluids and as MIM feedstocks have Non-Newtonian flow behaviour, certain corrections are required to get the true viscosity. The two most important are: Bagley end correction and Rabinowitsch Correction.

### 3.2.2.1 The Bagley end correction

In reality the MIM feedstock is not an incompressible fluid and its behavior might be disturbed at the entrance of the capillary, which might lead to instability if the velocity gradient is too high. It entails that the pressure at the entrance due to the force applied to extrude the feedstock is different from the pressure at the exit of the capillary [104, 128-130]. Thus, there are some pressure losses which have important consequences regarding the shear stress calculations, Figure 3.3.

![Fig. 3.3 Entrance pressure loss in case of a non-Newtonian fluid (right) compared with a Newtonian fluid (left) [125-127]](image)

For Newtonian fluid, the \(\Delta P\) versus capillaries of different L/R ratio will always be a straight line with zero intercepts, the slope of which is equal to twice the shear stress. But for Non-Newtonian fluid, the pressure drop will increase as die length will increase. Bagley end correction simply considers that pressure drop through a die length of L will be equivalent to the die length of L +e, as shown in Figure 3.4.
Fig. 3.4 Bagley end correction. The y-intercepts are the entrance pressure loss

The procedure to calculate Bagley end correction is quite simple. Pressure is plotted against different L/R ratio dies at a constant shear rate to obtain the e value. Thus, the true shear stress can be calculated as:

$$\tau(\text{true}) = \frac{P}{2\left(\frac{l}{\tau} + e\right)}$$  \hspace{1cm} \text{Eq. 3.1}

3.2.2.2 Rabinowitsch correction

The wall shear rate is generally greater for non-Newtonian fluid and the velocity profile is not parabolic, as shown in the velocity profile below.

Fig. 3.5 velocity profile for a Newtonian and non-Newtonian flow

A special step is used to determine this wall shear rate for non-Newtonian fluid and this is called as Rabinowitsch correction. And it is generally given by;
\[
\frac{(3n + 1)}{4n}
\]  

Eq. 3.2

Where \( n \) is the slope of the log-log graph of apparent shear rate and true shear stress. The true shear rates are thus calculated as;

\[
\dot{\gamma}(\text{true}) = \frac{(3n + 1)}{4n} \dot{\gamma}(\text{apparent})
\]  

Eq. 3.3

### 3.2.3 Injection moulding

Once the feedstock pellets were prepared, they were charged into an injection moulder either a twin-screw Arburg 220S (Singapore) or a BOY 15S (New Zealand). The injection moulding parameters are included in each chapter, while three tensile dog bone specimen standards (apart from chapter 5) were used to prepare test samples, Figure 3.6.

![Geometry of injection moulded tensile test bars](image)

**Fig. 3.6** Geometry of injection moulded tensile test bars, a) Tensile test sample proposed by the European MIM industry, b) MPIF standard 35, c) ASTM standard B925. In every case the thickness of test bars was 4 mm.
3.2.4 Water debinding

To remove water soluble PEG the green parts were placed on a perforated supporting plate either glass or ceramic. The stand was placed in distilled water bath with a magnetic stirrer underneath. Different debinding temperatures and times were used to construct a debinding profile. For this purpose the samples were weighed before and after water debinding at an accuracy of ± 0.0001 g. After removal of water-soluble binder all samples were dried in a vacuum oven at 40 ~ 55 °C for 12-h before the weight loss of the samples was recorded.

3.2.5 Thermal debinding and sintering

(Considering Ti-MIM, the quality of debinding and sintering furnace was not up to the mark especially in case of sintering furnace. Nonetheless, the following procedure was adopted for thermal debinding and sintering).

After removal of PEG, green parts were subjected to thermal debinding to remove the backbone polymers and lubricants. The green parts were either placed in a tube furnace (with flowing Ar) or in a vacuum furnace. However, in each case thermal debinding was carried out using the following profile, Figure 3.7.

![Figure 3.7 Thermal debinding profile](image-url)
Sintering was carried out in high vacuum sintering furnace at 1300 °C for 2-h (in most cases, otherwise stated) using the following heating profile, Figure 3.8.

![Sintering profile](image)

**Fig. 3.8 Sintering profile**

### 3.2.6 Characterization

The attendant density and open porosity of the as-sintered samples were measured by the Archimedes’ principle as specified in the ASTM B962-08 standard. Microstructures of the metal powders, and the feedstocks were observed using either a ZEISS scanning electron microscopy (SEM, Singapore) or an environmental scanning electron microscope (ESEM, FEI Quanta 200F, New Zealand) equipped with an energy dispersive X-ray spectrometer (EDX). To study the fracture surface under SEM, green parts were submerged in liquid nitrogen and were fractured.
Chapter 4 Effect of PEG molecular weight on rheological properties of Ti-MIM feedstocks and water debinding behaviour

This chapter is extracted from the publication (ref. [131]). The purpose of this chapter is to study the effect of PEG molecular weight on rheological properties of the feedstock and its water debinding behaviour which intriguingly, has not been well investigated. Four molecular weights of PEG, i.e. 1500, 4000, 10,000 and 20,000 g/mol were selected and PEG/PMMA based feedstocks were formulated with titanium metal powder. A systematic investigation of the rheological properties of the prepared feedstocks with capillary rheometry and the study of the effects of shear rate and temperature on viscosity was carried out. The water debinding behaviour of each feedstock was also investigated in terms of debinding temperature and PEG molecular weight.

4.1 Introduction

As explained earlier, the binder systems used in Ti-MIM fall into following groups according to the debinding routes used: wax based, polyoxymethylene based, aromatics-based, and water-soluble binder systems [21].

Water soluble binder systems have received increasing interest in recent years because they can be extracted in an environmentally friendly manner. Among these, polyethylene glycol (PEG) is the most extensively reported polymer due to its non-toxicity, commercial availability and solubility in water [22-25] as described in the previous sections. It is a crystalline polymer (chemical structure: HO-[CH2-CH2-O]n-H) with an open helical structure, which is responsible for its low melting point and solubility in water. PEG molecular weight has a profound effect on its physical properties. For instance, as molecular weight increases above 10,000 g/mol its viscosity increase significantly. On the other hand, the solubility in water at room temperature sharply decreases as molecular weight increases above 1000 g/mol, after which it levels off and slightly decreases in the range of 4000 g/mol to 35000 g/mol [108, 132, 133]. Thus, it is crucial to choose a suitable molecular weight for a successful MIM operation. In general, the PEG polymers with an average molecular weight in the range of 500 to 2000 g/mol are chosen for feedstock formulation [21].

Although rheological properties of PEG based feedstocks composed of ferrous metal powders are well documented in the literature [134-137], few work has been reported on the rheology of PEG based Ti-MIM feedstocks [104, 109, 110]. Thavanayagam et al. [104, 110]
investigated the effects of key parameters such as powder loadings and binder formulations on the rheological properties of the feedstock consisting of HDH Ti-6Al-4V powder with the binder system based on PEG, polyvinyl butyryl (PVB) and stearic acid (SA). Feedstocks with low viscosity, high shear rate dependence and low temperature dependence were selected for MIM operation. Sidambe et al. [27] reported that CP-Ti feedstocks, prepared using PEG (with a molecular weight of 1500 g/mol)/PMMA/SA binder system and with 69 vol. % powder loading, demonstrated good rheological properties and were injection moldable. Moreover, PEG was completely removed at 55 °C after 5-h soaking in water. However, it is noted that most of the research on the rheology of PEG-based MIM feedstocks intended to investigate the effects of metal powder shape, powder size, binder formulation and powder loading. The effect of PEG molecular weight on rheological properties has seldom been taken into account and it is therefore the main objective of this study. Similarly, other than molecular weight, studies of water debinding behavior of PEG binder systems in terms of water bath temperature, specimen thickness and powder shape etc. have been reported in the literature [138, 139]. The specific aim of this research is to characterize in detail the effects of PEG molecular weights on rheological behavior of Ti-MIM feedstocks in order to achieve excellent moulding operation. Secondly, water debinding performance is also studied with respect to PEG molecular weight. These studies will help establish a relationship between PEG molecular weight, rheological properties and debinding behaviour of the feedstocks.

4.2 Experimental procedures

Binder systems based on PEG/PMMA/SA were prepared. To study the effect of molecular weight, four different PEG molecular weights: 1500, 4000, 10,000 and 20,000 were selected for feedstock formulation and designated as Feedstock A, B, C and D respectively hereafter. Powder loading was selected as 60vol%.

For water debinding behaviour study, dog bone shaped specimens [Fig 3.6(c)] were made using a bench press at 25 MPa. Pressing die was preheated at 90 °C for 2-h. Each pressed bar was visually inspected and weighed after every run for quality control. The injection temperature was selected on the basis of rheological experiments, while the injection speed was 40 cm³/sec and the backing pressure was 14 MPa. Each moulded sample was visually inspected and weighed after every run for quality control.
The green parts were then subjected to water debinding to extract PEG. The parts were submerged in distilled water at 50 °C for different periods of time in order to construct a debinding profile.

4.3 Results and discussion

4.3.1 Yield stress

MIM feedstock generally possesses a yield shear stress at low temperatures and zero shear rate (i.e. Bingham behaviour), but exhibits a pseudoplastic behaviour over the shear rates that are encountered during injection moulding. Such fluids are termed as Herschel-Bulkley fluids and can be expressed as [140]:

\[ \tau = \tau_y + K\dot{\gamma}^n \]  
\[ \text{Eq. 4.1} \]

where \( K \) is a constant, \( \tau_y \) yield shear stress, \( \dot{\gamma} \) shear rate and \( n \) the exponent used to characterize the fluid. For Newtonian fluids \( n = 1 \), for pseudoplastic fluids \( n < 1 \) and for dilatant fluids \( n > 1 \). The yield stress can be calculated by the Bingham model [140]:

\[ \tau = \tau_y + \mu_p \dot{\gamma} \]  
\[ \text{Eq. 4.2} \]

where \( \tau_y \) yield shear stress, and \( \mu_p \) is the plastic viscosity, determined by the slope of the shear stress vs. shear rate line above the yield point. It represents the viscosity of the samples when extrapolated to infinite shear rate on the basis of the Bingham model. By plotting \( \tau \) vs \( \dot{\gamma} \), yield stress (\( \tau_y \)) and plastic viscosity (\( \mu_p \)) can be calculated. Figure 4.1 exemplifies the \( \tau \) vs \( \dot{\gamma} \) graphs for feedstocks at the two selected temperatures 80 °C and 100 °C. It is noted that the trend for other temperatures remains the same and therefore not included in Figure. 4.1.
Fig. 4.1 Shear stress vs. shear rate for feedstocks at (a) 80 °C and (b) 100 °C.

As shown in Figure 4.1, both yield stress ($\tau_y$) and plastic viscosity ($\mu_p$) increased as PEG molecular weight increased, suggesting lower flowability for the higher molecular weight. Since yield stress can be considered as a minimum force (stress) required for the flow, feedstocks composed of PEG with higher molecular weight will thus require a higher moulding pressure. However, the yield stress decreased with increased temperature, as shown in Figure 4.2.

Fig.4.2 Yield shear stress dependence on temperature for different feedstocks.

The decrease in yield stress with temperature was more prominent for the higher molecular weight feedstocks. It can also be seen from Figures 4.1 and 4.2 that the difference in yield stress values of feedstocks composed of PEG-1500 and PEG-4000 was only marginal and it further diminished as temperature increased. The effect of backbone polymer PMMA was
also evident from Figure 4.2. Except for Feedstock D (i.e., PEG-20,000), the decrease in yield stress for other feedstocks was relatively sharp between 90 and 100 °C (marked by the red line). This sharp decrease may be due to the softening of PMMA molecules (glass transition temperature of PMMA is approximately 104 °C). This emphasizes that the selection and content of backbone polymer should be chosen with great care. It is arguable that feedstocks A, B and C should not be injection moulded in the range of 90 to 100 °C. The temperature variation in this range during injection moulding will significantly affect flowability of the feedstocks. On the other hand, yield stress variation in feedstock D with temperature was gradual due to an inherently lower flowability of PEG-20,000. The yield stress of feedstock A and B was very low at higher temperatures, which was also confirmed by their plastic viscosity values (Fig. 4.1). In fact, it was observed that both feedstocks were able to flow without any pressure at higher temperatures during rheometry experiments. This implies that both feedstocks were not suitable for injection moulding at higher temperatures as flashing may occur during mould filling.

4.3.2 Shear sensitivity

The yield stress evaluation only gives an estimate of fluidity, pressure required to initiate the flow, and an approximated working temperature of feedstocks. However, in most cases the applied pressure in injection moulding is much higher than the yield stress. Viscosity dependence on shear rates is more desired due to the wide shearing range of injection moulders. Thus, the initial yield stress can be neglected. Equation (4.1) then becomes:

$$\tau = K\gamma^n$$  \hspace{1cm} Eq. 4.3

where $K$ is a constant and $n$ has the same meaning as in Eq. (4.1). This is known as power law model [141, 142]. Although it is widely used to characterize fluids, there are certain limitations. For instance, viscosity becomes infinite at low shear rates and vice versa. However, if used within the measured shear rates, this model can produce reasonably accurate results [142]. Eq. (4.3) is often used to describe shear rate dependence of viscosity and is given by [143]:

$$\eta = K\gamma^{n-1}$$  \hspace{1cm} Eq. 4.4

where $K$ is a constant and, $\eta$ is viscosity. The exponent $(n-1)$ value shows the viscosity dependence on shear rate (also termed shear sensitivity) and can be calculated from a double logarithm plot (log$\eta$ vs log$\gamma$). Generally a high $(n-1)$ value or a high negative slope is desired.
for MIM. However, too high \((n-1)\) values or too high shear sensitivity may also cause problems such as flashing during moulding. Figure 4.3 shows the viscosity dependence on shear rate for different feedstocks. Table 4.1 lists the \((n-1)\) values for these feedstocks.

Fig. 4.3 Plot of double logarithm of viscosity vs. shear rate in the temperature range of 80 °C to 140 °C for (a) feedstock \(A\), (b) feedstock \(B\), (c) feedstock \(C\) and (d) feedstock \(D\). It is noted that data for Feedstock \(A\) and \(B\) at 140 °C were excluded due to extremely low viscosities at this temperature.

**Table 4.1: The \((n-1)\) values for various feedstocks at different temperatures**

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>80°C</th>
<th>90°C</th>
<th>100°C</th>
<th>110°C</th>
<th>120°C</th>
<th>130°C</th>
<th>140°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock A</td>
<td>-0.53</td>
<td>-0.47</td>
<td>-0.41</td>
<td>-0.34</td>
<td>-0.27</td>
<td>-0.3</td>
<td>-</td>
</tr>
<tr>
<td>Feedstock B</td>
<td>-0.26</td>
<td>-0.32</td>
<td>-0.31</td>
<td>-0.47</td>
<td>-0.4</td>
<td>-0.51</td>
<td>-</td>
</tr>
<tr>
<td>Feedstock C</td>
<td>-0.31</td>
<td>-0.34</td>
<td>-0.3</td>
<td>-0.33</td>
<td>-0.37</td>
<td>-0.41</td>
<td></td>
</tr>
<tr>
<td>Feedstock D</td>
<td>-0.46</td>
<td>-0.45</td>
<td>-0.45</td>
<td>-0.43</td>
<td>-0.4</td>
<td>-0.38</td>
<td>-0.41</td>
</tr>
</tbody>
</table>

According to Refs. [19, 144], the shear rates may vary in the range of \(10^2\) to \(10^5\) s\(^{-1}\) during MIM. To achieve excellent moulding at the moulding temperature, upper limit of viscosity has been set at 1000 Pa-s for this shear rate range [129, 145]. It can be seen from Figure 4.3
that all the feedstocks were pseudoplastic in nature at all temperatures. Feedstocks A and B both had viscosities well below 1000 Pa⋅s and large variations of the shear rate dependency values. Feedstock A had good shear rate dependency at 80 and 90 °C but the shear rate dependency reduced readily as temperature increased, and therefore Feedstock A may only be used at lower temperatures. In contrast to yield stress results, Feedstock B had surprisingly low shear rate sensitivity at lower temperatures compared to Feedstock A. This may be caused by its low viscosity. The extremely low viscosity of both feedstock A and B makes it difficult to control the processing parameters, particularly at higher temperatures. Feedstocks C and D also had reasonably good viscosity in the entire shear rate range and demonstrated more consistent shear sensitivity values. It is noteworthy that Feedstock D possessed the highest shear sensitivity values over the entire temperature range. This better shear sensitivity of Feedstocks C and D is attributed to the higher PEG molecular weight. The flowability of feedstocks is dependent on the bonding between metal powder and polymeric binder. Increasing PEG molecular weight would increase the interaction between powder and polymeric binder, as a result of increased number of hydrogen bonds on the longer PEG molecule chains. This enhanced interaction gives rise to increased adhesion of binder onto the metal powders, which in turn, results in better flowability [146, 147].

It is also found that, in the case of Feedstock A and B, the maximum shear rate for pseudoplastic flow to occur varies from 8,000 s⁻¹ to 12,000 s⁻¹ (critical shear rate range), depending on temperature. The lowest value of 8,000 s⁻¹ is associated with the highest temperature used in this study (140 °C). Above these limiting shear rates (8,000 s⁻¹ to 12,000 s⁻¹), both feedstocks showed dilatant flow behavior due to feedstock separation. Inherently low viscosity as a result of the use of low molecular weight further decreases with shear rate. When the viscosity becomes too low, it is difficult for PEG to remain attached to metal powders. Therefore, feedstock A and B should not be injection moulded at higher injection speed and higher temperature, due to the risk of feedstock separation as shear rates vary in the range of 10² to 10⁵ s⁻¹. This critical shear rate range increases as PEG molecular weight increases. Feedstocks C and D both had this range in excess of 15,000 s⁻¹, with feedstock D having the highest workable shear rate range over the entire temperature range (80 °C to 140 °C). Under the practical MIM conditions, Feedstock D can thus be injection moulded over a wide range of temperature, pressure and speed. However, this wide range is realized at the expense of increased viscosity. Therefore, if a higher molecular weight is selected for
feedstock formulation, powder loading should be lowered in order to maintain an overall viscosity below 1000 Pa\cdot s.

4.3.3 Temperature dependence

Temperature sensitivity is another important factor that must be considered during feedstock design. In general, a good MIM feedstock should have a low temperature sensitivity of its viscosity. The higher sensitivity arises from large difference in coefficient of thermal expansion between binder polymer and metal powders. In addition, during injection moulding temperature decreases sharply from nozzle to cavity. If a feedstock viscosity is too sensitive to temperature change then a sudden decrease in viscosity can affect the final quality of the product by inducing cracks and stresses in the final part [90].

The temperature dependence of viscosity can be explained by the Arrhenius equation [148]:

$$\eta = \eta_0 \exp\left(\frac{E}{RT}\right)$$

Eq. 4.5

where $\eta_0$ is the viscosity at a reference temperature, $R$ is the universal gas constant, $E$ is the activation energy for viscous flow and $T$ is absolute temperature. A higher value of $E$ indicates a high sensitivity of viscosity to temperature change. The activation energy can be calculated from the plot of $\ln \eta \cdot \frac{1}{T}$, the slope of which is equal to $E/R$ (Figure 4.4).

![Fig. 4.4 Temperature dependence of viscosity for the feedstocks in the temperature range of 80 °C to 140 °C. It is noted that data for Feedstock A and B at 140 °C were excluded due to extremely low viscosities at this temperature.](image-url)
The result from Figure 4.4 indicates that the activation energy of feedstock decreased as PEG molecular weight increased. The lowest activation energy, 19.66 J/mol was achieved in feedstock $D$. The reason for such behaviour is still unclear. The highest $E$ value was observed in feedstock $A$ (28.19 J/mol). Thus, feedstock $A$ would require more accurate temperature control of the mould. Otherwise, temperature gradient across mould will induce residue stresses in the final part.

### 4.3.4 Water debinding behaviour

The goal of solvent extraction is to create interconnected pores throughout the moulded body so that the backbone component can be removed through these pores without distorting the shape when second debinding is applied. The water extraction process of PEG is driven by capillary action and concentration gradient across the water bath. The process starts from the surface of specimen. As water penetrates into the moulded body by capillary action, it extracts and dissolves the PEG molecules which are then transported into surrounding water bath due to concentration difference between green part and water bath. This process continues until the concentration equilibrium is achieved. The water debinding can be formulated using Fick’s diffusion model [109]:

\[
\ln\left(\frac{1}{F}\right) = \frac{D_e t \pi^2}{(2L)^2} + K
\]

Eq. 4.6

where $F$ is the fraction of remaining polymer, $t$ is the time, $2L$ is the specimen thickness, and $K$ stands for the change in the mechanism controlling the debinding. $D_e$ is the effective diffusion coefficient of polymer, a collective parameter that include the effects of water penetration, water-PEG interaction to form hydrated complexes and most significantly transportation of the hydrated PEG molecules [149]. Eq. (4.6) can be rewritten as:

\[
\ln\left(\frac{1}{100\% - F}\right) = \frac{D_e t \pi^2}{(2L)^2} + K
\]

Eq. 4.7

where $(100\% - F)$ is the percentage of polymer removal. Figure 4.5 presents the water debinding profile for the feedstock $A$, $B$ and $C$. The water debinding data for feedstock $D$ were not included in Figure 4.5 because the samples experienced significant swelling and cracking, Figure 4.6.
Fig. 4.5 PEG removal rate in feedstocks. The water bath temperature was 50°C.

Fig. 4.6 Cracking on the water debound specimen made from feedstock D. Cracks appeared after 30 min of debinding at 50 °C

It can be seen from Figure 4.5, PEG removal rate decreased as PEG molecular weight increased. More than 95% of PEG removal was obtained in the case of feedstock A just after 6-h of debinding, emphasising the benefit of PEG with a lower molecular weight. Surprisingly, difference between Feedstock B and C removal rate was not significant, given the viscosity difference and implies that PEG-10000 molecules have sufficient mobility for easy extraction.

The cracking in debound samples made from feedstock D is related to PEG molecular weight. Unfortunately the potential benefit of higher molecular weight for rheology is
compromised by the poor water debinding performance. The increase in molecular weight decreases the mobility of the PEG chains in water (solubility) because chain lengthening also increases the adhesion with metal powders [150]. As water penetrates into the samples, the dissolution of higher molecular weight PEG molecules is slower than the speed of water penetration, and therefore, the sample volume expands which ultimately leads to cracking. Figure 4.5 also validates the water debinding mechanism. It is clear that water debinding is a two-stage process. In the first stage, dissolution of PEG controls the entire process. The binder removal in this stage is rather rapid and depends on parameters such as water bath temperature, PEG molecular weight and sample thickness. As the process proceeds, porous channels are formed within the samples and a longer diffusion distance results. At this second stage, diffusion becomes the rate controlling step and binder removal rate slows down. The PEG removal rate significantly slows down after 6-h of leeching, and it is estimated that full removal in the case of feedstock C may not be obtained within feasible timeframe. However, from practical perspective thermal debinding can be employed after 75 wt% of PEG is removed, as enough open porosity is already created at this point.

4.4 Summary

PEG molecular weight plays an important role on rheological properties and debinding performance of feedstocks. The results reveal that the feedstock formulated from high molecular weight PEG as the primary binder component leads to a high yield stress. However, the shear sensitivity of feedstocks increases with PEG molecular weight due to more adhesion with metal powders provided by the molecular chain lengthening. Similarly, temperature sensitivity decreases as PEG molecular weight increases. On the other hand, feedstocks containing low molecular weight PEG show powder separation at higher temperatures and higher shear rates, and also have higher temperature sensitivity. The benefit of using high molecular weight binder is largely offset by the water debinding performance. The feedstocks formulated from PEG of too high molecular weight are prone to volumetric expansion and thus cracking. It was found that PEG-10000 not only had excellent rheological properties, but also good debinding performance. Thus, PEG-10000 was the best option as the primary binder component and the feedstock based on this polymer was most suitable for MIM.
Chapter 5 Compatibility improvement of Ti-MIM feedstock using liquid surfactant

This chapter is extracted from ref. [151] and documents the effect of different surfactants on the metal-and-binder interaction that has not been reported before. To study such effects, PEG and PMMA were used as the major and backbone constituents in the binder system. Three different surfactants – stearic acid, peanut oil and castor oil – were chosen to prepare feedstocks of 60 vol% solid loading. Rheological properties analysis, fracture surface, and flexural strength studies were carried out to identify the suitable surfactant that yields feedstock with excellent mouldability. It is found that castor oil as surfactant results in excellent overall properties of feedstock by enhancing metal-and-binder interaction.

5.1 Introduction

The formulation of binder systems has received much attention in recent years primarily because an ideal formulation is nearly impossible to attain, particularly in the case of Ti-MIM and often the same binder composition is applied to different powders as mentioned by Wen et al. [21]. Surfactants are generally added in binder systems to further enhance the interaction between metal powders and binder components by improving properties such as surface wetting, spreading, adsorption and binder strengthening [152]. In other words, surfactant can improve the compatibility of binder and powders by increasing adhesion between binder and powder particles, thereby leading to a better moulding operation. Therefore, the surfactant acts as a bridge between the powder and the binder. The surfactant is thus critical to the binder system and MIM process [153]. Furthermore, it can also reduce the friction between powders and die wall by acting as a lubricant and enhance miscibility between binder components [154].

The most commonly used surfactant in powder injection moulding is SA. The effects of SA on the properties of powder binder mixture have been studied extensively. For instance, Novak et al. [155] suggested that not only the activity and quantity of the surfactant, but also the type of bond between surfactant and powder surface is of essential importance. Lin and German [146] suggested that adsorption of organic surfactants on the powder surface is through hydrogen bonding. Song-lin et al. [156] found that chemical adsorption occurs on the 17-4PH stainless steel powder surface with the use of SA, which enhances the stability of feedstock and reduces the flow viscosity. Tseng and Teng [157] investigated the suspension
stability of Al$_2$O$_3$ powder–toluene mixture using various organic surfactants and found that the surfactant nature is critical to the suspension stability. This dependence is related to adsorption behaviour of the surfactant molecules to the powder surface and the adsorption affinity. Given the wide usage, SA is the first choice surfactant in Ti-MIM.

The reports on feedstocks comprising of surfactants other than SA in MIM are few and far between, palm stearin being one example. Ibrahim et al. [158] analyzed a feedstock comprising of palm stearin as surfactant and showed that this feedstock has properties comparable to conventional SA comprising feedstock. Similarly, the effects of nature of surfactants on rheological properties of feedstock are largely missing, particularly in the case of Ti-MIM. Owing to the importance of surfactant, a series of experiments were carried out to study the effects of different types of surfactant on the properties of Ti-MIM feedstock. The objective of this chapter is thus to find out a suitable surfactant which yields excellent properties of feedstock. It may be noted that results from this study can be also used for other powders injection moulding.

### 5.2 Experimental procedures

The binder system contained 83 wt% PEG ($M_w \sim 10,000$ g/mol), 15 wt% PMMA ($M_w \sim 45,000$ g/mol), and 2 wt% surfactant. We chose three different surfactants: solid stearic acid, liquid peanut oil, and Castor oil for feedstock formulation and designated as feedstock $A$, $B$, and $C$ respectively hereafter. The solid loading was fixed as 60 vol% for this purpose.

Homogeneity of feedstocks was determined with Accupyc II Gas Pycnometer.

To determine flexural strength, 4-point bending test was carried out using an Instron machine. ASTM standard (ASTM-C1161-13) flexural test rectangular specimen were made using Arburg 220S injection moulding machine as shown in Figure 5.1. The test-pieces had the dimensions of 45 mm (length), 3 mm (thickness) and 4 mm (width). Each moulded sample was visually inspected and weighed after every run for quality control.
Fig. 5.1 Flexural test specimen made by injection moulding in the temperature range of 95 °C to 115 °C. The injection pressure was varied between 120 to 350 bar, and the mould temperature was 27 °C.

5.3 Results and discussion

5.3.1 Yield stress

Figure 5.2 plots a graph of $\tau$ vs $\gamma$ for three feedstocks based on equation 4.2.

![Graph of Shear Stress vs Shear Rate](image)

**Fig. 5.2 Shear stress versus shear rate graphs for different feedstocks at 100 °C.**

It can be seen from Figure 5.2 that the use of liquid surfactants leads to a decrease in both yield stress and plastic viscosity. Since yield stress can be considered as minimum force required initiating the flow, feedstocks composed of liquid surfactants will thus require lower pressure for moulding. Figure 5.2 also indicates that there is little difference between yield stress and plastic viscosity values of feedstocks composed of liquid surfactants, feedstocks $B$ and $C$. The difference between yield stresses of the feedstocks further decreases as temperature increases, as shown in Figure 5.3.
Fig. 5.3 Yield stress dependence on temperature for different feedstocks. The decrease in yield stress with temperature is more prominent for feedstock containing SA (feedstock A).

The effect of backbone polymer PMMA is also evident from Figure 5.3 (as has been explained in the previous chapter section 4.3.1). It can also be extracted from Figure 5.3 that feedstock A should not be injection moulded in the range of 90–100 °C. The temperature variation in this range during injection moulding will affect flowability of the feedstock. Thereby, the best temperature range to achieve good control of moulding parameters with excellent rheology for all feedstocks is between 105 and 130 °C. It is worth noting that although high temperature processing is more attractive due to lower viscosities of feedstocks, it requires careful control of processing parameters. Therefore, it is advised to determine the temperature range by yield stress experiment that gives the best process control.

5.3.2 Shear sensitivity

Figure 5.4 shows the viscosity dependence on shear rate for the three feedstocks using equation 4.4 while Table 5.1 lists the \((n-1)\) values for them.
Fig. 5.4 Double logarithm of viscosity vs. shear rate plot for different feedstocks in the temperature range of 80 °C to 140 °C. It must be noted that due to extremely low viscosities of feedstock B and C, calculations at 140 °C were not possible.

Table 5.1: The (\(n-1\)) values for feedstocks at different temperatures

<table>
<thead>
<tr>
<th>Temp</th>
<th>80°C</th>
<th>90°C</th>
<th>100°C</th>
<th>110°C</th>
<th>120°C</th>
<th>130°C</th>
<th>140°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feedstock A</td>
<td>-0.31</td>
<td>-0.34</td>
<td>-0.3</td>
<td>-0.3</td>
<td>-0.33</td>
<td>-0.37</td>
<td>-0.41</td>
</tr>
<tr>
<td>Feedstock B</td>
<td>-0.19</td>
<td>-0.25</td>
<td>-0.26</td>
<td>-0.30</td>
<td>-0.31</td>
<td>-0.32</td>
<td>-</td>
</tr>
<tr>
<td>Feedstock C</td>
<td>-0.29</td>
<td>-0.25</td>
<td>-0.26</td>
<td>-0.25</td>
<td>-0.32</td>
<td>-0.39</td>
<td>-</td>
</tr>
</tbody>
</table>

During injection moulding shear rates may vary in the range of 10³ to 10⁵ s⁻¹, as stated in the literature [144]. To achieve excellent moulding the upper limit of viscosity has been set at 1000 Pa-s for this shear rate range at the moulding temperature as described in the literature [129, 145]. It can be seen from Figure 5.4 that all the feedstocks are pseudoplastic in nature at all temperatures and have viscosities well below 1000 Pa-s. Feedstock A has higher shear sensitivity values at most temperatures compared to feedstock B and C. It can also been seen from Table 5.1 and Figure 5.4 that there is an increasing trend of shear sensitivity values with
temperature, particularly in the case of feedstock B. This could be due to decreasing viscosities with increasing temperature. In fact, in the case of feedstock B and C viscosity became very low at 140 °C that rheometer calculations were not possible.

It is also found that, the nature of surfactant does not have significant effect on the critical shear rate range (the range up to which pseudoplastic flow occurs). In all three feedstocks, the maximum shear rate for pseudoplastic flow to occur varies from 12,000 s\(^{-1}\) to 15,000 s\(^{-1}\), depending on temperature. The lowest value of 12,000 s\(^{-1}\) is associated with the highest temperature used in this study (140 °C). Above these limiting shear rates (12,000 s\(^{-1}\) to 15,000 s\(^{-1}\)) all the feedstocks showed dilatant flow behavior due to separation caused by inherently low viscosity of PEG at higher shear rates.

Keeping in mind the higher shear sensitivity value requirement for MIM, feedstock A should be given preference over feedstocks B and C. However, feedstocks B and C have lower viscosities compared to feedstock A as shown in Figure 5.5.

![Double logarithm of viscosity vs. shear rate plot of different feedstocks at 120 °C.](image)

**Fig. 5.5** Double logarithm of viscosity vs. shear rate plot of different feedstocks at 120 °C.

It can be seen from Figure 5.5 that highest viscosity values are associated with feedstock A. Lower viscosities can be achieved when SA is replaced by liquid surfactants. In this case, almost 5% reduction in viscosity was achieved. This low viscosity is attributed to higher interaction between metal powder and binder system which increases the powder dispersion and thereby a higher solid loading can be employed. It should also be noted that there is a
nominal viscosity difference between feedstock B and C, suggesting that oil type has little effect over the shear sensitivity properties of feedstocks. It can be argued that this reduction in viscosity might not be of importance for low solid loading feedstocks. However, in the case of injection moulding of higher solid loading feedstocks, this reduced viscosity can have serious impact. In such cases, a lower viscosity at particular solid loadings is always sought upon.

5.3.3 Temperature dependence

Temperature sensitivity is another important factor that should be considered during feedstock designing. The temperature dependence of viscosity can be explained by the Arrhenius equation (Eq. 4.5). Figure 5.6 plots Arrhenius equation for different feedstocks.

![Temperature dependence of viscosity for feedstocks](image)

**Fig. 5.6 Temperature dependence of viscosity for feedstocks in the temperature range of 80 °C to 130 °C at a shear rate of 1500 s⁻¹.**

Figure 5.6 shows activation energies of feedstock A and C are marginally different. The lowest $E$ value was obtained for feedstock C containing castor oil, while the highest was obtained for feedstock B containing peanut oil as surfactant. Therefore, feedstock B will require more accurate mould temperature control. This increase in $E$ value of feedstock B may have occurred due to inherently high temperature dependence of peanut oil.

5.3.4 Mouldability index

Comparing the shear and temperature sensitivity and viscosity results, it becomes difficult to choose a feedstock that possesses excellent properties at lower viscosity. Hence, a
mouldability index has been introduced in the literature to counter this. It combines viscosity, shear sensitivity and temperature sensitivity in one formula and is given by [90]:

$$\alpha_{st\eta} = \frac{1}{\eta_o} \frac{1 - n}{E/R}$$

where $\eta_o$ is the reference viscosity at the reference temperature and a particular shear rate. The subscripts $s$, $t$ and $\eta$ represent the effects of shear sensitivity, temperature and viscosity respectively. The higher the value of $\alpha_{st\eta}$, the better rheological properties are. Table 5.2 compares the $\alpha_{st\eta}$ of feedstocks.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Feedstock A</th>
<th>Feedstock B</th>
<th>Feedstock C</th>
</tr>
</thead>
<tbody>
<tr>
<td>110°C</td>
<td>38</td>
<td>7</td>
<td>44</td>
</tr>
<tr>
<td>120°C</td>
<td>42</td>
<td>7.5</td>
<td>56</td>
</tr>
<tr>
<td>130°C</td>
<td>47</td>
<td>7.7</td>
<td>69</td>
</tr>
</tbody>
</table>

Feedstock C possesses the highest $\alpha_{st\eta}$ value at all temperatures, while the lowest are associated with feedstock $B$. Feedstock $C$ will therefore yield high quality MIM products. The lower value in the case of feedstock $B$ is attributed to its poor temperature sensitivity property. Therefore, it was discarded for further studies.

5.3.5 Fracture surface micrographs

The good rheological properties of feedstock $C$ arises from the higher interaction between binder system and Ti powders. By studying the fracture surface micrographs, this interaction can be verified as shown in Figure 5.7.

![Fracture surface morphologies of Feedstock A (left) and Feedstock C (right).](image)
For feedstock $A$, it can be seen that fracture surface is of a rounded nature (dimples) arising from the particle pull-out during fracture (Fig. 5.7, left). This particle pull-out occurs due to poor adhesion between metal particles and binder system. On the contrary, the fracture surface of feedstock $C$ is smooth and very few dimples are present (Fig. 5.7, right), which suggests good adhesion between binder system and titanium particles. This strong adhesion improves the powder dispersion in the binder during mixing, which in turn reduces the flow viscosity of the feedstock, and results in better rheological properties. This will be further explained in the subsequent section. The improved rheological properties ultimately lead to excellent moulding of green parts.

### 5.3.6 Feedstock homogeneity

Feedstock homogeneity is another tool that can be used to determine the powder-binder interaction. Poor powder-binder interaction causes inhomogeneous feedstock, which then leads to varying density within the feedstock. By monitoring density of a feedstock in randomly selected samples, estimation of feedstock homogeneity can be determined. A homogeneous feedstock will have a low standard deviation value. Table 5.3 compares the pycnometer density values of two feedstocks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Feedstock $A$ (g/cm³)</th>
<th>Feedstock $C$ (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.1404</td>
<td>3.1321</td>
</tr>
<tr>
<td>2</td>
<td>3.1397</td>
<td>3.1459</td>
</tr>
<tr>
<td>3</td>
<td>3.116</td>
<td>3.1151</td>
</tr>
<tr>
<td>4</td>
<td>3.1147</td>
<td>3.1394</td>
</tr>
<tr>
<td>5</td>
<td>3.1675</td>
<td>3.114</td>
</tr>
<tr>
<td></td>
<td>Standard Dev.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.022</td>
<td>0.014</td>
</tr>
</tbody>
</table>

The achieved standard deviation value of feedstock $C$ is lower than that of feedstock $A$. This implies that feedstock $C$ is more homogenous compared to feedstock $A$ and has higher powder-binder interaction.

The mechanism of good interaction between binder system and metal particles in the case of feedstock $C$ lies in the chemistry of castor oil [159]. Figure 5.8 compares the chemical formula of castor oil and SA.
Fig. 5.8 Comparison of chemical formula of stearic acid (left) and castor oil (right). It should be kept in mind that castor oil is a combination of different fatty acids. However, ricinoleic, oleic and linoleic acids are the three main ingredients.

The surfactants contain one polar group and a non-polar hydrocarbon chain. The polar group latches onto the metal powder surface via dipole-dipole attractive forces and the non-polar hydrocarbon chain keeps it in the binder matrix [159]. The more this attractive force, the better will be the powder dispersion. SA chain has only one polar ester functional group present. In contrast, the castor oil chain has at least three polar ester functional groups in addition to a hydroxyl group, which enhance the dipole-dipole attractive forces. Therefore, in the case of castor oil feedstock, a better powder dispersion and higher powder binder interaction can be achieved, which ultimately leads to lower viscosity and better rheological properties.

5.3.7 Green strength comparison

In MIM primary and backbone polymeric constituents control the green strength of the samples and the green strength is dependent on their respective contents. The surfactants can also increase the green strength by effectively increasing the dipole-dipole attractive forces. The green strength of samples produced from feedstock A and C is shown in Figure 5.9. The mean flexural strength value for feedstock A is 7.3 MPa and for feedstock C it is 8.1 MPa almost 10% higher than feedstock A. This is in conjunction with the homogeneity and rheological analysis results and hence proves the effectiveness of castor oil as surfactant.
It is arguable that the presence of extra ester groups in castor oil molecule may lead to higher contamination in the case of reactive powders during thermal debinding. However, the amount of surfactant added is usually minimal when MIM of reactive powders is sought. Furthermore, the amount of castor oil required is less, when compared to stearic acid for the same solid loading.

5.4 Summary

This study has shown the significant effects of surfactant on the properties of powder feedstocks. It was determined that viscosity of feedstock is decreased using oil as surfactant; thereby a higher solid loading can be achieved. Furthermore, feedstock containing castor oil as surfactant possessed a higher flexural strength and higher mouldability index value than feedstock containing stearic acid as surfactant. The improved properties are attributed to the more interaction between binder and titanium powder and better dispersion of the powder due to the presence of extra polar groups in castor oil molecule.
Chapter 6 A new lubricant based binder system for irregular Ti powder MIM feedstock preparation

This chapter focuses on the preparation of homogeneous HDH Ti-MIM feedstocks using solvent mixing with emphasis on the development of a binder system for producing higher solids loading for irregular HDH-Ti powder feedstocks. Homogeneous mixing and solids loading are the factors which have a strong influence over the final product properties. Simple hot mixing and emulsion mixing are commonly used techniques to prepare feedstock and have certain limitations and drawbacks. Solvent mixing provides an excellent alternative. The HDH-Ti powders are associated with poor rheological properties, and for successful moulding, solid loadings are kept much lower than for spherical powders. A binder system is designed to enhance the rheological properties in this chapter. To obtain PEG/PMMA/lubricants based homogeneous Ti feedstocks, the binder and metal powders were mixed in the common organic solvent acetone and vacuum dried. SEM analysis, rheometer tests and torque measurements were performed subsequently.

Contents of this chapter are currently under review process in the journal of Advanced Powder Technology.

6.1 Introduction

The MIM process starts with mixing of metal powders with a binder system to obtain a homogeneous feedstock. This process is crucial for successful MIM operation, as any inhomogeneity, including bubbles, will be carried over to the next processing step [31]. Hot mixing by shear mixers is a widely used mixing technique to prepare feedstocks. However, this technique has certain limitations. It must be carried out above the melting temperature of the backbone polymer using high shear mixers and generally requires long mixing times depending on the equipment used. Special care must be taken when dealing with Ti-MIM feedstocks and it is recommended to provide argon gas cover in order to reduce the impurity uptake [20, 160]. Another option is to prepare feedstocks using backbone polymer emulsions to pre-mix feedstocks followed by hot mixing at relatively low temperatures. However, polymers emulsions can be costly, and add extra cost on already expensive Ti-MIM products. Solvent mixing provides an alternative to emulsion mixing at lower cost.

To lower the cost of Ti-MIM products often HDH irregular powders are used, but irregular powders are associated with poor rheological properties and are generally replaced with spherical powders for better moulding process [19]. Park et al. compares the rheological
properties of different powder systems in detail [90]. It has been proposed to use a spheroidizing technique to improve the flowability of irregular powders. However, this technique may not be feasible due to the extra cost of the spheroidizing process. Another option is to use binder components which reduce the interparticle friction, thereby improving the flowability of irregular powders.

To facilitate the use of irregular Ti-HDH powder in MIM by improving rheological properties, a new binder system is developed and described in this chapter, and a mixing technique is also designed to improve the homogeneity of feedstocks at lower cost compared to emulsion mixing. The rheological behaviour of feedstock based on new binder system is presented and compared with already developed binder system.

6.2 Experimental procedures

Two binder systems based on PEG ($M_w \sim 4000 \text{ g/mol}$) / PMMA ($M_w \sim 45000 \text{ g/mol}$) were prepared. The first binder system (GAS) contained a major fraction of PEG as the primary component and PMMA as backbone polymer. SA was added as a minor fraction to act as surfactant. The second binder system (PPMC) contained two different lubricants (20% by weight of total binder) along with PEG and PMMA. Solids loading of 50, 55 and 60 vol.% were used to prepare the feedstocks. Water debinding was carried out at 40 $^\circ$C for 10-h. Dog bone shaped specimens [Fig. 3.6(c)] were injection moulded. The injection temperature was selected on the basis of rheological experiments, while the injection speed was 30 cm$^3$/sec and the backing pressure was 14 MPa. Each moulded sample was visually inspected and weighed after every run for quality control.

6.3 Results and discussion

6.3.1 Solvent mixing

The homogeneity of a feedstock is crucial for MIM processing. Inhomogeneous feedstocks can lead to poor rheological properties, void formation, density variation, and poor dimensional stability of the moulded part [39]. Thus, proper selection of a mixing technique is essential to obtain high quality products. Low shear mixers such as Sigma blade or twin screw mixers should be avoided for feedstock mixing in the case of simple hot mixing. The problem with such mixers is that the backbone polymer starts sticking to the blades because of higher viscosity, creating poor distribution even though stable torque values may be indicated. It is recommended to use high shearing mixers [31, 161]. Another common mixing
technique is to use polymer emulsions instead of powders/granules, and generally this involves mixing of primary polymer, surfactant and metal powders in a backbone polymer emulsion followed by hot mixing. Though good homogeneity can be achieved, high pricing of polymer emulsions makes it less favourable. Solvent-hot mixing is a potentially low cost technique for producing homogeneous Ti-MIM feedstocks compared to emulsion-hot mixing, as shown by the SEM micrographs at two different magnifications, Figure 6.1.

From Figure 6.1, covering of Ti particles with binder in both feedstocks can be seen. It is worth noting that better covering of Ti particles can be achieved by using PPMC binder system. This ultimately leads to lower viscosity of feedstock. This is further discussed in next section.

The time versus torque graph gives a good estimation of feedstock homogeneity. The torque value for inhomogeneous feedstocks can sometimes be very high, have high distinctive peaks and take a long time to stabilize. Time-torque graphs also give an idea about the feedstock
viscosity. Torque stability is generally achieved quite early with low torque values for low viscosity feedstocks, Figure 6.2.

![Fig. 6.2 Time versus torque graph for the feedstocks composed of two binder systems at 60vol% solids loading. PPMC Feedstock also has low torque value compared to GAS Feedstock suggesting lower viscosity.](image)

It is clear from the Figure 6.2, the irregular peaks disappear early suggesting the good homogeneity of pre solvent-mixed feedstocks. The mixing of metal powders with polymers-acetone mixture is thus very important. As acetone is evaporated it leaves behind a mixture in which both primary and backbone polymer molecules are evenly dispersed with the metal powders. If properly stirred, the resulting feedstock is homogeneous with little further mixing being required, and even low shearing mixers such as the sigma blade can be used to prepare homogeneous feedstock batches.

Homogeneity of the feedstocks can also be verified through use of the capillary rheometer [162]. For a homogeneous feedstock, the flow rate through a small die remains constant for a given pressure. Small variation of flow rate versus testing samples indicates homogeneous feedstock. In case of inhomogeneous feedstocks flow rates through a small die may vary sharply among testing samples at any given constant pressure, Figure 6.3.

It was observed that pre-solvent mixing of feedstocks not only decreases the time required to achieve homogeneity by hot mixing, but it also reduces the mixing temperature, thus further reducing the level of impurity pick-up during hot mixing. Figure 6.3 shows the variation in flow rates of feedstocks prepared at 120 °C by hand mixing for 20 mins after solvent mixing.
6.3 Flow rates behaviour of two feedstocks system at a constant pressure and temperature. There are very few fluctuations in the flow rates of two feedstocks even though only hand mixing was employed.

Time savings can also be achieved in solvent-hot mixing by optimizing parameters such as, acetone quantity, mixing speed, and mixing temperature.

6.3.2 Comparison of the two feedstocks systems

As explained earlier, In MIM, successful mould filling depends on the rheological properties of the feedstock. The two most important properties are flow behaviour and viscosity in particular [19]. Pseudoplastic flow (decreasing viscosity with increasing shear rate) of feedstocks upon shearing is usually sought in injection moulding to ease mould filling, minimize jetting and help in retaining component shape during the cooling process. The flow behaviour is characterized by the viscosity dependence on shear rates and is given by the modified power law (Eq. 4.4) [143].

A general rule of thumb is, the higher the packing density of the powder, the higher will be the solids loading with better rheological properties as more binder is available which in the case of poor packing density powder gets entrapped between the particles. The angular powder has a lower packing density and higher interparticle friction compared to spherical powders, so solid loadings are much lower to accommodate better rheological properties [19, 30]. As with homogeneity, solid loading is a crucial factor that determines the final product properties. Low solids loading are not desirable due to risk of slumping during debinding, high sintering time and high shrinkage during sintering. However, irregular powder particle feedstocks exhibit better shape retention during debinding because of high interparticle friction [19, 30].
For the GAS Feedstock system, 50vol% and 55vol% solids loading exhibited pseudoplastic behavior, while for 60vol% solids loading Feedstock separation occurred. On the other hand the 60vol% PPMC Feedstock system was pseudoplastic in nature. The two Feedstock systems are compared in Figure 6.4.

![Figure 6.4 Log shear rate versus Log true viscosity. The n-1 values are; -0.52 for 50vol% GAS, -0.06 for 60vol% GAS, -0.87 for 55vol% GAS and -0.47 for PPMC Feedstock systems respectively.](image)

From Figure 6.4, although 50vol% GAS Feedstock has the ideal n-1 value with low viscosity, such low solids loading are not desirable due to high shrinkage during sintering. The 55vol% GAS Feedstock has better shear rate dependency (n-1= -0.87) than 60vol% PPMC Feedstock (n-1= -0.47), but PPMC Feedstock will have better dimensional stability and sintering properties because of higher solids loading. The 60vol% GAS Feedstock first exhibited pseudoplastic behavior with high viscosity, but at higher shear rates its viscosity increases with shear rates due to feedstock separation. The plausible reasons for this feedstock separation are; poor packing density and lack of lubrication. When such feedstocks are injection moulded, feedstock separation occurs between the sprue and the runner due to increasing shear rates leaving behind highly compacted powders in the sprue bush. This compacted body can sometimes be very difficult to remove. This feedstock separation can also lead to explosion during injection process depending on the injection speed and injection volume. It is assumed that titanium powders behave in a fashion similar to aluminum and zirconium powders and will explode if dispersed at concentrations greater than 40 g/m³ [17]. The PPMC Feedstock system contains two different lubricants that significantly reduce the
interparticle friction thereby minimizing the risk of feedstock separation with reduced viscosity, Figure 6.5.

Fig. 6.5 Viscosity comparison of two Feedstock systems at different solids loading.

The difference in viscosity increases with increasing solids loading due to higher interparticle friction. In general, 40% reduction in viscosity can be achieved by using PPMC binder system. However, it may be noted that the viscosity is still not ideal for excellent moulding operation. According to German [31], for excellent moulding the viscosity of the feedstock should be below 1000 Pa.s at moulding temperature in the shear rate range of $10^2$ to $10^5$ S$^{-1}$. Viscosity at low to medium shear rates ($10^2$ to $10^4$ S$^{-1}$) is generally more important, as most of the injection moulding machines work in this shear rate range with highest shear rates occurring at the gates [163]. The desired viscosity was achieved at 53vol% for PPMC Feedstock (Figure 6.5) and at 50vol% for GAS Feedstock system respectively, indicating a 3% increase in solids loading can be achieved by using PPMC binder system. Further increase in solids loading can be achieved by mixing irregular and spherical powders. To keep the viscosity below 1000 Pa.s while keeping the solids loading above 55 vol%, a mixture of irregular and spherical powders was used to prepare PPMC Feedstock. Figure 6.6 compares the viscosity at different solids loading for different powder feedstocks determined by capillary rheometer (although torque measurements during mixing are generally used to determine the optimum solids loading, this technique may produce erroneous results, if low shear mixers are used. Capillary rheometer produces reliable and accurate results because of more realistic shear rates and conditions to injection moulding). [19]
It can be seen from Figure 6.6, that the highest critical solids loading are achieved in the case of GA- spherical powder PPMC Feedstock (65 vol%) due to inherently higher packing density with low interparticle friction as compared to irregular powders (53vol%). The ideal rheological properties can be achieved by using solids loading 1-2% lower than the critical value. It can also be extracted that critical solid loading of feedstock based on irregular and spherical powder mixture depends on the weight proportions of the two powders. This weight proportion should be chosen depending on the cost, and mechanical properties requirements.

The 58 vol% PPMC (50/50 wt% HDH-Ti + GA-Ti) Feedstock, hereafter called as “Feedstock A”, was also pseudoplastic in nature with low viscosity and better n-1 value compared to 60vol% HDH-Ti PPMC Feedstock at 190 °C. The low viscosity also provides an opportunity to use lower injection moulding temperature, as shown in the Figure 6.7.
Fig. 6.7 Shear sensitivity of Feedstock A at two different temperatures.

Feedstock A has a slightly lower n-1 value at 175°C mainly because of viscosity dependence of temperature. Even though it has higher viscosity at 175°C, it is just under the design limit. Thus, it can be injection moulded at 175°C, in the medium pressure range.

The sintered dog bone specimen (Figure 6.8) showed good shape retention, higher strength (~635 MPa) and low elongation (2%). The low elongation is justified considering the initial high impurity contents of HDH powder and the use of lubricants. Thus, this binder system is ideal for Ti-MIM applications where elongation is not the main requirement for instance, luxury items [60, 61].

Fig. 6.8 Sintered dog-bone sample

6.4 Summary

Solvent mixing is a low cost method to produce homogeneous Ti-MIM feedstocks compared to emulsion mixing. However, proper safety measures should be applied when dealing with organic solvents with high vapour pressure.

With the help of new binder system PPCMC, higher solids loading for irregular Ti powder feedstocks can be achieved. However, viscosity may not be ideal for injection moulding at solids loading higher than 53 vol%. The design viscosity at higher solids loading can be achieved by mixing irregular and spherical powders, the weight proportion of which depends
on the desired cost, rheological and mechanical properties requirements. By using this binder system high strength, good dimensionally stable Ti-MIM parts can be made at low cost which makes it ideal for less critical applications.
Chapter 7 Suitability of PEG/PMMA based metal injection moulding feedstock: An experimental study

This chapter extracted from ref. [164] comprehensively investigates the feasibility of PEG/PMMA for excellent MIM process. Feedstocks were made using stainless steel 17-4PH powder and subsequently conventional and micro injection moulding (μMIM) processes were carried out. DSC and fracture surface analysis of moulded samples were performed for complete evaluation. It was found that despite great potential there are certain drawbacks associated with this binder system. The main problem was the formation of shrinkage voids during solidification. It is proposed that this binder system is more suitable for μMIM process that has an inherently higher cooling rate.

7.1 Introduction

PEG/PMMA based binder system for PIM has been extensively reported in the literature. Sidambe et al. [27] reported that CP-Ti feedstocks, prepared using PEG (with a molecular weight of 1500 g/mol)/PMMA/SA binder system and with 69 vol.% powder loading, demonstrated good rheological properties. The PEG was completely removed at 55 °C after 5-h soaking in water. Moreover, the sintered samples showed excellent mechanical properties. Liu et al. [108] optimized compositions of PEG/PMMA binder system for ceramic injection moulding. They concluded that defects free debound parts can be obtained if the percentage of water soluble binder (PEGs) is about 62–66 wt%. Chuankrerkkul et al. [23] used PEG/PMMA binder for injection moulding of tungsten carbide-cobalt (WC-Co). Chen et al. [138] studied the water debinding kinetics of PEG/PMMA system for Ti-MIM. Omar et al. [165] investigated the influence of the PMMA content on the moulding, debinding and sintering behavior of injection moulded samples of 316L stainless steel feedstock. It is concluded that an increased PMMA content increases the apparent viscosity of the binder system, increases the strength of the mouldings and reduces the PEG leaching rate at the fixed volumetric powder fraction. Similarly, Sulong et al. [22] optimized injection moulding parameters for 16 μm Stainless Steel (SS316L) powder feedstock. The binder system contained PEG (73 wt%), PMMA (25 wt%) and stearic acid (SA-2 wt%).

However, certain drawbacks, such as higher mixing time and shrinkage voids were found during formulating PEG/PMMA feedstocks. This chapter addresses those problems and attempts are made to rectify them. Alternatively, solutions have been proposed. This research
will help improve the quality of PEG/PMMA based PIM feedstocks, thus leading to better quality PIM products.

7.2 Experimental procedures

Water atomised stainless steel 17-4PH powder was used. The binder system contained 83 wt% PEG ($M_w \sim 10,000 \text{g/mol}$), 15 wt% PMMA, $M_w \sim 45,000 \text{g/mol}$), and 2 wt% surfactant. Two solid loadings (60 vol.% and 62 vol.%) were selected to prepare feedstocks. In this chapter, we present the experimental results for the 60 vol.% feedstock only.

Homogeneity of feedstocks was determined with Accupyc II Gas Pycnometer.

Injection moulding was carried out with an Arburg 220S injection machine at various injection parameters. Since the injection pressure, nozzle temperature and injection speed did not noticeably affect the formation of moulding voids, we only report the results obtained from the samples prepared using the following two typical sets of injection moulding parameters. For conventional injection moulding, the MPIF standard dog bone [Fig. 3.6(b)] samples were made at 40 MPa moulding pressure, 128 °C nozzle temperature and with 15 cm$^3$/s injection speed. The micro metal injection moulding (μMIM) specimens were made at 10 MPa pressure, 110 °C nozzle temperature and with 8 cm$^3$/s injection speed. These two types of specimens are shown in Figure 7.1.

![Fig. 7.1 (a) Standard dog bone MIM specimen, (b) Micro-channel specimen for μMIM with the maximum thickness of 1mm, length 20mm, and width of 8.75mm. The wall thickness of micro channels is 0.2 mm](image)

DSC studies were carried out on TA instruments DSC Q200. The temperature was ramped from 30 °C to 190 °C during heating cycle and then dropped from 190 °C to 10 °C during cooling cycle. The heating cycle was first stabilised at 30 °C.
7.3 Results and discussion

7.3.1 Feedstock formulation

To prepare a homogeneous feedstock, PEG/PMMA binder based feedstocks require lengthy mixing at a high temperature (~ 170 °C) mainly due to the toughness of PMMA. Such high a temperature leads to PEG oxidation if mixing is done in air. This can be detrimental to final part properties in case of reactive materials. Anwar et al. [166] studied the PEG/PMMA binder feedstock formulation and a method was suggested which comprises of PMMA emulsion and PEG solution. The PEG solution, PMMA emulsion and metal powders were mixed together to make a homogeneous slurry, which was then dried to form the feedstock. The subsequent tests showed good homogeneity of feedstocks. Although this technique can produce fairly good homogeneous feedstocks at low temperatures, additional cost of PMMA emulsion can be a drawback.

Another mixing procedure that has been defined in the literature [167] and employed in this thesis is solvent-hot mixing. As explained in the previous chapter section (6.3.1), solvent-hot mixing is a potentially low cost technique for mixing PEG/PMMA based feedstocks and can produce homogeneous feedstocks at relatively low temperatures (130 °C). Although the effectiveness of this technique has been explained in detail in previous chapter section (6.3.1), Nonetheless Figure 7.2 compares the pycnometer densities of feedstocks prepared using either solvent-hot mixing at 130 °C or conventional hot mixing at 170 °C for 3-h. The standard variation of pycnometer density measured in five random samples was very small and thence both feedstocks exhibited excellent homogeneity.
7.3.2 Void nucleation

Even though both feedstocks were homogeneous and showed no abnormalities, such as agglomeration or binder pockets during mixing, irregular shaped voids appeared as the feedstocks reached room temperature, Figure 7.3.

Initially, it was thought that these voids were formed due to gas entrapment and may be rectified during injection moulding process. However, the voids were persistent even in injection moulded samples, regardless of the injection parameters. In most cases, the voids were found in the middle of the samples (Figure 7.4).
Fig. 7.4 Fracture surfaces of injection moulded samples of PEG/PMMA binder based feedstock (right) and a commonly employed binder system (left) are compared. Void is clearly visible and occurs in the middle of green part. It should be noted same injection parameters were applied in both cases.

The void formation is therefore an intrinsic result of PEG/PMMA binder; it is not related to the injection moulding parameters such as injection temperature, pressure and speed. Moreover, volume fraction of solid content also had no influence on void formation. This was verified by hot mixing the same binder system. Upon cooling, the similar voids appeared with a rough surface morphology.

7.3.3 Discussion and proposed solutions

The PEG used in this study is a crystalline solid and has a well-defined melting point depending on the molecular weight. Therefore, upon crystallization it undergoes a significant volumetric shrinkage [132, 168]. In comparison to PEG, PMMA is an amorphous polymer having glass transition temperature of 106 °C [169]. In the PEG/PMMA blends, solidification leads to segregation of PEG, concomitant of simultaneous rejection of the amorphous component [170]. Moreover, this segregation is interlamellar and takes place up to 40 wt% of PMMA content.

PEG/PMMA blends have been studied in literature albeit most of the times the PMMA contents are relatively high compared to compositions typically employed in MIM. Al-Hussam et al. [171] found that various ratios and concentrations of polymer blend systems were either miscible or compatible mixtures. Zhang and Zhang [172] studied coatings of PMMA/PEG copolymers with different PEG content and demonstrated that all of copolymer surfaces had island microphase separation structure and attributed it to columnar PEG phase dispersion on the PMMA matrix. Sari et al. [173] studied PEG/PMMA blends as novel form-
stable phase-change materials (PCMs) using the solvent casting method and found 70/30 w/w % PEG/PMMA blend as the potential form-stable PCM. They suggested that the interaction between PEG and PMMA is due to carbonyl–hydroxyl interaction. Although their blend surface was not smooth and showed some irregularities, no explanation was provided for such behaviour.

The void formation has also been reported in another blend containing PEG. He et al. [174] investigated the effects of blending chitosan with PEG on surface morphology and crystallization. It was found that with increasing PEG content, the crystallinity of chitosan-PEG blend decreased considerably. It is suggested that not only the stiff chitosan chain inhibited crystallization of PEG, but also the hydrogen bond interaction between chitosan and PEG restrained the movement of chitosan molecules and even partially destroyed the original crystalline structure of chitosan leading to reduced crystallization. Moreover with increasing the PEG content, the surface microstructure of blend films changed from smooth and featureless to the surface morphology filled with holes with varying sizes. This phenomenon was attributed to segregation of PEG and chitosan phases during solution volatilization due to the limited compatibility.

Based on our experimental results, it is proposed that these solidification defects are the result of difference between crystallization temperature of PEG and glass transition temperature of PMMA. During solidification, as temperature drops PMMA molecules starts to segregate at interlamellar regions (similar to solidification of metal castings, where impurities segregate in the centre) and form a network, while PEG spherulite starts to nucleate and grow around PMMA molecular chains with decreasing temperature. When temperature drops below the glass transition temperature of PMMA its molecular chains become rigid again. As temperature further falls and PEG crystallization temperature is reached, the rigid PMMA network impedes the volumetric shrinkage upon crystallization. This hindrance to volumetric shrinkage along with high interaction between PEG and PMMA molecules thus, results in void formation. In the case of MIM, the outer surfaces of samples cool down quickly, giving less time for PEG to crystallize. However, at centre PEG has enough time to crystallize and the PMMA chain resists this shrinkage, resulting in void formation upon solidification. That is why this phenomenon can be characterized as solidification defect of PEG/PMMA binder system. The tendency of PMMA segregation increases with PMMA content up to 40% [170] and results in more void nucleation. In fact, when PMMA content was increased to 15% void nucleation became more frequent.
It is possible that the high interaction between PEG and PMMA also results in void nucleation. However, nucleation of voids due to hydroxyl group and carbonyl group interaction or hydrogen bonding has not been reported in the literature.

Based on the above hypothesis, it is hypothesised that these voids could be avoided by inhibiting PEG crystallization, thereby limiting volumetric shrinkage upon cooling. One way to inhibit PEG crystallization is to incorporate sugar in the binder system. Izutsu et al. [175] studied the effects of sugars and different polymers on crystallization of PEG in frozen solutions. They demonstrated that sugars can be very effective in inhibiting PEG crystallization. Sugars such as sucrose and glucose are easy to remove and may be removed through water debinding along with PEG. The blending issues, high viscosity and high impurity uptake of feedstocks remain a concern especially in the case of sucrose that starts to decompose upon melting. Another option is to incorporate polyvinylpyrrolidone (PVP) into the matrix [175, 176]. PVP is hydrophilic, amorphous polymer and commonly used in pharmaceutical industry as a crystallization inhibitor. In addition, PVP is compatible with both PEG [177] and PMMA [178, 179]. Therefore, the incorporation of PVP may not increase overall viscosity of the system significantly and can be removed simultaneously along with PEG during water debinding. Given that PEG does not fully crystallize in the presence of PMMA, the amount of PVP could be minimal [180]. The molecular weight of PEG also affects the crystallization tendency of PEG in the presence of PMMA. As reported in Ref. [180], PEG crystallization decreases as its molecular weight decreases. However, it should be kept in mind that low molecular weight PEG results in poor rheological properties and leads to poor moulding operation [131].

Cooling rate has a profound effect on the crystallization of PEG [181]. As the cooling rate is increased, the PEG crystallization temperature ($T_c$) decreases. Similarly, crystallization of blends containing PEG can also be retarded by rapidly cooling blend from its melt temperature to below glass transition temperature. The degree of crystallization of Poly(Lactic Acid) PLA/PEG blends have been reported in Ref. [182]. In the case of PLA/PEG (70/30, wt/wt) blend maximum crystallinity was achieved with a cooling rate of $\leq 5 \, ^\circ\text{C/min}$. On the other hand, only 27% of crystallinity was achieved when cooling rate of 20 $^\circ\text{C/min}$ was employed, and $T_c$ was shifted from 32 $^\circ\text{C}$ to 15 $^\circ\text{C}$ [182]. However, it should be noted that at lower $T_c$ (below 40 $^\circ\text{C}$) a partial crystallization already occurs before reaching $T_c$ [183].
During conventional injection moulding process, it is difficult to achieve a high cooling rate for thick parts. However, in the case of μMIM, cooling rate can be very high. Figure 7.5 compares the DSC curves for micro and conventional injection moulded samples.

Fig. 7.5 DSC curves for micro and conventional injection mouldings with the (PEG/PMMA) binder system. The energy of melting for two samples was 10.86 J/g for μMIM sample and 15.44 J/g for conventional MIM sample. Furthermore, the T_c has been shifted to lower temperature for μMIM sample.

It can be seen from Figure 7.5, that μMIM sample has a broader but lower exothermic peak than the conventional MIM sample. It is worth noting that PEG does not fully crystallize even in the case of conventional MIM, particularly near surface. This explains that in case of conventional MIM most of the voids occurred along the centerline which is the last region to cool down and has the lowest cooling rate.
Fig. 7.6 PEG crystallization within the conventional injection moulded samples. This test was carried out for 3 different samples; the mean values of energy of melting are 9.4 J/g for region ~0.5 mm below top surface and 8.2 J/g for top surface region respectively. The thickness of the top surface region was selected as 0.3 mm

Figure 7.6 gives an illustration of how PEG crystallization varies within the samples. The degree of PEG crystallization increases as the distance from the top surfaces increases. Moreover, the melting curve has been shifted to higher temperature, which is in accordance with the literature [183]. This temperature gradient within the sample gives sufficient time for PEG to crystallize, thereby leading to void nucleation at the center-line. The thicker the sample, the higher will be this temperature gradient. On the other hand, in μMIM samples, the temperature difference between the center and top surfaces is considerably lower, giving PEG less time for complete crystallization. Therefore, due to inherently quicker cooling process during μMIM, PEG crystallization can be reduced to a level where it does not produce macro size voids inside the samples. This has been verified by the fracture surface analysis of moulded samples, Figure 7.7.
As shown in Figure 7.7, voids were clearly visible in the case of conventional injection moulding and occurred in the middle of the sample. This further validates the DSC results. It is interesting to note that there might be voids with size of below 10μm (marked by red circles). However, voids of the size > 50μm as in Figure 7.7(a) are of concern. Such voids are usually difficult to remove during subsequent sintering process. Moreover, it can also lead to excessive grain growth around such voids. Figure 7.8 shows the typical morphology of one void. It can be seen from Figure 7.8, that there are no particle pull-out impressions within the surface of void. Moreover, the irregular internal surface and a wormhole type appearance implies a typical solidification defect [184, 185], whereas voids due to air bubbles are round in shape and have smooth internal surfaces [185].
Fig. 7.8 Morphology of a void occurred during solidification of a conventional MIM sample

7.4 Summary

PEG/PMMA based binder system has been extensively reported in the literature. However, it was found that there are several problems associated with this binder system. This includes a higher mixing time and nucleation of macro-voids during solidification which are difficult to remove during sintering. The higher mixing time is associated with rigidness of PMMA molecules. This problem can be averted by using solvent-hot mixing. The nucleation of voids during solidification is associated to PMMA molecular chains hindering volumetric shrinkage of PEG upon cooling, which leads to void formation. The void formation can be minimized to a point where it is not detrimental to final properties by reducing PEG crystallization via applying higher cooling rates. This can be achieved by decreasing the mould temperature to a minimum operable temperature. Since the cooling rates in μMIM are inherently higher than conventional MIM process, it is suggested that the PEG/PMMA binder system is more suited to μMIM and this has been verified in our additional μMIM experiments. To fully realise the potential benefits of this system in the case of conventional MIM, a PEG crystallization inhibitor such as PVP should be incorporated in the binder system.
Chapter 8 Incorporation of PVP into PEG/PMMA based binder system to minimize void nucleation

In spite of its great potential, the PEG and PMMA binder system was found susceptible to void nucleation, as the rigid PMMA chains hinder PEG volumetric shrinkage upon cooling. It has been reported in the previous chapter (Chapter 7) that this void formation could be minimized by either using higher cooling rates or by incorporating a crystallization inhibitor in the binder system. Hence, it is suggested that this PEG/PMMA binder system is more suitable to μMIM where cooling rates are inherently higher. In this chapter, efforts have been made to increase the workability of this binder system for conventional metal injection moulding by adding a crystallization inhibitor, polyvinylpyrrolidone (PVP). DSC, rheological property measurements, solvent and thermal debinding behaviour, and fracture surface analysis of the moulded samples were performed. It was found that by incorporating PVP into PEG/PMMA binder system, high quality void-free MIM components can be produced while maintaining the clean nature of PEG/PMMA binder system.

This chapter is currently under review process in the journal of Materials & Design.

8.1 Introduction

Although PEG/PMMA binder system has been well documented and optimized in the literature, we found that this binder system leads to voids formation in the green parts as has been explained in the previous chapter (Ch 7) [164]. Based on the experimental results, it is proposed that these voids are a result of difference between crystallization temperature of PEG and the glass transition temperature of PMMA. Furthermore, it has been demonstrated that these voids can be minimized by reducing or retarding the PEG crystallization by either applying a higher cooling rate or using a crystallization inhibitor [164].

In the previous chapter it has been successfully proved that this voids formation can be minimized to a certain extent by applying higher cooling rates [164]. Therefore it is suggested that this binder system is more suited to μMIM, where cooling rates are inherently higher due to the much smaller sample thickness. In conventional MIM, cooling rates can only be increased to a certain extent by decreasing mould temperature; hence the voids may not be completely eliminated in the injection moulded parts. In addition, a high cooling rate poses the risk of distorting the moulded samples due to thermal stress. A more robust and
An effective approach is to incorporate a PEG crystallization inhibitor into the binder systems in order to fully savour the potential of this binder system.

Izutsu et al. [175] documented the effects of different polymers and sugars on crystallization of PEG in frozen solutions. They reported that sugars can be very effective in inhibiting PEG crystallization as mentioned in the previous chapter (Ch 7). However, the difficulty of blending, high viscosity and high impurity uptake associated with the use of sugar in the feedstocks rule out the suitability of sugars, particularly for reactive metal powders. An alternative option is to incorporate polyvinylpyrrolidone (PVP) into the PEG/PMMA blend. As explained in previous chapter (Ch 7), PVP is an amorphous, non-toxic and water soluble polymer. It is widely used in the pharmaceutical industry as a crystallization inhibitor, disintegrant, suspending agent, coating agent and tablet binder [186]. In addition, PVP is compatible with both PEG [177] and PMMA [178, 179]. Unlimited solubility of the high molecular weight PVP in the short chain PEG is well established, arising from the hydrogen bonding between the hydrogen atom of the PEG terminal groups and the electronegative oxygen atom in the carbonyl groups of the monomer units of the PVP chains [177]. Although PVP is not miscible in PEGs with a molecular weight of above 1000 g/mol, the blend may still be compatible, considering the functional groups of both polymers. Therefore, the incorporation of PVP may not increase the overall viscosity of the binder system. Equally importantly, it can be removed simultaneously along with PEG during water debinding. The one drawback associated with PVP usage could be its high cost. It is noted that the PEG crystallization is partially inhibited in the presence of PMMA, as reported in Ref. [180]. In addition, PEG crystallization temperature decreases as its molecular weight decreases. Considering these factors, the required amount of PVP may not be high to eliminate the void formation if lower molecular weight PEGs are used in this PEG/PMMA based binder formulation [181].

Nonetheless, the incorporation of PVP into PEG/PMMA binder system has not yet been studied in the literature. This chapter investigates the effects of PVP on the binder system in detail. The new findings obtained from this investigation will help increase the use of PVP-modified PEG/PMMA binder systems in the MIM industry, and potentially improve the quality of MIM products without compromising the environment-friendly nature of the binder mixture.
8.2 Experimental procedures

Water atomised stainless steel 17-4PH powder was used. The binder system contained PEG, 20 wt% of PMMA ($M_w \sim 45,000$ g/mol) as the backbone polymer and SA. PVP was added with respect to the weight proportion of PEG and three different proportions, 10, 30 and 32 wt/wt% respectively, were used. A solid loading of 60 vol% was used to prepare feedstocks for all binder formulations.

Feedstock preparation started with dissolving PEG, PMMA and SA in acetone as has been reported in experimental part of this thesis (Ch 3). When all three components were completely dissolved, the solution temperature was gradually increased to 80 °C to increase acetone evaporation rate. Once acetone was evaporated, PVP was then added in the binder system and mixed at 125 °C in double planetary mixer for 30 min. Afterwards, Stainless steel powders were gradually added into the binder system and kneaded at 30 rpm for 60 min. Homogeneity of feedstocks was determined with Accupyc II Gas Pycnometer.

DSC and TGA studies were carried out on TA instruments DSC Q200 and TGA Q500 respectively. In the case of DSC the temperature was ramped from 30 to 200 °C at 5 °C/min during heating cycle and then dropped from 200 to –5 °C during cooling cycle. The heating cycle was first stabilized at 30 °C. For TGA study the temperature was ramped from room temperature to 525 °C at 10 °C/min. Both DSC and TGA were performed in pure nitrogen atmosphere.

Injection moulding was carried out with an Arburg 220S injection machine. The injection moulding parameters were varied for full evaluation. For simplification purpose, the ranges of different parameters have been presented here. The injection pressure was varied from 20 MPa to 40 MPa. The nozzle temperature was varied between 110 °C and 130 °C, while the injection speeds were 8 to 15 cm$^3$/s.

Thermal debinding was performed in a Carbolite tube furnace (STF 15/450) in pure nitrogen atmosphere. The heating profile was selected based on the TGA result. The brown parts were then sintered in a Thermal Technology LLC sintering furnace under hydrogen atmosphere at 1325 °C for 2-h. Tensile test was carried out with an INSTRON Universal Mechanical Testing Machine.
8.3 Results and discussion

8.3.1 Inhabitation of PEG crystallization

PVP structure is shown below in Figure 8.1.

Fig. 8.1 Structure of PVP molecule, consisting of amide group [187].

Figure 8.1 presents the molecular structure of PVP. It is known that polymers consisting of an amide group, such as PVP, are good proton accepters. PEG, on the other hand, carries two proton-donating hydroxyl groups at its chain ends, giving rise to excellent compatibility between PVP and PEG [188]. It is generally agreed that PVP is also compatible with PMMA, although one report disputes this agreement [189]. However, no inhomogeneity was observed in any case during our feedstock formulations. All the binder formulations displayed single phase and excellent homogeneity, which affirms good compatibility amongst the components.

The initial binder composition included higher molecular weight PVP and PEG (Mw~10000 g/mol). However, higher molecular weight PVP started to crosslink at temperatures higher than ~130 °C, verified by DSC experiment as shown in Figure 8.2.

Fig. 8.2 Higher molecular weight PVP starts to crosslink around 130 °C in the presence of PEG. The release of energy around 140 °C during heating cycle of DSC thermal curve confirms this phenomenon.
It has been reported that the higher molecular weight PVPs start to crosslink at \(~150 \, ^\circ C\) in air; the presence of PEG may even accelerate this process. Additionally, the higher molecular weight PVP is difficult to remove during the subsequent water debinding process. The high molecular weight also increases the viscosity of the binder system. To mitigate these problems, PVP and PEG with lower molecular weights are recommended. In this study, we therefore selected PEG 1500 g/mol and a lower molecular weight PVP. Figure 8.3 presents the DSC results for the three different weight percentages of PVP in the PEG/PMMA binder system.

As shown in Figure 8.3, the heat absorption of PEG decreases as the PVP content is increased. The lowest PEG melting energy is observed when the PVP content is 32 wt/wt% of PEG. It is interesting to note that when the PVP content increased to above 30 wt/wt% of PEG, there was a sudden reduction in crystallization temperature. In the range of 10% and 30% of PVP, the crystallization temperature of PEG does not change much (around 17 °C). However, the crystallization temperature dropped to 6.7 °C when 32% of PVP was used. The simplest mechanism for PVP inhibiting PEG crystallization could be due to the interaction between PVP and PEG [190, 191]. Such interactions are well defined in the literature and are due to the hydrogen bonding between the hydrogen atom of the PEG terminal groups and electronegative oxygen atom in the carbonyl groups of the monomer units of the PVP chains [191].

In general, the crystallinity of polymers starts from the molecules assuming the lowest energy conformation and aligning themselves (partially or completely) like parallel rods [192]. When PVP is combined with PEG, the PVP molecules interact and encapsulate the PEG molecules,
destroying their molecular conformity and restraining the PEG molecules from packing together. Increasing the PVP content consequently enhances this restraining force and/or increases the time needed for the PEG molecules to attain packing order. Therefore, PEG crystallization temperature decreases sharply as the PVP content is increased above a certain concentration.

Although the samples containing the lowest amount of crystallized PEG are preferred, the difference in heat absorption between feedstocks containing 30 wt% and 32 wt% PVP is minimal. No voids were found in either feedstock during the SEM analysis of their green part fracture surfaces, as shown in Figure 8.4.

![Fracture surface morphologies for feedstocks with different PVP contents](image)

**Fig. 8.4 Fracture surface morphologies for feedstocks with different PVP contents, a) no PVP addition, b) PVP 10 wt/wt% of PEG, c) PVP 30 wt/wt% of PEG, d) PVP 32 wt/wt% of PEG**

As shown in Figure 8.4, an increased PVP content leads to the reduction of void formation. In the case of no PVP incorporation, macro-voids are visible on the fracture surface of the feedstock, with an average diameter of the voids being approximately 90 μm ± 6 μm (Figure 5 a, designated hereafter as Feedstock A). The size of voids was estimated by SEM observations and an optical micrograph analyzer. In the case of 10 wt% PVP addition, some
interconnected voids are still visible (marked by red circle in Figure 5 b). However, the size of the voids is reduced considerably, as compared to Feedstock A. A further PVP increase from 30 and 32wt% in the feedstocks has completely eliminated voids. The feedstock containing PVP 30 wt/wt% of PEG was analyzed hereafter and is designated as Feedstock B.

8.3.2 Shear sensitivity

Binders containing lower molecular weight PEG usually have poor rheological properties and tend to separate from powder at higher shear rates as has been explained in Chapter 4 of this thesis [131]. This phase separation causes technical problems when the injection molding of intricate shaped component is required. Due to interaction between PEG and PVP, the incorporation of PVP may lead to better rheological properties. Shear rate dependence of viscosity can be described by power law (Eq. 4.4). Figure 8.5 plots the log viscosity versus log shear rate for feedstock B.

![Log viscosity vs log shear rate for Feedstock B](image)

**Fig. 8.5 Viscosity dependence of Feedstock B on shear rate for three different temperatures**

Figure 8.5 displays the $\eta$ vs $\dot{\gamma}$ graph for Feedstock B. It can be seen that Feedstock B is pseudoplastic in nature and viscosity is well below 1000 Pa.s at the lowest shear rates at all temperatures. Such a viscosity value complies with the injection molding requirements. It is interesting to note that shear sensitivity does not change significantly as the temperature changes. This less sensitive shear with temperature will ease the injection molding operation. Furthermore, we did not observe any feedstock separation at higher shear rates; a common problem associated with feedstock composed of lower molecular weight PEG binders. The powder separation is related to a lower interaction between the powder particles and binder system arising from smaller molecular chains as mentioned before (Ch. 4) [131]. The longer
chains of PVP molecules increase the number of contacts with the metal powder, thereby increasing the shear rate dependency. Moreover, no effect on moldability was observed, thereby suggesting that good interactions between PVP, PEG and powder particles exist.

8.3.3 Solvent debinding

Solvent debinding is a crucial practice performed during the binder removal process. Its two main purposes are: 1) the clean removal of the main binder component, which would otherwise lead to excessive impurity content, 2) creation of interconnected pores throughout the molded body so that the backbone binder component can be removed through these porous channels, without distorting the shape during the second debinding process [149]. The PEG extraction process via water debinding is driven by capillary action and the concentration gradient across the water bath as explained in chapter 4 (section 4.3.4). It starts from the surface of specimen and as water penetrates into the moulded body via capillary action, it extracts and dissolves the PEG molecules which are then transported into surrounding water bath due to concentration difference between green part and water bath. The process continues until the concentration equilibrium is achieved. It can be reasonably assumed that a similar mechanism will be valid for PEG and PVP mixture, as these three interact with each other through hydrogen bonding [193, 194]. The water debinding can be formulated using Fick’s diffusion model [131]:

\[
\ln \left( \frac{1}{100\% - F} \right) = \frac{D_e t \pi^2}{(2L)^2}
\]

Eq. 8.1

where \((100\% - F)\) is the percentage of PEG and PVP mixture removal, \(t\) (sec) is the time, \(L\) is the specimen thickness (mm). \(D_e\) (mm\(^2\)/sec) is the combination of the effective diffusion coefficients of both PEG and PVP - a collective parameter that include the effects of water penetration, the water-PEG and PVP mixture interactions to form hydrated complexes, as well as the transportation of those hydrated complexes. The diffusion depends on the molecular mobility which, in turn, is generally a function of temperature, molecular weight and powder particle size [149]. The higher the molecular weight and the smaller the particle size, the lesser is the molecular mobility. Figure 8.6 presents the water debinding profile for the Feedstock B.
Fig. 8.6 PEG and PVP mixture removal rate for Feedstock B. The water bath temperature was 40°C

It can be seen from Figure 8.6 that more than 80% of the PEG/PVP mixture can be removed after 10 h of water debinding. The mixture removal rate significantly slows down after 6 h of leeching, and it can be estimated that full removal may not be obtained within a feasible timeframe. However, thermal debinding can be employed after 75 wt% removal of a PEG and PVP mixture is achieved. It is worth noting that mixture removal rate is increased by increasing the water bath temperature.

8.3.4 Thermal degradation behaviour

It is of extreme importance to study the thermal degradation behaviour of a feedstock in MIM. The thermal debinding cycle for MIM is chosen primarily based on the TGA analysis. The thermal degradation of the PEG/PMMA binder system is well documented in the literature [21, 195]. The PEG/PMMA binder decomposition starts at around 300 °C and ends at 430 °C. The maximum weight loss occurs in a narrow temperature range around 400 °C. The PVP thermal degradation has also been previously studied; one excellent report was by Loría-Bastarrachea et al. [196]. They reported that the decomposition starts at ~395 °C and ends at 525 °C with the highest mass loss occurring at 480 °C. The predominant decomposition mechanism is the depolymerization to monomer of the polymeric main chain which yields vinyl pyrrolidone as the main volatile product during thermal degradation. The percentage of residue mass is close to 3.5%. Figure 8.7 presents the weight loss over a temperature range for Feedstock B.
Fig. 8.7 TGA curve of Feedstock B. The initial weight loss below 100 °C for sample before thermal debinding is attributed to moisture content. No weight loss was observed after thermal debinding.

It can be seen from Figure 8.7 that the highest mass loss occurs in the temperature range of 325 °C to 420 °C. Therefore, a low heating rate should be applied during this temperature range for the thermal debinding to completely remove the binder. The second small weight loss below 200 °C is related to the decomposition of the low molecular weight PEG in the air/nitrogen atmosphere [197]. Interestingly, there is no second peak at 480 °C associated with the highest PVP weight loss. In fact, the theoretical calculations suggest that only ~ 94% of the binder has been removed. This implies the existence of interactions between PEG, PVP and PMMA. Although the higher residue content is undesirable, significant amounts of PEG and PVP (~90%) can be removed via solvent debinding, as shown in the previous section, therefore posing minimal threat. Figure 8.7 also reveals that there is no recorded weight loss from the sample after thermal debinding, thus confirming the complete removal of binder components.

8.3.5 Mechanical properties

The standard tensile bars sintered from Feedstock B are displayed in Figure 8.8. The mechanical properties of the samples sintered from the two feedstocks are compared in Table 8.1.

Fig. 8.8 Sintered dog bone tensile bar
Table 8.1: Comparison of mechanical properties for two feedstocks

<table>
<thead>
<tr>
<th>Feedstock A</th>
<th>Feedstock B</th>
<th>ASTM minimum mandatory tensile properties requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ultimate Tensile Strength (UTS) MPa</td>
<td>Ultimate Tensile Strength (UTS) MPa</td>
<td>Ultimate tensile strength = 795 MPa Elongation = 4%</td>
</tr>
<tr>
<td>Elongation (ε) %</td>
<td>Elongation (ε) %</td>
<td></td>
</tr>
<tr>
<td>950</td>
<td>966</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>921</td>
<td>953</td>
<td></td>
</tr>
<tr>
<td>1.8</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>970</td>
<td></td>
</tr>
<tr>
<td>&lt;1</td>
<td>8.2</td>
<td></td>
</tr>
<tr>
<td>875</td>
<td>950</td>
<td></td>
</tr>
<tr>
<td>&lt;1</td>
<td>5.5</td>
<td></td>
</tr>
</tbody>
</table>

It is clear that the ultimate tensile strength and elongation values obtained in Feedstock B fulfill the ASTM B883-10 specifications [198]. Although UTS values of Feedstock A are within the standard limit, the elongations are well below the minimum requirement of 4%. This corresponds to the significantly larger pores in the sintered samples made of Feedstock A, as shown in Figure 8.9. Compared with the much uniform small residue pores in the sintered samples from Feedstock B, clear bi-modal pores are observed in the sample from Feedstock A. These large pores originate from the shrinkage voids created during injection molding solidification [184], and deteriorate the final mechanical properties. It should be noted that the same solvent, thermal debinding and sintering processing parameters were applied to both feedstocks.

![Fig. 8.9 Comparison of the light microscope images of two feedstocks.](image)

Two distinctive pores are visible in case of Feedstock A. The pores shape indicates a typical shrinkage void created during solidification [184]. These pores will eventually lead to poor mechanical properties.

PVP incorporation in the PEG/PMMA binder system leads to excellent mouldability of the feedstock, with good rheological properties while maintaining the clean nature of this binder.
system. However, there is a main drawback associated with this new binder system. During injection moulding, longer cooling times had to be applied before the ejection of green parts. For instance, the cooling time of 75 sec at 20°C was used in this study for the injection moulding of green tensile test coupons with Feedstock B. For smaller moulding samples, where cooling rates are inherently higher, it may not pose a significant threat. Longer cooling times could, however, be a limiting factor for larger samples or for processes where a higher production rate is required. The cooling time can be decreased by decreasing the mould temperature. However, higher moisture condensation rates at the mould surface below 20°C may affect the final product quality. Initial assessments imply that the increase in cooling time may have been caused by interactions between the PVP and PMMA molecular chains. The cooling time decreased significantly (<60 sec) when lower molecular weight PMMA was employed in the binder mixture, while the opposite trend was observed by increasing PMMA molecular weight. The lower molecular weight PMMA however, led to poor sample shape retention during the water debinding step. Further development is needed to avert this problem by optimizing the contents of PVP and PMMA in this binder system.

It is also suggested that shrinkage voids could be eliminated by using an acrylic polymer other than PMMA, which has glass transition temperature (T_g) below the crystallization temperature of PEG, such as polybutyl methacrylate (PBMA with T_g ~ 16°C), while maintaining the clean nature of acrylate. PBMA seems to be a valid choice and was reported in the literature [89, 199] as a backbone polymer with no resulting voids observed during feedstock formulation. However, it was found that there are compatibility issues between PEG and PBMA, Figure 8.10. In addition, these samples had poor shape retention during water debinding.

![Fracture surface analysis of the feedstock comprising of PBMA as backbone polymer. Two phases can easily be seen.](image)

**Fig. 8.10** Fracture surface analysis of the feedstock comprising of PBMA as backbone polymer. Two phases can easily be seen.
8.4 Summary

A full investigation on PVP incorporation in PEG/PMMA binder system in metal injection moulding was carried out. The PVP incorporation reduces the voids formation by reducing PEG crystallization. However, the higher molecular weight PVP is prone to curing above 130 °C. Moreover, it is hard to remove during water debinding and may lead to cracking. This problem can be overcome by using lower molecular weights of PEG and PVP. It was found that reduction in PEG crystallization is directly proportional to PVP content in the binder system and at PVP content of 30wt/wt% of PEG no voids were visible both at macro- and micro- level. Furthermore, PVP can be removed during water debinding along with PEG without distorting the shape. The sintered samples fulfilled ASTM B883-10 specifications which were otherwise not possible because of the voids that are hard to remove during sintering. However, PVP addition leads to longer cooling time during injection moulding stage. This problem can be resolved by optimizing contents of PVP and PMMA in the binder system.
Chapter 9 An easy-to-decompose binder for Ti metal injection moulding: preparation and characterization of feedstock

This chapter is based on the published work of ref. [200] by the author. Impurity control is crucial to Ti-MIM success since titanium is a universal solvent to interstitial elements such as oxygen, carbon and nitrogen. A poorly selected binder system thus can fail the entire Ti-MIM process even if it produces excellent moulding properties. In this study, a low decomposition temperature binder system was developed and rheological and solvent debinding assessments of the feedstock were performed. Solvent mixing was employed to prepare homogeneous feedstocks. Effect of powder shape on rheological properties was evaluated. After injection moulding, solvent debinding was performed. The debound parts were then characterized by microstructural observation.

9.1 Introduction

It has been well established now that the interstitial elements such as oxygen, nitrogen, carbon and hydrogen have a significant effect on the mechanical properties of titanium and its alloys. Among these impurities oxygen has the highest impact due to its high solubility and high affinity for titanium particularly above 400 °C [20].

Baril et al. [20] found that sintering atmosphere contributes the most to overall oxygen content followed by debinding atmosphere and binder composition. The primary component of binder systems is usually removed completely by solvent extraction at low temperatures. Therefore, it does not increase the overall impurity level unless improper extraction is done. Contaminations during sintering can also be controlled by carefully controlling sintering atmosphere. However, contaminations during thermal debinding which arise from thermal decomposition of backbone polymers still remain a big concern for product designers. Hence, a comprehensive understanding of binder system and its thermal decomposition behaviour is crucial to achieve desired mechanical properties. Wen et al. [21] have recently reviewed the binder systems commonly used for Ti-MIM. It is suggested to use backbone polymers which leave minimum residue upon decomposition and have moderate decomposition temperatures, preferably below 400 °C [20, 21]. However, it must also be noted that the backbone polymer provides the necessary green strength until initial stage of sintering; too early decomposition may lead to shape distortion.
To minimize residue upon decomposition and impurity pick-up during debinding, efforts have been made to design and test a new binder system based on PEG and a low decomposition temperature polymer Q. Potential benefits and drawbacks of this binder system are also explained. The rheological behaviour and water debinding properties of feedstock based on this new binder system are also presented.

9.2 Experimental procedures

The binder system contained a major fraction of PEG ($M_w \sim 4000\text{g/mol}$) as the primary component and polymer Q as the backbone polymer. SA was added in a minor fraction to act as surfactant. This binder system is hereafter designated GQS. Feedstock preparation and rheological experiments were carried out as mentioned in Ch. 3. European MIM industry tensile bar test samples [Fig. 3.6 (a)] were injection moulded. The injection temperature was 90 °C, injection pressure was 14 MPa, injection speed was 40 cm$^3$/sec and the packing pressure was also 14 MPa. Each moulding was visually inspected and weighed after every run for quality control.

Water debinding was carried out at 40 °C, while thermal debinding and sintering were carried out in accordance with Ch. 3. Feedstock characterization was performed using FEI Quanta 200F environmental scanning electron microscopy (ESEM). Room temperature tensile properties were measured on an Instron 3367 universal testing machine with a cross-head speed of 0.5 mm/min as per ASTM E8 standard.

9.3 Results and discussion

9.3.1. Decomposition temperature of polymer Q

Commonly employed backbone polymers in Ti-MIM e.g. PP, PE, PMMA, and EVA have a decomposition temperature in excess of 400 °C and apart from PMMA others can leave residues behind [21]. The decomposition temperature of the Q, however, is below 400 °C; moreover this polymer is also a clean polymer and leaves no residue behind. Figure 9.1 compares the TGA behaviour of Q with PMMA.
Fig. 9.1 Weight loss of Polymer Q in argon atmosphere compared to PMMA. Decomposition starts around 190°C and ends at 340°C approximately. On the other hand, PMMA decomposition starts at 340°C and ends at 435°C

The TGA curve shows that most of the weight loss of polymer Q occurs in a narrow temperature range (marked by the black line) similar to PMMA. This characteristic is a typical of depolymerization reaction and has been noted in the literature before [201, 202]. However, after 300 °C the curve flattens suggesting that two depolymerization mechanisms; chain scission and unzipping reactions may be involved [203].

9.3.2. Feedstock optimization

9.3.2.1 Determination of optimal solids loading

After selecting the binder components and suitable binder composition the next step is to determine the optimum solids loading in order to achieve feedstocks with good rheological properties [19, 39]. Viscosity can be either increased or decreased by varying solids loading around the optimum value. Too much deviation from the optimum value can break down the entire process by either improper filling if excessive solids loadings are used or by deterioration of the mechanical properties in case of low solids loading, which is associated with slumping, long sintering time and high shrinkage during sintering. By using capillary rheometer optimum solids loading can be readily determined (as explained in Ch. 6, section 6.3.2), Figure 9.2.
Fig. 9.2 Optimum Solids loading for GQS feedstocks made of two different powder systems. The temperature was selected as 90°C. The viscosity values are the mean values calculated over the shear rate range of $10^2$ to $10^5$s$^{-1}$.

It is clear from Figure 9.2 that maximum solids loading that can be used while keeping good rheology and viscosity are 62vol% and 51vol% for spherical GA powder and irregular HD powder GQS feedstock systems respectively. Any increment above this limit will subsequently increase the viscosity of feedstock and pressure required for injection. It can also be seen from Figure 9.2 that by mixing spherical and irregular powders together adequate solids loading can be achieved.

9.3.2.2 Effect of powder shape

As a general rule of thumb, the higher the packing density of the powder, the higher will be the solids loading with better rheological properties [19]. The irregular powder has a lower packing density and higher interparticle friction compared to spherical powders, so solid loadings are much lower in order to have similar rheological properties [90]. The spherical powders also provide the additional benefit of low oxygen contents. However, irregular powders are preferred whenever low cost of final product is the main requirement instead of mechanical properties and irregular powder particle feedstocks exhibit better shape retention during debinding because of high interparticle friction [90].
Ideally, higher solids loading feedstocks are always preferred to reduce shrinkage during sintering. The 60vol% GA powder GQS feedstock (Feedstock A), however, had poor shape retention property during water debinding, Figure 9.3.

Fig. 9.3 Shape retention property of two feedstocks systems during water debinding. Feedstock B exhibited good retention while Feedstock A started disintegrating just after 30 min of water debinding. However, some swelling was also observed in case of Feedstock B.

As explained in the previous chapter (Ch 8), the goal of water debinding is to create interconnected pores throughout the moulded body so that the backbone component can be removed through these pores without distorting the shape when second debinding is applied [138, 139]. The role of backbone polymer thus becomes pivotal during and after water debinding [204]. As part becomes porous, the strength of backbone polymer should be enough to keep the part intact. The poor shape retention of feedstock A may be due to low strength of polymer Q and partly due to lack of friction between spherical particles. The green strength of the samples can be improved by using a mixture of spherical and irregular powders. However, the use of irregular powder has an adverse effect on rheological properties and solids loading subsequently. It also increases the overall impurity contents of feedstock. Thus, the irregular powder contents should be chosen just to provide the sufficient green strength and to keep the solids loading at moderate level. The 58vol% (50/50wt% GA+HDH powders) GQS feedstock (Feedstock B) showed better shape retention, Figure 9.3. Although feedstock B samples showed better shape retention, it still had low green strength and showed some swelling and shape distortion. Figure 9.4 shows SEM micrographs of feedstock A and B after water debinding.
9.3.2.3 Rheology of feedstock B

As explained earlier in section 4.4, pseudoplastic flow (decreasing viscosity with increasing shear rate) of feedstocks upon shearing is usually sought in injection moulding to ease mould filling, minimize jetting and help in retaining component shape during the cooling process. The flow behaviour is characterized by the viscosity dependence on shear rates and is given by the modified power law, (Eq. 4.4). The feedstock B not only exhibited better shape retention property than feedstock A, its rheological properties were comparable to feedstock A which had excellent rheological properties due to pure GA spherical powders. Figure 9.5 compares the rheological properties of the two feedstocks.
Fig. 9.5 Shear rate dependence of viscosity for two Feedstocks, a) Feedstock A & b) Feedstock B at 90°C, 100°C and 110°C.

It is clear from Figure 9.5 that both feedstocks are pseudoplastic in nature with feedstock A having small variation in n values at different temperatures. This implies that viscosity of feedstock A does not rapidly change with increasing temperature. On the other hand, feedstock B is more sensitive to temperature changes as n value changes with each temperature. This is due to irregular powders which have higher temperature dependence than spherical powders [90]. Therefore, the control of mould temperature for Feedstock B should be monitored closely in order to minimize residue stress.

The viscosities of both feedstocks are also well under the limit of 1000Pa.s in the shear rate range of injection moulding. The initial high viscosity can be rectified by extruding the feedstocks which align the particles thereby removing abnormalities. However, this step is not a necessary requirement given the shear mixing nature of injection moulder’s screw and most importantly, viscosities in the shear rate range of injection moulding machines must be considered.

The good rheology arises from the improved homogeneity of the two feedstock systems, which is verified by Figure 9.6.
Both feedstock systems are homogeneous with Ti particles in both are well covered with binder. The covering of Ti particles is more prominent for feedstock A because of higher packing density of spherical powders.

Nevertheless, the mechanical properties of feedstock B, particularly elongation, were not good. The final properties achieved were; UTS of approx. 450 MPa and elongation less than 2%. The poor properties may have been caused by low sintering density and high impurities contents because of HDH powder usage. To reduce the dependency on irregular powder while maintaining sufficient green strength, small amount of PMMA was incorporated into the binder system. The PMMA incorporation led to higher green strength and provided with the opportunity of higher solids loading feedstocks by using spherical powders only. A higher solids loading (> 63 vol.%) feedstock (Feedstock C) was made by using spherical powders and new binder composition. The green parts showed excellent shape retention during debinding and sintering, Figure 9.7.
Despite the unavailability of good quality thermal debinding and vacuum sintering furnaces, sintered samples showed good mechanical properties: average UTS of 600 MPa and average elongation of 5% were achieved, respectively. It is conceivable that higher elongation can be achieved by using good quality thermal debinding and sintering furnaces.

9.4 Summary

The decomposition temperature of polymer Q is below 400 °C which is essential in order to contain impurity uptake during debinding. However, this also presents a new challenge by decreasing the green strength required to retain the part during debinding. The green strength can be increased by using a mixture of irregular and spherical powders. However, the weight proportions of irregular powders should be optimized in order to savour the potential benefit of low impurity level that polymer Q brings with it. Alternatively, little amount of PMMA should be incorporated into the binder system. The PMMA incorporation provided the sufficient green strength thereby, eliminating the use of irregular powders and led to better mechanical properties sintered samples.
Chapter 10 Conclusions

This thesis focuses on the extensive study of water soluble PEG based binder systems for MIM. Efforts have also been made to produce a low decomposition temperature binder system for Ti-MIM. Some important findings are summarized below. We hope the findings described below could lay a foundation and lead to broader future investigations in these environment friendly binder systems.

1) It is found that PEG molecular weight has a significant effect on the rheological properties of MIM feedstocks. The results reveal that the rheological properties of feedstocks improve as PEG molecular weight is increased due to more adhesion with metal powders provided by the molecular chain lengthening. It was found that PEG-10000 not only had excellent rheological properties, but also good debinding performance. Thus, PEG-10000 is the best option as the primary binder component and the feedstock based on this polymer will result in excellent moulding operation.

2) The effects of different surfactants on the overall properties of powder feedstocks are shown in this thesis. It is determined that feedstock containing castor oil as surfactant possesses a higher flexural strength and higher mouldability index value than feedstock containing stearic acid as surfactant. The improved properties are attributed to the enhanced interaction between binder and titanium powder and better dispersion of the powder due to the presence of extra polar groups in castor oil molecule. It can be argued that the presence of extra ester groups in castor oil molecule may lead to higher contamination in case of reactive powders during thermal debinding. However, little amount of surfactant is added when MIM of reactive powders is sought. Moreover, less amount of castor oil will be required compared to stearic acid at a fixed solid loading.

3) Extensive study of PEG/PMMA binder system revealed that this binder system is prone to solidification defects (void nucleation), which badly affect the mechanical properties of the final product. The void formation can be minimized to a point where it is not detrimental to final properties by reducing PEG crystallization via applying higher cooling rates. This can be achieved by decreasing the mould temperature to a minimum operable temperature. Since the cooling rates in μMIM are inherently higher than conventional MIM process, it is suggested that the PEG/PMMA binder system is more suited to μMIM. To fully realize the potential benefits of this system in the case of conventional MIM, a PEG crystallization inhibitor such as PVP should be incorporated in the binder system.
4) A systematic investigation on the incorporation of PVP in PEG/PMMA binder systems showed that the PVP incorporation reduces the void formation by reducing the PEG crystallization. Furthermore, PVP can be successfully removed during water debinding along with PEG, without distorting the shape of injection moulded sample. Therefore, PEG/PMMA binder system incorporated with PVP can be used for conventional injection moulding while keeping the environment friendly nature of this binder system.

5) With the help of the new binder system PPMC, a higher solid loading for irregular Ti powder feedstocks can be achieved. However, viscosity may not be ideal for injection moulding at the solid loading higher than 53 vol.%. The proper viscosity at a high solid loading can be achieved by blending irregular and spherical powders. The low-cost MIM parts produced from the feedstock formulated by this binder system demonstrated a high strength and good dimensionally stability.

6) To minimize impurity uptake during thermal debinding process in Ti-MIM, a low decomposition temperature binder system is developed based on polymer Q and PEG. The decomposition temperature of polymer Q is below 400 °C which is essential in order to contain impurity uptake during debinding. However, this also presents a new challenge by decreasing the green strength required to retain the part during debinding. The green strength can be improved by incorporating little amount of PMMA into the binder system. The Initial trials have shown encouraging results despite processing constraints; strength 600 MPa and elongation of 5%. It is conceivable that higher elongation values can be achieved by using high quality vacuum furnaces.
Chapter 11 Recommendations and future work

One of the most important problems in Ti-MIM is the contamination occurring during the debinding and sintering processes. To intercept this issue, exhaustive efforts have been devoted to the development and design of specialty furnaces for Ti-MIM debinding and sintering, and a variety of debinding and sintering furnaces are available on the market. However, it should be kept in mind that titanium starts to significantly react with oxygen at a temperature above 400 °C. Impurities left in the debound “brown” parts after debinding would dissolve into titanium, causing undesirable properties. Therefore, the first and most important requirement in order to control the level of impurities is the development of binders and debinding method for easy removal of binders at temperature below 400 °C.

The primary component of binder does not contribute greatly to final impurity contents, unless insufficient removal is carried out. Therefore, the main focus in binder development should be on backbone polymer. The most common polymers include PE, PP, PMMA and EVA and apart from PMMA, significant quantities of other polymers are required in order to provide the necessary strength particularly in case of PP. Therefore, it is very important to optimize the contents of such polymers in the binder system. Moreover, polymers can be designed, synthesised, post-modified and assembled with a great degree of freedom. Therefore, if necessary, modification of common polymers such as PP should be done in order to improve the properties. Furthermore, due to increasing interest in environmental friendly systems, wherever possible water (or other environment friendly solvent) soluble primary component should be chosen.

In order to get titanium MIM products with minimum impurity, Ti-MIM processing should be carried out separately. Separate furnaces for thermal debinding and sintering should be dedicated to titanium.

Some recommendations for future works are listed below:

- The voids in case of PEG/PMMA binder system arise from interaction between the two components. Therefore, the molecular weight of PMMA may have an effect on this voids formation. Hence, it is suggested that the effect of PMMA molecular weight on PEG crystallization should be studied in detail.
- Although PVP incorporation into PEG/PMMA binder matrix did reduce the voids formation, it increased the subsequent cooling time which decreases the production rate. It is suggested that this higher cooling time may be due to interaction between
PMMA and PVP. Therefore, this interaction should be further studied in detail and the contents of both polymers should be optimized in the binder matrix in order to fully savour the potential benefits of this binder system.

- A detailed study of thermal debinding for titanium alloy feedstock is essential to the quality of Ti-MIM final sintered products. The next research should focus on the heating rate, holding time, inert atmosphere and debinding temperature of thermal debinding.

- Although castor oil as the surfactant showed excellent results in the case of Ti-MIM, it is recommended that a thorough evaluation of castor oil as surfactant for other metal powders MIM should be carried out.

- Ti-MIM feedstock recyclability has not been evaluated before and therefore, the next research should also focus on recyclability and if required, efforts should be made to improve it in order to reduce cost.

- PVP modified PEG/PMMA binder system should be tested for Ti-MIM and complete evaluation in terms of mechanical properties should be carried out. Similarly, further investigations on low decomposition temperature binder system are still required. It is recommended that samples made out of this binder should be sintered in a high quality sinter furnace. Mechanical properties assessment should be carried out. Improvisation of binder system should be carried out, if necessary.
References


