Development of an Environmentally Friendly POM-based Binder System for Titanium Metal Injection Moulding (Ti-MIM)

Keemi Lim

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Abstract

Metal Injection Moulding (MIM) of titanium (Ti) and its alloys have experienced a growing interest in both research and industry over the last decades. Due to titanium’s outstanding properties, such as its high strength-to-density ratio, excellent corrosion resistance, lightweight, and high biocompatibility, it has been used in various applications such as medical devices and implants, aerospace, and chemical processing industries. However, the annually produced mass is still relatively small compared to steel. The main reasons are its high manufacturing costs, and MIM has proven to offer a solution to reducing production costs. However, titanium’s affinity towards interstitial elements (i.e., oxygen and carbon) can strongly influence its mechanical properties. Hence, this dissertation is focused on developing a clean binder system for Ti-MIM.

Polyoxymethylene (POM), whose molecular formula is $\text{CH}_2\text{O}$, has found applications as a binder material for MIM due to its ability to decompose cleanly. This leaves the final product with very little to almost no contamination. Moreover, POM in the solid state has good mechanical properties, thus making handling moulded parts easier. Despite that, there are some limitations to using POM as a binder system. For one, POM decomposes into formaldehyde, which must be controlled under a particular concentration limit in the working environment because of its toxicity. Secondly, POM is relatively insoluble in most solvents and can only be dissolved in strong acids, oxidising agents, or alkalis. Hence, specially designed debinding furnaces are required. Concurrently, this adds additional pressure on the already existing expensive Ti feedstock. Therefore, an extensive study on POM-based binder systems was carried out in this research. This work aims to develop an environmentally friendly POM-based binder system for Ti-MIM. However, in the beginning, achieving superior mechanical characteristics with low impurity levels in Ti-MIM samples was challenging, if possible, due to different processing constraints. Nonetheless, POM is still a promising option for Ti-MIM due to its lack of decomposition residues. In this study, an alternative binder based on PPC/POM serves as a complementary approach that can minimise impurities during Ti-MIM processing.
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<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>C</td>
<td>Carbon</td>
</tr>
<tr>
<td>CP</td>
<td>Commercially pure</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential scanning calorimetry</td>
</tr>
<tr>
<td>EMA-GMA</td>
<td>Poly(ethylene methyl acrylate-glycidyl methacrylate)</td>
</tr>
<tr>
<td>EVA</td>
<td>Poly(ethylene vinyl acetate)</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier Transform Infra-red</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>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>MFI</td>
<td>Melt flow index</td>
</tr>
<tr>
<td>MIM</td>
<td>Metal Injection Moulding</td>
</tr>
<tr>
<td>N</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>O</td>
<td>Oxygen</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>PMMA</td>
<td>Polymethyl methacrylate</td>
</tr>
<tr>
<td>POM</td>
<td>Polyoxymethylene</td>
</tr>
<tr>
<td>PP</td>
<td>Polypropylene</td>
</tr>
<tr>
<td>PPC</td>
<td>Polypropylene carbonate</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 Microscopy</td>
</tr>
<tr>
<td>SS</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>s</td>
<td>Second</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>Ti</td>
<td>Titanium</td>
</tr>
<tr>
<td>Ti-MIM</td>
<td>Titanium and its alloy 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>UV-Vis</td>
<td>Ultraviolet-visible spectroscopy</td>
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Chapter 1 Introduction

1.1 Background

Titanium (Ti) is a material of great interest due to its unique properties, such as its lightweight, high specific strength, excellent biocompatibility, and corrosion resistance [1,2]. For instance, in medical applications, titanium exhibits the most suitable characteristics due to its non-toxicity and high biocompatibility with human tissues and bones, allowing reduced recovery time and rehabilitation [3]. Significant weight reduction can be achieved by using titanium or its alloys in aerospace structures and other high-performance applications, directly reducing energy costs. Nonetheless, the applications of titanium in these industries still need to be improved due to its expensive raw materials and processing limits. Against this background, metal injection moulding (MIM) is ideal for titanium processing.

Metal injection moulding (MIM) is an established net-shape manufacturing process that combines powder metallurgy and plastic injection moulding [4–6]. It takes advantage of the most valuable characteristics of powder metallurgy, offering high material utilisation capability with the versatility of plastic injection moulding to produce complex parts with fine details and tight tolerances in large quantities [7]. This makes it ideal for applications where precision and performance are critical, such as in the aerospace and medical industries. Additionally, MIM allows for the quick and efficient production of large parts, making it a cost-effective option for high-volume manufacturing [8].

Today, commercially available products based on titanium metal injection moulding (Ti-MIM) are the Hitachi Ti alloy watch case [9] and aircraft parts for Airbus A350 and Boeing B787 [9]. Others have been showcased for dental implants, medical devices, sunglasses frames, cell phones, and golf clubs [10,11]. However, from the economic perspective, processing titanium materials by MIM remains rare, especially when it is claimed that Ti-MIM technology is ready for industry [10]. Titanium owns only a tiny share of the overall MIM industry [5,9]. The lack of industrial confidence in Ti-MIM is due to the limited availability of commercially viable Ti-MIM feedstocks. In addition, the high affinity of titanium towards oxygen and carbon requires special considerations during MIM processing. Since carbon and oxygen are present in all binders, extreme care must be
considered during binder selection as oxygen has a high solubility and affinity to titanium above 400 °C. Hence, a comprehensive understanding of the binder system and its thermal decomposition behaviour is crucial to achieving the desired mechanical properties for titanium parts.

Herein, the attempts to use a catalytic debinding binder system, most commonly known as a polyoxymethylene (POM) binder system, is the new trend in the development direction for Ti-MIM. An essential characteristic of POM-based binders is their strong sensitivity to acid hydrolysis by acidic agents [12]. As such, parts can be quickly and defect-free degreased since debinding proceeds only at the gas/binder interface, avoiding cracks and bloating caused by boiling the binder [13,14]. In addition, it has been mentioned that POM in the solid state exhibited good mechanical performance, allowing easier handling of moulded parts, which can be fragile or easily deformed in another binder system [15]. Not only that, POM is also considered a clean polymer as it is depolymerised, yielding gaseous monomers. This leaves parts with little residues upon decomposition, which is critical when processing titanium using MIM technology.

Nonetheless, the literature on the POM-based binder system in the MIM industry, especially in Ti-MIM, is limited. This could be associated with the formaldehyde emission and the use of highly concentrated acids, which requires a capital investment around the catalytic debinding furnaces. Hence, in this thesis, particular focus has been given to developing an environmentally friendly POM-based binder system for Ti-MIM. Some interesting new findings of POM-based binder systems for Ti-MIM have been reported.

1.2 Objectives

The specific objectives are summarised below.

(1) Development of low formaldehyde POM binder for MIM

Polyoxymethylene (POM), with a molecular structure comprising of repeating unit carbon-oxygen linkage, [-CH2-O-]n, is evoked as a parent molecule for releasing formaldehyde gas. These gases usually occur thermally from excessive heat or chemically in the presence of acids or alkalis. Hence, during MIM processing, the release of formaldehyde gases must be controlled under specific concentration limits in the working environment. It has been
reported that exposure to high levels of formaldehyde is linked to rare nose and throat cancer in workers. Therefore, the solution has been proposed, and these discoveries will undoubtedly add value and shed new light on using POM as binders in the MIM industry.

(2) Compatibility improvement and optimisation of Ti-MIM feedstock
Considering the molecular structure of POM and PP, blending these two polymers is expected to be incompatible and demonstrates a two-phase system. In MIM, binder selection and formulation are critical. Binders play a crucial role in controlling the rheological properties of a feedstock and influence whether the resulting feedstock can be successfully injection moulded, debound and sintered without defects. To improve the homogeneity of the POM-based binder system for Ti-MIM, two different types of compatibiliser, poly(ethylene methyl acrylate-co-glycidyl methacrylate) (EGMA) and ethylene-vinyl acetate (EVA) are investigated. The objective is to understand better the interactions between the POM-based binder system and titanium metal powder, yielding excellent properties of the feedstock.

(3) Optimisation of the injected moulding process in MIM
The characteristic of a MIM part prior to sintering is its green density. The highest green density plays a vital role in achieving parts with better shape retention and ensuring full densification during sintering. Herein, optimisation of the Injection Moulding (IM) process is conducted via the Taguchi method using Minitab statistical software. An L9 orthogonal array experimental design was investigated, and several injection moulding parameters were optimised. The Taguchi method is a robust and effective tool for studying and analysing the injection moulding parameters in MIM to obtain high-quality moulded parts.

(4) Development of an environmentally friendly debinding technique for a POM-based binder system
The existing polyoxymethylene (POM) binder system in MIM uses a catalytic debinding technique involving a highly concentrated acid solution and an expensive debinding furnace. This dissertation adopted a simple, combined solvent-thermal debinding technique to overcome these drawbacks. This technique allows the removal of the main binder constituent (POM) in a reasonably short and environmentally friendly process. Moreover, the solvent debinding behaviour and mechanism of POM binder have yet to be reported in
the open literature. This knowledge could provide an interesting insight into the sustainable use of solvents for the POM debinding process.

(5) Development of a low decomposition temperature, clean binder system for Ti-MIM

To minimise the residue upon decomposition and impurity pick-up during the debinding of Ti-MIM feedstocks, we designed and tested a new binder system based on POM and polypropylene carbonate (PPC). PPC is another clean polymer that has attracted considerable attention in the MIM industry. The unique characteristic of PPC lies in its low decomposition temperature, widely reported in the range of 180 to 250 °C. This allows minimal oxidation with reactive metal powders like titanium. However, a preliminary study on PPC binder-based systems showed poor shape retention after solvent debinding. Therefore, adding polyethylene glycol (PEG) into PPC/POM might solve this problem. It may be noted that the results from this study can also be used for other powders injection moulding.

1.3 Thesis Outline

This thesis is divided into nine chapters. Chapter 1 provides an overview of this thesis. Chapter 2 is a literature review on MIM, particularly on developing polyoxymethylene-based binders and the current trends in processing titanium materials. The methodology used in this project is presented in Chapter 3. Chapter 4 introduces propylamine as a highly efficient formaldehyde absorbent for POM. Chapter 5 studies the compatibility of the POM-based binder system and its interactions with titanium powder. Chapter 6 employed a simple statistical Taguchi method to optimise the MIM- injection moulding process for optimum green density. Chapter 7 presents an environmentally friendly debinding technique to overcome the conventional catalytic debinding technique. Chapter 8 introduces a new low-temperature, clean binder system based on POM/PPC for Ti-MIM. Conclusions and recommendations for further work are presented in Chapters 9 and 10.
Chapter 2 Literature Review

2.1 The Metal Injection Moulding (MIM) Process

MIM was developed in the 1970s and 1980s as a process for net-shape manufacturing of small and complex metallic parts. With this technology, the capabilities of processing a wide range of metals and alloys known from conventional powder metallurgy (PM) are combined with the freedom of shape forming and efficient series manufacturing characteristic of polymer injection moulding [6,16]. Figure 2.1 illustrates the schematic diagram of a MIM process that includes four major processing steps: feedstock formulation, injection moulding, debinding, and sintering [17].

Figure 2.1 A schematic illustration of the MIM process [18].
The MIM process starts with preparing feedstock by mixing metal powders with a suitable binder system. The role of the binder is to hold the metal particles together while moulding the parts. The binder usually makes up 40–50 vol% of the feedstock composition, acting as a flowing agent for injection moulding and providing strength to parts at room conditions. Once shaped (also called the green part), the binder must be removed in the debinding step by either one or the sequential combination of several procedures, including solvent extraction, thermal degradation, or catalytic debinding. During debinding, shape stability is essential; hence, binders are usually formulated as a multi-component system. While one component is removed, the other(s) hold the metal particles in place. Once the binder is completely removed (known as the brown part), the particles are consolidated by sintering to obtain the final product. The density attained after sintering is typically close to the theoretical density of the metal in the range of 95-99%. Because of the densification during sintering, the part is subject to a 12–18% shrinkage, depending on the specific feedstock and its metal content. The sintered part may be used with or without further post-processing [4,12,19,20].

**2.2 Feedstock Preparation**

In the first MIM cycle, homogeneous mixing of the feedstock is vital for successful MIM processing. Any inhomogeneity, including bubbles, left during the mixing step will be carried over to the subsequent processing steps. Consequently, this would cause deleterious effects such as poor flowability during moulding and difficulty of densification and dimensional stability in the final products [12,21]. Hence, intensive mixing is preferred to achieve a homogeneous feedstock. This ensures that the whole surface of the metal powders is evenly coated with binder [21]. Besides, the binder and the metal particles should be inert concerning each other. For instance, the binder should not react with metal particles, and successively, the metal powders should not polymerise or degrade the binders [22]. Therefore, characteristics of metal powders such as the particle size, shape, size distribution of powders and selection of binder must be considered. Knowing the feedstock’s features, selecting the optimal injection moulding and sintering conditions, and understanding its behaviour during the production process of MIM parts could be realised.
2.2.1 Characteristics of Titanium Powders

The final properties of the MIM product are directly influenced by the properties of the titanium metal powders. As a result, the powder characteristics employed in MIM play a crucial role in controlling the overall process. A common guideline for the selection of titanium (Ti) powders based on the successful production of Ti-MIM is as follows [5,20,21,23]:

(a) Fine spherical powder – improves surface cleanliness,
(b) Optimal particle size of about 45 microns
(c) Low initial oxygen (max. 0.15 wt%) and carbon (max. 0.04 wt%) level
(d) High tap density (60-62 % of pycnometer density)
(e) Dense, discrete particle free of voids

2.2.2 Characteristics of Binders for Ti-MIM

A suitable binder for Ti-MIM should leave minimum oxygen and carbon residues after the debinding stage. This is because unless titanium powders are exposed to high temperatures, the forming feedstock of titanium powders does not cause oxygen pick-up during compounding and injection moulding. Therefore, the primary criterion for the binder system includes [20–22,24]:

(a) Good adhesion to Ti particles
(b) Low melting temperature and provide sufficient green strength at room temperature
(c) Good dimensional stability during debinding
(d) Low contact angle
(e) Complete decomposition at a temperature below 400°C [25] without any residue after thermal debinding
(f) Chemically passive to Ti powders
(g) Environmentally friendly and allow removal of binder in a reasonably short time
However, no single binder material can satisfy all of the above criteria. Hence, mixtures of different components are commonly used as the binder system. In general, binder formulations consist of at least two components: the primary and secondary. The primary binder, the major constituent in the binder system, is usually comprised of low molecular weight polymers (i.e. waxes) to wet the metallic powder particles and provide the necessary flowability for injection moulding. On the other hand, the secondary binder (high molecular weight polymer), known as a backbone component, ensures sufficient green strength after injection moulding and/or after the major component is removed. In most cases, the binder system also contains a third component, such as a surfactant [26], to enhance the compatibility between the metallic powders and the polymer.

2.3 Development of Binder System for Ti-MIM and its Challenges

The early attempts at developing a binder for Ti-MIM are primarily based on well-known binder systems designed for MIM of other materials, such as stainless steel. However, because titanium is a well-known universal solvent for many impurities such as hydrogen, oxygen, carbon and nitrogen, some of these requirements are even more stringent for the production of Ti-MIM [24,25,27]. One of the main challenges for the contamination control for Ti-MIM is the removal of the secondary binder. Because a secondary binder is added as the backbone component, it usually decomposes via thermal treatment before sintering at temperatures above 400 °C. It is known that when the processing temperature approaches 260 °C, the oxygen pick-up of titanium dramatically increases [24,25]. Therefore, the binder should be designed for removal at low temperatures. The selection of the major component should be based on whether it can be removed by solvent extraction (i.e. waxes or PEG) or low-temperature thermal debinding in the presence of an acid catalyst (POM). As for the backbone component, since polymers such as polyethylene and polypropylene are commonly used, oxidation and carbonisation are inevitably possible risks at this stage [8]. Hence, the backbone should contain as little oxygen as possible and have a decomposition temperature as low as possible [8,12].

In practice, polyethylene (PE) or polypropylene (PP), either mixed or copolymer with ethylene vinyl acetate, has been successfully used as a secondary component. A good value range would be between 20 wt% and 40 wt% [8]. Today, a choice of secondary binders has been focused on polymethyl methacrylate (PMMA). According to Jellineck [28], the
pyrolysis of PMMA leaves minimal residue within the component, producing about 95-100% gaseous monomers under vacuum or inert atmospheres. It is reported that the residual oxygen and carbon levels obtained in the sintered samples suggest that the titanium surfaces do not interact significantly with PMMA or its degradation products [28]. However, some literature suggests otherwise. Due to the depolymerisation of PMMA, which occurs close to those temperatures where titanium impurity uptake initiates (at approx. 260 °C to below 400 °C), PMMA could still introduce impurities into the sintered Ti MIM parts [17,25].

This shows that most of the binders being used for Ti-MIM are currently only suitable if the debinding and sintering cycle is carefully adjusted and care is taken to remove the binder decomposition products from the brown parts [4]. The development of binders for Ti-MIM can be categorised into three main groups: wax-based, water-soluble-based, and polyoxymethylene (POM) based binder systems.

### 2.3.1 Wax-based binder systems

In the late 1980s, Kaneko et al. attempted to develop a wax-based system for Ti-MIM [29]. This wax-based binder system generally comprises blends of waxes with one or several higher molecular weight polymers. Typically, the major component consists of waxes, which wet the metallic powder particles and impart feedstock with good flow properties. Some of the common classes of waxes used include paraffin wax (PW), beeswax, carnauba wax (CW), and several wax-like short oligomers [24]. However, because waxes have low molecular weight, a secondary backbone component is often required to improve dimensional stability during debinding. Among many, the most popular choices for wax-based backbone polymers are polyethylene (PE), polypropylene (PP), and ethylene vinyl acetate (EVA). In some cases, minor components are included to improve the chemical compatibility between titanium powders and polymeric binders. In Table 2.1, a list of the commonly used wax-based binder systems for Ti-MIM has been summarised by Froes [17] and Wen et al. [12] and collated with recent literature [29–32]. It is claimed that the binder systems listed are compatible with titanium powders and give acceptable levels of oxygen content, strength, and ductility.

Table 2.1. The wax-based binder system used for Ti-MIM
<table>
<thead>
<tr>
<th>Primary Binder</th>
<th>Secondary Binder</th>
<th>Other</th>
<th>Characteristic of Ti-MIM</th>
<th>Ref.</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td>UTS (ksi)</td>
<td>Elongation (%)</td>
</tr>
<tr>
<td>Wax+ EVA</td>
<td>PBMA</td>
<td>DBP</td>
<td>145.0</td>
<td>-</td>
</tr>
<tr>
<td>PW+ CW</td>
<td>PP + EVA</td>
<td>DOP</td>
<td>140.8</td>
<td>12</td>
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<tr>
<td>PW</td>
<td>PE</td>
<td>SA</td>
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<td>SA</td>
<td>121.9</td>
<td>14</td>
</tr>
<tr>
<td>PW</td>
<td>PEG+PE</td>
<td>SA</td>
<td>152.1</td>
<td>14.6</td>
</tr>
<tr>
<td>PW</td>
<td>Co-polymer</td>
<td>SA</td>
<td>136.1</td>
<td>14</td>
</tr>
<tr>
<td>PW+ CW</td>
<td>Atatic PP</td>
<td>SA</td>
<td>136.4</td>
<td>2.5</td>
</tr>
<tr>
<td>PW</td>
<td>PP+PEG+ PE</td>
<td>SA</td>
<td>56.4-60.8</td>
<td>2.0-4.0</td>
</tr>
<tr>
<td>PW+CW</td>
<td>PP</td>
<td>PE</td>
<td>73.1</td>
<td>19.0</td>
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<td>Palm stearin</td>
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<td></td>
<td>&gt;101.5</td>
<td>10-15</td>
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</tbody>
</table>


Even though wax-based binders have been the most prevalent binder system for MIM, it is particularly challenging to prepare Ti-MIM. In the early research, most wax-based binders focused on a single-step pyrolysis method. Consequently, the sintered parts do not meet the desired products' standards [29,41]. It was explained that the poor performance of the initial Ti-MIM parts is due to incomplete burnout, resulting in severe contamination [41]. These contamination issues have been the biggest hurdle for Ti-MIM. Hence, to solve this issue,
a two-step debinding process was studied by Kaneko et al. in 1990. The results revealed that performing a two-step debinding process could significantly reduce carbon and oxygen contamination after sintering [41]. Nonetheless, organic solvents such as heptane and hexane are involved in removing the wax component. This makes wax-based binders less attractive as the organic solvent deleteriously causes toxicological and environmental concerns [42]. As an alternative, considerations of using a green solvent (i.e. water or ethanol) to remove the binder system are explored.

### 2.3.2 Water-soluble binder systems

The first water-soluble binder (PEG-based) was disclosed by Cao and co-workers in 1992 [43]. He reported that after solvent debinding, the green parts remained rigid and gave excellent shape retention. In addition, the sintering shrinkage was isotropic [43]. Subsequently, in 1995, Anwar and co-workers [44] conducted a similar study on a PEG/PMMA binder system for stainless steel powders, and the results demonstrated sufficient green strength for handling after the removal of PEG. The use of PEG is almost similar to wax. Depending on their molecular weight (<10,000), they can exist either in a liquid state or solid at room temperature (with a low melting point) [42]. Besides, because PEG is commercially available, soluble in water at low temperatures, non-toxic and has a simple molecular structure (CH₂CH₂O)n, the use of these binders has been successful in formulating MIM feedstocks.

In PEG-based binders, the typical backbone polymers employed are PVB, EVA, HDPE, and PMMA. Among them, PMMA demonstrates the best performance, especially when used for reactive metals such as titanium [45]. This is because PMMA is a clean polymer that leaves little residue upon decomposition. For instance, Sidambe et al., who studied the binder system of PEG/PMMA on Ti-6-Al-4V alloy [46] and CP-Ti [47], reported that the backbone PMMA degraded cleanly with negligible carbon content over a narrow temperature (< 440 °C). He further mentioned that by comparing the Ti feedstock before and after pyrolysis using TGA analysis, the results demonstrated that the obtained brown part showed no weight loss after thermal pyrolysis. This confirmed the complete removal of the PMMA binder component in the feedstock. Besides, the residual oxygen and carbon content in the sintered samples was approximately 0.20% and 0.04%, satisfying the specifications according to the ISO 5832-3 and ASTM F67-06 standards, respectively.
Nonetheless, in recent years, some interesting problems have been related to using the PEG/PMMA system for Ti-MIM. For instance, Hayat and Cao have demonstrated that due to PEG crystallinity, the formation of shrinkage voids was detected in the PEG/PMMA system during solidification [48]. This led to defects such as voids and dimensional variations. Later that year, they revealed that by incorporating crystallisation inhibitors such as polyvinylpyrrolidone (PVP) or polyvinyl acetate (PVAc), the quality of Ti-MIM products was realised without compromising the environmentally-friendly nature of the binder mixture [49,50]. However, this adds additional cost at the expense of productivity. Moreover, water-soluble feedstocks demonstrated longer debinding time than wax-based systems [51].

### 2.3.3 Polyoxymethylene based binder systems

A US company, Celanese Corp, first disclosed the emergence of a polyoxymethylene (POM) based binder system in 1984 [12]. The binder was manufactured by BASF with the trade name Catamold® and is mainly sold as a feedstock for various metals. Currently, Catamold® MIM feedstock is available for a few materials, mainly carbonyl iron, low-alloy steels, and stainless steels [52]. In this system, POM acts as the primary component. In contrast, the backbone component comprises polyolefin polymers such as PE or PP as they do not adhere to metal powder surfaces [53]. The main advantages of this binder system are its rapid debinding at low temperatures (in the presence of an acid catalyst) and the possibility of shaping parts up to 35 mm thick without using any wax or low molecular weight polymers [12,54]. Due to its strong sensitivity to acid hydrolysis, POM feedstock can be removed at a temperature well below its softening temperature (approx. 110-140 °C). As such, the debinding is carried out directly from solid to gaseous state, avoiding defects such as warpage, sagging or slumping [54,55]. Besides, it is claimed that POM-based binder systems do not result in any latent defects or weak spots after sintering [56]. This is especially important for Ti-MIM as any interstitial contaminations (i.e. carbon and oxygen) during processing could affect the final sintered parts.

Zhang and colleagues [57] studied the fabrication of Ti-6Al-4V hollow sphere joints using two different binder systems: POM (polyoxymethylene) and PW (paraffin wax). They reported that the feedstocks based on the POM binder displayed better rheological
properties than the PW-based binder. It is also demonstrated that in feedstock containing PW, a higher impurity content was observed due to a longer debinding time required, which increased the binder residue. In contrast, the following properties of the sintered parts employing the POM binder system were achieved: carbon content (0.05 wt%), oxygen content (0.28 wt%), relative density (99.1%), tensile strength (978 MPa), and ductility (6.3%), respectively. Similar results have been reported by Ye et al. [58], using a POM-based binder system, producing engineering components such as thin-walled Ti glasses arm [59] and watch cases [53] from CP-Ti and Ti-6Al-4V with mechanical properties comparable to cast alloys. Hu et al. [60] employed POM-based binders and compared the spherical and irregular titanium (Ti) powders. It was claimed that using spherical titanium powder within the POM feedstock is easily removed during catalytic debinding (99.55%) with oxygen and carbon content of 0.3% and 0.12%, respectively, while the addition of titanium hydride (irregular) powder led to more residual of POM after debinding.

Nonetheless, this system has limitations despite the advantages of a POM-based binder system for Ti-MIM. The MIM feedstocks based on POM and the associated catalytic debinding technique pose high health and environmental hazards [20]. Besides, during depolymerisation, polyoxymethylene (POM) generates formaldehyde gas. In complying with environmental regulations and workplace hygiene standards, this binder system requires a special furnace to incinerate formaldehyde and nitrous gas [53]. Significantly, this put additional pressure on the already existing expensive MIM feedstock.

2.3.4 Comparison of the Binder Systems

Based on the different binder systems developed, a comparison of the properties and performance of each binder system is depicted in Table 2.2.

Table 2.2 The comparison of different binder systems for Ti-MIM.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Wax-based system</th>
<th>Water-based system</th>
<th>POM-based system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mouldability</td>
<td>+++</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>Green Strength</td>
<td>++</td>
<td>+++</td>
<td>+++</td>
</tr>
<tr>
<td>Debinding time (hrs)</td>
<td>++</td>
<td>+</td>
<td>+++</td>
</tr>
<tr>
<td>Solvent/Catalyst</td>
<td>Organic solvent</td>
<td>Water</td>
<td>Acid</td>
</tr>
</tbody>
</table>
Environmental concerns | Yes | No | Yes
Note: +++ - good or fast, ++ - fair or moderate, + - poor or slow

2.4 Polyoxymethylene (POM) Binder Systems

2.4.1 Characteristics of Polyoxymethylene (POM)

The favourable properties of POM as a binder material for MIM, especially titanium reactive metals, are attributed to their [20,61]:

a) Strong polar chain – allows powder surface to adhere and prevent separation during moulding.

b) High molecular weight – ensures high melt elasticity, high green strength and short moulding cycles.

c) Unstable oxymethylene linkage – cleanly decomposes into gaseous monomers.

d) Easy to mould and excellent shape retention.

e) Complete decomposition of the binder at a temperature well below its softening temperature in the presence of an acid catalyst – reduce thermal defects.

f) Shorter debinding time.

2.4.2 Development of POM Binder Compositions

In developing Ti-MIM, controlling carbon and oxygen content is necessary to meet high standards. Baril et al. [25] mentioned that additives such as binders or lubricants can also represent important sources of interstitial contamination. Interestingly, Kankawa and co-workers [62] reported that when a POM binder system contains lesser backbone polymers such as polybutyl methacrylate (PBMA) or polypropylene (PP), the system degrades faster, and the degree of distortion of the parts was observed to be smaller after thermal debinding. Simultaneously, the sintered part with a relative density of 96% and good control of carbon content (0.003%) was achievable with higher POM content and less PP. This agrees with the report by Kankawa et al. [63], who studied the amount of POM/PE polymer compositions in the binder system. Besides, they claimed that by improving the compatibility of POM binders with other organic binders, the final parts possess small
distortion with no cracks or swelling. Further, Parkhomenko et al. [55] investigated 32 different formulations based on the POM binder systems for 42CrMo4 powders. They reported that adding paraffin wax (PW) and/or stearic acid (SA) helped increase the plasticity of the overall mixture composition. Nonetheless, stearic acid was the best as it enhanced the specified fluidity level of the mixture. In another literature, it was demonstrated that adding additives such as ethylene vinyl acetate (EVA) could also aid in reducing the apparent viscosity of the POM/PP binder system while maintaining its original shape and structure after debinding [63].

Nonetheless, using POM-based binder systems on titanium powders is still in infancy. Even though the research and development of the titanium feedstocks based on the POM binder systems have displayed better quality parts than those supplied by BASF, there is still a serious lack of theoretical guidance [24]. Due to this, the practical process is still relatively slow as the research and development of this binder system is still in a large-scale trial-and-error stage. At present, the literature reports on POM binder design are very limited. Some examples of POM binder systems formulated for Ti-MIM feedstock are presented in Table 2.3.

Table 2.3. A compilation of POM binders used for Ti-MIM

<table>
<thead>
<tr>
<th>Base Metal</th>
<th>Binder</th>
<th>Solid loading (vol%)</th>
<th>Mixing Condition</th>
<th>Impurity (%)</th>
<th>Density (%)</th>
<th>Sintered Properties</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp-Ti</td>
<td>POM + PW + EVA + PE +SA</td>
<td>88 wt% POM, 5wt% EVA, 5</td>
<td>60</td>
<td>190°C, 30 mins</td>
<td>C: 0.09</td>
<td>95.9</td>
<td>UTS: 545</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>60</td>
<td>180°C, 90 mins, Ar atm</td>
<td>O: 0.22</td>
<td>UTS: 838</td>
<td>El: 15.4 %</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>C: 0.12</td>
<td>96.8</td>
<td>UTS: 838</td>
<td>[58]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>O: 0.30</td>
<td>YS: 729</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Material</td>
<td>wt% HDPE, 2 wt% SA</td>
<td>wt% POM, 5 wt% EVA, 5 wt% HDPE, 2 wt% SA</td>
<td>wt% TiH₂-Cp-Ti</td>
<td>wt% POM, 5 wt% EVA, 5 wt% HDPE, 2 wt% SA</td>
<td>wt% TiH₂-Cp-Ti</td>
<td>wt% POM, 5 wt% EVA, 5 wt% HDPE, 2 wt% SA</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>--------------------</td>
<td>----------------------------------------</td>
<td>----------------</td>
<td>----------------------------------------</td>
<td>----------------</td>
<td>----------------------------------------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>34.4 vol% POM (proprietary)</td>
<td>88 wt%</td>
<td>52</td>
<td>56</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-6Al-4V</td>
<td>65.6</td>
<td>60-63 POM + EVA + LDPE + SA</td>
<td>60-63 POM + PW + EVA + PE + SA</td>
<td>88 wt% TiH₂-Cp-Ti</td>
<td>180°C, 90 mins, Ar atm</td>
<td>60-63 POM + EVA + LDPE + SA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>160°C, 30 mins</td>
<td>60-63 POM + EVA + LDPE + SA</td>
<td>190°C, 30 mins</td>
<td>180°C, 90 mins, Ar atm</td>
<td>60-63 POM + EVA + LDPE + SA</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C: 0.12, O: 0.28, N: 0.02</td>
<td>185°C,120 rev/min, 60 mins</td>
<td>C: 0.05, O: 0.28, N: 0.04</td>
<td>C: 0.16, O: 0.37</td>
<td>180°C, 90 mins, Ar atm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>190°C, 30 mins</td>
<td>C: 0.08, O: 0.22</td>
<td>C: 0.07-0.08, O:0.25-0.30, N: 0.03</td>
<td>180°C, 90 mins, Ar atm</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>95.3</td>
<td>97.1-96.6</td>
<td>97.8</td>
<td>98.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>UTS: 913-928</td>
<td>UTS: 913-928</td>
<td>UTS: 683</td>
<td>UTS: 507</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>El: 7.8%</td>
<td>El: 5.2%</td>
<td>El: 5.1%</td>
<td>El: 6.3%</td>
<td></td>
</tr>
</tbody>
</table>
2.4.1 Challenges of POM-based Binder System

2.4.1.1 Formation of formaldehyde gas

Regardless of the promising potential of polyoxymethylene (POM) as a binder system for Ti-MIM, one disadvantage of POM is the formation of formaldehyde by-products upon decomposition. POM is inherently unstable with a molecular structure of repeating oxymethylene units (as depicted in Figure 2.2). Hence, POM tends to degrade upon exposure to high shear stresses and heat during compounding and moulding. Ebenhoch [61] mentioned that this degradation, which results in the evolution of formaldehyde, could create pores and shrinkage variations in the feedstock. Therefore, the thermal stability of the POM has to be improved with new additives that leave no residue after pyrolysis. The use of copolymers POM (Co-POM), in the presence of oxyethylene units, can improve the thermal stability of POM because depolymerisation of the unstable oxymethylene (-CH2O-) units can be stopped at the first oxyethylene (-CH2CH2O-) unit [59]. However, because Co-POM contains only small fractions of co-stabiliser, it still has the propensity to depolymerise into formaldehyde. Consequently, the generation of formaldehyde can easily oxidise to formic acid, which could induce polymer chain scission, thus accelerating the degradation of POM [65–67].
This is to emphasise that formaldehyde is an irritant regarded as a potential human carcinogen that could lead to serious health issues [68,69]. Hence, due to its toxicity, formaldehyde has limitations in the allowable quantity and concentration that can be present in the working environment. According to the work exposure standard (WES), the recommendable exposure to formaldehyde in the working environment in New Zealand should not exceed 1 ppm for the workplace ceiling limit, 0.5 ppm for an 8-hour time-weighted average (TWA), and 0.33 ppm for a 12-hour time-weighted average (TWA) [70].

Hence, in order to minimise the formaldehyde emission originating from POM, low molecular weight primary or secondary amine additives can be employed [81]. In one attempt, Sun et al. (2008) [71,72] demonstrated that the addition of hexamethylenediamine (HA) and triethanolamine (TEA) could reduce the amount of formaldehyde emission on POM. It is said that introducing an amine group serves three functions during melt treatment of POM, that is, to absorb the formaldehyde by an addition reaction, to neutralise the formic acid from the oxidised formaldehyde, and to promote the hydrolytic degradation of the unstable end groups of POM into stable groups [71,72]. Berardinelli et al. (2012) [73] described that basic hydrolytic treatment of POM with ammonium hydroxide successfully removed unstable oxymethylene chain end segments in the polymer. Another attempt was investigated by Mantaranon et al. (2016) [74] on a simple reactive blending of POM with bisphenol-A and aniline. It was found that by in situ mixing of the blends, benzoxazines were formed via the Mannich reaction and could effectively consume the formaldehyde generated from POM and retard the thermal degradation of POM.
2.4.1.2 High Viscosity of POM

Another complex of the existing POM binder system is its high viscosity, which makes it difficult to produce products with complex geometric shapes. It has been reported that adding small molecular weight components, such as wax, could reduce the viscosity of a POM-based binder system. However, in a recent study, Gonzalez-Gutierrez and co-workers demonstrated that adding wax (> 16wt%) causes defects such as phase separation. Thus, it can be concluded that adding wax is not the best option to decrease the viscosity of POM-based binders [15]. On the other hand, Zhang and Liu (2017) [63] found that the inclusion of a small amount of ethylene-vinyl acetate copolymer (EVA) and lithium stearate could help reduce the apparent viscosity of the POM-based binder system. In recent literature, hyperbranched polymer was employed as a processing aid to improve the rheological properties of POM-based binder systems [13]. The results revealed that the fluidity and uniformity of the feedstock are improved in the presence of hyperbranched polymer. Also, the tensile strength and dimensional accuracy of the sintered part were enhanced at 1121.92 MPa and 16%, respectively. Nonetheless, all of the binder components should be compatible with each other.

2.5 Injection Moulding Process

The second stage is injection moulding, in which the feedstock is injection moulded, similar to conventional thermoplastic injection moulding [88]. No special care is needed at this stage as titanium feedstock does not cause any important oxygen uptake [25]. The basic work principle of injection moulding is relatively simple. Initially, the feedstock is heated until it melts to fill the cavity, and then pressure is applied on the resin into the mould cavity of the desired shape. Once the moulded part is allowed to cool, the ejected solid part is known as the "green part" [75].

An injection moulding process typically comprises three main phases: filling, packing and cooling [76]. In MIM, these main phases are usually controlled and influenced by the injection parameters, such as the temperature of the barrel and nozzle, mould temperature, injection pressure, holding pressure, injection time, and cooling time [19,77]. Studies have shown that defects in injection moulding are attributed to bad materials and improper
operating conditions. For instance, flashes occur when a high moulding pressure is applied, forcing the feedstock into the clearances between mould components. Residual stress is another common defect caused during moulding, which will not be detected until later. This stress is frozen due to the rapid cooling by the relatively cold mould surfaces. However, during heating in the debinding step, the stress in materials is relieved, subsequently initiating the formation of distortion [78]. Furthermore, defects such as flow lines and incomplete fill are commonly detected, resulting in surface imperfections from low injection speed. Another common defect in MIM is the formation of gate marks due to powder/binder separation. Therefore, the appropriate process parameters are crucial in preparing parts without defects and with minimum porosity [79]. Some of the most common defects encountered during the moulding of MIM, including the ones described above, and the causes and solutions are tabulated in Table 2.4.

Table 2.4. Common defects encountered by parts during injection moulding, its causes and solutions [19,78].

<table>
<thead>
<tr>
<th>Defects</th>
<th>Causes</th>
<th>Solutions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flash</td>
<td>Too high a pressure inside the die, poor flatness of mould surface along the parting line, venting channel too large</td>
<td>Use a large tonnage machine, proper tool making, lower injection speed and moulding pressure, optimise the switch point.</td>
</tr>
<tr>
<td>Sink marks</td>
<td>Thermal shrinkage, low density</td>
<td>Increase moulding/holding pressure and injection speed, decrease mould temperature, increase gate area, add venting channels, and decrease speed when passing thick sections.</td>
</tr>
<tr>
<td>Voids</td>
<td>Trapped gas, absorbed moisture</td>
<td>Increase holding pressure, decrease injection speed, increase mould temperature, increase gate area, and move the gate to thick sections.</td>
</tr>
<tr>
<td>---------------</td>
<td>-------------------------------</td>
<td>----------------------------------------------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Burned marks</td>
<td>Overly heated binders</td>
<td>Decrease injection speed and feedstock temperature, increase gate area, and change gate location.</td>
</tr>
<tr>
<td>Weld lines</td>
<td>Cold feedstock in the die</td>
<td>Increase injection speed, mould temperature, and feedstock temperature, enlarge gate opening, add venting channels or overflow wells near weld line locations, move gate location, redesign parts to avoid stream partition.</td>
</tr>
<tr>
<td>Flow lines</td>
<td>Cold feedstock in the die</td>
<td>Increase injection speed, mould temperature, and feedstock temperature, enlarge gate opening, change gate location.</td>
</tr>
<tr>
<td>Incomplete fill</td>
<td>Insufficient material in cavity prior to gate freeze</td>
<td>Increase injection speed, shot size, pack pressure, venting, melt temperature, mould temperature.</td>
</tr>
<tr>
<td>Gate mark</td>
<td>Powder migration from a high shear rate region to a low shear rate region</td>
<td>Relocate gate with a wider opening at a thicker section, post-sintering surface treatment.</td>
</tr>
</tbody>
</table>

Further, the Taguchi method can be employed to optimise the moulding parameters and simultaneously satisfy the requirements for quality control of MIM parts in the green state - attaining the desired impact toughness in the sintered parts. For the past 20 years, the Taguchi method has been widely used as a powerful problem-solving technique due to its...
practicality in designing high-quality systems that provide much-reduced variance for experiments with an optimum setting of process control parameters. This method utilises orthogonal array (OA), signal-to-noise (S/N) ratios, main effects, and analysis of variance (ANOVA). The OA provides a set of well-balanced (minimum experimental runs) experiments, Taguchi’s S/N (which are logarithmic functions of desired output) serves as objective functions for optimisation, and main effects analysis is used to determine the optimal combination of processing parameters at the specific level with the highest mean response. ANOVA is then employed to estimate the error variance and determine the significance of the selected parameters [80,81]. The schematic flow chart of the Taguchi method used in MIM is depicted in Figure 2.3.

![Schematic flow chart of the Taguchi method in MIM](image)

**Figure 2.3.** The schematic flow chart of the Taguchi method in MIM [82].
The process of performing a Taguchi experiment begins with identifying several factors and levels that might affect the performance of the process. Then, the orthogonal array designs are utilised to advocate the assigned factors chosen for the experiment. The choice of the correct orthogonal array for a successful experimental design is essential, and it depends on the degree of freedom required to study the main effect and interacting parameters by minimising the number of experimental trials. The most used orthogonal array designs in MIM are L9 and L27 (as listed in Table 2.5). Next, to maximise the performance of a system or product, a signal-to-noise (S/N) ratio is conducted to complete the analysis of the experimental data. The S/N ratio is treated as a response (output) of the experiment. It measures variation when uncontrolled noise factors are present in the system. Several S/N ratio characteristics are available depending on the experiment's goal. The S/N ratio characteristics can be divided into three categories as shown in Equation 2.1, 2.2, and 2.3 when the characteristic is continuous [82,83]:

\[
\text{Smaller is/the better: } S_N = -10 \log \frac{1}{n} \left( \sum y^2 \right) \quad \text{Eq. 2.1}
\]

\[
\text{Nominal is/the better: } S_N = -10 \log \frac{1}{n} \left( \sum \frac{y}{S_y^2} \right) \quad \text{Eq. 2.2}
\]

\[
\text{Larger is/the better: } S_N = -10 \log \frac{1}{n} \left( \sum \frac{1}{y^2} \right) \quad \text{Eq. 2.3}
\]

where \( \bar{y} \) denotes the average of observed data, \( S_y^2 \) denotes the variation of \( y \), \( n \) indicates the number of observations, and \( y \) is the observed data. At this stage, the optimal combination of the control factors can be predicted. Response table and diagram are further plotted to identify significant main and interaction effects which influence the S/N ratio. Analysis of variance (ANOVA) is elaborated to finalise the optimum conditions for the considerable level of each variable in correlation to the S/N ratio. Once the optimal settings are established, it is helpful to undertake a confirmation trial before any onward actions are taken.

Recently, as the interest in the literature on this approach continues to grow, it has been considered an important technique in MIM to minimise performance variation at better cost efficiency. Table 2.5 lists some recent reports employing the Taguchi method focusing on optimising process parameters in metal injection moulding (MIM).
Table 2.5 Optimisation of the injection moulding process parameters in MIM by employing the Taguchi method.

<table>
<thead>
<tr>
<th>Optimisation</th>
<th>Orthogonal array (OA)</th>
<th>Signal-to-noise (S/N) characteristics</th>
<th>Main factors/levels</th>
<th>Optimal responses</th>
<th>S/N</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green strength of HDPE-palm kernel/ SS 316L</td>
<td>L₀</td>
<td>Larger is better Injection temperature (A), barrel temperature (B), injection pressure (C), speed (D)</td>
<td>A₀B₁C₁D₁</td>
<td></td>
<td>[84]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>A: 185 °C, B: 190 °C, C: 11 MPa, D: 90%</td>
<td>A, B, and C are the most influential factors.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Green strength of PEG-PMMA/ SS 316L</td>
<td>L₂₇</td>
<td>Larger is better Injection pressure (A), injection temperature (B), mould temperature (C), injection time (D), holding time (E)</td>
<td>A₀B₂C₀D₀E₀</td>
<td></td>
<td>[85]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>A: 10 bar, B: 160 °C, C: 55 °C, D: 5 sec, E: 5 sec</td>
<td>BxC is the most influential factor.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Green strength and surface appearance of PEG-PMMA/SS 316L

Injection pressure (A), melting temperature (B), powder loading (C), mould temperature (D), injection time (E), holding time (F)

A: 9 bar
B: 150 °C
C: 62 vol%
D: 70 °C
E: 6 sec
F: 7 sec

D is the most influential factor for green strength; C and D are the most significant factors for green appearance.

Surface roughness of hardened steel AISI H13 with TiN-coated P10 carbide

Cutting speed (A), feed rate (B), depth of cut (factor C)

A: 355 m/min
B: 0.1 mm/tooth
C: 0.5 mm

BXC is the most influential factor.
Green part dimension and shrinkage of SS 316L

Injection speed (A), mould temperature (B), material temperature (C), holding pressure (D), holding pressure duration (E), cycle time (F)

A: 20 mm/s  B: 40 °C  C: 200 °C  D: 50 MPa  F: 30 sec

B and C are the most influential factors.

B and D are the most influential factors.

Green density of PP-lipids/SS 316 L

Injection temperature (A), injection pressure (B), mould temperature (C), cool time (D), injection speed (E), injection time, (F), packing time, (G)

A: 190 °C  B: 80.5MPa  C: 80 °C  D: 10 sec  E: 105 rpm  F: 5 sec  G: 3 sec
Green density of PEG-PMMA/SS 316 L

Moulding pressure (A), moulding temperature (B), moulding temperature (C), holding pressure (D), moulding rate (E), holding time (F), cooling time (G)

A: 750 bar
B: 155 °C
C: 50 °C
E: 10 ccm/s
F: 15 sec

C and F are the most influential factors.

Green strength of PE-palm stearin/Ti-6Al-4V

Injection pressure (A), injection temperature (B), powder loading (C), mould temperature (D), holding pressure (E), injection speed (F)

A: 350 bar
B: 140 °C
C: 65 vol%
D: 50 °C
E: 600 bar
F: 10 ccm/s

D is the most influential factor.
<table>
<thead>
<tr>
<th>Property</th>
<th>Factor Levels</th>
<th>Result</th>
<th>Factors</th>
<th>Levels</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>The integrity of PE-palm stearin/ SS 316 L green part by solvent debinding</td>
<td>Larger is better</td>
<td>Solvent type (A), debinding temperature (B), debinding time (C)</td>
<td>A: methanol, B: 80 °C, C: 4 h</td>
<td>A is the most influential factor.</td>
<td>[92]</td>
</tr>
<tr>
<td>Green strength of LDPE-palm stearin/ SS 316 L</td>
<td>Larger is better</td>
<td>Injection Temperature (A), mould temperature (B), injection pressure (C), speed (D)</td>
<td>A: 170 °C, B: 50 °C, C: 55 %, D: 60 %</td>
<td>C is the most influential factor.</td>
<td>[83]</td>
</tr>
<tr>
<td>Feedstock homogeneity of HDPE-paraffin wax/ SS 316 L</td>
<td>Larger is better</td>
<td>Mixing temperature (A), mixing speed (B), mixing time (C)</td>
<td>A: 230 °C, B: 30 rpm, C: 15 min</td>
<td>A is the most influential factor.</td>
<td>[86]</td>
</tr>
<tr>
<td>Surface quality of PEG-PMMA/ SS 316 L</td>
<td>Smaller is better</td>
<td>Mould temperature (A), injection temperature (B), injection pressure (C),</td>
<td>A: 55 °C, B: 145 °C, C: 700 bar, D: 10 s</td>
<td></td>
<td>[93]</td>
</tr>
</tbody>
</table>
Green strength of PEG-PMMA/SS 316 L

Larger is better

Mould temperature

A: 55 °C

B: 145 °C

C: 700 bar

D: 10 s

A is the most influential factor.

2.6 Debinding Process

Next is the debinding. In MIM processes, debinding is one of the most complex and critical steps. Any defects generated during this step will only be exaggerated during the subsequent processing [94]. Since feedstocks consist of at least two or more binders, the debinding process is generally divided into multiple stages based on the formulation. The objective of debinding is to remove most of the binder with minimal remaining residue in the shortest time. In general, the removal of the primary binder component is to create a sufficient amount of porous structure. If the pore channels are unavailable or the amount and pore size are insufficient, the gas molecules produced during thermal treatment will expand, building up pressure. As a result, blistering, cracking, or even ruptures could occur when the parts can no longer contain the internal gas pressure [95]. Hence, only once the primary binders are completely removed can the interconnected porous network facilitate the rest of the remaining binder components to diffuse out of the compact surface without any pressure buildup [51]. One of the most common debinding techniques includes solvent debinding, followed by thermal debinding.
In the case of a polyoxymethylene (POM) based binder system, a catalytic debinding was performed, wherein a catalyst must be present at the surface for the reaction to proceed [51]. Due to the strong sensitivity characteristic of POM towards acid hydrolysis, POM breaks down into formaldehyde in the presence of a concentrated nitric acid catalyst (Fig. 2.4(a)) and leaves behind the metal powder skeleton held together by the remaining polyolefin. Typically, this process was performed below the melting point of POM, between 110-150 °C. As such, the decomposition of POM is carried out in the solid state. The debinding process proceeds exclusively at the gas-binder interface, with a nearly planar debinding advancing throughout the entire compact, wiping out the POM binder as illustrated in Figure 2.4(b) [12,96]. In this regard, parts produced with POM-based binders usually have good shape retention, minimal distortion, and precise dimensional control [56,97].

![Diagram of reaction](image)

Figure 2.4 (a) The decomposition of polyoxymethylene (POM) in the presence of a catalyst, and (b) the reaction of POM at the gas-binder interface over time [96].

The parts after removing the primary binders are often referred to as brown parts. Since primary binders are removed at a relatively low temperature, no diffusion bonding between powder particles occurs [51]. Therefore, it is unlikely that contamination of titanium will occur. However, to remove the secondary binders, thermal debinding is usually performed.
This is achieved by slowly heating the parts in an inert atmosphere to the temperature where the secondary binder evaporates and holding it at that desired temperature until all the binders are removed [20,51]. During thermal debinding, the risk of contamination on the titanium feedstock is relatively high (approx. 35-38% contribution), as represented in Figure 2.5 [25,98]. Since the carbon content determines the final properties of the titanium parts, careful designation of this step is critical to minimise any undesirable chemical reactions with the metal powders at elevated temperatures. Carburisation usually arises from binder decomposition, an inert atmosphere, and a fast heating rate.

The binder formulations, which generally include polymers such as polyethylene (PE), polypropylene (PP), polymethyl methacrylate (PMMA), ethylene vinyl acetate (EVA), and stearic acid (SA), have decomposition between 200 and 600 °C [99]. Therefore, the burnt out of these polymers at such high temperatures is enough to chemically react with titanium powders, forming contamination within the feedstock [98]. Moore and co-workers [100] reported that during thermal debinding, when the temperature reaches about 450 °C, carbon enrichment will occur if there are still binders remaining in part. Furthermore, Baril et al. [25] mentioned that thermal debinding should be performed below 400 °C when very fine titanium powders are involved. On the other hand, Benson and Chikwanda [98] mentioned that by using a higher debinding temperature, carbon contamination could be reduced to a certain extent but significantly affect the increase in oxygen level in titanium. Nonetheless, in practice, a degradation temperature between 400 °C and 500 °C is suitable [8].

Figure 2.5 The contributions of oxygen pick up at the thermal debinding stage (as represented by the asterisk*) of (a) CP-Ti and (b) Ti-6Al-4V MIM feedstock [25,98].
Hence, one way to reduce the contamination of Ti with carbon and oxygen is to reduce the number of decomposable substances in the binder system [35]. Kankawa et al. [101] revealed that the decomposition of depolymerisation polymers such as polyoxymethylene (POM) and polybutyl methacrylate (PBMA) in either air or nitrogen does not produce any carbon residue. Instead, they decompose into gaseous monomers, easily evaporated at a low temperature. On the other hand, random-type polymers such as polyolefins and ethylene vinyl acetate (EVA), when decomposed, tend to produce a broad spectrum of molecular fragments that contain little monomer, which results in residual carbon formation. Herranz [45] further explained that this is likely due to the cross-linked reactions between initially degraded chains. Moreover, this type of residue is hard to eliminate in an inert atmosphere. Therefore, it is crucial to choose an appropriate binder system that degrades into volatile components or includes additives that could help to volatilise the polymer components in inert atmospheres to ensure that the oxygen residue contents in the metallic feedstock are kept to a minimum [45]. Besides, Ebel [8] mentioned that the backbone binder should contain as little oxygen as possible and decompose in the proper temperature range. Typically, the thermal degradation should be as low as possible to minimise contamination of titanium during debinding. Some thermal debinding temperatures of typical secondary binder use in Ti-MIM are depicted in Table 2.5.

Table 2.5 The thermal debinding temperatures of some commonly used secondary binder

<table>
<thead>
<tr>
<th>Secondary Binder</th>
<th>Debinding Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene</td>
<td>500-600</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>450-500</td>
</tr>
<tr>
<td>Polymethyl methacrylate</td>
<td>200-450</td>
</tr>
<tr>
<td>Polyoxymethylene</td>
<td>300-450</td>
</tr>
<tr>
<td>Ethylene vinyl acetate</td>
<td>350-500</td>
</tr>
</tbody>
</table>

Another way to minimise contamination is the choice of the atmosphere under which thermal debinding is performed [15]. Heaney and German [102] studied the Ti-6Al-4V system and demonstrated that while an argon atmosphere results in lower residual carbon
content, a vacuum atmosphere favours the reduction of oxygen content. Since prevention of carbon contamination is much easier to achieve than it is for oxygen, the best option for Ti-MIM appears to be a vacuum process during heating while at the same time leaking argon into the vacuum chamber (sweep gas) [8,51,102–104]. Thian and colleagues [105] disclosed that a slow heating rate allows pores to slowly open up for the higher molecular weight components to escape without causing internal or external defects on the titanium parts. Indeed, often after primary debinding, a small amount of binder is sometimes left inside or on the surface of the parts. Therefore, a short hold for the remaining primary binder is customary [51]. Besides, the debinding process should not be extended for too long. It was found that at a debinding temperature of 600 °C with 1 hour holding time, the oxygen content increases dramatically [106,107].

The relationship between high temperature holding time with respect to carbon and oxygen contamination in Ti alloy feedstock during thermal debinding is illustrated in Figure 2.6. Nevertheless, the characteristics of the starting powder, such as low oxygen and carbon content, play the most important part in eliminating any residual contamination during MIM processing.

![Figure 2.6 A correlation of high temperature holding time vs. carbon and oxygen content on Ti-6Al-4V parts during thermal debinding [106].](image-url)
2.7 Sintering

After thermal debinding, another critical step is the sintering process. It is the process that gives MIM parts their strength. Until now, the parts have only been held together by particle friction and binder material. The sintering process transforms rigid powder compacts into proper solid metal products. These metal parts usually exhibit strength, hardness, ductility, wear resistance, conductivity, and visual resemblance similar to parts produced by conventional metalworking methods.

In general, the working principle of sintering is based on densification and shrinkage. An appreciable 10-20% shrinkage typically occurs in the final sintered part, and dimensional change is usually uniform and isotropic. However, thermal gradients can result in stresses that cause significant distortion. When debinding is incomplete, gaseous decomposition products at elevated temperatures can cause blisters and cracks in the part [108]. These defects arising in the parts due to sub-optimal conditions employed during the mixing, moulding and debinding phases cannot be corrected and are often magnified during the sintering stage [99]. Furthermore, contamination levels are another significant factor that defines the success of the debinding and sintering operations for Ti-MIM.

Oxygen is the most common interstitial element in titanium and its alloys. Although other interstitial elements such as nitrogen, carbon and hydrogen could have a detrimental influence on the properties of sintered parts, during MIM, the pickup of these elements is negligible compared to oxygen [8]. As depicted in Figure 2.6, interstitial oxygen positively influences the strength but deleteriously affects elongation. Increasing the oxygen level could significantly increase the tensile strength, however, at the expense of ductility. Therefore, the oxygen content in Ti-MIM should be kept at a low level. In the Materials Standards, it is required that the oxygen level be < 1800 ppm and < 4000 ppm for CP-Ti (grade 1) and CP-Ti (grade 4) products, respectively, following the ASTM F2989, while for Ti-6Al-4V products, the oxygen level should be < 2000 ppm (ASTM B348) [5,109,110]. However, as a guideline for MIM, the maximum oxygen level should be approximately 2000 ppm because oxygen pickup is unavoidable during sintering [110].
Figure 2.6 The effect of oxygen content on the mechanical properties of pure titanium [9].

The critical considerations for the Ti-MIM sintering cycle are peak temperature, holding time, rack material and, most importantly, sintering atmosphere [8]. Sintering of titanium is usually carried out in a high vacuum or argon. In general, high vacuum sintering provides better results than argon in terms of the final density and oxygen contamination. This is attributed to the fact that argon might be trapped in the pores of the sintering part, preventing full densification. Furthermore, impurities in the argon can lead to contamination of the titanium parts [8,51].

On the contrary, Banerjee and Joens [111] who studied the Ti alloy processed in a MIM furnace with a closed retort, proposed that parts sintered in an argon atmosphere demonstrated the best results with the lowest oxygen contamination and highest elongation. Besides, Ahmad et al. [112] also showed that the sintered Ti-6Al-4V parts in an argon atmosphere displayed improved densification compared to a vacuum atmosphere with higher tensile strength, elongation and decreased porosity. Nonetheless, with vacuum sintering, operating pressure sustained below or at 10^{-4} Pa is possible to minimise the contamination by oxygen. It is recommended that titanium be sintered at as low temperatures as possible. However, the low sintering temperature does not achieve the required densification of MIM parts [113]. Generally speaking, higher sintering temperatures and longer holding times led to higher density, resulting in higher strength and ductility. However, too high a sintering temperature damages, with loss of sintered strength due to either gas reactions or microstructure coarsening [5,113]. Therefore, the
optimal sintering cycle depends on the starting powder characteristics, desired density, alloying approach, microstructure, and final impurity level requirements. Typical sintering parameters for titanium and its alloy are around 1250 °C combined with a holding time of 2-3 hours [5,8,43]. If temperatures around and above 1300°C are involved, a reduction of ductility can be observed, attributed to either grain growth or higher oxygen pickup [51]. For instance, Ferri et al. [114] demonstrated that sintering gas atomised Ti alloy powder with an initial oxygen content of 0.088% at 1350 °C increased to 0.23% oxygen. In contrast, at 1250 °C, oxygen increases only to 0.21% after 120 min.

Another significant influence on sintering success for titanium and its alloys is known from the sintering substrates. Trays or plates made of zirconia or yttria are the most common for sintering Ti-MIM. However, these materials are expensive, and thus, a cost-saving alternative may be used, such as plasma spray coating on alumina substrates with a yttria layer [115]. Molybdenum is another sintering support that can be used when it involves reactive metals such as titanium. However, molybdenum is susceptible to grain coarsening at high temperatures, and therefore, its service time is relatively limited.

**2.8 Summary**

In general, the progress of titanium MIM and its alloys is still a relatively new process and is under continuous development compared to stainless steel MIM. Because titanium (Ti) has a high affinity towards oxygen and carbon, this complicates the whole MIM production chain from powder production to sintering. In particular, debinding is one of the most critical stages, as contamination can be easily introduced from the binders to titanium at elevated temperatures. Therefore, appropriate binder selection and debinding steps must be controlled more stringently to ensure the success of Ti-MIM. The emergence of the POM-based binder system has received increasing interest in recent years due to its clean decomposition, good shape retention, and shorter debinding time. In this dissertation, a novel, environmentally friendly POM-based binder system will be thoroughly investigated, and its drawbacks and limitations will be addressed accordingly. Furthermore, incorporating a low decomposition temperature polymer into a POM-based binder system will also be scrutinised.
Chapter 3 Methodology

This chapter describes the experimental work to develop a binder system and formulate a feasible Ti-MIM feedstock based on polyoxymethylene (POM). Raw materials, general experimental procedures, and equipment used in this PhD project are included here.

3.1 Materials

Commercial purity Ti powder was purchased from TLS Technik Spezialpulver (Germany). The powder was produced by gas atomisation (GA), resulting in a spherical shape with a nominal size of 45 µm. The GA Ti powder characteristics and morphology are presented in Table 3.1 and Figure 3.1, respectively. The mainly concerned impurity contents were 0.122% O, 0.003% C, and 0.008% N. Details of the polymers for the binder system are given in Table 3.2. The materials used for the preparation of powder binder feedstock include laboratory-modified polyoxymethylene (POM), isotactic polypropylene (PP), polypropylene carbonate (PPC), polyethylene glycol (PEG), poly(ethylene-co-methyl acrylate-co-glycidyl methacrylate) (EGMA), poly(ethylene-co-vinyl acetate) with 40% vinyl acetate (EVA), and stearic acid (SA).

Table 3.1 The elemental composition of Ti powder

<table>
<thead>
<tr>
<th>Powder type</th>
<th>Mean size (µm)</th>
<th>O (wt%)</th>
<th>C (wt%)</th>
<th>N (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GA Ti</td>
<td>45</td>
<td>0.122</td>
<td>0.003</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Table 3.2 Details of polymeric binder components

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Density (g/cm³)</th>
<th>Average Mw (g/mol)</th>
<th>Melting/Glass transition point (°C)</th>
<th>Supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>POM</td>
<td>1.42</td>
<td>~ 66,000</td>
<td>169</td>
<td>In-house</td>
</tr>
<tr>
<td>PP</td>
<td>0.9</td>
<td>250,000</td>
<td>160-170</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>PPC</td>
<td>1.26</td>
<td>150,000</td>
<td>25-45</td>
<td>Empower Materials</td>
</tr>
<tr>
<td>PEG</td>
<td>1.2</td>
<td>4,000</td>
<td>50-60</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>EMA-GMA</td>
<td>0.94</td>
<td>-</td>
<td>39</td>
<td>Sigma-Aldrich</td>
</tr>
<tr>
<td>EVA</td>
<td>0.941</td>
<td>-</td>
<td>75</td>
<td>Sigma-Aldrich</td>
</tr>
</tbody>
</table>
3.2 Experimental Procedures

3.2.1 Modification of Polyoxymethylene (POM)

In the first stage, POM is modified to reduce the formaldehyde emission for the MIM process. Melt-blending was performed by adding POM, propylamine (PA), and aluminium oxide in a Thermo Haake Brabender (Germany) mixer at 190 °C for 10 mins with a rotor speed of 50 rpm. Aluminium oxide is a formic acid absorber that prevents any aggravated degradation of POM during melt blending [116]. The formulations of POM blends are presented in Table 3.3. Figure 3.2 shows the physical appearance of the modified POM after pelletised. Compression moulding was conducted at 200 °C under a pressure of 10 MPa. The preheating, compression moulding, and cooling times were 3 min., 2 min., and 2 min., respectively. Samples with 120 µm and 3 mm thickness were used for characterisation. Solid density was measured using a helium micro-pycnometer AccuPyc 1200e (Micromeritics, Unterschleißheim, Germany), with a relative standard deviation of 0.005%. The reported value was the average of 10 determinations in a single run.
Table 3.3 Materials designation and composition of POM and its blends (POM-PA)

<table>
<thead>
<tr>
<th>Code</th>
<th>Compositions (wt%)</th>
<th>POM</th>
<th>Propylamine (PA)</th>
<th>Aluminium oxide (Al₂O₃)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POM</td>
<td>100</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.427</td>
</tr>
<tr>
<td>POM-PA1</td>
<td>98.8</td>
<td>1</td>
<td>0.2</td>
<td>-</td>
<td>1.426</td>
</tr>
<tr>
<td>POM-PA2</td>
<td>97.8</td>
<td>2</td>
<td>0.2</td>
<td>-</td>
<td>1.424</td>
</tr>
<tr>
<td>POM-PA3</td>
<td>96.8</td>
<td>3</td>
<td>0.2</td>
<td>-</td>
<td>1.425</td>
</tr>
<tr>
<td>POM-PA4</td>
<td>95.8</td>
<td>4</td>
<td>0.2</td>
<td>-</td>
<td>1.426</td>
</tr>
<tr>
<td>POM-PA5</td>
<td>94.8</td>
<td>5</td>
<td>0.2</td>
<td>-</td>
<td>1.425</td>
</tr>
</tbody>
</table>

Figure 3.2 Physical appearance of modified POM (POM-PA2) after melt-blending.
3.2.2 POM Binder System Formulation

Next, the POM-based binder component without metal powder was prepared similarly using an internal mixer (Thermo Haake Brabender, Germany) at 180 °C for 10 mins with a rotor speed of 60 rpm. The binder system was based on the polymer blend containing the laboratory-prepared POM as the primary binder, PP as the secondary binder, EMA-GMA and EVA as a compatibiliser, and SA as a surfactant. The compositions of the binder content are tabulated in Table 3.4. After mixing, the polymeric binder mixture is hot pressed into a thin film with a thickness of 1 mm for characterisation. Polymeric compatibility of the POM binder system was based on contact angle measurement and atomic force microscopy (AFM).

Table 3.4 The compositions of the binders (wt%)

<table>
<thead>
<tr>
<th>Binder</th>
<th>POM (%)</th>
<th>PP (%)</th>
<th>EGMA (%)</th>
<th>E40 (%)</th>
<th>SA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-0</td>
<td>80</td>
<td>15</td>
<td>0</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td>EGMA-2</td>
<td>78</td>
<td>15</td>
<td>2</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>EGMA-3</td>
<td>77</td>
<td>15</td>
<td>3</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>EGMA-5</td>
<td>80</td>
<td>15</td>
<td>5</td>
<td>-</td>
<td>5</td>
</tr>
<tr>
<td>EVA-2</td>
<td>78</td>
<td>15</td>
<td>-</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>EVA-3</td>
<td>77</td>
<td>15</td>
<td>-</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>EVA-5</td>
<td>80</td>
<td>15</td>
<td>-</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

3.2.3 Feedstock Preparation

Subsequently, the selected binder formulation was used to prepare the titanium feedstock. Mixing was performed at 180 °C, 60 rpm for 40 mins. The sequence of addition of the components for producing all sets of feedstocks is as follows. First, the dried powdered metal is added to the Brabender. Then, the first component is added. The second component is fed once the first is molten; the same is true with the third binder component, added after the second one is molten. The detection of the melting is accomplished by observing the increase in the torque evolution curves. When a polymer melts, the torque starts to increase
and reach peak torque, and then the torque decreases, stabilising afterwards. The mixing procedure and schematic of the torque evolution curves are shown in Figure 3.3. For Chapter 8, binder composition and feedstock preparation are explained in the experimental part of the chapter.

![Figure 3.3 Mixing procedure of MIM feedstock.](image)

### 3.2.4 Metal Injection Moulding

Once the feedstocks were prepared, they were charged into an injection moulder, the HAAKE MiniJet Piston Injection Moulder (ThermoFisher, Germany). The injection moulding parameters were chosen based on rheological experiments and the Taguchi method. The specific parameters are included in each chapter. Tensile dog-bone specimen standards are used to prepare test samples, as illustrated in Figure 3.4.

![Figure 3.4 Dimension of an injection moulded test sample in millimetres (mm).](image)
3.2.5 Solvent Debinding

A commonly used solvent debinding technique was performed on the injected parts (green parts) to remove POM benignly. Notably, POM is acid-sensitive; hence, acid is used as a solvent in decomposing the polymer binder. The solvent debinding was performed at 50 °C using different diluted and organic acids for varying time lengths. At a specific hour, the parts were removed from the solvent bath, washed with distilled water, dried in an oven at 60 °C for 3 h, and then conditioned to 25 °C for 12 hours. The debound parts were weighed and recorded to determine the percentage of the removed binder. Next, the debinding process was performed on the best-selected solvent at various temperatures. The effect of temperature on debinding time and kinetics was thoroughly investigated. The purpose of debinding is to create porosity in the green part to facilitate the escape of the gases produced during polymer decomposition, limiting the appearance of structural defects in the thermal debinding process.

3.2.6 Thermal Debinding

Subsequently, any remaining binder in the green parts was removed by thermal debinding. Thermal debinding was performed under a purging argon gas (quartz tube) and a high vacuum (ACME furnace, China) for comparison purposes. The heating profile was selected based on the TGA result. Since each binder system has its specific thermal debinding profile, the debinding profiles for different binder systems were demonstrated in the corresponding chapters.

3.2.7 Sintering

Sintering was carried out at 1300 °C for 120 mins with a 2 °C/min heating rate in ZSJ-20×20×30 high vacuum furnace. A cubic alumina crucible is used to cover the thermally debound samples during sintering to avoid contamination from the furnace chamber.

3.3 Characterisation and Testing

In this section, the characterisation and testing to develop an environmentally-friendly POM binder system for Ti-MIM were divided into two categories: (i) evaluation of the
modified POM formulation and (ii) study and optimisation of the different properties of POM-based binders system and MIM feedstock.

3.3.1 Evaluation of the modified POM Formulation

**Fourier transform infrared (FTIR)** spectra of POM and POM-PA blends were analysed using the Perkin Elmer Spectrum 100 series spectrophotometer (Shelton, Connecticut, USA) equipped with attenuated total reflectance mode (ATR) on a diamond crystal. All measurements were performed in the range of 4000–400 cm$^{-1}$ with a scanning resolution of 4 cm$^{-1}$ averaged over 16 scans.

Formaldehyde absorbance was measured photometrically at a wavelength of 412 nm using a **UV-Vis Spectrophotometer** (Shimadzu UV-2550, Japan). The procedure to determine formaldehyde emission followed the standard test method VDA 275 (German Automakers Association recommendation No. 275) with slight modifications. In brief, two test specimens with dimensions of 67 x 57 x 3 (mm) were hooked on copper metal in a 1 L glass bottle above 100 ml of distilled water. The glass bottle containing test specimens was heated in an air-circulating oven at 60 °C for three hours. After that, the test specimens were removed from the glass bottle, and 5 ml of the distilled water (known as sample solution) was extracted and transferred into a test tube. The sample solution was heated at 95 °C for 10 minutes. Then, 5 ml of acetylacetone reagent was added to the test tube. A blank solution was prepared without any test specimens. The concentration of formaldehyde was determined using the following Equation (3.1) [24]:

\[
G = f \times (A_d - A_b) \times 100 \times \frac{1}{S} \quad (3.1)
\]

where G is the concentration of formaldehyde (mg L$^{-1}$), $A_b$ is the absorbance of a blank solution, $A_d$ denotes the absorbance of the sample solution, f is the gradient of the calibration curve for the standard formaldehyde solution (which is 2.466), and S is the total surface area of the samples (cm$^2$).

**Thermal gravimetric analysis (TGA)** was performed on SDT Q600 at a heating rate of 10 °C/min under an argon atmosphere. The temperature range was 25 to 500 °C. The decomposition temperatures at initial weight loss ($T_{onset}$) and the maximum weight loss ($T_{u}$)
were determined from the TGA graph. The highest decomposition temperature \( T_{\text{max}} \) was obtained from the derivative thermogravimetric (DTG) curves.

The **melt flow index (MFI)** values of POM and POM-PA blends were measured using a Dynisco melt flow indexer weighing 2.16 kg at 190 °C, as specified in ASTM D 1238 standard [25]. The results are expressed in grams per 10 min.

**Scanning electron microscopy (SEM)**, micrographs of the gold-coated fractured surfaces (broken in the liquid nitrogen) of POM and POM-PA blends were analysed using a Hitachi SU-70 Scanning Electron Microscope.

### 3.3.2 Characterisation of POM Binders and MIM Feedstock

The compatibility of POM with other polymeric components was studied via **contact angle measurement**. The POM binder constituents were initially determined on four test liquids (deionised water, ethylene glycol, di-iodomethane, and hexadecane). A drop test was performed by depositing a single drop of liquid (volume, \( V = 3-5 \mu L \)) on the sample surface, and the sessile drop and the contact angle were measured. Contact angles measured on 3 different areas for each sample were averaged to obtain one representative value. Using the above data, the total surface energy \( \gamma^{(\text{tot})} \), disperse part \( \gamma^{(d)} \), and polar part \( \gamma^{(p)} \) were obtained, following the Owens–Wendt method [117–119]. Afterwards, the interfacial tension between the polymers was calculated using the geometric and harmonic mean equations (Eq. (3.2), (3.3)):

\[
\gamma_{ij} = \gamma_i + \gamma_j - 2 \left( \sqrt{\gamma_i^d \gamma_j^d} + \sqrt{\gamma_i^p \gamma_j^p} \right) \quad (3.2)
\]

\[
\gamma_{ij} = \gamma_i + \gamma_j - \frac{4 \gamma_i^d \gamma_j^d}{\gamma_i^d + \gamma_j^d} - \frac{4 \gamma_i^p \gamma_j^p}{\gamma_i^p + \gamma_j^p} \quad (3.3)
\]
After that, contact angle measurement using deionised water was performed on the formulated POM binder system and selected titanium feedstock. Each measurement was repeated four times for each specimen for an accurate measurement.

Tapping mode atomic force microscopy (AFM) was used to characterise the POM binder system. Atomic force microscopy was performed on an Asylum Research MFP-3D Origin with Budget Sensors silicon 150 probes. The nominal scans include a line rate from 0.5 to 1 Hz, with a frequency of 150 kHz and a spring constant of 1.5-15 Nm\(^{-1}\). The images obtained were analysed using commercial Gwyddion software.

Fourier Transform Infrared (FTIR) using a Perkin Elmer 100 spectrophotometer (Waltham, MA, US) was performed to evaluate the chemical interactions between the POM-based binder system and the MIM feedstock. The spectra were collected over a scan range of 450-4000 cm\(^{-1}\) at a resolution of 16 cm\(^{-1}\).

Accupyc II Gas Pycnometer is another tool to determine the interaction between the powder and binder. A homogeneous feedstock will demonstrate low standard deviation values. On the other hand, an inhomogeneous feedstock caused by poor powder-binder interaction will lead to varying density within the feedstock and can further cause distortion within the moulded part. The homogeneity of the feedstock was determined by randomly selecting 5 samples from the prepared batch. Subsequently, to ensure the highest possible density with no voids, the injection moulded and crushed injected parts were compared to the feedstock's theoretical density [120]. The density of the final sintered sample was also obtained using the gas pycnometer.

Capillary rheometers are designed to calculate viscosity based on Newtonian fluids, and because MIM feedstocks have non-Newtonian flow behaviour, certain corrections were applied to obtain their true viscosity. Rheological experiments were performed on a CFT-500D capillary rheometer (Shimadzu) from 180 °C to 200 °C. Different pressure values and die sets with different length-radius (L/D) ratios (D1 = 1 mm, L1 = 1 mm; D2 = 1 mm, L2 = 2 mm) were used for calculations based on the Bagley & Rabinowitsch corrections [121–124]. The mouldability index (α) can be calculated using Eq. (3.4) [121]:

\[
\alpha = \frac{1}{n} \frac{1-n}{E/R} \quad (3.4)
\]
where $E$ is the activation energy, $R$ is the gas constant, and $\eta_0$ is the reference viscosity at 190 °C and a shear rate of 6000 s$^{-1}$. A high value of $\alpha$ denotes better rheological stability of the feedstock [124].

Microstructures of the metal powder, green samples, and sintered parts were observed using the **Scanning Electron Microscope** (SEM Hitachi SU-70).

**An optical microscope coupled with Image J software was used** to measure the porosity and the pore size distribution of the sintered parts.

**LECO Analyzers** (LECO Series ON 736 and CS 744) were conducted on at least 3 samples (average) to determine the oxygen and carbon content of the sintered samples.

**Tensile testing** was conducted on an Instron 3367 machine with an extensometer. The gauge length for each sample is 50 mm, and the crosshead speed is 0.5mm/min. The final mechanical properties for each binder system were taken as the average data from at least 3 samples.
Chapter 4 Development of Low Formaldehyde POM Binder for MIM

Polyoxymethylene (POM) can be easily decomposed when exposed to heat and oxygen, releasing undesired carcinogenic formaldehyde products. Therefore, in this chapter, POM modifications were intended to reduce the formaldehyde emission while maintaining its original properties as a potential binder system for metal injection moulding (MIM). The role and effect of employing amine as a formaldehyde scavenger at different concentrations were thoroughly studied. The data in this chapter has been published in ref. [125].

4.1 Introduction

The emergence of the polyoxymethylene (POM) binder system is one of the hot topics in the powder injection moulding industry for metals and ceramics [13,15]. POM is one of the preferred binders for MIM feedstocks due to its excellent properties, such as high dimensional stability, high rigidity, good warm strength, and fast debinding time [12,61,126]. However, upon exposure to heat and high shear stresses during compounding and moulding, POM degrades into formaldehyde [68]. Notably, the vapours of formaldehyde are known to be irritants and have been regarded as a potential human carcinogen that could lead to serious health issues [69,127]. According to the Occupational Safety and Health Administration (OSHA) Formaldehyde Standard 29 CFR 1910.1048, the permissible exposure limit to formaldehyde is 0.75 ppm for an 8-hour time-weighted average (TWA) and the airborne concentration of formaldehyde should not exceed 2 ppm on a short-term exposure limit [127].

Moreover, binder systems based on POM require expensive capital equipment to manage the decomposition of the formaldehyde oligomers [128]. Therefore, it is believed that a safer working environment can be realised by reducing the production of formaldehyde in POM. Secondly, this will lower the operational cost of disposing of the formaldehyde emission originating from POM.

---

In the literature, different types of formaldehyde scavengers have been reported; for the leather substrates, plant extracts (for instance, gallic acid, pyrogallol and ethylene urea) have been studied to reduce the formaldehyde content [129]. For wood substrates, adding formaldehyde scavengers such as tannins, phenolic compounds, sodium metabisulphite, and amines has successfully reduced formaldehyde emissions [130,131]. Nonetheless, the amine group is the best functional reacting group for formaldehyde absorption [130]. For polymer substrates, Sun et al. demonstrated that the addition of hexamethylenediamine (HA) and triethanolamine (TEA) helps reduce the formaldehyde emission in POM [71,72]. It has been suggested that the addition of an amine group serves three functions during melt treatment of POM: (1) absorbing the formaldehyde by an addition reaction, (2) neutralising the formic acid from the oxidised formaldehyde, and (3) promoting the hydrolytic degradation of the unstable end groups of POM into stable groups [71,72]. Mantaranon et al. [74] investigated a simple reactive blending of POM with bisphenol-A and aniline. They found that by in situ mixing of the blends, benzoazines were formed via a Mannich reaction and could effectively consume the formaldehyde generated from POM and retard the thermal degradation of POM. Interestingly, Xu et al. [132] reported that not all organic amines can remove formaldehyde. The results showed that amines with two -NH groups could not effectively remove formaldehyde compared to those with one -NH group.

Nonetheless, these approaches use a complex amine group, which can significantly change the structure of the POM backbone and its mechanical properties. Herein, we used a simple amine group, propylamine, to modify POM. Besides, the use of propylamine to modify POM for MIM has not yet been reported in the literature. Therefore, this study aims to understand the decomposition mechanism of POM and how it can be modified to minimise the release of formaldehyde while maintaining its good rheological properties for MIM. A preliminary study was investigated to compare the properties of commercial POM and modified POM (i.e., POM-PA2 in this study) on the MIM feedstock in terms of its rheological properties and green strength.
4.2 Results and Discussion

4.2.1 Reaction mechanism of POM and propylamine (PA)

The previous literature has found that the oxidative scission reaction of POM starts at approximately 160 °C [67]. Our melt-blending process was carried out at 180 and 190 °C; thus, the oxidative scission reaction is expected. During melt blending, an intermediate product containing hydroperoxide groups is produced from POM in the presence of heat and oxygen. As shown in Figure 4.1(a), the hydroperoxides on the methylene groups can induce a β-scission reaction, followed by the formation of formaldehyde, which later oxidises into formic acid, causing acidolysis of the polymer and further accelerating degradation [65–67].

However, when propylamine is added, a different reaction route is expected. During the β scission, formaldehyde gas generated from POM will react with propylamine to form an imine (N=C) group [133]. Since imine is unstable, it undergoes an addition reaction with the POM to form a new and stable mixture of POM polymer containing a nitrogen functional group (Fig. 4.1(b)). However, if basicity is continuously increased (with an increased pH) by adding excessive propylamine and at lower formaldehyde concentrations, imine will not form. Instead, the excessive amine will react with formaldehyde and form protonation of hydroxymethyl amine that would reversibly convert back to its free base form and formaldehyde gas (Fig. 4.1(c)) [134]. Besides, a certain degree of polymerisation is necessary for the propylamine to be stable during the processing of POM.
Figure 4.1 The (a) oxidative scission reaction of POM in the presence of heat and oxygen, (b) reaction of formaldehyde with propylamine, and (c) formation of tertiary amine due to excess amine.

4.2.2 FTIR analysis

Figure 4.2 demonstrates the typical stretching vibrations of POM, propylamine (PA), and POM-PA blends. Figures 4.3 and 4.4 elucidate the interaction between POM and PA at different concentrations. As shown in Figure 4.2, the stretching mode of POM C-O-C bonds can be observed at 1088 and 891 cm\(^{-1}\). Meanwhile, the moderate bands at 2920, 1237, and 630 cm\(^{-1}\) are attributed to the stretching of CH\(_2\) [67,135]. As for the propylamine (PA), a twin peak can be observed at 3364 cm\(^{-1}\) and 3289 cm\(^{-1}\), corresponding to primary amines -NH stretching vibration. On the other hand, the characteristic absorption peak at 1070 cm\(^{-1}\) belongs to the C-N stretching vibrations of propylamine.

After adding propylamine, it is notable that POM-PA blends demonstrate a single weak band at 3297 cm\(^{-1}\) (Fig. 4.3). This is well attributed to the stretching vibrations of -NH groups (secondary amine), suggesting the successful incorporation of propylamine within the POM main chain. Furthermore, Figure 4.4 shows that the peak of POM-PA blends at 1088 cm\(^{-1}\) (C-O-C absorption bands) becomes sharper and slightly shifts to a lower wavenumber (1087 cm\(^{-1}\)) after modification. This shift towards a lower wavenumber proves an interaction between POM and propylamine, feasibly forming a stronger C-N bond within the C-O-C bond. Interestingly, the addition of 2 wt.% propylamine reveals the highest intensity increase. The strong intensity at 2 wt.% propylamine corresponds to a maximum amount of molecular bonding between POM and propylamine. However, beyond 2 wt.% propylamine, the intensity at the C-O-C and CH\(_2\) absorption bands slightly decreases. We suggest that the degradation of POM and propylamine generates a stable product (as proposed in Fig. 4.1).
Figure 4.2 The FTIR spectra of POM, PA, and POM-PA blends.
The formaldehyde emission values of POM and POM-PA blends are shown in Figure 4.5. All POM-PA blends demonstrate a lower formaldehyde emission than unmodified POM. Besides, a comparison between POM and POM-Al₂O₃ has been made (with constant wt% of aluminium oxide), and the results show that the reduction of formaldehyde emission is not significant without propylamine. This suggests that the addition of propylamine (PA) is necessary to absorb or react with the formaldehyde produced from the decomposition of POM through an addition reaction (Fig. 4.1(b)). Besides, it has been reported that the mixture of polyoxymethylene with amine functional groups produces a synergistic effect in reducing formaldehyde [71,136]. As seen, at a low concentration of propylamine (1 and 2 wt.%), the formaldehyde emission of the POM-PA blends decreases. At 2 wt.% concentration, the formaldehyde emission is reduced by 35% compared to unmodified POM (2.04 mg/L). This reveals that propylamine, with its basic properties, could remove
the unstable ends groups of POM and replace them with a relatively stable -NH group. However, beyond 2 wt.% concentration, the formaldehyde emission level increases again. It is stipulated that the reaction proceeds rapidly at a higher propylamine concentration, leading to the formation of hydroxymethyl (R-OH) groups (Fig. 4.1(c)). As a result, this creates product molecules with less content of the remaining active hydrogen group. These observations agree with the study by Sun et al. [72], who reported that the produced molecules with a lack of active hydrogen atoms are the reason for the poor scavenging efficiency of formaldehyde. It is also noteworthy that adding a simple amine, propylamine, to the POM matrix can achieve much lower emissions than the latest commercial POM grades – Duracon Low Volatile POM. The low level of formaldehyde emission of POM-PA2 allows compliance with the current and future more formidable emissions industry norms [137].

Figure 4.5 The formaldehyde emission with increasing propylamine concentration compared with commercial POM grades (Note that commercial POM grades are tested at 60 °C according to the VDA 275 standard testing method [137]).

4.2.4 TGA Analysis

Figure 4.6 shows the thermal decomposition of the unmodified POM and modified POM-PA blends, while Table 4.1 tabulates the T$_{onset}$, T$_d$, T$_{max}$, and MFI values of POM and its
blends. MFI value is an inverse function of viscosity and can be used to estimate the interaction between the phases in polymer mixtures [138].

Table 4.1 Thermal decomposition and MFI value of POM and POM-PA blends

<table>
<thead>
<tr>
<th>Material Designation</th>
<th>$T_{\text{onset}}$ (°C)</th>
<th>$T_d$ (°C)</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>MFI (g/10 min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POM</td>
<td>275.59</td>
<td>350.74</td>
<td>326.84</td>
<td>9.84 ± 0.19</td>
</tr>
<tr>
<td>POM-PA1</td>
<td>285.83</td>
<td>372.74</td>
<td>330.25</td>
<td>9.82 ± 0.13</td>
</tr>
<tr>
<td>POM-PA2</td>
<td>294.72</td>
<td>387.21</td>
<td>358.39</td>
<td>9.73 ± 0.17</td>
</tr>
<tr>
<td>POM-PA3</td>
<td>302.27</td>
<td>406.38</td>
<td>365.95</td>
<td>9.77 ± 0.24</td>
</tr>
<tr>
<td>POM-PA4</td>
<td>301.48</td>
<td>399.70</td>
<td>362.98</td>
<td>9.95 ± 0.13</td>
</tr>
<tr>
<td>POM-PA5</td>
<td>284.09</td>
<td>386.97</td>
<td>354.18</td>
<td>9.98 ± 0.04</td>
</tr>
</tbody>
</table>

As presented in Figure 4.6, the POM and POM-PA blends display a single-step degradation behaviour at 500 °C. The thermal degradation of POM is due to the randomly initiated bond cleavage in the carbon-oxygen backbone [139]. The influence of increasing propylamine
concentration on POM can be analysed by the decomposition temperature. From Table 4.1, the thermal degradation characteristic temperature for all POM-PA blends is higher than that of pure POM. This indicates that propylamine can hinder the tendency of molecular degradation of POM during processing. However, it appears that the addition of propylamine increases the thermal stability of POM in a manner dependent on amine concentration. Increasing propylamine concentration increases the degradation temperature; beyond a certain concentration, it shifts towards a lower temperature. Besides, when comparing the MFI value, we found that thermal stability increases at a lower MFI value. The maximum decrease in MFI value at 2wt.% propylamine demonstrates higher viscosity due to the formation of a higher molecular weight chain mechanism that effectively retard the thermal degradation of POM. Therefore, the relationship between high thermal stability and low MFI value of the POM-PA matrix are important factors in reducing formaldehyde emission, as they inhibit the tendency of molecular degradation of POM. Furthermore, it is worth noting that at 589 °C, neither POM-PA 1 nor POM-PA2 produce any residues. However, for the blends of POM, POM-PA3, POM-PA4, and POM-PA5, the residues were 0.32%, 0.59%, 0.69%, and 1.60%, respectively. The residue of pure POM detected less than 1% is mainly attributed to the thermally degraded processing aid and stabilising compound [65]. In the case of high PA contents (such as POM-PA 3 to POM-PA 5), we assume that the structures produced differ from those formed in POM-PA1 and POM-PA2.

4.2.5 SEM observations

As shown in Figure 4.7(a), the fracture surface of the unmodified POM reveals a smooth, wave-like structure, indicating the characteristic of a brittle fracture behaviour [140,141]. However, after adding propylamine, the fractured surface of the polymer blends (POM-PA) becomes craggy. The craggy fracture surface can be ascribed to the good interaction of the dispersed phase within the continuous matrix [142]. Figures 4.7(a) and (b) reveal that no aggregation or formation of voids is observed when propylamine concentrations are low. Besides, it is most evident in the blends of POM-PA2, where the fracture surface is the craggiest. This reveals that adding 2wt.% of propylamine could generate the most substantial interaction between propylamine and POM. Nonetheless, at higher propylamine concentrations (3 wt.% and above), the fractured surface of the polymer blends exhibits some micro-cracks (Fig. 4.7(d-f)). This phenomenon is not well understood. However, we
speculate that the possible degradation of POM within the blends during melt blending may contribute to the formation of these cracks. This is reflected in the MFI value. When too much amine is added, the MFI value increases, suggesting the presence of lower molecular weight within the polymer blends.

4.2.6 Rheological Properties

Based on the above results, POM-PA2, with the lowest formaldehyde emission, was used to formulate the metal injection moulding (MIM) feedstock. For comparison purposes, a feedstock using commercial POM was also prepared. Figure 4.8 shows the rheological behaviour of two feedstocks containing POM and POM-PA2 as the primary binder component. Both feedstocks display pseudoplastic behaviour. Notably, the feedstock containing POM-PA2 demonstrates a slightly lower viscosity than the feedstock containing unmodified POM. This might be due to the better interaction between the modified polymeric binder (POM-PA2) and titanium powder attributed to the increased hydrogen bonds on the POM molecular chains. Nonetheless, it is discernable that both feedstocks show reasonably good viscosity in the entire shear rate range of $10^2$ to $10^5$ s$^{-1}$, where the upper viscosity limit has been set at 1000 Pa·s [122].

Figure 4.7 SEM micrographs of the fracture surface of (a) POM, (b) POM-PA1, (c) POM-PA2, (d) POM-PA3, (e) POM-PA4, and (f) POM-PA5.
Figure 4.8 Plot of the double logarithm of viscosity vs shear rate in the temperature range of 180 °C to 200 °C for (a) POM feedstock and (b) POM-PA2 feedstock.

Table 4.2. Comparison of the rheological properties of POM and POM-PA2 feedstock

<table>
<thead>
<tr>
<th>Properties</th>
<th>POM</th>
<th>POM-PA2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow behaviour index (n)</td>
<td>180 °C: 0.58</td>
<td>180 °C: 0.60</td>
</tr>
<tr>
<td></td>
<td>190 °C: 0.53</td>
<td>190 °C: 0.50</td>
</tr>
<tr>
<td></td>
<td>200 °C: 0.54</td>
<td>200 °C: 0.57</td>
</tr>
<tr>
<td>Activation Energy (E_a)</td>
<td>9.45 J/mol</td>
<td>9.78 J/mol</td>
</tr>
<tr>
<td>Mouldability index (α_{stv})</td>
<td>52.4 x 10^{-4}</td>
<td>58.1 x 10^{-4}</td>
</tr>
</tbody>
</table>
Other important factors that must be considered during MIM feedstock design are shear sensitivity \((n)\) and temperature sensitivity \((E_a)\). A suitable MIM feedstock should have a low \(n\) value and low \(E_a\). However, if the \(n\) value is too low, it may cause problems such as flashing or jetting during moulding [122,143,144]. As shown in Table 4.2, the difference in shear sensitivity \((n)\) values between feedstocks containing POM and POM-PA2 at each temperature does not differ significantly. Moreover, the change in the thermal sensitivity of both feedstocks is considered negligible (with a difference of only 0.3 J/mol). Therefore, we further consider the general mouldability index to determine the final decision for the best selection of titanium feedstock. A high mouldability index value is desirable for the MIM process since it indicates that the feedstocks will possess a better ability to be moulded during the injection moulding process. We observe that the feedstock containing POM-PA2 has a higher mouldability index than the feedstock containing POM, with values of 0.0058 and 0.0052, respectively (see Table 4.2). Nevertheless, the overall rheological properties of the feedstock containing POM-PA2 are almost similar to that containing POM. This fulfils our main objective, which is to retain the excellent properties of POM after modification with propylamine.

### 4.2.7 Green Strength of the MIM Parts

The high green strength of the moulded parts is necessary for subsequent handling. The green strength is usually dependent on the binder constituents. Table 4.3 shows the highest mean flexural strength in the feedstock containing POM-PA2, with a value of 20.3 MPa. This is 7.3% higher than feedstock containing POM (18.8 MPa). It is suggested that the higher flexural strength is due to the additional polar group in the modified POM binder constituent, which is attributed to the more significant interaction between the binder and titanium powder. It is noted that, after mixing titanium powder with the modified POM, the amount of aluminium oxide present in the formulated feedstock is only 0.03 wt%, which does not cause defects in the final product.

Table 4.3. The green strength of POM and POM-PA2 feedstock

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Flexure load (N)</th>
<th>Flexural Strength (MPa)</th>
<th>Standard Deviation (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POM</td>
<td>6.03</td>
<td>18.79</td>
<td>± 1.02</td>
</tr>
</tbody>
</table>
4.3 Summary

This study focuses on preparing low formaldehyde- polyoxymethylene (POM) binder for metal injection moulding (MIM). The results reveal that adding propylamine in polyoxymethylene (POM) can significantly reduce formaldehyde emissions. However, the concentration of propylamine should be carefully decided. At low propylamine concentration (typically 2 wt.%), formaldehyde emissions have been effectively reduced by 35%. When amine concentration is low, the unstable terminal groups of POM are easily removed via the addition reaction. However, a different reaction route occurs at a high amine concentration, wherein the molecule could reversibly convert back to its free base form and formaldehyde gas. Nonetheless, the feedstock formulated from the modified POM-PA2 binder displays characteristics almost identical to the feedstock containing POM. Thus, POM-PA2 is a better alternative than POM as a binder for MIM due to its significantly reduced formaldehyde emission while maintaining its excellent rheological and mechanical properties without causing any defects to the final product.
Chapter 5 Compatibility Improvement of Ti-MIM Feedstock Using Compatibiliser

Partial data in this chapter is extracted from ref. [145]. More findings from the following investigation are presented here. Due to the different characteristics of each of the multiple polymers, obtaining a homogenous metal injection moulding (MIM) feedstock blend is challenging. Therefore, studying interactions between the polymeric components is vital for achieving suitable MIM feedstocks. Two different compatibilisers – EGMA and EVA – were chosen to study the interactions in polyoxymethylene (POM) and polypropylene (PP) blends. Contact angles, Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM) were performed to identify the suitable compatibiliser that yields a feedstock with excellent properties. It was found that the binder system based on EGMA-3 demonstrates the lowest contact angle and best miscibility for the POM/PP blends. Subsequently, the rheological properties of the best feedstock were assessed and compared to feedstock without compatibiliser.

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. Hence, the initial stages, such as mixing and moulding, are considered critical in the MIM process [146,147]. During mixing, every metal powder particle is ideal to be covered with a thin layer of binder to provide sufficient fluidity to fill the mould during injection [21]. In this regard, the significance of binders cannot be overstressed to achieve such characteristics, as explained in detail by German [148]. Since the initial interaction is to wet the metal powder surface, good compatibility between binder components is essential to prevent phase separation or segregation of feedstock during processing via injection moulding [42].

Commonly in MIM feedstocks, binders comprise multicomponent polymeric mixtures containing minor additives, such as stearic acid. The additives promote adhesion to the powder surface, coating the particles and preventing powder aggregation [149]. However, due to the relatively short chain lengths of stearic acid, interlinking strength among binder components is often weak [147,150]. Hence, including polymers with a polar group as interfacial agents among binder components is beneficial in enhancing the interlinking strength of binder components and improving the adhesion force on the powder surface [151,152].

At present, the interaction of the binder and powder is mainly assessed by rheological and thermogravimetry measurements [13,59,153,154]. Very little is known about the specific interactions among binder components and how such interaction affects the MIM of reactive powders, such as Ti-MIM. In one attempt, Hausnerova et al. [147] studied the adhesion of binder components to ceramic powders via contact angle measurement. The results show that among the binder components, the acrawax/polyethylene glycol (PEG) polymer blend with the highest polar component values is more suited for powder injection moulding. In addition, Subuki et al. [146] investigated the molecular interactions of three different binder systems comprising polystyrene/polyethylene (PS/PE), PS/polypropylene (PP), and thermoplastic natural rubber/paraffin wax (TPNR/PW) for stainless steel (316L) using Fourier-transform Infrared (FTIR). It is reported that PS/PP blends displayed the highest interaction with the metal powder. On the other hand, Bleyan et al. [155] propose that studying the interaction of low-molecular analogues of binder components via FTIR and calorimetric measurements could provide necessary information on the miscibility of the polymers. It is claimed that the interactions between the two polymers can noticeably enhance the debinding and sintering characteristics.

In this work, polyoxymethylene (POM) was used as a primary binder, polypropylene (PP) as the backbone binder, and stearic acid (SA) as a surfactant. Thus far, no reports are available in the literature studying the interactions of POM-based binders. Considering the molecular structure of POM and PP, blending these two polymers is expected to be incompatible and demonstrates a two-phase system [138,156,157]. Therefore, to improve the homogeneity of the POM-based binder system for Ti-MIM, two different types of compatibiliser, poly(ethylene methyl acrylate-co-glycidyl methacrylate) (EGMA) and ethylene-vinyl acetate (EVA) will be investigated. This study aims to better understand the
interactions between the POM-based binder system and titanium metal powder, which can lay the foundation for developing a novel binder system for Ti-MIM.

5.2 Results and Discussion

5.2.1 Contact angle measurement

Contact angle measurement for each binder is studied to determine the components' wettability and interaction. The Owens–Wendt theory (geometric and harmonic method) was applied to calculate the surface and interfacial tensions of POM, PP, and compatibiliser blends [117]. Table 5.1 shows that the contact angles for all given binder components are highest with deionised water (DI) and lowest with hexadecane (HD). It is well known that a decrease in contact angle allows the binder to spread over the powder particles easily, resulting in better wettability [158]. As can be seen from Table 5.1, POM has a lower contact angle value in the polar liquids with the highest polar component, $\gamma^p = 3.9$ mJ/m$^2$. This can be related to POM's polar functional group, (-CH$_2$O-), which can easily form hydrogen bonds with powder via acid-base interactions. This proves that POM is suitable for acting as a primary binder. On the other hand, PP demonstrates a hydrophobic characteristic. Since molecular interactions among binder components are critical to achieving good homogeneity of feedstocks and necessary green strength, compatibiliser is introduced.

The Owens–Wendt theory was used to predict the compatibility of POM/PP blends. Table 5.2 reveals that POM and PP blends demonstrated the highest interfacial tension. This signifies that the combination of these two polymers is immiscible. The high polarity POM blended with the apolar PP is not favourable from a thermodynamic point of view, which results in clearly separated phases, as seen previously by morphological investigations.

Table 5.2 shows that POM/EGMA/PP blends have the lowest interfacial tension value compared to EVA. Besides, EGMA has a similar surface tension to POM with respect to the polar component ($\gamma^p$) and PP in terms of the dispersive component ($\gamma^d$). This demonstrates the preferential miscibility of EGMA over E40 in POM/PP ternary blends.

Table 5.1. Contact angle [°] and calculated free surface energy ($10^{-3}$ J/m$^2$) of the binder components on 4 different liquids (deionised water (DI), ethylene glycol (EG), diiodomethane (DIM), and hexadecane (HD,))

<table>
<thead>
<tr>
<th>Materials</th>
<th>DI</th>
<th>EG</th>
<th>DIM</th>
<th>HD</th>
<th>$\gamma^{(tot)}$</th>
<th>$\gamma^{(d)}$</th>
<th>$\gamma^{(p)}$</th>
</tr>
</thead>
</table>

62
Table 5.2. The interfacial tension of the binder components using geometric and harmonic mean equations

<table>
<thead>
<tr>
<th></th>
<th>Geometric mean</th>
<th>Harmonic mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>POM/PP</td>
<td>1.21</td>
<td>2.39</td>
</tr>
<tr>
<td>POM/EGMA</td>
<td>0.69</td>
<td>1.37</td>
</tr>
<tr>
<td>POM/EVA</td>
<td>1.05</td>
<td>2.09</td>
</tr>
<tr>
<td>PP/EGMA</td>
<td>0.54</td>
<td>1.05</td>
</tr>
<tr>
<td>PP/EVA</td>
<td>0.69</td>
<td>1.37</td>
</tr>
</tbody>
</table>

As can be seen from Figure 5.1, the POM-based binder system with no compatibiliser (C-0) has the highest contact angle value, 94.3°. However, when compatibiliser is introduced into the POM-based binder system, the contact angle values in all the samples are less than 90°, displaying a hydrophilic characteristic. Nonetheless, the POM-based binder system with EGMA demonstrated greater wettability than E40. The wettability trend is as follows: EGMA-3 (66.9°) > EVA-3 (73.3°) > C-0 (94.3°). The low contact angle of the binder is critical to ensure sufficient wetting of the metallic powder, subsequently promoting appropriate mixing and moulding of metal powders [159].

As anticipated, the resulting titanium MIM feedstock based on the EGMA-3 binder formulation shows the lowest contact angle value of 87.6° (presented in Figure 5) when compared to feedstock based on C-0 (101.3°) and EVA-3 (98.9°) composition, respectively. This better dispersibility is the result of a stronger powder-binder adhesion. The powder particles are dispersed more homogeneously with the EGMA-3 binder formulation, which will induce less powder-binder separation during injection moulding at high shear stress.
Figure 5.1 Contact angle of POM-based binder system with different compatibiliser composition. Note that F.C-0, F. EGMA-3, and F.EVA-3 represent feedstock C-O, EGMA-3 and EVA-3.

5.2.2 FTIR

Figure 5.2 depicts the FTIR spectra of the titanium MIM feedstocks based on formulations C-O, EGMA-3, and EVA-3 and compares them with their respective binder constituents. Figure 5.2 (a) shows that there is not much significant change in the wavenumber arising from the interaction between the metal powder and the binders. Moreover, the FTIR spectra of Feedstock C-0 display all the characteristic peaks for pure POM and pure PP, indicating the absence of interaction.

However, after the addition of compatibiliser, a significant shift in the wavenumber of the feedstock is observed. From Figure 5.2 (b) and (c), both EGMA and EVA have a carbonyl group (C=O) at absorption bands 1733 and 1734 cm\(^{-1}\), respectively. It has been reported that a shift towards a lower wavenumber, usually less than 30 cm\(^{-1}\), can be expected after forming a Lewis acid-base reaction between binder and powder [160]. However, it is noteworthy
that the presence of stearic acid (SA) as a surfactant in the MIM feedstock is often one of the reasons for this interaction. Nonetheless, it can be seen that Feedstock EGMA-3 (Figure 5.2 (b)) demonstrates a shift from 1733 cm$^{-1}$ to 1705 cm$^{-1}$ with a difference of 28 cm$^{-1}$, while Feedstock EVA-3 (Figure 5.2 (c)) displays a difference of 35 cm$^{-1}$ after the band shifts from 1734 cm$^{-1}$ to 1699 cm$^{-1}$. This stipulates that in the presence of EGMA-3, the POM-based binder system has a stronger bond or acid-base interaction towards titanium powder than EVA. It is suggested that compatibilisers – EGMA and EVA – interact and overlap with the binder system, forming possible hydrogen bonding between the OH group from POM and the C=O group from compatibiliser (Figure 5.3).

Besides, a new peak can be distinguished at 2955 cm$^{-1}$ in Figure 5.2(b). This corresponds to the symmetrical and asymmetrical CH$_2$ stretching vibrations. Interestingly, the peaks of the epoxy group located at wavenumber 844 and 911 cm$^{-1}$ on the EGMA group have disappeared. This indicates a chemical reaction between the epoxy groups of EGMA and the end hydroxyl groups of POM (Figure 5.3(ii)) [161,162]. In the case of Feedstock EVA-3 (Figure 5.2 (c)), no new peaks are observed. This proves that the addition of EGMA has a more effective interaction in improving the compatibility between POM and PP blends than EVA. Hence, developing the ternary blend system based on EGMA-3 would improve binder adhesion on powder particles.
Figure 5.2 The FTIR spectra of feedstock (a) C-0, (b) EGMA-3, and (c) EVA-3 with its respective binder constituent.

Figure 5.3 Possible interactions between POM and different compatibilisers in the binder system.
5.2.3 Microstructural Observations

The compatibility of the POM-based binder system with and without compatibiliser is illustrated in Figure 5.4. Typically, a blend with poor miscibility exhibits distinctly separate phases of components, while a homogeneous surface morphology is observed for the blend with good compatibility [163]. In Figure 5.4 (a), the island-like morphology shows a clear phase separation between POM and PP blends, where the darker regions correspond to PP, and the lighter regions correspond to POM. This indicates the high level of immiscibility between the two polymer phases. However, an elongated structure can be seen in the ternary blends after the addition of compatibiliser. A compatible blend has been reported to demonstrate surface morphology with smaller holes and larger extended-like morphology [164]. Figure 3 (b) depicts that the POM-based binder system with EGMA-3 revealed better miscibility, dominated by more elongated-like morphology dispersed in the continuous phase. On the other hand, the morphology of the POM-based binder system with EVA-3 shows both island-like and elongated-like characteristics (Figure 5.4 (c)). Similarly, from the optical micrograph, the POM-based binder system with EVA-3 presents many holes dispersed in the continuous phases compared to the binder system with EGMA-3 formulation.

Further, the SEM micrograph of the MIM feedstock is presented in Figure 5.5. Some unfilled voids or gaps were observed at the interface between titanium particles and the binders for feedstock C-0 (Figure 5.5 (a)). The presence of voids or gaps in the feedstock blend is usually a result of poor compatibility and interfacial stability [50]. For feedstock EGMA-3 and EVA-3, the binder is melted and uniformly distributed in the feedstock matrix. No voids were found, indicating a good binder adhesion on metal powder. Nonetheless, from Figure 5.5(b) and (c), feedstock EGMA-3 shows better wetting between powder and binder than feedstock E40-3. The clusters of binders are embedded surrounding the powder particles in feedstock E40-3 (Figure 5.5 (c)). The difference in wetting can be ascribed to the presence of oxygen-containing functional groups in the binder system. Feedstock EGMA-3 containing more carboxyl groups reveals better interaction between binder-binder components, enhancing the powder-binder adhesion, as reflected from the FTIR.
Figure 5.4 AFM phase images (with optical micrograph) of POM-based binder system with formulation (a) C-0, (b) EGMA-3, and (c) EVA-3.

Figure 5.5 SEM fractographs on Titanium MIM feedstock (green parts) with binder formulation (a) C-0, (b) EGMA-3, and (c) EVA-3.
5.2.4 Gas Pycnometer

The homogeneity between the best and worst feedstocks was then compared with the gas pycnometer. Table 5.3 demonstrates the pycnometer density of the best feedstock (EGMA-3) and compares it to the worst feedstock, C-0. It is observed that Feedstock EGMA-3 exhibits a much smaller standard deviation, 0.009, compared to Feedstock C-0 (0.012). This indicates that Feedstock EGMA-3 is more homogeneous and has higher powder-binder interaction. Interestingly, Feedstock C-0 exhibits a density of more than 100%. Some of the primary binders are believed to have been lost during the moulding process [149].

Furthermore, when comparing the density of the moulded part, we found that Feedstock EGMA-3 reveals a higher value than C-0. The high-density green part is ideal for improving the final MIM product [165]. It is important to ensure that the moulded part is filled before continuing the MIM process, as this could affect the final product.

Table 5.3 Pycnometer density of feedstock C-0 and EGMA-3 at three different conditions

<table>
<thead>
<tr>
<th>Sample condition</th>
<th>Experimental density (g/cm³)</th>
<th>Theoretical density (g/cm³)</th>
<th>% Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-0 Feedstock</td>
<td>3.3417 ± 0.012</td>
<td>3.2836</td>
<td>99.28</td>
</tr>
<tr>
<td>Moulded Part</td>
<td>3.2810</td>
<td>3.3049</td>
<td>99.28</td>
</tr>
<tr>
<td>Crushed moulded part</td>
<td>3.2793</td>
<td>3.2982</td>
<td>99.48</td>
</tr>
<tr>
<td>EGMA-3 Feedstock</td>
<td>3.1768 ± 0.009</td>
<td>3.2836</td>
<td>98.32</td>
</tr>
<tr>
<td>Moulded Part</td>
<td>3.2836</td>
<td>3.2982</td>
<td>99.56</td>
</tr>
<tr>
<td>Crushed moulded part</td>
<td>3.2810</td>
<td></td>
<td>99.48</td>
</tr>
</tbody>
</table>

3.1 Rheological Behaviour

Figure 5.6 shows the viscosity versus shear rate for Feedstocks C-0 (worst feedstock) and EGMA-3 (best feedstock). The results demonstrate that the viscosity for both feedstocks decreases with an increasing shear rate, indicating pseudoplastic behaviour. Both feedstock C-0 and EGMA-3 have viscosities well below 1000 Pa.s, which is considered suitable for injection moulding [166,167]. Nonetheless, a lower viscosity can be seen associated with
Feedstock EGMA-3. Figure 5.6 and Table 5.4 show that Feedstock EGMA-3 demonstrates a more consistent and higher shear sensitivity value at most temperatures. In contrast, a significant variation of the shear rate dependency values can be observed for Feedstock C-0. This better shear sensitivity of Feedstock EGMA-3 can be attributed to the excellent compatibility between the binder systems. Since the flowability of a feedstock depends on the bonding between metal powder and polymeric binder, adding compatibiliser EGMA into the immiscible POM/PP blends improves the interaction between powder and the polymeric binder. Consequently, this increased binder adhesion on the metal powder surface leads to better flowability (Figure 5.7 (b)). On the other hand, a poor powder-binder interaction can be seen in Feedstock C-0 (Figure 5.7 (a)).

![Figure 5.6](image)

Figure 5.6 The log-log plot of viscosity vs shear rate plot of feedstock (a) C-0 and (b) EGMA-3 in the temperature range of 180-200°C.
Table 5.4 The (n-1) value and moldability index for feedstock C-0 and EGMA-3 at three different temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>180°C</th>
<th>190°C</th>
<th>200°C</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Feedstock C-0</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(n-1)</td>
<td>-0.467</td>
<td>-0.375</td>
<td>-0.293</td>
</tr>
<tr>
<td>Moldability index, α</td>
<td>4.37E-03</td>
<td>4.88E-03</td>
<td>4.30E-03</td>
</tr>
<tr>
<td><strong>Feedstock EGMA-3</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(n-1)</td>
<td>-0.441</td>
<td>-0.466</td>
<td>-0.406</td>
</tr>
<tr>
<td>Moldability index, α</td>
<td>7.13E-03</td>
<td>8.31E-03</td>
<td>9.25E-03</td>
</tr>
</tbody>
</table>

Figure 5.7 The comparison between the poor (a) and good (b) flow behaviour of feedstock.
A stable feedstock will flow consistently and extrude nicely through the capillary die.

Another critical characteristic of MIM feedstock is temperature sensitivity. Low activation energy, E, indicates that viscosity is less affected by temperature [57]. Thus, any slight temperature fluctuation during injection moulding will not result in sudden viscosity change that can cause moulding defects. From Figure 5.8, the lowest E value was obtained for Feedstock EGMA-3 at 5.41 kJ mol⁻¹. Further, the moldability index, α, from Table 5.4 reveals the highest value for feedstock EGMA-3 at all temperatures. It is worth concluding that a binder system must have miscible or partially miscible blends to ensure better compatibility between metal powders and binders. Adding a compatibiliser such as EGMA
helps modify the interfaces between the immiscible POM/PP blends. As a result, it reduces the binder system's interfacial energy and improves the binder interlinking strength, which leads to the creation of MIM feedstock with enhanced performance.

![Graph showing temperature dependence of viscosity for feedstock C-0 and EGMA-3 at a shear rate of 6000 s⁻¹.]

**Figure 5.8** Temperature dependence of viscosity for feedstock C-0 and EGMA-3 at a shear rate of 6000 s⁻¹.

### 5.3 Summary

This study has shown the significant effects of compatibiliser on the properties of powder feedstocks. It has been demonstrated that the addition of compatibiliser, EGMA and EVA aids in lowering the interfacial tension between the immiscible POM/PP blends. The POM-based binder system with EGMA-3 demonstrates the lowest contact angle and best miscibility for the POM/PP blends compared to EVA-3. Due to the active site of the EGMA molecule (i.e., epoxy and carbonyl functional group), chemical reactions and hydrogen bonds are possible within the ternary polymeric blend. As reflected, the ternary binder blends containing POM, EGMA-3, and PP have provided feedstock with a more homogeneous and higher-density moulded part than feedstock C-0. Besides, from the rheological analysis, feedstock containing compatibiliser EGMA-3 demonstrates low viscosity, high shear sensitivity, low-temperature sensitivity, and high mouldability index, which is suitable for MIM production.
Chapter 6 Green Density Optimization of Titanium Metal Injection Moulding Process (Ti-MIM) Using Taguchi Method

This chapter aims to optimise the Metal Injection Moulding (MIM) process through the Taguchi technique. For this purpose, green density has been identified as a quality characteristic of green parts or as an output for this study. The highest green density is essential in achieving parts with better shape retention. An L9 orthogonal array experimental design was conducted, and several injection moulding parameters were optimised. The results concluded that injection temperature significantly contributes to the parts' density. Subsequently, a confirmation test yielded results with optimum green density on all the injected moulded samples.

6.1 Introduction

The next main challenge for producing MIM parts is to achieve dimensional accuracy at the end of the process chain. Due to the multi-phase character of the feedstock systems, the moulding conditions can induce inhomogeneity in the injection moulding parts, which in turn could cause inhomogeneous binder extraction or anisotropic shrinkage during sintering. This is because, during injection moulding, extremely high shear rates of $10^6 \text{ s}^{-1}$ can occur [168]. As a result, this may lead to powder binder separations or orientation effects of the powder particles in the flow direction, subsequently affecting the following processing steps [169, 170]. Therefore, injection parameter optimisation is necessary to produce a high-quality green component and ensure successful debinding and sintering processes [171].

The Taguchi method is recognised as a systematic approach to designing and analysing experiments to improve product quality [172]. Taguchi has been utilised widely in the MIM process to minimise performance variation at better cost efficiency and time. This method provides an in-depth understanding of the process parameters and reduces defects with minimum experimental runs. For instance, [171] employed the Taguchi method for optimising the green density of injection moulded samples using a variety of factors like injection pressure, injection temperature, mould temperature, injection time and holding time. The results showed that mould temperature, injection time and pressure significantly optimised the sample green density. Other researchers who employed Taguchi as a medium
tool to optimise their MIM parameters include Mustafa et al. [85], Li et al. [87], Amin et al. [90], Nor et al. [92], Wahab et al. [83], Mustafa et al. [86], and Prasad et al. [93].

Since the performances of MIM green parts can be quantified by their density, strength, and surface quality [174], the optimisation parameter to achieve the highest green density will be investigated using the Taguchi method. To conduct the optimisation stage, four imperative factors: (A) injection temperature, (B) mould temperature, (C) injection pressure, and (D) injection time will be studied. The objective is to determine the optimum injection moulding parameters condition to produce green components with high density.

6.2 Experimental Procedures

6.2.1 Taguchi (Design of Experiment)

In this study, the density optimisation of MIM feedstock was conducted by implementing the Taguchi orthogonal array (Statistical Method). The injection process was run in 3 3-level design of the experiment with 4 parameters, as tabulated in Table 6.1. Consequently, the experiments were configured in an L₉ (3⁴) orthogonal array with 9 trials, as depicted in Table 6.2.

<table>
<thead>
<tr>
<th>Injection Parameters</th>
<th>Symbol</th>
<th>Level 1</th>
<th>Level 2</th>
<th>Level 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection temperature (°C)</td>
<td>A</td>
<td>180</td>
<td>190</td>
<td>200</td>
</tr>
<tr>
<td>Mould temperature (°C)</td>
<td>B</td>
<td>80</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>Injection pressure (bar)</td>
<td>C</td>
<td>550</td>
<td>650</td>
<td>750</td>
</tr>
<tr>
<td>Injection time (s)</td>
<td>D</td>
<td>4</td>
<td>6</td>
<td>8</td>
</tr>
</tbody>
</table>

Table 6.1. Injection parameter for three levels of Taguchi Design

Table 6.2. Orthogonal array of L₉ structure
Then, the outcome quality obtained from each experimental run is assessed using a signal-to-noise (S/N) approach. The Signal-to-Noise ratios (S/N) are logarithmic functions of desired output that are objective functions for optimisation, helping in data analysis and predicting optimum results. This work uses "nominal-the-best" characteristics (Eq. 1) to reduce density variations between the injection moulded parts.

\[
\frac{S}{N} = 10 \log \frac{\bar{y}^2}{\sigma^2_{N-1}} \quad \text{(Equation 1)}
\]

where \(\bar{y}\) is the average density, and \(\sigma_{N-1}\) is the standard deviation. The density of the injected parts is determined using a gas pycnometer (ASTM standard 63).

### 6.3 Results and Discussion

#### 6.3.1 Interpretation of response table and plot graph

Table 6.3 shows the green density of three injected moulded parts (R1, R2, and R3). The optimised injection moulding process parameters were calculated based on the average density of the replications for each level structure of the L9. The depiction of the variability of the S/N ratio can be found in Table 6.4. In a detailed explanation, S/N ratios help predict

<table>
<thead>
<tr>
<th>Trial</th>
<th>Injection Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
</tr>
<tr>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td>8</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>3</td>
</tr>
</tbody>
</table>
the optimal result and improve the quality via variability reduction of the measurement based on repetition [173].

Table 6.3. Density replication, mean, and S/N ratio of L9 structure experiment

<table>
<thead>
<tr>
<th>Trial</th>
<th>Density (g/cm³)</th>
<th>Mean, ( \bar{y} )</th>
<th>S/N ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R1</td>
<td>R2</td>
<td>R3</td>
</tr>
<tr>
<td>1</td>
<td>3.2659</td>
<td>3.2736</td>
<td>3.2674</td>
</tr>
<tr>
<td>2</td>
<td>3.2706</td>
<td>3.2685</td>
<td>3.2673</td>
</tr>
<tr>
<td>3</td>
<td>3.2477</td>
<td>3.2721</td>
<td>3.2627</td>
</tr>
<tr>
<td>4</td>
<td>3.2674</td>
<td>3.2633</td>
<td>3.26318</td>
</tr>
<tr>
<td>5</td>
<td>3.2655</td>
<td>3.2647</td>
<td>3.2626</td>
</tr>
<tr>
<td>6</td>
<td>3.2524</td>
<td>3.2607</td>
<td>3.2543</td>
</tr>
<tr>
<td>7</td>
<td>3.2505</td>
<td>3.2647</td>
<td>3.2555</td>
</tr>
<tr>
<td>8</td>
<td>3.2678</td>
<td>3.2684</td>
<td>3.2662</td>
</tr>
<tr>
<td>9</td>
<td>3.2713</td>
<td>3.2610</td>
<td>3.2643</td>
</tr>
<tr>
<td>Total</td>
<td>29.37326</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 6.4. Response table of S/N ratio variability analysis

<table>
<thead>
<tr>
<th>Level</th>
<th>Injection Temperature</th>
<th>Injection Pressure</th>
<th>Mould Temperature</th>
<th>Injection Time</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(A)</td>
<td>(B)</td>
<td>(C)</td>
<td>(D)</td>
</tr>
<tr>
<td>1</td>
<td>57.41</td>
<td>57.97</td>
<td>61.52</td>
<td>60.26</td>
</tr>
<tr>
<td>2</td>
<td>62.28</td>
<td>67.12</td>
<td>61.38</td>
<td>58.74</td>
</tr>
<tr>
<td>3</td>
<td>59.32</td>
<td>53.93</td>
<td>56.12</td>
<td>60.02</td>
</tr>
<tr>
<td>Delta</td>
<td>4.87</td>
<td>13.18</td>
<td>5.40</td>
<td>1.52</td>
</tr>
<tr>
<td>Rank</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>4</td>
</tr>
</tbody>
</table>
Table 6.4 shows that injection pressure contributes to the most significant factor in optimising the green density of the moulded parts (Delta= 13.18) compared to the other factors. The second most influential factor is mould temperature since mould temperature could assist the melt flow of feedstock inside the mould cavity [90]. On the other hand, injection temperature and time came in as the third and fourth contributing factors to the green density, according to the delta values. The Delta values were then plotted and shown in Figures 6.1 and 6.2 for further analysis of significant factors contributing to the moulded parts' green density.

![Main Effects Plot for SN ratios](image)

Figure 6.1. S/N ratio main effects plot of green part density at various levels of injection parameters.
From Figure 6.1, the S/N ratio plot indicates the significant effect in obtaining optimum density. It is discerned that the control factor levels that can maximise the S/N ratio of the process are A2, B2, C1 and D1, which are 190 °C, 650 bar, 80 °C and 4 sec. As for Figure 6.2, the mean plot illustrates the significant factors in reducing the fluctuations of density obtained. Figures 6.1 and 6.2 show that maximised factor levels B and D are the same. This signifies that 650 bar (injection pressure) and 4 sec (injection time) are the best injection moulding parameters to optimise the green density. However, there is disagreement in factor levels A and C, representing the injection and mould temperatures, respectively. For injection temperature, the S/N ratio displayed that level 2 has a significant effect in obtaining optimum density. However, this result contradicted the Mean analysis, which indicates that level 1 significantly reduces the fluctuations of density obtained. Nonetheless, when comparing the gradients of the A factor for Mean analysis between levels 1 and 2 (Table 6.5), the injection temperature shows only slight changes affecting the density variations. Conversely, a more significant change between levels 1 and 2 is denoted for the S/N ratio analysis (Table 6.4). This means that injection temperature has a more substantial influence on the S/N ratio than mean analysis. Hence, changing the injection temperature might
significantly change the S/N ratio of the process. Therefore, based on the analysis of factors and levels, the optimised level to obtain optimum green density with low variations of the moulded parts is A2, B2, C1 and D1.

Table 6.5. Response table of means variability analysis

<table>
<thead>
<tr>
<th>Level</th>
<th>Injection Temperature (A)</th>
<th>Injection Pressure (B)</th>
<th>Mould Temperature (C)</th>
<th>Injection Time (D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.266</td>
<td>3.264</td>
<td>3.264</td>
<td>3.266</td>
</tr>
<tr>
<td>2</td>
<td>3.262</td>
<td>3.267</td>
<td>3.266</td>
<td>3.261</td>
</tr>
<tr>
<td>3</td>
<td>3.263</td>
<td>3.261</td>
<td>3.261</td>
<td>3.264</td>
</tr>
<tr>
<td>Delta</td>
<td>0.005</td>
<td>0.006</td>
<td>0.006</td>
<td>0.006</td>
</tr>
</tbody>
</table>

6.3.2 Prediction and Confirmation Experiment

Further, a confirmation experiment was performed on 10 injection moulded parts replicates to verify the effectiveness of the optimal injection moulding process parameter described above. The predicted quality characteristic is calculated based on the optimum performance of the injection moulding parameters as below;

\[
\frac{S}{N} \text{ ratio} = \bar{T} + (\bar{A}_2 - \bar{T}) + (\bar{B}_2 - \bar{T}) + (\bar{C}_1 - \bar{T}) + (\bar{D}_1 - \bar{T})
\]

where \(\bar{T}\) is the average S/N ratio, \(\bar{A}, \bar{B}, \bar{C}\), and \(\bar{D}\) are the injection moulding parameters, and subscript 1 and 2 denotes the level at each parameter.

Therefore, the predicted S/N ratio is:

\[
\frac{S}{N} \text{ ratio} = 61.433 + (62.28 - 61.433) + (67.12 - 61.433) + (61.52 - 61.433) + (60.26 - 61.433)
\]

\[
\frac{S}{N} \text{ ratio} = 66.88
\]
From Table 6, the results of the S/N ratio of green density obtained from 10 replications are 66.09, which has a difference of 0.8% compared to the predicted S/N ratio. This shows that the experimental result is strongly correlated with the estimated result.

Table 6. Mean and S/N ratio of confirmation experiment based on 10 replication samples

<table>
<thead>
<tr>
<th>Average Density, $\bar{y}$</th>
<th>Standard deviation, $\sigma_{N-1}$</th>
<th>S/N ratio (Nominal-the-best)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.2589</td>
<td>0.001616</td>
<td>66.09132</td>
</tr>
</tbody>
</table>

6.4 Summary

The optimisation of injection parameters in the metal injection moulding (MIM) process to produce the highest green density parts was successfully investigated through Taguchi Method L9 ($3^4$). It can be observed that injection temperature plays the most significant contribution in optimising the green density of MIM parts, and the optimum injection moulding parameter is found to be at an injection temperature of 190 °C, injection pressure at 650 bar, mould temperature at 80°C, and injection time at 4 sec. The green density of MIM parts obtained at the optimum processing parameters is 3.26 g/cm$^3$. The results obtained from Taguchi analysis strongly support the experimental findings, exhibiting a difference of less than 1%.
Chapter 7 Development of an environmentally friendly debinding technique for a POM-based binder system

To reduce cost, this chapter focuses on designing an alternative debinding technique for the POM binder system on Ti-MIM feedstocks. In this chapter, the solvent debinding technique is proposed. The solvent debinding technique has been widely accepted in the metal injection moulding (MIM) industry due to its inherent advantages, such as reduced energy consumption, ease of preparation, and cost-effectiveness. Besides, to the best of the authors' knowledge, there has not been any literature on the solvent-debinding behaviour of POM binders.

7.1 Introduction

The main advantage of polyoxymethylene (POM) in MIM, especially for reactive metals like titanium, is its ability to decompose rapidly and cleanly into its starting gaseous monomers [62]. These advantages make it possible to reduce the risk of oxygen or carbon contamination in the final metal parts. Additionally, POM has good mechanical properties, allowing easy handling of the moulded part. However, the limitation of this binder system is its reliance on highly concentrated acidic catalysts (i.e. nitric acid or oxalic acid) for POM degradation. This exacerbates corrosion to the surrounding debinding equipment and poses a severe risk to human health. Additionally, using concentrated acids is hazardous and generates much waste. As a result, the need for a special catalytic debinding oven is often a prerequisite for POM-based binder systems to manage the acid vapours and gaseous monomers [12,20,42]. This, in turn, adds additional pressure on the already existing expensive Ti feedstock.

Therefore, a commonly used debinding technique, solvent debinding followed by thermal debinding technique [51,174] is proposed to resolve this issue. This technique allows the removal of the primary binder from the outside of the part, slowly moving into the core. In such a manner, interconnected pores within the green parts are created, facilitating the removal of other binder components during the subsequent thermal debinding stage [83,175].
This work studied polyoxymethylene (POM) as a main constituent in the binder system and its solvent-debinding behaviour to produce Ti-MIM. To the best of the authors' knowledge, the solvent debinding behaviour of POM binders has not been studied in the literature. This chapter highlights the utilisation of diluted nitric acid and benign organic acids (i.e. formic acid and acetic acid) to remove the POM binder. Additionally, the study explores the possibilities of solvent recycling. Further, the sintered parts were characterised using mechanical testing, a LECO analyser, SEM, optical microscopy, and a gas pycnometer. New findings through this investigation could provide an environmentally benign substitute for the highly corrosive acids used in the conventional POM debinding process.

7.2 Experimental procedures

To study the effects of debinding time and solvents, we performed solvent debinding at 50 °C using different acid solvents for varying time lengths. Notably, POM is acid-sensitive; hence, it is used as a solvent. Subsequently, we investigated how debinding temperature affects the debinding kinetics. For this purpose, the green parts were debound at different temperatures (i.e. 55°C, 60°C, and 70°C) with 5M nitric acid as solvent. The parts were then dried and weighed to determine the fraction of binder removed. Mathematical modelling was used to describe the kinetics of the debinding process. The effective diffusivity and activation energy of POM were calculated using Eq. (1) and (2), respectively [176,177]:

\[
\ln \frac{C}{C_0} = \frac{D_e \pi^2}{4L^2} \quad \text{(Eq. 1)}
\]

\[
\ln D_e = \ln D_o - \frac{Q}{RT} \quad \text{(Eq. 2)}
\]

where \(C_0\) is the initial amount of soluble binder inside the green parts, \(C\) is the total amount of the remaining soluble binder in the parts, \(D_e\) is the effective diffusion coefficient of POM, \(t\) is time, \(L\) is the diffusion distance, \(D_o\) is the pre-exponential factor of the effective diffusion coefficient, \(Q\) is the effective activation energy, \(T\) is the debinding temperature and \(R\) is the universal gas constant, namely 8.314 J mol\(^{-1}\)K\(^{-1}\). A plot of \(\ln(C_0/C)\) against \(t\), at a constant temperature, is constructed where the slope of the straight line gives an approximate value for the effective diffusivity, \(D_e\). Meanwhile, activation energy, \(Q\), is obtained by plotting the graph of \(\ln(D_o)\) against \(-1/T\).
Once the solvent debinding was completed, thermal debinding and sintering were carried out. The heating profile was selected based on TGA and shown in Figure 7.1.

Figure 7.1 Thermal debinding profile for POM/PP/EGMA-3 binder system

7.3 Results and Discussion

7.3.1 Influence of Different Solvents on POM

The solvent debinding process of the POM binder system in different solvents (1M, 3M, and 5M nitric acid, concentrated formic acid, and concentrated acetic acid) at 50°C is shown in Figure 7.2. As shown in Figure 7.2, 5M nitric acid solvent has the highest extraction efficiency for the POM binder. After 7 hours, the percentage of soluble binder removed is about 70 wt%. This is well reflected in Figure 7.3 (d), where the green compacts revealed more pores than other solvents. The increase in pores suggests that binders are more easily extracted from the green compacts. As expected, as nitric acid concentration decreases, the amount of extracted POM binder reduces (Fig. 7.3(b, c)). Hamamura et al. [178], studying the dissolution of POM bulk film in nitric acid, reported that the degradation rate decreases by 90% when nitric acid concentration changes from 30 mass% to 5 mass%, which is equivalent to 5M to 1M nitric acid concentration, respectively.
Interestingly, the debinding rate of POM in concentrated formic acid is comparable to that of a 5M nitric acid solvent. The results are consistent with the microstructure observations in Figures 6.3 (d) and (e). However, the time needed to completely remove POM in formic acid is almost twice the amount of 5M nitric acid (*Fig. 7.4*). On the other hand, in the case of concentrated acetic acid, POM's binder extraction is the slowest, achieving only 0.7 wt% after 7 hours. The phenomenon is unclear, but it is stipulated that increasing solvent size could limit the dissolution rate of polymers [179,180]. Acetic acid, having methyl group CH₃, has larger acetate anions and hence is not as penetrating as the smaller formate HCOO⁻ molecules. Nevertheless, no defects were observed on all green parts after solvent debinding. The debinding rate of POM decreases as follows: 5M HNO₃ > HCOOH > 3M HNO₃ > 1M HNO₃ > CH₃COOH, suggesting that the acid concentration and solvent size strongly influence the dissolution of POM.

![Figure 7.2 Influence of different solvents on the debinding rate of POM at 50°C.](image)
Figure 7.3 SEM images of green parts in (a) its original state, (b) 1M nitric acid, (c) 3M nitric acid, (d) 5M nitric acid, (e) formic acid, and (f) acetic acid after 7 hours.

Figure 7.4 The weight loss of POM binder in 5M nitric acid and concentrated formic acid with respect to time.
7.3.2 Influence of Temperature on POM

Temperature is one of the critical variables in the solvent debinding process. It is noteworthy that samples immersed in formic acid at 55 oC result in distortion after an hour. Hence, the debinding process of POM proceeded in 5M nitric acid, as shown in Figure 7.5. As expected, at higher debinding temperature, the solubility of POM increases due to higher molecular mobility and diffusivity. Figure 7.6 demonstrates a plot of ln(Co/C) vs time (in seconds) for each debinding temperature. The effective diffusion coefficient can be calculated from the gradient of the straight line according to Eq. (1). From Figure 7.6, the effective diffusion coefficient is in the following order: 70 > 60 > 55 > 50 oC. This suggests that debinding temperature strongly influenced the debinding rate. At 70 oC, the solvent penetration rate is the fastest, with a high diffusivity rate of $1.05 \times 10^{-4}$ mm²/s. The activation energy of POM extraction is estimated to be 33 kJ/mol (Fig. 7.7). This value is comparable to that reported by Absesoltan et al. [181], suggesting that the debinding of POM proceeds via acid hydrolysis reaction. As nitric acid is a mineral acid, all protons are readily available for the hydrolysis of POM. However, it should be noted that a debinding time that is too high is not recommended as it will result in strength loss, formation of cracks and blisters, distortion, or even complete collapsing of the parts [177,182,183]. From Figure 7.8, it can be seen that solvent debinding at 70°C for 2 hours resulted in blister formation. Hence, the optimum solvent debinding temperature for POM is 60 °C, with an efficient debinding time of 5 hours. The result is comparable to the debinding time utilised by the conventional catalytic debinding technique reported by Chen et al. [184] and Jiang et al. [13].
Figure 7.5 Influence of temperature on the debinding rate of POM in 5M nitric acid

Figure 7.6 $\ln(C_0/C)$ plotted vs time at three different temperatures. It is noted that the slopes of the straight lines denote the values of the effective diffusion coefficient.
Figure 7.7 \( \ln(\text{De}) \) plotted against \( T^{-1} \) at 50, 60, and 70 \(^\circ\)C. The slope of the regressed straight line gives the effective activation energy of 33 kJ/mol.

Figure 7.8 Defects on green samples after solvent debinding at 70\(^\circ\)C for 2 hours

### 7.3.3 Binder Removal Mechanism of POM

It is well-known that POM depolymerises catalytically under acidic conditions at 120\(^\circ\)C, yielding formaldehyde - a direct transition from solid to gas [185]. Hence, one crucial highlight in the solvent debinding of POM is its chemical reaction in the presence of acid. It is stipulated that the fast removal mechanism of POM is driven by three simultaneous processes: dissolution, diffusion, and chemical reaction. The process begins from the green compact surface due to direct contact of the solvent with the POM binder. During the initial
contact of POM and solvent, acid hydrolysis and dissolution occur. The main chain of POM is broken into numerous POM-OH molecules due to random chain scission. Continuously, the depolymerisation of these molecules evolves into formaldehyde [178,186]. As the solvent gradually penetrates the interior of the green compacts, it dissolves and extracts POM binder, which is then transported from the inter-particle spaces through the metal powder into the surrounding solution. However, as debinding proceeds, diffusion becomes the rate-determining step; a longer diffusion distance is required through the porous channels to dissolve the POM binder. Ultimately, the solvent debinding process stabilised when both dissolution and diffusion are restricted. The mechanism is illustrated in Figure 7.9.

![Diagram of solvent debinding process](image)

**Reaction:**

\[
\begin{align*}
\text{HO-CH}_2\text{-OH} + \overset{n}{\text{C-O-C-O-C-O}} & \rightarrow \\
\overset{n}{\text{C-O-C-O-C}} + \overset{n}{\text{C-O}} + \overset{n}{\text{H}} \quad \text{H}^+ \\
\overset{n}{\text{C-O-C-C}} + \overset{n}{\text{C}}^+ & \rightarrow \\
\overset{n}{\text{C}}^+ + \overset{n}{\text{O=CH}} \quad \text{(formaldehyde)}
\end{align*}
\]

Figure 7.9 The schematic mechanism and chemical reaction of POM (via acid hydrolysis) during solvent debinding.
7.3.4 Solvent Recyclability

However, due to solvents being widely recognised as of great environmental concern, solvent recyclability was studied to enhance the environment-friendliness of solvent debinding process. Four samples were performed in the same 5M nitric acid solvents until completion. From Figure 7.10, the POM extraction remains high, averaging 69.6%. It can be deduced that the solvent remained active after each experiment. This phenomenon could be explained by the inherent ability of the POM main chain, -CH2O- to degrade into formaldehyde in acid, leaving the solvent almost clean with little residues. Alternatively, studies have shown that HNO$_3$ can be isolated and reclaimed from industrial chemical operations, reducing HNO$_3$ consumption and waste generation [187,188]. This significantly minimises nitric acid waste and contributes to green chemistry.

Figure 7.10 The efficiency of POM removal in 5M nitric acid solution after 4 runs.
7.3.5 TGA

Further, a thermogravimetric (TGA) test was performed to investigate the decomposition behaviour of each binder constituents to establish a temperature profile for the thermal debinding process [189]. Figure 7.11 shows that stearic acid (SA) and polyoxymethylene (POM) are easily decomposed when the temperature approaches 400°C. On the other hand, the maximum decomposition temperature \( T_d \) of polypropylene (PP) occurs around 425°C and poly(ethylene-co-methyl acrylate-co-glycidyl methacrylate) (EMA-GMA) at 463°C, respectively. When the temperature increases to 600°C, the curve flattens, suggesting all binders are finally decomposed. Hence, based on the TGA evaluation, a suitable thermal debinding profile was constructed, as depicted in Figure 7.1. Subsequently, after thermal debinding (TD), no weight loss was recorded for the samples, *(Fig. 6.11)*. This confirms the complete removal of binder components.

![TGA profile of the binder constituents and after thermal debinding (TD) process.](image-url)
7.3.6 Properties of sintered Titanium parts

Sintering of the thermally debound samples was performed at 1300°C. It can be seen in Figure 7.12(a) that the resulting final parts exhibited an arch-like deformation. This is because sometimes samples get stuck on the surface after sintering. Therefore, to prevent bonding of the titanium to the supporting base, some loose yttrium oxide powder was applied to the base before positioning the thermally debound samples. As reflected, the introduction of yttrium oxide as a base material prevented any deformation during sintering (Fig. 7.12(b)). The properties of the sintered parts with and without yttrium oxide are tabulated in Table 7.1.

Figure 7.12 Sintered Ti-MIM parts (a) without yttrium oxide and (b) with yttrium oxide as an additional supporting base.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Ti-MIM (without Y$_2$O$_3$)</th>
<th>Ti-MIM (with Y$_2$O$_3$)</th>
<th>MPIF 64 (Grade 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm$^3$)</td>
<td>4.38</td>
<td>4.33</td>
<td>&gt; 4.230</td>
</tr>
<tr>
<td>Relative density (%)</td>
<td>97.5</td>
<td>96.2</td>
<td>&gt; 95</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>2.0</td>
<td>3.8</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>Shrinkage Factor (%)</td>
<td>14</td>
<td>14</td>
<td>&lt; 15</td>
</tr>
<tr>
<td>Oxygen Content (%)</td>
<td>1.19 ± 0.13</td>
<td>1.21 ± 0.06</td>
<td>0.3 (max)</td>
</tr>
</tbody>
</table>

Table 7.1 The properties of sintered Ti-MIM with and without yttrium oxide
Interestingly, a dramatic microstructure difference was observed when comparing the sintered samples with and without yttrium oxide as a supporting base. As depicted in Figure 7.13(a), samples with the aid of yttrium oxide demonstrated a significant increase of pores, about 8%, when compared to samples without yttrium oxide (Fig. 7.13(b)). The sintered samples with yttrium oxide as a supporting base displayed homogeneously distributed small pores throughout the compact. In contrast, samples without yttrium oxide showed only a population of small, rounded pores with occasionally large, elongated pores near the outer compact. The results are intriguing; however, the cause of this phenomenon remains unclear.
Figure 7.13 Optical macrographs of sintered Ti sample (a) with yttrium oxide and (b) without yttrium oxide as supporting base. The total porosity and pore size distribution with Gaussian fitting were quantified using ImageJ and Origin analysis software.

The tensile properties of the sintered Ti samples are summarised in Table 7.1. Note that testing cannot be carried out for parts without the aid of yttrium oxide as a supporting base owing to its inherent property of physical deformation. As reflected, the increase in porosity weakens the mechanical properties and causes great variability, resulting in premature failure. The final titanium parts have an average ultimate tensile strength of 328 MPa (similar to Grade 2 titanium – used in dental implant applications) and ductility of 3.8%. Figure 7.14 depicted the typical fracture surface of Ti parts after mechanical testing, demonstrating smooth facets and river patterns, indicating a brittle fracture mode. This can be attributed to the high oxygen content in Ti samples of more than 1 wt%. Yan et al. [190] have reported that oxygen contents above 0.6 wt% drastically affect mechanical properties, and ductile materials can become brittle.

In addition, when comparing samples supported by yttrium oxide and those not supported by it, the oxygen impurities levels displayed no discernable differences. The high oxygen levels in the final Ti parts may be due to the high thermal decomposition of EMA-GMA at temperatures above 400°C. Due to the presence of many oxygen functional groups in the molecular structure of EMA-GMA, during heating at high temperatures, oxygen can diffuse through the open pores formed during solvent debinding, hence facilitating impurity uptake [8]. Another reason for such high impurity levels is the static furnace atmosphere during thermal debinding [64,104,191].
Nevertheless, owing to the considerable porosity and oxygen content, an investigation was conducted to introduce Ar gas to the samples during the thermal debinding process. Results revealed that the implementation of this technique yielded reduced impurity absorption in the final sintered samples, demonstrating a nearly two-fold decrease of oxygen content value at 0.48 wt%. The thermal debinding profile, mechanical properties, and impurities of the resulting sintered parts are attached in Appendices 1 and 2. Nonetheless, in both instances, the impurity levels of the resulting samples exceeded the maximum allowable limits set forth by the ASTM standard. However, it is noteworthy that performing thermal debinding under an argon gas environment before sintering resulted in diminished oxygen and carbon content compared to the thermal debinding process conducted in a high vacuum setting.

6.3 Summary

A simple yet effective approach was employed to solve the conventional catalytic debinding process issue for the POM-based binder system in MIM. By using the solvent debinding technique, this process can effectively extract POM binder while being environmentally friendly. The optimal debinding parameters were found at a temperature of 60 °C and a solvent concentration of 5M nitric acid (wherein the solvent concentration is three times lesser than in the catalytic debinding process). Moreover, this process demonstrated a high debinding rate with complete removal in 5 hours, similar to the conventional method.
Overall, the solvent debinding process for POM shows promise in improving the sustainability of industrial processes while reducing production costs. The resultant titanium-MIM parts revealed good dimensional tolerance, a high density of over 4.3 g/cm³ on all samples and an average ultimate tensile strength of 328-406 MPa. However, the impurity contents of the resultant samples under high vacuum and argon gas purging conditions are well above the maximum permitted limits of ASTM standards. This problem can be resolved by i) employing inert gas on the sample during thermal debinding and ii) introducing a low-temperature, clean binder system based on polypropylene carbonate (PPC) and POM for Ti-MIM. It is noteworthy that thermal debinding under argon gas leads to a lower oxygen and carbon content than thermal debinding in high vacuum.
Chapter 8 Formulating Titanium Powder Feedstocks for Metal Injection Moulding from a Clean Binder System

This chapter introduced a newly developed binder system based on polypropylene carbonate/polyoxymethylene (PPC/POM) to tackle the challenges associated with impurity control in titanium Metal Injection Moulding (Ti-MIM) processes. The data in this chapter has been published in ref.[192]. The binder system primarily focused on PPC as the dominant backbone binder, owing to its advantageous properties of clean and low-temperature decomposition. However, due to the poor shape retention of the PPC/POM binder system in the early trials, the use of polyethylene glycol (PEG) was incorporated to facilitate the formation of the porous network within the compact structure, allowing efficient removal of the residual binder for subsequent debinding process. After injection moulding, solvent debinding was performed and assessed. Microstructural observations and impurity analysis (oxygen, carbon, nitrogen) were conducted to characterise the debound parts and evaluate their performance.

8.1 Introduction

This work aims to develop a low-temperature and clean binder system for Ti-MIM. Among the binder systems, polypropylene carbonate (PPC) has recently found its applications in MIM due to its ability to burn cleanly and decompose entirely at a low temperature (below 400°C), leaving almost no residue [154,193]. This makes PPC an interesting material for Ti-MIM. Another polymer that decomposes completely into its gaseous state is polyoxymethylene (POM). Owing to its molecular structure (CH₂-O), the methyl-oxygen bonds are easily broken under heat and oxygen, yielding its monomer gas [15]. Additionally, POM possesses excellent properties, such as high dimensional stability, rigidity, and good warm strength, making handling moulded parts easier [125].

---

However, in early trials of the PPC/POM binder system, samples have shown complete disintegration during solvent debinding, attributed to the poor green strength of PPC. Therefore, in this work, polyethylene glycol (PEG) is incorporated into the PPC/POM binder system to facilitate the formation of open pores within the samples for an effective thermal debinding process. By creating sufficient open pores within parts, efficient thermal debinding could be realised without structural defects. The main objective of this work is to develop a low-temperature, clean binder system for Ti-MIM. Herein, PEG acts as a primary binder, which will be removed in the solvent debinding stage. PPC, having low decomposition temperature, serves as the major backbone polymer, while POM provides clean and necessary green strength to parts until the initial sintering stage. This research will guide the selection of an environmentally friendly binder system specifically for Ti-MIM.

8.2 Experimental procedures

The feedstock was prepared using a ThermoHaake Brabender mixer (Germany) at 165 °C, with a rotor speed of 50 rpm for 30 mins. A formulation of 63 vol% powder loading of titanium powder was used for investigation. The binder system is composed of polyethylene glycol (PEG) as the primary component, polypropylene carbonate (PPC) and polyoxymethylene (POM) as the majority and minority backbone component, and stearic acid (SA) as a surfactant. The Ti feedstocks will be designated according to Table 8.1. The weight fractions of SA were kept constant at 2 wt.%, respectively, for all binder compositions.

Table 8.1 Binder compositions for titanium feedstock

<table>
<thead>
<tr>
<th>Code</th>
<th>Binder component content, % w/w</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PEG</td>
</tr>
<tr>
<td>30PEG</td>
<td>30</td>
</tr>
<tr>
<td>40PEG/5POM</td>
<td>40</td>
</tr>
<tr>
<td>50PEG</td>
<td>50</td>
</tr>
<tr>
<td>8POM</td>
<td>40</td>
</tr>
<tr>
<td>10POM</td>
<td>40</td>
</tr>
</tbody>
</table>
The injection moulding parameters were: injection pressure 19 MPa, holding pressure 16 MPa, injection time 5s, and injection temperature and mould temperature were 165 °C and 32 °C, respectively. The green parts were then subjected to water debinding to remove the major fraction of PEG. Water debinding was performed at 30 °C for different time intervals up to 21h, so a debinding profile was constructed.

Thermal debinding was carried out under purging argon gas following the profile shown in Figure 8.1. Thermal gravimetric analysis (TGA) measurement was performed under an argon atmosphere with a flow rate of 100ml/min and a heating rate of 10°C/min. Rheological experiments were performed on a CFT-500D capillary rheometer (Shimadzu) at 170 °C. Different pressure values and die sets with different length-radius (L/D) ratios (D1 = 1 mm, L1 = 1 mm; D2 = 1 mm, L2 = 2 mm) were used for calculations based on the Bagley & Rabinowitsch [194]The morphologies of feedstocks were observed on an FEI Quanta 200F scanning electron microscope (SEM) at an accelerating voltage of 5 kV. The C, N, and O impurity contents of thermally debounded samples were determined with LECO analysers (LECO, Series ON736 and CS744).

Figure 8.1 Thermal debinding profile for PEG/PPC/POM binder system
8.3 Results and Discussion

8.3.1 Thermal Degradation of Backbone Polymer

Commonly employed backbone polymers in Ti-MIM, such as PP, PE, and PMMA, have a high decomposition temperature above 400°C [12]. It is well-known that at about 260°C, binders may introduce impurities in the titanium parts [10]. Hence, in Ti-MIM, it is impossible to avoid impurities completely. However, using a low-temperature binder system can aid in lowering the risk of contamination to a minimum. The advantages of using PPC and POM are their low to moderate decomposition temperature and clean decomposition behaviour. As can be observed from Figure 8.2, PPC and POM degrade entirely in a single step at 275°C and 370°C, respectively, which is below 400°C. Moreover, it has been reported that PPC and POM decomposed by a depolymerisation mechanism, yielding gaseous monomer propylene carbonate and formaldehyde, which volatise leaving minimal residue on final metal parts [101,195]. It is postulated that the utilisation of a binder system comprising polypropylene carbonate (PPC) and polyoxymethylene (POM) holds the potential to lower the impurities in reactive metals, such as titanium.

Figure 8.2 The TGA-DTG curve of backbone binder PPC and POM.
8.3.2 Rheological properties

To achieve optimal moulding conditions at specified temperatures, the upper viscosity limit has been set at 1000 Pa.s for the given shear rate range[122] As depicted in Figure 8.3, all feedstocks exhibited pseudoplastic behaviour, indicating rotation and re-arranging of polymeric binders and metallic particles within the feedstock along the flow direction. This facilitates inter-particle motion, making the feedstock well-suited for MIM [196,197].

However, the influence of feedstock viscosity was found to be directly related to the proportion of PEG content in the binder system. Figure 8.3(a) illustrates an increase in PEG content from 30 wt.% to 50 wt.% resulted in a decrease in viscosity. Conversely, adding a POM backbone binder into the feedstock did not significantly affect its viscosity, as shown in Figure 8.3(b).

Furthermore, as depicted in Figure 8.4, the feedstock with a composition of 40PEG/5POM showed a high (n-1) value of -0.67. A high (n-1) value or a steep negative slope is generally considered desirable in metal injection moulding. However, excessively high (n-1) values or shear sensitivity may lead to issues such as flashing during moulding [122,198]. It is noteworthy, however, that all feedstocks were successfully injected moulded without any defects. The viscosity data for other feedstocks 40PEG/8POM and 40PEG/10POM is presented in Appendix 3.
Figure 8.3 The viscosity of titanium MIM feedstocks as a function of shear rate on the influence of increasing (a) PEG content and (b) POM backbone binder content at 170 °C
Figure 8.4 The plot of the double logarithm of viscosity versus the shear rate of PEG/POM feedstock at 170 °C

### 8.3.3 Solvent Debinding

The removal of PEG in water has been widely studied in previous works [177,194,199–202]. During debinding, water slowly diffused into the PEG to produce a swollen gel. As the molecular weight of the water is significantly lower than that of PEG, water can diffuse into compact faster than the PEG diffuses out. This mechanism is driven by capillary forces and concentration gradients of dissolved binder in the compact and water bath [203]. Consequently, this forces PEG to diffuse out of the compact through a network of pore channels. Since the diffusion distance for the water and PEG is short in the initial stage, the debinding rate is relatively fast. As debinding proceeds, pores are extended to the inner core of the compact, and PEG leaching gradually slows down until equilibrium approaches. The advantage of this approach is to create interconnected open-pore channels within injected compacts for subsequent rapid removal of the residual binder.

### 8.3.3.1 Influence of PEG Content

Figure 8.5 shows that an increase in PEG content substantially improves the removal rate of PEGs. Specifically, after 11 hours, 54% of the PEG was removed for the 50PEG sample,
followed by 52% and 36% for the 40PEG and 30PEG samples, respectively. This improvement can be attributed to the decrease in resistance to diffusion resulting from the lower content of backbone binders in higher PEG samples. It is demonstrated that increasing PEG content decreases the amount of backbone binder, improving PEG molecules' molecular mobility during solvent debinding. As a result, this leads to a higher PEG removal rate. This observation is consistent with previous literature [194,204]. Nonetheless, sufficient backbone binder is crucial in binding Ti powder particles together, preventing swelling and cracking during solvent debinding. Figure 8.6 shows defects in the 50PEG sample after 11 hours. This finding suggests that the enhanced dissolution and low backbone content in the 50PEG create internal stresses, ultimately leading to structural damage. As debinding proceeded to 16 and 21 hours, 40PEG eventually swelled and demonstrated the formation of blisters on the compacts. This can be explained by the slower dissolution rate of PEG molecules compared to the speed of water penetration. In turn, the sample volume expands, forming blisters within the samples. Nonetheless, from a practical perspective, the PPC/POM binder system containing 40% PEG content is preferred for the subsequent study, with a shorter debinding time and higher removal rate of PEGs compared to 30PEG.

![Figure 8.5 PEG removal rate in feedstock sample](image)

Figure 8.5 PEG removal rate in feedstock sample (a) 30PEG, (b) 40PEG, and (c) 50PEG at 30°C
To enhance the green strength of the sample during solvent debinding, an investigation was conducted on the influence of the POM backbone binder on the PEG removal rate. As observed in Figure 8.7, an increase in POM backbone binder had a negligible effect on the overall PEG removal rate. However, increasing the POM content facilitated the prevention of deformation on the debound samples. This suggested that POM as a secondary, minor backbone binder plays a vital role in securing the stability of the samples throughout debinding. On the other hand, PPC, serving as the predominant backbone binder, fosters compatibility within the binder system and enhances the adhesion between the powder and binder. As depicted in Figure 8.8, after 21 hours, 5POM demonstrated the most defects, followed by 8POM with slight slumping, while 10POM displayed the best shape retention with no defects. It is believed that 60% of PEGs removed during solvent debinding could successfully create sufficient pores for the subsequent thermal debinding stage [202]. This is well reflected when no visible structural defects were observed on sample 10POM after thermal debinding (i.e. Fig.8.8(d)).
Figure 8.7 PEG removal rate in feedstock sample (a) 5POM, (b) 8POM, and (c) 10POM at 30°C

Figure 8.8 Comparison of the samples (a) 5POM, (b) 8POM, and (c) 10POM after completion of solvent debinding at 30°C and on sample (d) 10POM after thermal debinding
8.3.4 Maximal open porosity and microstructural observations

Subsequently, the maximal open porosity was investigated using Archimedes’ principle [205] to determine the optimal porosity level necessary to effectively remove residual binders during the subsequent debinding phase. Table 8.2 presents the maximal open porosity observed in samples after the completion of solvent debinding. Notably, a discernible trend emerges, indicating that the open porosity is directly proportional to the amount of POM backbone. This is expected because increasing the POM backbone binder content increases the amount of insoluble binder remaining in the samples after solvent debinding. As reflected in Figure 8.9(a-c), increasing the POM backbone binder reduces open pore size. Nonetheless, it is crucial to emphasise the significance of the amount of POM present, as it maintains structural integrity and prevents defects during processing (Fig. 8.8c). From Table 2.2, the maximal open porosity of 10POM is about 10%. According to Fan et al.[95], a minimum porosity of about 8% is sufficient to form an interconnected pore structure reaching the centre of the samples, allowing for a successful thermal debinding process. Similar findings by Rolere et al. [174] on paraffin wax were observed when maximal open porosity is approximately 12%, showing an efficient removal of the remaining binder during the thermal debinding step. As Figure 8.9(d-f) demonstrated, no binder was presented in the samples after thermal debinding. This signifies the complete combustion of the binder, resulting in binder-free titanium compacts.

Table 8.2 Maximal open porosity of samples after approximately 60% PEG removal measured by Archimedes principle

<table>
<thead>
<tr>
<th>Code</th>
<th>Maximal open porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5POM</td>
<td>19.5 ± 0.5</td>
</tr>
<tr>
<td>8POM</td>
<td>12.1 ± 0.2</td>
</tr>
<tr>
<td>10POM</td>
<td>10.1 ± 0.3</td>
</tr>
</tbody>
</table>
Figure 8.9 SEM micrographs of feedstock (a) 5POM, (b) 8POM, (c) 10POM after solvent debinding and (d) 5POM, (e) 8POM, (f) 10POM after thermal debinding

8.3.5 Impurity Content

The impurity contents of the thermally debounded samples at 800°C were obtained via LECO impurity analysis provided in Table 8.3. It is apparent that increasing the POM backbone binder does not yield a proportional increase in the carbon and oxygen content. This reveals the efficacy of the backbone binder POM to decompose cleanly. Furthermore, it is noteworthy to mention that the incorporation of PPC binder as a major backbone binder also decomposes cleanly and facilitates decomposition at lower to moderate temperatures, thereby minimising the presence of impurities. All samples showed contamination within the tolerances for Grade 3 (ASTM F2989) titanium surgical implants after thermal debinding.

Table 8.3 Impurity content of thermally debound samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>O (wt%)</th>
<th>C (wt%)</th>
<th>N (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5POM</td>
<td>0.26 ± 0.004</td>
<td>0.052 ± 0.002</td>
<td>0.03 ± 0.02</td>
</tr>
<tr>
<td>8POM</td>
<td>0.25 ± 0.001</td>
<td>0.058 ± 0.010</td>
<td>0.05 ± 0.005</td>
</tr>
<tr>
<td>10POM</td>
<td>0.27 ± 0.005</td>
<td>0.052 ± 0.010</td>
<td>0.03 ± 0.010</td>
</tr>
<tr>
<td>ASTM F2989 (max.)</td>
<td>0.30</td>
<td>0.08</td>
<td>0.05</td>
</tr>
</tbody>
</table>
8.4 Summary

A promising environmentally friendly system based on PPC/POM was successfully developed for Ti-MIM. Owing to the inherent characteristics of polypropylene carbonate (PPC) and polyoxymethylene (POM) such as, their low decomposition temperature and propensity for clean degradation, titanium feedstocks made from this novel binder systems has been proved to effectively mitigate the introduction of impurities during the debinding process. As reflected from the SEM and LECO analysis, the resultant samples demonstrated a complete absence of binder and exhibited admissible impurity levels, with oxygen content of 0.27 wt% and carbon content of 0.05 wt%. These findings demonstrate compliance with the stringent requirements outlined in ASTM F2989 for Grade 3 titanium products.
Chapter 9 Conclusions

This thesis focuses on developing an environmentally friendly POM-based binder system for MIM. Additionally, efforts have been made to introduce a clean, low decomposition temperature binder system for reactive metals injection moulding, such as titanium. Some of the important findings are summarised below. We hope the findings described below could provide insight and lead to broader future investigations of environmentally friendly POM-based binder systems for MIM.

1) Initial efforts on preparing low formaldehyde- polyoxymethylene (POM) binder for metal injection moulding (MIM) were successfully fabricated. The results revealed that adding propylamine in polyoxymethylene (POM) can significantly reduce formaldehyde emissions. Among the various compositions tested, POM-PA2 exhibited the most promising results, achieving a notable 35% reduction in formaldehyde emission. This phenomenon can be attributed to 2wt% propylamine, which facilitates the optimal molecular bonding between POM and propylamine. Consequently, this interaction forms a novel and stable POM polymer mixture containing nitrogen functional groups, enhancing its formaldehyde scavenging capabilities. Furthermore, the titanium feedstock formulated using the POM-PA2 binder displayed nearly identical characteristics to the feedstock containing conventional POM. This observation establishes POM-PA2 as a superior alternative to POM as a binder for MIM, owing to its substantially lower formaldehyde emission and excellent mechanical properties.

2) The best POM-based binder system was obtained by incorporating the compatibiliser EGMA at a 3% w/w concentration, which exhibited the lowest contact angle and best miscibility. This is attributed to the active site in the EGMA molecule (i.e. epoxy and carbonyl functional group), enabling chemical reaction and hydrogen bonding within the ternary polymeric blend. The resulting ternary binder blends POM-PA2/PP/EGMA-3 demonstrated several advantageous characteristics for titanium feedstock production. Firstly, they yielded a more homogeneous and higher-density moulded part than the control feedstock without compatibiliser. Additionally, the rheological analysis revealed that the feedstock containing the EGMA-3
compatibiliser exhibited low viscosity, high shear sensitivity, low temperature sensitivity, and a high moldability index, rendering it highly suitable for MIM production. These findings highlight the potential of the POM-PA2/PP binder system with EGMA as a promising formulation for achieving improved performance and processability in metal injection moulding applications.

3) A robust design method to optimise the injection parameters in the MIM process to produce the highest green density parts were successfully investigated through the Taguchi Method L9 (3⁴). The optimum injection moulding parameter is found at an injection temperature of 190°C, injection pressure at 650 bar, mould temperature at 80°C, and injection time of 4 sec. The green density of feedstock obtained at the optimum processing parameters is 3.26 g/cm³, which strongly supports the Taguchi analysis, exhibiting a difference of less than 1%.

4) Next, a solvent debinding technique was employed as a simple and environmentally friendly approach to extract the POM binder effectively. This process exhibited a high debinding rate, achieving complete removal of the binder within 5 hours, comparable to the conventional method. The optimal debinding parameters were found at a low temperature of 60 °C and solvent concentration of 5M nitric acid, three-times lesser than that used in the catalytic debinding process. Furthermore, the use of solvent debinding process to extract POM holds promise in enhancing sustainability by mitigating environmental impact.

5) The optimised binder system (POM-PA2/PP/EGMA-3) provided good mechanical properties for the titanium feedstocks. The resulting sintered samples revealed good dimensional tolerance and a high density of over 4.3 g/cm³ on all samples. However, the average ultimate tensile strength was limited to a range of 328-407 MPa, primarily due to the presence of pores and oxygen impurities. In addition, it is noteworthy to mention that the oxygen content in the sintered samples was found to be significantly lower when the thermal debinding process was conducted in argon condition as opposed to a vacuum.

6) Nonetheless, to mitigate impurity uptake during the thermal debinding process in Ti-MIM, a novel binder system based on polypropylene carbonate (PPC) and polyoxymethylene (POM) was developed. The unique characteristics of
polypropylene carbonate (PPC) and polyoxymethylene (POM), such as its low decomposition temperature and propensity for clean degradation, have proved to be a suitable backbone binder for titanium feedstocks. As reflected from the SEM and LECO analysis, the obtained samples exhibited a complete absence of binder. They demonstrated minimal impurities, with an oxygen content of 0.27 wt% and carbon content of 0.05 wt% after the thermal debinding process. In this regard, the application of this binder system in fabricating Ti-MIM parts holds promising potential for addressing concerns related to low impurity levels and environmental impact throughout the MIM process.
Chapter 10 Recommendations and Future Work

The current study has successfully undertaken a comprehensive investigation to develop an environmentally friendly binder system based on POM for Ti-MIM. To further advance this research field, the following recommendations are proposed for future work:

1) Conduct an in-depth analysis of the recyclability and proper disposal methods for the solvent employed in POM extraction. This exploration will unlock the potential benefits of solvent-debinding techniques for POM-based binders.

2) Implement a dedicated furnace exclusively for thermal debinding and sintering of titanium to prevent contamination issues in the final parts.

3) Undertake a more extensive examination of the PEG/PPC/POM binder system after sintering, focusing on mechanical properties and impurity content.

4) Optimize the solvent debinding efficiency of the PEG/PPC/POM binder system to minimize both time and cost requirements.
Appendices

Appendix 1. Thermal debinding profile for POM/PP/EGMA-3 binder system

Appendix 2. Mechanical properties and impurities content of sintered samples (averaged to 3 samples)

<table>
<thead>
<tr>
<th>UTS (MPa)</th>
<th>Elongation (%)</th>
<th>Oxygen (wt%)</th>
<th>Carbon (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>406 ± 82</td>
<td>nil</td>
<td>0.483 ± 0.02</td>
<td>0.16 ± 0.03</td>
</tr>
</tbody>
</table>

Appendix 3. The plot of the double logarithm of viscosity versus the shear rate of POM feedstock at 170 ºC
References


S. Guo, X. Qu, B. Duan, M. Qin, Y. Zhang, Influence of sintering time on mechanical properties of Ti-6Al-4V compacts by metal injection molding, Xiyou Jinshu Cailiao Yu Gongcheng/Rare Metal Materials and Engineering 34 (2005).


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A. ASTM, B962-17-Standard Test Methods for Density of Compacted or Sintered Powder Metallurgy (PM) Products Using Archimedes’ Principle,