

Characterization of feedstocks for hybrid advanced technologies

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ABSTRAKT

Tato diplomová práce se zabývá složením a charakterizací vysoce plněných směsí na bázi karbonylového železa určených pro hybridní technologie zpracování kovů vstřikováním kovových prášků (PIM) a materiálovou extruzí (MatEx). První část práce je teoretická a popisuje základní principy formulace směsí, se zaměřením na vlastnosti prášku — velikost částic, jejich distribuci velikostí a morfologii — a také na složení polymerního pojiva a tokové chování. Strukturální a reologické aspekty jsou podrobně diskutovány s ohledem na analytické metody, jako jsou skenovací elektronová mikroskopie a kapilární reometrie. Zvláštní pozornost je věnována tokovému chování, které ovlivňuje stabilitu směsi, včetně kritického objemového podílu prášku, dilatantního chování, prahového napětí, skluzu na stěně a fázové separace.

V experimentální části jsou hodnoceny dva typy karbonylového železného prášku (CIP HQ a CIP OS), každá v kombinaci s pojivem na bázi polyetylénu (PE) nebo acrawaxu (AW). Prášky byly nejprve morfologicky charakterizovány pomocí SEM a následně analyzovány pomocí vysokoteplotní mikroskopie za účelem posouzení jejich slinovacího chování. Byly aplikovány dva slinovací profily — zkrácený a standardní; zkrácený profil vedl k částečnému spečení se zřetelnými defekty, zatímco standardní profil umožnil úplnou densifikaci a mikrostrukturu bez viditelných vad.

Směsi byly připraveny pomocí dvourotorového hnětiče Brabender a kritický objemový podíl prášku byl stanoven na základě měření a průběhu krouticího momentu. Reologické vlastnosti byly hodnoceny pomocí kapilární reometrie, přičemž u všech složení bylo potvrzeno pseudoplastické chování. Vliv morfologie prášku a chemického složení pojiva na viskozitu a stabilitu toku byl systematicky zhodnocen. Dále byla provedena SEM analýza v klíčových fázích procesu — od smíchané směsi až po sintrovaný výrobek — která potvrdila homogenitu, účinné odstranění pojiva a úspěšnou densifikaci prášků. Vstřikované vzorky vykazovaly optimální mikrostrukturální kvalitu, zatímco díly vyrobené pomocí MatEx vykazovaly lokální porozitu a povrchové defekty, což poukazuje na nutnost další optimalizace procesu.

Keywords: CIP, prášek karbonylu železa, PIM, vstřikování práškových materiálů, materiálová extruze, slinování, charakterizace, prášková směs, reologie,

ABSTRACT

This thesis investigates the formulation and characterization of carbonyl iron-based feedstocks for hybrid manufacturing technologies - powder injection molding (PIM) and material extrusion (MatEx). The first part of the thesis is purely theoretical and outlines the fundamental principles of feedstock formulation, with emphasis on powder characteristics—particle size, size distribution, and morphology—as well as binder composition and flow behaviour. Structural and rheological aspects are discussed in detail, with reference to analytical methods such as scanning electron microscopy (SEM) and capillary rheometry. Special attention is given to flow phenomena relevant to feedstock stability, including critical solid loading, dilatancy, yield stress, wall slip, and phase separation.

The experimental section evaluates two grades of carbonyl iron powder (CIP HQ and CIP OS), each combined with either a polyethylene (PE)-based or acrawax (AW)-based binder. Powders were first characterized morphologically using SEM and then subjected to high-temperature microscopy to analyse their sintering behaviour. Two sintering profiles—a shortened and a standard profile—were applied; the short cycle resulted in partially sintered structures with visible defects, while the standard profile achieved full densification and a defect-free microstructure.

Feedstocks were prepared using a counter-rotating twin-screw mixer and critical solid loading was determined from torque measurements. Rheological properties were evaluated with capillary rheometry, confirming pseudoplastic behaviour across all compositions. The effects of powder morphology and binder chemistry on viscosity and flow stability were systematically assessed. Additionally, SEM analysis was conducted at key stages of the process—from mixed feedstock to sintered part—confirming homogeneity, effective binder removal, and successful densification. Injection-molded samples demonstrated optimal microstructural quality, whereas MatEx-produced parts exhibited localized porosity and surface defects, indicating the need for further process refinement.

Keywords: CIP, carbonyl iron powder, PIM, powder injection molding, material extrusion, sintering, characterization, feedstock, rheology,

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INTRODUCTION

Advanced manufacturing technologies have revolutionized the production of complex metal and ceramic components by integrating conventional plastic processes and sintering manufacturing techniques. Two processes in this evolution are Powder Injection Moulding (PIM) and Material Extrusion (MatEx), both of which allow for high-precision shaping of materials with intricate geometries. PIM is a technology that combines the principles of powder metallurgy with plastic injection moulding, enabling the mass production of small, high-density components with excellent mechanical properties. In contrast, MatEx, particularly Fused Filament Fabrication (FFF), is an additive manufacturing approach that deposits material layer by layer, offering greater design flexibility and material efficiency. The combination of these two technologies opens new possibilities for fabricating metal and ceramic parts with enhanced performance and reduced production costs, making them highly relevant for aerospace, biomedical, and automotive applications.[1; 2; 3]

The processing of feedstock through PIM or MatEx requires careful control of various parameters to ensure defect-free and high-quality components. PIM involves injection moulding of the feedstock into moulds, followed by debinding and sintering to remove the binder and consolidate the powder into a dense structure. MatEx, on the other hand, relies on extrusion-based additive manufacturing techniques where the feedstock is deposited in layers to build a final shape. Once shaped, the part is referred to as the green.[4]

The feedstock used in both PIM and MatEx consists of a mixture of fine metal or ceramic powder and a polymer-based binder. The binder acts as a temporary carrier, enabling the shaping of the feedstock before it undergoes debinding and sintering to achieve the final component properties. Achieving an optimal volume loading of powder in the binder is essential for successful processing, requiring thorough material characterization and testing. Important tests include rheological analysis, thermal analysis, and structural analyses.[5; 6]

Especially, an understanding the rheological behaviour of the feedstock is crucial in both processes, as it affects flowability, extrusion performance, and mould filling. Rheological testing helps optimize processing parameters such as temperature and pressure, ensuring stability and consistency in the final products examined with the help of structural analyses.[1; 3; 5]

I. THEORETICAL PART

1 FEEDSTOCK

In PIM and MatEx, the feedstock is the mixture of fine powder and binder that serves as the essential material for the moulding and/or printing process, Figure 1. The properties of the feedstock are determined by several factors, including powder characteristics, binder composition, the powder-to-binder ratio, mixing method.[7]

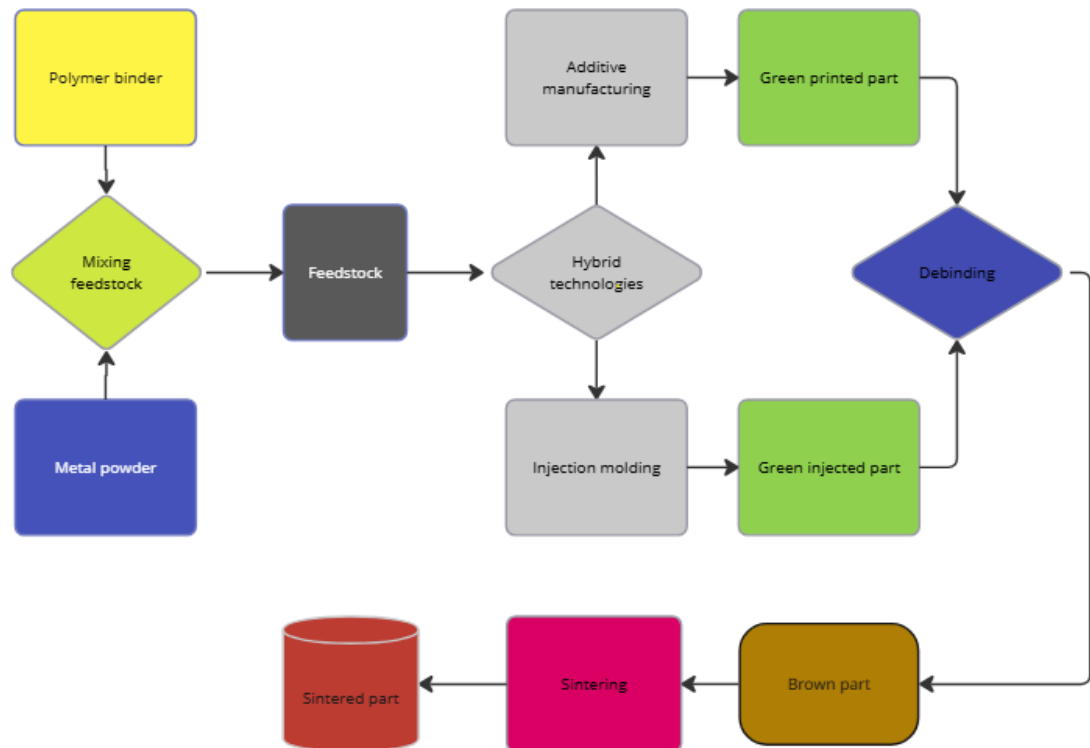


Figure 1 Hybrid processing of powder feedstocks.

A well-designed feedstock must balance processability with the ability to maintain the required final dimensions of the component. This balance is typically achieved through the use of low molecular weight polymers in the binder to reduce viscosity, facilitating smooth flow during moulding. Additionally, the feedstock should be free of voids and pores, ensuring that the binder sufficiently fills all interparticle spaces. Optimizing particle packing density by adjusting particle size distribution or incorporating bimodal size distributions further enhances the flow properties and stability of the feedstock.[7]

In majority industrial processes, commercial ready-to-use feedstocks are commonly used. These feedstocks contain an optimized mixture of powder and binder, allowing manufacturers to focus on the moulding process without adjusting individual feedstock compositions. While this approach simplifies production, it may limit the ability to fine-tune dimensional properties by reformulating the feedstock.[7]

1.1 Powder features

Powder characteristics are important to successful processing, influencing every manufacturing stage from feedstock preparation to final sintering. Highly important attributes such as particle size, shape, and size distribution as they directly affect packing density, flow behaviour, and sintering performance. Other powder properties like magnetism, thermal conductivity, chemical reactivity and electrical conductivity are also important for specific products but might also alter the manufacturing process. Thus, they might introduce additional considerations potentially complicating handling and processing stages. Alternation to equipment or manufacturing conditions may be necessary to ensure consistent performance and product quality. Modifications such as implementing antistatic equipment, controlling environmental factors (e.g., humidity, atmosphere), or adapting process parameters (e.g., mixing speeds, compaction pressures, or sintering conditions) are specifically designed to mitigate issues caused by these specific characteristics. [7; 8; 9]

Different types of powder fabrication techniques define the size, shape, and properties of the resulting powder, Figure 2. Gas atomization produces spherical powders with sizes ranging from 5 to 40 μm . This method is commonly used for metals and alloys but comes with high costs. Water atomization, on the other hand, results in rounded or ligamental shapes, with particle sizes between 6 and 40 μm , offering more cost-effective alternative. Centrifugal atomization creates spherical particles within the 25 to 60 μm range, and it is also used for metals and alloys, though its cost is moderate to high. Plasma atomization allows the production of small spherical powders, typically between 2 and 40 μm , making it suitable for metals, alloys, and ceramics, albeit at a high cost. Plasma rotating electrode process is a centrifugal atomization method which allows to influence flow of the droplets to reach better results.[10; 11]

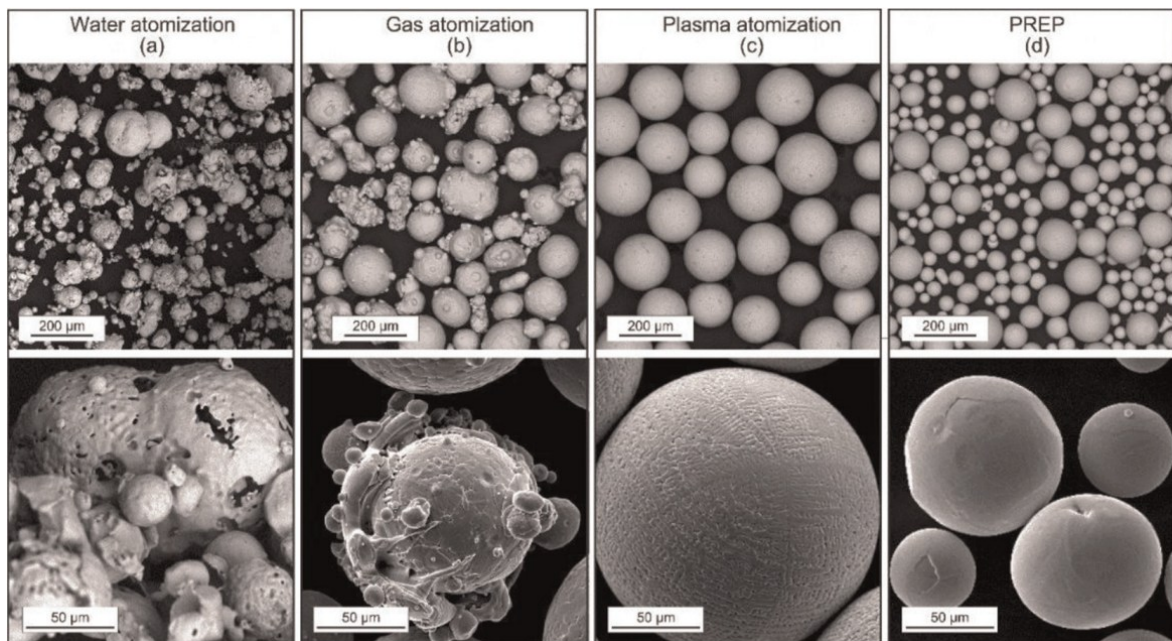


Figure 2 Powder surface: (a) iron powders produced by water atomization; (b) 316 L powders produced by gas atomization; (c) 316 L powders produced by plasma atomization; and (d) Ti-6Al-4 V powders produced by plasma rotating electrode process.

Source: Features of the Powder Application in Direct Laser Deposition [11]

Chemical processes also play an important role in powder fabrication. Oxide reduction, which involves reducing metal oxides using gases such as hydrogen or carbon monoxide, leads to powders with polygonal to rounded shapes and sizes ranging from 1 to 10 μm . This technique is relatively low in cost. Carbonyl decomposition produces rounded to spiky particles, typically between 0.2 and 10 μm in size, at a moderate cost. Another chemical method, chemical vapor decomposition, generates ultra-fine powders with sizes between 0.1 and 2 μm , but at a high production cost.[12]

Other techniques include precipitation, milling, and fine grinding. Precipitation can produce powders with equiaxed or needle-like shapes in the 0.1 to 3 μm size range, while milling and fine grinding generate angular or irregular particles, with sizes varying from 0.2 to 40 μm . These methods are typically used for ceramics and other brittle materials. Milling often results in sharp particles that inhibit packing and flow, making them less ideal for applications such as injection moulding.[12]

Atomization remains one of the most effective means of producing high-quality powders with controlled size and shape. Gas atomization, performed under inert conditions, produces highly homogeneous spherical particles with high packing densities. Water atomization, while more cost-effective, leads to less spherical particles that often require

additional processing, such as tumbling, to improve their packing behaviour. Plasma atomization is particularly useful for creating spherical powders of refractory metals and ceramics. The process involves melting and accelerating agglomerated material in a plasma torch, resulting in small, well-formed particles.[10; 12]

1.1.1 Particle size

The size of particles determines how they interact during flow and packing. Smaller particles provide a larger surface area relative to their volume, enhancing sintering rates by increasing surface energy. However, excessively fine particles can lead to agglomerations, these then leads to poor feedstock homogeneity and high interparticle friction, longer debinding times, which negatively impacts process. In contrast, larger particles reduce surface energy and friction. Also, coarser powders are much cheaper and easier to handle.[13; 7]

This perspective is supported by study by Tafti *et al.* [14], which highlights the impact of fine powders (10 μm) on sintering and flowability in irregular iron-based feedstock. The study confirms that smaller particles enhance sintered density and mechanical properties, such as tensile strength and elongation at break, by increasing surface area and promoting better particle bonding during sintering. However, it also notes challenges while formulating near critical solid loading (CLS) with flowability due to increased interparticle friction, as smaller particles create higher resistance to flow. Conversely, coarser powders (25–45 μm) were easier to process due to lower friction but resulted in lower sintered density and reduced mechanical strength. The differences in flow behaviour can be observed in Figure 3.[14]

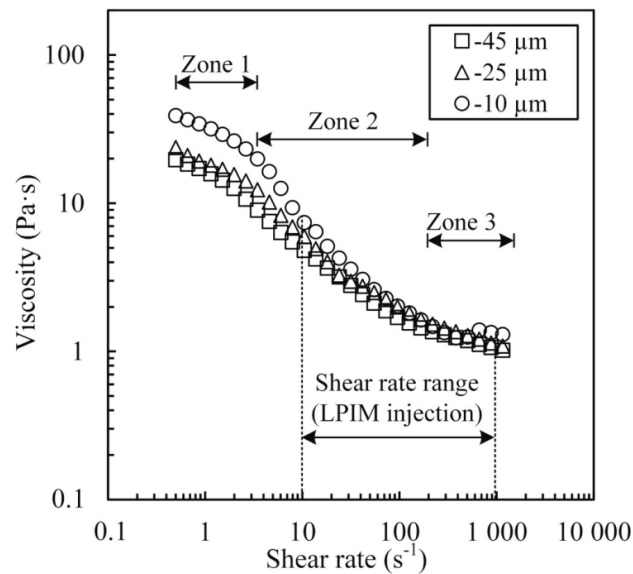


Figure 3 Influence of particle size on the feedstock viscosity (all feedstocks formulated with an identical solid loading of 57 vol% and tested at 90 °C).

Source: Influence of powder size on the moldability and sintered properties of irregular iron-based feedstock used in low-pressure powder injection molding.[14]

Another study by Mukund and Hausnerova [13] report essential effect of small size differences. In feedstocks containing finer powders, such as water atomized (WA) of mean particle size of 24 μm , hence WA_24. WA_24 exhibit better flow properties, facilitating easier cavity filling at lower temperatures, for instance at a nozzle temperature of 180 °C. On the other hand, feedstocks with larger, coarser powder particles, like WA_44, experience greater resistance to flow, requiring higher nozzle temperatures, up to 195 °C, to achieve complete mould filling. [13]

1.1.2 Particle size distribution

Particle size distribution is as critical as a particle size. A narrow size distribution ensures uniform flow and predictable behaviour during compaction and sintering. However, in some cases, a bimodal distribution, which includes both large and small particles, can optimize packing density by allowing smaller particles to fill voids between larger ones. This results in higher density and fewer defects in the final moulded or sintered part.[7]

In MIM and MatEx, particle size distribution is typically assessed using laser scattering or diffraction techniques. This method relies on measuring the diffraction patterns produced by particles dispersed in a liquid. As the particle size increases, the angle of diffraction also

increases. This approach is particularly effective for characterizing particles within the range of 0.1–1000 μm . A representative particle size distribution measurement for a standard powder, obtained using this technique, is illustrated in Figure 4.[7]

Trad *et al.* [15] highlighted the role of particle size distribution in powder injection moulding. A narrow distribution was found to enhance flow uniformity and reduce segregation, making it suitable for predictable and stable processing. However, the study also emphasized the advantages of a bimodal distribution, where finer particles filled voids between coarser ones, optimizing packing density and minimizing porosity in sintered parts. While this distribution improved densification, it also presented challenges in handling and processing due to increased segregation risks during moulding. These observations confirm the critical balance required in particle distribution to achieve both process stability and high-quality final components.[15]

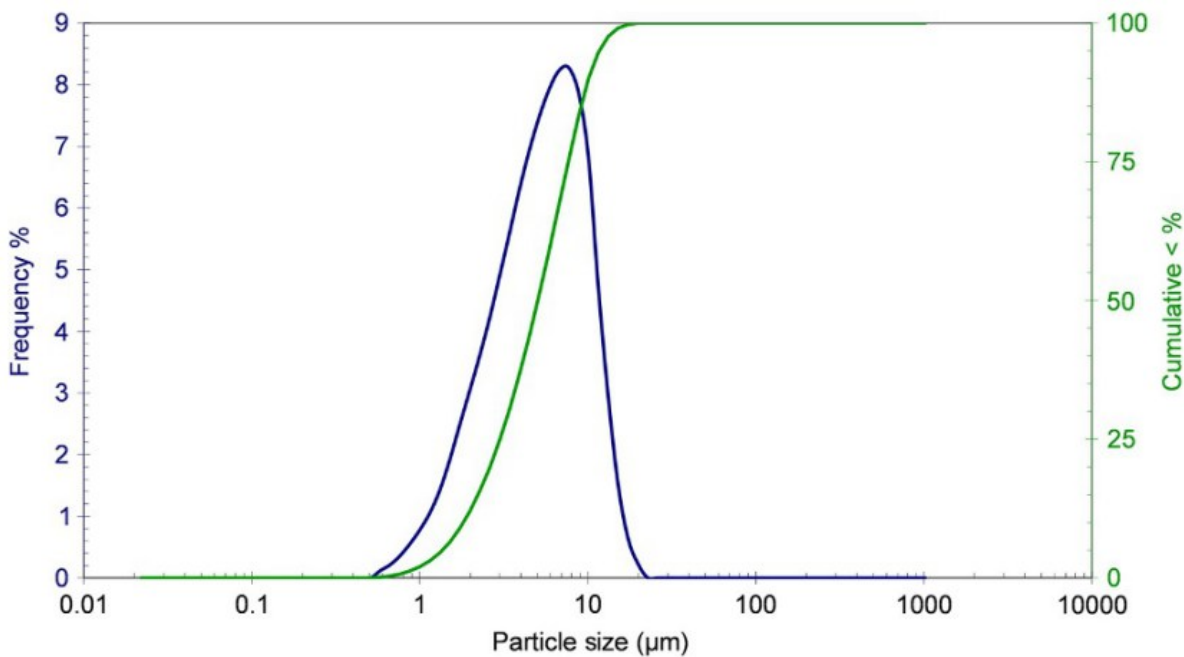


Figure 4 A typical PIM and MatEx powder particle size distribution where the $D_{10} \sim 2 \mu\text{m}$, the $D_{50} \sim 5 \mu\text{m}$, and the $D_{90} \sim 10 \mu\text{m}$.

Source: Handbook of Metal Injection Molding [7]

Particle size distribution has high impact on the mouldability, there are two parameters that can help with prediction of mouldability. The first one is distribution slope parameter (S_w) and second one is the flow behaviour index (n). Flow behaviour index will be further discussed in future chapters. [16]

D_{10} , D_{50} , and D_{90} are parameters used to describe the size distribution of particles in a material. These values come from a cumulative distribution curve as can be seen in Figure 4 and represent specific points in the dataset. D_{10} is the particle size where 10% of the total volume (or mass) of the sample consists of specified particle size. D_{50} , also known as the average particle size, is the point where half of the total volume consists of specified particle size. Lastly, D_{90} is the size at which 90% of the sample is made up of specified particle size. These values help in understanding how fine or coarse a material is.[13; 7]

The S_w value represents the slope of the log-normal cumulative distribution and functions similarly to a variation coefficient or standard deviation. A narrow particle size distribution corresponds to higher S_w values, whereas a broader distribution is associated with lower S_w values. In the Eq. 1 the numerator signifies that D_{10} and D_{90} are 2.56 standard deviations separately on a Gaussian distribution. However, powders typically follow a log-normal distribution, and the logarithmic size is suitable for gaining Gaussian cause. [16]

$$S_w = \frac{2,56}{\log\left(\frac{D_{90}}{D_{10}}\right)} \quad \text{Eq. 1}$$

1.1.3 Particle shape

Particle shape significantly impacts the flowability, packing density, and sintering behaviour of powders in powder injection moulding. Spherical particles are preferred for their superior flow and efficient packing, while irregular shapes increase interparticle friction, potentially causing flow defects. Quantitative measures like aspect ratio and qualitative SEM descriptors categorize shapes from spherical to dendritic or angular. Optimizing particle shape is essential for achieving uniform flow, high packing density, and defect-free sintering in PIM.[7]

An experimental study by Hausnerova *et al.* [17] was conducted to compare the performance of 17-4PH stainless steel powders produced via gas atomization and water atomization. Gas atomized powders, characterized by their spherical shape, were contrasted with the more irregularly shaped water atomized powders. Results showed that higher torque fluctuations at elevated solid loadings indicated proximity to the critical solid loading, where binder becomes locked in interparticle spaces, resisting flow. This was also confirmed by another study by Mukund *et al.* [18], where powder of the Co-Cr-Mo-Si alloy was used to distinguish the effects of size and shape. Clear differences emerge when observing viscosity

as a function of time in Figure 5, with Gas atomized (GA) feedstocks exhibiting stable and repeatable viscosity profiles. In contrast, WA feedstocks demonstrate notable viscosity instability. Although flow instability is common in polymer melts, it is less expected in highly filled materials. The irregular shape and lower symmetry of WA powder particles increase interparticle friction, limiting binder penetration into particle interstices, which can lead to particle-binder separation due to inadequate lubrication.[17; 18]

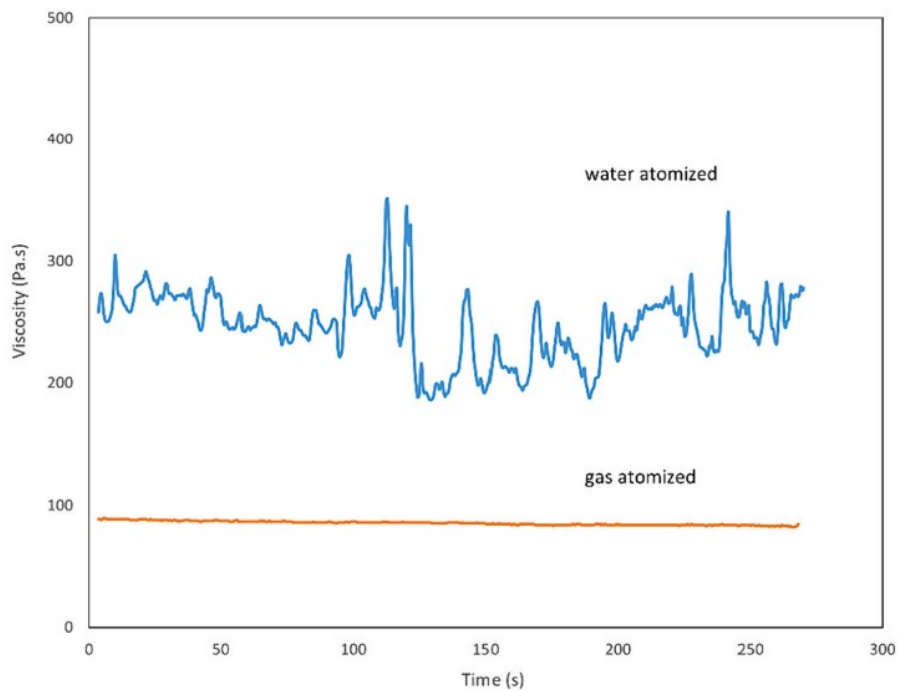


Figure 5 Viscosity as a function of time for gas- and water-atomized feedstocks.

Source: Quantification of shape parameters of Co-Cr-Mo-Si multiphase compounds and their role in the processing of metal injection molding feedstocks[18]

Spherical-shaped powders exhibited superior packing characteristics, achieving higher powder loading in feedstocks and higher theoretical density upon sintering. Spherical particles attained a maximum theoretical density of 99.3 %, demonstrating a clear packing advantage compared to irregular-shaped particles, which reached only 97.9 % of theoretical density.[19; 20]

However, irregular-shaped particles demonstrated certain beneficial traits, notably better dimensional precision and mechanical strength in moulded compacts after debinding. The improved shape stability observed in irregular-shaped particles resulted from particle interlocking, reinforcing structural integrity in both green and debound states. Additionally,

irregular-shaped particles exhibited higher viscosity compared to spherical-shaped powders, due to increased interparticle friction and reduced flowability.[20; 21]

Viscosity measurements indicated distinct flow behaviours influenced by particle shape. Spherical powders showed consistently lower viscosity during the moulding process, enhancing processability and mould-filling capability. Conversely, irregular-shaped powders, despite their higher viscosity, provided improved dimensional accuracy and structural robustness, highlighting the significant role of particle geometry in shaping final product quality.[20; 21]

In the review by Naranjo *et al.* [5] the importance of shape of powder for MatEx is mentioned, where the spherical shape of powder particles obtained through gas atomization significantly benefits the feedstock flowability, which is advantageous MatEx processes. This improved flowability is essential as it enables smooth material processing during printing and injection moulding and prevents issues like clogging or inconsistent material extrusion through the printer nozzle. The use of spherical powders, therefore, plays an important role in enhancing the processability and the overall quality of printed parts[5]

In summary, powder particle shape significantly influences feedstock processing and performance. While spherical powders offer enhanced packing density and flow properties beneficial for achieving higher densities, irregular powders provide improved shape stability and precision, underscoring a trade-off between packing efficiency and structural precision.[21; 20; 5]

1.2 Binder

Binders serve as a temporary medium to homogeneously mix powder particles, shape them into a desired form, and hold them in place until sintering begins. Although binders do not directly affect the final composition of the moulded material, their formulation significantly influences the success of the process, from feedstock preparation to the sintering phase.[7]

1.2.1 Binder composition

The composition of binders, and consequently debinding methods often differ across PIM and MatEx applications, reflecting specific requirements for flow behaviour, powder interaction, and manufacturing conditions. Most binders consist of multiple components, including a primary base that governs flow properties and modifiers to suit specific

applications. Main attributes of an ideal binder include low viscosity during moulding, strong adhesion to the powder, wettability, complete removal during debinding, and no residual contamination.[7]

The binder system in PIM and MatEx is designed to provide suitable processing properties by incorporating a complex mixture of up to five different polymers and waxes. This complexity makes it challenging to fully investigate the individual reaction pathways and chemical mechanisms occurring within the system. The binder system consists of three main components: the main binder, backbone, and additives.[22; 23]

The main binder makes up 50–90% of the system and is typically a low molecular weight polymer, such as polyethylene glycols with various molecular weights or paraffin wax. This component is removed first during the debinding stage, and its low viscosity ensures smooth flow, preventing interference with the powder and heavier components. [24; 7]

The backbone, which can constitute up to 50 %, provides structural support to the brown part after debinding. The majority of binder systems rely on polyolefin backbones, such as polyethylene or polypropylene, as they remain intact during the initial stages of debinding but thermally degrade in the early stage of sintering step.[23; 22; 24]

Additives-comprising up to 5 % of the binder system-include dispersants, compatibilizers, plasticizers, waxes, and stabilizers. These components help the powder particles disperse uniformly into the binder, preventing phase separation and agglomeration. The inclusion of multiple polymeric and wax-based ingredients enhances the feedstock's processing behaviour, but it also complicates the analysis of the binder's degradation and interaction mechanisms throughout the PIM and MatEx process.[23; 22]

A binder's performance depends on its ability to wet the powder surface effectively, aid in uniform mixing, and provide sufficient rigidity after moulding. Common binder components include waxes, thermoplastic polymers, surfactants, and lubricants, which collectively reduce viscosity, improve particle packing, and enhance process reliability. For optimal performance, binders must maintain a delicate balance between providing low viscosity at high powder loadings and preventing powder-binder separation during high-shear processes.[7; 25]

The study by Bleyan *et al.* [22] compared the interactions between polyethylene glycol and two waxes: acrawax and carnauba wax, using FTIR and calorimetric analysis. The

findings reveal that AW forms significantly stronger interactions with PEG than CW, as evidenced by the FTIR. These results demonstrate that binder formulations with higher interaction strength, such as AW/PEG, are more favourable for PIM and MatEx processes. The enhanced interactions improve powder wetting, uniformity, and structural integrity, aligning with the theoretical requirements of binders in PIM and MatEx. [22]

Another study by Kukla *et al.* [26] investigates the rheological behaviour of binder systems for powder injection moulding using a rotational rheometer (MCR501, Anton Paar) in oscillation mode with a plate-plate geometry. Viscosity measurements were conducted at 175°C under a nitrogen atmosphere to prevent degradation. Binary and ternary binder systems, composed of polypropylene, polypropylene wax, and paraffin wax, were analysed to assess the impact of composition on viscosity.[26]The results showed that viscosity varied significantly with binder composition, with paraffin wax reducing overall viscosity. Different mixing rules were tested for viscosity prediction, including logarithmic, Grunberg-Nissan, and Van der Wyk models. Models incorporating interaction parameters provided better agreement with experimental data, particularly for zero-shear viscosity, but struggled at high shear rates.[26]

1.2.2 Testing of binders

Differential Scanning Calorimetry (DSC) measures the differential heat flow between a sample and reference as both are subjected to controlled heating or cooling cycles. DSC effectively detects and quantifies thermal transitions such as melting, crystallization, glass transitions, and other phase changes. In analysing binder systems, DSC precisely identifies melting points, softening temperatures, and thermal events critical for defining processing parameters.[27]

DSC provides valuable information regarding the thermal transitions of polymeric components within binder systems, essential for evaluating their processability. For instance, distinct melting peaks identified by DSC for binder constituents such as waxes or polymers like polypropylene pinpoint exact temperatures required to achieve complete melting and flowability. The identification of glass transition temperatures through DSC further aids in ensuring appropriate viscosity and mechanical properties during shaping processes.[28]

Processing temperatures in PIM and MatEx are determined primarily using DSC data. Mixing and extrusion temperatures are chosen slightly above the highest melting point detected among binder constituents. Selecting temperatures significantly above identified

melting points ensures complete polymer melting and suitable viscosity, facilitating moulding and extrusion without initiating premature thermal degradation or adversely affecting binder integrity.[28]

Thermogravimetric Analysis (TGA) is a thermal characterization technique used to measure changes in a sample's mass as a function of temperature or time under controlled heating conditions. This method provides critical insights into the thermal stability and decomposition characteristics of materials. In the context of binder systems for PIM and MatEx, TGA evaluates binder decomposition, identifies thermal stability limits, and quantifies residual mass after decomposition.[29; 7]

The thermal degradation behaviours of polymeric binder systems are extensively studied using TGA. By heating binder materials at controlled rates and monitoring weight loss, engineers can precisely identify the decomposition onset temperatures and ranges for individual binder components. This information is essential for defining safe processing windows, preventing polymer degradation during mixing, moulding, or extrusion.[30; 7]

TGA results directly guide the selection of temperature hold points during thermal debinding and sintering. Binder systems commonly contain multiple polymeric components, each with distinct decomposition ranges. TGA profiles, showing clear stepwise mass losses, indicate precise temperature ranges suitable for incremental debinding holds. Each decomposition step in the TGA curve corresponds to a specific binder component, requiring corresponding temperature plateaus during sintering to effectively remove each polymeric fraction without causing structural defects due to rapid gas formation or internal pressure buildup.[30; 7]

Fourier Transform Infrared Spectroscopy (FTIR), when coupled with TGA, significantly enhances the understanding of the thermal degradation mechanisms of polymeric binder systems in PIM and MatEx. While TGA alone provides quantitative insights into mass loss and degradation temperature ranges, the addition of FTIR allows for real-time identification and qualitative analysis of evolved gaseous decomposition products. This integration of TGA and FTIR, enables precise identification of specific volatile species, such as carbon dioxide, carbon monoxide, and various organic molecules, evolving during thermal decomposition. This combined analysis provides comprehensive insights, allowing us to accurately identify not just the temperatures at which binders degrade but also the chemical nature and sequence of decomposition reactions, and so greatly improving process optimization for debinding and sintering in hybrid technology processes.[31; 32]

2 STRUCTURAL ANALYSES

PIM and MatEx processes inherently produce parts with some porosity and complex microstructures due to their multi-step nature. These hybrid techniques involve sequential stages: mixing feedstock materials, shaping a "green" part, debinding, and finally sintering. Each of these stages significantly influences the final structure and properties of the finished part. [33; 34]

The quality of the final product begins with the green part, which consists of a feedstock, which is shaped either by injection molding or material extrusion. A homogeneous, defect-free green body is very important because structural inconsistencies such as binder segregation or incomplete mould filling can lead directly to cracks, pores, and non-uniform densities after subsequent processing. Structural characterization at this early stage allows the early detection and correction of potential defects, ensuring optimal outcomes in later stages. [23; 5]

Debinding, the subsequent critical step, involves the controlled removal of the polymeric binder from the shaped green part before sintering. This step can be performed using solvent extraction, thermal decomposition, or catalytic methods. Each debinding method has a subtle influence on the microstructure and porosity of the intermediate product, impacting the subsequent sintering process. Proper debinding reduces residual stresses and potential defects, facilitating successful sintering.[7; 35]

Sintering, the final processing stage, subjects the debound part to high temperatures to achieve densification and material strengthening. During sintering, the remaining binder residues are fully eliminated, and particle bonding occurs through mechanisms such as diffusion and grain boundary migration, leading to reduced porosity and enhanced mechanical properties. The microstructural characteristics established in previous stages (green body quality and debinding effectiveness) directly determine the final density, homogeneity, and mechanical performance of the sintered part. Consequently, structural analyses including microscopy, density measurement, X-ray imaging, and mechanical testing (e.g., hardness and tensile strength) are important to assess and optimize the final properties, ensuring reliability and comparability to materials produced by conventional manufacturing methods.[33; 34]

2.1 Feedstock structure

2.1.1 X-ray computed tomography

X-ray computed tomography (CT) is a powerful non-destructive tool to examine the internal structure of PIM and MatEx parts. It uses X-rays to produce 3D reconstructions, revealing internal features such as porosity, cracks, or inclusions that are invisible externally. This is invaluable because PIM and MatEx parts can trap voids or binder pockets inside. Widianlara *et al.* [33] studied PIM steel parts and X-ray CT scans of the green compacts showed only a small number of pores and confirmed the absence of internal cracks, surface weld lines, or binder-rich separations. Such CT analysis complements surface inspections and validates the process. X-ray CT can also quantify the amount, size, and spatial distribution of pores in 3D. Muchavi and Machaka [34] used micro-CT to track porosity through each processing step (moulding, debounding, and sintering) of a 17-4PH stainless steel MIM part. The 3D scans identified where pores were located and how they evolved, information that traditional 2D microscopy could not fully capture. This ability to locate internal defects helps pinpoint process issues. Moreover, X-ray inspection is often used for quality control of complex parts to detect hidden flaws prior to service. Moreover, X-ray inspection is often used for quality control of complex parts to detect hidden flaws prior to service. While typical micro-CT may miss sub-micron pores, modern systems can achieve resolutions down to 2–5 μm , particularly when particles are well separated. Laboratory-based nano-CT systems offer significantly enhanced resolution up to 450 nm per voxel allowing detection of features in the sub-micrometre range. These systems are therefore often complemented by even higher-resolution techniques to ensure comprehensive structural characterization. [33; 34; 36; 37]

2.1.2 Scanning Electron Microscopy / Energy-Dispersive X-ray Spectroscopy

Scanning Electron Microscopy (SEM) is one of the most useful characterization methods in PIM and MatEx, offering high-resolution imaging of surfaces and cross-sections. Especially when these technologies usually employ micro-scale powders, SEM's magnification is important for examining powder and microstructure details that optical microscopes might not resolve. [7]

SEM cross-sectional micrographs can verify that metal powders are evenly distributed within the binder. A uniform dispersion with good particle-binder contact is essential for

defect-free parts. For example, in Jacob *et al.* [38], an SEM image of a MatEx part showed very uniform filler distribution and strong adhesion at the polymer–metal interface indicating good wettability of the powder by the binder. Such images confirm that the binder has properly coated the particles to prevent agglomeration or separation.[38]

This method is also routinely used to observe the shape and size of the metal powders (and any pore structures). It can measure if powders are spherical or irregular and whether their size distribution is as expected. In material extrusion, feedstock granules and printed filament cross-sections are SEM-inspected to ensure powder homogeneity. If particles were agglomerated or unevenly distributed, SEM would reveal those inconsistencies, which could lead to local defects.[7]

Spotting surface and microstructural defects is what SEM excel in. On green parts, SEM can detect issues like small cracks, knit lines, or surface wrinkles that result from the moulding or extrusion process. The study by Widianlara *et al.* [33] SEM was employed to examine a region where two feedstock flows met. The SEM images confirmed there were no surface wrinkles or voids in that critical area. After sintering, SEM is used to evaluate fracture surfaces and cross-sections for signs of incomplete sintering (such as visible particle boundaries or insufficient neck growth) and residual porosity. If a part breaks in testing, SEM fractography can show whether the failure originated at a pore or flaw. SEM imaging of sintered 15-5PH stainless parts from Chang *et al.* [39], clearly showed the formation of necks between particles Figure 6 and how higher sintering temperatures reduced residual pore size on the fracture surface.[33; 39]

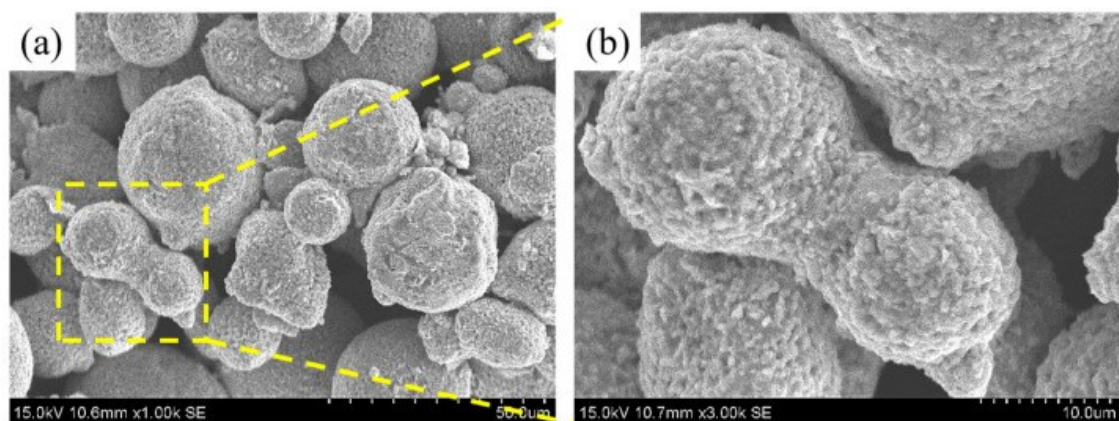


Figure 6 SEM morphology of the parts after thermal debinding and pre-sintering. (a) the sintering neck between the metal powder, (b) left image magnified 3000×.

Source: Printing, Debinding and Sintering of 15-5PH Stainless Steel Components by Fused Deposition Modeling Additive Manufacturing [39]

The Scanning Electron Microscopy analysis in study by Nor *et al.* [40] provided critical insights into the morphology, size distribution, and dispersion of stainless steel 316L powder within the polymer binder. High-magnification images (500×, 2000×, 5000×) revealed spherical particles of ~5 μm, concentrated in the cross-section and uniformly distributed in well-mixed samples—contributing to high packing density, essential for successful injection molding. SEM also identified defects in poorly mixed feedstocks, including air entrapment, agglomeration, and uneven binder coverage, which caused non-homogeneous regions. These defects negatively impact injection molding by impairing binder wetting, promoting phase separation, and leading to internal stresses and surface cracking. The clear contrast between homogeneous and defective regions highlighted the importance of proper mixing and formulation for consistent feedstock performance.[40]

SEM is commonly equipped with Energy-Dispersive X-ray Spectroscopy (EDX) detectors, allowing point or area analysis of elemental composition. While the metal powders and binder chemistry are known, EDX can detect unwanted elements or verify alloy homogeneity. This is particularly useful if there are suspicions of contamination (for example, oxygen from residual binder or carbon that might form carbides). In the study by Siedlecki *et al.* [41] comparing micro-PIM and extrusion, EDX mapping on sintered samples revealed carbon-rich phases at grain boundaries – attributed to binder decomposition residues forming carbides. Detecting these via SEM/EDX alerted the researcher to adjust the binder or sintering cycle to reduce such impurities. Generally, EDX helps ensure that no significant chemistry changes, for example oxidation, carbide formation, or ingredient segregation, which could occur during processing.[41]

A comparable application of SEM-EDX analysis is described by Hausnerova *et al.* [42], who employed this technique to quantitatively assess phase separation in highly filled powder/polymer compounds. Their study demonstrated that the distribution of elements characteristic of the powder and polymer could be accurately distinguished. EDX spectra revealed that in polymer-rich areas, the concentration of metallic elements was significantly reduced, confirming material segregation during flow.[42]

2.1.3 Transmission Electron Microscopy

While SEM covers microscale features well, Transmission Electron Microscopy (TEM) can probe the nanoscale structure of materials. TEM involves transmitting electrons through an ultrathin foil of the sample, achieving atomic-level resolution. In PIM and metal extrusion

contexts, TEM is not routinely used for every part (due to the intensive sample prep), but it becomes very important in research and detailed failure analysis. [7]

Many alloys form nano-sized precipitates during sintering or post-heat-treatments. TEM is able to image these precipitates and measure their size and distribution, which might be below SEM's resolution. For example, in Zhang *et al.* [43], in a MIM-fabricated nickel-base superalloy, a high-volume fraction of $\sim 0.5 \mu\text{m}$ γ' precipitates were observed homogeneously in the matrix (those were large enough for SEM), but smaller secondary phases like $0.2 \mu\text{m}$ carbides were also present at grain boundaries. TEM could further clarify the crystal structure or morphology of such precipitates if needed and indeed is often used in alloy development to confirm the nature of strengthening phases. TEM is also extremely useful for examining the interfaces in composite or multi-material parts. TEM can show dislocations, grain boundary films, or wetting layers that indicate how well the binder or a second phase interacted with the base metal at the microscopic level.[44; 43]

With techniques like selected area electron diffraction and high-resolution imaging, TEM can identify crystal structures of phases or reveal defects like dislocations and nano-voids within grains. If a sintered part had an unexpected brittleness, TEM analysis might uncover brittle intermetallic phases at the nanoscale or a network of nanometre pores not visible in SEM.[45]

2.2 Sintered part structure

The structure after sintering is evaluated to assess densification, grain growth, and defect presence. Key factors influencing the final structure include porosity reduction, phase composition, and mechanical integrity. The success of the sintering process is confirmed through microstructural analysis, density measurements, and mechanical testing, all of which determine its impact on the material's final properties.[16; 7]

The structural and mechanical properties of PIM and MatEx components are predominantly assessed through microstructural analysis, with porosity being a key characteristic influencing performance. Both PIM and MatEx produce components with microstructural features that can often surpass those achieved through conventional powder metallurgy. A fundamental distinction among these manufacturing routes lies in the nature, distribution, and morphology of pores in the final structure.[16]

Metallographic etching reveals the grain boundaries in polycrystalline metals. Grain size has a direct impact on mechanical properties (Hall–Petch relationship, where smaller grains generally mean higher strength). In sintered PIM parts, grain growth can occur during the high-temperature hold. By etching and measuring grain size, one can tell if the sintering cycle produced an appropriate microstructure or if abnormal grain growth occurred. For instance, one study by Hwang *et al.* [46] measured an average grain size of $\sim 88 \mu\text{m}$ via SEM after etching. They found that the yield strength of the sintered steel still followed Hall–Petch behaviour – smaller grain regions were stronger – even though the part had about 5% porosity. This highlights why knowing the grain size is important: it allows engineers to predict strength and adjust sintering parameters (temperature, time) to refine or coarsen the grains as needed for a balance of strength and ductility.[46; 47]

A polished cross-section observed under an optical microscope (or SEM) allows quantitative analysis of porosity: one can measure the area fraction of pores, their size distribution, and where they tend to reside (e.g. along grain boundaries or in clusters). Metallography is often the simplest way to check if a part has any large voids or unbonded areas internally. For quality control, a metallographic inspection might ensure that porosity is below a threshold and that there are no gross defects like cracks inside. In practice, metallographic images of sintered parts often complement density measurements – they visually confirm that pores are small and isolated. For example, etched cross-sections of solvent-debound and sintered micro-PIM samples in Siedlecky *et al.* [41] study showed that higher powder loading (60 vol% vs 55 vol%) led to more residual carbon impurity after sintering: dark spots at grain boundaries in the microstructure indicated carbide formation from binder residue. This finding, made via metallographic observation, demonstrated how porosity and binder removal affect the final chemistry. It underscored the importance of a proper binder gasification to avoid such micro-defects.[41; 48]

Metallography can reveal if the microstructure is uniform throughout the part or if there are gradients. In additive material extrusion, for instance, each printed layer could potentially show a slightly different microstructure (due to cooling rates or orientations). By taking cross-sectional micrographs through different orientations, one can detect any layering effect (perhaps different grain sizes near the part surface vs interior, or variations in porosity). A homogeneous microstructure is usually desired for consistent properties. If metallography shows, say, a denser skin and a more porous core, process adjustments might be needed (such as altering sintering profiles or print parameters).[49; 50]

Part density is often measured using electronic densitometer via Archimedes' principle to evaluate densification and residual porosity after sintering. Porosity directly impacts mechanical properties by reducing the load-bearing area and acting as stress concentrators, which influence tensile strength and fatigue life. Tensile testing determines ultimate tensile strength, elongation, and fracture behaviour, with porosity contributing to strength reduction while potentially enhancing ductility. Fatigue testing assesses the material's resistance to cyclic loading, with stress levels set as a percentage of ultimate tensile strength. The fatigue limit is determined at stress levels where the material can endure over a million cycles without failure.[46; 16]

In PIM and MatEx, the sintering process results in fine, well-dispersed pores throughout the microstructure. This homogeneous pore distribution enhances mechanical properties by reducing stress concentration points and improving load-bearing capability. In contrast, components manufactured via conventional powder metallurgy often exhibit a network of interconnected, irregularly shaped pores along grain boundaries. These pores, resulting from incomplete densification, compromise mechanical properties by promoting crack initiation and propagation under stress. The higher porosity in powder metallurgy parts generally leads to lower overall density and reduced strength, making these materials less suitable for high-performance applications.[16; 46]

Beyond inherent differences in pore morphology among manufacturing techniques, process parameters such as sintering temperature, time, and atmosphere significantly influence final porosity. Vacuum sintering mitigates gas entrapment within pores, enhancing densification and improving mechanical performance. Additionally, the debinding stage plays a crucial role in pore evolution; improper debinding can result in carbon residues that hinder full densification, leading to retained porosity in the final structure. While increased sintering temperatures typically enhance density, exceeding the optimal sintering window may induce grain coarsening and isolated pore formation, negatively affecting mechanical performance and component reliability.[46; 16]

Microstructural analysis involves (etching and) SEM imaging to examine grain structure, porosity, and fracture characteristics. Fractography reveals failure mechanisms, while Electron Backscatter Diffraction analysis provides insights into strain distribution and grain boundary behaviour.[46]

3 FLOW ANALYSES

Understanding the flow behaviour of feedstock is essential for optimizing processing conditions in PIM and MatEx processes. Analysing feedstock flow properties from initial mixing to final extrusion or injection enables manufacturers to precisely control processing parameters, ensuring consistency and quality in the final components. The structure of the feedstock, specifically the distribution, shape, and size of particles, and the composition of the binder, significantly influences its rheological properties.[7]

Proper knowledge of feedstock structure helps in anticipating and managing challenges like viscosity variations, yield stress, pseudoplasticity, dilatancy, and wall slip phenomena. A well-designed feedstock structure, featuring optimal particle packing density and appropriate binder composition, facilitates smooth flow during processing, minimizes defects, and enhances dimensional accuracy and mechanical performance of the final product.[7]

Therefore, detailed structural analysis of the feedstock, including particle characteristics and binder interactions, not only deepens the understanding of flow behaviour, but also changes how feedstock formulations are perceived and optimized. Accurate flow analysis, supported by structural insights, is indispensable for achieving high-quality, defect-free, and reliably reproducible products in advanced hybrid manufacturing applications.[7]

3.1 Rheometry

Utilizing capillary and rotational rheometry techniques, is important for characterizing the flow behaviour of polymer melts and highly filled composite materials. Each rheometric method provides specific advantages but also poses distinct limitations, particularly when applied to filled polymeric systems.[51; 7]

Capillary rheometers are core instruments in analysing high shear rate behaviour relevant to industrial processes such as extrusion and injection moulding. The capillary rheometer comprises a heated cylindrical barrel, through which polymers are melted and forced via a piston through a narrow-diameter tube (capillary) at constant shear rates or pressures. This allows for accurate measurements of pressure drop and volumetric flow rate, enabling calculations of apparent viscosity. Critical corrections, such as Rabinowitch (for true shear rates) and Bagley (for entrance pressure losses), are applied to improve measurement

accuracy. The ability to isolate wall slip and analyse the effects of viscous dissipation on flow properties makes capillary rheometers invaluable for characterizing filled polymers.[51; 52; 53]

In contrast, rotational rheometers typically employ cone-and-plate or parallel plate geometries to measure steady shear properties. Cone-and-plate geometries feature a uniform shear rate due to their small cone angle, facilitating precise viscosity and shear stress measurements. Parallel plate geometries, although experiencing variable shear rates across their radius, offer simpler sample handling. However, rotational rheometers encounter specific challenges with highly filled polymers, such as pronounced wall slip, which occurs due to a polymer-depleted boundary layer at the measurement surface. This issue distorts viscosity readings and, while mitigable by textured or serrated plates, complicates measurement reliability. Additionally, the presence of particle-particle interactions, agglomerates, and yield stress makes accurate measurements challenging. Furthermore, rotational rheometers are inherently limited to moderate shear rates (typically below 200 s^{-1}), restricting their ability to characterize significant dilatant or pseudoplastic behaviours fully.[51; 7; 6]

3.2 Rheology of feedstock

Flow in non-Newtonian fluids, refers to the behaviour of materials where viscosity is not constant but varies with shear rate or stress. These fluids exhibit complex flow properties such as dilatancy, pseudoplasticity, viscoelasticity, and yield stress, depending on the forces applied and the material structure. [51]

Viscosity in highly filled polymers refers to the material's resistance to flow, heavily influenced by the high concentration of solid particles dispersed within the polymer matrix. Unlike unfilled polymers, where viscosity primarily depends on the molecular structure of the polymer chains, highly filled systems exhibit complex rheological behaviour due to particle interactions and the influence of fillers on the flow.[54; 55]

Changes in viscosity during flow indicate structural rearrangements of particles and polymer chains, such as orientation, filler network formation, or particle interlocking. These structural shifts significantly impact the rheological behaviour of filled materials.[53]

Filled melts leverage the flowability of the polymer binder and the performance-enhancing properties of the fillers to produce high-precision and high-performance components. [6; 51]

In PIM and MatEx applications, feedstock comprises a polymeric binder and a solid filler, typically metal or ceramic powders. The binder ensures adequate flow properties during the moulding process and binds the powder particles together until the part undergoes debinding and sintering. Common binders include thermoplastics and waxes, combined with additives to optimize flow behaviour and reduce defects like phase separation.[7]

The solid fillers play a role in determining the mechanical and thermal properties of the final product. Factors such as particle size, shape, and distribution significantly influence the viscosity and homogeneity of the feedstock. Powders with high sphericity and uniform size distribution enhance flowability and minimize defects in the moulded parts.[7]

3.2.1 Critical solid loading

Critical solid loading represents the maximum volume fraction of powder that can be incorporated into a binder system while maintaining sufficient flowability for processing. It is a fundamental parameter in powder injection moulding as it directly affects feedstock viscosity, homogeneity, and the quality of moulded parts. Achieving optimal solid loading requires balancing particle packing efficiency, powder-binder interactions, and flow properties to prevent issues like phase separation or excessive viscosity.[7]

In study by Wei *et al.* [56], alumina ceramics were fabricated via injection moulding using multi-component binder systems. Increasing solid loading elevated the viscosity and stabilized torque of feedstocks, which exhibited pseudoplastic behaviour below 52 vol.% and dilatant behaviour at 54 vol.%, indicating proximity to critical powder concentration. Bending strength of green bodies initially increased, peaking at 25 MPa with 52 vol.% solids loading, before declining due to porosity at higher loadings. Higher solid loadings also increased bulk density and reduced shrinkage in sintered ceramics, enhancing mechanical properties. Alumina ceramics with 52 vol.% solid loading displayed uniform microstructures and achieved best bending strength.[56]

Experimental investigations by Mukund and Hausnerova [13] using water atomized (WA) powders confirmed the theoretical understanding of CSL as a key parameter in PIM. The powders (WA_24, WA_34, and WA_44) represent the percentage of particles sized between 10 μm and 20 μm obtained from water atomization. Torque measurements were

employed to determine the CSL values, revealing 71 vol% for WA_24, 70 vol% for WA_34, and 69 vol% for WA_44. These differences are attributed to the particle size distribution, with WA_24 having the broadest distribution (lowest slope of the log-normal cumulative distribution value) and thus achieving the highest CSL due to enhanced packing efficiency.[13]

3.2.2 Dilatancy

Dilatancy is the phenomenon where a suspension's viscosity increases with shear rate – the opposite of pseudoplasticity. In the context of PIM and MatEx feedstocks, dilatant behaviour is generally undesirable and less common, but it can occur under certain conditions. Most well-formulated feedstocks are pseudoplastic to facilitate mould filling. If a feedstock were dilatant, it could lead to high injection pressures and even incomplete cavity filling, since the material would resist flow more as the injection speed increases. Therefore, desired aim for flow index $n < 1$ (pseudoplastic), and avoid $n > 1$ which indicates dilatant behaviour. In practice, dilatancy in powder-polymer mixtures tends to appear when the particle fraction is extremely high, or the particle interactions become strongly frictional, essentially when the system approaches a jamming condition.[21; 51; 57]

Malkin *et al.* [57] review provides a detailed perspective. As shear rate increases, especially in dense suspensions, particles can start to collide and form transient clusters, causing resistance to flow to shoot up. The onset of this thickening is influenced by factors like particle surface roughness and binder viscosity. Rough or angular particles have higher inter-particle friction, so they tend to jam, and more dilatant at lower shear rates compared to smooth particles. Conversely, a more viscous binder can lubricate the particles better; higher continuous-phase viscosity has been shown to suppress dilatancy by damping out sudden frictional contacts. In other words, a thick, oily binder can help the suspension remain in a pseudoplastic regime even at high shear rates, whereas a very runny binder might allow the particles to hit and clump, triggering dilatancy. This insight is important for feedstock design: it implies that if one is pushing the powder content to the maximum, using a slightly more viscous binder or adding internal lubricants could prevent dilatant flow spikes.[57]

3.2.3 Yield stress

Yield stress fluids transition from viscoelastic solid-like behaviour, where deformations are recoverable, to plastic deformation, where deformation becomes unrecoverable, once the applied stress exceeds a critical threshold. [58]

Highly filled polymer feedstocks often behave as yield-pseudoplastic fluids, meaning they exhibit a yield stress followed by pseudoplastic viscosity. The yield stress is the minimum stress required to initiate flow – below this stress, the material behaves like a soft solid with the powder particles locked in a network. For PIM and MatEx feedstocks, a finite yield stress at processing temperature is commonly observed, indicative of inter-particle friction and cohesive forces within the binder-powder structure. In practical terms, this yield stress characterizes the “strength” of the packed powder-binder structure: the higher the yield stress, the more injection pressure is needed to get the feedstock moving. Studies have noted that feedstocks at very low shear rates – close to zero behave like Bingham plastics – a certain stress must be overcome for flow to start, after which viscosity drops with increasing shear rate (pseudoplasticity). This behaviour is crucial for moulding and extrusion stability. A modest yield stress is actually beneficial. It ensures that the material doesn’t flow under gravity or minor stresses, helping the part retain its shape (important for MatEx deposition or for avoiding sag in filled moulds). However, if the yield stress is too high, it can make filling the mould or extruding filament very difficult and can lead to incomplete filling or high pressures. [53; 54]

3.2.4 Wall slip

Wall slip is a critical phenomenon observed in the flow of all polymers. It occurs when a thin layer of the binder or polymer matrix forms near the wall of the flow channel, creating a slip interface between the material and the wall. This behaviour arises due to the separation of binder and filler particles under shear, leading to a binder-rich layer that facilitates flow. Wall slip significantly impacts the apparent viscosity of the material, often leading to underestimation of shear stress during rheological measurements.[59; 60]

In PIM and MatEx feedstocks, wall slip is influenced by factors such as the die surface roughness, particle size, and binder composition. For example, smoother die surfaces promote more pronounced wall slip, as the lack of mechanical interlocking allows the binder layer to slide more easily. Conversely, textured or roughened surfaces can mitigate wall slip by disrupting the binder layer and promoting adhesion between the material and the die wall. The particle size and distribution also play a role, as smaller particles are more likely to migrate to the slip layer, enhancing the effect.[59; 60; 61]

Wall slip presents both challenges and opportunities in the processing of highly filled polymers. While it can reduce flow resistance, facilitating material movement through

narrow channels, it can also lead to processing inconsistencies, such as non-uniform flow and defects in the final product. Measuring and quantifying wall slip is essential for accurate rheological characterization and process optimization. Techniques like the Mooney method, which involves using capillaries of varying diameters to measure slip velocity, are commonly employed to address this phenomenon.[59; 60; 61]

3.2.5 Phase separation

Powder–binder separation is a significant issue in powder injection moulding and material extrusion, as it directly influences the quality and dimensional accuracy of the final components. This phenomenon occurs when the powder and binder components of the feedstock separate during the moulding process, leading to defects such as voids, cracks, or distortions in the sintered part.[7; 62; 63]

One of the primary causes of powder–binder separation is the large density difference between the powder and binder. During mould filling, particularly when the flow direction changes, denser powder particles tend to continue along their original trajectory, accumulating unevenly in the cavity. This creates density gradients in the moulded component and results in preferential erosion at locations where separation occurs. Such issues lead to inhomogeneous binder removal during debinding, which in turn causes uneven shrinkage during sintering.[7; 62; 63]

A particle in the suspension experiences various forces, including hydrodynamic, electrostatic, steric, and van der Waals interactions, which collectively influence the suspension's microstructure. Factors like particle size distribution, particle concentration, binder properties, and shear rates during moulding significantly impact the extent of phase separation. Low inter-particle spacing or insufficient "lubricating" binder content amplifies the likelihood of separation.[7; 62; 63]

To address this, study by Shivashankar *et al.* [62] introduces a view based on inter-particle spacing, which depends on particle diameter, solid volume fraction, and maximum packing fraction. This parameter provides a quantitative approach to evaluating and minimizing powder–binder separation. The research demonstrated that small inter-particle spacing increases the risk of separation, while feedstocks with larger spacing, such as those with spherical particles and sufficient binder content, are less prone to this issue.[62]

The experimental findings by Shivashankar *et al.* [62] emphasize the importance of designing feedstocks with optimal particle and binder characteristics to resist separation. By

maintaining proper inter-particle spacing and ensuring homogeneity, the study offers valuable guidance for achieving correct dimensions and reducing defects in resulting components.[62]

II. PRACTICAL PART

4 OBJECTIVES OF THE MASTER THESIS

The objectives of the master thesis were set as follows:

- Prepare mixtures for Powder injection molding and additive manufacturing.
- Determine and evaluate the flow behaviour of mixtures.
- Analyse the structure before and after processing cycle.

The theoretical part was created based on these objectives to provide the necessary background for understanding the results obtained and collected in the practical section.

The practical part of this thesis includes a description of the materials, equipment, and processes used in the experimental investigation. The focus is on carbonyl iron powders (CIP HQ and CIP OS) with different particle size distributions, analysed using high-temperature microscopy to study their sintering behaviour. Scanning electron microscope (SEM) micrographs of both raw and sintered powders will be evaluated.

Feedstocks will be prepared by mixing the powders with either acrawax-based or polyethylene-based binder systems. Their flow behaviour will be examined using capillary rheometry. Additionally selected feedstock will be observed by SEM throughout all key stages of the hybrid process.

The aim is to gain a deeper understanding of the microstructural evolution and rheological behaviour of these materials during processing. Experimental work was conducted at the Tomas Bata University in Zlín, with selected high-temperature analyses performed at AGH University in Kraków during the ERASMUS stay.

5 EXPERIMENTAL

This chapter will describe the materials and apparatus employed in this master's thesis.

5.1 Materials

5.1.1 Powder

Iron powder used in this study was Carbonyl Iron Powder (CIP) supplied by BASF, Table 1. CIP is produced through the thermal decomposition of iron pentacarbonyl ($\text{Fe}(\text{CO})_5$), a process first industrialized in 1924 [64]. The resulting particles are characteristically spherical, typically below 10 μm in diameter, formed via a gas-phase synthesis reaction.[64]

CIP optimized silicate (OS) is a mechanically hard grade of carbonyl iron powder engineered for high-performance Metal Injection Molding (MIM) applications. It retains the characteristic onion-skin microstructure formed during carbonyl decomposition, which enhances sintering behaviour and supports stable magnetic properties at high frequencies. The powder is surface-silicated to improve flowability, enabling efficient feedstock compounding and high solid loadings. With a particle size distribution of $D_{50} \approx 3.4\text{--}4.4 \mu\text{m}$ and slightly higher oxygen content ($\text{O} \leq 0.9 \text{ wt.}\%$) compared to other market available powders, CIP OS offers good sintering performance and dimensional control. It is well suited for the production of geometrically complex parts requiring consistent and reproducible processing.[65]

CIP high quality (HQ) is mechanically hard, ultra-fine carbonyl iron powder tailored for applications that demand the highest precision, such as micro-MIM and hybrid manufacturing technologies including material extrusion (MatEx). Its particles retain the onion-skin structure, Figure 7, typical of non-annealed carbonyl iron, contributing to high sintering activity and excellent high-frequency magnetic performance. The extraordinary particle fineness of CIP HQ allows for high packing density, superior surface finish, and excellent part resolution, especially in miniaturized or geometrically complex components. Due to its unique microstructure and magnetic behaviour, CIP HQ interacts strongly with the magnetic component of microwave radiation, making it an effective absorber of microwave frequencies. This property supports its use in demanding electromagnetic shielding applications, ranging from civilian to military technologies.[65]

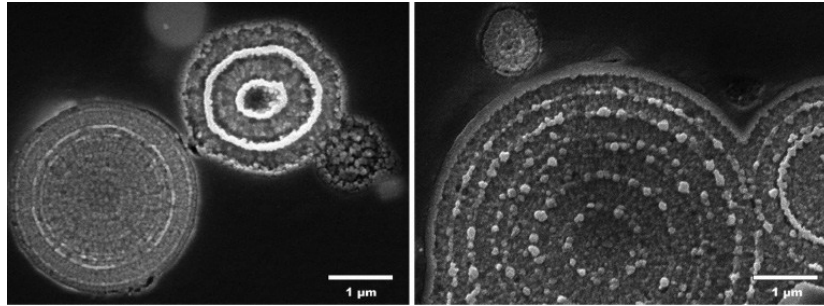


Figure 7 Typical SEM-images (SE, 20 kV) showing the onion-type structure of CIP after preparation of a metallographical section.[64]

Table 1 List of powders.

Type of powder	Label	Mean size distribution	Shape	Manufacturing process	Composition
Iron powder	CIP HQ	$D_{50} = 2\mu\text{m}$	Spherical	Carbonyl decomposition	Fe min. 97.8%; C max. 0.6-0.9%; N max. 0.6-0.9%; O max. 0.3-0.5%
	CIP OS	$D_{50} = 3,4\mu\text{m} - 4,4\mu\text{m}$	Spherical	Carbonyl decomposition	Fe min. 97.5%; C max. 0.7-0.9%; N max. 0.5-0.9%; O max. 0.6-0.9%

5.1.2 Binder

Two types of binders were used in the study. They are abbreviated a PE for polyethylene-based binder and an AW for acrawax-based binder, according to the backbone component in the binder composition.

The polyethylene-based binder, Table 2, consists of LDPE (53 wt.%), EVA (26 wt.%), and PW (21 wt.%), each serving a specific role in the process. LDPE acts as a backbone polymer, providing mechanical strength before sintering and remaining in the structure until late debinding. EVA, functioning as an elastic and compatibilizing component, enhances interfacial adhesion and compatibility among the binder constituents, particularly improving cohesion between non-polar LDPE and polar additives such as PEG. PW serves as the main binder, offering flowability during injection moulding due to its low melting temperature and is removed early in the debinding process.[66]

Table 2 PE-binder component characteristics

Component	Full Name	Density [g/cm ³]	Melting Temp. [°C]	Supplier	Location
EVA	Ethylene vinyl acetate	0.95	67.00	ExxonMobil	Houston, United States
LDPE	Low density polyethylene	0.91	102.00	ExxonMobil	Houston, United States
PW	Paraffin wax	0.9	58	FAGRON	Olomouc, Czech Republic

The second binder system Table 3 consists of PEG 4000 (29.5 wt.%), PEG 6000, AW (28 wt.%), PW (12 wt.%), and SA (1 wt.%), each playing its specific role in the processing and debinding stages. PEG 4000 and PEG 6000, as water-soluble main binders, ensure excellent flowability during injection moulding and enable easy removal in the early-stage solvent debinding due to their water solubility, leaving open pores for gaseous products of backbone polymers. AW a high-melting-point wax, serves as the backbone polymer, providing structural integrity during moulding and retaining shape stability until late debinding. PW further enhances flow properties, lowering viscosity and improving injection performance, while SA acts as a surface-active agent, improving powder dispersion and reducing viscosity during mixing.

Table 3 AW-binder component characteristics

Component	Full Name	Density [g/cm ³]	Melting Temperature [°C]	Supplier	Location
AW	Acrawax C (Ethylene bis stearamide)	0.51	145	LONZA	Basel, Switzerland
PEG4000	Polyethylene glycol 4000	1.41	62	Sino-Japan Chemical Co., Ltd.	Taipei, Taiwan
PEG6000	Polyethylene glycol 6000	1.21	62	Sino-Japan Chemical Co., Ltd.	Taipei, Taiwan
PW	Paraffin wax	0.9	58	FAGRON	Olomouc, Czech Republic
SA	Stearic acid	0.85	70	P-LAB a.s.	Prague, Czech Republic

5.2 Apparatus

5.2.1 Material testing

Knowing powder characteristics is important to understanding why and how feedstock will behave.

Microstructural evaluation of the carbonyl iron-based powders and feedstocks at various processing stages—including after mixing, injecting, debinding and sintering—was performed using a scanning electron microscope (SEM; VEGA II LMU, Tescan Ltd., Czech Republic) operated at an accelerating voltage of 5 kV. To assess the homogeneity and powder–binder interaction within the feedstocks, as well as morphological changes during processing, both BSE Full and TOPO B imaging modes were employed. The BSE (Backscattered Electron) Full mode provides compositional contrast based on atomic number differences, facilitating the distinction between metallic powder particles and the polymeric or pore regions. In contrast, TOPO B mode emphasizes surface topography, enabling detailed analysis of morphological features.[45]

For this measurement, cylindrical specimens were prepared from the carbonyl iron powders using a manual press and a steel mould. Each sample was weighed prior to testing and subsequently placed into the heating chamber of the high-temperature microscope (EM301 Heating Microscope, Hesse Instruments GmbH, Osterode am Harz, Germany). The instrument utilizes a non-contact optical method to monitor dimensional changes of the sample during controlled heating, with sample temperatures reaching up to 1600 °C. The analysis is performed using EMI III software, which automatically processes silhouette images of the specimen to determine key geometric parameters and to identify characteristic thermal events, such as onset of sintering, deformation, and melting. The measuring cell is specifically designed to accommodate measurements beyond the melting point, making it particularly suitable for studying sintering behaviour and high-temperature material responses. After the experiment, the sample was reweighed to assess any potential mass loss. All experiments were conducted under an inert argon atmosphere to prevent oxidation.[67]

The CIP feedstocks, formulated with both AW and PE binders, were evaluated using a capillary rheometer (Göttfert 50, GÖTTFERT Werkstoff-Prüfmaschinen GmbH, Buchen, Germany). The measurements were conducted with a capillary die featuring a length-to-diameter (L/D) ratio of 10/1, across an apparent shear rate range of 35–2000 s⁻¹.

5.3 Processing techniques

Mixing of the binder and powder was carried out using a counter-rotating twin-screw extruder (Plasti-Corder PL 2000, Brabender GmbH & Co, Duisburg, Germany). This equipment enables the uniform dispersion of the powder within the binder, ensuring the production of a homogeneous feedstock. Additionally, the extruder is equipped with a torque measurement capability. For the preparation of AW-based feedstocks, the temperature profile across the chamber zones was maintained at 80 °C / 80 °C / 80 °C, while PE-based feedstocks were processed at 140 °C / 140 °C / 140 °C.

For each measurement, the individual components of the binder system and powder were accurately weighed and introduced into the mixing chamber. The solid loading was systematically increased in each experiment, typically by 1 or 2 vol.%, depending on the feedstock behaviour and torque response observed in the previous step. This stepwise approach was employed to identify the critical solid loading characteristic for each formulation. Specifically, eight solid loading increments were conducted for the CIP HQ powder with a polyethylene (PE)-based binder system, and ten increments for the CIP HQ powder with the acrawax (AW)-based binder. These measurements were utilized to construct the critical solid loading curve, essential for determining the optimal powder content at which homogeneous and processable feedstocks can be formulated.

Injection molding of the feedstocks was performed using an injection molding machine (Allrounder 370S 700-100, Arburg; ARBURG GmbH + Co KG, Lössburg, Germany). AW-based feedstocks were processed with a nozzle temperature of 75 °C and a barrel temperature profile of 95 °C (Zone 1), 85 °C (Zone 2), 80 °C (Zone 3), 75 °C (Zone 4), and 20 °C (Zone 5). The screw stroke was set to 60 mm, cooling time to 30 s, and injection pressure to 1000 bar. Hold pressure was applied in two stages: 800 bar for 5 s and 150 bar for 2 s.

Additive manufacturing of 3D printed parts from the AW CIP HQ feedstock was carried out using the Arburg Freeformer (ARBURG GmbH + Co KG, Lössburg, Germany). The temperature of the discharge unit was set to 80 °C, with Zone 2 and Zone 1 temperatures at 75 °C and 70 °C, respectively. The material feed temperature was 40 °C, and the build chamber was maintained at 30 °C. The melt speed was 20 mm/s, and the melt pressure reached 249 bar.

Debinding was conducted at 60 °C for approximately 8 hours. exclusively to feedstocks based on the AW binder system. Aqueous debinding was carried out using deionized water

supplemented with 2 vol% of a corrosion inhibitor (Inhibitor 4000; Zschimmer & Schwarz GmbH & Co KG, Lahnstein, Germany).

Sintering of the green parts was provided on both a high-temperature microscope (EM301 Heating Microscope, Hesse Instruments GmbH, Osterode am Harz, Germany) under an inert argon atmosphere, and in Sintering oven MIM 3016 (CLASIC CZ s.r.o., Revnice, Czech Republic)

Two distinct sintering profiles were employed to evaluate the thermal densification behaviour of the samples. The shortened profile used on a high...consisted of a multi-step heating cycle as follows: heating at 3 °C/min to 250 °C with a holding time of 10 minutes; followed by 2 °C/min to 460 °C with an additional 10-minute hold; and then a final ramp at 10 °C/min to a peak temperature of 1300 °C, maintained for 30 minutes.

Sintering provided in sintering oven was carried out according to an optimized profile featuring a prolonged thermal exposure: heating at 3 °C/min to 250 °C with a 60-minute hold; followed by 2 °C/min to 460 °C with another 60-minute hold; and then heating at 5 °C/min to 1300 °C, with an extended holding time of 180 minutes.

6 RESULTS AND DISCUSSION

6.1 Powder characterization

The morphology and particle size distribution of the Carbonyl Iron Powder (CIP) powders were characterized using scanning electron microscopy (SEM).

The SEM Figure 8a shows CIP HQ powder with spherical morphology and a broad size distribution, dominated by fine particles. The satellite free surface and absence of agglomerates indicate high purity and excellent packing potential, but the fine size implies high surface area.

As can be seen from Figure 8b, the CIP OS powder exhibits predominantly spherical particles; however, the particle size distribution is coarser and more heterogeneous in comparison to CIP HQ. Numerous particles display partial plastic deformation into ligamental shapes or satellite structures, indicating a less uniform and more irregular overall morphology.

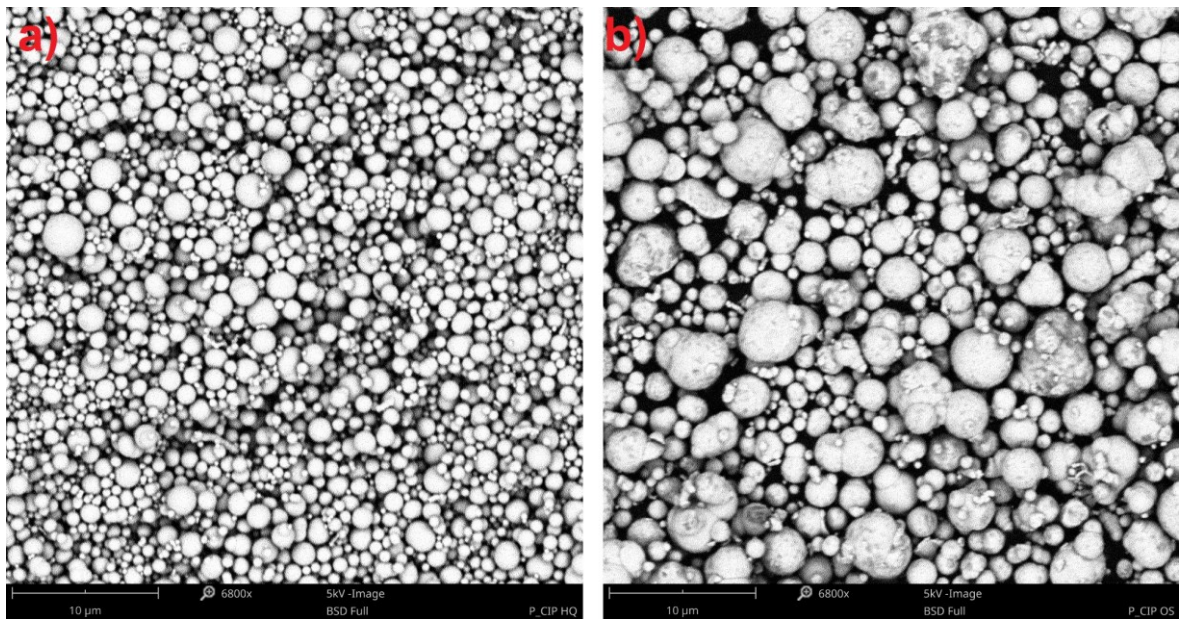


Figure 8 A SEM image of two iron powders 6800x magnification; a) CIP HQ, b) CIP OS (SEM; VEGA II LMU, Tescan Ltd., Czech Republic)

The CIP HQ powder consists predominantly of spherical particles with a fine and broad size distribution and minimal morphological defects. The high sphericity facilitates improved flowability by reducing interparticle friction[15] Additionally, the wide size distribution enables smaller particles to fill voids between larger ones, enhancing packing density, which is beneficial for achieving a uniform green body (injected or printed part).[7]

However, the fine particle size results in a high surface area, which leads to increased powder-powder interactions during compounding.[15; 7] These manifests as higher feedstock viscosity and mixing torque, potentially complicating injection or extrusion.[14] Moreover, the finer particles form a more closed pore network, which can impede binder removal during debinding and requires careful thermal control to avoid defects.[23]

The CIP OS powder also features generally spherical particles, but with a coarser and more heterogeneous size distribution, and notable defects such as satellite structures and plastic deformation into ligamental forms.[21] These irregularities increase mechanical interlocking and reduce particle mobility, leading to poorer flowability[21; 13] The morphological deviations also lower packing efficiency, increasing green body porosity and reducing uniformity.[41]

On the other hand, the coarser particles and more open pore network in CIP OS favour faster binder removal and reduce the risk of internal defects during debinding and the powder is cheaper.[16; 23] The lower surface area also contributes to reduced viscosity, simplifying feedstock preparation.[15] However, the reduced driving force for sintering and less uniform particle contact limit the achievable final density and mechanical properties.[38]

The average weights before and after sintering remained unchanged within the precision of the measurement for both (CIP HQ and CIP OS) powder types, Table 4, recorded as 0.77 ± 0.01 g and 0.78 ± 0.01 g, respectively. These values confirm that no significant material loss occurred during thermal exposure, which is consistent with the expected behaviour under a stable argon atmosphere, free from oxidative or reductive reactions.[68]

Table 4 Weight measurements of powder.

Powder	Weight before [g]	Weight after [g]
CIP HQ	0.77 ± 0.01	0.77 ± 0.01
CIP OS	0.78 ± 0.01	0.78 ± 0.01

The sintering behaviour of the CIP HQ and CIP OS powder, as recorded via high-temperature microscopy (Figure 9 and Figure 10), displays zones, which were defined based on the evolution of shrinkage behaviour observed via high-temperature microscopy. Although both powders are composed of carbonyl iron, the different particle sizes result in shifted thermal responses. By aligning the zones with equivalent sintering phenomena (e.g.,

initiation, densification, melting), rather than with fixed temperature points, enables a more meaningful comparison of thermal behaviour and diffusion-driven kinetics.

To facilitate a more precise and structured evaluation of these behaviours, the sintering process was subdivided into six thermally defined zones (A–F), each corresponding to a characteristic stage of microstructural/shrinking evolution. Zone A represents the initial phase, characterized primarily by thermal expansion and minor particle rearrangement without significant densification. Zone B marks the onset of sintering, identified by the first measurable shrinkage. In Zone C, the highest activity is observed, indicating the peak of sintering activity and bulk densification. Zone D follows as the rate of dimensional change decreases, consistent with intermediate sintering accompanied by the initiation of grain growth. Zone E captures the final stage of solid-state sintering, where the material approaches theoretical density and further structural changes become minimal. Finally, Zone F represents the onset of surface softening and potential melting, evidenced by the spheroidization of the test pieces.

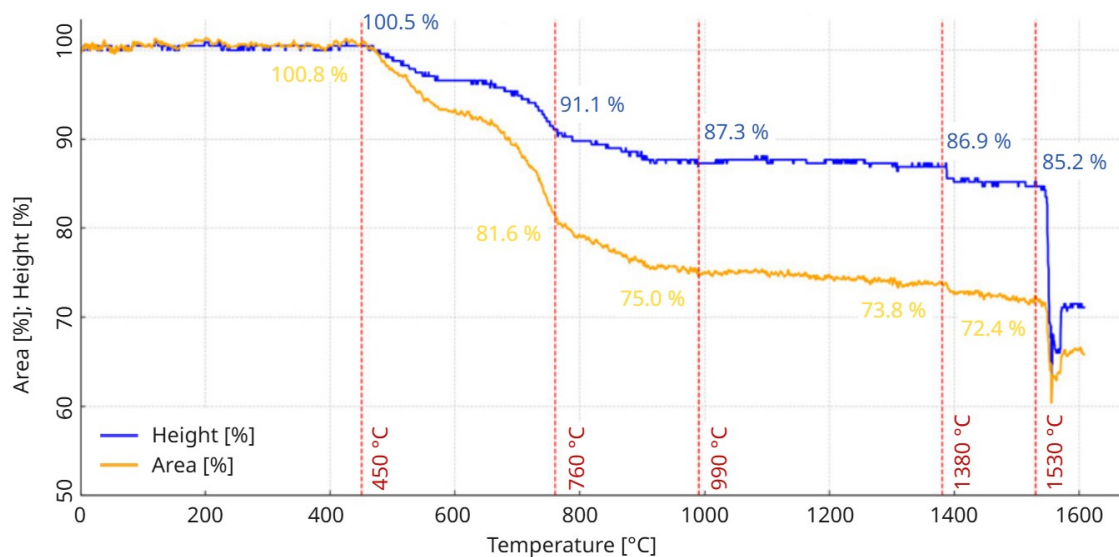


Figure 9 Graph of heating powder CIP HQ in high temperature microscope; characteristic temperatures and corresponding height and area are highlighted in red.

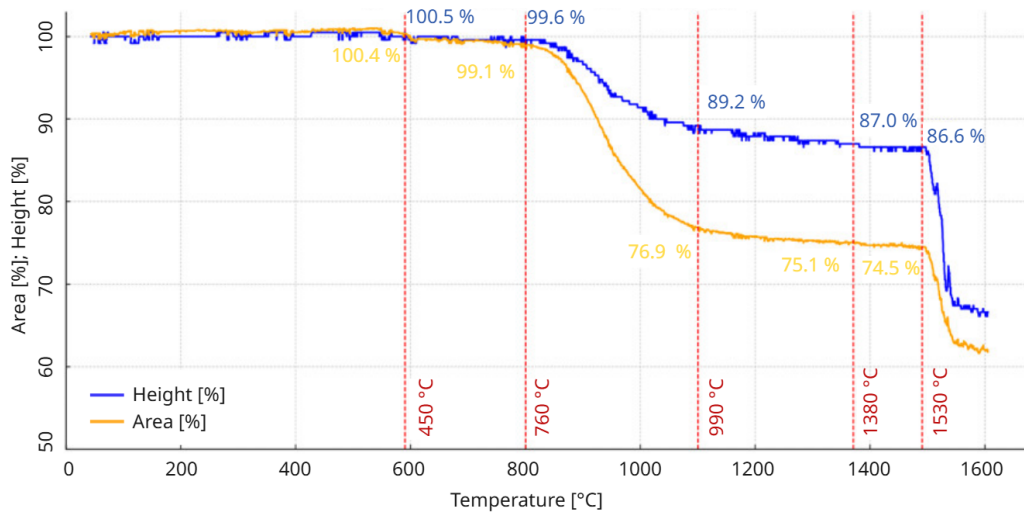


Figure 10 Graph of heating powder CIP OS in high temperature microscope; characteristic temperatures and corresponding height and area are highlighted in red.

To quantitatively assess and compare the shrinkage behaviour of carbonyl iron powders across the defined sintering zones, the first derivative of dimensional change with respect to temperature was calculated for each zone as showed for CIP HQ and CIP OS in Table 5 and Table 6, respectively. This allows the shrinkage rate to be expressed as the change in projected area or specimen height per unit temperature, normalized per 10 °C. The derivative was approximated numerically using the finite-difference method between two boundary points of each thermal zone, as given by Eq. 2:

$$\frac{dX}{dT} \approx \frac{X_{i+1} - X_i}{T_{i+1} - T_i} \quad \text{Eq. 2}$$

where X is either the projected area [%] or the specimen height [%], and T represents temperature. The result was then scaled by a factor of 10 to obtain the shrinkage rate per 10 °C.

Table 5 Area and height shrinkage in temperature zones for CIP HQ powder.

Zone	Temperature from [°C]	Temperature to [°C]	$d(A)/dT$ [%/10°C]	$d(H)/dT$ [%/10°C]
HQ-A	22	450	0.01778	0.01111
HQ-B	450	760	-0.61935	-0.30323
HQ-C	760	990	-0.28696	-0.16522
HQ-D	990	1380	-0.03077	-0.01026
HQ-E	1380	1530	-0.09333	-0.11333
HQ-F	1530	1608	-0.84615	-1.80769

The sintering behaviour of the CIP HQ powder, as presented in Figure 9 and Table 5, demonstrates a well-defined sequence of thermally driven transformations across Zones A to F, characteristic of fine carbonyl iron powders. In Zone A (22–450 °C), both the projected area and specimen height increase slightly, with shrinkage rates of +0.01778 %/10 °C and +0.01111 %/10 °C, respectively. This zone reflects the initial thermal expansion phase, where particles undergo minor rearrangement without initiating densification. The transition into Zone B (450–760 °C) is marked by a sharp increase in shrinkage rate, reaching –0.61935 %/10 °C in area and –0.30323 %/10 °C in height. This indicates the onset of sintering, likely governed by surface diffusion and early-stage neck formation, which are facilitated by the high surface energy of the fine particles.[69; 70]

In Zone C (760–990 °C), the material continues to densify, although at a reduced rate compared to the previous zone. Shrinkage rates in this interval remain significant (–0.28696 %/10 °C in area and –0.16522 %/10 °C in height), suggesting that bulk diffusion and particle bonding are actively progressing. As sintering enters Zone D (990–1380 °C), the shrinkage rates decrease substantially to –0.03077 %/10 °C for area and –0.01026 %/10 °C for height. This reduction signifies a transition into the intermediate sintering regime, characterized by grain growth and pore isolation, with slower densification due to diminishing diffusion gradients.[70]

Further heating into Zone E (1380–1530 °C) leads to a moderate shrinkage (–0.09333 %/10 °C in area and –0.11333 %/10 °C in height), which may be attributed to increased grain boundary mobility or enhanced sintering kinetics at elevated temperatures. In Zone F (1530–1608 °C), the powder undergoes an abrupt increase in shrinkage, particularly in height (–1.80769 %/10 °C), indicating the onset of surface softening, partial melting, or collapse of the pore structure. The extremely high shrinkage rates in this zone means a transition from solid-state to liquid-state and spheroidization into liquid drop. [71; 72]

For improved visualization, Figure 11, presents six selected images captured during the high heat microscopy test. The imaging system acquires an initial image at the start of the heating process, and subsequently begins capturing images at every 1 °C increment after reaching 800 °C. This approach is employed to optimize memory usage, as no significant morphological changes occur in the early stages of heating. The selected images correspond to temperatures near the boundaries of predefined thermal zones, allowing observation of the sample's behaviour throughout the process. As anticipated, the most prominent visible

change is a progressive reduction in sample size, indicative of shrinkage due to sintering. In the final image, the sample adopts a near-spherical shape, suggesting it has entered a molten state.

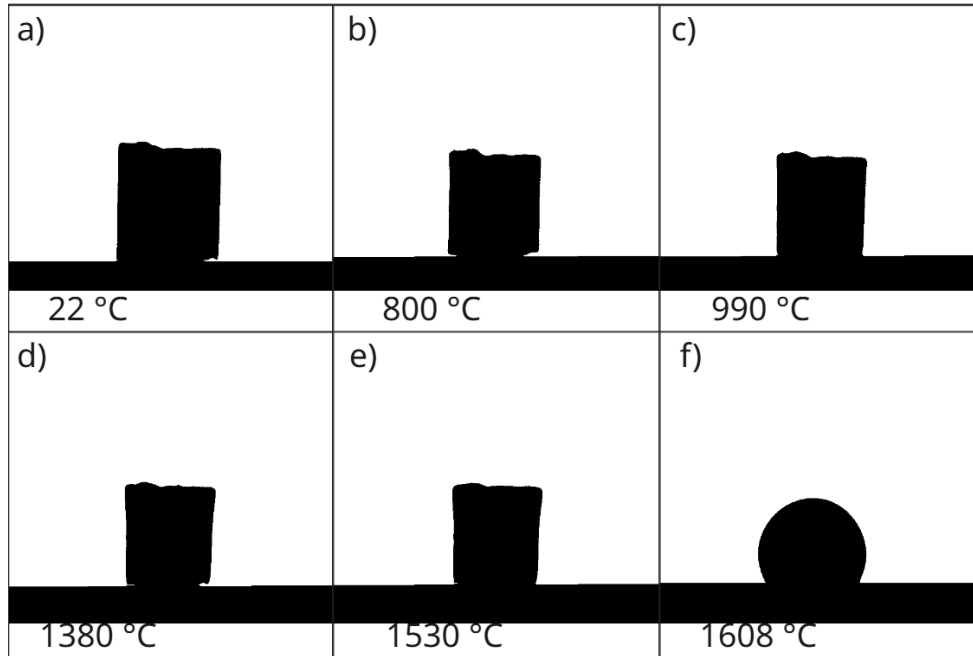


Figure 11 Heating of the CIP HQ sample (EM301 Heating Microscope, Hesse Instruments GmbH, Osterode am Harz, Germany)

The sintering behaviour of the CIP OS powder, as depicted in Figure 10 and Table 6 , reveals a progressive sequence of microstructural transformations across Zones A to F, driven by thermally activated diffusion mechanisms. In Zone A (22–590 °C), the material exhibits a slight increase in both projected area and height, reflected by low positive shrinkage rates of $+0.00169\%/10\text{ }^{\circ}\text{C}$ and $+0.00847\%/10\text{ }^{\circ}\text{C}$, respectively. This trend indicates that the system is primarily undergoing thermal expansion, without structural densification at this stage. Entering Zone B (590–800 °C), the first signs of shrinkage appear, marking the onset of sintering. The shrinkage rates remain relatively low ($-0.06190\%/10\text{ }^{\circ}\text{C}$ in area and $-0.04286\%/10\text{ }^{\circ}\text{C}$ in height), consistent with early-stage neck formation and limited particle rearrangement.[69; 71; 70]

Table 6 Area and height shrinkage in temperature zones for CIP OS powder.

Zone	Temperature From [°C]	Temperature To [°C]	$d(A)/dT$ [%/10°C]	$d(H)/dT$ [%/10°C]
OS-A	22	590	0.00169	0.00847
OS-B	590	800	-0.06190	-0.04286
OS-C	800	1100	-0.74000	-0.34667
OS-D	1100	1370	-0.06667	-0.08148
OS-E	1370	1490	-0.05000	-0.03333
OS-F	1490	1605	-1.10435	-1.73913

A dramatic increase in shrinkage is observed in Zone C (800–1100 °C), which exhibits the highest rates across all zones: $-0.74000\%/10\text{ °C}$ for area and $-0.34667\%/10\text{ °C}$ for height. These values correspond to the active sintering stage, characterized by rapid densification and the development of robust interparticle bonds. As the temperature continues to rise into Zone D (1100–1370 °C), the shrinkage rate decreases significantly ($-0.06667\%/10\text{ °C}$ for area and $-0.08148\%/10\text{ °C}$ for height), suggesting a transition to intermediate sintering accompanied by grain coarsening and reduced pore mobility. In Zone E (1370–1490 °C), the shrinkage process slows further, with modest rates indicating that the system is approaching its maximum packing density. The behaviour here is characteristic of late-stage sintering, where densification becomes increasingly limited by pore closure and grain boundary stability.[70; 73]

Finally, in Zone F (1490–1605 °C), the powder undergoes a final intensification of shrinkage, particularly in area ($-1.10435\%/10\text{ °C}$), with a similarly high rate in height ($-1.73913\%/10\text{ °C}$). These pronounced changes suggest the onset of surface softening or partial melting, leading to morphological transformations such as spheroidization. This behaviour confirms that the material has entered liquid-state. [70; 73]

Figure 12 presents six images illustrating the CIP OS sample's behaviour during heating. Images were selected near the boundaries of thermal zones to highlight key transitions. Progressive shrinkage is evident with increasing temperature, culminating in a near-spherical shape in the final frame, indicating the onset of melting.

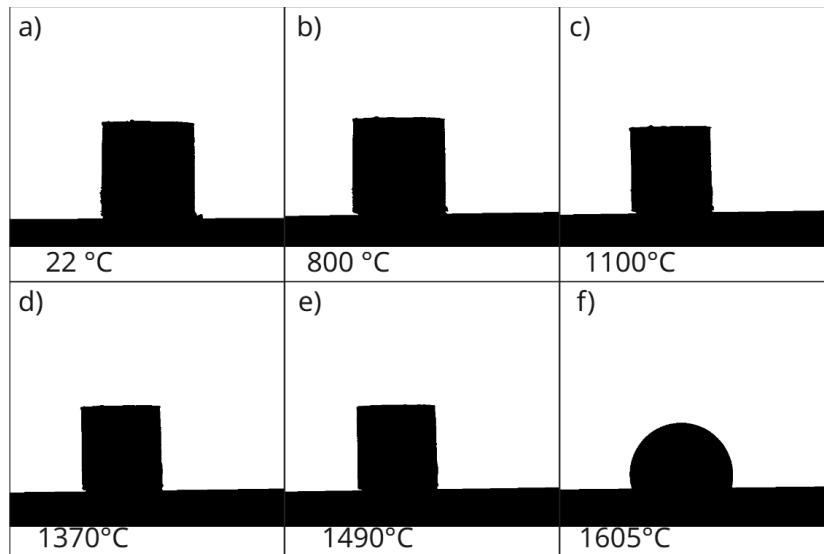


Figure 12 Heating of the CIP OS sample (EM301 Heating Microscope, Hesse Instruments GmbH, Osterode am Harz, Germany).

The observed differences in sintering behaviour between the CIP HQ and CIP OS powders can be directly correlated with their respective particle size distributions. Specifically, the finer particles of the CIP HQ powder demonstrated earlier onset of sintering and more rapid densification at lower temperatures, while the coarser CIP OS powder exhibited delayed shrinkage and required higher thermal input to initiate sintering. These findings are strongly supported by the study of Wu *et al.* [74], which systematically investigated the effect of particle size on sintering dynamics in stainless steel feedstocks processed via metal injection molding. Their results confirmed that finer powders, such as 17-4PH with a mean particle size of $6.87\ \mu\text{m}$, possess a higher sintering driving force due to increased surface area, resulting in enhanced densification, higher shrinkage rates, and reduced porosity. In contrast, coarser powders, exemplified powder (mean particle size $9.65\ \mu\text{m}$), exhibited slower diffusion kinetics, elevated residual porosity, and less uniform shrinkage due to reduced surface energy and hindered particle rearrangement during sintering.[74]

Figure 13 presents the thermal deformation profiles of CIP HQ (a–d) and CIP OS (e–h) feedstocks captured via high-temperature microscopy at progressive temperatures up to the onset of melting. CIP HQ, with finer particles ($D_{50} \approx 2\ \mu\text{m}$) and lower oxygen content ($\text{O} \leq 0.5\ \text{wt.}\%$), begins deforming around $1548\ ^\circ\text{C}$ and reaches a spherical shape by $1558\ ^\circ\text{C}$, reflecting its higher sintering activity due to increased surface area. In contrast, CIP OS—despite having coarser particles ($D_{50} \approx 3.4\text{--}4.4\ \mu\text{m}$) and higher oxygen content ($\text{O} \leq 0.9\ \text{wt.}\%$)—shows melting-related deformation at an earlier temperature, around $1517\ ^\circ\text{C}$.

This is contrary to the trend described by Yang et al. [75], where higher surface oxidation typically raises the melting point. A likely explanation is the presence of a silicate coating in CIP OS, which may soften at lower temperatures and influence the behaviour of molten iron, effectively reducing the temperature at which deformation begins. Additionally, the visibly different contact angles between the molten droplet and the ceramic plate suggest a difference in molten sample composition.[75]

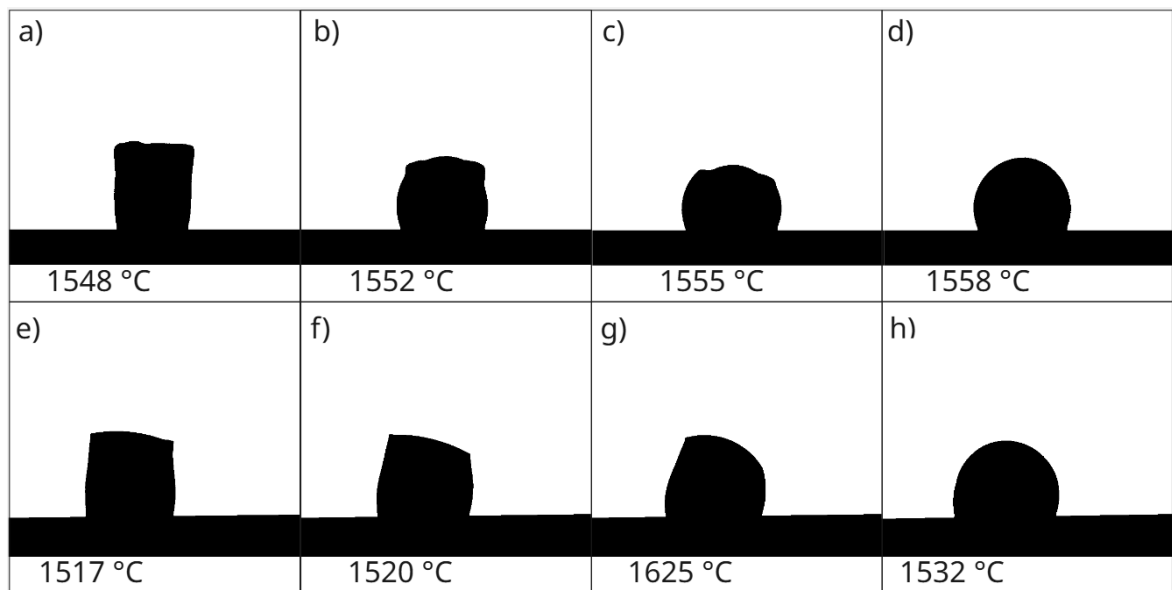


Figure 13 Thermal deformation of CIP feedstocks observed via high-temperature microscopy during heating: a)–d) CIP HQ and e)–h) CIP OS captured at progressive stages of deformation up to the liquid state (EM301 Heating Microscope, Hesse Instruments GmbH, Osterode am Harz, Germany).

To visually compare the sintering behaviour of CIP HQ and CIP OS across the defined zones, shrinkage rate bar charts were constructed for Zones B to E, as shown in Figure 15 and Figure 14. These zones represent the sequential stages of solid-state sintering, from initial onset of shrinkage to final densification. By expressing the rate of shrinkage in both projected area and specimen height per 10 °C, the charts allow for a direct and quantitative comparison of sintering kinetics between the two powders. Zones A and F, which corresponds to the early heating and onset of melting, respectively, was excluded from the comparison due to its almost zero values and significantly higher shrinkage values. Including these zones would have distorted the vertical scale of the charts and reduced the visual resolution of the shrinkage trends in the earlier zones. Therefore, the focus on Zones B–E ensures proportional representation and improved interpretability of the comparative sintering behaviour.

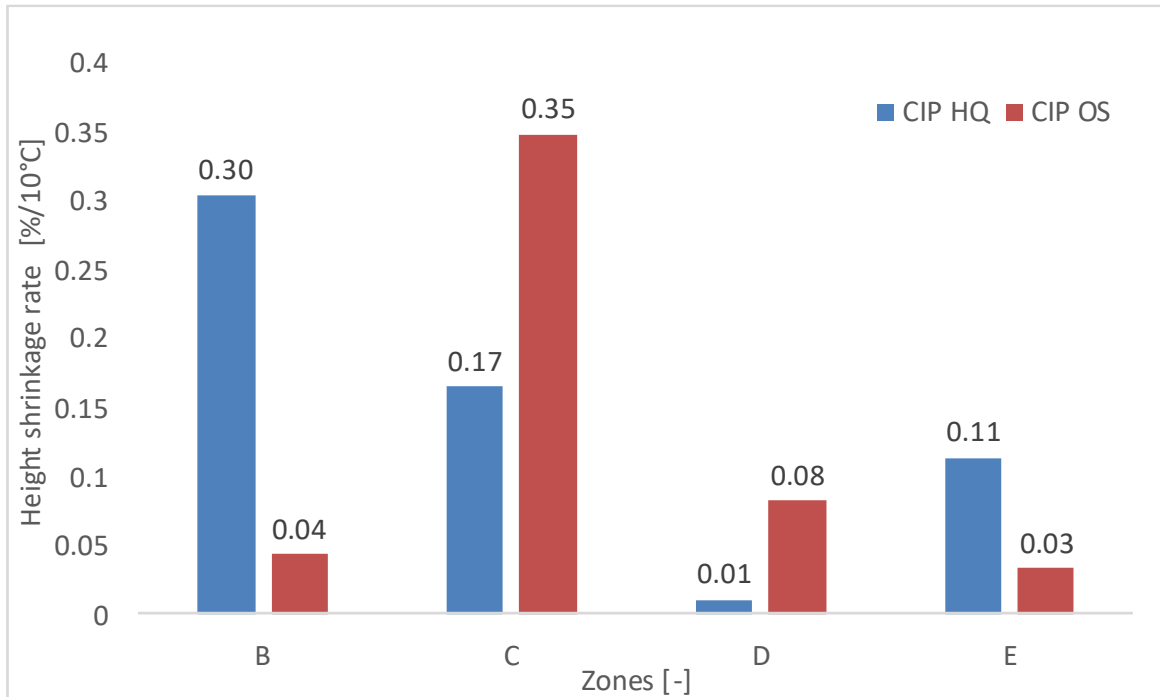


Figure 14 Height shrinkage rate comparison charts for Zones B–E.

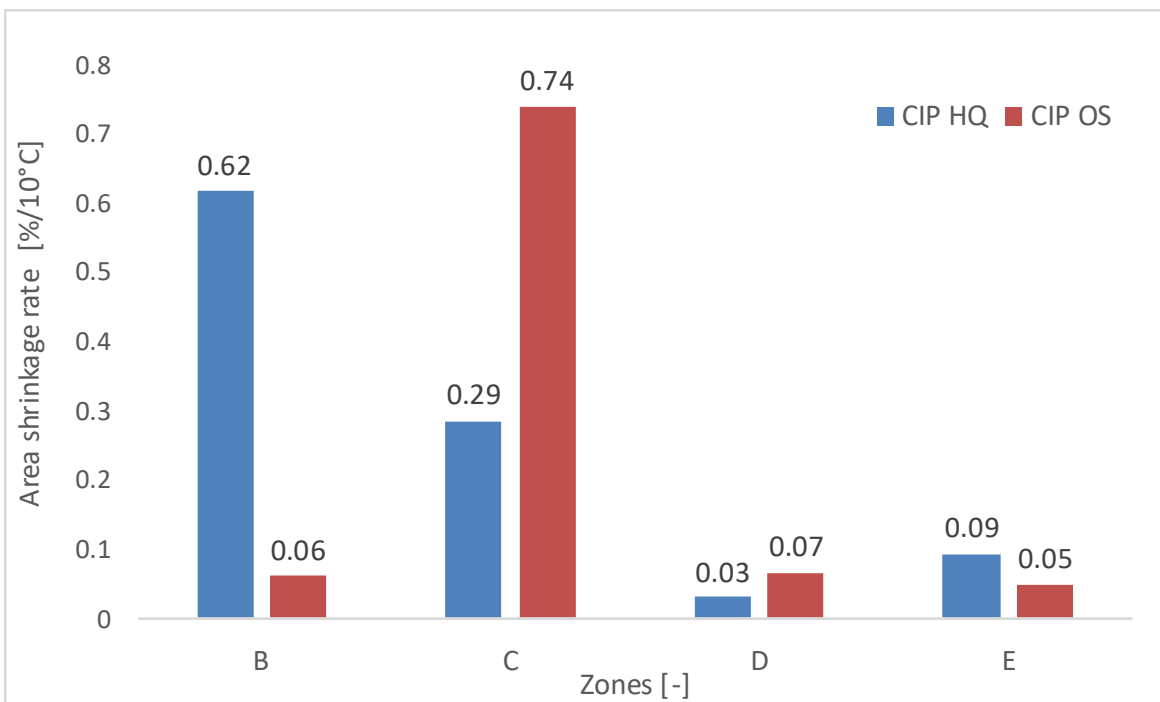


Figure 15 Area shrinkage rate comparison charts for Zones B–E.

A comparative analysis of the sintering behaviour of CIP HQ and CIP OS reveals distinct differences in the onset, intensity, and progression of shrinkage, primarily driven by differences in particle size distribution. CIP HQ exhibits a significantly earlier initiation of sintering, with the shrinkage rate in Zone B more than ten times higher than that of CIP OS in the same zone. This early activation is attributed to the finer particle size and higher

specific surface area of CIP HQ, which enhance diffusion-driven consolidation at lower temperatures. In contrast, CIP OS shows a delayed response, with its maximum shrinkage shifted to Zone C, where the shrinkage rate in area increases by over 1100 % compared to its previous zone — indicating a thermally activated threshold required to initiate densification in coarser particles.

From Zone C to D, the shrinkage rate in CIP HQ decreases by approximately 89 %, marking a transition toward structural stabilization and grain growth. In contrast, CIP OS maintains elevated shrinkage activity through Zone D, with its height reduction rate increasing by nearly 91 % compared to the previous zone. This suggests that OS progresses more slowly through the sintering cycle, with active densification continuing over a broader temperature range.

In Zone E, both powders exhibit a decline in shrinkage rates. However, CIP HQ still demonstrates roughly 87 % higher area shrinkage and over 240 % greater height reduction than OS, reflecting its continued microstructural responsiveness even in late-stage sintering. This may be attributed to residual porosity and finer internal features that continue to densify under elevated thermal energy.

Finally, in Zone F, both materials undergo rapid dimensional collapse, indicative of melting or spheroidization. Overall, CIP HQ demonstrates earlier and more intense sintering kinetics, whereas CIP OS follows a more delayed but extended densification profile. If the results are compared with study done by Staab *et al.*[70], It's possible to see that the dominant sintering mechanism in carbonyl iron powder, as confirmed by positron annihilation spectroscopy, is grain boundary diffusion. Dislocation contributions vanish above ~630 °C, and the shrinkage observed in the range of 1050–1500 °C in this study aligns with this grain boundary-controlled mass transport mechanism. [70]

This behaviour means that the densification observed in this temperature range is not driven by defect-assisted diffusion, but rather by thermally activated atomic migration along grain boundaries, which become the primary diffusion pathways once dislocations have annealed out. For hybrid applications, this insight is highly valuable, as it confirms that, under appropriate thermal conditions, CIP exhibits a predictable and diffusion-controlled sintering behaviour, governed primarily by its grain boundary network. This supports the use of carbonyl iron powders in hybrid feedstocks, as their fine particle size and high purity favour efficient neck formation and shrinkage during sintering.

6.2 Rheological behaviour of feedstock

The critical solid loading of the carbonyl iron powder CIP HQ with a PE-binder system was evaluated by monitoring the torque during mixing at incrementally increasing powder volume fractions. As illustrated in Figure 16, the torque increases gradually from 7.5 N·m at 55 vol.% to 10.6 N·m at 59 vol.%, indicating good dispersion and sufficient binder wetting in this range. That's why an optimal solid loading was selected 59 vol.% for PE-binder.

However, a pronounced non-linear increase in torque is observed beyond 59 vol.%, with values reaching 14.3 N·m at 60 vol.%, 18.9 N·m at 61 vol.%, and peaking at 23.8 N·m at 62 vol.%. This sharp rise indicates a transition in flow behaviour, primarily due to insufficient binder content to fully wet and separate the powder particles. As a result, particle mobility becomes increasingly restricted, and the system exhibits a greater number of direct particle-particle contacts, enhancing mechanical interlocking and frictional resistance. Additionally, at such high solid loadings, the feedstock may begin to deviate from typical shear-thinning behaviour, showing characteristics of yield stress or dilatant systems, which further increase the torque response during mixing.[35; 76]

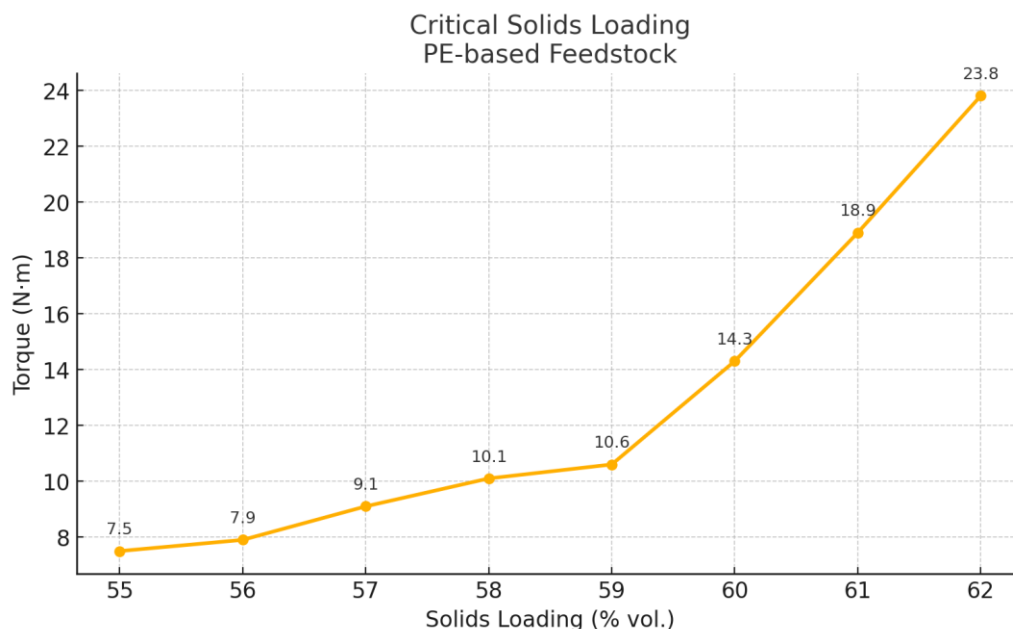


Figure 16 Torque evolution with time for CIP HQ feedstock with PE-binder.

Figure 17 shows the solids loading increased from 50% to 61%, the mixing torque exhibited a gradual yet consistent rise, increasing from 2.9 N·m at 50 vol.% to a peak value of 15.5 N·m at 61 vol.% for AW-based binder. This trend is characteristic of increasing particle-particle interactions within the binder matrix, where the reduced volume of polymer

relative to powder content results in higher internal friction and greater resistance to flow. The steadily rising torque suggests the feedstock maintained homogeneous dispersion of particles up to this point, with sufficient binder available to fill the interstitial spaces among particles.[77; 76]

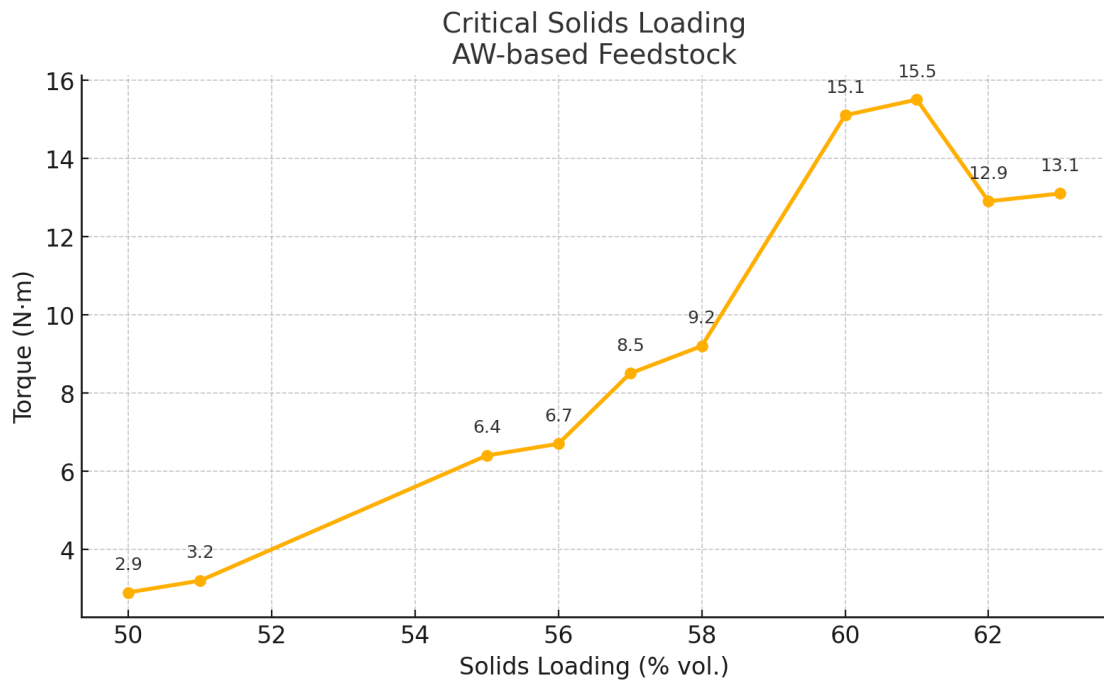


Figure 17 Torque evolution with time for CIP HQ feedstock with AW-binder.

Another way to determine critical solid loading (CSL) is a density measurement, where a drop in measured feedstock density (Figure 18) below the theoretical linear trend due to void formation, would be an indication of CSL as shown by Mukund *et al*[18]. Apparent similarity to the behaviour of the AW-based feedstock, where the torque increases up to 15.5 N·m at 61 vol.% solids loading and subsequently decreases at 62 vol.% and 63 vol.%, has different reason. At solids loadings above CSL, the material can no longer maintain a homogeneous, flowable cause. Instead, it may begin to show phase separation, the formation of agglomerates, or loss of cohesion, resulting in lower measured torque despite the higher particle content. The reduced torque suggests that the internal structure supporting viscous resistance breaks down. Instead of a plastic or pseudoplastic flow, the material may shift toward granular flow, where particles slide over each other, leading to decreased mechanical resistance. Furthermore, in overloaded systems, excess particles may begin to act as a solid lubricant, reducing overall shear resistance. This creates an artificial drop in torque, not due to improved flow, but due to poor wetting and inefficient mixing.

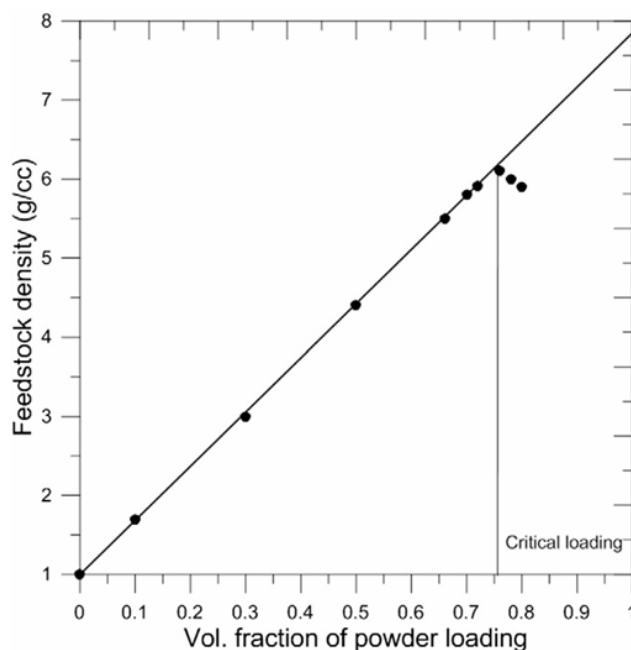


Figure 18 Density analysis of the critical solid loading for (6/20) μm feedstock.[18]

To ensure reliable mixing behaviour and maintain feedstock uniformity, 58 vol.% was selected as the optimal solid loading, offering a high powder content while remaining within the range of stable and homogeneous processing.

Analysing the torque measurements for the feedstocks at their optimal solid loading conditions, Figure 19 reveals distinct differences influenced by both the type of powder and the binder system used. Specifically, CIP OS powder exhibits lower torque values (AW binder: 6.2 N·m, PE binder: 7.7 N·m) compared to CIP HQ powder (AW binder: 9.2 N·m, PE binder: 10.6 N·m). Based on the literature, it can be discussed that this disparity arises from several powder characteristics. The CIP OS powder is surface-silicated to enhance flowability, thereby facilitating efficient feedstock compounding and enabling high solid loadings. Finer particles exhibit larger specific surface areas and higher inter-particle friction, which enhances the tendency to form agglomerates. This increased friction and agglomeration typically lead to higher mixing torque values and elevated feedstock viscosity. Particle size distribution (PSD) also plays a crucial role; a broader PSD facilitates more efficient particle packing, often resulting in lower feedstock viscosity, whereas a narrow PSD generally leads to poorer packing efficiency and higher viscosity. Powder morphology further influences flow behaviour and packing characteristics. Spherical powders, commonly produced by gas atomization, are generally favoured due to their superior packing density and improved flow during injection moulding compared to irregularly shaped powders produced by water atomization. However, work by Hausnerova

et al. [17] suggest that for fine powders, irregular morphologies may actually offer advantages in terms of critical solid loading and rheological performance.[77; 78; 17; 65].

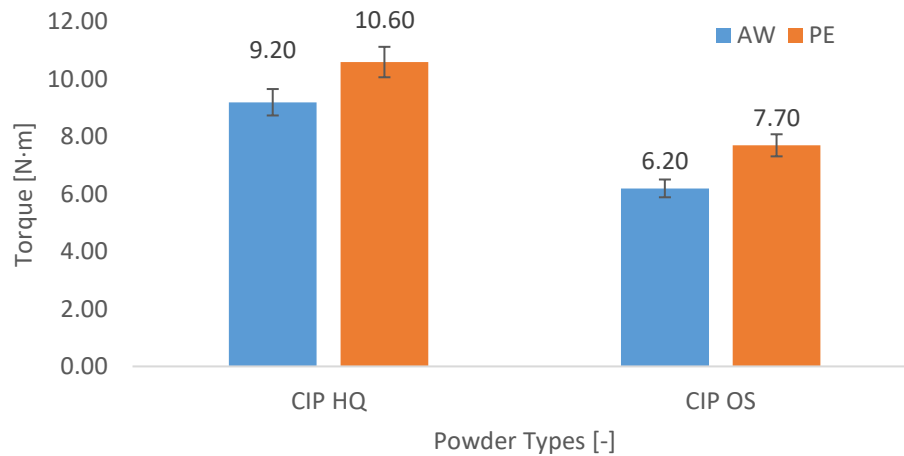


Figure 19 Torque of the feedstocks based on solid loadings

Regarding the influence of binder systems, the AW binder consistently demonstrates lower torque values compared to the PE binder for both powder types. Specifically, AW-based feedstocks yield lower torque despite their marginally lower optimal solid loading (58%) compared to PE-based feedstocks (59%). Quantitatively, for the CIP HQ powder, the torque of the AW-based feedstock is approximately 14.1% lower than that of the PE-based feedstock. Similarly, for the CIP OS powder, the AW-based feedstock exhibits a torque approximately 21.6% lower than the corresponding PE-based feedstock. This consistent reduction in torque values indicates that the AW binder system provides enhanced flowability, making it superior to the PE-based system within this composition range, even at a slightly reduced solid loading.

Capillary rheometer was employed to investigate the shear-dependent viscosity behaviour of feedstocks formulated from two types of carbonyl iron powders and two binder systems. The rheological profiles indicate typical pseudoplastic behaviour across all compositions; however, substantial variations were observed depending on powder morphology and binder formulation.

The flow curves presented in Figure 20 and Figure 21 illustrate the effects of binder system and powder morphology, respectively, and are supporting the discussion throughout this section.

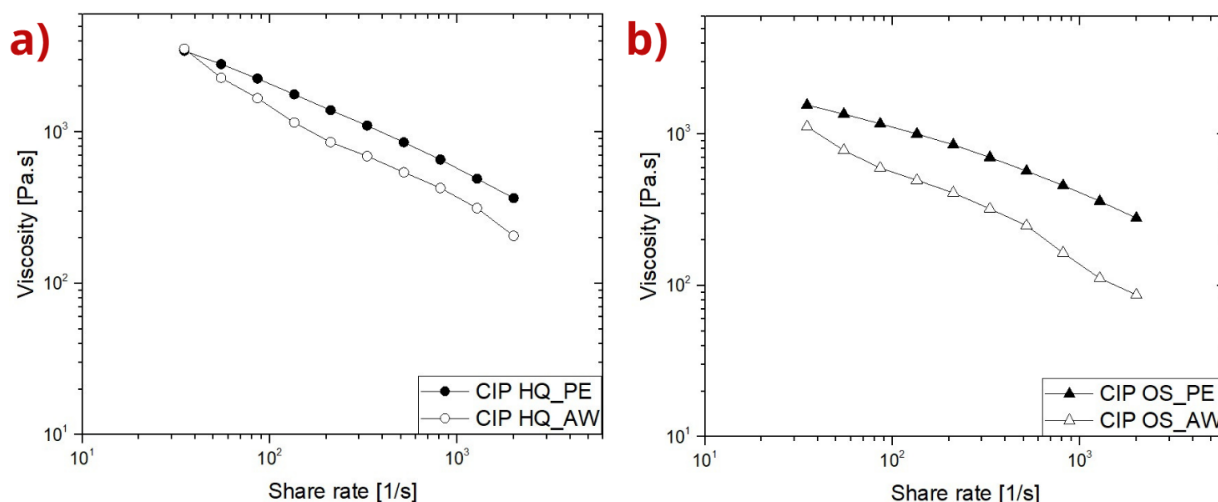


Figure 20 Viscosity as a function of shear rate for CIP OS (a) and CIP HQ (b) feedstocks: influence of binder

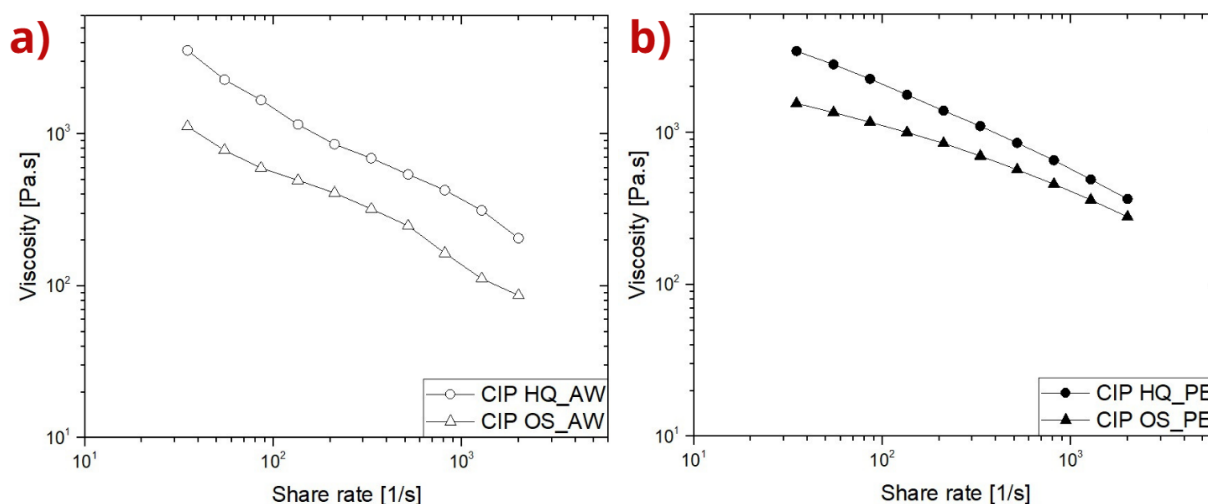


Figure 21 Viscosity as a function of shear rate for AW-based (a) and PE-based (b) feedstocks: influence of powder

Across all measured shear rates, feedstocks based on CIP HQ consistently exhibited higher viscosity than those formulated with CIP OS. This behaviour is attributed to the finer particle size and higher specific surface area of CIP HQ, which enhances interparticle contact and friction, leading to increased flow resistance and greater binder demand. In contrast, CIP OS, with its coarser morphology, exhibited lower viscosity and improved flowability. Additionally, the silica coating on CIP OS may further improve flowability and powder–binder interactions, contributing to easier flow during processing. These findings are consistent with literature reports that finer powders require more binder to achieve comparable wetting, thereby increasing viscosity.[5; 15; 14; 79; 17; 78; 13; 65]

Binder chemistry played a significant role in the overall rheological behaviour of the feedstocks. AW-based feedstocks demonstrated lower viscosity compared to their PE-based counterparts. This is attributed to the presence of low molecular weight binder constituents in the AW formulation, such as paraffin waxes, polyethylene glycol, and stearic acid. These components act as primary plasticisers and surface-active agents, which effectively minimise friction between powder particles during flow. Due to their lower intrinsic viscosities and earlier melting behaviour, they enhance wetting and lubrication at particle interfaces, significantly reducing the viscosity of the feedstock.[80; 79; 32; 22; 24] In contrast, the PE binder system, composed of higher molecular weight polyolefins, exhibits greater chain entanglement and a higher melting point, resulting in higher overall viscosity and lower flowability. Furthermore, the deliberate inclusion of ethylene-vinyl acetate as a thickening agent contributes to the increased viscosity of the PE-based feedstock. While components like paraffin wax within the PE formulation help reduce viscosity, their effect is moderated by the structural contribution of PE and EVA. The presence of EVA enhances dispersion homogeneity and suppresses powder-binder separation, contributing to improved stability and green strength. Thus, although PE-based systems are more viscous, they offer better rheological consistency and part integrity during and after moulding.[32; 24; 21; 25]

In the low shear region, feedstocks with CIP HQ exhibited similar initial viscosities for both AW and PE binders, suggesting that both binders are initially effective in mobilizing the fine particle network. For CIP OS, the AW-based feedstock displayed slightly lower initial viscosity, indicating superior flow initiation, likely due to the rapid melting and spreading of the AW binder.

At intermediate shear rates, distinct differences in viscosity decline were noted. The PE-based CIP HQ feedstock exhibited a stable, steady pseudoplastic profile, while the AW-based counterpart showed a slight flattening, possibly which could represent a transition zone where a particular mode of structural breakdown or alignment is saturated, or a new mechanism of flow is initiating, alternatively increased viscosity of waxes way beyond a melting point are not able to cover all of the area of particles and thus increasing particle-particle interactions. This intermediate region precedes the re-establishment of dominant pseudoplastic mechanisms at higher shear rates. Such behaviour might also reflect the Payne effect, where a decrease in storage modulus with increasing strain indicates progressive breakdown of particle-particle interactions under shear, especially intensified by higher filler concentration. A similar trend was observed with CIP OS, where the AW binder's viscosity

reduction decelerated temporarily. These differences suggest that while the AW binder provides excellent low-viscosity flow, it may be more prone to localized instability or poor dispersion at mid-range shear.[79]

All feedstocks continued to exhibit pseudoplastic behaviour at high shear rates. PE-based systems showed a steady decline in viscosity, maintaining a relatively linear slope. AW-based feedstocks, particularly with CIP HQ, displayed more pronounced pseudoplasticity, indicating greater sensitivity to shear but also potential for flow instability. Among all formulations, CIP OS with AW binder achieved the lowest viscosity, confirming it as the most processable in high-shear applications.

In summary, CIP HQ feedstocks demonstrated the highest overall viscosity, while the combination of CIP OS with AW binder achieved the best low-viscosity performance. The most pseudoplastic system was CIP HQ with AW, whereas CIP HQ with PE showed the most stable and predictable flow behaviour. AW binders are advantageous for low-pressure, high-flow applications, particularly with CIP OS. PE binders, on the other hand, provide superior flow stability and are better suited for fine powders such as CIP HQ.

6.3 Structure of feedstock

The structural evolution of the feedstock during processing can be effectively visualized using scanning electron microscopy (SEM), which provides high-resolution insight into morphological changes at each critical stage. The following micrographs illustrate the feedstock structure after mixing, after injection molding, after solvent debinding, and after sintering. This comparative overview supports the evaluation of powder dispersion, defect formation, binder removal efficiency, and densification behaviour.

Figure 22 presents SEM micrographs of the feedstocks after mixing, with emphasis on evaluating homogeneity, and powder dispersion within binder. All samples exhibit good overall homogeneity, with powder particles uniformly distributed and adequately coated by the binder phase. Sample a) shows a well-mixed structure with no visible binder pooling; b) displays a similar morphology, though a slightly thicker binder layer surrounds the particles. In c), the binder coverage is particularly uniform, while d) shows slightly increased interparticle distances, though homogeneity remains satisfactory. No significant agglomerates are present in any sample; only minor particle clustering is observed in c) and d), likely attributable to the satellite morphology typical of CIP OS powders rather than inadequate dispersion. The powder–binder interface appears well-

defined across all samples, indicating effective wetting and adhesion. The original particle morphology is preserved in all cases, with no evidence of deformation or mechanical damage from the mixing process. In backscattered electron mode, the binder appears as a greyish-black phase surrounding the metallic powder, while darker black regions observed sporadically may correspond to voids or entrapped air introduced during the mixing process.

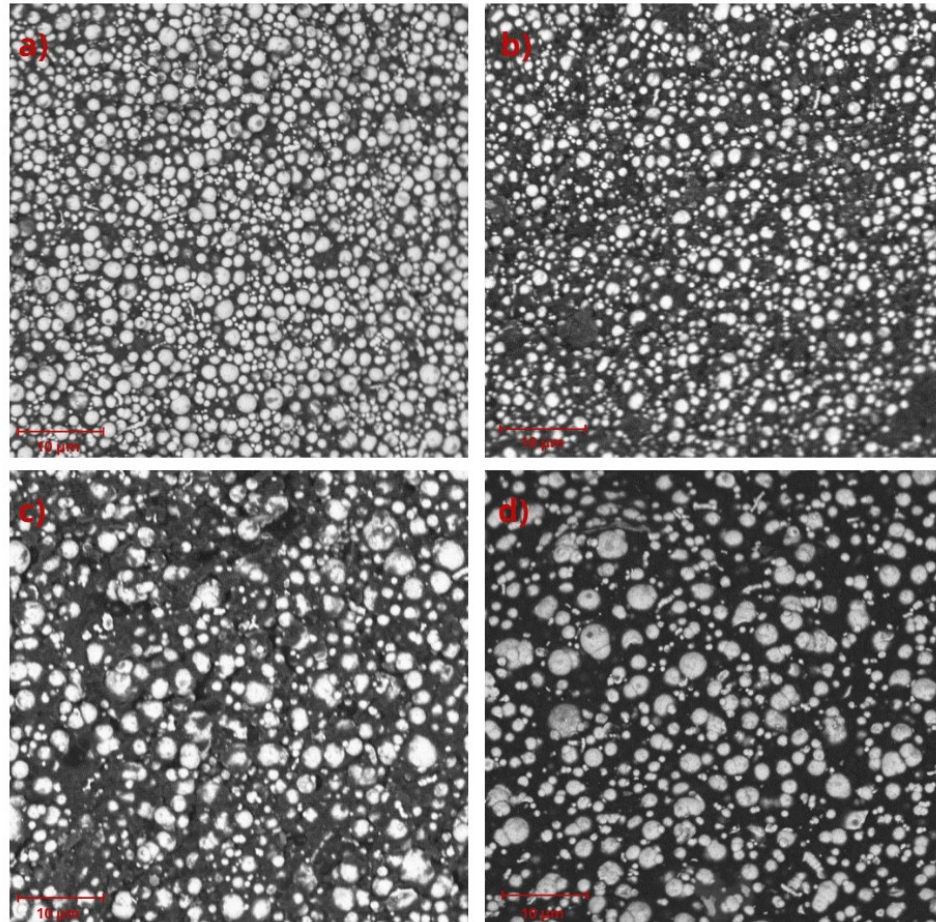


Figure 22 Microstructure of feedstocks after mixing observed by SEM (BSD Full mode, 5 kV, 5000×): a) CIP HQ + AW (58 vol.%), b) CIP HQ + PE (59 vol.%), c) CIP OS + AW (58 vol.%), d) CIP OS + PE (59 vol.%).

The finer particle sizes of CIP HQ enables reliable extrusion through standard nozzle geometries and ensures good densification, therefore the following processability tests were performed using CIP HQ with AW binder. The AW binder, while less stable than PE, offers lower viscosity, which is beneficial for both extrusion and injection molding. Additionally, AW is more environmentally friendly and easier to debind. Figure 23 presents the SEM microstructure of the CIP HQ AW feedstock after injection molding. The image reveals a highly homogeneous microstructure, confirming that the uniform powder–binder

distribution achieved during mixing was successfully preserved during forming. The powder particles are densely packed and exhibit no signs of segregation; no binder-rich or powder-rich zones are evident. The carbonyl iron particles appear well coated by the binder phase, with clear particle–binder interfaces and no evidence of phase separation or inhomogeneity. Furthermore, no visible pores or voids are detected, indicating that the molding process was free of significant air entrapment. The microstructure is compact, without large binder pools, and exhibits excellent uniformity

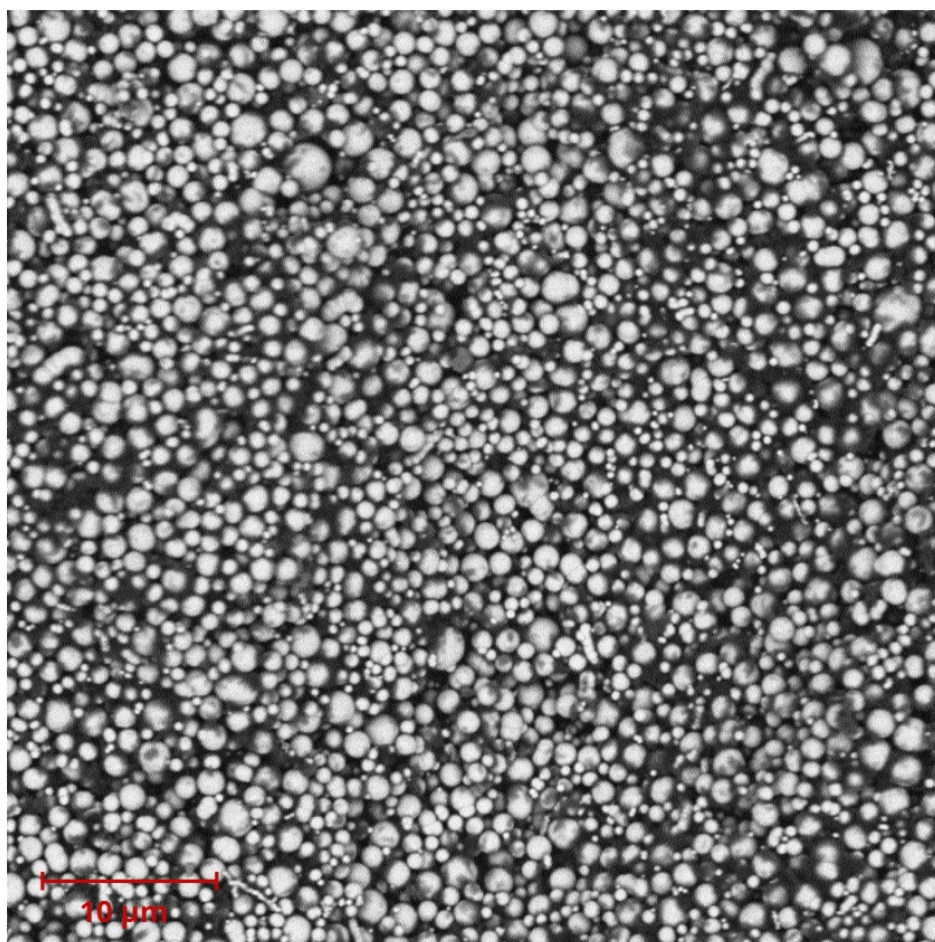


Figure 23 Microstructure of the CIP HQ AW feedstock (58 vol.%) after injection molding, observed with SEM (BSE Full mode, 5 kV, 5000×).

Figure 24 shows the microstructure of the CIP HQ AW feedstock after solvent debinding, where powder particles remain in close contact and are visibly held together by the residual backbone binder, while darker regions indicate the presence of pores formed by the removal of the soluble binder component. These pores appear well-distributed and begin to form interconnected pathways, which are essential for facilitating the subsequent thermal debinding and sintering stages. In TOPO B mode (Figure 24b), the topographical contrast

highlights slight surface depressions in pore-rich regions, further confirming the presence of an emerging pore network. The absence of major defects, such as cracking or delamination, suggests that the solvent debinding process was uniform and did not compromise the structural integrity of the green part. However, minor surface unevenness, visible as local shading or “shadowing,” indicates topographical variation, likely associated with the onset of internal porosity development.

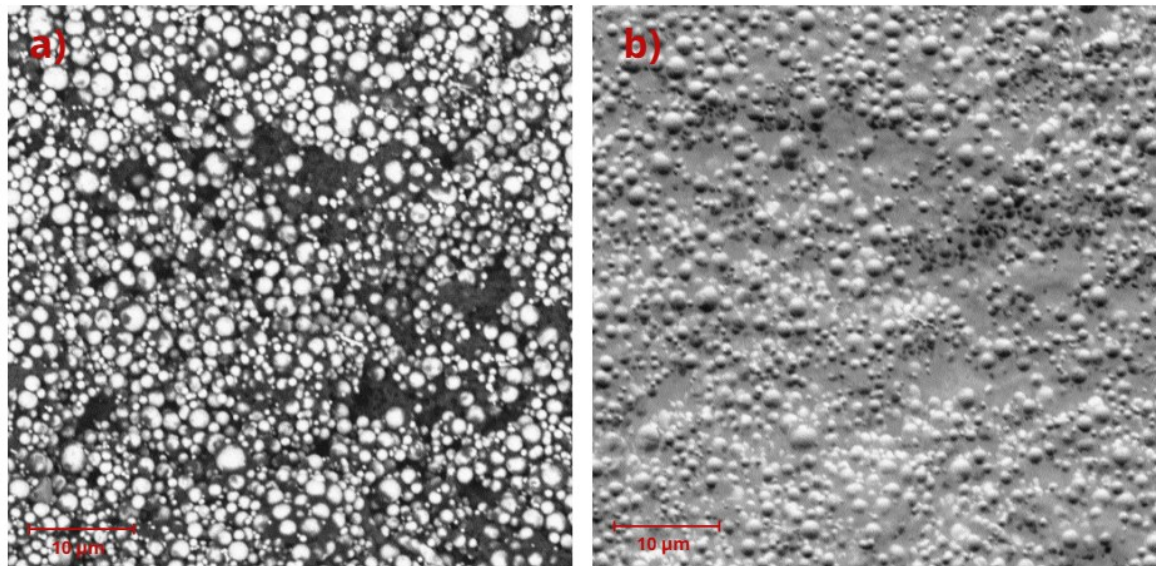


Figure 24 Microstructure of the CIP HQ AW feedstock (58 vol.%) after solvent debinding, observed by SEM at 5 kV and 5000 $\times$ magnification: a) BSD Full mode; b) TOPO B mode.

Figure 25 presents SEM images of the CIP HQ AW feedstock after sintering. The microstructure reveals well-developed grains with clearly distinguishable grain boundaries, reaching sizes up to approximately 5 μm . Only small residual porosity is observed, indicating that densification was largely successful. However, a few individual round particles appear unsintered and remain embedded in the material. These may be attributed to an insufficient sintering duration or suboptimal thermal profile, leading to incomplete diffusion. The topographical image in Figure 25b shows a moderately rough surface, typical of sintered metallic materials, but no signs of severe surface defects or delamination. Overall, the microstructure confirms a high degree of densification with localized areas of incomplete sintering, offering insight into potential optimization areas for the sintering protocol.

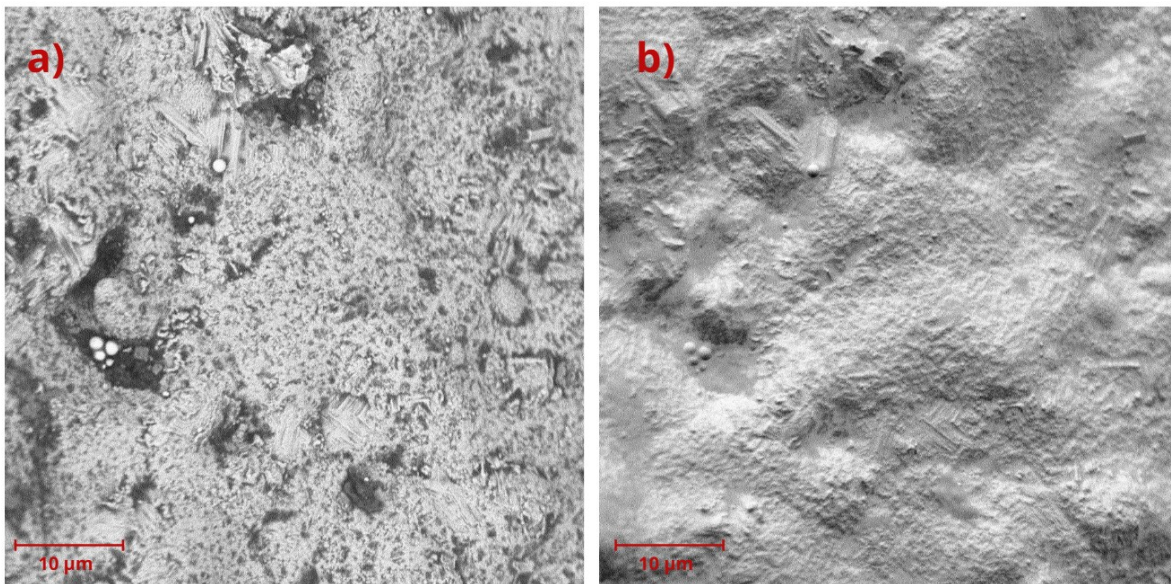


Figure 25 Microstructure of the injecting molded CIP HQ AW feedstock (58 vol.%) after sintering, observed by SEM at 5 kV and 4600 $\times$ magnification: a) BSE Full mode; b) TOPO B mode.

Figure 26 shows the microstructure of the sintered 3D printed CIP HQ AW feedstock. The micrograph reveals a partially developed microstructure, with some grains and grain boundaries becoming distinguishable. Indications of residual porosity are present, although the extent and distribution appear localized. Additionally, surface features suggest possible defects such as fracture lines or delamination, likely originating from processing stresses or suboptimal layer bonding typical in additive manufacturing.

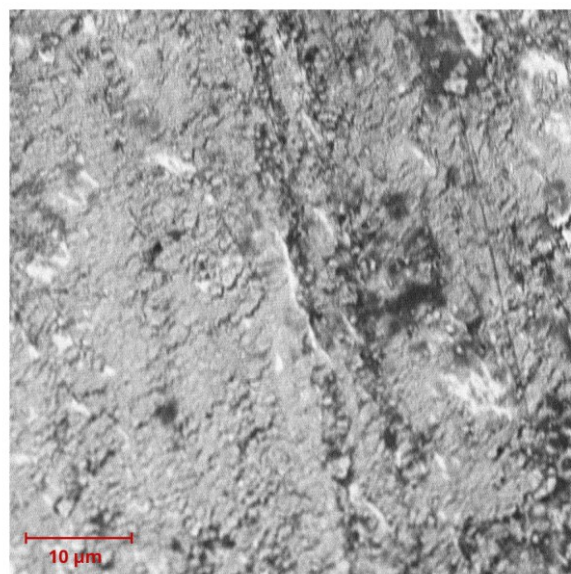


Figure 26 Microstructure of 3D printed CIP HQ AW feedstock (58 vol.%) after sintering, observed by SEM (BSE Full mode, 5 kV, 4600 $\times$).

Figure 27 presents the microstructure of the sintered injected feedstock, the microstructure reveals well-defined grains with distinct boundaries and sizes reaching up to approximately 10 μm . No residual porosity is observed, indicating effective densification. The image shows a uniform, coherent metallic structure, with the previously noted defects—such as unsintered particles observed in earlier sintering trials—no longer present. In Figure 27b) (TOPO B mode), the surface exhibits a spiky morphology due to the reliefs created by protruding grains. The structure appears homogeneous, with no signs of segregation or delamination. These observations confirm that the modified sintering profile improved microstructural development and eliminated the defects associated with insufficient thermal processing.

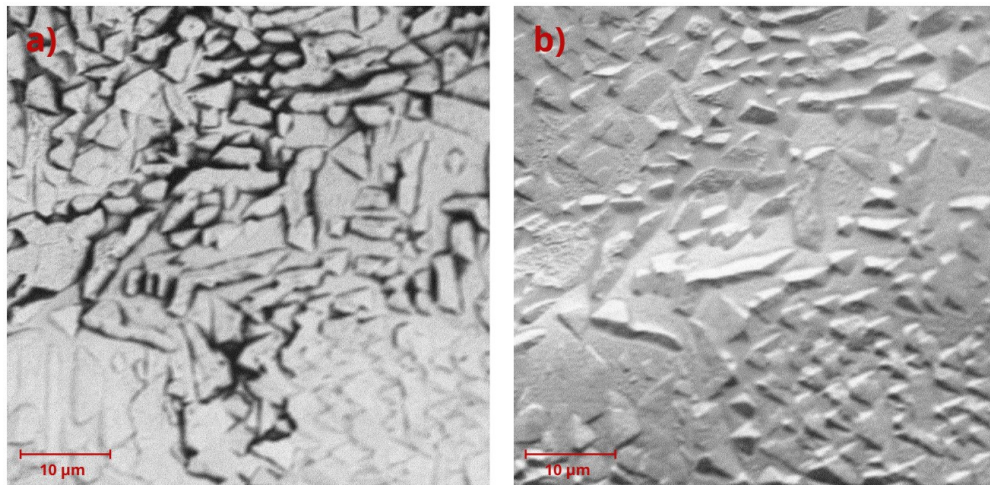


Figure 27 Microstructure of the injected CIP HQ AW feedstock (58 vol.%) after modified sintering profile, observed by SEM at 5 kV and 4600 $\times$ magnification: a) BSE Full mode, b) TOPO B mode.

SEM observations confirmed that all feedstocks were well-mixed, showing uniform powder dispersion and good binder coverage without significant voids or agglomerates. Injection molding preserved this homogeneity, producing green parts with densely packed particles and no segregation or defects. Solvent debinding successfully created a uniform porous network while maintaining structural integrity. The initial sintered sample from injection molding displayed unsintered particles, attributed to a short sintering profile. After adjusting the thermal cycle to the standard time, the final injection-sintered structure showed complete densification, visible grain boundaries, and no residual porosity or defects. In comparison, the sintered part produced by additive manufacturing exhibited surface roughness, possible delamination.

CONCLUSION

The formulation, processing, and characterization of carbonyl iron-based feedstocks for hybrid applications encompassing powder injection molding (PIM) and material extrusion additive manufacturing (MatEx) were comprehensively investigated. The study focused on two grades of carbonyl iron powder—CIP HQ and CIP OS—processed with polyethylene (PE)-based and acrawax (AW)-based binder systems. The results provide an in-depth understanding of powder morphology, sintering behaviour, rheological properties, and microstructural evolution throughout the processing cycle.

Scanning electron microscopy (SEM) confirmed that both CIP HQ and CIP OS powders exhibit predominantly spherical morphology, which is beneficial for flowability and packing efficiency. CIP HQ demonstrated a finer particle size distribution with minimal surface defects, while CIP OS presented coarser and more heterogeneous particles, including occasional satellite and spheroidal to ligamental structures. These morphological differences significantly influenced subsequent sintering and rheological behaviours. The fine size and high surface area of CIP HQ are advantageous for densification but pose challenges for binder wetting and removal.

Sintering analysis using high-temperature microscopy revealed that both powders undergo a thermally driven densification process governed primarily by grain boundary diffusion. CIP HQ exhibited an earlier onset of sintering and higher shrinkage rates, attributable to its high surface energy and finer particle size. Conversely, CIP OS required higher thermal input to initiate densification and showed a slower but more stable sintering profile. These findings validate that the sintering behaviour is predictable and diffusion-controlled, supporting the suitability of both powders for sinter-based processing.

Feedstock mixing experiments identified optimal solid loadings of approximately 59 vol.% for PE-based and 58 vol.% for AW-based systems using CIP HQ and CIP OS powders. Torque measurements indicated that AW-based feedstocks exhibit lower mixing resistance due to enhanced binder lubrication. CIP HQ consistently required higher torque due to its fine particle size and greater surface area, increasing binder demand. CIP OS feedstocks showed lower torque responses, suggesting easier processing and reduced binder viscosity requirements.

Capillary rheometry confirmed pseudoplastic flow behaviour for all feedstocks. Formulations containing CIP HQ exhibited higher viscosities than those with CIP OS, due

to higher specific area and thus greater interparticle friction in finer powders. AW-based binders, formulated with low molecular weight components such as PEG and stearic acid, demonstrated significantly reduced viscosity, offering superior flowability. PE-based binders, although more viscous, provided enhanced rheological stability. CIP HQ with AW binder remains the most suitable for hybrid processing, as its fine particles support extrusion through standard 3D printing nozzles, and the AW binder offers improved environmental compatibility and more efficient debinding.

SEM evaluation throughout the hybrid process—after mixing, injection molding/material extrusion, debinding, and sintering—confirmed that feedstocks were well-dispersed and morphologically stable. Injection molding preserved powder–binder homogeneity, while solvent debinding resulted in a uniform and interconnected porous network essential for effective thermal debinding and densification. Two distinct sintering profiles were employed to evaluate densification behaviour: a shortened profile and a standard profile with extended holding times. SEM analysis of samples sintered using the shortened profile revealed incomplete densification, with individual, unsintered particles still visible in the microstructure. These defects were attributed to insufficient thermal exposure. Consequently, a second sintering cycle employing the standard profile was conducted, which resulted in fully sintered structures with well-developed grains, no residual porosity, and no observable defects. In contrast, sintered parts produced via extrusion-based AM exhibited surface roughness, localized porosity, and signs of delamination.

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LIST OF ABBREVIATIONS

PIM	Powder Injection Molding
MatEx	Material Extrusion
CIP	Carbonyl Iron Powder
CIP HQ	Carbonyl Iron Powder – High Quality
CIP OS	Carbonyl Iron Powder – Optimized Silicated
AW	Acrawax (Ethylene bis stearamide)
PE	Polyethylene
LDPE	Low-Density Polyethylene
EVA	Ethylene Vinyl Acetate
PEG	Polyethylene Glycol
PW	Paraffin Wax
SA	Stearic Acid
SEM	Scanning Electron Microscopy
EDX	Energy-Dispersive X-ray Spectroscopy
TEM	Transmission Electron Microscopy
CT	Computed Tomography
FTIR	Fourier Transform Infrared Spectroscopy
TGA	Thermogravimetric Analysis
DSC	Differential Scanning Calorimetry
HTM	High-Temperature Microscopy
CSL	Critical Solid Loading
Sw	Slope of the Log-Normal Distribution
FFF	Fused Filament Fabrication
μm	Micrometer
wt. %	Weight Percent

vol.%	Volume Percent
°C	Degrees Celsius
g/cm ³	Grams per Cubic Centimeter
cc	Cubic Centimeter
n	Flow Behaviour Index
N·m	Newton meter (Torque)
TOPO B	Topographic B Mode (SEM imaging mode)
BSE	Backscattered Electrons
PSD	Particle Size Distribution
$D_{10}/D_{50}/D_{90}$	Particle Size Distribution Percentiles