CHARACTERIZATION OF POLYMERIC BINDERS FOR METAL INJECTION MOLDING (MIM) PROCESS

A Dissertation
Presented to
The Graduate Faculty of The University of Akron

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

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December, 2007
ABSTRACT

The Metal Injection Molding (MIM) process is an economically attractive method of producing large amounts of small and complex metallic parts. This is achieved by combining the productivity of injection molding with the versatility of sintering of metal particulates. In MIM, the powdered metal is blended with a plastic binder to obtain the feedstock. The binder imparts flowability to the blend at injection molding conditions and strength at ambient conditions. After molding, the binder is removed in a sequence of steps that usually involves solvent-extraction and polymer burn-out. Once the binder is removed, the metal particles are sintered.

In this research several topics of the MIM process were studied to understand how the polymeric binder, similar to the one used in the sponsoring company, works. This was done by examining the compounding and water debinding processes, the rheological and thermal properties, and the microstructure of the binder/metal composite at different processing stages. The factors studied included the metal contents, the composition of the binder and the processing conditions.

The three binders prepared during the course of this research were blends of a polyolefin, polyoxymethylene copolymer (POM) and a water-soluble polymer (WSP). The polyolefin resins included polypropylene (PP), high-density polyethylene (HDPE) and linear low-density polyethylene (LLDPE). The powdered metal in the feedstocks was 316 L stainless steel.
The compounding studies were completed in an internal mixer under different conditions of temperature, rotational speed and feedstock composition. It was found that the metal concentration was the most important factor in determining the torque evolution curves.

The observation of microstructure with Scanning Electron Microscope (SEM) at different stages during compounding revealed that the metal particles neither agglomerate nor touch each other.

The liquid extraction of the water-soluble polymer (WSP) from the molded parts (or water debinding) was investigated using two configurations of flow of water relative to the samples. Both permitted the reduction of the mass transfer resistance outside the parts, revealing information on the diffusion of the WSP inside the part exclusively.

The debinding studies showed that a single effective diffusivity could be used to model the extraction process of the binder from molded parts. This approach is more accurate when the debinding time is above 2 hours.

Steady shear and dynamic experiments were conducted on the binder and feedstocks samples containing LLDPE. The results of both experiments revealed that the feedstocks did not show yield stress even though the highest metal content was 64 % by volume. Therefore, it was concluded that there were only hydrodynamic interactions between the metal particles.

The thermal characterization of binders, polymers and feedstocks included differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The DSC tests were performed after preheating and quenching of the samples. The heating rate was 20 °C/min. The TGA scans were conducted from room temperature to 700 °C at 20 °C/min.
The DSC tests revealed that the melting point of the polymers depressed when blended in the binders and feedstocks. The depression was more intense for POM and the water-soluble polymer than for the polyolefins. Therefore, it was concluded that the melting point depression of POM and the water-soluble polymer was caused by their entrapment in the polyolefin matrix and in between the metal particles.

The TGA scans showed that the feedstocks with higher metal concentration had higher final decomposition temperature, but similar onset temperature. The reason was that the higher the metal concentration the more difficult the diffusion of the products of the decomposition of the binder out of the samples.

The morphological studies revealed that the binders were heterogeneous showing domains of the polar resins, embedded in a continuous phase composed of polyolefin. This distribution of phases was the result of the immiscibility between the polymeric components, and of the higher concentration (>70 vol%) of the polyolefin with respect to the polar components (polyoxymethylene and water-soluble polymer).

The deformation during steady shear testing and compounding of the binder with the metal modified the size of the dispersed domains. The steady shearing increased the size of the dispersed domains by coalescence of the particles. On the other hand, the presence of powdered metal during compounding forced a redistribution of the dispersed phases. Apparently, a thin heterogeneous layer of binder surrounded the metal particles while most of the polyolefin occupied the space between the coated metal particles. The SEM study on samples obtained after water debinding revealed that the water-soluble polymer did not distribute uniformly on the surface of the molded disk of feedstock used for water debinding tests.
DEDICATION

To Jogis, my wife, for her support, love and help during the last years. To my Mom Elvira who taught me how to overcome obstacles, to fight against the circumstances, to be generous and to always keep a positive mind. To my father, who taught me the love of books, of teaching, of education and of being handy. To my brothers Jorge, Pablo and Rafael who helped me pursue my dream of being an Instructor in my home country. To Jeronimo who teaches me every day the wonders of being a full time Mr. Mom. To Josephine who will be another smiling start in my sky. To my “suegritos” who have been there for my family when we needed it the most. Lastly, I want to dedicate this project to my friends in Akron: Mayela, Antonio, Guillermo, Jairo and their families for becoming our second family in the US.
ACKNOWLEDGMENT

The author wishes to acknowledge the support and guidance of his advisor Dr. Arkady Leonov, the help received from Dr. Johanna Baena and the support provided by Dr. Majid Daneshvar who not only provided a topic for this dissertation but also friendship, materials and a salary through an Industrial Assistantship.
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CHAPTER I
INTRODUCTION

The metal injection molding process is a manufacturing process intended to produce large amounts of small and complex metal parts\textsuperscript{1-5}. It combines the versatility and high productivity of the (plastics) injection molding\textsuperscript{1,2} with the powder metallurgy technique of sintering. Then, since the sintering of a compacted powder is alike for a part obtained by injection or press molding, the key points in MIM turned out to be how to make the metal flow into the mold and how to retain the shape of the molded part until it begins the sintering. This problem is commonly solved by dispersing the powdered metal into a binder to form a paste that flows at high temperature and becomes solid at room temperature. Consequently, the molded part retains its shape after injection molding and may be handled and processed safely.

The binders used in MIM are usually compounds of several materials. However, the binders may be broadly classified in two groups, those based on wax/polymer or, on polymer/polymer compounds. According to the MIM literature\textsuperscript{1,2}, the wax/polymer binders are composed of a high polymer, a wax (or waxes) and additives. The purpose of the polymer is to impart rigidity to the part when cold, while the wax reduces the viscosity of the binder and the additives reduce particle separation and segregation.

The wax/polymer binders are eliminated from the molded part in the debinding step by either, solvent extraction followed by thermal treatment, or by thermal debinding alone. It has been well established however; that when one or various binder
components are leached out and the others get burnt the part preserves its shape and dimension well until the sintering. The reason is that the porosity created during leaching open paths allowing the gasses resulting from the decomposition of the other components to escape out of the part during burnt out. In this way, the generation of internal stresses is reduced avoiding the deformation of the parts.

The wax/polymer binders are difficult to remove from the parts because of two reasons. First, if only thermal debinding is used, very slow heating rates are required in order to avoid the buildup of internal stresses and hence part deformation. Second, if both solvent debinding and thermal debinding are used, then the leaching should be done using hydrocarbon solvents. This poses an obvious safety and environmental hazard concern. These reasons motivated the development of water debindable binders like the one used in this research.

The binders based solely on polymers are not very common in industry and have received little attention by researches everywhere. The reason is that the MIM process originated as an extension of the older Ceramic Injection Molding (CIM) process in which water soluble binders were infrequent. In addition, in the MIM industry there is not much interest on the development of new binders because of the lack of knowledge of why and how a particular binder system works. This fact motivated this research project.

This research is intended to understand why and how the binder currently used at the Sponsoring Company (Precision Made Products LLC) works. To accomplish this, the polymeric binders and feedstocks were studied in a variety of aspects including, compounding, water debinding, rheological behavior, thermal properties and microstructure. To the best of the Sponsoring Company and the proponent’s knowledge
this is the first work in which the polymeric binders are characterized in such a wide range of facets. The resins used were based on, polypropylene (PP), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), polyoxymethylene copolymer (POM) and water-soluble polymer (WSP). The metal used to produce the metal/binder compound (or feedstock) was powdered 316 L stainless steel.

The compounding studies were performed in an internal mixer to evaluate the effect of temperature, rotational speed, binder composition and metal contents on the torque evolution curves. Several binders and a variety of feedstocks were produced to proceed with the characterization and debinding studies. The compounding permitted the production of feedstocks of up to 64 vol% of solids.

The rheological characterization included steady shear, frequency sweep and dynamic time sweep experiments. The focal point of the rheological studies was to determine the effect of the metal contents on the flow properties of the feedstocks. To accomplish this, the series of feedstocks based on LLDPE were used in these studies. In addition, the effect of the concentration of binder components on the rheological properties was also evaluated.

The water debinding was studied using two configurations of flow of water relative to the molded parts. In one of them, the parts were rotated while submerged in water. In the other configuration, a water jet impacted the parts in such a way that the samples could be positioned in two orientations with respect to the water jet. The experimental results were input in a diffusion model to obtain the effective diffusivity of the water-soluble polymer inside the parts.

The thermal studies included differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC results revealed the effect of the metal and
different binder compositions on the melting points of the binder constituents. The results indicated that the metal and binder composition affected the crystallization of the polymers. On the other hand, TGA tests gave information on the effect of the metal on the degradation curve of the neat polymers and binders.

Scanning Electron Microscopy (SEM) was used to study the microstructure of binders and feedstocks. The binder and the feedstocks based on LLDPE with different metal concentrations were studied with SEM. The observations revealed that the heterogeneous structure of the binder changed upon addition of metal particles. The micrographs of the feedstocks also showed that a binder layer surrounded the metal particles. This layer was multiphase as found from the observation of fracture surfaces and from the micrographs of feedstocks after water debinding.

In addition, it was found that the water-soluble polymer did not distribute uniformly through the surface of the injected samples.
The Metal Injection Molding Process (MIM) is an economical method to produce small and complex metallic parts\textsuperscript{1-5}. In MIM process, the powdered metal is mixed with a blend of diverse materials called “binder” to form the “feedstock.” The role of the binder is to hold the metal particles together while molding the parts. In addition, it provides flowability at injection molding conditions and strength at room conditions. After shaping the parts, the binder must be removed in the debinding step by either one or the sequential combination of several procedures including solvent extraction, thermal degradation, or catalytic cracking. To accomplish the debinding while keeping shape stability, binders are formulated as multicomponent systems. Therefore, while one component is removed the other(s) hold the metal particles in place. Once the binder is completely removed, the particles are weld together by sintering to obtain the final product. The density attained after sintering is close to the theoretical density of the metal.

Many metals have been processed in metal injection molding process\textsuperscript{2}. Some typical materials are stainless steel, iron, iron-nickel, superalloys (e.g. Inconel), titanium, titanium alloys, and copper. The more important characteristics of the powdered metal are\textsuperscript{2} particle size, particle size distribution, and particle shape. These parameters, especially particle shape, depend on the method of producing the powder. Processes
including gas atomization, water atomization, electrochemical, and plasma are common nowadays to produce pulverized metals. The relation between the process to produce the powder and the particle shape is very well defined, for instance, gas atomization yields round particles while water atomization gives irregular particles, on the other hand, electrochemical methods gives spongy particles of irregular contour. The reason for a distinct shape is the dynamic details of powder formation from the molten or dissolved metal or alloy. The preferred powder shape in MIM is spherical since more packing is possible than with irregular shaped particles. In addition, powders with wide size-distributions are favored because of the higher packing possible as compared to monosized powders. Thus, the better powders are round and wide size-distributed.

As mentioned before, the feedstock is the material that is molded in MIM. Therefore, the properties of the feedstock determine largely the success of the whole MIM process. If the feedstock is homogeneous and stable, then the parts will have good qualities. Most properties of the feedstock will depend, then, on the compounding of the binder with the metal. The mixing equipment to compound the binder and the metal should provide intense shearing. Planetary mixers, z-blade mixers, Banbury mixers, and twin-screw extruders have been used for feedstock compounding. The major objective of the mixing process is to ensure the whole surface of each particle is coated with binder. From the experience of compounding of polymers with fillers, it is clear that distributive mixing should dominate when the metallic powder does not agglomerate, while dispersive mixing is necessary when processing agglomerating powders. However, the mixing mechanism cannot only be elucidated based on blending powder and binder alone. Sometimes, the binder components are mixed with each other as well as with the
powder during the same operation. As a result, it is not easy to decide what mechanism should dominate feedstock production, or which mixer to use.

It is important to highlight that the role of the binder is to give fluidity to the feedstock. Therefore, the binder must be seen as a temporary vehicle for shaping the feedstock and, once the shape is attained, the binder is removed making permanent the shape of the metal part. The final consolidation of the metal particles is attained by sintering, process in which the binder plays no role.

2.1. Binders for Metal Injection Molding

A binder is either a neat or a blend of materials that is solid at ambient temperature and viscous at feedstock processing temperature. The binder purposes are to hold the metal particles together, and to give fluidity to the feedstock. When these functions are satisfied, the feedstock will show no problems during shaping or during mixing and debinding.

Binders for MIM can be categorized according to the major components in two groups: wax-based binders modified with polymers (or wax/polymer) and polymer-based (or polymer/polymer) binders. The wax-based binders modified with polymers are composed of one or more waxes of different origin, and one or more polymers. In some instances, oils are added; these binders will be considered in the group of wax/polymer binders. The second set of binders, polymer-based binders, consists of blends of two or more polymers. The polymeric binder systems have several advantages over wax/polymer binders including improved flow properties, possibility of sequential debinding and better shape retention during debinding.

Apart from the major components, contemporary MIM binders usually contain additives\textsuperscript{10}, which improve flow properties of the feedstock, and increase the interaction
between the metal and the binder. According to Liang et al\textsuperscript{10}, the MIM additives include dispersants, stabilizers, plasticizers, and inter-molecular lubricants. Dispersants increment the wetability of the powder reducing the surface energy. Stabilizers, prevent particle agglomeration mostly by forming an adsorbed layer on the surface of the particles producing steric stabilization. Plasticizers and lubricants, on the other hand do not act on the solid-binder interface but on the binder itself. Plasticizers increase the flow behavior while intermolecular lubricants decrease the interaction between stabilizer molecules and the binder molecules. The great variety of additives makes binders for each application rather unique.

The composition of binder and its possible interaction with the metal determines the debinding procedure. Three types of debinding are commonplace in MIM industry: thermal debinding, solvent debinding, and catalytic debinding. The first is the most frequent in MIM processing. In thermal debinding, a part containing binder is heated at a given rate in a special oven under controlled atmosphere. The binder decomposes by thermal cracking in small molecules that are swept away by the gas leaving the oven. The final part represents a porous body of metallic particles held together by the Van der Waals forces. The second method of debinding uses dissolving the binder by contacting the part with an appropriate solvent. In catalytic debinding, the part is brought into contact with an atmosphere that contains a gaseous catalyst. The catalyst accelerates the cracking of the binder in small molecules that can be carried by inert gas out of the oven. In the MIM industry, the preferred way of debinding is a sequential process consisting of two debinding methods one after another. Obviously, this process is possible when the binder is multicomponent; otherwise, sequential debinding is not practical. The typical sequence is solvent extraction followed by thermal debinding.
An important aspect of the debinding process is the ability of the part to retain its shape during debinding. Part deformation is likely if a binder becomes soft during solvent debinding or thermal debinding. In those situations, the parts will deform because of their own weight. If this happens, the parts become scrap and the starting materials are irrecoverable. Other aspects of debinding process include the use of toxic and dangerous solvents, the generation of toxic vapors and gases, and the need for toxic materials. Solvents and processes that are inert and environmentally friendly are favored.

2.1.1 Wax/polymer binders

The wax/polymer binders are blends of waxes with one or several polymers. These binders impart the feedstocks good flow properties and dimensional stability during debinding. Waxes provide the binder low viscosity because of their low molecular weight, while the part’s dimensional stability being due to the polymers. This is because polymers have broader and higher melting range as compared to waxes.

The wax/polymer binders are thermoplastic binders. They do not contain polymers, which crosslink physically or chemically. These binders can be shaped when heated and become solids when temperature decreases. Other wax/polymer systems contains thermosets that crosslink when injected molded. Thermosets may be advantageous for the reason that a crosslinked polymer transforms from solid to gas during debinding avoiding melting, which is consider the cause of deformation during debinding\(^2\). However, thermosets are impractical because they hamper reusing the feedstock in scrapped parts. This is an important economical reason because of a high cost of metal in feedstock.
Different waxes have been used in wax/polymer binders. They may be natural or synthetic. In some cases when natural waxes are modified to improve their properties, they are called modified waxes. The common classes of waxes are\textsuperscript{11}: paraffin, microcrystalline, synthetic hydrocarbon, and oxidized polyethylene waxes. Paraffin and microcrystalline waxes are derivative form petroleum. Paraffin waxes are blends of linear chain compounds and are marketed in various grades accordingly to their melting point. Microcrystalline waxes are blends of different types of molecules including linear, branched, monoclinic, and polyclinic. This kind of waxes contains crystalline domains of submicron diameter. Microcrystalline waxes have higher melting point than paraffinic and are more flexible. The synthetic hydrocarbon waxes are mixtures of linear hydrocarbons. Examples of these waxes are polyethylene or polypropylene waxes. These waxes are similar to paraffin waxes but with longer chains. They have higher strength and flexibility than paraffin waxes. The last groups of waxes, oxidized polyethylene, have paraffinic structure, high melting points, and low molecular weights of about 10000. They have good properties for MIM feedstocks.

Examples of pure wax binders are very seldom in the literature. Nevertheless, Chung et al\textsuperscript{12} provides such an example with iron powder mixed with polyethylene wax (an oligomer with degree of polymerization of 29). The rheological behavior of the feedstocks was studied using a capillary rheometer. The unsteady flow curve obtained in the measurements indicated the separation of the binder from the powder, which was attributed to the incompatibility of the polyethylene wax and the metal. Therefore, the necessity of polymers was recognized in wax-based binders in following works by this group\textsuperscript{13}. 

\textsuperscript{11} Chung et al. 12. 
\textsuperscript{12} Chung et al. 13.
Several polymers that have been used in wax/polymer binders are polyethylene\textsuperscript{7,8,10,14-30}, (both low\textsuperscript{23} and high density\textsuperscript{24-30}, LDPE and HDPE), poly(ethylene-co-acrylic acid, EAA)\textsuperscript{19,31,32}, ethylene-diene-propylene terpolymer (EPDM)\textsuperscript{23}, polypropylene (PP)\textsuperscript{7, 8, 10, 13, 16, 17, 19, 21, 24-27, 30, 31, 33-36}, polybutenes (PB)\textsuperscript{37}, poly(ethylene-co-vinyl acetate) (EVA)\textsuperscript{13, 17,19,22,24-27,32,38}, polystyrene (PS)\textsuperscript{10,17,22}, poly(methyl methacrylate) (PMMA)\textsuperscript{10, 32}, poly(ethylene glycol)\textsuperscript{7, 8, 10, 15, 17, 28, 40}, poly(vinyl acetate) (PVA)\textsuperscript{15, 28, 33,40}, poly(vinyl butyral) (PVB)\textsuperscript{7, 8, 33}, and polyacetal (POM)\textsuperscript{7, 8, 10, 33,41-43}.

Polymers are added into waxes to improve properties and to facilitate processing. Polymers improve homogeneity, stability and flow properties of the feedstock\textsuperscript{13, 24-27, 29, 30}, mechanical properties of the green part\textsuperscript{7, 23, 26, 27}, reduce debinding time\textsuperscript{13, 22}, and improve dimensional stability during debinding\textsuperscript{7, 23, 26, 27, 30}.

Binders are presented in the patent literature as early as binders based in polymers/wax blends for MIM were presented in the patent literature since 1980. In the patent granted to Adee and MacPherson\textsuperscript{14} in 1980, a binder based on a plasticizer and two binders were patented. The two binders were extractable and they might be polyethylene or polystyrene, polystyrene and camphor or polyethylene and beeswax. The patent claims that the binder reduces the carbon contents to less than 1% in the final part. Other materials contained in the binder are Hunt Wesson oil 101 (a cooking oil) and stearic acid.

In 1985, Wiech Jr. and Raymond\textsuperscript{34} patented an invention regarding to a method to make feedstock. They presented the sizes of the particulate metals used and the mixing procedure. The binders were not discussed in detail; however, in one example the components were PP, carnauba wax and paraffin wax.
Johnson K\textsuperscript{16}, was granted a patent in 1988 that claimed a new method for fabricating parts from particulate material. The binder proposed consisted of at least two components of different melting point, one of high m.p. and the other of low m.p. The first component was to be removed by dissolution, while the second by thermal degradation. The high melting point components were PP and PE, and the low melting point was a blend of peanut oil and paraffin or carnauba wax.

In another patent, granted to Kiyota\textsuperscript{18} in 1989, the starting materials for MIM were the object of the invention. In this patent, several polymers including PP, PE, polystyrene (PS), or a mixture of them was compounded with a wax chosen among any of the following: Bee’s wax, Japanese wax, montant wax, PE wax, microcrystalline wax or paraffin wax and lubricants and plasticizers. The plasticizers included 2-ethylhexylphthalate (DOP), di-ethylphthalate (DEP) and di-n-buthylphthalate (DBP). Among the lubricants, they used fatty acids, fatty acid amides and fatty acid esters.

Nagai et al\textsuperscript{45} were granted a patent in 1990 for the invention of a binder for injection molding (either MIM or ceramic injection molding –CIM-) composed of a condensation polyether of polyoxymethylene and polyoxypropylene (POM) blended with a compound from the group of natural waxes, synthetic waxes, fatty acids and fatty esters. The waxes included carnauba, candelilla, cerasin, montan, paraffin, microcrystalline, and PE or PP wax.

The patent 5030677 was granted to Achikita and Ohtsuka in 1991\textsuperscript{46}. They invented a composition for injection molding of metals. Their binder consisted of LLDPE and paraffin wax with boric acid ester. The metal could be present in 30\% to 70\% by volume. The boric acid ester plays the role of lubricant. The conditions for thermal debinding were also given in the patent.
Miura et al\textsuperscript{19}, patented a process for the production of sinters and the binder used in that process in 1993. The binder consisted of one of the following groups: i) EVA, EEA or a mixture of the two, ii) PP or atactic PP or a mixture of the two, iii) PS or PE or a mixture of the two, and a wax. The wax might be paraffin, carnauba or a mixture of the two. In addition, a plasticizer was added, DBP, DOP were possibilities.

In two patents granted in 2000 to Schofalvi\textsuperscript{47,48}, the object of the invention was a binder system and a method for particulate material. The binder proposed consisted of a blend of polycarbonate, ethylenebisamide wax and a guanidine. In addition, in his latter patent, Schofalvi\textsuperscript{48}, proposed a fourth compound to accelerate the debinding rate. This material was organic peroxide. A list of about 20 possible peroxides was provided.

The effect of polymers on wax-based binder was studied by Rhee et al\textsuperscript{13}. Several polymers were studied, including low molecular weight PP, EVA with 26.5% vinyl acetate (EVA-A), EVA with 9.5% vinyl acetate (EVA-B), HDPE, and a blend of EVA-A and HDPE. Each polymer or blend was presented in the binder in concentration of 20% by weight, the rest being wax. The feedstocks were prepared with modified iron (98wt\% Fe and 2wt\% Ni), and 17-4PH stainless steel. The characterization of the feedstocks included rheological properties, debinding, sintering, and injection molding behavior. Rhee et al concluded that EVA with low VA content was the best polymer based on the great improvement of binder performance in both injection molding and thermal debinding. Additionally, EVA improved feedstock homogeneity, stability, and shape retention during debinding. On the other hand, PP and HDPE showed poor adhesion to the powder, PP being the worst. The miscibility of PP and wax, and of HDPE and wax revealed that HDPE was miscible with the wax, while PP was immiscible.
Cao et al\textsuperscript{24} studied the homogeneity of wax/polymer feedstocks based on paraffin wax, carnauba wax, low molecular weight PP, HDPE, and EVA. They concluded that a homogeneous feedstock shows good injection molding properties, stability, and low dimensional variability. Several other researchers investigated flow properties of wax/polymer based feedstocks using capillary rheometry. Li et al\textsuperscript{25-27}, and Huang et al\textsuperscript{29} studied the rheology of several Fe-2Ni based wax/polymers feedstock with binders contained paraffin wax, EVA, HDPE and PP. Binders containing PW/EVA, PW/HDPE, PW/PP and PW/HDPE/PP were prepared and tested in capillary rheometer. The results indicate that PW/PP binder was useless because of binder separation in the capillary flow. On the other hand, the binder based on PW/HDPE/PP showed the best flow behavior having the lowest shear sensitivity and the lowest activation energy in flow.

Another tested binder studied by Li et al\textsuperscript{22} was based on blend of oil and wax modified with polymers, which improved solvent debinding in chloroethylenes. The solvent extracts oil and wax leaving the PE to be removed by thermal debinding. Thus, the debinding process is improved. The authors found that the oil decreases the green strength but also, the mixing torque and the debinding rate. They also found that presence of EVA was not appropriate because of the swelling of the EVA in oil causing failure of the parts during solvent debinding. The authors concluded that the best polymer to use with oil-wax was polyethylene.

Hens et al\textsuperscript{7} tested several binders based on polymers, including two based solely on polymers. The binders included polypropylene/paraffin wax/stearic acid and palm oil/polyethylene/stearic acid. The metals were Inconel and 17-4PH. The authors studied the mixing, injection molding, solvent debinding, thermal debinding, and sintering. The
debinding was carried out using solvent. The debinding of the wax and the oil in the solvent was fast and shape retention was very good.

The usefulness of polymer modified wax binder was demonstrated in a paper by Zhu et al. These authors tested a multicomponent binder with tungsten-cemented carbide. The binder contained paraffin wax (60 wt% of binder), liquid paraffin wax (5 wt% of binder), HDPE (10 wt% of binder), polypropylene (10 wt% of binder), dioctyl phthalate (DOP) (5 wt% of binder), ethylene-co-polypropylene (5 wt% of binder) and stearic acid (5 wt% of binder). In their research, Zhu et al found that the rheological properties of the binder were highly improved showing homogeneity and stability. The debinding was done in two steps because of the presence of more than one polymer in the binder. The first was liquid extraction using heptane and the second thermal decomposition. The thermal debinding could be adjusted to avoid decarburization of the metallic alloy through atmosphere control in the debinding oven. From their results, Zhu et al concluded that the reason for having excellent rheological properties is the presence of liquid paraffin and DOP; no separation phenomena were observed during molding. Additionally, the binder permitted both solvent and thermal debinding giving gradual debinding and increased shape retention.

Another wax/polymer binder was used by Heaney et al in a study of the effect of powder characteristics on dimensional variability of part. The authors used a binder composed of 50 wt% wax, 40 wt% PP and 10 wt% of a polymeric surfactant. The interesting feature of this binder is the inclusion of a polymeric surfactant that is nonionic, instead of the usual stearic acid. The binder required solvent debinding in heptane followed by thermal debinding.
Although the polymer/wax binders are common in MIM industry, the binder selection is still mostly empirical. In an attempt to address this issue, Liang et al\textsuperscript{10}, studied several systems and presents some ideas on how to select a thermoplastic for binder formulation. The systems reviewed included pure wax-based, wax-polymer, pure polymeric, water-soluble polymeric, and catalytic-debindable polymeric systems. Properties of the polymers such as molecular weight, melting range, and molecular structure were analyzed. Additionally, a list of classes of additives was presented, as mentioned in the introduction to section 2.1. The authors concluded that a binder should have a linear chain polymer with polar or polarizable functional group. Additionally, Liang et al affirmed that the solubility between binder constituents should be considered when preparing a binder, because when components are incompatible additives are required to make them compatible with each other. Furthermore, the authors give some recommendations on the desirable structure of the dispersants, stabilizers, plasticizers, and inter molecular lubricants.

Analysis of papers mentioned in this Section makes clear that polymers are a very important component of binders. Polymers used as modifiers of wax-based binders, improve several properties of feedstocks including feedstock homogeneity and stability, reduce debinding time, improve dimensional stability in thermal debinding, and make possible a sequential debinding i.e. solvent and thermal feedstocks purely based in polymers are possible, the properties are good, and sequential debinding becomes available.

2.1.2. Polymer/polymer binders

Metal injection binders based solely on polymers have been studied by several researchers. Several systems included polyacetal binders with catalytic debinding\textsuperscript{42,49},
polyacetal modified binders with non-catalytic debinding, binders based on polyethylene glycol binders using POM, binders using EVA, block copolymers, methyl cellulose and polyamides.

The polyacetal binder requiring catalytic debinding is very common in PIM industry for both metal injection molding and ceramic injection molding. The binder is manufactured by BASF with the trade name Catamold® and is mostly sold as in feedstocks of various metals. According to Krueger et al., from BASF Corporation, the Catamold® system consists of a blend of polyacetal (POM) and several additives that include copolymer, stabilizer, and dispersant. The role of the additives is diverse. The copolymers reduce the crystalline fraction in the POM reducing the shrinkage while cooling the mold during injection. Thermal stabilizers are used to avoid thermal degradation of the POM during molding due to friction and dissipative heating of the blend. In addition, organic buffers are added to reduce the affect of acid moieties on the metal. However, these moieties are generated during the thermal decomposition of POM even though thermal stabilizers are added. To enhance the dispersion of the powder in the binder, several surfactants are added to the blend. The character of these surfactants is not specified. Each metal requires a balance of additives to work well in the MIM processing. The debinding of the Catamold® binder is catalytic by depolymerization mechanism; the catalyst is gaseous nitric acid.

The main advantage of Catamold® is its rapid debinding that permits continuous processing and the reduction of slumping or dimensional instabilities because of the absent of a liquid phase during debinding. Even though the processing speed is good for certain MIM products, it is not the only criterion for binder selection.
To avoid the handling of nitric acid in both liquid and gaseous state, and to avoid the appearance of flow lines and binder-rich zones, Wang et al\textsuperscript{50} modified the polyacetal based binder by adding a very small amount of a undisclosed agent. The experiments were conducted with both, thermal and catalytic debinding. The authors concluded that the defects disappear during injection, and that the debinding was possible using only the thermal decomposition, which avoids the environmental and personal dangers of handling nitric acid in gaseous state.

The polymeric binders based on water soluble polymer were investigated by Hens et al\textsuperscript{7-9} and proposed in the patents by Herrmann\textsuperscript{15}, Kihara et al\textsuperscript{17} Menke et al\textsuperscript{40} The motivation for developing these binders was the poor behavior of wax/polymer binders, such as low green strength, poor shape retention during debinding, the use of environmentally unsound solvents, and very narrow processing windows. One example of a polymeric binder was given by Hens et al\textsuperscript{7-9}. It was a blend of water soluble polymer, acetal copolymer, and undisclosed component. This binder can be solvent debound in water, ethanol, methanol, or mixtures of these solvents. Once the water-soluble polymer is removed, the other polymers are removed thermally.

Another example of binders based on water-soluble polymer is given by Herrmann\textsuperscript{15} in patent 3330892 granted to him in 1967. The binder consisted of a fluid vehicle, a binder and a deflocculant. The organic vehicle was one of the following components: paradichlorobenzene, chloroacetic acid, naphthalene, benzoic acid, phallic anhydride and camphor. The deflocculants proposed were, surfactants and aliphatic monocarboxylic acids and their salts. The binder was water-soluble polymer, or a non water soluble component, like PE, PS PVA, etc. The debinding was dome by sublimation of the organic vehicle followed by thermal debinding.
The binder proposed by Kihara et al\textsuperscript{17} in the invention patented in 1991 a binder with at least two components, one water-soluble and the other water insoluble was proposed. The purpose was to have water debinding followed by thermal debinding of the insoluble components. The water soluble polymers however, not only included water-soluble polymer but also, hydroxymethylcellose, polyacrylamide, poly(vinyl ether), poly(acrylic acid) and poly(methacrylic acid).

Menke et al\textsuperscript{40}, in patent 5098942 invented a binder based on water soluble polymers, such as poly(ethylene oxide) and other components, such as poly(vinyl acetate). The binder was not intended for water debinding but for thermal debinding exclusively. It seems that the water-soluble polymer is used to lower the viscosity and help during injection molding process.

The use of POM in binders is reported by Hens et al\textsuperscript{9}, Covatch\textsuperscript{3} and in a patent by Ebenhoech et al\textsuperscript{41}. The binder presented by Hens was mentioned before and it contained POM because this material increased the strength of the green part when compared to other polymers. In the paper by Covatch, POM as binder component is just mentioned without giving details. On the other hand, in the patent granted to Ebenhoech et al, the binders are presented in detail. In this patent, POM homo or copolymer was used in binders together with a polymer immiscible with POM, such as polyolefin or aromatic vinyl polymer and a dispersant that could be PEO oligomer, stearic acid, fatty alcohols and block copolymers. The method of debinding proposed was catalytic with vapor of nitric acid.

Other polymers that have used as main polymers in MIM feedstocks, included EVA, block polymers, methyl cellulose and polyamides. The EVA was mentioned in the patents granted to Kihara et al\textsuperscript{17} and Miura et al\textsuperscript{19}, block copolymers were mentioned in
the patent granted to Pett et al\textsuperscript{20}, methyl cellulose in the patent granted to Menke et al\textsuperscript{10} and in the patent granted to Takayama et al\textsuperscript{52}. It is interesting to note that the binder proposed by Takayama et al. was a blend of a water soluble amide or amine and a polyamide resin. Either, the amine or amide was water soluble, while the polyamide resin was removed by thermal degradation.

2.2. Characterization of MIM feedstocks

Several instrumental and processing techniques have been used to characterize binders and feedstocks\textsuperscript{2}. The common instrumental techniques in MIM binder development include capillary rheometry, torque rheometry, differential scanning calorimetry (DSC), microscopy, and thermo gravimetric analysis (TGA). The processing techniques include torque rheometry, injection molding, and solvent debinding. The processing techniques are usually only practical with the feedstock, e.g. injection molding and debinding. Furthermore, in most practical situations the evaluation of a given binder is solely based on the testing of a resulting feedstock. This is because of the great effect of adding a metal on binder properties, and because what is processed in MIM is the feedstock.

In the following Sections, both instrumental techniques and processing will be reviewed.

2.2.1. Capillary and Torque rheometry in MIM

Both torque and capillary rheometry are used in MIM feedstock evaluation. The capillary rheometry is commonplace because of its usefulness in determining feedstock homogeneity, stability, and constitutive properties. Torque rheometry, on the other hand, is useful in determining maximum and optimum solids loading, homogeneity of feedstocks as result of a mixing process, and the amount of energy required for mixing.
The difference between the two rheometric techniques is that torque rheometers record the torque while mixing while the capillary rheometers start with a premixed feedstock.

2.2.1.1. feedstock maximum solids loading (critical loading) and optimum loading by torque rheometry

The maximum solid loading (or critical loading) in MIM feedstocks is the volumetric concentration of solids at which the viscosity reaches an infinite value\(^2\). An alternative definition is based on density: when the density deviates from the additive prediction, the critical loading has been reached. The feedstock loses fluidity at the critical solids loading. From a structural viewpoint, in this condition, the metal particles are touching each other and the binder fills the voids between particles but does not cover the whole surface of the particles.

The solid loading is an important parameter because of its role in part shrinkage, dimensional stability, and final density. Low solids loading causes part dimensional variations during debinding and sintering, as well as product with low density. On the other hand, if the solid concentration is very high, the feedstock will be inhomogeneous and will not flow steadily in the injection-molding machine generating dimensional inconsistencies in molded parts, with each part having different dimensions.

The critical solid loading is an experimental parameter, which is usually determined by either density measurements or torque rheometry\(^2\). In the first method, the density of feedstock is measured with incremental amounts of powder. The volume fraction at which the actual density deviates from the density predicted by the additive rule is considered as the critical solid loading. In the second method, the powder is added incrementally into the mixing chamber of rheometer and the torque is recorded.
When the critical solid loading is reached, a dramatic increase in torque occurs and the torque of mixture becomes erratic \(^2, 7-9, 36, 44\).

An example of the density method to determine critical solid loading is presented in papers by Rei et al\(^{53}\) and Qu et al\(^{23}\). In Rei et al paper, a curve of the density variation is showed. It is apparent that the experimental density fell below the theoretical density at about 64 vol\% solid loading. Similarly, in the paper by Qu et al, the density method is used to determine the critical loading of WC-TiC-Co in a polymer modified wax binder. The critical solid loading was found to be 64 vol\%. A typical experimental and theoretical density curves are presented in Figure 2.1.

In a series of papers by Hens et al\(^{7-9}\), the critical solids loading was determined for several feedstocks of Inconel 624 and Inconel 718 and 17-4PH stainless steel in wax/PP and water-soluble polymer/POM binders. The torque rheometer was a Haake System 90 Rheomix. In their experiments, Hens et al added increasing amounts of powder and waited for torque stabilization between the additions. The torque curves were depicted to show when the critical loading is attained. In Figure 2.2, one of the curves is shown for Inconel 718 in water-soluble polymer/POM binder.

Torque rheometry was also used by Dihoru and coworkers\(^{37}\) to determine the critical solid loading. They used a Rheomix 600p from Haake Polylab Systems at a temperature of 160 °C. The binder and the initial quantity of powder (stainless steel) were mixed until the torque reached a constant value. The powder amounts were added in 20- minute intervals after stabilization of the torque. They considered attaining the critical solid loading when the mixing torque exhibited a steep increase and no longer stabilized.
Figure 2.1 Loading curve of WC-5TiC-10Co powder in polymer-modified wax-based binder\textsuperscript{23}

Figure 2.2 Torque rheometry for feedstock with IN718
The optimum particulate-solid loading is calculated from the critical loading. The optimum particulate-solid loading is the volumetric concentrations of solids that will be used in the actual MIM process. The recommended solids concentration varies from 2 to 5% less than critical\(^2\). The optimum solids loading depend on the actual feedstock, which is being measured. For that reason, finding the optimum should involve experimental work and some criteria for its selection.

The relationship between the two methods to determine the critical solids loading has not been presented in the literature. However, this relation should shed light on the MIM feedstock microstructure since one measuring method is founded on suspension flow while the other is not. Accordingly, it is expected that both methods give different results for the critical solid loading.

2.2.1.2. Rheological determination of homogeneity of MIM feedstocks

A feedstock is considered as homogeneous, if the flow curve in capillary rheometer is smooth. The homogeneity of a feedstock relates to how well the particulate solid is distributed in the binder matrix. Feedstock homogeneity promotes dimensional consistency of injected parts and helps preventing such defects as binder separation and powder segregation. To measure the homogeneity of a feedstock several methods are available including\(^2,5,53\) density measurements, binder burnt-out, capillary rheometry, and torque rheometry. From these four methods, the last two are reviewed.

There are both capillary and torque rheometers in use. They operate in different way. In capillary rheometers, the material is forced through a small gap channel from a reservoir by a piston. The pressure at the entrance of the capillary and the flow rate are recorded. On the other hand, torque rheometers are rotary equipments in which torque is recorded as a function of time of mixing.
The principal difference between capillary and torque rheometers in determining homogeneity is explained in Ebenhoech and Krueger’s paper. According to these authors, the capillary rheometer permits rheological measurements without any further mixing of the feedstock, while torque rheometers requires some degree of mixing to let a reading. As a result, Ebenhoech and Krueger recommend the capillary rheometer when no mixing studies are simultaneously conducted.

In principle for determining feedstock homogeneity, separately from mixing studies, any rheometer should work. However, the capillary rheometers are preferred over any rotational types, such as parallel plates and cone and plate, because of three reasons. Capillary rheometers cover wider range of shear rates, the shear rates are closer to those created in injection molding, and the flow conditions are closer to those found during mold filling. Therefore, the capillary rheometer reproduces the MIM processing conditions very closely.

Torque rheometers, on the other hand, can be used to study the whole mixing process, from the beginning of mixing to the end when the feedstock is produced. This is advantageous when a complete study of feedstock mixing is required. Nevertheless, the impossibility of obtaining rheological information in terms of shear rate and shear stress limits their use.

Capillary rheometers measurements include pressure at the entrance (or force applied to the piston) and mass flow. Homogeneous feedstocks show time-independent pressure (or force) while inhomogeneous blends show erratic values. The usefulness of this simple observation was demonstrated in a paper by Chung et al. In their investigation, a feedstock was run several times through a capillary rheometer. In between runs, the feedstock was remixed in their particular mixer (Ross mixer). They
found that the force reading decreased to a stable value as the number of repetitions
was about 5. Based on these results, Chung et al concluded that the stabilization of the
force reading in the capillary rheometer was caused by homogenization of the feedstock.

In early 90s Cao et al\textsuperscript{24} reviewed the importance of rheometry in MIM processes.
They recognized that capillary rheometers were the best equipment to determine
homogeneity of feedstocks. They also argued that the most homogeneous blend had the
best dimensional stability and consistency during injection, debinding, and sintering.

Other authors\textsuperscript{2, 5, 7-9, 54} have also recognized the usefulness of capillary rheometry
as a tool to determine homogeneity. Typical pressure curves of homogeneous and
inhomogeneous feedstocks in capillary rheometers are shown in Figure 2.3\textsuperscript{9}. Both blends
have the same solids loading.

MIM feedstock homogeneity determination using torque rheometers is used
when mixing is additionally studied. E.g. Supati et al\textsuperscript{55} studied the effects of mixing time,
mixing speed, mixing temperature and, solids loading on feedstock homogeneity using a
torque rheometer. They concluded that when the torque curve becomes flat, the
feedstock is homogeneous. Similar result was obtained by Dihoru et al\textsuperscript{37} combining
torque and capillary rheometry.

In torque rheometers, homogeneous feedstocks display smoother torque curves
than inhomogeneous feedstocks. A schematic of typical curves for homogeneous and
inhomogeneous feedstocks in torque rheometers is given in Figure 2.4.

In conclusion, rheometry plays an important role in feedstock’s homogeneity
determination. Capillary rheometers are preferred over torque rheometers because the
latter alter the structure of the blend itself. However, rheometers are not only used to
study the homogeneity of blends. They are additionally used to understand new or
improved feedstocks regarding mixing and processability. For these reason in almost every work on MIM moldability there is a rheometric study involved.

Figure 2.3 Comparison of poorly mixed and well-mixed feedstocks using capillary rheometer

Figure 2.4 Comparison in torque rheometers of homogeneous and inhomogeneous feedstocks
2.2.1.3. Rheological determination of stability, separation and segregation of MIM feedstocks

The term stability refers to the steadiness of feedstock viscosity with respect to shear rate. The separation indicates separation of the binder from the feedstock, and segregation to classification of particles by sizes through the binder. The stability, separation and segregation testing is useful in previewing flow defects in injection molding. The causes of instabilities in flow have not been studied in detailed in the MIM literature. Additionally, the experimental testing of stability, separation and segregation is infrequent. Feedstock stability, separation and segregation are tested in capillary rheometers or in injection molding. Obviously, because of the cost of running an injection molding machine it is preferable to use capillary rheometry for evaluating the feedstock characteristics.

Dihoru et al.\textsuperscript{37}, determine stability of several feedstocks composed of stainless steel powders obtained by different processes, and binder based on wax/PP. The effect of the particle shape, solids volumetric fraction, and particle size on feedstock stability and viscosity was studied. The authors found that the stability of powders based on gas-atomized and high pressure water atomized powders with small diameter particles gave improved stability. In Figure 2.5 the viscosity $\nu$. shear rate curves for stable and unstable feedstocks are shown.

One example of testing separation is described in the paper by Cao et al.\textsuperscript{24}. The feedstock was tested in a capillary rheometer at low shear rate for a long time (more than one hour). The shear rate was set to 3.5 s$^{-1}$ and the temperatures were varied from 110 °C to 140 °C. These experiments showed that after one hour, the viscosity of the feedstock increased sharply. They interpreted this result as the binder separation.
To test this assumption they took samples from skin and core of the material in the barrel of the rheometer and evaluated them using TGA. The TGA results confirmed that the skin had higher binder content than the core. Similarly, they proved that the material left in the barrel had higher content of solids than the initial feedstock. In this work, three binders were tested. They were composed of paraffin wax, carnauba wax and low molecular weight PP (LMW-PP), EVA and HDPE in each one of the binders. The binder with LMW-PP showed less stability, and the one based on EVA showed higher stability. The binder based on HDPE was moderately stable.

The separation and segregation of powders in MIM feedstocks have not been thoroughly studied in terms of rheological characterization. However, several papers can be found on how to control and avoid separation effects in injection molding. Although the separation and segregation of concentrated suspensions and their flow in
pipes were amply discussed\textsuperscript{58, 59}, the MIM feedstocks have not been studied. More work in this field is required.

2.2.1.4. Constitutive equations of MIM feedstocks

Capillary rheometry may be used for determining constitutive equations (CE’s) of MIM feedstocks. The constitutive equations are usually of the power-law type, without consideration of any elastic effect. Only one paper\textsuperscript{60} acknowledged that MIM feedstocks are viscoelastic materials. However, no measurements of viscoelastic behavior have been reported and no viscoelastic CE’s have been used to model the MIM feedstocks.

The suspension data can be fit to two kinds of equations. When the suspensions are Newtonian or when there is a region of Newtonian behavior, the viscosity data may be correlated with the solids concentration. Several of these equations are given in the paper by Chung et al\textsuperscript{12} and are shown on Table 2.1.

It the general instance of non-Newtonian behavior it is common to fit rheological data to more general equations that include the shear rate as variable. These include, the power-law, Bingham, Casson, Cross, and modified Cross equations.

Chung et al\textsuperscript{12} fitted the viscosity data obtained from a wax-based feedstock with iron powder to the different equations presented in Table 2.1. the authors found that the best fit was obtained with the equation the Frankel and Acrivos. To fit the data, the Newtonian viscosities obtained at different temperatures were divided by the viscosity of the neat wax at the respective temperature. This ratio of viscosities is known as reduced viscosity. The data for these suspensions fell into a single curve that was then fitted to the above equations.
Table 2.1 Equations for viscosity of concentrated suspensions at zero shear

<table>
<thead>
<tr>
<th>Equation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \eta_r = (1 - \varepsilon \cdot \varphi)^{-2} )</td>
<td>Maron and Pierce\textsuperscript{61}</td>
</tr>
<tr>
<td>( \eta_r = (1 - \varphi / \varphi_{\text{max}})^{-2} )</td>
<td>Quemada\textsuperscript{62}</td>
</tr>
<tr>
<td>( \eta_r = [A/(1 - \varphi / \varphi_{\text{max}})]^2 )</td>
<td>Chung et al\textsuperscript{12}</td>
</tr>
<tr>
<td>( \eta_r = C {(\varphi / \varphi_{\text{max}})^{1/3} / [1 - (\varphi / \varphi_{\text{max}})]^{1/3}} )</td>
<td>Frankel and Acrivos\textsuperscript{63}</td>
</tr>
</tbody>
</table>

Several authors reported the usefulness of the Maron and Pierce equation for modeling the viscosity of feedstocks of about 60% of metal in volume\textsuperscript{24, 27}. In the paper of Li et al\textsuperscript{27}, the data were well fitted by the equation. The calculated values were useful in establishing that at injection molding temperature the viscosity was low. In the paper of Cao et al\textsuperscript{24}, the feedstocks showed yielding, therefore the Bingham and Casson equations were also used to model the feedstock viscosity at low shear rates.

The use of the power law is widespread in MIM literature. However, when yielding is observed the Bingham fluid or the Casson equations incorporating a yielding term are preferred\textsuperscript{24, 64}. Another model that incorporates yielding is a modified Cross model used in a paper by Chung et al\textsuperscript{65}. Table 2.2 represents some empirical CE’s containing a yield term, which is useful for modeling the MIM feedstocks.

In some cases, empirical equations are developed for particular feedstocks. E.g. Huang et al\textsuperscript{66} developed an equation for predicting the viscosity as a function of shear rate, temperature, and powder loading, intended for injection molding modeling.
Table 2.2 Empirical models for viscosity of MIM feedstocks

<table>
<thead>
<tr>
<th>Equation</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\tau = \tau_y + \eta \dot{\gamma}$</td>
<td>Bingham</td>
</tr>
<tr>
<td>$\tau^{1/2} = \tau_y^{1/2} + C \dot{\gamma}^{1/2}$</td>
<td>Casson</td>
</tr>
<tr>
<td>$\eta = \frac{\eta_0}{1 + (\eta_0 \dot{\gamma} / \tau)} + \frac{\tau_y [1 - \exp(-a \dot{\gamma})]}{\dot{\gamma}}$</td>
<td>Modified Cross</td>
</tr>
</tbody>
</table>

The dependence of viscosity on shearing rate is very important in MIM processes. If the variation of shear induces great variations in viscosity, the molding will be difficult because of uncontrolled random variation in molding conditions are always present. Therefore, a good feedstock should have a low sensitivity to shear rate. For particular case of MIM feedstock that behaves as a power-law fluid, low sensitivity to shear is expected if the exponent is close to unity.

In most of MIM feedstock CE’s, the dependence of viscosity on temperature is expressed as an Arrhenius equation. However, in some instances, the dependence is expressed as WLF type\textsuperscript{64, 67}. The temperature dependence of viscosity is getting important when selecting binders. If the variation of viscosity is low under temperature changes, the feedstock is said to have low sensitivity to temperature. This translates in viscosity stability during molding and then fewer defects during molding cause by unavoidable random variations in injection conditions.
2.2.2. Thermal Characterization

MIM feedstocks are thermally characterized mainly for thermal debinding cycle specification and thermal stability studies. In some instances, the thermal characterization includes determining melting peaks, and thermal capacity. In addition, other data that have been measured using specialized equipment is the thermal conductivity. Among the instruments used in thermal analysis, the most used are thermo gravimetrical analyzer (TGA) and differential scanning calorimetry (DSC). Additional instruments include dynamical mechanical analyzer (DMA), and thermo mechanical analyzer (TMA) as shown by Rhee et al\textsuperscript{13}.

The measurement of the heat capacity has been reported in several papers\textsuperscript{12, 24}, which reported the use of a power compensated DSC calibrated with graphite standard to determine the heat capacity. In both publications, heat capacity data were fitted with a polynomial useful for the particular feedstocks studied.

The thermal conductivity of MIM feedstocks was measured by Liu et al\textsuperscript{68}, Kowalsky et al\textsuperscript{69}, and Mamunya et al\textsuperscript{70}, using specialized equipment based on LASER pulse emission. Kowalsky et al, determined the thermal conductivity of molten and solid feedstocks based on polyacetal The experimentally measured thermal conductivity was compared to the predictions using the rule of mixtures as presented by the Maxwell, and Lewis and Nelson equations. The calculations showed that the Maxwell equation underestimate the conductivity, while the Lewis and Nelson equation showed results closer to experimental data. None of the two methods could reduce the error to less than 15\%, and none took into account phase changes (specific volume variation) in the range of processing temperature. The theoretical models of conductivity were not tested for concentrations above ca. 29\% according to the author. Mamunya et al found that
the thermal conductivity of metal filled polymers increases as compared to the neat polymer.

DSC thermograms were used by Cao et al.\textsuperscript{24} to determine the compatibility between binder components examining the behavior of the melting peak before and after the blending. If the peaks’ maximum shift after mixing, then the components are compatible. Another example of compatibility determination was presented by Khalil et al.\textsuperscript{31}. DSC studies revealed that the melting peaks of the constituents in the binder were slightly lower than the melting peaks of the neat components. The authors concluded that there were interactions between the components without complete dissolution of each component in the others.

Another application of DSC thermograms is in determining the injection temperatures. For instance, Rhee et al.\textsuperscript{13} set the minimum injection temperature based on the higher melting peak of the binder. Additionally, the maximum temperature of the mold was set to be lower than the minimum recrystallization temperature.

Kowalsky et al.\textsuperscript{69} used DSC to determine the behavior of BASF feedstock based on 316L stainless steel. The experiments were conducted at different cooling rates, from 10 to 90 °C/min. The maximum of the specific heat decreases, as well as the average heat capacity when the cooling rate is high. The reason for this is the different degree of crystallinity for rapid cooled semi-crystalline containing feedstocks. At very rapid cooling rates, the maximum of the heat capacity is shifted to lower temperatures that may be below the processing range; therefore the maximum should not be taken into account when simulating injection molding.

Thermogravimetric analysis has been used to determine the thermal stability of feedstocks, and more importantly, the thermal debinding procedure. Chung et al.\textsuperscript{12} and
Cao et al\textsuperscript{24} performed TGA measurements under nitrogen atmosphere at 20 °C/min to determine the binder content and to establish the rate of thermal debinding. In the second experiment, Cao et al, heated the sample to 210 °C and left it loses weight isothermally.

The shape retention during thermal debinding was studied by Li et al\textsuperscript{27}. They found that the best binder should give a gradual decomposition, with remaining binder components holding the metal particles together while other components pyrolyze. Therefore, the authors concluded that a multicomponent binder (PW/HDPE/EVA in their case) must be used on order to have good shape retention during thermal debinding.

Other use of TGA analysis was found by Petzold et al\textsuperscript{35} who used TGA to determine the oxygen, carbon, and nitrogen pick up by titanium during debinding. The experiments were performed under nitrogen and oxygen atmospheres with recording the weight increment.

Other thermal methods used in MIM research include thermo mechanical analysis (TMA) by Cao et al\textsuperscript{24}, and Dynamic Mechanical Analysis (DMA) by Liu et al\textsuperscript{68}. Cao et al used TMA to determine the softening points of the binder and feedstocks. The probe penetrates a flat sample with a round tip of 0.51 mm diameter. The temperature dependent penetration was recorded under the 100mN force applied to the probe. The authors found a correlation between interacting binders and penetration temperature. The penetration temperatures increased when the binder is highly interacting with the metal. The authors stated that the penetration temperature could be used to measure the adhesion strength of the binders to the powders. DMA was used to determine the coefficient of thermal expansion (CTE) of MIM feedstock. Rectangular samples were inserted in the DMA and the position of the probe was recorded as a function of
temperature. The slope of the curve gives the CTE. When the temperature dependent position reaches a maximum the softening starts, therefore the DMA allows determining both the CTE and the softening points of the feedstocks.

2.3. The Metal Injection Molding process

The processing of feedstocks includes several steps: mixing or compounding, injection molding, debinding, and sintering. The first three processes will be reviewed in the next three Subsections.

2.3.1. Feedstock compounding

The mixing of the metal powder and the binder is a critical step in MIM process, since an inhomogeneous feedstock cannot be corrected in the following steps in the MIM process.  

The MIM feedstocks were compounded in a variety of equipments ranging from handmixers with marine propeller type blade to twin-screw extruders. The compounding usually takes more than one step. For instance, Hens et al, mixed first in a high shearing devices and then in a twin screw extruder. The authors argued that the mixing was more effective than mixing in a sigma blade or double planetary mixer because of higher shearing and shorter residence time.

The mixing temperature is different for different materials. E.g. Chung et al mixed iron powder with polyethylene wax, an oligomer of degree of polymerization 30 at 129 - 140 °C for about 30 minutes. Similarly, Cao et al mixed LMW-PP at 150 °C, EVA at 129 °C and HDPE at 160 °C in polymer/wax systems.

Most mixing studies used torque rheometers to determine the mixing parameters, including the torque. Examples of studies using Haake rheometer include one by Loh et al, Supatti et al, and Dihoru et al. Loh et al used the Taguchi method.
to study the compounding of MIM feedstock with 70% volume content of solids. The variables studied included mixing temperature, mixing time, powder loading rate, speed of rotor blade, type of rotor and particle size at three levels each. The three rotor types were roller, sigma and cam. Feedstock homogeneity was evaluated using density and binder burn-out. The results based on density indicate that the ranking of factors determining feedstock homogeneity were powder loading rate, speed of rotor blade, type of rotor blade, mixing temperature, mixing time, and particle size. In the case of binder burnt-out the factors were powder loading rate, speed of rotor blade, mixing temperature, type of rotor blade, particle size and mixing time. The authors concluded that powder loading rate and speed of rotor blade were the most important factors affecting feedstock homogeneity. Dihoru used a torque rheometer to produce a homogeneous feedstock. The mixing was done at 50 rpm for 2 hours at 140 °C. Supatti et al55 mixed a feedstock in Haake instrument after mixing in a Turbula blender for 15 minutes. The rotors were of roller type. The metal powder was added gradually to the mixing chamber. The feedstock produced was homogeneous.

The relation between feedstock viscosity variability and dimensional variability of green powder injected molded components was studied by Zauner et al67. The feedstock components were dry mixed in a Turbula mixer. The compounding of the wax/polymer binder with metal was done in two equipments to compare the effect of shear. A sigma-blade batch-mixer of 0.5 L capacity was used at 160 °C for 29 min. The other feedstock was compounded in a 2 in co-rotating twin screw extruder at 160 °C in two passes with granulation between passes. The water-atomized powder was 316L stainless steel. The results indicate higher viscosities and variability of viscosity for the material compounded in the sigma blade equipment than for that compounded in twin-screw extruder.
Additionally, the variability of viscosity nonlinearly depended on temperature for the feedstock mixed in sigma blade mixer, and practically linearly for the material mixed in a TSE. The authors attributed these differences to poor wetting of the powder when mixed in the sigma blade mixer.

Most of the studies on mixing use a torque rheometer with the capability of recording the torque and control the temperature of mixing. No studies have been found in which the sequence of addition of materials during compounding is evaluated or correlated in some way to the properties and morphology of the feedstocks.

In many situations, the inhomogeneity or separation defects of feedstocks cannot be clearly explained by inappropriate mixing. It can also be attributed to other factors including binder composition, metal characteristics, and mixing processes. Therefore, the studies should be focus on finding the interrelation between these factors and on isolating the effect of each one from the others.

2.3.2. Injection molding studies in MIM

The injection molding is a very important stage in MIM processing, because the properties of the green part cannot changes too much during the following processing steps. For instance, if a part comes with defects such as, weld lines or sink marks, or if the green parts are not consistent and if the dimensional variation cannot be controlled in this step, nothing can be done after injection to fix the problem.

In the technical literature nothing to the author’s best of his knowledge has been published in regard to the injection molding processing (that is the procedure to determine the injection molding conditions to obtain consisted and repeatable parts). Therefore, no comments are done about this topic in this section.
2.3.2.1. Injection molding modeling

In this Section, a brief description of the MIM injection molding is reviewed. The proposed research will not include modeling of the injection step as a consequence this Section is intended for contextualization of the proposed research.

Several approaches have been used for modeling MIM injection molding stage. The most important works are commented in this Section.

In a series of papers from the Rensselaer Polytechnic University\textsuperscript{72-81}, a study of powder injection molding was developed. Lee et al\textsuperscript{72} and Najmi et al\textsuperscript{74, 73-75} modeled the mold filling stage using the finite element method (FEM) for pressure calculation coupled with the finite volume method (FVM) for determining the front position, and the finite difference method (FDM) to calculate the temperature profile. They employed a 2D modeling using the Helle Shaw generalized approximation. In these studies, different feedstocks were used to inject a circular ring shape part and a rectangular part. The numerical results and analytical results for the circular ring part agreed well with experimental results. Najmi et al\textsuperscript{76} found different temperature profiles and therefore, different pressure profiles for different feedstocks during mold filling. The authors attributed this result to the differences in thermal conductivity and thermal capacity of different feedstocks. Najmi et al\textsuperscript{75} described the application a software to the gate optimization, including in the goal function several factors important in the injection molding, and evaluated the temperature and pressure profiles.

Fox et al\textsuperscript{73} optimized the injection molding for having no defects using an experimental design based on orthogonal arrays. The results were analyzed using the Taguchi methods. The variables studied included barrel and die temperature, injection speeds and profiles, packing pressures and profiles, packing times and cooling times.
The results permitted a better control over the green part dimensions and the elimination of voids in molded parts. The sintered parts were tested for mechanical properties and observed with X-ray radiography.

Fox et al analyzed cooling process in a series of papers\textsuperscript{76, 79-81}. The motivation for this study was finding the effect of mold temperature profile on the “frozen” stresses occurrence. The modeling was performed with 3D-FEM to determine the positions of the cooling channels before producing the mold and to determine the magnitude of the possible stresses in the parts.

The full 3D modeling of injection molding process of MIM feedstocks is presented in two papers by Wang et al\textsuperscript{82, 84}. The mold filing stage was modeled combining the FDM and the volume of fluid method (VOF) to track the melt front. The program output includes pressure, temperature, shear stresses, shear rates, and velocity profiles. The modeling program allows describing almost any geometry with the advantage of being 3D capable. The only drawback is related to the description of edges and curve surfaces because of the inherent limitations of the FDM. However by making denser the numerical grid many details can be studied.

In a subsequent paper, Wang et al\textsuperscript{84} compared experimental short shots with numerical predictions from the simulation software developed before\textsuperscript{82, 83}. It was found that short shots are minimized by increasing the injection pressure, melt temperature, and die temperature. The results obtained from the numerical solutions were in agreement with the experimental results demonstrating that the software could be used to substitute costly short shot testing in MIM injection molding process. Additionally, injection conditions can be determined before designing the mold.
In a series of papers by Kwon et al\textsuperscript{85-87}, the apparent slip phenomena in concentrated suspension were studied and incorporated into injection molding simulation software. The apparent slip is caused by the migration of metal particles toward the center of the conduction under high level non-uniform shear. The migration phenomenon has been observed in other concentrated noncolloidal\textsuperscript{88,89} suspensions and in MIM feedstocks\textsuperscript{24}.

Kwon and Anh\textsuperscript{85} characterized the apparent slip using the Mooney method where the slip velocity is directly calculated. They also treated the slip in terms of a thin “slip layer” with calculating its thickness and corresponding slip velocity. The authors obtained experimental results for flow of a PIM feedstock in capillary rheometer and used them to predict the flow rate in pipes. They found that with using the slip velocity calculations the prediction of flow rates coincide with the experimental results. These authors, additionally, modified a FEM/FDM scheme for injection molding including the slip corrected viscosity. The results showed that the pressure profiles and clamping force obtained without slip corrected viscosity were significantly different from those obtained with slip correction. Additionally, both methods to correct the viscosity for slip were found to be essentially the same because of the small thickness of the slip layer (maximum 3.5 µm) when the thickness of the part was small.

Kwon and coworkers\textsuperscript{86} used the slip layer approach to correct the injection molding predictions because of the presence of the layer in molding. The main motivation of this work was to increase the predictive capacity of the injection molding software. Because the slip layer acts as a lubricant and a thermal insulator, it affects both the flow behavior and heat transport between the mold and the feedstock. The modeling approach was based on the Helle Shaw approximation that is usually
considered as 2.5D. However, in a more recent publication by Hwang and Kwon\textsuperscript{87}, fully 3D simulation software for MIM injection molding incorporating apparent slip was also presented. The numerical results were tested against short shot experimental results. The coincidence of predicted and real profiles was good. The authors concluded that the software might be a useful tool for MIM injection molding designers.

Another 3D modeling of injection molding in MIM was accomplished by Ilinca and coworkers\textsuperscript{64, 90–92} using a code developed by the National Research Council of Canada for the injection molding of plastics. The code was fully 3D and used the pseudo concentration technique to track the flow front position. The properties of MIM feedstocks were involved in the code and results obtained for the injection molding of a feedstock gel based. The results showed that the simulation software was appropriate to describe the MIM injection molding.

Barriere and cowokers\textsuperscript{58, 59, 93} integrated the segregation in the injection molding modeling of MIM feedstocks. They employed a two-phase model for the MIM feedstock avoiding the use of equivalent viscosity for the mixture. The model was able to predict phase separation. Each phase was modeled as a fluid interacted with another via a momentum exchange term. Two variables, namely solids and fluid volumetric fractions were used to determine the condition of the feedstock at any point. The model was solved with a FEM scheme, using VOF method to track the front position. The implementation of the two-phase model in injection molding allowed a good prediction of the filling of two tensile samples cavities filled in different ways. The simulation software was used as a tool to avoid segregation effects considering the values of the volumetric fractions of binder and solid required eliminating the defect.
The above brief review shows that the modeling and simulation of the injection molding process in MIM is well developed. However, it seems that every specific situation requires experiments to find the right parameters for numerical simulation. Therefore, in this sense, the injection molding software is useful when the production of a given part must be optimized. This is usually the situation when good molding conditions have been found by trial and error in a corresponding injection molding machine.

2.3.2.2. Injection molding as a tool to test MIM feedstocks

The injection molding processing has been used in several studies as a mean to characterize feedstock. The quality of parts determined as the number of defective parts has been used in MIM to compare the quality of feedstocks. Additionally, the proper injection molding conditions can be determined using these studies.

The comparison of two feedstocks is possible with using injection molding. E.g. Wang et al\textsuperscript{50} injected discs (of 32 mm diameter and 2 mm thickness) to test a modified acetal feedstock. The authors tested mold temperatures from 90 to 134°C finding an optimum at 95°C. The “flow number” i.e. the integral of the melt pressure over a portion of the filling stripe was used as a measure of the quality of the feedstocks. The results show that the flow number for the modified feedstock was lower than that of the unmodified one, even at lower temperature. Wang et al also showed photographs of the injected molded parts and argued that the surface of the parts produced with the modified feedstock gave better finishing than the surface of those parts produced with unmodified feedstock.

Homogeneous feedstocks as compared to inhomogeneous ones should be easier to mold. This result was confirmed by Cao et al\textsuperscript{24} who also injected molded parts. They
used a speed of 1.73 cm/s (4.4 in/s) for the injection to avoid freezing of the material in the cavity. Additionally they presented a correlation between shear sensitivity, viscosity at molding temperature and flow activation energy. The feedstocks with low viscosity, low shear sensitivity, and low activation energy behave better in injection molding. These authors also noted the appearance of defects including binder separation, or wrinkles.

Heaney et al\textsuperscript{44} studied the relation between different powders and the dimensional variability of molded parts. The parts were produced in injection molding at 150 °C with mold at 34 °C. The injection speed was 20 cm\textsuperscript{3}/s and the hold pressure was 24 MPa. The authors determined the dimensional variability for 120 pieces molded using different feedstocks, and indicated a great variability for the first 20 molded parts. The results were used to evaluate the relation between powder characteristics and final part dimensional variations.

Several authors introduced the moldability parameter has been used in the plastics processing practice. Li et al\textsuperscript{27} injected molded tensile testing bars for MIM feedstocks, comparing several feedstocks with different rheological characteristics. They concluded that the feedstock with lower viscosity, lower power-law exponent and lower flow activation energy is suitable for injection molding. The authors presented the moldability parameter $\alpha_{STV}$ as defined by Weir\textsuperscript{94} for polymer processing:

$$\alpha_{STV} = \frac{1}{\eta_0} \frac{\partial \log(\eta)/\partial \log(\gamma)}{\partial \log(\eta)/\partial (1/T)}$$

Equation 2-1

In equation 2-1 $\eta$ is the viscosity, $\eta_0$ the reference viscosity, $\gamma$ the shear rate, and $T$ the temperature. Li et al calculated the moldability parameters for the feedstocks

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at a reference temperature and shear rate. They concluded that the feedstock with the larger moldability parameter could be the most easily injected molded.

In summary, it is possible to use the injection molding of parts as a mean for testing the feedstocks. Several variables that could be additionally studied are the effect of binder components, metal shape and size distribution, mixing protocols, and rheological characteristics.

2.3.2.3. Molding defects and feedstock characteristics

According to Miura et al\textsuperscript{95}, molding defects in metal injection molding include cracks, powder-binder separation and segregation effects, short shots, weldlines, sink marks, and internal voids. The defects may be attributed to a combination of bad material and improper operating conditions. However, in some cases when to mold an inhomogeneous or unstable material is impossible the injection molding defects necessitate the changes in feedstock formulation.

Miura et al\textsuperscript{95} studied several factors that could caused crack defect in MIM thin-wall parts, including molding conditions, binder content, binder and powder characteristics, and binder recycling. They found that the crack was caused by a poor flowability of the feedstock in the mold near a hole. Short shot studies were made to understand the mechanism of crack formation. The results indicate that higher holding pressures and higher injection speed reduce the frequency of the appearance of the defect in sintered parts. Similar effect was found with the increase in binder content and the use of recycle material, which increase the flowability of the feedstocks. Thus, a less viscous, more homogeneous and more stable feedstock would avoid the crack defect in the particular case studied. It is important to notice that even though the frequency of
defects decreased they were not eliminated. The reason might be a bad quality of the feedstock that could not be corrected when changing the processing conditions.

Two other important defects in MIM injection molding are binder separation and powder segregation. Both defects occur in feedstocks under high and nonuniform shearing in injection molding. The binder separation is due to the formation of a layer of neat binder near the surface of the sprue or mold, which results in the acceleration of the feedstock because of the lubricating action of the low viscosity layer near the wall. In this occurrence, the high velocity feedstock hits the surface of the mold bouncing back creating voids and weld lines during freezing. Chung et al.\textsuperscript{32, 12} attributed those defects to low adhesion between binder and powder.

The powder segregation occurs simultaneously with the binder separation, with the powder segregating according to particle size. In this instance, the larger particles migrate towards the centerline of the conduction and the smaller to the wall. Particle migration has been taken into account in MIM injection molding modeling via introducing a diffusion coefficient for the particles\textsuperscript{67}.

Binder separation in MIM was studied by Kwon and coworkers\textsuperscript{85-87}, and by Barriere and coworkers\textsuperscript{58, 59, 93}. Both research groups incorporated the binder separation in injection modeling as presented in the Section devoted to the injection molding modeling. Fundamental studies of the cause for particle migration have not been developed. However, the phenomenon is attributed, as mentioned before, to low adhesion between binder and particles. The mechanics of particle migration in suspensions was discussed elsewhere\textsuperscript{88,89,97}. 

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2.3.3. Solvent Debinding in MIM

The removal of the binder, or debinding, can be accomplished in three ways: thermal debinding, solvent debinding, and catalytic debinding. In the thermal debinding, the binder is removed as a gas either under vacuum or in atmosphere. When thermal debinding occurs under vacuum it is called diffusion, while under atmosphere permeation. In solvent debinding, the parts are brought into contact with a fluid that dissolves the binder or one of its components. The solvent may be liquid, gaseous or a supercritical fluid. When a fraction of the binder is removed by solvent extraction, pores are open allowing further thermal debinding. In catalytic debinding, a gaseous catalyst is contacted with the molded parts to accelerate the binder depolymerization reaction. The small molecules are swept out of the oven by a carrier gas.

Nowadays, the common practice is to use multiple component binders amenable for sequential debinding. A typical sequence is solvent debinding followed by thermal decomposition. In this sequence, pores created during solvent debinding are used for easing migration of decomposition products during thermal debinding. Using this sequence, the part does not deformed because during solvent debinding the particles are hold together by the insoluble polymer. While during thermal debinding, the pores avoid the building up of internal pressure that could cause deformation, bursting and other defects. Additionally, the porosity accelerates the thermal debinding as compare to the same process in a non-porous compound.

The solvent debinding can be accomplished by immersion in liquid solvent at low pressure and temperature (immersion debinding), by immersion in supercritical solvent at high pressure and temperature (supercritical debinding), or by contacting with a saturated vapor of a liquid solvent (condensed solvent debinding). In the third extraction
procedure, the solvent vapor condensates on the surface of the parts forming a liquid film that extracts the soluble component of the binder. In the following, a brief review of solvent debinding is presented.

The solvent debinding process has been used for ceramic injection molding (CIM). In the text by Mutssudy and Ford, the advantages of the solvent debinding are mentioned including faster removal, less equipment costs, and possibility of process automation. In the usual solvent extraction, the parts are immersed in the extracting fluid, and then dried in a drier or in air. The remaining binder is removed by thermal debinding. The solvents use in CIM and mentioned in the book by Mutssuddy and Ford. They include chlorofluorohydrocarbons, chlorohydrocarbons, hexane, and heptane. It is clear that the intention in solvent debinding was to remove waxes.

In MIM papers by Hens et al, the use of the solvents mentioned in the previous paragraph is criticized because these solvents are carcinogenic, and flammable. Therefore, Hens et al proposed to use a polymer, which is soluble in water, ethanol, methanol or their solutions. The authors compared the debinding rate of water-soluble polymer based binder in several solvents. They found that debinding in methanol was the fastest, ethanol the second and water the slowest. The solvent debinding did not cause any deformation changes in the parts, while in the case of wax/polymer binders there were deformation in heptane and trichloroethane.

Tsai and Chen studied the debinding of CIM parts with three solvents. Cylindrical samples were submerged in the solvents and then removed after a prescribed time. Then, they measured the penetration of the diffusing front by TGA technique scraping the samples at different position toward the center. Their results showed that the penetration seems to follow a shrinking core behavior. A model for diffusion was
stated and an effective diffusivity resolved. The three solvents used were compared to determine which one gave the faster debinding.

In a paper from Krauss et al\textsuperscript{99}, the debinding of water-soluble polymer from a CIM part was investigated using water. The study included de modeling with the shrinking core model to find an effective diffusivity. The data fitted the model very well and an effective diffusivity was determined to be appropriate for the modeling of the debinding at all times. The shrinking core was also followed with mercury porosimetry experiments. The porosimetry corroborated that the water extraction proceeded as a shrinking core.

Hwang and Hsieh\textsuperscript{100} compared the evolution of porosity in straight thermal debinding with the porous structure evolution in solvent debinding. They measured porosity using mercury porosimetry. The binder was wax/polymer and the solvent was heptane. The results indicate that the binder dissolution started from the surface and progress toward the center of the compounds. As debinding proceeds the volume and size of pores increase and pore size distribution broadens. In contrast, in straight thermal debinding, the distribution of pore sizes is narrow and the average pore size decreases as debinding proceeds. The authors also concluded that followed by solution debinding, the thermal debinding is very fast because of the pores formed during solvent debinding. In contrast, at intermediate stages of straight thermal debinding the binder accumulates near the surface of the compounds forming a layer that hinders the diffusion and reduce the speed of debinding. This could be a reason why the solvent debinding is faster than straight thermal one.

Hwang et al\textsuperscript{101} also compared the mechanisms of thermal, vacuum and solvent debinding. The results and conclusions are similar to their previous work. They
presented, however, some new results on dimensional changes of the parts when the solvent is added and drained. The details of the laser device used in their measurements are given in Lin and Hwang’s paper\textsuperscript{102}. The results indicate that the parts expand and contract upon addition and drainage of solvent (heptane in this case). The dimensional changes occurred because of swelling of PP in heptane during wax extraction. This is expected since PP structure is hydrocarbon-like.

Li et al\textsuperscript{22} described the use of dichloroethylene. The binder was of the wax/oil/polymer type, containing either polyethylene or EVA. Molded parts of 6 mm thickness were debound in the solvents to determine the kinetics of debinding. The experimental results show that swollen parts containing EVA produced cracks making impossible the use of dichloromethane for debinding wax/oils/EVA based parts. On the other hand, parts containing PE showed no defects and the debinding rate was high, reaching up to 2mm/h. The authors also mentioned that the recycle ratio of the solvent is 95 wt%.

Condensed solvent debinding is described by Zhu and coworkers\textsuperscript{30}. A custom-made binder for tungsten-cemented carbide based on waxes, polyethylene, polypropylene and ethylene-diene-propylene terpolymer (EPDM) was debound in heptane. The system depicted in Figure 2.6 consists of two containers at different pressure and temperature under inert atmosphere (Argon). The solvent flows from the container with pure solvent to the container where the parts are, and condensates on the surface of the parts. The condensate extracts the binder soluble components and falls toward the porous substrate, being finally collected at the bottom of the low-pressure container.
Qu et al\textsuperscript{23} presented the evidence of the pore formation after solvent debinding. Rectangular specimens of 6 x 6 x 42 mm made from WC-TiC-Co feedstock with wax/polymer binder were debound in heptane. The picture of fracture surface shows many interconnected pores that were created during solvent debinding. Additionally, the authors presented figures of time dependent mass loss as a function of part thickness.

2.4. MIM feedstock as dispersed system

MIM feedstocks are dispersed systems of metallic particles in a continuous polymeric matrix. It means that MIM feedstock may be considered as a highly filled polymer with volumetric fractions about 64%.

Filled polymers or composites are blends of polymer and solids made for either decreasing price or improving mechanical properties of final part\textsuperscript{103}. If a filler reduces cost by taking up volume it is called extender, if it improves any mechanical property, it is called reinforcer. Reinforcing fillers may have any particle shape, ranging from plates to elongated cylinders. On the other hand, extenders are usually irregular or spherical.

To improve the properties of filled polymers it is necessary to increase the interaction between the polymer and the reinforcing solid particles. This is accomplished
by using coupling agents whose molecules have their heads and tails of different chemical nature, where one part of the molecule interacts with the particle and the other with the polymer.

The rheology of concentrated suspensions has been studied in many papers. An excellent review of the results on concentrated suspensions of small active particles with attractive forces is presented by Leonov\textsuperscript{104}. The same idea, but applied to particles in low molecular fluids was studied by Coussot et al\textsuperscript{105}. In both works, the particles are considered to form networks that rupture in flow and restore again at rest. This process of destruction and restoration was modeled with a kinetic equation, and it is responsible for yield and thixotropy. One of the more remarkable aspects of this modeling is that the existence of yield is described without considering any mathematical yield criterion. In paper by Leonov et al\textsuperscript{104}, the viscoelasticity of concentrated suspensions was also taken into consideration. In contrasts, the usual approaches to concentrated suspensions have three disadvantages: i) the inclusion of the Von Mises’ yield criterion, which complicate mathematical treatment and required additional assumptions on yielding and thixotropy. ii) unclear thermodynamics of viscoelasticity, and iii) appearance of unknown dependencies of parameters on volume fraction of particles and particle size. In the modeling presented by Coussot et al\textsuperscript{84}, the transition from solid-like behavior to flow is predicted as a bifurcation with continuous evolution of the state of the materials.

The appearance of structuring in suspensions has been mentioned by several authors and has been attributed to strong interactions between the filler particles\textsuperscript{104-109}. For instance, Vinogradov et al\textsuperscript{106}, used acetylene black filler in polybutylene of low molecular weight in concentrations of 0.5 to 13 % by volume. Experimental results showed that the black formed a 3D network capable of causing a high yield stress, while
the elasticity of the suspensions was less than that of the unfilled polymer. Tanaka and White\textsuperscript{110} used a cell model for theoretical calculations of the shear viscosity of concentrated suspensions, assuming that the particles interact by either Van-der Waals-London or Coulomb electrostatic forces. The authors found good agreement of the model predictions with available experimental data. Metzner\textsuperscript{108} considered that the interaction between particles is important when the solid particles are suspended in a low viscosity liquid. The formation of structure and yielding is attributed to the interaction of adsorbed polymer layers on the particles’ surfaces. Malkin\textsuperscript{109} discussed the possible nature of the interaction between the particles in polymeric matrices. The particles are considered to interact via layers of adsorbed polymer or by contacting between particles forming a solid-like structure, which causes yield, non-Newtonian viscosity, and thixotropy.

The majority of filled polymers studied in the literature include particles in a single polymer, showing yield and thixotropy. Only in few cases in the filled polymer literature, several polymers were used. One example of a filled polymer that behaved like a concentrated suspension was reported by Suetsugu and White\textsuperscript{110}. They studied the behavior of a suspension of calcium carbonate particles in a PS. The authors found that coating the particles with stearic acid greatly reduced the viscosity, decreased the apparent yield, and reduced aggregation. Therefore, coating the particles with stearic acid reduced particle-particle interactions. It was presumed that the carboxylic groups attached to the calcium carbonate and the hydrocarbon tail point away from the interface into the bulk phase. This paper of Suetsugu and White shows the behavior of the typically steric stabilized suspensions that are discussed in several references in the context of colloidal and noncolloidal suspensions.
Three methods are commonplace to stabilized suspensions\textsuperscript{111-116}: electrostatic, steric and a combination of the two. According to Tadros\textsuperscript{113}, electrostatic stabilization is based on charge separation and formation of an electrical double layer. On the other hand, steric stabilization is accomplished by the adsorption of surface-active polymers on the surface of particles. Following Tadros\textsuperscript{113}, this stabilization mechanism can be applied in the presence of electrolytes and at high temperature. The stabilizing polymer has a strong anchor to the particles and a stabilizing chain that extent into the suspension forming a layer of adsorbed polymer.

The steric stabilization has been used in stabilizing particulate polymers, examples include PVC in several solvents\textsuperscript{117}, and polystyrene latex stabilized with poly(ethylene oxide) in aqueous media\textsuperscript{118, 119}. Other examples include particles in non-aqueous media\textsuperscript{110, 120}. The sterical stabilization occurs because of two contributions. The first is a mixing interaction, which arises from the unfavorable mixing of the adsorbed or grafted layers under good solvent conditions. The second is an elastic interaction caused by the loss of configurational entropy of adsorbed chains when particles approach each other.

The mixing interaction occurs when the stabilizing layer of two particles overlap. In this situation, the chemical potential of the adsorbed polymer in the overlapping zone increases because of concentration effect. Then, a repulsion force appears to lower the chemical potential of the adsorbed polymer in the stabilizing layer. This effect is illustrated in Figure 2.7.

The elastic interaction takes into account that the closest the particles, the less space for the adsorbed molecules causing change in molecular shape and volume. Consequently, there is repulsion intended to increase entropy in the stabilizing layer.
From the aforementioned two interaction mechanisms, it is clear that steric stabilization leads to steep repulsion as soon as the interparticle distance becomes smaller than the double thickness of the stabilizing layer. According to Tadros\textsuperscript{111, 113}, this is the case when the grafted chains are in good solvent condition. In case of non-aqueous dispersions, the adsorbed chains are densely packed. Therefore, the thickness of the stabilizing layer is less than under good solvent conditions and the interactions may be treated as hard-sphere one.

Interparticle interactions in stabilized suspensions are commonly determined by direct measurement of the force between stabilized surfaces\textsuperscript{120-127}, or by rheological methods\textsuperscript{111, 129}. The direct measurements can be carried out using force balances\textsuperscript{120-127} or AFM\textsuperscript{127}. According to Israelachvili\textsuperscript{124}, the force balance consists of two macroscopic surfaces made of mica or glass. The attractive or repulsive forces are measured by the deflection of a spring or balance arm and distance using optical methods. The basic force balance is depicted in Figure 2.8.

Rheological methods to determine the interparticle forces are presented by Tadros\textsuperscript{111}. According to Tadros, there is a good correlation between rheological properties and interparticle forces, making it possible to understand the interparticle interactions in concentrated suspensions. One of the more useful methods is rheology in
dynamic regime. The relation between elastic and loss modulus reveals any overlapping of the adsorbed layers. For example, Croucher and Milkie\textsuperscript{128} obtained the dynamic results for a suspension of poly(vinyl acetate) stabilized with poly(2-ethylhexyl methacrylate) dispersed in Isopar G (an isoparaffinic oil), presented in Figure 2.9. It is seen that as volumetric concentration increases the elastic modulus becomes more important than the loss modulus and the suspension behavior becomes more solid-like. According to Crouchet and Milkie\textsuperscript{128} and Tadros\textsuperscript{111}, the reason for this trend is that the particle interactions become more important as particles get closer to each other. At a solids fraction of 0.54 the elastic modulus is larger than the loss modulus. This behavior is interpreted as interpenetration of the stabilizing layers, which causes increase in elasticity.

![Figure 2.8. Force balance\textsuperscript{124}](image)

![Figure 2.9. G’ and G” v. frequency at three particle volumetric fractions of PVA\textsuperscript{129}](image)
The relation between sterically stabilized suspensions and MIM feedstock is presumed from the information available on the behavior of different binders. The binders used in MIM practice are usually composed of a functional polymer, a nonfunctional polymer, and some additives. Examples of binders are shown in Table 2.3.

As seen from Table 2.3, the binders that showed no separation were composed of immiscible or partially miscible materials, with one of them having polar groups. The polar groups in the polymers include ester groups (CW, EVA), and ether group (PEO), POM, PVB). Additionally, the stearic acid is commonly used as coupling agent to increase adhesion from the binder to the metal. However, from binders 7 and 8 it can be concluded that stearic acid is not necessary when proper polymers are chosen.

Table 2.3 Example of binders used in MIM

<table>
<thead>
<tr>
<th>Components</th>
<th>Metal</th>
<th>Observation</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PEW</td>
<td>Iron</td>
<td>Separation</td>
</tr>
<tr>
<td>2</td>
<td>LMW-PP, PW, CW, SA (20-69-10-1)</td>
<td>Fe-2Ni (60%) 17-4PH (64%)</td>
<td>Separation, Poor adhesion to powder</td>
</tr>
<tr>
<td>3</td>
<td>EVA-A, PW, CW, SA (20-69-10-1)</td>
<td>Fe-2Ni (60%) 17-4PH (64%)</td>
<td>No defects Good adhesion to powder</td>
</tr>
<tr>
<td>4</td>
<td>EVA-A, PW, CW, SA (20-69-10-1)</td>
<td>Fe-2Ni (60%) 17-4PH (64%)</td>
<td>No defects Good adhesion to powder</td>
</tr>
<tr>
<td>5</td>
<td>HDPE, PW, CW, SA (20-69-10-1)</td>
<td>Fe-2Ni (60%) 17-4PH (64%)</td>
<td>Separation Poor adhesion to powder</td>
</tr>
<tr>
<td>6</td>
<td>PP, PW, CW, SA (40-48-10-2.5)</td>
<td>Stainless steel</td>
<td>Separation</td>
</tr>
<tr>
<td>7</td>
<td>PEO, POM</td>
<td>IN718 (up to 68%)</td>
<td>No defects</td>
</tr>
</tbody>
</table>
Table 2.3 Example of binders used in MIM. Continued

<table>
<thead>
<tr>
<th>Components</th>
<th>Metal</th>
<th>Observation</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>8 PEO, POM, PVB</td>
<td>IN718 (up to 68%)</td>
<td>No defects</td>
<td>7</td>
</tr>
<tr>
<td>9 EVA-C, PW, SA (20-79-1)</td>
<td>Fe-2Ni (58%)</td>
<td>No separation</td>
<td>27, 28</td>
</tr>
<tr>
<td>10 PW, HDPE, SA (79-20-1)</td>
<td>Fe-2Ni (58%)</td>
<td>No separation</td>
<td>27, 28</td>
</tr>
<tr>
<td>11 PW, PP, SA (79-20-1)</td>
<td>Fe-2Ni (58%)</td>
<td>Severe separation</td>
<td>27, 28</td>
</tr>
<tr>
<td>12 PW, EVA, HDPE, SA (79-10-10-1)</td>
<td>Fe-2Ni (58%)</td>
<td>No separation</td>
<td>27, 28</td>
</tr>
</tbody>
</table>

PEW: polyethylene wax. Degree of polymerization: 29
PW: Paraffin wax
SA: Stearic acid
EVA-B: poly(ethylene-co-vinyl acetate) 9.5% VA
PP: Polypropylene
PVB: Poly(vinyl butyral)

LMW-PP: Low molecular weight polypropylene
CW: Carnauba wax
EVA-A: poly(ethylene-co-vinyl acetate) 26.5% VA
HDPE: High density polyethylene
PEO: Polyethylene oxide
EVA-C poly(ethylene-co-vinyl acetate) 14% VA
3.1. Materials

The materials comprised one powdered metal and five resins. The metal was 316L stainless steel (SS) and the resins were based on: high-density polyethylene (HDPE), linear-low-density polyethylene (LLDPE), polypropylene (PP), polyoxymethylene copolymer (POM), and water-soluble polymer (WSP).

3.1.1. Metal

The 316L SS, an austenitic stainless steel, was chosen because of its availability and high demand. It had wide particle-size-distribution and its particles were spherical. These characteristics were considered representative of other metal powders used at the Sponsoring Company. Metal powders with different particle-size-distributions or composed of other alloys were not tested because of limitations in material availability and proprietary restrictions.

The 316 L SS is an austenitic stainless steel containing up to 0.03 wt% carbon and up to 3 wt% of molybdenum. The austenitic stainless steel is a solution of iron with another element (or elements) having a face centered cubic (fcc) lattice. Austenitic steel exists at temperatures above the eutectoid point that depends on the composition but that is around 710°C. When slowly cooled, the austenitic steel becomes a mixture of ferrite (bcc) and cementite (a compound of iron and carbon with chemical formula...
Fe₃C). When quenched, the austenitic molten steel becomes martensitic steel that has body centered tetragonal lattice. However, at moderate cooling rates, some of the austenitic structure can be kept in the solid together with other steel structures giving alloys with varying properties. The austenitic steels are soft and ductile while martensitic steel is very hard, strong and brittle.

The austenitic stainless steels may contain several additional elements, which give certain properties to the steels. In the instance of the 316 L stainless steel, the combination of low carbon content and high proportion of molybdenum impair outstanding corrosion resistance and avoid carbide precipitation at the grain boundaries. Therefore, the 316L stainless steel has higher toughness, creep, stress to rupture, and tensile strength than chromium-nickel austenitic stainless steels.

The powdered 316L Stainless Steel may be manufactured by water, gas or centrifugal atomization⁵,⁶. In water and gas atomization, the metal is force through a nozzle producing a stream of molten metal, which is impinged upon by a jet of water or gas. The impact breaks up the metal stream into fine particles of diverse sizes. Even though the principle of both atomization methods is the same, the shape and surface qualities of the resultant particles is different. The water atomization produces non-spherical particles of rough surface, while gas atomization yields spherical and smooth particles. The reason is that in water atomization the solidification of the metal particles occurs very quickly freezing the turbulent structure of the metal droplets attained during impact. On the other hand, in gas atomization enough time is provided to allow shape relaxation of the metal particles.

In contrasts to the water and gas atomization methods, in centrifugal atomization the particles are produced by freezing droplets that are tangentially ejected
from a spinning disk. The droplets solidify into spherical particles while cooling in inert gas or vacuum. The disadvantage of this method is that large room should be provided for the flying particles not to collide with any surface and to cool down while keeping enough sphericity.

The 316L SS used in this research was manufactured by UltraFine Powder Technology. The powder was produced by the gas atomization method from the pre-alloyed metal. The fact that the atomization starts from a prealloyed steel and that the argon is used in the cooling stage guarantees the uniformity of the chemistry among batches of powdered 316L. The chemical composition of the steel is presented in Table 3.1\textsuperscript{130}.

As in most processes for manufacturing powdered solids, the gas atomization produces particles with a distribution of sizes. The size distribution of the stainless steel used in this study is shown in Table 3.2\textsuperscript{130}. In addition, both, the size distribution and the cumulative distribution are shown in Figure 3.1.

The size distribution graph is very useful when comparing different batches of powdered solids. However, numerical parameters are more useful to qualify the particulate solids used in a given application. Therefore, some parameters of the distribution are calculated and shown in Table 3.3. These parameters were calculated following the methodology presented elsewhere\textsuperscript{131,132,133}. The parameters so calculated are: mode, median, geometric mean, coefficient of uniformity, standard deviation and specific area.

Table 3.1 Chemical composition of the metal\textsuperscript{130}

<table>
<thead>
<tr>
<th>Element</th>
<th>Fe</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>C</th>
<th>S</th>
<th>O</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt %</td>
<td>Balance</td>
<td>16.9</td>
<td>10.5</td>
<td>2.13</td>
<td>1.3</td>
<td>0.50</td>
<td>n.d</td>
<td>0.02</td>
<td>0.01</td>
<td>0.07</td>
<td>0.26</td>
</tr>
</tbody>
</table>
The Figure 3.1 and Table 3.3 indicate that the particulate 316L SS size distribution is monovariate, with a mode of 11.0 μm. It can be observed that the mode, median and geometric mean are very close to each other demonstrating that the distribution is not very wide. However, the coefficient of uniformity and the standard deviation, which measure the width of the distribution, indicate that the distribution is relatively wide. To understand this is important to notice that a monodisperse distribution of particle sizes would have a coefficient of uniformity of 1 and nil standard deviation. Therefore, it is possible to say that the 316L SS distribution is relatively wide.

The broadness of the distribution guarantees that more metal could be packed in a given volume. The reason is that using particles of various sizes fills more space because small particles tend to occupy the space left between larger particles making possible high loads of powder.

Table 3.2 Size distribution of the powdered metal

<table>
<thead>
<tr>
<th>Micron</th>
<th>Cum Pass (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.4</td>
<td>0.0</td>
</tr>
<tr>
<td>1.9</td>
<td>0.2</td>
</tr>
<tr>
<td>2.8</td>
<td>3.2</td>
</tr>
<tr>
<td>3.9</td>
<td>10.1</td>
</tr>
<tr>
<td>5.5</td>
<td>19.3</td>
</tr>
<tr>
<td>7.8</td>
<td>31.6</td>
</tr>
<tr>
<td>11.0</td>
<td>47.8</td>
</tr>
<tr>
<td>16.0</td>
<td>64.1</td>
</tr>
<tr>
<td>22.0</td>
<td>90.2</td>
</tr>
<tr>
<td>31.0</td>
<td>98.5</td>
</tr>
<tr>
<td>44.0</td>
<td>100</td>
</tr>
</tbody>
</table>
Figure 3.1 Particle size distribution of the 316L SS powder

Table 3.3 Several parameters of the Particle Size Distribution

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Formula</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mode</td>
<td>Higher wt fraction in size distribution</td>
<td>11.0 µm</td>
</tr>
<tr>
<td>Median</td>
<td>Diameter at 50 % cumulative</td>
<td>11.5 µm</td>
</tr>
<tr>
<td>Geometric mean</td>
<td>$\exp\left[\frac{\ln(d_{16}) + \ln(d_{50}) + \ln(d_{84})}{3}\right]$</td>
<td>10.3 µm</td>
</tr>
<tr>
<td>Coefficient of uniformity</td>
<td>$\frac{\phi_{50}}{\phi_{10}}$</td>
<td>3.51</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>$\sigma = \left(\frac{\ln(d_5) - \ln(d_{95})}{4.6}\right) + \left(\frac{\ln(d_{16}) - \ln(d_{84})}{2.8}\right)$</td>
<td>0.956</td>
</tr>
<tr>
<td>Specific Area</td>
<td>$a = \sum_j f_{mj} \frac{A_{pj}}{V_{pj}\rho}$</td>
<td>1297 cm²/g</td>
</tr>
</tbody>
</table>

90% of the spherical particles are finer than 22 µm

(1) The letter $d_x$ represents the diameter of particles at which $x$% of the sample is coarser than that size.
(2) The symbol $\phi_x$ represents the particle diameter for which $x$% of the sample is finer than.
(3) The symbol $f_{mj}$ represent the mass fraction of solids in the channel $j$. The symbol $A_{pj}$ and $V_{pj}$ the area and volume of one particle of the channel $j$, respectively. $\rho$ is the intrinsic density of the 316L SS.
3.1.2. Polymers

The polymers used in this investigation included HDPE, PP, LLDPE, POM and a water-soluble polymer (WSP). The polymers were used as commercial resins without any purification to simulate the industry practice. The resins were combined in three binders with the following combination of resins: i) HDPE, POM and WSP. ii) PP, POM and WSP. iii) LLDPE, POM and WSP.

Many polymers could be use as binder components according to the recommended properties that a binder should have. These are \textsuperscript{2, 5, 12, 134}: i) Ability to fill the mold at the injection molding conditions without giving defective parts, ii) Good shape retention after mold cooling and during debinding, iii) Debindability at low cost and with minimum environmental impact, minimum effect on the shape and dimensions of the parts and negligible affect on the chemistry of the metal. iv) Capability to bear more than 45 vol\% of metal particles. In addition to these conditions, in this research, the binder should contain the water-soluble polymer provided by the Sponsoring Company, POM and a polyolefin as major component. The polyolefins chosen were HDPE, PP and LLDPE.

The feedstocks obtained by combining the three resins aforementioned satisfied the first, second and fourth requirements as well as the water debindability. However, the impact of the thermal debinding on shape and dimension stability and on the metal chemistry was not tested. Similar binders systems in use nowadays in industry have shown no effect on these parameters. Therefore, no impact on the shape and chemistry was anticipated from the binders proposed here.

As it is apparent, the thermal debinding is a key operation in determining dimensional stability of the molded parts. Therefore, two important findings regarding
shape stability were considered when specifying the binders used in this research. The first, is that solvent debinding improves the shape retention during thermal debinding because of the pores created avoid the build up of internal stresses\textsuperscript{7, 8, 99-102}. The second finding that using several polymers with different thermal decomposition profiles seems to improve the shape stability of the parts during debinding\textsuperscript{22, 23, 26, 27, 30}.

The solvent debinding create pores that provide room for the less dense liquid byproducts of polymer decomposition at early stages of chain thermal degradation and in addition, provide a mean for evacuation of liquids and gasses produced during debinding. In addition, when several polymers with different thermal decomposition profiles are used it seems that even if one of the polymers has been almost completely removed, the other still provides support to the metal particles retaining the shape. However, the same effect is attained by using polymers that degrade by unzipping mechanism\textsuperscript{42}. In conclusion, the binder must contain at least one water-soluble polymer and at least two more polymers of different thermal decomposition behavior or one that degrades by unzipping mechanism.

Besides the relation between thermal debinding and shape retention, the relation between binder decomposition and metal chemistry depends on the amount of metal atoms present in the resin additives. It is important to realize that the term resin is used because neat polymers are not used in Metal Injection Molding industry. However, many additives in use nowadays do not contain metals and are purely organic molecules. In addition, since the thermal debinding is usually done at a very low temperature rate and up to temperatures of more than 600 °C it is evident that even if the resin contains thermal stabilizer their affect on the chemistry of the metal and on the rate of debinding is none. The cause is simple: the thermal stabilizer also pyrolizes!
3.1.2.1. High Density Polyethylene (HDPE) resin

The HDPE used in this project was manufactured by DOW. This material is identified as DOW Polyethylene 17450N. According to the manufacturer\textsuperscript{135}, this HDPE resin is injection-molding grade and complies with the US FDA 21 CFR 177.1520 (c) 3.2a. The FDA Code of Federal Regulations 177 imposes rules on the resins in contact with food and the section 177.1520 regulates resins based on polyolefins specifically\textsuperscript{136}.

The FDA regulation, CFR 177.1520 (c) 3.2a, is applicable to resins based on olefin copolymers for use in articles used for packing or holding food during cooking. The maximum amount of extractables should be less than or equal to 2.6 wt\% (by weight of the polymer) at 50°C in n-Hexane. The FDA also establishes the proportion of monomers that the copolymer may have to fulfill the rule. The copolymer may contain ethylene and 1-alkenes (2-8 carbon atoms) with no less than 96 wt\% of units derived from ethylene. The rule gives several exceptions based on the type of alkenes and the required proportions for comonomers.

If the HDPE resin 17450-N is intended for used in contact with food, the additives are also regulated by the FDA. Approved processing aids are given in the CFR 177.1520, as well as surface lubricants, anti-blocking agents and a deactivator of Ziegler-Natta type catalyst. Antioxidants are specified in CFR 178.2010, antistatics in CFR178.3130 and clarifying agents in CFR 178.3295. The CFR can be consulted for detailed information. The most important conclusion is that these additives are organic molecules most of them oligomers without heavy metals. They will decompose thermally without leaving any residue. Therefore, it is considered that the detailed investigation of the structure of these additives is irrelevant in studying the thermal debinding.
The chemical structure of the HDPE was not determined in this study. However, based on the manufacturer information and the FDA regulations, this HDPE is a copolymer of ethylene and alkene that may be 1-butene, 1-pentene, 1-hexene or 1-octene. Some of the properties of the HDPE are shown in Table 3.4.

The DSC curve of the HDPE used in this research is shown in Figure 3.2. The scan was conducted at a heating rate of 20 °C·min$^{-1}$ after preheating and quenching. A single peak is observed at 132.3 °C. Glass transitions were not observed. The heat of melting was 162.9 J/g.

The TGA Curve is depicted in Figure 3.3. The experiment was conducted in nitrogen atmosphere at a heating rate of 20 °C/min from room temperature to 700 °C. The data indicate that no residue was left after the total decomposition of the resin.

The DSC and TGA scans reveal that the HDPE had a narrow molecular weight distribution since the DSC melting peak is narrow and the decomposition curve varies from 100 wt% to 0 wt% in a narrow temperature range. The melting occurs over an interval of 80 °C determined from the point any melting begins to the end. However, most of the area of the peak covers a span of 50 °C around the melting point. The thermal degradation occurs in an interval of 130 °C approximately. In addition, the TGA curve showed that the resin decomposes completely before reaching 700 °C. Therefore, this material will degrade completely before the sintering starts causing no changes in the chemistry of the metal.

Regarding the rheological behavior, the only information for the polymer is the melt index that reveals that the polymer has low average molecular weight.
Table 3.4 Properties of the Polyethylene resin

<table>
<thead>
<tr>
<th>Property</th>
<th>Conditions</th>
<th>Value</th>
<th>Units</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melt Index</td>
<td>190 °C, 2.16 kg</td>
<td>17.0</td>
<td>g/10 min</td>
<td>Dow Technical Data</td>
</tr>
<tr>
<td>Density</td>
<td>N/A</td>
<td>0.950</td>
<td>g/cm³</td>
<td>Dow Technical Data</td>
</tr>
<tr>
<td>Melting point</td>
<td>20 °C/min</td>
<td>134.5</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>DSC crystallization point</td>
<td>10 °C/min</td>
<td>115.0</td>
<td>°C</td>
<td>DOW Technical Data</td>
</tr>
<tr>
<td>Onset Thermal degradation</td>
<td>20 °C/min</td>
<td>260.3</td>
<td>°C</td>
<td>At 0.5% weight loss</td>
</tr>
<tr>
<td>End thermal degradation</td>
<td>20 °C/min</td>
<td>497.9</td>
<td>°C</td>
<td>At 99.5 % weight loss</td>
</tr>
</tbody>
</table>

Figure 3.2 DSC scan of HDPE resin
3.1.2.2. Linear-Low-Density Polyethylene (LLDPE) resin

The LLDPE used in this project was manufactured by NOVA Chemicals. According to the manufacturer\textsuperscript{137}, the "NOVAPOL\textsuperscript{®} GI-2024-A is an LLDPE masterbatch resin that features medium flow, easy processability, an excellent balance of properties, good moldability, and good environmental stress crack resistance. Some properties of this resin are given in Table 3.5.

The LLDPE resin from NOVA Chemicals complies with the US FDA 21 CFR 177.1520 (c) 3.2a, which implies that the resin may be used in articles intended to be in contact with food including packaging and articles for holding food\textsuperscript{137}. Therefore, the maximum extractables in Hexane at 50 °C is 2.6 wt% (by weight of the polymer). The additives approved by the FDA does not include organometallic compounds. Therefore, the byproducts of the thermal decomposition of the resin would not alter the chemistry of the metal.

Figure 3.3 TG scan of HDPE resin
According to the product information\textsuperscript{138}, the LLDPE manufactured by NOVA contains 1-butene comonomer. It was manufactured by a medium pressure gas process using Ziegler-Natta catalyst.

The DSC curve of the LLDPE resin is shown in Figure 3.4. The heating rate of 20 °C·min\textsuperscript{-1} and the melting point read after quenching. A single peak is observed at 126.4 °C. Glass transitions were not observed. The heat of melting was 82.41 J/g.

The TGA Curve is depicted in Figure 3.5. The experiment was conducted in nitrogen atmosphere from room temperature to 700 °C at a heating rate of 20 °C/min. The data indicate that no residue was left after the total decomposition of the resin. The thermal decomposition occurs in an interval of about 200 °C.

The shear viscosity of the LLDPE was provided by the NOVA Chemicals. Figure 3.6 depicts the shear viscosity as function of the shear rate

Table 3.5 Properties of the LLDPE resin

<table>
<thead>
<tr>
<th>Property</th>
<th>Conditions</th>
<th>Value</th>
<th>Units</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight $M_w$</td>
<td></td>
<td>46618</td>
<td>Mol/s</td>
<td>Ref. 138</td>
</tr>
<tr>
<td>Polidispersity index</td>
<td></td>
<td>2.72</td>
<td></td>
<td>Ref. 138</td>
</tr>
<tr>
<td>Melt Index</td>
<td>190 °C, 2.16 kg</td>
<td>20</td>
<td>g/10 min</td>
<td>NOVA Technical Data</td>
</tr>
<tr>
<td>Density</td>
<td></td>
<td>0.926</td>
<td>g/cm$^3$</td>
<td>NOVA Technical Data</td>
</tr>
<tr>
<td>Melting point</td>
<td>20 °C/min</td>
<td>126.4</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>Onset Thermal degradation</td>
<td>20 °C/min</td>
<td>155.2</td>
<td>°C</td>
<td>At 0.5% weight loss</td>
</tr>
<tr>
<td>End thermal degradation</td>
<td>20 °C/min</td>
<td>591.8</td>
<td>°C</td>
<td>At 99.5 % weight loss</td>
</tr>
</tbody>
</table>
Figure 3.4 DSC scan of LLDPE resin

Figure 3.5 TG scan of LLDPE resin
Figure 3.6 Shear viscosity of LLDPE at 180 °C

3.1.2.3. Polypropylene (PP) resin

The PP resin used in this project was manufactured by A Schulman under the commercial name POLYAXIS PD 8020. It is a resin design for rotational molding with a good stiffness and environmental stress cracking resistance. The polypropylene was produced by Exxon Mobil.

The DSC curve of the PP resin is shown in Figure 3.7. The scan was conducted at a heating rate of 20 °C·min⁻¹ after preheating and quenching. A single peak is observed at 126.4 °C. Glass transition of PP was not observed. The heat of melting was 82.41 J/g.

The TGA Curve is depicted in Figure 3.8. The experiment was conducted in nitrogen atmosphere from room temperature to 700 °C at a heating rate of 20 °C/min. The data indicate that no residue was left after the total decomposition of the resin.
The TGA curves revealed that the PP decomposed in a wide range of temperature. This may be the result of the thermal stabilizers, since this resin was compounded for rotomolding. The thermal decomposition occurs in an interval of about 150 °C.

Table 3.6 Properties of the polypropylene resin

<table>
<thead>
<tr>
<th>Property</th>
<th>Conditions</th>
<th>Value</th>
<th>Units</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td></td>
<td>0.902</td>
<td>g/cm³</td>
<td>A Schulman Technical Data</td>
</tr>
<tr>
<td>Melt Index</td>
<td>190 °C, 2.16 kg</td>
<td>20</td>
<td>g/10 min</td>
<td>A Schulman Technical Data</td>
</tr>
<tr>
<td>Melting point</td>
<td>20 °C/min</td>
<td>170.2</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>Onset Thermal degradation</td>
<td>20 °C/min</td>
<td>315.2</td>
<td>°C</td>
<td>At 0.5% weight loss</td>
</tr>
<tr>
<td>End thermal degradation</td>
<td>20 °C/min</td>
<td>492.7</td>
<td>°C</td>
<td>At 99.5 % weight loss</td>
</tr>
</tbody>
</table>

Figure 3.7 DSC scan of PP resin
The Poly(oxy methylene) (POM) used in this study is a copolymer of formaldehyde and a cyclic ether that contains an ethoxy group. It is end-capped to increase the ceiling temperature and avoid depolymerization. The POM copolymer was manufactured by Ticona® Engineering Polymers with trade name CELCON®. This resin is injection-molding grade. Some of the properties of the POM resin are shown in Table 3.7.

Figure 3.9 shows the DSC scan of the POM resin. The DSC scan was conducted at a heating rate of 20 °C·min⁻¹ after preheating and quenching at 173.9 °C. A single peak is observed at 126.4 °C. Glass transitions were not observed. The heat of melting was 145.0 J/g.
Figure 3.10 shows the TGA curve for this material. The experiment was conducted in nitrogen atmosphere from room temperature to 700 °C at a heating rate of 20 °C/min. The data indicate that no residue was left after the total decomposition of the resin.

The Thermogravimetric curve shows that the depolymerization of the POM copolymer started well above 200 °C. The resistance to thermal degradation is attributed to end capping, the presence of the comonomer on the POM and thermal stabilizers.

Table 3.7 Polyoxymethylene copolymer resin properties

<table>
<thead>
<tr>
<th>Property</th>
<th>Conditions</th>
<th>Value</th>
<th>Units</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td></td>
<td>1.40</td>
<td>g/cm³</td>
<td>Ticona polymers</td>
</tr>
<tr>
<td>Melting point</td>
<td>20 °C/min</td>
<td>173.9</td>
<td>°C</td>
<td></td>
</tr>
<tr>
<td>Onset Thermal degradation</td>
<td>20 °C/min</td>
<td>260.1</td>
<td>°C</td>
<td>At 0.5% weight loss</td>
</tr>
<tr>
<td>End thermal degradation</td>
<td>20 °C/min</td>
<td>447.6</td>
<td>°C</td>
<td>At 99.5 % weight loss</td>
</tr>
</tbody>
</table>

Figure 3.9 DSC scan of POM resin
3.1.2.5. Water-soluble polymer

The nature and structure of the water-soluble polymer is not revealed in this section because of the need of protecting the technology of the Sponsoring Company that supplied materials for this research.

3.2. Processing Equipment

To understand the properties of the metal injection molding feedstocks it is necessary to conduct debinding and rheological tests with samples of reproducible shape. In order to obtain samples, two processing stages are required. First, the feedstock has to be produced and secondly, samples must be molded. The production of the feedstock was accomplished using an internal mixer and the samples were produced by using a micro-injection molding machine. Both pieces of equipment are described first.
3.2.1. Internal Mixer

The production of the MIM feedstocks and binders was accomplished using a batch internal mixer. A Brabender Plasticorder, manufactured by C. W. Brabender, with cam rotor was used to compound both, the metal with the polymeric binder components and the neat binders. The mixer has three temperature zones independently controlled and a chamber’s volume of 82 cm³. The process signals are sent to a data acquisition system that permits the recording of the torque and the temperatures of each of the three heated zones as a function of mixing time. Additionally, the stock temperature is measured by a thermocouple located closely to the internal wall of the mixing chamber, making it possible to record the stock temperature during mixing.

3.2.2. Micro-Injection Molding Machine

To produce the samples for debinding and rheological testing a micro-injection molding machine was used. A DSM Solutions micro-injection molding machine with a shot size of 3.5 mL and variable injection force was employed. In this piece of equipment, the material is heated inside a barrel until ready to flow. Once the stock is ready, a piston is inserted in the barrel and the whole set up is put in the machine assembly to allow the instrument to push the piston and force the material into a single-cavity mold. The barrel and the mold are heated independently permitting to keep the mold colder than the barrel. In most situations, more than one shot is possible with one load of the barrel, depending on the size of the cavity.

3.3. Experimental Procedures for compounding and debinding

The effect of different contents of metal and polymers on compounding torque evolution curves, feedstock debinding rate and properties was studied. For that reason, two sets of feedstocks were prepared and water debound using a home-made piece of
equipment. The procedures for compounding and water debinding the different feedstocks and neat binders are presented in the following sections.

3.3.1. Feedstock and binder compounding

Four sets of feedstocks were produced. The first set consisted of 4 blends obtained using a proprietary binder which components were provided by the sponsoring company. In preparing the first set of feedstocks, two different mixing speeds and three different concentrations of metal were used. The four feedstocks are identified with the letters A to D as shown in Table 3.8.

The second set of feedstocks consisted of 8 compounds with different concentration of polymers and metal. They were based on HDPE as backbone polymer and were mixed at two different temperatures but at the same rotational speed. The blends are identified with the number 1 to 8 followed by the letter H that means that the materials were based on HDPE. The composition of these feedstocks is given in Table 3.9.

The third and fourth sets contain different polyolefin and different concentration of metal. One set is based on PP resin while the other on LLDPE. During the compounding of the third and fourth sets, the mixer speed and temperature were not varied among samples. The blends obtained are noted with a number followed by a letter, for the feedstocks based on PP the letter is P and for those based on LLDPE, the letter L. The composition of the third and fourth set of feedstocks is given in Table 3.10 and Table 3.11, respectively.

Each set was mixed bearing an objective in mind. For instance, the first set of feedstocks was carried out to study the effect of mixing speed and of concentration of metal on the torque-evolution-curves obtained during mixing. Similarly, the second set
was intended to evaluate the effect of different variables including, mixing temperature and various concentration of binder components on several properties of the feedstocks. Lastly, the third and fourth sets were proposed to find the effect of metal concentration on the properties of the feedstocks.

Table 3.8 Compounding conditions of the feedstocks based on proprietary binder

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Fill Factor</th>
<th>Temp. (°C)</th>
<th>Speed (RPM)</th>
<th>M/F (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.64</td>
<td>170</td>
<td>150</td>
<td>60</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td>170</td>
<td>180</td>
<td>60</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>D</td>
<td></td>
<td></td>
<td></td>
<td>33</td>
</tr>
</tbody>
</table>


Table 3.9 Compounding conditions of the feedstocks based on HDPE resin

<table>
<thead>
<tr>
<th>Feeds.</th>
<th>Speed (RPM)</th>
<th>Fill Factor</th>
<th>Temp. (°C)</th>
<th>M/F (vol%)</th>
<th>WSP/B (wt%)</th>
<th>POM/B (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-H</td>
<td>100</td>
<td>0.72</td>
<td>150</td>
<td>63</td>
<td>40</td>
<td>5</td>
</tr>
<tr>
<td>2-H</td>
<td></td>
<td></td>
<td>150</td>
<td>63</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>3-H</td>
<td></td>
<td></td>
<td>150</td>
<td>64</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>4-H</td>
<td></td>
<td></td>
<td>150</td>
<td>64</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>5-H</td>
<td></td>
<td></td>
<td>180</td>
<td>63</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>6-H</td>
<td></td>
<td></td>
<td>180</td>
<td>63</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>7-H</td>
<td></td>
<td></td>
<td>180</td>
<td>64</td>
<td>40</td>
<td>5</td>
</tr>
<tr>
<td>8-H</td>
<td></td>
<td></td>
<td>180</td>
<td>64</td>
<td>50</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 3.10 Compounding conditions of the feedstocks based on PP resin

<table>
<thead>
<tr>
<th>Feeds.</th>
<th>Speed (RPM)</th>
<th>Fill Factor</th>
<th>Temp. (°C)</th>
<th>M/F (vol%)</th>
<th>WSP/B (wt%)</th>
<th>POM/B (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-P</td>
<td>100</td>
<td>0.75</td>
<td>180</td>
<td>22</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>2-P</td>
<td></td>
<td></td>
<td></td>
<td>45</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>3-P</td>
<td></td>
<td></td>
<td></td>
<td>63</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>4-P</td>
<td></td>
<td></td>
<td></td>
<td>45</td>
<td>21</td>
<td>10</td>
</tr>
<tr>
<td>5-P</td>
<td></td>
<td></td>
<td></td>
<td>63</td>
<td>21</td>
<td>10</td>
</tr>
<tr>
<td>6-P</td>
<td></td>
<td></td>
<td></td>
<td>63</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>


Table 3.11 Compounding conditions of the feedstocks based on LLDPE resin

<table>
<thead>
<tr>
<th>Feeds.</th>
<th>Speed (RPM)</th>
<th>Fill Factor</th>
<th>Temp. (°C)</th>
<th>M/F (vol%)</th>
<th>WSP/B (wt%)</th>
<th>POM/B (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-L</td>
<td>100</td>
<td>0.75</td>
<td>180</td>
<td>22</td>
<td>21</td>
<td>10</td>
</tr>
<tr>
<td>2-L</td>
<td></td>
<td></td>
<td></td>
<td>45</td>
<td>21</td>
<td>10</td>
</tr>
<tr>
<td>3-L</td>
<td></td>
<td></td>
<td></td>
<td>63</td>
<td>21</td>
<td>10</td>
</tr>
<tr>
<td>4-L</td>
<td></td>
<td></td>
<td></td>
<td>45</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>5-L</td>
<td></td>
<td></td>
<td></td>
<td>63</td>
<td>50</td>
<td>10</td>
</tr>
<tr>
<td>6-L</td>
<td></td>
<td></td>
<td></td>
<td>63</td>
<td>0</td>
<td>10</td>
</tr>
</tbody>
</table>

The sequence of addition of the components for producing all sets of feedstocks is as follows. First, the previously dried powdered-metal is added to the Brabender and let there until its temperature reaches the desire mixing temperature. Once the temperature is stable the first component is added. The second component is fed once the first is molten and the same with the third binder component, which is added after the second one, is molten. The detection of the melting is accomplished by observing the increase in the torque evolution curves. When a polymer melts, the torque curve grows reaching a peak torque, then the torque decreases stabilizing afterwards. The mixing procedure is shown in Figure 3.11 together with a schematic of the torque evolution curves.

Figure 3.11 Compounding of MIM feedstocks.

The compounding of binders is accomplished using a procedure similar to the one mentioned for feedstock production. However, not all the neat binders were produced because of the difficulties in mixing binders with high content of water-soluble polymer. The reason is the partial miscibility of the water-soluble polymer with the other two polymers. The binders obtained are presented in the Table 3.12.
Table 3.12 Binders compounded

<table>
<thead>
<tr>
<th>binder</th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>M/F</th>
<th>C3/B (wt%)</th>
<th>C2/B (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIN3PP</td>
<td>PP</td>
<td>POM</td>
<td>WSP</td>
<td>0.00</td>
<td>7</td>
<td>10</td>
</tr>
<tr>
<td>BIN2LL</td>
<td>LLDPE</td>
<td>POM</td>
<td>WSP</td>
<td>0.00</td>
<td>21</td>
<td>10</td>
</tr>
<tr>
<td>BIN3LL</td>
<td>LLDPE</td>
<td>POM</td>
<td>WSP</td>
<td>0.00</td>
<td>7</td>
<td>10</td>
</tr>
</tbody>
</table>

Conventions: M: metal, F: feedstock, B: binder, C1, C2 and C3: Polymeric components, WSP is the water-soluble polymer

The composition of the binders is the same as to the composition of the binders in the feedstocks sets 3 and 4. The purpose is to present rheological results based on reduce viscosity, which requires information of the neat binder. With this in mind, it was planned to have more neat binders than those presented in Table 3.12. However, this was hindered because of the impossibility of attain higher concentrations of water-soluble polymer in either, the binders based on PP or LLDPE.

3.3.2. Injection Molding of Test Samples

Test samples for rheology testing and debinding studies were obtained using the micro-injection molding machine already described. 20 samples of each material were injected molded. The conditions used for the different compounds are as follows. For the samples 1 to 8, MIM380 and MIM700 the pressure was 3 bar and 190 °C. For all other samples the temperature was 180 °C. The difference is due to the lower viscosity of the samples with less metal requiring less temperature for the onset of flow.

The tip of the barrel was pre-heated for 10 s before each shot. This procedure is required since the industrial-scale injection molding machines use either hot sprue or hot tip to avoid the solidification of the material in the sprue. If the tip is not heated the feedstocks could not be injected molded.
3.3.3. Water Debinding

The water debinding is the process in which the water-soluble polymer is removed from the MIM molded parts. The rest of the binder is removed by thermal debinding that consists in thermally decomposing the remaining polymers. In this context, the purpose of the water debinding is to create porosity in the injected part to facilitate the escape of the gases produced during polymer decomposition and to allow for thermal expansion limiting the appearance of residual stresses in the part.

In the usual experimental approach to water debinding, the parts are immersed in a water bath and leave there for a certain length of time. The water is not agitated or refreshed. Because of such a setup, the concentration of the extractable polymer in the water varies continuously. After a certain debinding time the part is removed and the weight loss calculated to obtain an intraparticle diffusion coefficient through diffusion models that assume negligible concentration of polymer at the surface of the particle. The result of such an experiment and its analysis lumps the extraparticle and the intraparticle mass transport phenomena, leading to dubious results in respect to the intraparticle diffusivity.

To improve the results obtain in water debinding tests, two setups are proposed in this research having a common purpose: to isolate the extra and intraparticle mass transport phenomena. To accomplish this, two water flow configurations relative to the particles were selected. In the first one, the particles rotated in the water while in the second one a water jet impinged on the particles. In both flow situation, the effect of the extraparticle phenomena is reduced (particles rotating) or it is well understood and transport coefficients correlations are available (water jet impinging).
With the approach proposed, the results obtained from the experiments could be separated in those attributable to the extraparticle phenomena and those that depended on the intraparticle transport. In this way, the results obtained in this research will permit the modeling of any debinding situation that uses the same material. The reason is that if a fluid flow model can be constructed for a given situation, the intraparticle transport model can be coupled to it to model the whole debinding process. This experimental procedure can be use in any solvent debinding situation. This is the most relevant aspect of the debinding studies in this research.

3.3.3.1. Water debinding of immersed rotating cylinders

The first debinding setup consists of a heated tank with continuous flow of water in and out. The tank has a volume of 3800 cm³ and the water flows in and out at 20 ml/min. The molded parts are attached to a cylindrical plate through plastic ties leaving a distance from the shaft of about 5 cm. The parts rotate at 200 rpm. The tank is heated with a heating plate that has bath temperature controller. The setup is depicted in Figures 3.12 (a) and (b).

The cylindrical samples had diameter of 6.5 mm diameter and 5 cm length. To have samples of different length, the parts were cut with a circular saw at different lengths and one extreme and the sides were coated with epoxy resin to eliminate radial diffusion inside the particle. A typical coated particle is shown in Figure 3.13. Figure 3.14 shows the details of the shaft and how the samples were attached to it using a circular plate with three perforations. Therefore, three samples were tested simultaneously. A list of the samples is shown in Table 3.13.
Figure 3.12 First water debinding setup

Figure 3.13 Cylindrical samples for water debinding

Figure 3.14 Cylindrical samples for water debinding
Table 3.13 Dimensions and debinding time of debinding with submerged cylinders

<table>
<thead>
<tr>
<th>Experiment #</th>
<th>Length (mm)</th>
<th>Debinding Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.66</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>10.87</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>5.42</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>19.40</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>6.09</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>22.13</td>
<td>40</td>
</tr>
<tr>
<td>7</td>
<td>8.98</td>
<td>40</td>
</tr>
<tr>
<td>8</td>
<td>2.40</td>
<td>40</td>
</tr>
<tr>
<td>9</td>
<td>22.49</td>
<td>60</td>
</tr>
<tr>
<td>10</td>
<td>9.90</td>
<td>60</td>
</tr>
<tr>
<td>11</td>
<td>7.62</td>
<td>60</td>
</tr>
<tr>
<td>12</td>
<td>20.92</td>
<td>90</td>
</tr>
<tr>
<td>13</td>
<td>9.65</td>
<td>90</td>
</tr>
<tr>
<td>14</td>
<td>19.46</td>
<td>120</td>
</tr>
<tr>
<td>15</td>
<td>12.32</td>
<td>120</td>
</tr>
<tr>
<td>16</td>
<td>2.29</td>
<td>120</td>
</tr>
<tr>
<td>17</td>
<td>18.64</td>
<td>150</td>
</tr>
<tr>
<td>18</td>
<td>9.32</td>
<td>150</td>
</tr>
<tr>
<td>19</td>
<td>8.86</td>
<td>150</td>
</tr>
<tr>
<td>20</td>
<td>22.05</td>
<td>840</td>
</tr>
<tr>
<td>21</td>
<td>11.88</td>
<td>840</td>
</tr>
</tbody>
</table>

The coated samples were dried for 24 hours in a vacuum oven at 64 °C previously to the experiments. After drying, the parts were weighed and tied to a perforated disk using a plastic tie (see Figure 3.14). The perforated disk was fastened to
the end of a shaft that was attached to a variable speed motor. Once, three of the
samples are tied to the disk, and the water bath is at the experimental temperature, the
shaft is lowered, and the experiment begins. The parts were subjected to different
debinding times including, 5, 12, 40, 60, 90, 120, 150, and 840 minutes. The debinding
temperature was 40 °C. The time to lower the shaft and start the motor was less than
10 seconds.

After the debinding was concluded, the parts were removed from the water,
untied from the rotating disk and then dried in a convection oven for 12 h. Following
that, the parts were weighed to find out how much mass was loss during debinding.
From the initial and final weights, the amount of mass extracted was recorded and an
average rate of debinding calculated. With this information and a simple mathematical
model for the diffusion, the effective diffusion coefficient was calculated. The details of
the modeling are shown in Chapter 4.

3.3.3.2. Water debinding with water jet impingement on samples

The second experimental setup consisted of device to produce a water jet using
water from a heated container. The home-made device is presented in Figure 3.15. The
plates A and B could be leveled to allow for a perpendicular water jet impinging on the
sample disks.

Two kinds of samples were used in the water debinding studies with water jet. The
first kind consisted of circular plates glued to glass plates as shown in Figure 3.16
(a). The second one consisted of plates sandwiched in between two metal plates. This
configuration is shown in Figure 3.16 (b).

The dimensions of the system are shown in the Figure 3.17. The distance from
the nozzle to the cylindrical plate in the configuration shown in the Figure 3.16 (a) is
35.50 mm. The distance from the nozzle to the plate in configuration given in Figure 3.16 (b) is 12.00 mm. The nozzle diameter is 1.98 mm.

Figure 3.15 Debinding setup with water jet.

Figure 3.16 Debinding with water jet
Debinding with water jet. Dimensions

The water jet experiments of the first type mentioned were conducted at three different temperatures including, 30 °C, 40 °C and 50 °C using samples based on HDPE. The reason to choose these temperatures is that the debinding is currently carried out at 40 °C at the sponsoring company. The time of the tests was 2, 4, 8, 16 and 32 minutes.

The water jet experiments using the configuration of sample between plates was used to study the concentration front inside the part. To accomplish this, rectangular samples were cut from molded disks of approximately 20 mm length and 10 mm width. Three of the edges of the sample were coated with epoxy resin leaving one side exposed. The surfaces of larger area of the sample plates were cover with rubber sheets to avoid the effect of water on them, as shown in Figure 3.18.
The samples were put under the water jet for a period and then removed and dried in a convection oven for 24 h. After this, small squares were removed at different positions from the exposed edge of the samples. Each square was tested in a thermogravimetric analyzer (TGA) to evaluate the amount of water-soluble polymer removed from the sample by leaching. The tests were done for 32, 64 and 128 minutes at 40 °C.

3.4. Characterization techniques

Several characterization techniques were used to study different properties of the MIM feedstocks and binders. The characterization included, rheological, calorimetric and microscopic techniques aimed to determine the effect of composition on the properties.

3.4.1. Differential Scanning Calorimetry (DSC)

A Differential Scanning Calorimeter (TA DSC 2922) in the scanning mode was used to determine the melting point and heat of melting in all the feedstocks and binders investigated. The samples were carefully weighted to 10±2 mg and sealed in aluminum hermetic pans and lids, placed in the DSC and heated at a rate of 20°C/min.

The temperature range was from -120 °C to 200 °C for all the binders and feedstocks. The thermal transition temperatures of the materials are influenced by the processing and thermal histories during processing. Therefore, first and second (after-quenching) scans were conducted to gather evidence of thermal and/or processing histories of the feedstocks and binders studied.

3.4.2. Thermogravimetric Analysis

A Thermogravimetric Analyzer manufactured by TA Instruments was used to study both, the thermal stability of the MIM feedstocks prepared during this study and
the concentration of water-soluble polymer after debinding. The temperature range in both kinds of tests was from room temperature to 700°C with a scanning rate of 20°C/min.

3.4.3. Scanning Electron Microscopy (SEM)

The Scanning Electron Microscopy (Hitachi S-2150 microscope) was used to study the MIM feedstocks prepared. Samples at different stages of compounding and before and after debinding were observed. To obtain the samples, the material was immersed in liquid nitrogen and cryogenically fractured. Afterwards the samples were fastened on conductive tape to aluminum mounts and coated with silver by sputter coating machine (Emitech K575X).

Feedstock samples after compounding, molding, rheological testing and water debinding were observed using SEM. The results are presented in section 4.5.

3.4.4. Rotational rheometry

A rheometer controlled strain rheometer ARES (Advanced Rheometric Expansion System), manufactured by Rheometrics Scientific (now TA Instruments) was used in the rheology tests. Steady shear, frequency sweep and dynamic temperature sweep experiments were performed on different samples as shown in Table 3.1. All the experiments were conducted using the parallel disks of 25 mm diameter and leaving a gap of 1 mm. The Steady Shear testing was conducted at different temperatures using the Steady Rate Sweep template offered by the ARES Control software (Winrhios). The initial rate was 1.51x10^-5 s^-1 and the final rate 100 s^-1, taking 9 points per decade in logarithmic sweep and clockwise rotation.

The frequency sweep testing was conducted at different temperatures using the Dynamic Frequency Sweep Test template that comes with the Winrhios control.
Software. The test was performed at a given strain and at frequencies varying from 0.01 rad/s to 100 rad/s. The time per measurement was 30 s.

Before starting the tests, the fixtures were loaded and let to warm up for about 30 minutes. Then, the fixtures were zeroed using the Autozero capability of the rheometer and the upper fixture rose to about 5 mm. The tempered chamber was then opened and the sample inserted. After closing the furnace, the upper plate was lowered to about 1 mm until the force was close to zero and the sample left unperturbed until the temperature was stable again. Once at the test temperature, the upper plate was adjusted to give a normal force close to zero. Then the furnace was open and the samples’ edge trimmed. The sample was left to reach the experimental temperature again for about 10 minutes, then, the test begun.

The Dynamic Time Sweep tests were done using the Dynamic Time Sweep template included in the Winrhios control Software. The test was performed at three temperatures. Each test was done at a given strain and frequency for a length of time of 11 h. and varying from 0.01 rad/s to 100 rad/s. The time per measurement was 30 s.

Table 3.14 Rheology tests

<table>
<thead>
<tr>
<th>Type of tests</th>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Frequency or rate</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steady shear</td>
<td>Binder BIN2LL</td>
<td>160, 170, 180</td>
<td>Shear rate: 1.5x10^{-5} to 100 s^{-1}</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Feedstock 1-L 22% vol Met</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Feedstock 2-L 45% vol Met</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Feedstock 3-L 63% vol Met</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Frequency sweep</td>
<td>Binder BIN2LL</td>
<td>160, 170, 180</td>
<td>1x10^{-2} to 1x10^{2} rad/s</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>Feedstock 1-L 22% vol Met</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Feedstock 2-L 45% vol Met</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Feedstock 3-L 63% vol Met</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 3.14 Rheology tests. Continued

<table>
<thead>
<tr>
<th>Type of tests</th>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>Frequency or rate</th>
<th>Strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Frequency sweep</td>
<td>Feedstock 1-L 22% vol Met</td>
<td>160, 170, 180</td>
<td>1x10^{-2} to 1x10^{2} rad/s</td>
<td>3.8</td>
</tr>
<tr>
<td></td>
<td>Feedstock 2-L 45% vol Met</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Feedstock 3-L 63% vol Met</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Feedstock 5-L 63% vol Met</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Feedstock 5-P 63% vol Met</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Feedstock 6-H 63% vol Met</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Feedstock 6-L 63% vol Met</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The composition of the feedstocks and binder are given in Tables 3.6 (6-H), 3.7 (5-P), 3.8 (1-L, 2-L, 3-L, 5-L and 6-L) and 3.9 (BIN2LL)

The shear and normal stresses differences in parallel disks rheometer are obtained from the measurements of the angular velocity \( \Omega \), the torque \( M \) and the thrust \( F \) on the upper disk. If the coordinate \( z \) coincides with the rotation axis, the torque and thrust are expressed as follows:

\[
M = 2\pi \int_0^R \tau_{oz}(r)r^2 dr
\]  
3-1

and,

\[
F = -2\pi \int_0^R \sigma_{zz}(r)rdr
\]  
3-2

where, \( \tau_{oz} \) and \( \sigma_{zz} \) are components of the extra stress and stress tensors, respectively. \( R \) is the radius of the disks.

The expression of the shear stress as a function of the torque is obtained by inverting the equation 3-1. To do this, the integration variable (radius, \( r \)) is transformed into the shear rate \( (\dot{\gamma}) \) using the expression of the shear rate \( (\dot{\gamma} = \Omega \cdot r / h) \), where \( h \) is the gap.
between the two disks. Then, the equation obtained is differentiated with respect to the maximum shear rate \( \dot{\gamma}_R = \Omega \cdot R / h \) using the Leibnitz' rule of differentiation of an integral to give, after rearrangement, the following expression for the shear stress in terms of the torque \( M \):

\[
\tau_R = S \left[ \frac{3}{4} + \frac{1}{4} \frac{\partial \ln(S)}{\partial \dot{\gamma}_R} \right]; \quad S = \frac{2 \cdot M}{\pi \cdot R^3}
\]

where, \( \tau_R \) is the shear stress evaluated at the shear rate \( \dot{\gamma}_R \).

The expression of the normal stress differences in terms of the thrust is obtained from the equation 3-2. First, the expression of the stress \( \sigma_{zz} \) in terms of the ambient pressure and the normal stress differences is replaced in 3-2. Then, the resultant equation is integrated by parts and finally inverted to obtain the expression of the normal stress differences in terms of the thrusts. The stress \( \sigma_{zz} \) is:

\[
-\sigma_{zz}(r) = p_0 - (\tau_{zz} - \tau_n)(r) + \int_r^R \left( \frac{\tau_{\text{op}} - \tau_n}{r} \right) dr
\]

where, \( p_0 \) is the ambient pressure and \( \tau_n \) are components of the extra stress tensor. The integration of equation 3-5 by parts gives the following expression of the thrust:

\[
F' = \pi \int_0^R (N_1 - N_2) dr; \quad F' = F - \pi \cdot R^2 \cdot p_0
\]

where, \( N_1 \) and \( N_2 \) are the first and second normal stress differences.

To invert the equation 3-5 the variable of integration, \( r \), is replaced by the shear rate \( \dot{\gamma} \) and the resultant equation differentiated with respect to \( \dot{\gamma}_R \) using the Leibnitz' rule. Accordingly, the expression of the normal stress differences in terms of thrusts is:
\[
(N_1 - N_2) = \frac{2 \cdot F'}{\pi \cdot R^2} \left[ 1 + \frac{1}{2} \frac{d \ln F'}{d \ln \dot{\gamma}_R} \right]
\] 3-6

The manufacturer of the ARES gives the following equations to calculate the flow curve and \( N_1 \), they are:

\[
\tau_{\phi z} = M \cdot K_\gamma
\] 3-8

and,

\[
N_1 = F \cdot K_Z
\] 3-9

where \( K_\gamma \) is the geometric stress constant and \( K_Z \) is the normal constant. Both parameters are determined from calibration experiments.

The parameters determined in the dynamic experiments include the storage and loss modulus. These parameters are calculated with the following equations:

\[
G' = \cos \delta \cdot \left( \frac{\tau_{\phi z}}{\gamma} \right)
\] 3-10

and,

\[
G'' = \sin \delta \cdot \left( \frac{\tau_{\phi z}}{\gamma} \right)
\] 3-11

where \( G' \) and \( G'' \) are the elastic and loss modulus, \( \delta \) the phase angle, \( \tau_{\phi z} \) the stress and \( \gamma \) the strain. According to the information provided by the manufacturer of the rheometer ARES, the stress is given by equation 3-8 and the strain by the following equation:

\[
\gamma_{\phi z} = \theta \cdot K_\gamma
\] 3-12

where \( \theta \) is the angular displacement and \( K_\gamma \) (=\( R/h \)) the strain constant that is determined by calibration for the parallel disks configuration. Here, \( R \) is the radius of the disks and \( h \) the separation between the disks.
CHAPTER IV
RESULTS AND DISCUSSION

In this chapter, the results of two MIM process steps and three characterization techniques are presented. The processes include MIM feedstocks compounding and water debinding of the water-soluble polymer. The three characterization techniques were rheology, Differential Scanning Calorimetry (DSC) and Thermogravimmetrical Analysis (TGA).

The MIM feedstock compounding results and analysis is presented in the first section. The results included the effect of blending conditions and feedstock composition on the torque evolution curves. The second section presents the experimental results of water debinding and the modeling of this process. The last three sections of this chapter present the results of the characterization of the MIM binder and feedstock. The more important result of the rheology testing was that the feedstocks did not show yield stress. In addition, the thermal characterization by DSC and TGA revealed that the metal contents influenced the melting point of the binder components and the end temperature of degradation of the feedstocks.

This chapter has five parts. The first one presents the feedstock compounding results. The second part the water debinding results and modeling. The following three parts present the results of rheology, DSC and TGA analysis and SEM microscopy studies.
of the binders and feedstocks. The effect of the feedstock composition on the processing and characterization was presented through this chapter.

4.1. Compounding of MIM feedstocks

The preparation of the feedstock is a very important step in the MIM process since the quality of the feedstock determines how the shaping and debinding processes occur. The feedstock must be homogeneous enough to permit the filling of the mold with the maximum load of metal possible and with the maximum shape stability after cooling.

In the compounding study, 316L SS were mixed with five different polymers including, HDPE, PP, LLDPE, POM and water-soluble polymer (WSP). The polymers were combined in three binders that included i) HDPE, POM and WSP. ii) PP, POM and WSP. iii) LLDPE, POM and WSP. The metal contents varied between 0 vol% to 64 vol%, accordingly to the experiments proposed in Chapter 3.

The objective of the compounding experiments was to obtain the torque-evolution-curves and determine how several variables including, temperature, metal concentration, and binder formulation affected the torque curves. The results showed that it was possible to obtain feedstocks with 64 % of metal by volume (89.0 wt%) at a mixing temperature of 180 °C and 100 rpm.

4.1.1. Torque and Temperature Evolution Curves

The typical torque and temperature evolution curves are depicted in Figure 4.1. The point of addition of each component is indicated by the arrows next to the time axis. The shape of both curves was typical of compounding done with sequential addition of components. At the beginning, the torque was zero but after adding the first polymeric component, the torque increased rapidly, reached a peak and decreased...
afterwards to a steady value greater than zero. This behavior indicated that melting occurred. The torque varied similarly upon addition of the second component. However, after adding the third component, the water-soluble polymer, the torque decreased reaching its final value without presenting peak.

Figure 4.1 also presents the temperature evolution curve. It is apparent that the stock temperature decreased upon addition of each polymeric component but rose again after the polymers melt. However, the temperature decreased more notoriously upon addition of the first binder component possibly because it was added in larger quantity than the other polymers.

4.1.2. Affect of the mixing temperature on the torque evolution curves

The different mixing temperatures influence the torque evolution curve as shown in Figure 4.2. The curves were obtained during compounding of feedstocks based on HDPE. The feedstocks 1-H to 8-H contained high-density polyethylene in proportions of 40 to 55 weight %. The metal content was 63 vol% to 64 vol%. The detailed composition was given in Table 3.6.

The feedstocks 1-H to 4-H were compounded at 150 °C while the feedstocks 5-H to 8-H at 180 °C. Figure 4.2 shows that the area under the torque-evolution-curves resulting from compounding feedstocks at 150 °C (Figure 4.2 a) was larger that the corresponding area resulting from the compounding at 180 °C (Figure 4.2 b). This difference could be attributed to the effect of temperature on the viscosity of the continuous phase. As a result, at low compounding temperature the mechanical energy required for mixing would be greater than at higher mixing temperature. The relative areas under the torque-evolution-curves of feedstocks based on HDPE are presented in Table 4.1.
Figure 4.1 Typical torque and temperature evolution curves. The arrows indicate the time of addition of the different components.

Figure 4.2 Comparison of torque evolution curves of feedstocks based on HDPE compounded at (a) 150°C and (b) 180°C. The metal content was 63 vol% and 64 vol%.
Table 4.1 Relative area under the torque evolution curves

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Temperature (°C)</th>
<th>Relative area</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-H</td>
<td>150</td>
<td>1.61</td>
</tr>
<tr>
<td>2-H</td>
<td>150</td>
<td>1.39</td>
</tr>
<tr>
<td>3-H</td>
<td>150</td>
<td>1.44</td>
</tr>
<tr>
<td>4-H</td>
<td>150</td>
<td>1.22</td>
</tr>
<tr>
<td>5-H</td>
<td>180</td>
<td>1.28</td>
</tr>
<tr>
<td>6-H</td>
<td>180</td>
<td>1.01</td>
</tr>
<tr>
<td>7-H</td>
<td>180</td>
<td>1.08</td>
</tr>
<tr>
<td>8-H</td>
<td>180</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Figure 4.3 Typical temperature evolution curve during compounding of 1-H to 4-H
Another important difference between the torque-evolution-curves at 150 °C and 180 °C is realized by observing the encircle regions B in Figures 4.2 (a) and (b). The encircle regions B reveals that the torque-evolution-curve after adding POM is different when mixing at 150 °C than when compounding at 180 °C. It is observed that after adding the second polymer (POM) to the blend at 150 °C, the torque reached a lower value than when adding POM to the blend at 180 °C for all feedstocks although torque after adding the HDPE was the same (see region A in the Figures 4.2). In addition, the torque evolved differently at low temperature than at 180 °C. At the lower mixing temperature, the torque grew continuously while in the instance of high temperature the torque stabilized very rapidly.

The different shape of the torque-evolution-curves mentioned may be attributed to either, miscibility between the POM and the PP in the melt, or shear effect due to the increased amount of mass in the compounder. Both reasons seem plausible, however. On one side, the miscibility in the melt would imply colligative effect of the POM and the PP reducing both melting temperatures. On the other side, more heat dissipation increased the mixing temperature causing melting by heat transfer. The typical temperature evolution curve of blends 1-H to 4-H, is shown in Figure 4.3.

Figure 4.2 also reveals that the torque attained at the end of compounding at 150 °C was higher than at 180 °C. This result would confirm the effect of temperature on the viscosity of the continuous phase as the dominant factor on the viscosity of the feedstocks. In the instance of the feedstocks based on HDPE, the continuous phase is the polyolefin that was present in 55 wt% approximately.
4.1.3. Affect of the rotor speed on torque and temperature evolution curves

The influence of the rotor speed on the melting behavior of binder components was studied in two compounding tests involving the proprietary binder provided by the Sponsoring Company. The feedstocks were part of the first set and corresponded to the feedstocks A and B that had a ratio of metal to binder of 2.6 by volume. These two compounds had the exact same composition being the only difference the speed of the rotors during mixing. The two torque-evolution-curves are shown in Figure 4.4.

Figure 4.4 shows that when the rotors speed was reduced from 180 RPM to 150 RPM the melting of the first binder component was hampered. This result made evident that the range of shearing rates imposed on the material during compounding, and not only the mixing temperature, determined the occurrence of melting of the blend components. This fact was pointed out elsewhere.\textsuperscript{143}

4.1.4. Affect of Metal Concentration on the Torque Evolution Curves

The concentration of metal had an important affect on the torque-evolution-curves as it is observed in Figures 4.5 to 4.7. Three feedstocks, the proprietary one, the one based on PP and the feedstocks based on LLDPE were tested. The maximum metal concentration in any of the compounds was 63\% by volume. This value corresponded to 89\% by weight.

Increasing the metal concentration raised the torque along the whole torque evolution curve. However, the area under the torque-time curve (that was assumed proportional to the mechanical power) did not grow linearly but semi-logarithmically with respect to the concentration of metal. For instance, if the volumetric concentration of metal was doubled in the compounding of feedstocks B, C and D (see Figure 4.5) the mechanical power did not double, but grew by a factor of 5.
The fitted lines showing that the area under the torque curves depended semi-logarithmically on the metal volume are shown in Figures 4.8 to 4.10. The feedstocks were B, C and D (proprietary binder), the feedstocks based on PP and those based on LLDPE. The relative area was calculated by dividing all the areas by the larger one obtained for the respective feedstock.

Figures 4.8 to 4.10 show that the semilogarithmic correlation of relative area v. metal volume fitted the data well. Therefore, it is possible to estimate the area under the torque evolution curve of a blend with different metal concentration in between that of the blends studied.

4.1.5. Binder composition and the torque evolution curves

The relation between the composition of the feedstocks and the torque-evolution-curves was determined by studying five selected points of the torque curves. The selected points are shown in Figure 4.11 and they are: The maximum torque reached after addition of component 1 (T1). The torque attained after stabilization immediately before adding component 2 (T2). The peak torque reached upon addition of component 3 (T3). The torque attained immediately before adding the third component (T4) and lastly, the torque reached at the end of mixing (T5).

The torques selected correlated with parameters that characterized the feedstock composition. The possible “composition” parameters included: i) The ratio of the mass of metal to the mass of one or various components (e.g. mM/mC1). ii) The ratio of volume of metal to the volume of one or the sum of the volumes of several components (e.g. VM/Vc1 or VM/(Vc1+ Vc2)). And, the ratio of metal surface to the volume of one or sum of the volumes of several components (e.g. AM/Vc1 or AM/(Vc1+ Vc2)). The correlation coefficient between a given characteristic torque and any of the parameters.
concentration parameters were alike. Therefore, the selection of the composition parameter was arbitrary. The ratio of the surface area of metal to the volume of one or the sum of the volumes of various components was used.

Figure 4.4 Effect of mixing speed on torque evolution curves. The arrows indicate the moment of addition of components 1, 2 and 3. The mixing temperature was 180 °C.

Figure 4.5 Torque evolution curve during compounding of feedstocks B, C and D. The mixing temperature was 180 °C and the rotational speed 180 RPM.
Figure 4.6 Torque evolution curve of feedstocks based on PP. The mixing temperature was 180 °C and the rotational speed 100 RPM.

Figure 4.7 Torque evolution curve during compounding of feedstocks based on LLDPE. The mixing temperature was 180 °C and the rotational speed 100 RPM.
Figure 4.8 Relative area v. metal volume concentration of feedstocks B, C and D. The mixing temperature was 180 °C and the rotational speed 180 RPM.

Figure 4.9 Relative area v. metal volume concentration of feedstocks based on PP. The mixing temperature was 180 °C and the rotational speed 100 RPM.
Figure 4.10 Relative area v. metal volume concentration of feedstocks based on LLDPE. The mixing temperature was 180 °C and the rotational speed 100 RPM

Figure 4.11 Characteristic torques on the typical torque-evolution-curves
Each of the characteristic torques selected correlated well with one composition variable and very poorly with others. For example, torque $T_4$ obtained while compounding feedstocks based on LLDPE and PP correlated well only with the ratio of the surface area of metal to the volume of component 3 ($A_M/V_3$). The correlation coefficient ($r^2$) was 0.94 and the standard deviation 0.33. The correlation with other composition variables gave correlation coefficients between 0.10 and 0.38. The respective standard deviations were between 1.5 and 1.7.

Table 4.2 shows the torques and the variable with which they correlated well. In addition, Figures 4-12 to 4-21 show the fitted curves to the experimental data. Tables 4.3 and 4.4 show the value of the composition variable for each feedstock based on PP (Table 4.3) and LLDPE (Table 4.4).

Table 4.2. Relation between characteristic torques and composition

<table>
<thead>
<tr>
<th>Torque</th>
<th>Feedstock</th>
<th>Correlate with</th>
<th>$r^2$</th>
<th>Stdev</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_1$</td>
<td>Based on PP</td>
<td>$A_M/V_1$</td>
<td>0.95</td>
<td>2.400</td>
</tr>
<tr>
<td>$T_2$</td>
<td></td>
<td>$A_M/V_1$</td>
<td>0.99</td>
<td>1.191</td>
</tr>
<tr>
<td>$T_3$</td>
<td></td>
<td>$A_M/(V_1+V_2)$</td>
<td>0.89</td>
<td>2.237</td>
</tr>
<tr>
<td>$T_4$</td>
<td></td>
<td>$A_M/V_2$</td>
<td>0.96</td>
<td>0.337</td>
</tr>
<tr>
<td>$T_5$</td>
<td></td>
<td>$A_M/V_{BIN}$</td>
<td>0.97</td>
<td>0.087</td>
</tr>
<tr>
<td>$T_1$</td>
<td>Based on LLDPE</td>
<td>$A_M/V_1$</td>
<td>0.99</td>
<td>0.673</td>
</tr>
<tr>
<td>$T_2$</td>
<td></td>
<td>$A_M/V_1$</td>
<td>0.98</td>
<td>0.397</td>
</tr>
<tr>
<td>$T_3$</td>
<td></td>
<td>$A_M/(V_1+V_2)$</td>
<td>0.97</td>
<td>2.984</td>
</tr>
<tr>
<td>$T_4$</td>
<td></td>
<td>$A_M/V_2$</td>
<td>0.94</td>
<td>0.412</td>
</tr>
<tr>
<td>$T_5$</td>
<td></td>
<td>$A_M/V_{BIN}$</td>
<td>0.98</td>
<td>0.354</td>
</tr>
</tbody>
</table>

Note: A stands for surface area, M refers to metal and Bin for binder, respectively.
Figure 4.12 Torque $T_1$ versus $A_{md}/V_{pp}$.

Figure 4.13 Torque $T_2$ versus $A_{md}/V_{pp}$.
Figure 4.14 Torque $T_3$ versus $A_M/(V_{PP}+V_{POM})$

$T_3 = 4.0\times10^{4} \cdot \frac{A_M}{V_{PP}+V_{POM}} + 13.3$

Figure 4.15 Torque $T_4$ versus $A_M/V_{WSP}$

$T_4 = -1.2\times10^{-5} \cdot \frac{A_M}{V_{WSP}} + 14.8$
Figure 4.16 Torque $T_5$ versus $A_M/V_{BIN}$

Figure 4.17 Torque $T_1$ versus $A_M/V_{LLDPE}$
Figure 4.18 Torque $T_2$ versus $\frac{A_W}{V_{LLDPE}}$.

Figure 4.19 Torque $T_3$ versus $\frac{A_W}{(V_{LLDPE}+V_{POM})}$.
Figure 4.20 Torque $T_4$ versus $\frac{A_M}{V_{WSP}}$

Figure 4.21 Torque $T_5$ versus $\frac{A_M}{V_{BIN}}$
Table 4.3 Composition of feedstocks that corresponds with characteristic torques (PP)

<table>
<thead>
<tr>
<th>Torque</th>
<th>Feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sequence</td>
</tr>
<tr>
<td>T₁ and T₂</td>
<td>Aₘ/Vₚₚ</td>
</tr>
<tr>
<td></td>
<td>Aₘ/(Vₚₚ+Vₚₒₘ)</td>
</tr>
<tr>
<td>T₃</td>
<td>Sequence</td>
</tr>
<tr>
<td></td>
<td>Aₘ/Vₚₒₘ</td>
</tr>
<tr>
<td>T₄</td>
<td>Sequence</td>
</tr>
<tr>
<td></td>
<td>Aₘ/Vₚₒₘ</td>
</tr>
<tr>
<td>T₅</td>
<td>Sequence</td>
</tr>
<tr>
<td></td>
<td>Aₘ/Vₜᵢₙ</td>
</tr>
</tbody>
</table>

Table 4.4 Composition of feedstocks that corresponds with characteristic torques (LLDPE)

<table>
<thead>
<tr>
<th>Torque</th>
<th>Feedstock</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sequence</td>
</tr>
<tr>
<td>T₁ and T₂</td>
<td>Aₘ/Vₚₚ</td>
</tr>
<tr>
<td></td>
<td>Aₘ/(Vₚₚ+Vₚₒₘ)</td>
</tr>
<tr>
<td>T₃</td>
<td>Sequence</td>
</tr>
<tr>
<td></td>
<td>Aₘ/Vₚₒₘ</td>
</tr>
<tr>
<td>T₄</td>
<td>Sequence</td>
</tr>
<tr>
<td></td>
<td>Aₘ/Vₚₒₘ</td>
</tr>
<tr>
<td>T₅</td>
<td>Sequence</td>
</tr>
<tr>
<td></td>
<td>Aₘ/Vₜᵢₙ</td>
</tr>
</tbody>
</table>

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4.1.6. Dispersion of metal during compounding

The dispersion of the metal in the polymeric matrix was observed at three times during the compounding. Samples were taken before adding component 2 (POM), before adding component 3 (water-soluble polymer) and at the end of mixing as shown in Figure 4.22. The feedstocks studied were the 3-P, based on polypropylene resin, and 3-L, based on LLDPE, both with 64 vol% of metal. The pieces of compound taken from the Brabender were cryogenically fractured after immersion in liquid nitrogen.

Figure 4.23 shows two micrographs of the metal and polypropylene blend after the mixing torque stabilized. The ratio of resin to metal is 0.0522 by weight or 0.427 by volume. It is observed that the metal is well dispersed in the PP matrix, given the large volumetric ratio of the polyolefin resin. No agglomerates are visible in neither Figure 4.23 (a) nor (b).

Figure 4.24 depicts two micrographs of the metal blended with polypropylene and POM. The ratio of POM and PP to metal is 0.0583 or 0.461 by volume. The micrographs were taken after the stabilization of the torque upon adding POM. The micrographs show no agglomeration of the metal.

Figure 4.25 shows the micrograph of the final feedstocks obtained after adding the water-soluble polymer. The micrographs show no agglomeration of metal particles.

Figures 4.23 to 4.25 reveal that the metal particles were always surrounded by the binder and that no agglomerates are observed. In some of the micrographs, it is even possible to see the dispersed particles behind the layer of polymer left after removal of large particles upon fracture. See for instance the encircled regions in Figure 4.23 (a) and (b), Figure 4.24 (a) and 4.25 (a).
Figures 4.26, 4.27 and 4.28 show the micrographs of the feedstock based on LLDPE with 64 vol% of metal. It is apparent that the metal particles did not agglomerate when LLDPE was the only polymer present. Similarly, the metal did not agglomerate after adding either POM or water-soluble polymer. The ratios of LLDPE to metal and of the sum of the LLDPE and POM to metal were 0.044 by weight (0.363 by volume) and 0.0506 by weight (0.398 by volume), respectively.

Figures 4.26 to 4.28 show that there is no agglomeration of metal particles. The circles in Figures 4.26 to 4.28 enclose metal particles behind binder layers left after removal of particles during fracture. It is apparent that the small particles were not separated by the binder layer from the big particle that was removed during fracture. Then, it is clear that there is no agglomeration of metal particles during compounding.

![Graph showing torque over time](image)

**Figure 4.22 Points of sampling for SEM during compounding**
Figure 4.23 Micrographs of a composite of metal and polypropylene resin obtained during compounding (a) at low magnification, (b) at larger magnification
Figure 4.24 Micrographs of a composite of metal, polypropylene resin and POM obtained during compounding (a) at low magnification, (b) at larger magnification.
Figure 4.25 Micrographs of the feedstock based on PP, 3-P, at the end of compounding:
(a) at low magnification, (b) at larger magnification.
Figure 4.26 Micrographs of a composite of metal and LLDPE resin obtained during compounding (a) at low magnification, (b) at larger magnification
Figure 4.27 Micrographs of a composite of metal, LLDPE resin and POM obtained during compounding (a) at low magnification, (b) at larger magnification
Figure 4.28 Micrographs of the feedstock based on LLDPE, 3-L at the end of compounding (a) at low magnification, (b) at larger magnification.
4.2. Water debinding

The water debinding was the operation of extraction of the water-soluble polymer (WSP) by dissolving it in water. Because of this process, porous formed inside the part at the sites where the WSP was situated. This porosity will play an important role in the subsequent thermal debinding because it will provide the gases, resulting from the thermal decomposition, a route to escape from the solid avoiding the buildup of stresses, deformation and distortion.

This section presents the results of the water debinding studies using two flow configurations that consisted on rotating cylinders submerged in water and on water jet impingement on MIM parts. The purpose of using these flow configurations was to reduce the ratio of external to internal resistance to mass transfer. In this way the experimental results would give information on the transport of mass inside the solid exclusively and not the combined effects of external and internal mass transport.

In this section, the results concerning each of the flow configurations are presented according to the following plan. First, the extraparticle mass transport is evaluated using a flow model, an equation to calculate the heat transfer coefficient and an analogy between heat and mass transfer. Then the experimental results are presented and finally, a mathematical model of debinding including simplifications based on the experimental results is proposed and developed.

4.2.1. Debinding studies with rotating cylinders submerged in water

The experimental setup using molded-cylinders coated with epoxy resin was presented in Chapter 3 and was shown again in Figure 4.29. The molded MIM cylinders had a diameter of 5.5 mm and a length of 25 mm. The cylinders were cut to various lengths between 2 and 22 mm to have more samples available for the debinding tests.
The sides and the bottom end of the cylinders were coated with epoxy resin to guarantee one-dimensional diffusion along the cylinders’ axis. The resultant outside diameter of the coated cylinders was 6.5 mm. The MIM feedstock used to make the cylinders contained 63 vol% of metal and the binder had 50% of water-soluble polymer equivalent to 3 wt% based on the mass of the feedstock.

The experiments consisted in rotating the cylinders while submerged in water as shown in section 3.3.3.1. The resistance to mass transport outside the samples was reduced by keeping the concentration of the water-soluble polymer close to zero at the exposed surface of the cylinders. To accomplish this, the water was fed and removed continuously from the tank at a flow rate of 20 ml·min⁻¹ and the cylinders rotated at 200 rpm.

4.2.1.1. Evaluation of the extraparticle mass transport

The evaluation of the mass transport of the water-soluble polymer from the exposed surface of the cylinders toward the bulk of the water required the adoption of a simplified flow model. This model was based on two conditions: i) The cylinder was at rest and the water flowed around it, and ii) the water impinged on the exposed surface as a free unconfined water jet. This flow model is depicted in Figure 4.30.

The first condition was proposed because of the relativity of motion between the cylinder and the water permitted to assume that the cylinder was at rest and the water past it. The second condition was stated to establish a flow situation that had been studied and for which there was an equation for the calculation of the heat transfer coefficient. Even more, the convective coefficient calculated gave a conservative value because of the implicit assumption that only one cylinder was moving in quiescent water. However, since three cylinders were rotating simultaneously during the
experiment, the turbulence was higher than assumed in the model and if the extraparticle transport calculated was high, in the real situation it would be even higher.

To calculate the mass transfer coefficient, the Chilton-Colburn analogy between heat and mass transfer was used. This analogy is accurate in situations in which the boundary layer around the solid is not distorted because of high rates of heat or mass transfer\textsuperscript{144}. This condition was satisfied in the debinding experiments as the concentration of water-soluble polymer (WSP) in the solid was low. The expression of the Chilton-Colburn analogy is:

\[ Nu \cdot Pr^{-1/3} = Sh \cdot Sc^{-1/3} \]  \hspace{1cm} (4-1)

where \( Nu \) is the Nusselt number, \( Pr \) is the Prandtl number, \( Sh \) is the Sherwood number and \( Sc \) is the Schmidt number. These nondimensional parameters are defined as follows:

\[ Nu_d = \frac{h \cdot d}{k_w} \]  \hspace{1cm} (4-2)

\[ Pr = \frac{\mu_w \cdot C_w}{k_w} \]  \hspace{1cm} (4-3)

\[ Sh_d = \frac{k \cdot d}{c \cdot D_{WSP,w}} \]  \hspace{1cm} (4-4)

\[ Sc = \frac{\mu_w}{\rho_w \cdot D_{WSP,w}} \]  \hspace{1cm} (4-5)

where, \( h \) is the convective heat transfer coefficient between the solid part and the water, \( d \) is the diameter of the cylinder and when used as subscript indicates that the calculations are based on the diameter \( d \). \( k_w, C_w, \rho_w, \mu_w \) are the thermal conductivity, heat capacity, density and viscosity of water at the debinding temperature, respectively.
k is the convective mass transfer coefficient in the water, $D_{WSP,w}$ is the diffusion coefficient of the water-soluble polymer (WSP) in water and $c$ is the molar concentration of the solution composed of WSP and water.

Figure 4.29 Cylinders for water debinding test

![Diagram](image.png)

Figure 4.30 Water debinding with the submerged rotating cylinder. (a) Experimental situation with the cylinder moving relative to the water. (b) In the flow model, the cylinder is at rest and the water flows around it. The water impinges on the exposed surface of the cylinder as a free and unconfined jet.
The Nusselt number was calculated using the empirical equation for the flow situation depicted in Figure 4.30 (b):

\[ \text{Nu}_d = 0.278 \cdot \text{Re}_d^{0.633} \cdot \text{Pr}^{1/3} \] 4-6

where \( \text{Re}_d \) is the Reynolds number calculated using the diameter of the cylinder. The correlation was taken from the heat transfer literature\(^{145} \). The Reynolds number was computed using the following definition:

\[ \text{Re}_d = \frac{d \cdot \nu \cdot \rho_w}{\mu_w} \] 4-7

where, \( \nu \) is the velocity of the cylinder relative to the water.

The properties of the water at 40 °C are given in Table 4.5 along with the values of the nondimensional parameters. Two notes are that the velocity of the cylinders relative to the water was calculated using the frequency of 200 rpm and the mean distance from the shaft to the part was 5 cm. The mass transfer coefficient required the molar concentration (\( c \) in equation 4-4), which was taken as that of the water because of the low concentration of the water-soluble polymer.

The nondimensional parameters and the coefficients of heat and mass transport are shown in Table 4.5. The results indicated that the mass transfer of water-soluble polymer (WSP) outside the cylinder was very high compared to the total amount of WSP in the largest part (55 mg). In other words, the 55 mg would be removed in 6 hundredths of a second. Therefore, the extraparticle mass-transfer did not control the process of debinding of the water-soluble polymer and hence, the experimental results gave information on the intraparticle diffusion process exclusively.
4.2.1.2. Experimental results

The experimental results of water debinding from rotating cylinders are presented in Figure 4.31 and Figure 4.32. Figure 4.31 presents the weight percentage of water-soluble polymer (WSP) extracted from the part against the debinding time for parts of four different lengths. Similarly, Figure 4.32 shows the weight percentage of WSP extracted against the square root of the debinding time for four part lengths. The percentages are based on the total amount of water-soluble polymer present in the part.

Figure 4.31 indicates that the rate of WSP debinding decreased as time increased for all the samples. Therefore, the rate of debinding was fast at the beginning but decreased at longer times of contact. The wt% of WSP removed at any given debinding time decreased with increasing part length because the amount of WSP was greater in the longer parts.

Figure 4.32 shows that the transport inside the particle controlled the debinding since the experimental points fitted well with straight lines. This behavior is typical of systems in which diffusion is the controlling step of the whole extraction process. In addition the good correlation indicated that the diffusivity was approximately constant.

These results may be interpreted by analyzing the processes involved in the extraction of the water-soluble polymer (WSP) at any given time greater than zero. The three steps occurring simultaneously at different locations in the MIM molded part were: i) Diffusion of water inside the material through the previously open pores. ii) Interaction of water with the solid WSP creating a liquid hydrated WSP (hWSP) that was much less mobile than the small water molecules, and iii) diffusion of the hWSP out though the porous media toward the exposed surface of the cylinder. According to the experimental results presented in Figure 4.32, the last stage controlled the whole
extraction process kinetics. In other words, the experimental results indicated that the rate limiting process was the transport of the hWSP rather than their dissolution or the diffusion of the water in.

Figure 4.31 Weight percentage of water-soluble polymer removed with respect to debinding time

Figure 4.32 Weight percentage of water-soluble polymer removed with respect to the square root of the debinding time
Table 4.5 Parameters of the flow of water around the cylinder at 40 °C

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density of water (kg·m⁻³)</td>
<td>992.2</td>
<td>Experimental¹⁴⁶</td>
</tr>
<tr>
<td>Viscosity of water (Pa·s)</td>
<td>6.35x10⁻⁴</td>
<td>Experimental¹⁴⁶</td>
</tr>
<tr>
<td>Heat capacity (J·kg⁻¹·K⁻¹)</td>
<td>4177.3</td>
<td>Experimental¹⁴⁶</td>
</tr>
<tr>
<td>Thermal conductivity of water (w·m⁻¹·K⁻¹)</td>
<td>0.627</td>
<td>Experimental¹⁴⁶</td>
</tr>
<tr>
<td>Diameter of the cylinder</td>
<td>6.5 mm</td>
<td>Measured</td>
</tr>
<tr>
<td>Reynolds number</td>
<td>10300</td>
<td>Equation 4-7</td>
</tr>
<tr>
<td>Prandtl number</td>
<td>4.4</td>
<td>Equation 4-3</td>
</tr>
<tr>
<td>Nusselt number</td>
<td>157.8</td>
<td>Equation 4-2</td>
</tr>
<tr>
<td>Heat transfer coefficient (h)</td>
<td>15300 W/(m²·K)</td>
<td>h=νu_d*k_w/d</td>
</tr>
<tr>
<td>Diffusivity coefficient (D_{WSP,w}) m²·s⁻¹</td>
<td>8x10⁻¹¹</td>
<td>Estimated using the Wilke-Cheng method¹⁴⁷</td>
</tr>
<tr>
<td>Molar concentration (c) (kmol·m⁻³)</td>
<td>55.1</td>
<td>Calculated</td>
</tr>
<tr>
<td>Schmidt number</td>
<td>8230</td>
<td>Equation 4-4</td>
</tr>
<tr>
<td>Sherwood number</td>
<td>1950</td>
<td>Equation 4-5</td>
</tr>
<tr>
<td>Mass transfer coefficient</td>
<td>1.3x10⁻³ kmol/(m²·s)</td>
<td>K_w=Sh_d·c·D_{WSP,w}·µ_w⁻¹</td>
</tr>
<tr>
<td>Rate of transport of water-soluble polymer in the boundary layer</td>
<td>8540 mg/s</td>
<td>Estimated</td>
</tr>
</tbody>
</table>
4.2.1.3. Modeling of the debinding process

A model of the debinding process may be formulated using the conservation of hydrated water-soluble polymer (hWSP) and solid water-soluble polymer (WSP) in the molded part. Such a model would require, besides the kinetic equation of WSP hydration, a description of the transport of the hWSP inside the porous part.

The mass transport of the hydrated water-soluble polymer is a complex phenomenon because of the combination of several mechanism of mass transport and the effect of geometrical intricacies of the pores. Therefore, to simplify the model, the concept of “effective diffusivity” is used. The effective diffusivity would account for the porosity, the shape and diameter of the pores inside the solid and would allow picturing the heterogeneous media as a continuum.

According to the previous discussion, the model of the debinding of water-soluble polymer is given by the conservation equations of hydrated WSP, hWSP, and solid WSP. The control volume is represented in Figure 4-33 along with the real concentration profiles of the hydrated WSP, the solid WSP and the water.

The first equation of conservation of the hydrated WSP is stated as:

\[ \frac{\partial (\varepsilon_s c_{hWSP})}{\partial t} = D_{eff} \frac{\partial^2 c_{hWSP}}{\partial z^2} + r_{hWSP} \rho_s \]

where, \( \varepsilon_s \) is the porosity of the solid after hydration of the water-soluble polymer (WSP) has started and is expressed in \( m^3_{\text{liquid}}/m^3_{\text{Feedstock}} \). \( c_{hWSP} \) is the molar concentration of hydrated water-soluble polymer expressed in \( \text{kmol}_{hWSP}/m^3_{\text{liquid}} \). \( D_{eff} \) is the effective diffusivity of the hydrated WSP in the porous solid expressed in \( m^3_{\text{liquid}}/(m_{\text{Feedstock}} \cdot \text{s}) \). \( r_{hWSP} \) is the rate of generation of hWSP by hydration of solid WSP expressed in \( \text{kmol}_{hWSP}/(kg_{\text{Feedstock}} \cdot \text{s}) \). \( \rho_s \) is the density of the feedstock in \( (kg_{\text{Feedstock}}/m^3_{\text{Feedstock}}) \). The
terms in the equation are given in units of moles of hWSP per unit volume of feedstock and per second. The convective term did not appear in equation 4-8 because the concentration of hWSP in water is presumed to be low as expected from its low concentration in the solid.

The second equation of the model is the balance of solid water-soluble polymer. This equation is:

\[ \frac{\partial (c_{WSP})}{\partial t} = -r_{WSP} \rho_s \]

where \( c_{WSP} \) is the molar concentration of solid water-soluble polymer (before hydration) given in \( \text{kmol}_{WSP}/\text{m}^3_{\text{Feedstock}} \), \( r_{WSP} \) is the rate of hydration of expressed in \( \text{kmol}_{WSP}/(\text{kg}_{\text{Feedstock}} \cdot \text{s}) \), and \( r_{WSP} = r_{hWSP} \). \( \rho_s \) is the density of the feedstock in \( \text{kg}_{\text{Feedstock}}/\text{m}^3_{\text{Feedstock}} \). All the terms in the equation are given in units of moles of WSP per unit volume of feedstock and per second.

The initial and boundary conditions are:

i) For equation 4-8:

**IC:** \( at \quad t = 0, \quad 0 \leq z \leq L, \quad c_{hWSP} = c_{hWSP}^0 \)

**BC1:** \( at \quad t > 0, \quad z = L, \quad \frac{\partial c_{hWSP,L}}{\partial z} = 0 \)

**BC2:** \( at \quad t > 0, \quad z = 0, \quad c_{hWSP} = c_{hWSP,0} \)

ii) For equation 4-9:

**IC:** \( at \quad t = 0, \quad z = 0, \quad c_{WSP} = c_{WSP}^0 \)

where \( c_{WSP}^0 \) and \( c_{hWSP}^0 \) are the initial molar concentration of WSP and hWSP, respectively. \( c_{hWSP,0} \) and \( c_{hWSP,L} \) are the molar concentrations of hydrated WSP at \( z=0 \) and \( z=L \), respectively.
The model expressed in the previous equations can be simplified according to the experimental results previously discussed. Specifically, if the ratio of the rate of hydration to the rate of diffusion of the hydrated water-soluble polymer were large, a core of unhydrated WSP would exist in the interior of the part with a boundary that recedes at slow rate. This assumption permits the removal of the transient term and the reaction term in equation 4-8, and the removal of equation 4-9 altogether. This simplification is known as the pseudo-steady-state approximation. Similarly, the existence of a core of reducing dimension gave the name of shrinking-core model to this representation.

The simplified physical situation is shown at the top of Figure 4.34. Two domains are clearly distinguished. One is the shrinking-core, named Zone I, containing unhydrated water-soluble polymer in solid phase trapped in the MIM feedstock. The other domain is a porous media containing a solution of water and hydrated WSP in the pores. This zone is named Zone II. This model is called the shrinking unhydrated core model.

With the simplifications mentioned above, the new model is given by the differential equation for diffusion of the hydrated water-soluble polymer in Zone II as:

$$D_{\text{eff}} \frac{\partial^2 c_{\text{hWSP}}}{\partial z^2} = 0$$  \hspace{1cm} 4-14

with the following boundary conditions

BC1: \hspace{1cm} at \hspace{0.5cm} z = 0, \hspace{0.5cm} c_{\text{hWSP}} = c_{\text{hWSP,0}} = 0 \hspace{1cm} 4-15

BC2: \hspace{1cm} at \hspace{0.5cm} z = B, \hspace{0.5cm} c_{\text{hWSP,B}} = c_{\text{hWSP,eq}} \hspace{1cm} 4-16

where $D_{\text{eff}}$ is the effective diffusivity of the hydrated water-soluble polymer in the porous solid (m$^3$liquid/(mFeedstock·s)). $c_{\text{hWSP}}$ represents the molar concentration of hWSP in the
liquid inside the pores in zone II (kmol\textsubscript{hWSP}/m\textsuperscript{3}\textsubscript{liquid}). B is the position of the boundary of the shrinking core. \(c_{\text{hWSP},0}\) is the concentration of the hWSP at the position of \(z=0\). \(c_{\text{hWSP},B}\) is the molar concentration of the hydrated water-soluble polymer at the shrinking-core boundary and is equal to \(c_{\text{hWSP,eq}}\), which is the molar concentration of hWSP (dissolved in water) in phase equilibrium with the solid WSP.

The boundary condition 4-15 was proposed because of the results of the analysis of the mass transport outside the part. That is, the mass transport of hWSP outside the part is so fast that the concentration at the exposed surface of the cylinder is practically zero. The second boundary condition (4-16) corresponds to the impermeability of the epoxy resin to water at the bottom of the sample.

Equation 4-14 may be integrated twice to obtain the concentration profile in zone II:

\[
c_{\text{hWSP}}(z) = \frac{z}{B} c_{\text{hWSP,eq}}
\]

and this linear profile is depicted in Figure 4-27.

![Figure 4-33 Actual concentration profiles of unhydrated and hydrated water-soluble polymer in the cylinders](image)
4.2.1.4. Shrinking unhydrated core model

The velocity of the receding border line between the core and zone II gives an equation for the evaluation of the diffusivity of the hydrated water-soluble polymer (hWSP). The mass balance of water-soluble polymer (WSP) in Zone I gives the following equation:

$$A \cdot c_{WSP} \cdot M_{WSP} \cdot \frac{dB}{dt} = -J_{hWSP} \bigg|_{z=B} \cdot A \cdot M_{WSP}$$

In this equation, $A$ is the cross-sectional area perpendicular to the direction of mass flow of hWSP. $M_{WSP}$ is the molecular mass of WSP. $J_{hWSP}$ is the molar flux of hydrated WSP at the boundary between zones I and II, expressed in kmol$_{hWSP}/$(m$^2_{Feedstock}$·s).
Expressing the molar flux of hWSP with the Fick’s law in equation 4-18, the following is obtained:

\[
c_{\text{WSP}} \cdot \frac{dB}{dt} = D_{\text{eff}} \cdot \frac{dc_{\text{WSP}}}{dz} \bigg|_{z=B}
\]

4-19

The derivative on the right-hand-side of equation 4-19 can be evaluated from equation 4-17. Then, equation 4-19 becomes:

\[
B \cdot \frac{dB}{dt} = D_{\text{eff}} \cdot \frac{c_{\text{hWSP, eq}}}{c_{\text{WSP}}}
\]

4-20

By separating variables and integrating the equation, the result is:

\[
B(t) = \sqrt{2 \cdot D_{\text{eff}} \cdot t} \cdot \sqrt{\frac{c_{\text{hWSP, eq}}}{c_{\text{WSP}}}}
\]

4-21

The weight percent of water-soluble polymer removed is expressed in term of the initial mass of WSP and the mass at time t as:

\[
100 \varphi^t = 100 \frac{m^0_{\text{WSP}} - m^t_{\text{WSP}}}{m^0_{\text{WSP}}}
\]

4-22

where, \( \varphi^t \) is the mass fraction of the WSP removed after a debinding time of t. The mass of solid WSP at time t, \( m^t_{\text{WSP}} \), is given by the difference between the initial mass and what has been removed at t. Thus,

\[
m^t_{\text{WSP}} = m^0_{\text{WSP}} - m^t_{\text{WSP, removed}}
\]

4-23

The last term in 4-23 may be expressed in terms of B based on geometric arguments as:

\[
m^t_{\text{WSP, removed}} = c^0_{\text{WSP}} \cdot A \cdot B \cdot M_{\text{WSP}}
\]

4-24

Equation 4-24 gives the amount of WSP that is not in the solid anymore because of dissolution and transport. Then, equation 4-22 becomes:
\[
100\varphi_t = 100 \frac{m_{WSP}^0}{m_{WSP}^0} - \left(\frac{m_{WSP}^0 - c_{WSP}^0 \cdot A \cdot B \cdot M_{WSP}}{m_{WSP}^0}\right) 
\]

Simplifying \(m_{WSP}^0\) and replacing the expression of \(B\) the following equation is obtained:

\[
100\varphi_t = 100 \cdot \sqrt{2 \cdot D_{eff} \cdot \frac{c_{hWSP,eq}}{c_{WSP}^0} \cdot \frac{\sqrt{t}}{L}} \quad 4-26
\]

This equation makes clear that a plot of 100\(\varphi_t\) versus the ratio of the square root of the debinding time to the length of the part would give a straight line. Such a plot is shown in Figure 4-35. The slope is given by:

\[
slope = 100 \cdot \sqrt{2 \cdot D_{eff} \cdot \frac{c_{hWSP,eq}}{c_{WSP}^0}} \quad 4-27
\]

Equation 4-27 shows that the slope of the fitted line includes the initial molar concentration of WSP \((c_{WSP}^0)\), the molar concentration of hWSP in equilibrium with the solid WSP \((c_{hWSP,eq})\) and the effective diffusivity \(D_{eff}\) of hydrated water-soluble polymer through the porous metal/polymer matrix (Zone II). In order to calculate the effective diffusivity of the hWSP, in the porous section of the part (Zone II), the equilibrium concentration of hWSP with solid WSP must be found. This equilibrium concentration was calculated by the personnel at the Sponsoring Company. The value was 5.92x10^{-2} kmol\(hWSP/m^3_{\text{liquid}}\) or 919.5 kg\(hWSP/m^3_{\text{liquid}}\). With this information and the slope of the line presented in Figure 4-35 that is 13.303 wt%·mm·min^{-1/2}, the effective diffusivity is calculated as:

\[
D_{eff} = \frac{(slope)^2}{1.2 \times 10^{12} \cdot \frac{c_{WSP}^0}{c_{hWSP,eq}}} = 3.6 \times 10^{-11} \frac{m^2}{s} \quad 4-28
\]

where, the number in the denominator is a conversion factor to convert the units of the slope to \(m\cdot s^{-1/2}\).
This diffusivity obtained is of the same order of magnitude as other data reported in the MIM literature\textsuperscript{148, 149}.

The effective diffusivity can be used to estimate the "tortuosity factor". The definition of the effective diffusivity, used in the development of the previous equations, may be expressed including the tortuosity and the porosity as follows:

\[ D_{\text{eff}} = \frac{\varepsilon_s}{\tau} D_{\text{hWSP, w}} \]  \hspace{1cm} 4-29

where, \( \varepsilon_s \) is the porosity of the solid after hydration of the WSP has started and can be expressed in m\(^3\) liquid/m\(^3\) Feedstock, \( \tau \) is the tortuosity factor expressed in m\(^2\) liquid/m\(^2\) Feedstock and \( D_{\text{hWSP, w}} \) is the diffusivity of the WSP in water (given in Table 4.5 and expressed in m\(^2\) liquid·s\(^{-1}\)). The tortuosity factor was originally defined as the ratio of the length of the diffusion path of the molecules to the length of porous solid\textsuperscript{150-153}. This definition is based on the parallel pores model that assumes that the pores are sinuous but parallel\textsuperscript{150}.

If the porosity of the MIM feedstock, after the debinding has begun, is taken as the porosity based on the formulation of the feedstock, the tortuosity would be:

\[ \tau = \varepsilon_s \cdot \frac{D_{\text{hWSP, w}}}{D_{\text{eff}}} = 0.173 \cdot \frac{8.0 \times 10^{-11}}{3.6 \times 10^{-11}} = 0.318 \]  \hspace{1cm} 4-30

The tortuosity obtained is less than one, which is surprising given its definition. However, in the author’s opinion, this value must be taken as a numerical factor since the porous structure is apparently far from the parallel porous model, as revealed in Figure 4.95 in section 4.5.4. It is also important to realize that the calculation of the tortuosity is based on experimental mass transfer data. Therefore, the pore structure and the diffusion mechanisms determine the value of tortuosity. In addition, in previous
work, tortuosity factors of less than one have been obtained\textsuperscript{154}. This outcome was explained as the consequence of surface diffusion\textsuperscript{150}.

It is important to mention, that the pores inside the debound MIM feedstock must be arranged more complexly than in a simple parallel pores structure. This is supported by the experimental results that indicate that there is a maximum limit of WSP removable. In other words, there are no pores reaching every region containing WSP in the molded parts. The structure of the porosity in MIM feedstock parts is the result of the interaction between the metal particles and the polymers contained in the binder. The metal particles and the polymers may arrange in many ways. However, the value calculated could be used in the modeling of the initial stages of thermal debinding that follows the water debinding in the MIM process studied.

Figure 4.35 Experimental data fitted to equation 4-26
4.2.2. Debinding studies with water jet

The debinding experiments with water jet were conducted impinging MIM samples arranged in two positions relative to the water jet. In the first set up, the water jet impacted the molded disks perpendicularly to its larger surface as shown in Figure 4.36. In the second arrangement, the samples were impacted on one of the smallest sides to determine the penetration of the diffusing front as depicted in Figure 4.37.

Figure 4.36 water jet impinging on the larger surface of the molded disk

Figure 4.37 Penetration experiment

The diameter of the disks was 25 mm and their thickness was 1 mm. The samples for penetration were cut out from disks. Their length was 20 mm and its width 10 mm. The disks were glued to glass plates while the samples for the penetration tests were sandwiched between rubber sheets and metal plates. The three sides of the samples for penetration were coated with epoxy resin to force the one-dimensional diffusion.
The purpose of the debinding experiments with water jet was to reduce the resistance to mass transport outside the samples. To accomplish this, two conditions were fulfilled. First, the water that impinged on the samples was free of water-soluble polymer and second, the jet had enough speed as to attain high mass transfer coefficient. The calculation of the extraparticle mass transport is presented next.

4.2.2.1. Evaluation of the mass transport outside the samples

The evaluation of the extraparticle mass transport is done using the empirical equation for heat transfer and the Chilton-Colburn analogy between heat and mass transport. The analogy was expressed in the equation 4-1. It included the nondimensional numbers defined in equations 4-2 to 4-5.

To calculate the Nusselt number, the following empirical equation was used:

\[ Nu = 1.648 \cdot Re^{1/2} \cdot Pr^{1/3} \] 4-31

The Reynolds number was calculated with the nozzle diameter. The Nusselt number was evaluated using the properties of water at 40 °C and a flow rate of 3.12 cm³·s⁻¹. The results of the calculations are presented in Table 4.6.

The results indicate that the extraparticle mass transport was fast and that the extraction rate was controlled by the intraparticle phenomenon. Therefore, the experiments gave information on the mass transfer inside the particles, exclusively.

4.2.2.2. Experimental results of water jet impingement normal to the samples

In the series of experiments with water jet impinging normal to disks the presence of hydraulic jump was determined by direct observation. The hydraulic jump was identified by the abrupt increase in the film thickness that reduced the average film velocity and hence, the heat transfer coefficient. The typical profile of the water in the experiments conducted is shown in Figure 4.38.
Table 4.6 Calculated parameters of the water jet impinging at 40 °C

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water properties</td>
<td>Same as in Table 4.5</td>
<td>Experimental\textsuperscript{144}</td>
</tr>
<tr>
<td>Diameter of the nozzle</td>
<td>2.012 mm</td>
<td>Measured</td>
</tr>
<tr>
<td>Reynolds number</td>
<td>3000</td>
<td>Equation 4-7</td>
</tr>
<tr>
<td>Prandtl number</td>
<td>4.4</td>
<td>Equation 4-3</td>
</tr>
<tr>
<td>Nusselt number</td>
<td>145.28</td>
<td>Equation 4-2</td>
</tr>
<tr>
<td>Heat transfer coefficient (h)</td>
<td>45300 W/(m\textsuperscript{2}·K)</td>
<td>h=\textit{Nu}_d^*k_w/d</td>
</tr>
<tr>
<td>Diffusivity coefficient (D_{hWSP,w}) m\textsuperscript{2}·s\textsuperscript{-1}</td>
<td>8x10\textsuperscript{-11}</td>
<td>Wilke-Cheng\textsuperscript{151}</td>
</tr>
<tr>
<td>Molar concentration (c) (kmol·m\textsuperscript{-3})</td>
<td>55.1</td>
<td>Calculated</td>
</tr>
<tr>
<td>Schmidt number</td>
<td>8226.5</td>
<td>Equation 4-4</td>
</tr>
<tr>
<td>Sherwood number</td>
<td>1823.5</td>
<td>Equation 4-5</td>
</tr>
<tr>
<td>Mass transfer coefficient</td>
<td>3.9x10\textsuperscript{-3} kmol/(m\textsuperscript{2}·s)</td>
<td>\textit{K_w}=\textit{Sh}<em>d·c·D</em>{WSP,w}·\mu_w\textsuperscript{-1}</td>
</tr>
<tr>
<td>Rate of transport of water-soluble polymer in the boundary layer</td>
<td>3400 mg/s</td>
<td>Estimated</td>
</tr>
</tbody>
</table>

Figure 4.38 Water profile on the disks showing the hydraulic jump
The causes of the hydraulic jump in jet impinging include the presence of obstacles to the flow along the flow path and low jet speed. In the experiments conducted, the jet speed could not be changed and no visible obstacles were present along the flow path. Therefore, no changes to the experimental setup were possible and hence, the hydraulic jump was unavoidable.

The first series of experiments were conducted with the feedstocks based on HDPE. The experiments were intended to find the dependence of the debound mass with respect to the temperature. The flow rate of water impinging the samples was 3.01 g/s, the temperatures were 30 °C, 40 °C and 50 °C. The results are presented in Figures 4.39 to 4.46 along with the fitted curve of the water-soluble polymer removed expressed in weight percentage as function of the debinding time.

![Figure 4.39 Water debinding of feedstock 1-H at different temperatures by jet impinging at 30 °C, 40 °C and 50 °C](image-url)
Figure 4.40 Water debinding of feedstock 2-H at different temperatures by jet impinging at 30 °C, 40 °C and 50 °C.

Figure 4.41 Water debinding of feedstock 3-H at different temperatures by jet impinging at 30 °C, 40 °C and 50 °C.
Figure 4.42 Water debinding of feedstock 4-H at different temperatures by jet impinging at 30 °C, 40 °C and 50 °C.

Figure 4.43 Water debinding of feedstock 5-H at different temperatures by jet impinging at 30 °C, 40 °C and 50 °C.
Figure 4.44 Water debinding of feedstock 6-H at different temperatures by jet impinging at 30 °C, 40 °C and 50 °C

Figure 4.45 Water debinding of feedstock 7-H at different temperatures by jet impinging at 30 °C, 40 °C and 50 °C
Figure 4.46 Water debinding of feedstock 8-H at different temperatures by jet impinging at 30 °C, 40 °C and 50 °C

Figure 4.47 Weight percent extracted from disks at 32 min of debinding
Figures 4.39 to 4.46 show that the amount of WSP debound varied non-linearly with respect to time. More precisely, the data followed a power law with exponent less than one indicating that the rate of debinding decreased with respect to time. In addition, the Figures 4.39 to 4.46 also reveal that the rate of debinding was higher at higher temperature.

The effect of the temperature on the amount debound is shown in Figure 4.47 where the amount debound at the longest debinding time was plotted against the kind of feedstock. It is apparent that the amount debound increased with increasing temperature. It is also observed that the feedstocks that lost more weight had more water-soluble polymer to binder ratio.

4.2.2.3. Experimental results of penetration experiments

The penetration experiments were conducted on samples of the feedstocks 1-L, 2-L and 3-L. The mass lost by each sample is presented in Table 4.7 and Figure 4.48. The non-dimensional concentration profiles are presented in Figure 4.49.

The Table 4.7 reveals that the samples lost more mass at longer debinding times and less metal concentration. For instance, the feedstock 1-L lost more mass at 128 min than at 32 minutes of debinding. In addition, the feedstock 1-L lost more mass than feedstocks 2-L or 3-L at the same debinding time. Feedstock 1-L had a contents of 68.4 wt% of metal, while feedstocks 2-L and 3-L 84.3 wt % and 89.0 wt%, respectively.

The dependency of the amount of mass lost on the metal concentration may be attributed to two factors. First, less metal concentration implied more binder and hence more water-soluble polymer (WSP) available. Second, less metal in the feedstock implied different processing history that could have increased the connectivity between WSP domains. Both factors may have played a role.
Figure 4.49 shows the non-dimensional concentration profiles and reveals how the penetration increased with decreasing metal concentration. Then, as it was mentioned in the previous paragraph, the higher concentration of metal made more difficult the extraction of the WSP because of the less WSP availability and possibly because of less connectivity of WSP domains.

4.2.2.4. Modeling of the penetration

In this section, a model of the penetration experiments is proposed. The coordinate system and the basic dimensions are presented in Figure 4.50. The model was intended to calculate the effective diffusivity of water-soluble polymer (WSP) in the feedstocks and to evaluate the linearity of the diffusion coefficient. The model proposed has the general expression given as:

\[
\frac{\partial \rho}{\partial t} = D \frac{\partial^2 \rho}{\partial z^2}
\]  

With the following initial and boundary conditions

IC: at \( t= 0, 0<z<L \), \( \rho = \rho_{z,0} \)

BC1: at \( z= 0, t>0 \), \( \frac{\partial \rho}{\partial z} = 0 \)

BC2: at \( z = L, t>0 \) \( \rho = \rho_L = 0 \)

Where \( D \) is the effective diffusivity of the WSP in the solid, \( \rho_{z,0} \) is the initial concentration of WSP and \( \rho_L \) is the concentration at the exposed edge of the sample.

The analytical solution of the equation 4-14 with the initial and boundary conditions 4-15 to 4-17 is:

\[
\rho(z,t) = 2 \cdot \rho_{z,0} \sum_{i=1}^{\infty} \left[ (-1)^{i+1} \cos(\mu_i z/L) \exp(-\mu_i^2 t \cdot D/L^2) / \mu_i \right]
\]  

149
Where, $\mu_i$ is given by:

$$\mu_i = (2i - 1)\frac{\pi}{2}$$

### Table 4.7 Experimental results of penetration experiments

<table>
<thead>
<tr>
<th>Feedstock</th>
<th>Debinding time (min)</th>
<th>Weight lost (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-L</td>
<td>32</td>
<td>0.823</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>1.390</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>2.162</td>
</tr>
<tr>
<td>2-L</td>
<td>32</td>
<td>0.523</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>1.122</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>1.273</td>
</tr>
<tr>
<td>3-L</td>
<td>32</td>
<td>0.299</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>0.726</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>1.221</td>
</tr>
</tbody>
</table>

Figure 4.48 Total mass of water-soluble polymer extracted as a function of debinding time
Figure 4.49 Non-dimensional water-soluble polymer concentration profiles of feedstocks based on LLDPE at different debinding times.

Figure 4.50 Scheme of the system for penetration modeling.

The procedure to obtain the diffusivity was to use equation 4-18 and 4-19 with the data obtained from the TGA data. Specifically, the average position of the section analyzed by TGA and its concentration of water-soluble polymer (WSP) were taken as z and ρ in equation 4-18. Then the diffusivity was obtained for each position as a fitting factor. The results are presented in Figures 4.80 to 4.82. The average diffusivity at each time is given in Table 4.8.
The Figures 4.51, 4.52 and 4.53 show that the diffusivity decreased with respect to the position measured from the end of the part, as shown in Figure 4.50. This result means that the diffusivity obtained after using equation 4-18 is lower near the exposed edge. This could be a consequence of the fact that the dissolution of WSP is controlling the global rate of debinding. The reason is that given the model of diffusion chosen, the diffusivity calculated is not the same for all times and positions. In other words, the diffusivity is accounting not only for diffusion but also for the WSP dissolution.

Another observation from Figures 4.51 to 4.53 is that at increasing debinding time the diffusivity at any position was less. The reason for this result may be the same as given above. That is, the dissolution of WSP was slow enough as to have a notorious effect on its extraction even if more porous are opened after a long time.

The results indicate that the diffusivity depended on the position in the solid. Therefore, a correlation between the diffusivity and the concentration was sought as a mean to represent the non-linearity of the diffusion of WSP out of the parts. The data and fitted curves are shown in the Figures 4.54 to 4.56.

The Figures 4.54 to 4.56 indicate that there was a good correlation of the diffusivity data with respect to the concentration of WSP. The correlation coefficients were close to 1, especially for the diffusivities obtained for feedstock 1-L and 2-L at 32, 64 and 128 min. The goodness of the log-log correlations indicated that the effective diffusivity depended on the WSP concentration through a power law. This dependency was found for diffusivity in porous solids before however, the exponents are not the usual for common porous solids used in heterogeneous catalysis, for instance. The usual exponents for power law were between 2 and 3. The exponent 2 corresponded to random porosity.
Table 4.8 Average diffusivities calculated from the equation 4-32 and TGA data

<table>
<thead>
<tr>
<th>feedstock</th>
<th>Debinding time (min)</th>
<th>Diffusivity (m²/s) x 10⁻¹⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-L</td>
<td>32</td>
<td>13.11</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>10.43</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>7.23</td>
</tr>
<tr>
<td>2-L</td>
<td>32</td>
<td>8.97</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>7.71</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>7.54</td>
</tr>
<tr>
<td>3-L</td>
<td>32</td>
<td>12.20</td>
</tr>
<tr>
<td></td>
<td>64</td>
<td>8.50</td>
</tr>
<tr>
<td></td>
<td>128</td>
<td>5.76</td>
</tr>
</tbody>
</table>

Figure 4.51 Diffusivity obtained from TGA data of feedstock 1-L
Figure 4.52 Diffusivity obtained from TGA data of feedstock 2-L

Figure 4.53 Diffusivity obtained from TGA data of feedstock 3-L
Figure 4.54 Effective diffusivity v. concentration. Feedstock 1-L

Figure 4.55 Effective diffusivity v. the concentration. Feedstock 2-L
4.3. Rheological characterization of the feedstock

The steady shear, frequency sweep and dynamic time sweep of several Feedstocks based on LLDPE, HDPE and PP resins were tested in parallel disks configuration to determine the affect of the metal concentration and binder composition on the rheological properties. The Advanced Rheometric Expansion System (ARES) available at the Olson Research Center was used to carry out all tests. Parallel disks of 25 mm in diameter were used to test the samples leaving a gap between disks of 1 mm. The testing temperatures were 160 °C, 170 °C and 180 °C under different shear rates, frequencies and strains depending on the type of test. The experiments were set up using the ARES Control software (Winrhios) provided by the manufacturer of the rheometer. The experimental details along with the equations to calculate the stress and the first normal stress difference were presented in Chapter 3.
4.3.1. Steady shear viscosity of MIM feedstocks

Steady shear experiments were conducted to evaluate the affect of the metal on the rheological behavior of the binder. The materials tested include, the binder BIN2LL (21 wt% water-soluble polymer, 10 wt% POM, 69 wt% LLDPE) and three feedstocks with the same binder and different metal content: Feedstock 1-L, 22 vol%, feedstock 2-L, 45 vol% and feedstock 3-L, 63 vol%. The metal particles were spherical and the particle size distribution is polydispersed. The coefficient of uniformity (ratio of the diameter of particle for which 60 wt% of the sample is finer than to the diameter of the particle for which 10 wt% of the sample is finer than) is equal to 3.51. In addition, the metal particles are considered non-agglomerating because of the results shown in the compounding studies. Finally, it is important to mention that the particles are non-colloidal since their diameters are larger than 1 µm. Specifically, the mode of the particle size distribution is 11 µm and as 0.2 wt% of the particles is finer than 2 µm.

The samples for rheology testing were obtained by injecting molding of disks in a mini-injection molding machine. The disks were 1mm thick and had a diameter of 25 mm. The samples were tested up to 100 s⁻¹. However, the viscosity curves became erratic after shear rates between 10⁻¹ and 1 depending on the sample. The shear viscosity curves obtained up to 100 s⁻¹ for the binder and for the feedstock 2-L are presented in Figure 4.57 and 4.58, respectively.

Figure 4.57 depicts the shear viscosity of the binder BIN2LL. It reveals that after a shear rate of about 1 s⁻¹, the viscosity became unstable and decreased sharply. The curves at 160 °C and 170 °C showed even shear-thickening behavior at larger shear rates. This result may be attributed to inertial effects, viscous dissipation and particle segregation at large shear rates. The same behavior is observed in the Figure 4.58.
Figure 4.57 Log-Log Shear viscosity of binder based on LLDPE at different temperatures

Figure 4.58 Log-Log Shear viscosity of feedstock 2-L at different temperatures
The logarithm of the shear viscosity of the different materials is plotted against
the logarithm of the shear rate in Figures 4.59, 4.60, 4.61 and 4.62 for low shear rates.

Figures 4.59 to 4.62 indicate that the binder and the feedstocks showed shear-
thinning behavior. The data were fitted to the power law equation given in 4-38. The
results are presented in Table 4.9. The equations are of the form:

\[ \eta = m \dot{\gamma}^{\alpha-1} \]  

4-38

where, \( \eta \) is the apparent viscosity, \( m \) a constant, \( \dot{\gamma} \) the shear rate
and \( n \) the flow behavior index. The dependency of \( m \) on the temperature was found according to the
equation \( m = m_0 \exp[-A(T - T_0)] \) where, \( m_0 \) is a reference value taken at \( T_0 \), a reference
temperature. \( A \) is a constant and \( T \) is the temperature.

Table 4.9 shows that the power-law parameters corresponding to the feedstock
3-L are very different from those of the binder and feedstocks 1-L and 2-L. The reason
may be the increased hydrodynamic interactions among particles because of the large
metal concentration in feedstock 3-L when compared to the other samples.

The experimental data show in Figures 4-57 to 4-62 may be difficult to
interpret if the viscous dissipation is high as to render the sample non-isothermal. To
estimate the intensity of the viscous dissipation, the energy equation for a parallel disk
rheometer is solved. The rheometer is sketched in Figure 4.63 (c). The energy equation
is:

\[ k \left( \frac{\partial^2 T}{\partial z^2} + \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) \right) = -\text{tr} \left( \sigma \cdot \varepsilon \right) \]  

4-39

where, \( k \) is the thermal conductivity of the material, \( T \) the temperature, \( z \) and \( r \) the axial
and radial coordinates as shown in Figure 4.63 (a) and (b). “\( \text{tr} \)” represents the trace and
$\sigma$ and $\varepsilon$ are the stress and strain rate tensors, respectively. The boundary conditions will be given after simplifying the equation as described below.

Figure 4.59 Log-Log Shear viscosity of binder based on LLDPE

Figure 4.60 Log-log shear viscosity of feedstock 2-L. The metal content was 22 vol%
Figure 4.61 Log-log shear viscosity of feedstock 2-L. The metal content was 45 vol%.

Figure 4.62 Log-log shear viscosity of feedstock 3-L. The metal content was 63 vol%.
Table 4.9 Power Law parameter for binder BIN2LL and feedstocks 1-L, 2-L and 3-L

<table>
<thead>
<tr>
<th>Material</th>
<th>N</th>
<th>A (°C⁻¹)</th>
<th>m₀ (Pa·s⁻¹)</th>
<th>T₀ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIN2LL</td>
<td>0.917</td>
<td>49.3</td>
<td>677.6</td>
<td>160</td>
</tr>
<tr>
<td>1-L</td>
<td>0.948</td>
<td>33.4</td>
<td>1552.6</td>
<td>160</td>
</tr>
<tr>
<td>2-L</td>
<td>0.952</td>
<td>37.1</td>
<td>2199.1</td>
<td>160</td>
</tr>
<tr>
<td>3-L</td>
<td>0.375</td>
<td>25.9</td>
<td>28294.1</td>
<td>160</td>
</tr>
</tbody>
</table>

Figure 4.63 Parallel disk rheometer (a) Cylindrical coordinates, (b) dimensions and (c) rheometer.
The second derivative of the LHS term in equation 4-39 could be eliminated if the gap between the disks is smaller that the disks radius. Therefore,

\[
\text{if } h \ll R \Rightarrow \frac{\partial^2 T}{\partial z^2} \gg \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right)
\]

where \( h \) is half of the gap distance and \( R \) the radius of the disks. The condition expressed in equation 4-40 means that if the gap is very small compared to the radius of the disks, the variation of temperature along the axial direction is going to be much higher than the temperature variation along the radial direction. In the instance of the rheology experiments \( h=0.5 \text{ mm} \) and \( R \) was 12.5 mm. Therefore, the ratio \( h/R \) was 0.04, which is much less than 1. After simplifying the equation 4-39, and by substituting the only component of rate of strain tensor \( \dot{\gamma}_{\varphi z} \) and replacing the expression of the power law, the following equation so obtained:

\[
k \frac{\partial^2 T}{\partial z^2} = -m\dot{\gamma}_{\varphi z}^{n+1}
\]

with the following boundary conditions:

BC1: \( \text{at} \ z = +h, \ T = T_D \)

BC2: \( \text{at} \ z = -h, \ T = T_D \)

Where \( T_D \) is the temperature of the disks and \( 2h \) is the gap. The solution of equation 4-41 is then:

\[
T(z) = \frac{m}{2k} \dot{\gamma}_{\varphi z}^{n+1} h^2 \left[ 1 - \left( \frac{z}{h} \right)^2 \right] + T_D
\]

The maximum temperature rise would occur at \( z=0 \). The increment of temperature would be:
\[ \Delta T_{\text{max}} = \frac{m}{2k} \gamma^2 \rho \varepsilon \]

The values of \( \Delta T_{\text{max}} \) obtained for the binder and the different feedstocks are shown in Table 4.10. The maximum shear rate is also given in the Table. The thermal conductivity was calculated by weight averaging the conductivities of the binder and the metal. The binder was assumed composed of neat LLDPE, because it forms the continuous phase. The conductivity of the 316 L SS was provided by the Sponsoring Company. The conductivity of the feedstock at 170 °C was then, 14.3 W·m\(^{-1}\)·K\(^{-1}\).

Table 4.10 Maximum temperature increment in the steady shear experiments

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
<th>Shear rate (s(^{-1}))</th>
<th>( \Delta T_{\text{max}} ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BIN2LL</td>
<td>160</td>
<td>6.3x10(^{-1})</td>
<td>2.4x10(^{-6})</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>6.3x10(^{-1})</td>
<td>2.2x10(^{-6})</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>6.3x10(^{-1})</td>
<td>1.6x10(^{-6})</td>
</tr>
<tr>
<td>1-L</td>
<td>160</td>
<td>6.3x10(^{-2})</td>
<td>5.9x10(^{-8})</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>6.3x10(^{-2})</td>
<td>4.7x10(^{-8})</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>6.3x10(^{-2})</td>
<td>3.5 x10(^{-8})</td>
</tr>
<tr>
<td>2-L</td>
<td>160</td>
<td>4.0x10(^{-2})</td>
<td>3.3x10(^{-8})</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>4.0x10(^{-2})</td>
<td>3.1x10(^{-8})</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>4.0x10(^{-2})</td>
<td>2.2x10(^{-8})</td>
</tr>
<tr>
<td>3-L</td>
<td>160</td>
<td>1.6x10(^{-2})</td>
<td>7.6x10(^{-7})</td>
</tr>
<tr>
<td></td>
<td>170</td>
<td>1.6x10(^{-2})</td>
<td>5.5x10(^{-7})</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>1.6x10(^{-2})</td>
<td>4.4x10(^{-7})</td>
</tr>
</tbody>
</table>
4.3.2. Dependence of the viscosity at zero shear rate on the metal concentration

The relative effective-viscosity at low shear rate depended on the volumetric fraction of particles according to a Mooney exponential equation. The relative viscosity is plotted against the volumetric fraction of solids in the Figure 4.64. The Mooney equation is expressed as

\[ \eta_r = \exp \left( \frac{B\phi}{1 - \phi / \phi_c} \right) \]

where B is a fitting parameter and \( \phi \) and \( \phi_c \) are the volumetric fraction of solids and the critical volumetric fraction of solids in the suspension. The critical fraction of solids was taken in equation 4-46 as another fitting parameter. The values of the parameters were B=0.7053 and \( \phi_c = 0.7097 \). The correlation coefficient was of order \( 10^{-1} \).

The Mooney equation was the only empirical model for non-interacting and large particles that fitted the data. The models of the Krieger-type (non-exponential) could not fit the data since the rapid growth of relative viscosity with the increment of solids content.

Figure 4.64 Effective relative viscosity at low shear rate \( \eta_r \) v. volumetric fraction of solids
4.3.3. Brownian effects

The Brownian effects were estimated by calculating the Péclet number (Pe), which relates the shear rate to the diffusion rate. Accordingly, if Pe were less than one the interaction among particles due to Brownian effects would be more important than the purely hydrodynamic interactions due to the shearing of the suspension. The opposite would be true if the Péclet number were larger than one. To calculate the Péclet number the following equation\(^{158}\) was used:

\[
Pé = \frac{\eta_b \dot{\gamma} a^3}{kT}
\]

where, \(\eta_b\) is the viscosity of the binder in Pa\(\cdot\)s, \(\dot{\gamma}\) is the shear rate expressed in s\(^{-1}\), \(a\) is the particle diameter in m, \(k\) is the Boltzman constant (J\(\cdot\)K\(^{-1}\)) and \(T\) the temperature in K.

In the instance of the samples studied, the diameter of the metal particles was taken as the mode of the particle size distribution that was 11 µm. Therefore, at the conditions that would give the smallest Pé i.e. at \(\dot{\gamma} = 0.5\) s\(^{-1}\), with binder viscosity of 551.1 Pa\(\cdot\)s and temperature of 433 K (160 °C) the Pé number would be:

\[
Pé = \frac{\eta_b \dot{\gamma} a^3}{kT} = \frac{551.1 \times 0.5 \times (11 \times 10^{-6})^3}{1.38 \times 10^{-23} \times 443} = 6.14 \times 10^7
\]

Therefore, the interaction between particles was purely hydrodynamic, since Pé\(\gg\)1.

The results are shown in the following Table.

Table 4.11 Péclet numbers calculated for feedstocks 1-L, 2-L and 3-L

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Shear rate (s(^{-1}))</th>
<th>Pé</th>
</tr>
</thead>
<tbody>
<tr>
<td>160</td>
<td>0.5</td>
<td>6.14(\times)10(^7)</td>
</tr>
<tr>
<td>170</td>
<td>0.5</td>
<td>6.00(\times)10(^7)</td>
</tr>
<tr>
<td>180</td>
<td>0.5</td>
<td>5.86(\times)10(^7)</td>
</tr>
</tbody>
</table>
4.3.4. Yield stress from steady shear data

From the steady shear data, it was found that the binder and the feedstocks based on LLDPE resin did not show yield stress. According to Malkin and Vinogradov and Malkin, a filled polymeric material shows yield stress if the stress becomes independent of the shear rate at low shear rate, in other words, if the slope of the shear rate v. shear stress curve becomes infinite. The reason for the existence of a yield stress in filled system is the formation of a structural skeleton through the entire material because of the interaction between filler particles. The skeleton strength depends on the strength of the filler, the intensity of interparticle interactions and the number of contact points between filler particles. Therefore, if yield stress is not found in the MIM feedstocks studied in steady shear then, it is possible to affirm that the particles do not interact strongly and are not in contact with each other. The plot of logarithm of the shear rate v. logarithm of the shear stress for the binder and feedstocks at 170 °C are presented in Figure 4.65.

![Figure 4.65 Shear rate versus shear stress for binder and feedstocks based on LLDPE at 170 °C](image-url)
Figure 4.65 shows that the slope of the shear rate v. shear stress curve is not infinite at the lowest shear rates attained in the experiments. Therefore, the feedstocks and binder did not show yield stress.

4.3.5. Normal stresses

The normal stresses were observed in some of the samples tested. In the instance of feedstock 3-L, negative normal stresses were observed. The Figure 4.66 depicts the first normal stress difference ($N_1$) of feedstocks 2-L at 160 °C, 170 °C and 180 °C. Figure 4.67 shows the normal stress difference of feedstock 3-L.

Figure 4.66 shows that the first normal stress difference of feedstock 2-L depended directly on the shear rate and inversely on temperature. It increased with increasing shear rate and decreased with increasing temperature. Therefore, the elasticity of the feedstock was more important at low temperature and higher shear rates.

Figure 4.67 shows the first normal stress difference of feedstock 3-L versus the shear rate. Two different zones are observed. The first, at shear rates below $1 \times 10^{-3}$ s$^{-1}$, is characterized by positive $N_1$. The second zone, at shear rates between $1 \times 10^{-3}$ s$^{-1}$ and $1 \times 10^{-1}$ s$^{-1}$ is typified by negative $N_1$ values. This result is surprising, however, negative normal stresses observation have been reported by other authors$^{160, 161}$, even in noncolloidal suspensions in Newtonian liquids$^{162}$. In Laun$^{160}$, the negative $N_1$ values were found in suspensions at steady state in the shear thickened state. While in Lem and Han$^{161}$, the negative $N_1$ were found in the shear thinning section of the viscosity curve. In the instance of feedstock 3-L, the first normal stress difference was positive at low shear rates where the logarithm of the viscosity varied more non-linearly with the logarithm of the shear rate than at higher shear rates.
Figure 4.66 First normal stress difference of neat binder and feedstocks 2-L

Figure 4.67 First normal stress difference of feedstocks 3-L
Figure 4.67 also reveals that the first normal stress difference depended inversely on the temperature, i.e. increasing temperature decreased $N_1$. This dependence was maintained in the zone of negative $N_1$, where at higher temperatures the first normal stress difference was more negative.

4.3.6. Frequency sweep tests

The effect of the metal on the dynamic behavior of the binder was investigated in frequency sweep experiments. The samples included, the binder BIN2LL (21 wt% water-soluble polymer, 10 wt% POM, 69 wt% LLDPE) and three feedstocks with the same binder and different metal content: Feedstock 1-L, 22 vol%, feedstock 2-L, 45 vol% and feedstock 3-L, 63 vol%. The samples were disks of 25 mm in diameter and 1 mm of thickness, produced by injection molding in a micro-injection molding machine. The frequency was varied from $10^2$ to $10^2$ rad/s and the strain was kept at 0.01 % while, the temperatures were: 160 °C, 170 °C and 180 °C. The equations used to calculate the modulae and tan δ were presented in section 3.4.4. The elastic and dynamic modulue are presented in Figures 4.68 and 4.69, respectively. The tan δ curves are depicted in Figure 4.70. The results obtained with the feedstock 1-L are not shown in order to make the figures more clear.

Figure 4.68 show the frequency dependence of the storage moduli ($G'$) at 0.01% strain. The results indicate that the slope of the moduli curves of all blends varied with respect to frequency. In the instances of feedstocks 2-L and 3-L, at low frequencies (ca. $1x10^{-2}$ rad/s), the slope was positive and large; while in the medium range ($1x10^{-1}$ to 10 rad/s) the slope was positive but smaller than at low frequency. At high frequency (ca. $1x10^{2}$ rad/s) the slope was positive and larger than in the middle range of frequencies but smaller than at low frequency. In contrast to the feedstocks, the binder showed a
more constant slope however, larger than that of the feedstocks. The shape of the loss moduli (G’’) curves is similar to that of the G’ curves. The loss moduli versus frequency curves are depicted in Figure 4.69.

Figures 4.68 to 4.69 indicate that the elastic modulus G’ and the loss modulus G’’ depended on the metal concentration. This is observed in Figure 4.68 that shows that G’ increases with increasing metal contents. Similar behavior is displayed by the loss moduli in Figure 4.69. However, the elasticity increases with increasing concentration of metal as shown Figure 4.70 that depicts the tan δ curves.

The affect of temperature on the modulae is shown in the Figures 4.68 to 4.70. It is apparent, that the storage and loss modulae increase with increasing temperature. However, the dependence is in such a way that the elastic response is more important at high temperature as shown by the tan δ curves.

Another observation from the Figures 4.68 and 4.69 is that the storage modulae curves of a given material at different temperatures are almost parallel to each other. However, the curves are separated at low frequency but become closer at higher frequency. In the instance of G’’, the curves actually crosses each other at a frequency between $1 \times 10^{-1}$ and $1 \text{ rad/s}$. The curves of tan δ does not cross each other and are fairly parallel, as shown in Figure 4.70.

In summary, it is evident that the dynamic response of the binder to frequency and temperature was similar to that of the feedstocks. Therefore, it is possible to conjecture that most of the viscoelastic behavior of the feedstocks is due to the inherent viscoelastic behavior of the binder. This implies that the interaction between metal particles was negligible confirming the results regarding yield stress under steady shear.
Figure 4.68 Storage Modulus of binder BIN2LL and feedstocks 2-L and 3-L

Figure 4.69 Loss Modulus of binder BIN2LL and feedstocks 2-L and 3-L
4.3.7. Yield stress from frequency sweep data

The feedstocks based on LLDPE did not show yield stress according to the dynamic data because of the increasing viscous behavior at low frequency. According to previous knowledge summarized by Malkin\textsuperscript{109}, a filled polymeric material does not show yield stress if the dynamic behavior at low frequency and low strain is fluid-like.

Figure 4.70 indicates that at low frequency the binder and the feedstocks show fluid-like behavior since the slope of the tan δ curves are negative at low frequency. Therefore, it is possible to reaffirm that the feedstocks based on LLDPE show no internal structure and that the interaction between particles are purely hydrodynamic.

4.3.8. Affect of the presence of water-soluble polymer on the dynamic response

To study the influence of the water-soluble polymer (WSP) on the rheological behavior of feedstocks, two sets were chosen. The first one, based on LLDPE, comprises
the feedstock 5-L (with WSP) and 6-L (without WSP). The second set was based on PP resin and comprised the feedstocks 5-P (with WSP) and 6-P (without WSP). The frequency sweep experiments were conducted at frequencies between $1 \times 10^{-2}$ and $1 \times 10^{2}$ rad/s at 3% strain. The tan δ curves corresponding to feedstocks based on LLDPE and PP are presented in Figures 4.71 and 4.72, respectively. In addition, the complex viscosity are shown in Figures 4.73 and 4.74 for feedstocks based on LLDPE and PP, respectively.

Figure 4.71 to 4.72 show that the feedstocks with water-soluble polymer (WSP) behave more fluid-like than the feedstocks without WSP at a given temperature. This result may be attributed to the possible plasticizing effect of the WSP on the POM. The reason is that these two materials are polar and may interact with each other showing even, specific interactions.

The behavior of the feedstocks based on LLDPE with and without WSP with respect to temperature is similar. Figure 4.71 shows that the blends with and without WSP behave more fluid-like at lower temperature. Similar trend is observed in the instance of the blends based on PP resin, except that the curves at 170 °C and 180 °C are inverted. This behavior may be attributed to rearrangement of the phases in the binder upon variations of temperature and addition of WSP.

4.4. Thermal Characterization of MIM feedstocks

The thermal characterization of the feedstocks comprised differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of several feedstocks, neat resins and neat binders. The affect of the metal contents and binder composition on the melting point was studied using DSC. The DSC scans of binders and feedstocks were compared to those of neat resins. In addition, TGA experiments complemented the
study of the effect of the metal and different compositions on the thermal behavior of the blends. Kinetics studies of thermal degradation were not competed.

Figure 4.71 Tan δ versus frequency of feedstocks 5-L and 6-L

Figure 4.72 Tan δ versus frequency of feedstocks 5-P and 6-P
Figure 4.73 Complex viscosity versus frequency of feedstocks 5-L and 6-L

Figure 4.74 Complex viscosity versus frequency of feedstocks 5-P and 6-P
4.4.1. Differential Scanning Calorimetry of the Binders and feedstocks

The DSC scans obtained for the feedstocks based on LLDPE and PP is presented in Figures 4.75 and 4.76. All the peaks were endothermic. Tables 4.12 and 4.13 lists the melting temperatures corresponding to the peaks depicted in the DSC scans.

Figure 4.75 and 4.76 show melting point depression of the polymers in the different compounds based on LLDPE and PP resins, respectively. Each chart includes the binder components’ scans at the top, the binders’ scans at the bottom and the feedstock’s DSC scans in the middle. It is apparent that the melting peaks of the blends displaced to the left with respect to the peaks of the binder components. In the instance of LLDPE-based blends, the melting point depression was larger with respect to WSP and POM than with respect to LLDPE. In the instance of the blends based on PP, the melting point depression of the WSP is large. However, the depression with respect to PP or POM is difficult to evaluate because of the proximity of the melting points of POM and PP that render the discrimination of the two peaks impossible. Therefore, two melting point depression are shown in Table 4.13.

Tables 4.12 and 4.13 reveal that the average melting point depression of the polymers was larger when the binder components were in the feedstocks than when they were in the binders. However small, this differences may be attributed to the presence of the metal. It is also apparent in the Tables 4.12 and 4.13 that the melting point depression of the POM did not change if WSP was or not present in the blends.

The melting point depression of the polymers is shown in Figure 4.77 and 4.78. Where the value of the m.p.d are shown with respect to the material.
Figure 4.75 DSC scans of polymers, binders and feedstocks based on LLDPE

Figures 4.76 DSC scans of polymers, binders and feedstocks based on PP
Table 4.12 Melting points of the feedstocks components in the blends based on LLDPE

<table>
<thead>
<tr>
<th>Component or blend</th>
<th>Metal to binder ratio</th>
<th>Melting point of Polymer (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>WSP</td>
</tr>
<tr>
<td>Neat polymers</td>
<td></td>
<td>69.7</td>
</tr>
<tr>
<td>BIN1LL</td>
<td>0.0</td>
<td>62.2</td>
</tr>
<tr>
<td>BIN2LL</td>
<td>0.0</td>
<td>64.2</td>
</tr>
<tr>
<td>BIN3LL</td>
<td>0.0</td>
<td>62.0</td>
</tr>
<tr>
<td>1-L</td>
<td>2.2</td>
<td>63.1</td>
</tr>
<tr>
<td>2-L</td>
<td>6.3</td>
<td>61.7</td>
</tr>
<tr>
<td>3-L</td>
<td>15.6</td>
<td>62.6</td>
</tr>
<tr>
<td>4-L</td>
<td>2.2</td>
<td>61.1</td>
</tr>
<tr>
<td>5-L</td>
<td>14.9</td>
<td>63.6</td>
</tr>
<tr>
<td>6-L</td>
<td>16.2</td>
<td></td>
</tr>
<tr>
<td>Average (°C)</td>
<td></td>
<td>62.6</td>
</tr>
<tr>
<td>Average Binders (°C)</td>
<td></td>
<td>62.8</td>
</tr>
<tr>
<td>Average for feedstocks (°C)</td>
<td></td>
<td>62.4</td>
</tr>
<tr>
<td>Average m.p.d. (°C)</td>
<td></td>
<td>7.2</td>
</tr>
<tr>
<td>Average m.p.d. Binders °C)</td>
<td></td>
<td>6.9</td>
</tr>
<tr>
<td>Average m.p.d. feedstocks (°C)</td>
<td></td>
<td>7.3</td>
</tr>
</tbody>
</table>

Note: m.p.d. stands for melting point depression. WSP: water-soluble polymer
Table 4.13 Melting points of the feedstocks components in the blends based on PP

<table>
<thead>
<tr>
<th>Component or blend</th>
<th>Metal to binder ratio</th>
<th>Melting Point of polymers</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>WSP</td>
</tr>
<tr>
<td>Neat polymers</td>
<td></td>
<td>69.7</td>
</tr>
<tr>
<td>BIN2PP</td>
<td>0.0</td>
<td>63.5</td>
</tr>
<tr>
<td>BIN3PP</td>
<td>0.0</td>
<td>64.4</td>
</tr>
<tr>
<td>1-P</td>
<td>2.2</td>
<td>65.0</td>
</tr>
<tr>
<td>2-P</td>
<td>6.4</td>
<td>59.9</td>
</tr>
<tr>
<td>3-P</td>
<td>15.9</td>
<td>61.8</td>
</tr>
<tr>
<td>4-P</td>
<td>6.3</td>
<td>65.1</td>
</tr>
<tr>
<td>5-P</td>
<td>14.9</td>
<td>65.9</td>
</tr>
<tr>
<td>6-P</td>
<td>16.2</td>
<td>-</td>
</tr>
<tr>
<td>Average (°C)</td>
<td></td>
<td>63.6</td>
</tr>
<tr>
<td>Average Binders (°C)</td>
<td></td>
<td>63.9</td>
</tr>
<tr>
<td>Average for feedstocks (°C)</td>
<td></td>
<td>63.5</td>
</tr>
<tr>
<td>Average m.p.d. (°C)</td>
<td></td>
<td>6.1</td>
</tr>
<tr>
<td>Average m.p.d. Binders °C)</td>
<td></td>
<td>5.8</td>
</tr>
<tr>
<td>Average m.p.d. feedstocks (°C)</td>
<td></td>
<td>6.2</td>
</tr>
</tbody>
</table>

Note: m.p.d. stands for melting point depression. WSP: water-soluble polymer
The DSC scan results may be summarized as follows: i) The melting point depression of the water-soluble polymer (WSP) and the POM were more intense than the reduction in the melting point of the LLDPE or the PP. ii) The extend of the melting point depression was higher in the blends that contained metal. iii) The occurrence and span of the melting point depression of POM was not affected by the presence or absence of WSP.

Additional evidence supporting the first two observations mentioned in the previous paragraph was obtained from the results of the DSC scans performed on the feedstocks based on HDPE. The results are presented in Table 4.14 and in Figure 4.79. In this instance, it was apparent that the order of magnitude of the melting point depression of both WSP and POM was similar. However, as in the blends based on PP and LLDPE, the melting point depression of the HDPE was lower than for the other two binder components.

The melting point depression of polymers in blends has been attributed to several factors including, higher heating rates, diluent effect and changes in the crystal size\textsuperscript{163}. In this study, the melting point depression was attributed to changes in crystal size because of the presence of the other components in the blends. This reason seems plausible when considering the way the melting points were obtained.

The DSC tests consisted of two runs. In the first, the sample was heated up at the heating rate of 20 °C/min up to about 200 °C and then quenched until it reached -110 °C. The second run was done at the same heating rate and up to 200 °C. The melting points were taken from the second scan. This procedure implies that the polymers were first melted in succession until the blend was in the liquid state and then quenched, freezing up the melt structure. During the quenching phase, the polymers
crystallized in a sequence that depended on the rate of crystallization of the polymers. In this regard, the polyolefins crystallized first, then the POM and finally the WSP. In this process, one polymer not yet crystallized could have been “trapped” in the crystalline structure of a polymer already crystallizing reducing the space available for crystallites. This kind of phenomena would explain the reduction of crystallite size and hence, in meting point of POM and WSP and the little change of the polyolefin’s melting point.

However the explanation given above seems reasonable, one major factor in determining if a polymer could have been trapped by another during crystallization is that there should be miscibility or at least partial miscibility of the polymers in the melt. This is the only way to in which a polymer can trap another during crystallization. Accordingly, it is possible to conjecture that there is at least partial miscibility of WSP and POM in LLDPE, in PP and in HDPE in the melt.

The effect of the metal on the melting point depression could be explained in a similar way as to the effect of binder components. Specifically, the dispersed metal restricted the mobility of the polymers enough as to produce further reduction in the size of the crystalline domains and increased melting point depression. However, the effect of metal was less important indicating that the mayor mechanism for melting point reduction of POM and WSP is the rapid crystallization of the polyolefin components in the blends.

The relative heats of melting of the binder components are presented in Figures 4.80, 4.81 and 4.82 in binders and feedstocks. The relative heats of melting are calculated with reference to the heat of melting of the neat polymers and in the instance of the binders based on PP to the mass-averaged heat of melting of PP and POM.
Figures 4.77 Melting point depression of polymers in blends based on LLDPE

Figures 4.78 Melting point depression of polymers in blends based on PP
Table 4.14 Melting points of the feedstocks components in the blends based on HDPE

<table>
<thead>
<tr>
<th>Blend Polymers</th>
<th>Melting point of Polymer (°C)</th>
<th>WSP</th>
<th>HDPE</th>
<th>POM</th>
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</thead>
<tbody>
<tr>
<td>69.7</td>
<td>132.3</td>
<td>173.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Component or blend</td>
<td>Metal to binder</td>
<td>57.0</td>
<td>128.2</td>
<td>162.8</td>
</tr>
<tr>
<td>1-H</td>
<td>14.9</td>
<td>62.4</td>
<td>128.5</td>
<td>163.5</td>
</tr>
<tr>
<td>2-H</td>
<td>17.4</td>
<td>61.6</td>
<td>129.0</td>
<td>163.6</td>
</tr>
<tr>
<td>3-H</td>
<td>17.5</td>
<td>57.4</td>
<td>128.1</td>
<td>161.8</td>
</tr>
<tr>
<td>4-H</td>
<td>15.1</td>
<td>59.2</td>
<td>128.9</td>
<td>163.4</td>
</tr>
<tr>
<td>5-H</td>
<td>15.2</td>
<td>59.2</td>
<td>128.9</td>
<td>163.4</td>
</tr>
<tr>
<td>6-H</td>
<td>17.7</td>
<td>54.0</td>
<td>129.1</td>
<td>161.4</td>
</tr>
<tr>
<td>7-H</td>
<td>16.1</td>
<td>54.7</td>
<td>128.5</td>
<td>161.0</td>
</tr>
<tr>
<td>Average (°C)</td>
<td></td>
<td>58.2</td>
<td>128.6</td>
<td>162.6</td>
</tr>
<tr>
<td>Average m.p.d. (°C)</td>
<td></td>
<td>11.5</td>
<td>3.7</td>
<td>11.3</td>
</tr>
</tbody>
</table>

Note: m.p.d. stands for melting point depression. WSP: water-soluble polymer

Figures 4.79 Melting point depression of polymers in blends based on HDPE
Figures 4.80 Melting heats of polymers in blends based on LLDPE

Figures 4.81 Melting heats of polymers in blends based on PP
Figures 4.82 Melting heats of polymers in blends based on HDPE

Figures 4.80 and 4.81 reveal that the heat of melting of the polyolefinic component (LLDPE and PP, respectively) in the binders is very close to the heat of melting of the neat polymers. On the other hand, the heat of melting points of the LLDPE and the PP decreased with respect to that of the neat polymers when present in the feedstocks. Therefore, the degree of crystallinity of the polyolefin in the binders was essentially the same as that in the neat polymers. In other words, POM and water-soluble polymer (WSP) did not affect the melting point of LLDPE and PP. In contrast, the melting heat of the WSP and POM were as low in the binder as in the feedstocks. This result indicated that the crystallinity of the WSP and POM was greatly reduced when blended with the polyolefin. This conclusion was confirmed for the POM, in the blends that did not contain WSP

Figure 4.82 shows that in the instance of the feedstocks based on HDPE, the affect of blending HDPE with POM and WSP on HDPE heat of melting was more intense
than in the instances of LLDPE and PP based feedstocks. This observation might be the result of the increased proportion of metal in the feedstocks based on HDPE (up to 17.7 Metal/binder) as compared to the feedstocks based on LLDPE or PP (up to 16.2 Metal/binder).

4.4.2. Thermal stability of the binders and feedstocks

The thermal stability of the blends was determined using thermogravimetric analysis. The TGA tests were run under nitrogen atmosphere from room temperature to 700 °C at a heating rate of 20 °C/min. The tests were done to determine the affect of the metal on the TGA curves of the binders. The discussion begins with the presentation of the thermo-gravimetric curves of decomposition of binder components and binders. The second section presents the TGA curves of feedstocks and reveals the effect of adding metal to the binders.

It is important to realize that the TGA tests were not intended to determine the kinetics of thermal decomposition of the binder components or to study the mechanism of degradation. That is another area of research in MIM processing.

4.4.2.1. TGA of binder components and binders

Figure 4.83 to 4.85 present the thermogravimetric (TG) curves of the polymeric resins that compose the binders which polyolefin is LLDPE, PP or HDPE, respectively. The Figures reveal that the temperature at the onset of thermal degradation of water-soluble polymer was lower than at the onset of degradation of LLDPE, PP or POM. In addition, POM was the component with higher temperature at the beginning of degradation.

The temperatures at the onset of degradation of LLDPE, water-soluble polymer, PP, HDPE and POM are presented in Table 4.15.
Figure 4.83 TG curves of the constituents of the binders based on LLDPE

Figure 4.84 TG curves of the constituents of the binders based on PP
Figure 4.85 TG curves of the constituents of the binders based on HDPE

Figure 4.86 TG curves of the three polyolefinic resins used in this research
Table 4.1 Temperature at the onset of thermal degradation (0.5% weight loss)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water-soluble polymer (WSP)</td>
<td>170</td>
</tr>
<tr>
<td>POM</td>
<td>260</td>
</tr>
<tr>
<td>LLDPE</td>
<td>155</td>
</tr>
<tr>
<td>PP</td>
<td>185</td>
</tr>
<tr>
<td>HDPE</td>
<td>210</td>
</tr>
</tbody>
</table>

Table 4.15 indicates that the initiation of degradation of LLDPE resin occurred at the lowest temperature. In particular, LLDPE started the degradation before HDPE. The reason seems to be that the random scission (the first reaction of thermal degradation of Polyethylene) is favored when the chain is branched.\textsuperscript{164}

Table 4.15 also shows that the degradation of PP begun at higher temperature than LLDPE but at lower than HDPE. The reason seems to be the presence of great amount of additives in the PP resin since it was a rotomolding grade. The antioxidants and anti thermal degradation additives were added to the PP in order to avoid thermal damage during the relatively long residence time in the mold. The additives are free radical stabilizers that stop the mechanism of degradation by stabilizing primary radicals after random scission. However, during TGA testing the stabilizer molecules will also thermally degrade since the temperatures reached are enough to break any covalent bond. For comparison purposes, the TG curves of the polyolefins are presented in together in Figure 4.86.

Finally, Table 4.15 indicates that the POM begun to degrade at higher temperature than the other resins. The reason is that the POM used in this research was a copolymer with –C-O- and –C-O-O- segments randomly distributed along the main
chain. It has been demonstrated that POM copolymer degrades at higher temperature than the homopolymer because sequential depolymerization (unzipping) of the chain is interrupted by the –C-O-O- comonomer\textsuperscript{165}.

Figures 4.87 and 4.88 show the thermograms of the binders based on LLDPE and those based on PP, respectively. For reference, the TG curves of the constituents of the binders are also depicted.

The thermogravimetric curves of thermal decomposition of the binders are shown in Figure 4.87. It is apparent that at temperatures close to that of the onset of degradation of the binder the binder’s TG curve is close to that of the POM and the water-soluble polymer (WSP). The different shape of the curves of BIN2LL and BIN3LL may be caused by their different composition. Binder BIN2LL contains less LLDPE but more WSP and POM than the binder BIN3LL. Therefore, BIN2LL decomposes more like WSP and POM do than the binder 3LL. In the instance of the binder based on PP, it is found that this binder degrades similarly to POM and WSP at early stages but more like PP at late stages, as shown in Figure 4.88.

4.4.2.2. TG curves of feedstocks. Affect of the metal

The TG curves of the feedstocks based on LLDPE are shown in Figure 4.87 and of the feedstocks based on PP in Figure 4.88 along with the TG curves of the polymer components and the binders tested. In both the Figures, the end of thermal degradation of the feedstocks is indicated by the arrows near the TG curves.

Figures 4.87 and 4.88 show that the metal present in the feedstocks delayed the end of thermal degradation of the resins. The temperature at the end of degradation of feedstocks is pointed to by a light arrow and that of the corresponding binder by a heavy arrow.
Figure 4.87 reveals that the end of the degradation of the feedstocks occurred at larger temperature than that of the binders. For instance, the feedstock 3-L finish decomposing at about 514.5 °C, while the binder BIN3LL at 498.3 °C. However, the temperature at the end of degradation of feedstock 2-L was only 2°C larger than that of the binder BIN2LL. In other words, the reduction of the metal contents decreases the difference between the temperatures at the end of degradation of the feedstocks and of its respective binder. The same result is observed in Figure 4.88, between the feedstock 3-P and its respective binder BIN3PP. Therefore, the metal affected the rate of decomposition of the feedstocks. The reason may be the restriction that the metal imposes on the flow of gasses and liquids resulting from the degradation of the binder. Increasing concentration of metal makes more difficult the evacuation of the thermal degradation byproducts. Upon this, the chemical equilibrium of the decomposition reactions is displaced toward higher temperature. Table 4.16 shows the temperatures at the onset and end of the thermal degradation of binders and binders in feedstocks.

![Figure 4.87 TGA curves of the binders based on LLDPE and their constituents](image-url)
Figure 4.88 TGA curves of the binder based on PP and their constituents

Table 4.16 Temperatures at the onset and end of thermal decomposition

<table>
<thead>
<tr>
<th>feedstock</th>
<th>Metal Concentration Wt%</th>
<th>Initial Temperature of decomposition(°C)</th>
<th>Final Temperature of decomposition(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-P</td>
<td>94.0</td>
<td>118.2</td>
<td>508.1</td>
</tr>
<tr>
<td>BIN3PP</td>
<td>-</td>
<td>238.8</td>
<td>483.5</td>
</tr>
<tr>
<td>2-P</td>
<td>86.2</td>
<td>77.5</td>
<td>483.8</td>
</tr>
<tr>
<td>1-P</td>
<td>68.7</td>
<td>52.3</td>
<td>470.3</td>
</tr>
<tr>
<td>3-L</td>
<td>94.1</td>
<td>95.9</td>
<td>514.5</td>
</tr>
<tr>
<td>BIN3LL</td>
<td>-</td>
<td>155.0</td>
<td>498.3</td>
</tr>
<tr>
<td>2-L</td>
<td>86.1</td>
<td>79.4</td>
<td>499.5</td>
</tr>
<tr>
<td>BIN2LL</td>
<td>-</td>
<td>134.7</td>
<td>497.1</td>
</tr>
<tr>
<td>1-L</td>
<td>68.8</td>
<td>34.0</td>
<td>470.3</td>
</tr>
</tbody>
</table>
4.5. Morphological studies of the binders and feedstocks

The morphology of the binders and feedstocks was studied with scanning electron microscopy (SEM) of cryogenically fractured samples. Micrographs were taken on different samples and at different stages of the MIM process. For instance, some samples were observed during compounding, while others after water debinding or after rheological testing.

The SEM study was conducted to observe microstructural changes caused by processing or testing and to characterize the microstructure of the compounds.

4.5.1. Powdered Metal

The powdered metal is shown in Figure 4.89. The micrograph shows that the sizes of the particles are polydispersed and that the surface of the particles looks smooth.

![SEM micrograph of the 316L Stainless Steel used to prepare the feedstocks](image)

Figure 4.89 SEM micrograph of the 316L Stainless Steel used to prepare the feedstocks
4.5.2. Microstructure of the binders

The binders were observed with SEM after their compounding in the internal mixer. Figure 4.90 (a) and (b) shows micrographs of the binder based on PP. The microstructure is typical of a heterogeneous blend with dispersed domains of oblong shape in light color. Some of the oblong domains are encircled in Figure 4.90 (a). Figure 4.90 (b) shows that the dispersed domains are oriented. This orientation may have been caused during compounding. It is also apparent, that after fracture, the particles that were removed left holes in the continuous matrix. Therefore, the adhesion between the dispersed and continuous phase is weak. The weak adhesion between domains might be attributed to the different polarity of the components of each phase. It is presumed that the dispersed domains are composed of POM or water-soluble polymer (WSP) that are the polar polymers and the continuous phase of PP resin. Furthermore, the composition of the binder is 72 wt% of PP resin, 7 wt% of POM and 21 wt% of WSP.

Figure 4.91 (a) and (b) show micrographs of the binder that contained LLDPE. The microstructure is similar to that of the binders that contained PP. It is evident that the blend was multiphase displaying clear colored spherical domains some of which are encircled in the Figure 4.91 (a). In addition, the holes left after fracture of the sample seems to indicate that the adhesion between phases is weak. In this instance, the continuous phase is composed of LLDPE and the POM and WSP constitute the dispersed phase. The binder observed was compounded with 69 wt% of LLDPE, 10 wt% of POM and 21 wt% of WSP.

In addition to the features mentioned above, it is apparent in Figures 4.90 (a) and 4.91 (a) that the binders had a platelet like structure. The white color edges of the platelets are observed in both micrographs.
Figure 4.90 SEM micrographs of neat binder based on polypropylene after brittle fracture (a) 50 μm and (b) 10 μm
Figure 4.91 SEM micrographs of the binder BIN2LL at (a) 50 μm and (b) 10 μm
4.5.3. Microstructure of the feedstocks

The feedstocks were observed after cryogenic fracture of disks obtained by injection molding of the feedstocks. Figures 4.93 (a) – (c) show the micrographs of feedstocks based on PP and with different metal contents. The metal contents increased from Figure 4.93 (a) to Figure 4.93 (c). The volumetric metal contents were 22 vol%, 45 vol% and 63 vol%. It is clear that the metal affected the microstructure through rearrangement of the phases during feedstock compounding or molding.

Figures 4.93 (a) reveals that polymeric oblong domains seems to exist along with metal particles. Some of these domains are encircled in Figure 4.93 (a). However, in feedstocks with more metal contents these domains are not observed. Therefore, it is presumed that redistribution of the polymers contained in the dispersed domains occurred upon increase in metal content from 22 vol% to 45 vol%.

Figures 4.93 (b) and (c) show that the metal particles are surrounded by a layer of polymer. The Figures show structures that look like “craters” left after the removal of metal particles upon cryogenic fracture. The walls of these structures suggest that the metal particles removed were surrounded by binder. A schematic of the process of formation of the crater-like structures is shown in Figure 4.92.

![Diagram](image)

**Figure 4.92 Formation of crater-like structures upon cryogenic fracture**
The structure of the binder layer that surrounds the metal particles is observed in the micrographs shown in the Figures 4.94 (a) and (b). Figure 4.94 (a) shows that after fracture, holes are observed in the binder layer. One of these holes is encircled in the Figure 4.94 (a). Furthermore, the piece that left the hole seems to be attached to the corresponding particle as shown in Figure 4.95 (b). Therefore, the adhesion between the piece that left the hole and the rest of the binder layer is weak. The reason may be different polarity of the materials that rendered the adhesion to each other poor. It might be speculated that the layer is composed of polyolefin and the piece that left the hole may be composed of POM or water-soluble polymer.

4.5.4. Microstructure of disks after water debinding

Figure 4.95 (a) and (b) show the surface of a molded disk after water debinding by water jet impingement at 40 °C. Figure 4.95 (a) reveal that irregular shaped holes appeared on the surface of the disks after water debinding, meaning that those regions were composed of water-soluble polymer (WSP) exclusively. This observation implies that the WSP did not distribute homogeneously through the surface of the disks. Therefore, the porous structure is not simple as in the case of solids found in other engineering applications such as heterogeneous catalysis.

Figures 4.95 (a) and (c) also confirm that i) a binder layer surrounds the metal particles, and ii) the water-soluble polymer did not distribute homogeneously in the layer of binder. The first observation regards with the dispersion of the metal in the polymeric matrix. It demonstrates that agglomeration of metal particles did not exist in the feedstocks. On the other hand, the second observation seems to back the hypothesis that the layer that surrounds the metal particles is multiphase and that the WSP is dispersed in it rather than wetting the metal particles exclusively.
Figure 4.93 Micrographs of the feedstocks 1-P (a), 2-P (b) and 3-P (c)
Figure 4.94 Micrograph of a fracture surface of a disk of feedstock (a) based on LLDPE (b) based on PP
Figure 4.95 Micrograph of the surface of a disk perpendicular to the water jet after debinding of water-soluble polymer from the feedstock based on LLDPE
4.5.5 Microstructure of disks after steady shear tests

The SEM micrographs of binder BIN2LL before and after steady shear are shown in Figure 4.69 (a) and (b). The micrographs are oriented as in between the parallel disks, i.e. the top of the micrograph coincide with the topmost surface of the sample. The binder was tested at shear rates between $1 \times 10^{-5}$ s$^{-1}$ to 100 s$^{-1}$ in parallel disks geometry at 180 °C.

Figure 4.69 (a) and (b) reveal that the size of the dispersed domains near the surface of the disk changed because of the steady shear test. It is apparent, that the sizes of the holes left by the particles upon cryogenic fracture are larger in the micrograph of Figure 4.69 (b). Therefore, particle coalescence due to shearing must have occurred as has been shown elsewhere\textsuperscript{166}.

Figure 4.70 (a) and (b) show the micrographs of feedstock 3-L before and after steady shear test in parallel disks configuration. The feedstock 3_L contained 63 vol% of metal particles. The test was carried out at shear rates from $1 \times 10^{-5}$ s$^{-1}$ to 100 s$^{-1}$ and at 180 °C. The sample observed was taken at the end of the steady shear test.

Figures 4.70 (a) and (b) do not reveal any redistribution of migration of metal particles because of the shear rate imposed. In both micrographs, large and small particles are distinguishable through the surface of the fracture. Small particles under the binder layer left after removal of larger particles are visible everywhere in the sample. Therefore, it seems that the shearing during steady shear did not cause migration or separation of particles in this feedstock. Separation, however, can occur at larger shear rates as those present in injection molding.
Figure 4.96 Binder BIN2LL based on LLDPE (a) after compounding and (b) after steady shear test
Figure 4.97 Feedstock 3-L (a) after compounding and (b) after steady shear test
CHAPTER V
CONCLUSIONS

This chapter summarizes the more important conclusions of this research:

- The mechanical energy of mixing increased exponentially with respect to the volumetric concentration of metal in the feedstocks. Therefore, the concentration of metal in the feedstocks has a maximum limit that was not reached in this research.

- The shape of the torque evolution curves is predictable if the composition of the binder and the concentration of metal are known. This conclusion was derived from the experimental results that showed that there is correlation of certain characteristic torques with composition variables expressed as surface area of metal per unit volume of binder component.

- Scanning Electron Microscopy revealed that there is neither agglomeration nor segregation of metal particles during compounding. This proves that the binder is capable of keeping the powdered metal suspended.

- The proper experimental setup makes it possible to isolate the mass transport inside feedstocks during solvent debinding. This is possible if the flow of the solvent and the concentration of debindable substance are properly controlled. In particular in this research, the fluid moved fast with respect to the parts, and the concentration of debindable material was kept close to zero.
- The water-soluble polymer (WSP) is not completely removable. The reason seem to be the lack of connectivity between WSP domains inside the parts.

- The water debinding of the water-soluble polymer could be modeled using one single parameter determined from few experiments. As shown in this research, few water debinding experiments were required to calculate the effective diffusivity. In addition, this parameter could model the debinding results, especially at long times of debinding.

- The shear viscosity of the feedstocks followed a power law model.

- The feedstocks showed no yield stress even though the metal concentration was 63 % by volume of compound.

- The melting temperature of the feedstocks is determined by the polyolefin used. The reason is that the melting point of the polyolefin was not depressed more than 2 °C because of the presence of other polymers or metal in the feedstocks. Therefore, this temperature is appropriate to estimate the processing temperature of the feedstocks.

- The thermal decomposition of the binder is affected by the concentration of metal. Increased concentration of metal raised the temperature at the end of decomposition.

- The water-soluble polymer domains did not distribute uniformly on the surface of the molded disks.

- The microstructure of the parts before and after rheological test did not change. However, microstructural changes may occur in injection molding, which occurs at higher shear rates than the shear rates applied during rheological studies.
REFERENCES


208
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<th>Title and Source</th>
</tr>
</thead>
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<td>Johnson, K.</td>
<td>Patent 4765950, 1988</td>
</tr>
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