Development and Characterization of a Metal Injection Molding Bio Sourced Inconel 718 Feedstock Based on Polyhydroxyalkanoates

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Abstract: The binder plays the most important role in the metal injection molding (MIM) process. It provides fluidity of the feedstock mixture and adhesion of the powder to keep the molded shape during injection molding. The binder must provide strength and cohesion for the molded part and must be easy to remove from the molded part. Moreover, it must be recyclable, environmentally friendly and economical. Also, the miscibility between polymers affects the homogeneity of the injected parts. The goal of this study is to develop a feedstock of superalloy Inconel 718 that is environmentally friendly. For these different binders, formulations based on polyethylene glycol (PEG), because of his water solubility property, and bio sourced polymers were studied. Polyhydroxyalkanoates (PHA) were investigated as a bio sourced polymer due to its miscibility with the PEG. The result is compared to a standard formulation using polypropylene (PP). The chemical and rheological behavior of the binder formulation during mixing, injection and debinding process were investigated. The feedstock was characterized in the same way as the binders and the interactions between the powder and the binders were also studied. The results show the well adapted formulation of polymer binder to produce a superalloy Inconel 718 feedstock.

Keywords: metal injection molding; Inconel 718; polyhydroxyalkanoates; polyethylene glycol

1. Introduction

Metal injection molding (MIM) is a process to produce on mass small parts of less than 50 g with complex geometry from varied materials such as stainless steel, superalloys, carbides or ceramics. The MIM process provides good dimensional accuracy (tolerances < 5 microns), a good surface finish (Ra < 1.5 microns) and high mechanical strength similar to those of the powder material [1,2]. The MIM is a process that involves many industrial sectors such as automotive, aerospace, information technology or medical. This process is based on the injection of a fluid material composed of powder of the desired material for the final part, and of a binder of several polymers. The piece is then subjected to debinding to remove the binder and then the piece is sintered to obtain a dense part [2].

The binder plays the most important role in the MIM process. It has to be able to support an important load rate of powder, typically 60%, and to carry the powder in the mold. Enneti, Quinard and Tam [2–4] showed that the binder must give strength and cohesion to the molded part and be easily removed from the molded part, while being recyclable, environmentally friendly and economical. These authors also explained the importance of a low viscosity, good adhesion to the powder, no chemical reaction with the powder which can contaminate the powder or scissor the polymeric chains, and a low coefficient of thermal expansion for binders. The binders are generally composed of three components [2]. One provides the necessary fluidity (polyethylene glycol (PEG) or waxes are

generally used). Another one serves to provide strength of the injected piece, for which polypropylene or polyethylene is commonly employed. The last one is a surfactant which prevents the possible aggregation of the powder particles. Stearic acid is often used.

The different polymers of the binders used in this study are choose due to their environmentally friendly behavior in the MIM process. First the PEG permits the realization a water debinding due to its solubility in water [2,5]. This is environmentally important because the solvent debinding is generally realized using hazardous chemical solvent. Moreover the water and the PEG can be separated and then the water recycled. The PEG is a biocompatible thermoplastic semi-crystalline homopolymer which his characteristics depend on the molecular mass. It contains terminal hydroxyl groups which provides water-solubility for molecular masses ranging from 400 to 40,000 g·mol^{-1} [5–7]. PEG is not soluble in hydrocarbons but is soluble in acetone and alcohol [5]. Accordingly, a PEG with a molecular weight of 20,000 g·mol^{-1} was chosen as it ensures solubility in water while keeping a sufficient binder viscosity.

The choice of the primary binder polymer is driven by its affinity with the PEG. Moreover, to reduce its environmental impact, bio-sourced polymer was choosen because the primary binder has to be removed by thermal debinding to make the shape of the piece as long as possible. In addition, the influence of the binder on both homogeneity and rheological properties of the feedstock has been established [8]. Taking into account all these aspects, polyhydroxyalcanoates (PHA) was choose because it is well known to be miscible with the PEG [5]. Moreover, PHA is one of the most common bio sourced polymers and grades are available for mold injection application [9]. The PHA is a polyester obtained directly from the bacterial metabolism. More than 250 species of bacteria synthesized PHAs granules size from 0.2 to 0.5 µm as carbon and energy storage materials under condition of limiting nutrients and in the presence of excess carbon source. PHA is a biodegradable and biocompatible polymer with good physical, mechanical and thermal properties [5,9].

In this study, a micro powder of Inconel 718 was investigated for an application in the MIM process. A micro powder was chosen because it is well adapted for µMIM experiments, including injection, debinding and sintering stages [3,10]. The use of Inconel for MIM process has been studied by Özgün [11] and a formulation was developed. Inconel superalloys are used in aviation, aerospace and nuclear power due to their high resistance to corrosion and oxidation but also for their excellent mechanical strength at high temperature [11]. Currently, the most popular superalloys used for the above applications are Inconel 718 and 625. Here, an Inconel 718 powder was chosen as the final material of the piece. The binders developed by Özgün [11] were composed of polypropylene (PP), carnauba wax, paraffin wax and stearic acid.

The process to remove the PEG using the CO_2 supercritical as solvent was studied. This process heated and pressurised the CO_2 below his critical point (304.1 K and 7.38 MPa). The supercritical CO_2 has the behavior of a gas: this facilitates the penetration of the CO_2 inside the samples, and of a liquid: this increases the solubility of the PEG in the CO_2. The debinding method using the CO_2 supercritical as solvent was first reported by Chartier *et al.* in 1995 [12] but the tests were performed on feedstocks made of different waxes and ceramics powders. Shimizu *et al.* [13] also used this method of debinding with feedstock made of paraffin wax. Federzoni *et al.* [14] were the first to use the CO_2 supercritical as solvent debinding method to remove the PEG. Federzoni *et al.* [14] showed that the PEG can be removed entirely by using 65 °C, 300 bar and 7 h as conditions of the process.

The goal of the present study is to develop an environmentally friendly binder formulation adapted to the use of a micro powder of Inconel 718 with the use of bio sourced polymers as binder and the CO_2 supercritical as solvent debinding method.

2. Materials and Methods

Two grades of PHA are used, namely PHA and PHBV provided by NaturePlast and adapted to the injection process. The powder used is an Inconel 718 atomized by argon provide by Sandvik Osprey (Neath, UK). The powder was characterized by a granulometer laser LA-950 V2 provided by Horiba (Kyoto, Japan), the tests were realized in water.

The polymer blends are made in a twin screw mixer provided by Brabender (Duisburg, Germany) which has a volume capacity of 50 cm^3, a speed of 50 rpm and at a temperature of 180 °C. The temperature of the test is determined between the higher melting temperature of the polymer and the lowest temperature of degradation of the polymers. According to this requirement, the mixtures were made for all the different kinds of mixture at 180 °C. The higher melting temperature corresponds to the PHA at 175 °C and the lowest temperature of degradation at the SA at 180 °C. The speed of the mixture was determined according to previous work in our laboratory [15]. First, the primary binder and the PEG were introduced in the mixer and then the SA and the powder. The mixture is homogenized when the mixing torque is stable.

The rheological tests were performed on a capillary rheometer Rosand RH2000 provided by Malvern Instruments (Malvern, UK). The tests are realized at 180 °C, the temperature selected for injection, in order to characterize the viscoelastic properties of the binders. The feedstocks were characterized at shear rate corresponding to the usual injection shear rate, between 2000 s^{-1} and 50,000 s^{-1} in a range of shear rates matching those encountered in injection process. The injection was realized on an injection machine (Arburg, Loßburg, Germany) at 180 °C. Cylinders of 100 mm of length and 10 mm of diameter were injected.

The choice of the PEG was made due to his possibility to be removed by water. To study this method of debinding, a cylinder of the different mixtures were injected. Different methods of water debinding were tested. First the samples are put on a bath of heat water [16,17]. Two different temperatures were tested, 50 °C and 60 °C, and the test were made during 24 h and 48 h because these conditions correspond to removal of the entire PEG from the feedstock made with the PP. Another test was made using a magnetic stirrer in the water bath [16,18]. To compare the result with the previous test, the same temperature and time were studied. Finally, an ultrasonic bath was used [18]. The ultrasonic bath use a 35 KHz and 50 W ultrasonic waves. Images of the samples before and after debinding were also made to characterize the possible defaults which can appear during the different process. To determine the weight loss of PEG the samples are weighed before and after each test. This is an approximation but only the PEG is logically soluble in water so the results are close to reality. To confirm the results, some TGA on the samples have to be made.

According to the work of Federzoni *et al.* [14] a preliminary test was made at 70 °C, 300 bar during 4 h. However, a previous test on the samples injected with the feedstock with PP shows only 40% of weight loss of PEG. Another test at 150 °C and 400 bars during 4 h was made and the results were better. These conditions were choosen because, according to the data from the National Institute of Standards and Technology [19], the density and the viscosity of the supercritical CO_2 are similar at 70 °C, 300 bar (257.34 kg/m^3, 26.004 µPa·s) and 150 °C, 400 bar (259.50 kg/m^3, 29.180 µPa·s). So the coefficient of diffusivity and solubility of the PEG in the CO_2 does not change because of the properties of the CO_2 but due to the increase of the temperature and the pressure that enhance these coefficients. The supercritical debinding was realized in a SFE2.2 supercritical fluid reactor provided by Separex (Champigneulles, France).
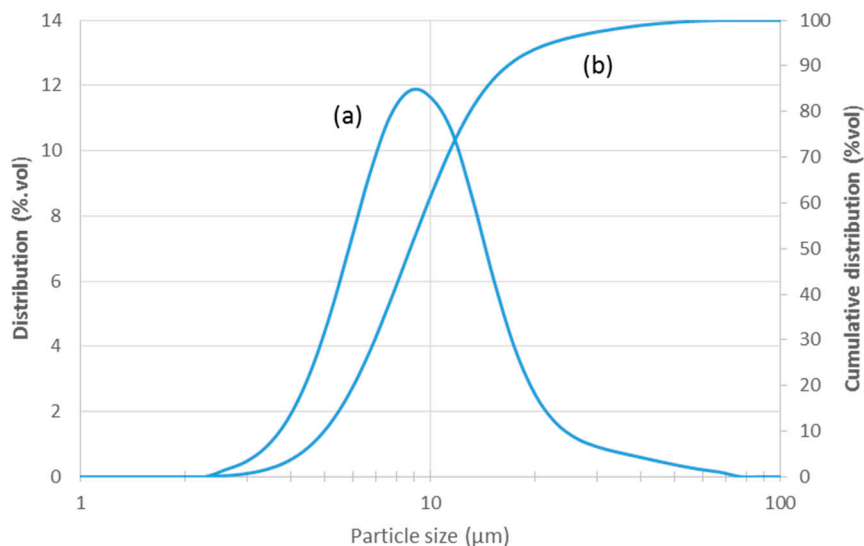
3. Results

3.1. Powder Characterization

The Inconel 718 powder was characterized by laser granulometer to determine the particle size and distribution. The Table 1 gives the D_{10}, D_{50} and D_{90} of the powder and the Figure 1 gives the distribution and the cumulative distribution. The size of the powder is in accordance with the requirements of the MIM process with a size smaller that 20 µm. The distribution is relatively thin with a span of 1.35 µm. This shows that the powder chosen is adapted to our process.

Table 1. Characteristics of the Inconel 718 powder.

Particles Size Distribution	D_{10}	D_{50}	D_{90}
Size	4.95 μm	8.7 μm	16.7 μm

Figure 1. Size distribution (**a**) and cumulative volume (**b**) of the Inconel 718 powder.

3.2. Mixing

To characterize the different mixtures (Table 2), the critical volume fraction of powder was determined for each formulation [3,20]. The results are given Table 3 and Figure 2. To determine the critical volume fraction of powder, the incremental method was used. This method consists of adding the powder progressively until the mixing torque cannot stabilize. The maximum volume fraction of powder corresponds to the last mixture that is stabilized. The results for the mixture show a lower critical volume fraction of powder for the In718/PEG/PP/SA mixture. The volume fraction of powder determines the value of the shrinkage during the sintering and also the uniformity of the shrinkage. A high value of volume fraction reduces the value of the shrinkage because the distance between the particles of powder become lower and less porosity remains after debinding. The mixtures based on PHBV and PHA are interesting at this point. The critical volume fraction was determined to characterize and compare the different mixtures but the other analyses were made on feedstock with 60% of volume fraction. This fraction was chosen because it is a usual volume fraction in industry.

Table 2. Composition of the formulations.

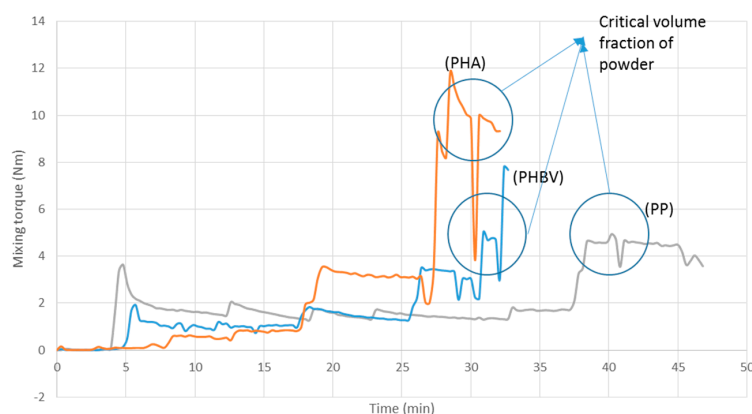| Volume Fraction (%)	Materials of Feedstock 1	Materials of Feedstock 2	Materials of Feedstock 3
60	Inconel 718	Inconel 718	Inconel 718
22	PEG20K	PEG20K	PEG20K
16	PP	PHA	PHBV
2	Stearic Acid	Stearic Acid	Stearic Acid

Figure 2. Mixing torque *versus* time of the feedstocks with polyhydroxyalkanoates (PHA), Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and polypropylene (PP) during the incremental method.

Table 3. Critical volume fraction of powder and maximum volume fraction of powder of the different feedstock.

Formulation	Critical Volume Fraction of Powder (%)	Maximum Volume Fraction of Powder (%)
In718/PEG/PHA/SA	92	90
In718/PEG/PHBV/SA	87	85
In718/PEG/PP/SA	80	78

3.3. Rheology

The feedstocks were characterized by capillary rheometer to determine their ability to be injected. The results are shown Figure 3. The results shows pseudo plastic behavior of all the mixtures and the results are in accordance with the mixing results. The pseudo plastic behavior of the feedstocks can be confirmed using the flow behavior index of the Ostwald's law (1). The results are available in Table 4 and the value of the flow behavior index of all the feedstocks corresponds to a pseudo plastic behavior (<1). Moreover the feedstock with PHA show low shear viscosity. This low shear viscosity can be easy to inject and makes it easier to fill the thin part of the component. The two other feedstocks have similar shear viscosity.
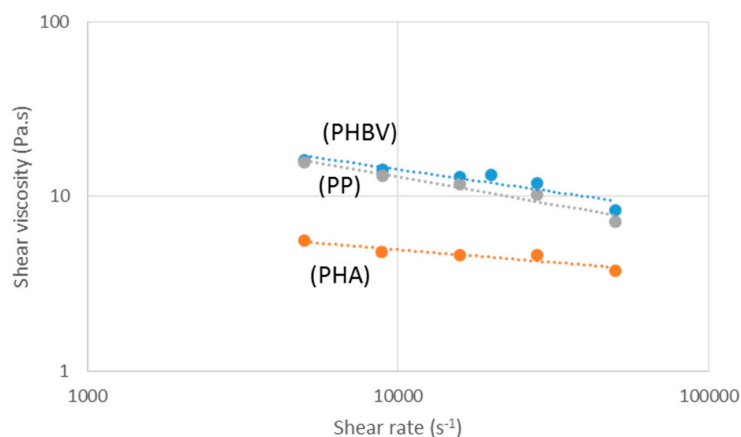

Figure 3. Shear viscosity *versus* shear rate of the feedstock with PP, PHBV and PHA and 60% of volume fraction of powder.

$$\eta = K\dot{\gamma}^{n-1} \tag{1}$$

Ostwald's law of fluid where n is the flow behavior index, η is the shear viscosity (Pa· s), *K* is the flow consistency index and $\dot{\gamma}$ is the shear rate (s^{-1}).

Table 4. Value of the flow behavior index of the different feedstock.

Formulation	PP	PHA	PHBV
Value of the flow behavior index *n*	0.686	0.855	0.743

3.4. Water Debinding

The different results of the debinding test in water are available in Figures 4 and 5. In water, the weight loss of PEG of the feedstocks with PP and PHBV are similar and after 48 h at 60 °C the PEG is totally removed. The PHA lost only 40% of PEG after this process. This lower weight loss of PEG can be explained by the affinity, or even miscibility, between the PEG and the PHA. This can induce a smaller inclusion of PEG in the PHA compared with PHBV or PP. The PEG is so much more difficult to access for the water and the time of debinding increase. The images of the cylinder with PHA may confirm this hypothesis because some cracks appear on the surface and may be due to the difficulty for the water to access to the PEG. Moreover, the use of 60 °C as temperature of the water reveals better results for the PHBV and PP mixture, contrary to the PHA feedstock that lost more PEG at 50 °C.

The water debinding test with magnetic stirrer shows better results for each formulation. After 48 h at 60 °C all the formulations have lost 100% of PEG. Moreover, after 24 h at 60 °C the components have lost more PEG than after 24 h in water at 60 °C without stirring. This is probably due to the replacement of the water around the samples. This refresh water has a better possibility to remove the PEG. The results for water at 50 °C are similar to the previous test in water. However, the images show more cracks for the samples with PHA and PHBV. This is probably because more tension appears on the samples due to the mobility of the water.

The debinding by ultrasonic water was studied and the results show between 150% and 350 % of weight loss of PEG. This is due to the loss of some powder during the process. Moreover, as shown in the images in Figure 6 the samples made with the feedstock with PHA or PHBV isare seriously damaged. The sample of the feedstock with PP does not show any default or crack. The tests were made in a bath fill with water at 60 °C.
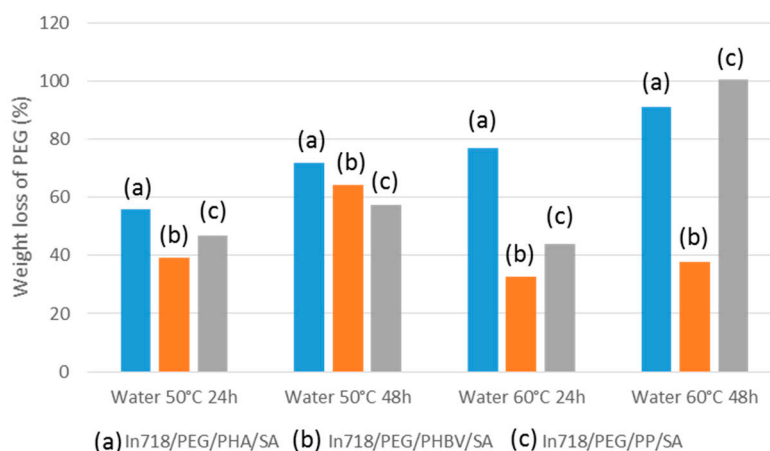

Figure 4. Weight loss of polyethylene glycol (PEG) for the different feedstocks after debinding in water at 50 °C and 60 °C during 24 h and 48 h.
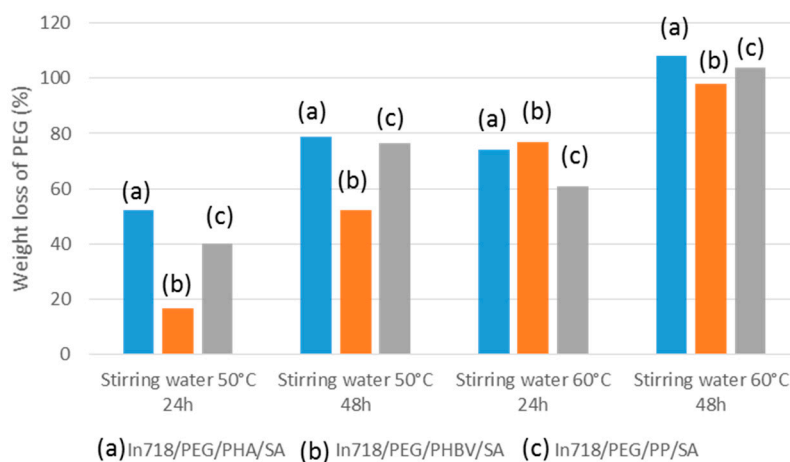
Figure 5. Weight loss of PEG for the different feedstocks after debinding in stirring water at 50 °C and 60 °C during 24 h and 48 h.

Figure 6. Images of the different samples after injection, after 48 h of debinding in water at 60 °C, after 6 h of debinding in ultrasonci water at 60 °C, and after 48 h of debinding in stirring water at 60 °C.

3.5. Supercritical Debinding

The results of the different tests are shown in Figure 7 and images of the samples after the tests are available in Figure 8. The results show better weight loss for the feedstock with PP. The feedstock with PHA was totally destroyed during this process. This is probably due to the more fragile backbone of the PHA induced by the littlest inclusion of PEG. This fact decreases the strength of the sample, which, with the high temperature, cannot maintain the shape of the component. Regarding the others feedstocks, this process is softer than the debinding by water because the samples show no cracks or deformations.
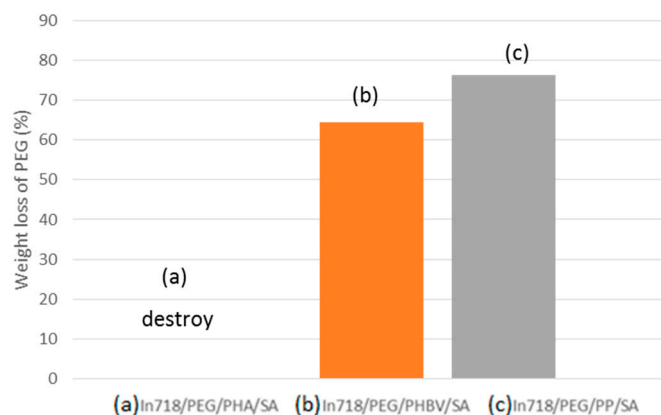
Figure 7. Weight loss of PEG for the different feedstocks after supercritical CO_2 debinding process at 150 °C and 400 bar during 4 h.
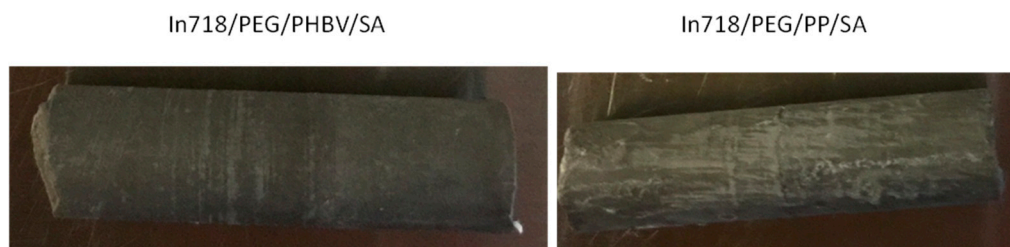

Figure 8. Images of the different samples after 4 h at 150 °C and 400 bar of supercritical CO_2 debinding.

4. Discussion

The results show the PP can be substituted by the PHBV in a MIM feedstock. The results obtained with the feedstock with PHA show that the properties of this feedstock are not compatible with the MIM process. The PHA could be a primary binder but maybe the ratio with the PEG should be changed for a higher rate of PHA. The change of the ratio could more deeply modify the properties of the feedstock due to the possible modification of the parameters of miscibility between the PEG and the PHA. This could avoid the cracks, reduce the time of debinding and increase the strength of the component. This could be interesting because the viscosity of the feedstock with PHA is relatively low and an increase of the rate of PHA should not make the mixture too viscous to inject. Some analyzes like TGA or DSC will be done to analyze the possible miscibility between the PHA and the PEG and so optimize the ratio of the mixture. Finally, maybe the PHA should be mixed with another polymer which is more adapted.

The conditions of the CO_2 supercritical debinding process have to be optimized to successfully entirely remove the PEG in a short time. Maybe the increase of the time is not the best solution; the influence of the temperature and of the pressure could be studied more. A lower temperature can probably reduce the defaults because the polymers will be more resistant to the mechanical stress. According to our composition of feedstock, a test around 100 °C should be more compatible. This temperature is higher than the melting temperature of the PEG and sufficiently lower than the melting temperature of the PP. Moreover, a higher pressure between 400 bars and 600 bars should be tested because our equipment is limited to 600 bars. This would determine the influence of pressure on the debinding process. The influence of the different polymers and of the different debinding processes on the final densified part is an important study. This will be studied in future works because the modification of the surface of the samples by the polymers or the process can induce some problems during the thermal debinding and also during the sintering.

5. Conclusions

The results show that the PHBV can be a solution to substitute the PP and realize a green feedstock. Indeed, the behavior of the feedstock made with PHBV shows similar rheological properties, better maximal volume fraction of powder and no more defaults after debinding process. The time of debinding is longer but the use of the CO_2 supercritical debinding process reduces this time which becomes much shorter than for the water debinding. Moreover, this debinding process is smoother for the components during debinding. The feedstock made with PHA is interesting due to his low viscosity but too much default appears during debinding and the time to remove the PEG is too long. The tests of debinding have to be confirmed by TGA and the influence of the different process and the different polymers on the final densified piece will be studied.

Author Contributions: Alexandre Royer designed and performed the experiments. Alexandre Royer analyzed the data and wrote the paper. Thierry Barrière and Jean-Claude Gelin supervised the study and corrected the paper.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

PP	polypropylene
PEG	polyethylene glycol
PHA	polyhydroxyalkanoates
PHBV	poly(3-hydroxybutyrate-co-3-hydroxyvalerate)
SA	stearic acid
TGA	thermogravimetric analysis
MIM	metal injection moulding

References

1. German, R.M. *Powder Injection Moulding—Design and Applications*; Innovative Material Solution, Inc.: State College, PA, USA, 2003.
2. Enneti, R.K.; Onbattuvelli, V.P.; Atre, S.V. Powder binder formulation and compound manufacture in metal injection molding (MIM). In *Handbook of Metal Injection Molding*; Heaney, D.F., Ed.; Woodhead Publishing Series in Metals and Surface Engineering; Woodhead Publishing: Cambridge, UK, 2012; pp. 64–92.
3. Quinard, C.; Song, J.; Barriere, T.; Gelin, J.C. Elaboration of PIM feedstocks with 316L fine stainless steel powders for the processing of micro-components. *Powder Technol.* **2011**, *208*, 383–389. [CrossRef]
4. Tam, K.C.; Yap, S.P.; Foong, M.L.; Loh, N.H. Metal injection molding: Effects of the vinyl acetate content on binder behavior. *J. Mater. Process. Technol.* **1997**, *67*, 120–125. [CrossRef]
5. Thomas, S.; Grohens, Y.; Jyotishkumar, P. *Characterization of Polymer Blends: Miscibility, Morphology and Interfaces*; John Wiley & Sons: New York, NY, USA, 2014.
6. Sheth, M.; Kumar, R.A.; Davé, V.; Gross, R.A.; McCarthy, S.P. Biodegradable polymer blends of poly(lactic acid) and poly(ethylene glycol). *J. Appl. Polym. Sci.* **1997**, *66*, 1495–1505. [CrossRef]
7. Castillo, R.V.; Müller, A.J. Crystallization and morphology of biodegradable or biostable single and double crystalline block copolymers. *Prog. Polym. Sci.* **2009**, *34*, 516–560. [CrossRef]
8. Thavanayagam, G.; Pickering, K.L.; Swan, J.E.; Cao, P. Analysis of rheological behaviour of titanium feedstocks formulated with a water-soluble binder system for powder injection moulding. *Powder Technol.* **2015**, *269*, 227–232. [CrossRef]
9. Jiang, L.; Zhang, J. Biodegradable Polymers and Polymer Blends. In *Handbook of Biopolymers and Biodegradable Plastics: Properties, Processing and Applications*; Ebnesajjad, S., Ed.; William Andrew Publishing: Boston, MA, USA, 2013; pp. 109–128.
10. Quinard, C.; Barriere, T.; Gelin, J.C. Development and property identification of 316L stainless steel feedstock for PIM and μPIM. *Powder Technol.* **2009**, *190*, 123–128. [CrossRef]

11. Özgün, Ö.; Gülsoy, H.Ö.; Yılmaz, R.; Fındık, F. Microstructural and mechanical characterization of injection molded 718 superalloy powders. *J. Alloy. Compd.* **2013**, *576*, 140–153. [CrossRef]

12. Chartier, T.; Ferrato, M.; Baumard, J.-F. Influence of the debinding method on the mechanical properties of plastic formed ceramics. *J. Eur. Ceram. Soc.* **1995**, *15*, 899–903. [CrossRef]

13. Shimizu, T. Solvent debinding of injection moulded parts with supercritical carbon dioxide. *Met. Powder Rep.* **1997**, *52*, 41.

14. Federzoni, L.; Revirand, P.; Lumia, D.; Rossignol, G. Evaluation of the supercritical CO2 as method of debinding for PIM parts. In Proceedings of the Internationnal Congress & Exibition, Euro PM, Copenhagen, Denmark, 12–14 October 2009.

15. Djoudi, H.; Gelin, J.-C.; Barrière, T. Experiments and FE simulation for twin screw mixing of nanocomposite of polypropylene/multi-walled carbon nanotubes. *Compos. Sci. Technol.* **2015**, *107*, 169–176. [CrossRef]

16. Chen, G.; Cao, P.; Wen, G.; Edmonds, N. Debinding behaviour of a water soluble PEG/PMMA binder for Ti metal injection moulding. *Mater. Chem. Phys.* **2013**, *139*, 557–565. [CrossRef]

17. Hidalgo, J.; Jiménez-Morales, A.; Barriere, T.; Gelin, J.C.; Torralba, J.M. Water soluble Invar 36 feedstock development for μPIM. *J. Mater. Process. Technol.* **2014**, *214*, 436–444. [CrossRef]

18. Shbeh, M.M.; Goodall, R. Design of water debinding and dissolution stages of metal injection moulded porous Ti foam production. *Mater. Des.* **2015**, *87*, 295–302. [CrossRef]

19. US Department of Commerce. National Institute of Standards and Technology. Available online: http://www.nist.gov/ (accessed on 25 March 2016).

20. Hidalgo, J.; Abajo, C.; Jiménez-Morales, A.; Torralba, J.M. Effect of a binder system on the low-pressure powder injection moulding of water-soluble zircon feedstocks. *J. Eur. Ceram. Soc.* **2013**, *33*, 3185–3194. [CrossRef]