DEBINDING PROCESS OF SS316L METAL INJECTION MOULDING UNDER ARGON ATMOSPHERE

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ABSTRACT: Solvent and thermal debinding acted as binder in removing Restaurant Waste Lipid (RWL) and Polypropylene (PP) from the stainless steel 316L. This investigation was carried out to determine the effect of thermal debinding variables on density, shrinkage and surface morphology of the brown parts other than to remove the binder from the SS316L under the Argon atmosphere with flow rate of 5 ml/min. The parameter used for solvent debinding process was solvent temperature at 60°C for six hours, while thermal debinding process was conducted at various temperature of 400°C, 500°C and 600°C, heating rate of 10 °C/min, 20 °C/min and 30 °C/min, dwell time of 30 min, 60 min and 90 min, and cooling rate of 5 °C/min, 10 °C/min and 15 °C/min. Analysis of weight loss percentage was done on the brown part after the solvent debinding and thermal debinding processes. Scanning Electron Microscope (SEM) was used to confirm the removal of RWL and PP from the compacts based on the porosity form, and attachment of PP in the powder particles. This investigation showed that debinding parameters were important in terms of their effects on the physical properties. Based on the observation through SEM and consideration of the factors that affected the physical properties of the parts, it was found that RWL was completely extracted out at 60°C for six hours, while the thermal temperature of 500°C with heating rate of 10 °C/min, dwell time of 60 min and cooling rate of 15 °C/min were the optimal thermal debinding parameters in PP removal.

KEYWORDS: *Thermal Debinding; Injection Moulding; Polypropylene*

1.0 INTRODUCTION

Metal injection moulding (MIM) is an advanced technology that can produce high performance, intricate and complex-shaped metal parts. MIM is employed to process metal powders into the desired shapes, where it involves the process of mixing metal powder and binder to form a feedstock. MIM involves four processing steps which include mixing, injection moulding, debinding and sintering [1].

Stainless steel 316L has long been known as a biomaterial for medical implant or other medical equipment. Besides its capability, the cost of this metal is also considered low compared to other substitute metals such as Titanium. Preparation of feedstock is usually done by mixing the SS316L powder with binder, consisting of two or three components of polymeric binder along with surfactants. This composition of binder is characterized as backbone binder which holds the metal particles in its place after injection, and the primary binder increases the flowability of the powder particles during injection moulding [2]. Since the final product is based on the metal itself, removing or debinding the binder is crucial since it will affect the sintering process due to unburnt binder or residue from the binder which causes contamination [3].

Several debinding techniques have been recognised in removing the binder out from the green parts including thermal [4], solvent [5] and wicking [6-7], where different methods have their own capability or advantages. Two methods of debinding process are usually employed to shorten the time for binder removal, other than minimizing the possibility of cracking and swelling [8]. First, the solvent debinding process allows the primary binder with low molecular weight to diffuse out from the green components to the solvents by immersion. The types of solvents used ranged from heptane, Hexane, and water is usually preferable since this type of solvent is more environmentally friendly compared to other types of solvents. This method creates pores which form interconnected tunnel or channel which is used to diffuse out the backbone binder or high molecular weight binder from the components during thermal debinding process [9-11].

The green part is thermally debound at elevated temperature to remove the remaining minor binders inside the green part. The existing porosity makes the thermal removal of the insoluble binders to be completed in a short period compared to usual thermal debinding process [12]. Debinding temperature, heating rate, cooling rate and surrounding atmosphere give great influence on the outcomes of the brown part. Too steep of elevated temperature could increase the possibility of the parts to crack, swell and warp. It is also shown that incorrect atmosphere, temperature, dwell time and cooling time setting could result in elevated oxidation level [13-15].

During thermal debinding, the strength of the compact would decrease due to thermal softening and loss of polymer. Therefore, the compact will become more porous and more exposed to the surrounding air, which then increases the oxidation level under air atmosphere. Apart from that, heating rate with dwell time also affects the oxidation level since shorter dwell time with high heating rate could reduce the percentage of built up of oxidation level on the powder particle surfaces [14]. Although high heating rate is good in reducing the formation of oxide layer, too high rate could increase the stresses that act on the compact which generate cracks or distortion during thermal debinding [12]. Therefore, optimum heating rate and dwell time during debinding process also need to be considered in order to obtain a good final product, either in physical or mechanical properties [16].

In this research, the effects of two-step debinding via solvent and thermal techniques under Argon atmosphere on the SS316L green part injection mould are analysed for optimum binder removal based on heating rate, temperature, cooling rate and dwell time. The characteristics of the brown part after debinding process of SS316L green part injection mould are based on XRD and SEM analysis.

2.0 METHODOLOGY

The green part in this study consisted of 316L water atomized stainless steel powder with mean particle size of 6μm and powder loading of 60 percent. Particle size was measured via particle analyser Fritsch analysette 22 compact. The stainless steel powder had the physical properties and chemical composition as shown in Table 1, as supplied by Epson Atmix Japan.

For binder components, polypropylene (PP) and restaurant waste lipids (RWL) were used with compositions and thermal properties as shown in Table 2.

Table 1: Physical properties and chemical composition of 316L stainless steel metal powder

<table>
<tr><td colspan="9">Powder size and density</td></tr>
<tr><td colspan="2" rowspan="2">Powder SS316L Epson Atmix Corp</td><td>Size</td><td>D10</td><td colspan="2">D50</td><td>D90</td><td colspan="2">Density</td></tr>
<tr><td>6.0μm</td><td>2.87μm</td><td colspan="2">5.96μm</td><td>10.65μm</td><td colspan="2">8.0471 g/cm^3</td></tr>
<tr><td colspan="9">Powder chemical composition (% wt)</td></tr>
<tr><td>Ci</td><td>Si</td><td>Mn</td><td>P</td><td>S</td><td>Ni</td><td>Cr</td><td>Mo</td><td>Cu</td></tr>
<tr><td>0.027</td><td>0.84</td><td>0.19</td><td>0.016</td><td>0.012</td><td>12.20</td><td>16.40</td><td>2.10</td><td>0.03</td></tr>
</table>

Table 2: Binder composition and thermal properties of binder components

Binder	Fraction in binder	Density (gcm^{-3})	Melting Temperature (°C)	Degradation Range (°C)
Polypropylene (PP)	0.4 (5.6g)	0.90	165	350~470
RWL derivatives	0.6 (8.3g)	0.90	50	270~360

Temperature selection for solvent (heptane) must be set below the melting temperature of backbone binder, which in this case, PP in order to prevent the green part from slumping. The temperature selected must also be slightly higher than the melting temperature of the lowest melting temperature of the binder components, in this case RWL, where RWL could dissolve in heptane, and diffuse out from the injected part or green part. In order to achieve this, differential scanning calorimeter (DSC) Q20 was used to gain the data of melting temperature of the binder inside the injected part using the heating rate of 10 °C/min under nitrogen atmosphere with flow rate of 50 ml/min.

Thermal debinding was done under the Argon atmosphere with flow rate of 5 ml/min range of temperature, heating rate, dwell time and cooling time setting as shown in Table 3 to understand the effect of each parameter on the injected part. Improper thermal debinding cycle induces the defects such as cracks, blister, distortion and contamination [1, 17].

First, the weight of the green parts was weighted and recorded. The green parts were subject to solvent extraction process, where the soluble binder of RWL was leached out by immersing the part in heptane solution at temperature of 60 °C for six hours in the convection drying oven. Then, the parts were dried for two days at room temperature before the weight after solvent was taken. The weight loss percentage of the parts was calculated by Equation (1). The parts after solvent were analysed by Scanning Electron Microscope (SEM, FKMP, UTHM) to evaluate the formation of porosity formed and X-ray diffraction (XRD, FKMP, UTHM) to analyse the phases of the parts.

$$W_{loss} = \frac{W_i - W_a}{W_i} \times 100\% \qquad (1)$$

The initial weight of the green part is Wi, and Wa is the weight after solvent debound. The parts after solvent debinding then underwent thermal debinding process to remove the backbone binders (PP) by using tubular furnace (AMMC, UTHM) under argon atmosphere at constant flow rate.

Table 3: Thermal debinding parameter range

Variables	Ranges
Temperature (℃)	400, 500, 600
Heating rate (℃/min)	10, 20, 30
Dwell time (min)	30, 60, 90
Cooling rate (℃/min)	5, 10, 15

The brown part after thermal debinding was weighted to determine the weight loss. Cross section of the parts was analysed through SEM to determine the burned off of PP, and sample phases were conducted through XRD. The compact that has completely undergone debinding process was examined on the surface with naked eyes, such as the surface of the compact. A debound compact that resulted in crack and swell was separated and labelled as a failure compact.

3.0 RESULTS AND DISCUSSION

3.1 Solvent Debinding Process

Solvent debinding is a process to extract low molecular weight binder from the part which can be enhanced to shorten the time of thermal debinding process. For this research, results from differential scanning calorimeter (DSC) analysis were used in solvent debinding process to extract the major binder (RWL) from the green part in heptane solution. Figure 1 shows that the minimum temperature for solvent was found to be 48°C, and temperature of 60°C was chosen to increase the diffusion of the RWL into the heptane solution. This selection of temperature has been used by other researchers since it is below the melting temperature of PP, and no observation of crack or swelling was found during the experiment.

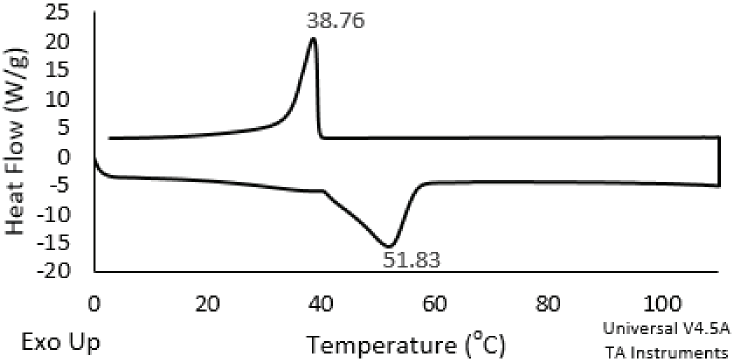


Figure 1: RWL DSC data curves under heating rate of 10°C/min in Nitrogen atmosphere with 50 ml/min gas flowrate

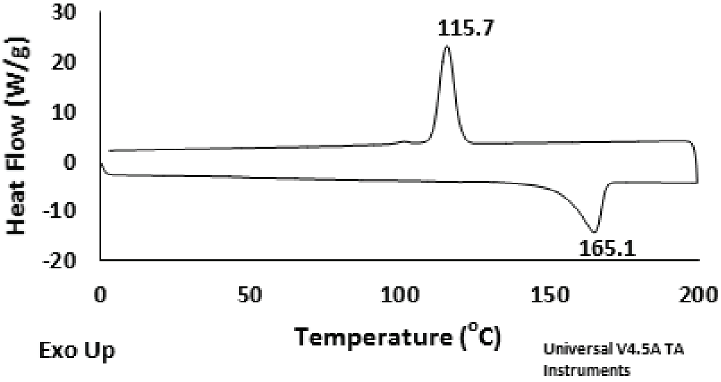


Figure 2: PP DSC data curves under heating rate of 10°C/min in Nitrogen atmosphere with 50 ml/min gas flow rate

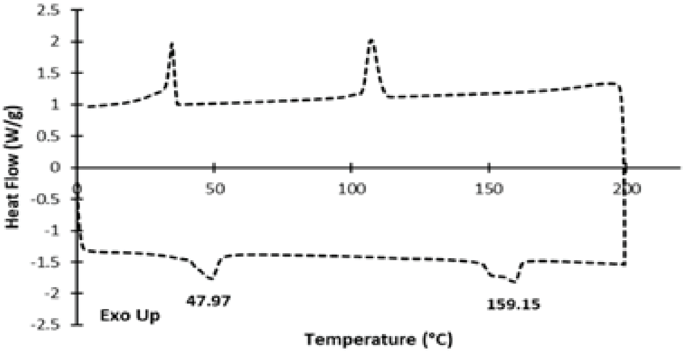


Figure 3: DSC data curves under heating rate of 10°C/min and Nitrogen atmosphere with 50 ml/min flowrate for green part

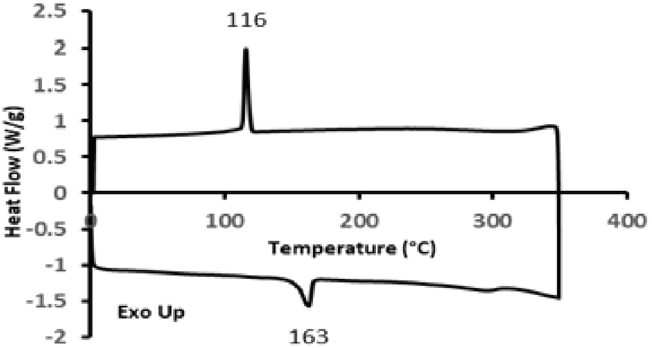
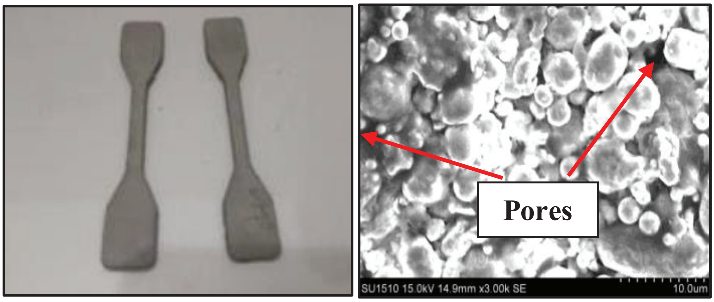


Figure 4: DSC data curves under heating rate of 10°C/min and Nitrogen atmosphere with 50 ml/min flowrate for part after solvent

Figures 1 and 2 show the DSC curves of RWL and PP, respectively. This is to show that the melting temperature of both components of binder is 51.8°C and 165°C, respectively. Figure 3 shows the results of melting temperature of both components after being mixed to form a green part with SS316L powder. It shows that the melting temperature of RWL and PP was shifted to the left due to the melting point depression. 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 reasonable when considering the way, the melting points were obtained [18]. Figure 4 shows the result of DSC after solvent debinding process, indicating that there are only single peaks appear on the profile which interpreting that RWL components is successfully being remove out of the green part which remains only PP inside the green part.

Figure 5(a) shows no sign of swell or crack occurring at the surface of the brown parts. The result of SEM analysis after solvent at temperature of 60°C for six hours is presented in Figure 5(b). From this figure, it can be clearly seen that there are open pore channels formed due to the removal of RWL. This open pore channel contributes to the success of the thermal debinding process where with this channel, pressure from the gas residue of burnout PP will allow to flow out through this channel. This is important to reduce the stress in the green part surface as a result produce good surface finish after thermal debinding process. Other than that, Polypropylene (PP) binder can also be seen still attached to powder particles which to keep the powder particles in place and retain the part shapes. From the result obtained, the parameters of the solvent debound in the heptane solvents are optimized in removal of the RWL from the parts without any distortion occurring on the surface.



(a) (b)

Figure 5: (a) Brown part after solvent debinding and (b) microstructure of green part after solvent debinding for 6 hours at temperature of 60°C

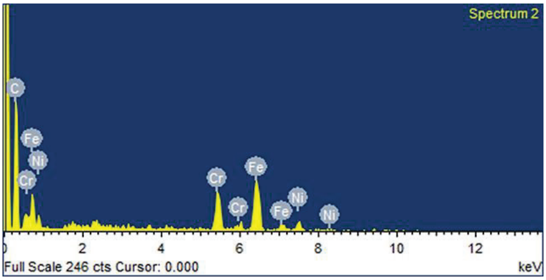


Figure 6: Weight Loss against samples of solvent debinding for 6 hours at temperature 60°C

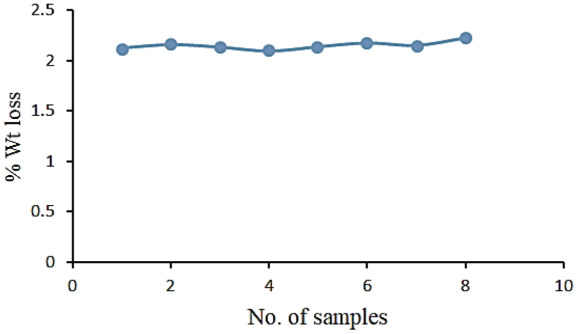


Figure 7: Energy Dispersive Spectroscopy (EDS) of green part after solvent debinding for six hours

From Figure 6, weight loss results of the samples taken after solvent debinding process show that the weight of the RWL in each green part is nearly constant and successfully being extracted. Equation (1) is used to calculate the variety of percentage weight different for 10 parts and the result shows that there is a decrease in the weight of the brown part after solvent extraction process. The variety shows less difference and most of the percent weight loss is above 2%. Analysis from Energy Dispersive Spectroscopy (EDS) in Figure 7 shows that the content of carbon element during solvent process is still obvious. This is due to the presence of PP that has not been unburned inside the part.

3.2 Thermal Debinding Process

Thermal debinding process is a step to remove minor binder that is left after solvent debinding process at an elevated temperature [3]. In this research, heating rate to debinding temperature was identified as parameter that could affect the physical properties of the debound part. According to Hayat et al. [5], this parameter can affect the change of the content of interstitials and final density of the part.

Heating rate is defined as the temperature change per minute from room temperature to the debinding temperature. As seen from Figures 8 and 9, the part that was debound at low heating rate from room temperature to specific debinding temperature in argon gas produced was defect-free compared to the debound part at high heating rate [3]. Debound part at heating rate of 20°C showed that swells occurred at the surface of the brown parts. However, no crack was observed for all the debound parts. For this result, the formation of the distortion occurring at high heating rate was related to the pressure build-up at the brown parts due to the accelerated debinding [5]. Accelerating the heating rate causes particle migration, and binder flow increases, leading to deformation at the surface of the parts.

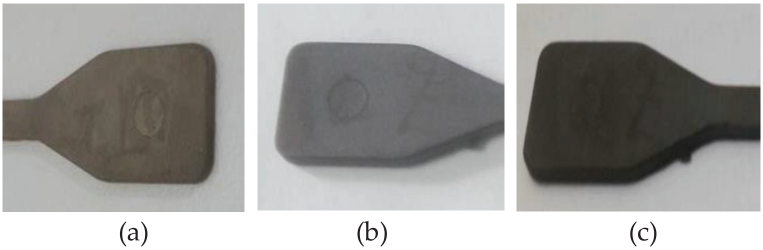
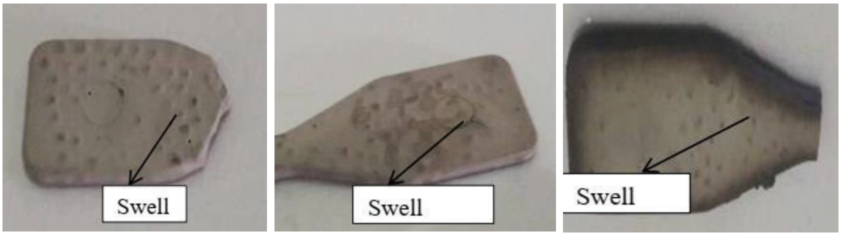

(a) (b) (c)

Figure 8: Thermal debound part or brown part at temperature and heating rate of (a) 400°C and 10°C/min, (b) 500°C and 10°C/min and (c) 600°C and 10°C/min



(a) (b) (c)

Figure 9: Thermal debound part or brown part at temperature and heating rate of (a) 400°C and 20°C/min, (b) 500°C and 20°C/min and (c) 600°C and 20°C/min

Although higher heating rate increase the weight loss of the brown part, part, swelling is found after being heated at 20°C/min at all range of temperature as shown in Figure 9. The swelling is due to quick burnout of the binder which results in increase the pressure and stress inside the green part from the residue gases where the pores created from the solvent debinding cannot accommodate the sudden increase in gas pressure. The sudden increase internal pressure from the burnout gas will push the top powder particles of the part and this process results in swelling occurs at the surface of the brown part for gas to release in the atmosphere [5]. This part defect is not found when 10°C/min heating rate was applied shown in Figure 8. Clean brown part appears for Figure 8(b) as compare with (a) and (b) in Figure 8 which shows brownish and carburizing particles appear on its surface. The brownish color of the part is due to the incomplete burnout of the binder at the surface of the part while the dark color indicates of the carbon residue from the binder being covered on the surface of the SS316L powder particles [3]. At 500°C and heating rate of 10°C/min, shows clear color of SS316L powder and almost clean from residue of binder burnout which indicate the better choice of heating temperature and heating rate. Since part appearance of the sintered part will replicate the appearance of the brown part, it is a choice to avoid heating rate of 20°C/min for all temperature.

SEM analysis was done to determine the effect of the temperature used in thermal debinding on the removal of PP from the brown parts after solvent debinding. Based on the observation, polypropylene (PP) binder was still seen attached to powder particles, proving that PP binder was not completely burned at temperature of 400 °C (Figure 10) with different heating rate. Figure 10 shows one of the examples taken from the temperature of 400 °C with heating rate of 10 °C/min. Figure 11 shows that at temperature of 500 °C, PP has been completely removed from the brown parts after solvent, and this also happened at temperature of 600°C (Figure 12). No PP can be observed attached to the stainless steel powder.

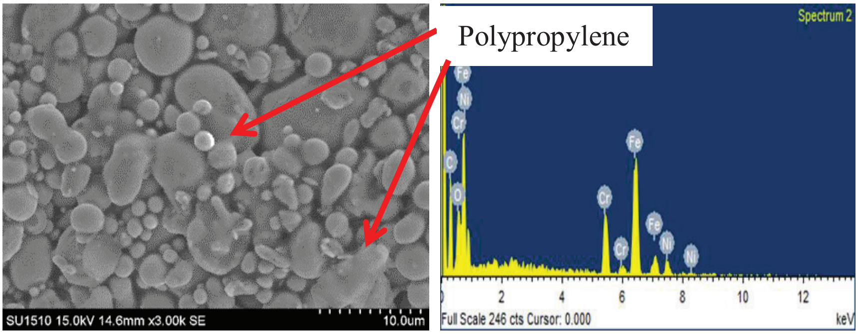


Figure 10: Scanning electron microscope (SEM) and EDS at temperature of 400°C with heating rate of 10°C/min

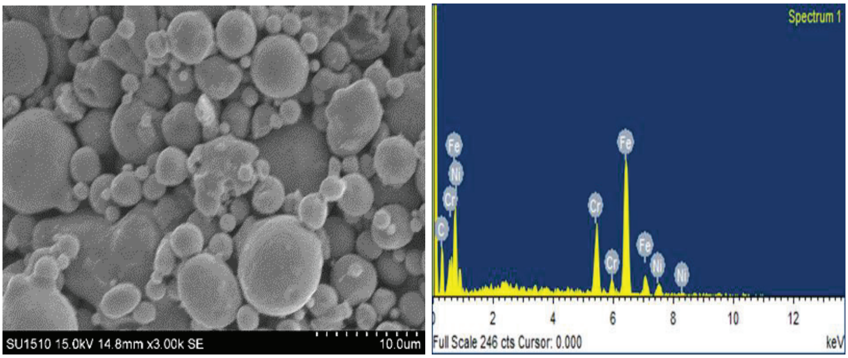


Figure 11: Scanning electron microscope (SEM) and EDS at temperature of 500°C with heating rate of 10°C/min

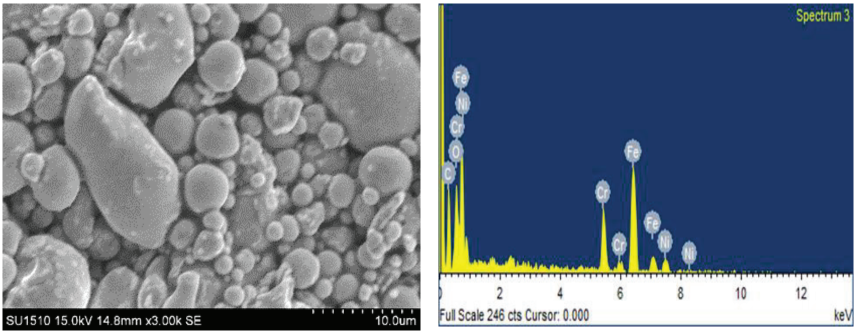


Figure 12: Scanning Electron Microscope (SEM) and EDS at temperature of 600°C with heating rate of 10°C/min

From Figure 10, the analysis from Energy Dispersive Spectroscopy (EDS) shows that the content of carbon element after thermal debinding process was reduced compared to carbon content after solvent debinding as compare to Figure 7 which is EDS from after solvent part. This phenomenon was due to the burning of PP from the brown part which caused the amount of carbon to be reduced. Comparison was made for the carbon content at temperature of 400 °C and 500 °C. From the observation, the carbon content in 500 °C was reduced much more compared to 400 °C. This was due to the completely burned PP from the brown part at 500 °C. This comparison can be proven through the comparison of EDS element peak in Figures 10 and 11 and 12.

Dimensions of the parts before and after undergoing thermal debinding were measured in two dimensions (width and length) in order to study the shrinkage percentage. Shrinkage percentage of brown part was calculated based on Equation (2) where the initial dimension of the green part is D_i and D_a is the dimension after thermal debound.

$$\%\text{shrinkage} = \frac{D_i - D_a}{D_i} \times 100\% \tag{2}$$

From the measurement of the part dimension, the results from Figures 13 and 14 show that shrinkage occurred in all parts of different heating rates and temperature for both dimensions. Based on the result, part shrinkage occurring in the temperature of 400°C was lower compared to part shrinkage in temperature of 500°C and 600°C. This was due to the presence of unburn binder inside the parts that made the shrinkage process less to occur. Comparison between the part shrinkage of 500°C and 600°C shows that part shrinkage for temperature of 600°C was lower compared to 500°C at 10°C/min. While for 20°C/min heating rate, the shrinkage of parts under 600°C shows increment in numbers as compare to 500°C temperature. This might due to at 600°C temperature the PP quickly be burned as compare to 500°C where there are still remain unburn PP inside the brown part.

At 30°C/min heating rate, both temperatures show equal in shrinkage percentage for both dimensions which might due to at both temperature and heating rate there is still remaining PP inside the brown part. The higher temperature results in increase of oxidation of the brown part [15].

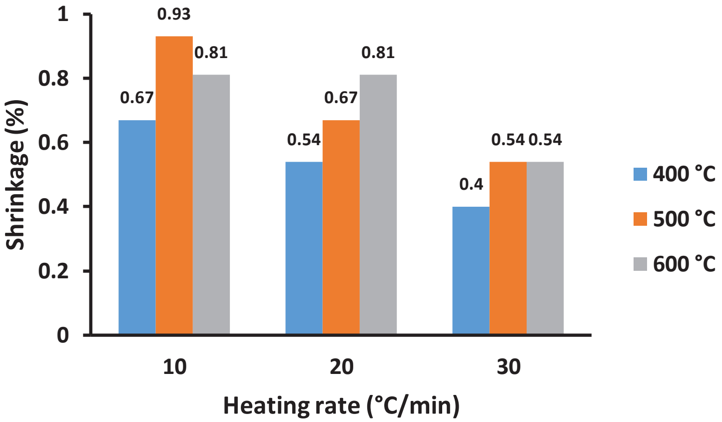


Figure 13: Shrinkage percentage of different heating rate at different temperature (part length)

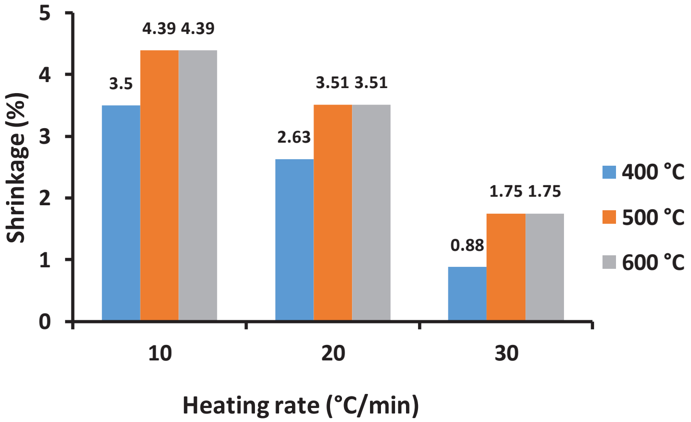


Figure 14: Shrinkage percentage of different heating rate at different temperature (part width)

Weight measurement was taken for all the brown parts after thermal debinding process in order to determine the relation of weight loss of binder with temperature. From Table 5, it was observed that weight loss of the part increase with the increasing heating rate and temperature and the result obtained shows the similarity outcome with the previous research [7]. This only true for temperature of 400°C and 500°C only. For parts with debinding temperature of 600°C, the weight loss become decrease with higher heating rate. This is due to oxidation level of the SS316L powder particles which results in increase of weight of the parts [19] and also proven by the shrinkage percentage shown in Figures 13 and 14. This shows that certain high temperature will only increase the oxidation level of the debound part and optimum level of debinding temperature need to be optimised.

Table 5: Weight loss of different debinding temperature and heating rate

Samples	Heating Rate (°C)	Average Initial Weight (g)	Average Weight After thermal (g)	Average Weight Loss (g)
Temperature: 400 °C				
1	10	6.285	6.164	0.121
2	20	6.301	6.165	0.136
3	30	6.318	6.158	0.160
Temperature: 500 °C				
1	10	6.300	6.089	0.211
2	20	6.360	6.100	0.260
3	30	6.368	6.103	0.265
Temperature: 600 °C				
1	10	6.360	6.119	0.185
2	20	6.279	6.078	0.201
3	30	6.301	6.116	0.241

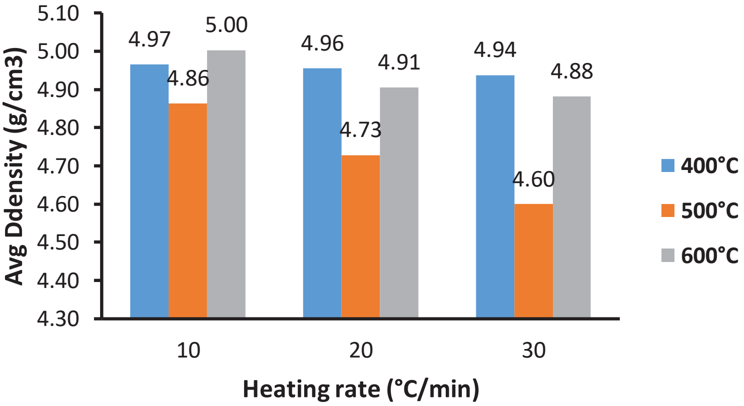


Figure 15: Average density of brown part under different temperature and heating rate

Average density of the thermal debound part were measured and being plotted as Figure 15. It shows that highest density of thermal debound part is at 10°C/min heating rate for all heating temperature. Result of 400°C temperature shows slightly decrease in density which indicating that the weight of remaining unburn PP is still inside the brown part. This is where the weight of SS316L powder with the remaining PP has led to less shrinkage in volume results in high density of the brown part. This is proven as explained in its shrinkage properties, weight loss and EDS analysis. While for 600°C temperature, at lower heating rate density is higher and decrease towards increasing the heating rate is best explained due to oxidation of the powder particles where the density is higher due to the oxygen element attached together with the powder particles of SS316L which results in additional weight of the brown part although most of the PP is completely decomposed. With this additional weight and decrease in volume the density become higher as compare to brown part which undergo 500°C temperature. The density decreases with increasing the heating rate was due to less oxidation occurs at higher heating rate. For 500°C temperature, the brown part density shows decrease in value with higher heating rate. The average density is higher at 10°C/min is due to the rearrangement of packing order of the powder particles and the highly numbers of pore created at this stage. This can be described by higher shrinkage percentage as explained in Figures 13 and 14 where higher shrinkage results in high packing order of the powder particles. The low in density of brown part at this temperature is due to the number of pores created after the thermal debound process which results in increase the volume of the brown part which inversely proportional to the density. Although the density at this thermal debound temperature is not high, results from the EDS, shrinkage and weight loss properties is strongly recommended that this temperature and heating rate of 10°C/min is suitable in removing remaining PP inside the thermal debound part without any swelling or high oxidation of powder particles.

4.0 CONCLUSION

From this research, the process parameters for thermal debinding within the metal injection moulding (MIM) processing of stainless steel SS316L under Argon gas atmosphere were vary to determine the removal of the binder from the parts, and investigate their specific influence on the physical properties of the debound parts. For the solvent debinding process, SEM images indicate that the Restaurant Waste Lipid (RWL) is completely removed at the temperature of 60°C, where porosity can be seen after solvent debinding. The result also shows that there is weight loss for all parts and a good surface finish is obtained. Thus, the result obtained from this research has achieved the objective of the study to remove the RWL binder through solvent debinding process. For thermal debinding process, polypropylene is completely removed at the temperature of 500°C and 600°C based on the observation of the SEM images, weight loss, density and shrinkage analysis. This is due to no polypropylene attached to the powder particles which also proven by the weight loss, and shrinkage properties as compared to the parts debound at the temperature of

400°C. Observations based on the physical properties of the part show that heating rate to debinding temperature can only vary within 10°C/min due to the swell that occurs at higher debinding. Compared to higher debinding rate, slower heating rate causes the part to result in a good surface finish where there is no defect. In conclusion, the process parameters for thermal debinding greatly influence the microstructure, density and surface finish of the parts. This is because thermal temperature at 400°C results in the presence of PP binder which has not completely burned off compared to 500°C and 600°C. Higher heating rate applied to part leads to formation of swell on the part surface, while low heating rate results in high density of the part. Therefore, thermal extraction at temperature of 500°C with the heating rate of 10 °C/min and the cooling rate of 15°C/min is the most appropriate for the removal of polypropylene in stainless steel (SS316L) part where the binder is completely removed from the part, and the surface is free from any defect. However further analysis needs to be conducted since the argon being kept fixed and variety of gas flow rate need to analyze besides different gas atmosphere could also result in different optimum conditions of thermal debound parameters.

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