

CHARACTERIZATION BY INFRARED SPECTROSCOPY OF BINDER BASED ON POLYETHYLENE GLYCOL AND INCONEL 718 FEEDSTOCK FOR POWDER INJECTION MOULDING

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Abstract

Metal injection moulding (MIM) has over the past decade established itself as a competitive manufacturing process to produce in large quantities small precision components with complex shape which would be costly to produce by alternative methods. MIM is a process which combines the versatility of plastic injection moulding with the strength and integrity of machined, pressed or otherwise manufactured small, complex metal parts. MIM consists in shaping powder particles and sintering them. During the injection phase, segregation appears in the feedstock and defects will be appear in the component during the sintering. To limit this effect, during decades a vast variety of binder systems have been developed. Binder systems are formulated as a mixture of different organic or inorganic substances with several functions. Binder system has the main commitments of giving the necessary rheological behavior to the feedstocks for injection moulding to transport the powder particles into the mould cavity and the cohesion of the green part.

In this paper a study of chemical interactions between polymers in binder and in Inconel feedstocks was investigated by Fourier Transform InfraRed spectroscopy (FTIR) and by differential scanning calorimetry (DSC). These methodologies were also investigated to study the thermal behavior of the binder at a temperature close to the temperature of injection. Analyzes shows relationship between chemical interactions and miscibility of polymer and different rheological and mechanical behavior. All methodologies revealed no interactions between the different component of the binder and the powder. This result shows the necessity to develop a better formulation of binder to improve the homogeneity of the feedstock and reduce the segregation during injection phase.

Key words: metal injection moulding, feedstock, binder, FTIR analysis

1. INTRODUCTION

Metal injection moulding (MIM) is a process for competitive manufacturing to produce in mass (more than 10,000 units per year) small parts (less than 50g) 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 ($R_a < 1.5$ microns) and high mechanical strength similar to those of the powder material. The PIM is a process that has great potential and involves many industrial sectors such as automotive,

aerospace, information technology or medical. This method is based on the injection of a fluid material composed of powder of the desired material for the final part, and of a binder generally consisting 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 (Enneti, 2012).

The binder is the most important part in the MIM process as it contributes fully to multitask like to be able to support a load rate by importing powder, typically 60%, and to direct the powder in the mold (Enneti, 2012). For this it must give strength and cohesion to the molded part and be easily re-

moved from the molded part and be recyclable, environmentally friendly and economical. It thus requires a low viscosity, good adhesion to the powder, no chemical interactions with the powder (Enneti, 2012; Tam et al., 1997; Scott Weil et al., 2006) and a low coefficient of thermal expansion. Binders are usually classified into three categories:

- Based on thermoplastic: the most currently used binders formulations are generally based on thermoplastic and compound of polyethylene, propylene and natural or synthetic wax and / or stearic acid (Scott Weil et al., 2006; Enneti, 2012).
- Based on thermoset: binders based on thermoset are used to achieve greater resistance of the work piece after injection but are not recyclable. They are generally composed of polycarbosilane or epoxy resin.
- Based on gel: the gel binders reduce the use of polymers and may be formed of an aqueous gel or silica gel (Hidalgo et al., 2013). Some polysaccharides are used as a component due to their gelling properties in water.

In this study, a powder of Inconel 718 was investigated to an application in the MIM process. Inconel superalloy is used in aviation, aerospace and nuclear power for its high resistance to corrosion and oxidation but also for its excellent mechanical strength at high temperature (Özgün et al., 2013a, 2013b). Superalloy use most often is currently Inconel 718 and 625. Here we are using an inconel 718 whose composition is given in table 1. The binders used in these superalloys are generally composed of PP, CW, PW and SA (Özgün et al., 2013a, 2013b). However, here we will work with a conventional formulation of MIM (Urterkin et al., 2011; Enneti, 2012) and already used in the laboratory.

The objective of this study is to determine the behavior of binders used in MIM on an Inconel 718. For this, a study of the temperature behavior and chemical interactions between polymers was performed. The morphological characteristic of the powder used has also been studied.

2. MATERIALS AND METHODS

The polymers used for this study are polypropylene, polyethylene glycol and stearic acid (Urterkin et al., 2011). The PEG used in this study has a molar weight of 20000 g/mol. The polypropylene is a PP670Kh supplied by Sabic. The polymer blended are made in a Brabender twin screw mixer which have a volume capacity of 50 cm³ at a speed of 30 rpm and at a temperature of 180°C. The behavior of polymer and binder are further characterized by FTIR and DSC.

The powder used is an Inconel 718 atomized by argon. The powder was supplied by Sandvik Ospreys Ltd. The chemical composition of the powder is given by table 1. The morphological characteristic of the powder was characterized by laser granulometer and by krypton physical adsorption and by infrared spectroscopy. FTIR studies were performed on a Rheonaut Resultec. This device couples a ThermoScientific Smart OMNI-Transmission Nicolet iS10 infrared spectrometer. This device allows for testing the temperature to 400°C, which is used to study the chemical and thermal behavior of polymers, binders and feedstocks. Temperatures used in tests are choose to be the nearest of the injection temperature conditions.

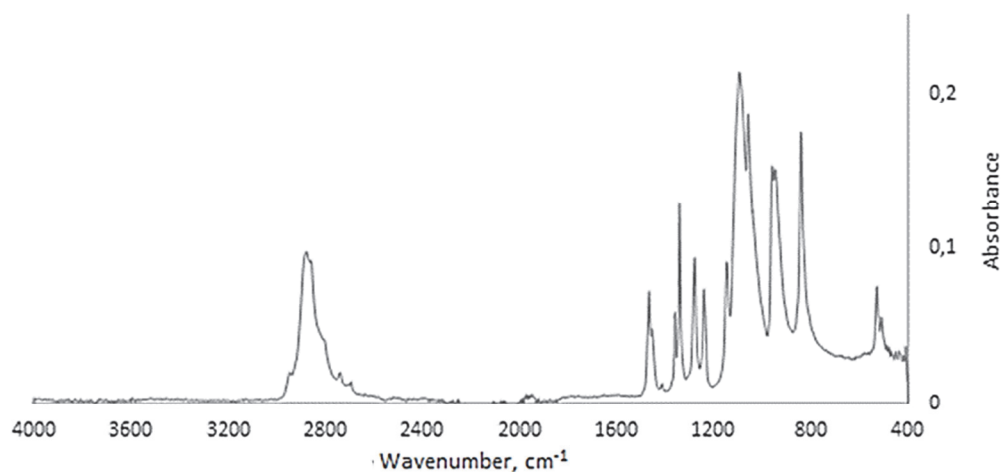


Fig. 1. Spectrum FTIR of PEG 20K at 40°C.



3. RESULTS AND DISCUSSION

3.1. Thermal behavior of PEG20K

The FTIR absorption spectrum of PEG at 40°C is shown in figure 1. PEG spectrum shows the characteristic peak of pure PEG (Finocchio et al., 2014). A broad band centered at 2890 cm^{-1} corresponds to the CH_2 band. The peaks of the CH_2 are detected at 963 cm^{-1} and 842 cm^{-1} (rocking), 1467 cm^{-1} (asymmetric deformation) 1360 cm^{-1} and 1343 cm^{-1} (wagging vibration mode), 1280 and 1242 (twisting), 1280 cm^{-1} and 1242 cm^{-1} (twisting) and 1148 (symmetric deformation). The other peaks correspond to the C-O-C stretching mode (1116 cm^{-1}) and to the C-OH stretching mode (1060 cm^{-1}).

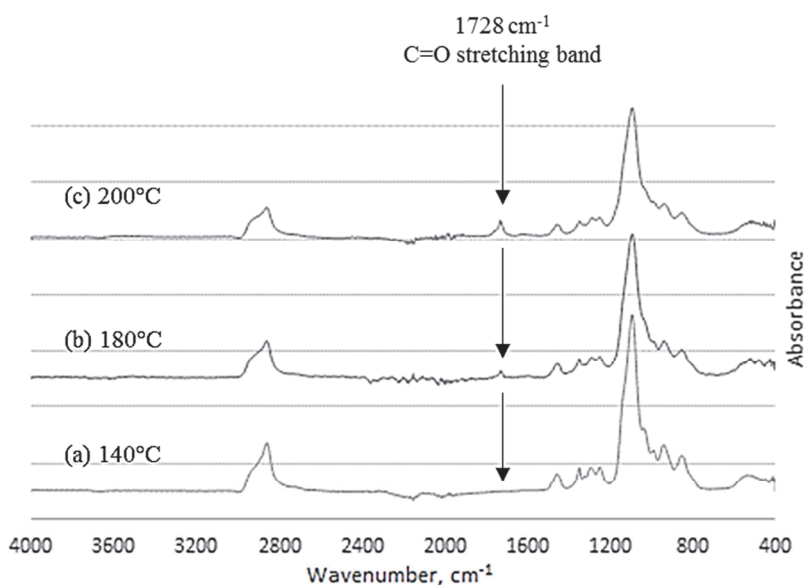


Fig. 2. Spectra FTIR of PEG 20K at 140°C (a), 180°C (b) and 200°C (c).

denser phase characterized by a C=O stretching band at 1728 cm^{-1} , with a shoulder at 1754 cm^{-1} (figure 2). These bands appear at 175°C and reach their maximum intensity between 200°C and 250°C. This effect indicates the formation of a complex mixture of decomposition products, likely low-molecular-weight fractions formed as a result of chain scission processes at the weak carbon-oxygen bonds in the PEG backbone.

3.2. Thermal behavior of polypropylene

Figure 3 shows the thermal behavior of the PP analyzed by FTIR. At 40°C, the spectra show the characteristic peaks of the polypropylene. The peaks at 1370 cm^{-1} and 2964 cm^{-1} correspond to the CH_3 deformation and stretching respectively. The peaks of the CH_2 are detected at 1465 cm^{-1} (asymmetric deformation), 963 cm^{-1} and 842 cm^{-1} (rocking). A broad band centered at 2890 cm^{-1} corresponds to the CH_2 band with the peak of the CH_3 at 2964 cm^{-1} . No differences are visible between the spectra at 40°C and the spectra at 200°C. The peaks are not shifted and no distorted. The result shows a stable behavior of the polypropylene at this temperature.

3.3. Mixing behavior

Figure 4 shows the temperature behavior of the mixture. The FTIR

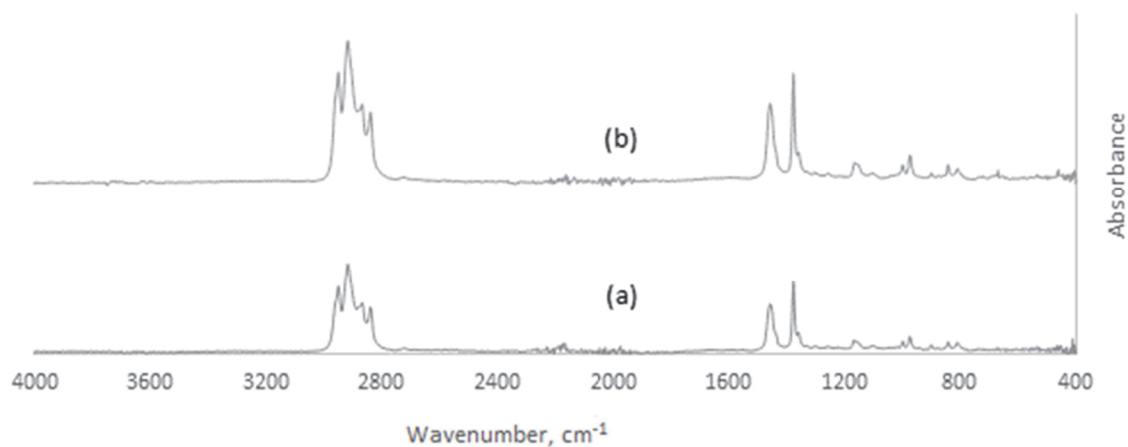


Fig. 3. Spectra FTIR of PP670KH at 40°C (a) and 200°C (b).

The thermal decomposition of PEG investigated by FT-IR (figure 2) at increasing temperature shows the formation of decomposition products in the con-

analysis shows that at 40°C the spectra obtained for the PEG60% +PP40% mixture is the superposition of the spectra of pure PEG and pure PP. The peaks



of the PEG and of the PP are not shifted and not distorted. This shows no chemical change and therefore no interactions between the two polymers. At 200°C the appearance of C = O peak of degradation of the PEG is visible, it means that the behavior of the PEG is not modified by the addition of PP. This result was confirmed by DSC, see figure 5. The DSC curve shows a melting temperature at 69°C for the PEG and at 151°C for the PP. These results are the same that the pure PEG and PP and show a non-interaction between the two polymers because the melting temperature of the polymer doesn't change in the mix (Belhaneche-Bensemra & Bedda, 2001). These results also show an immiscibility of PP with the PEG (Belhaneche-Bensemra & Bedda, 2001).

Figure 6 shows the spectra of the mixture PP40%+PEG60% after the mixing process and after the injection process. This result shows the decomposition of the PEG with the presence of the carbonyl's peak. Moreover the presence of the band of the C=C at 1640 cm⁻¹, which correspond to an intermediate component of the degradation's reaction, shows the decomposition is not over after the mixing process. The spectrum of the PEG after the injection process, with the growth of the carbonyl's peak, shows the decomposition going on during the injection phase.

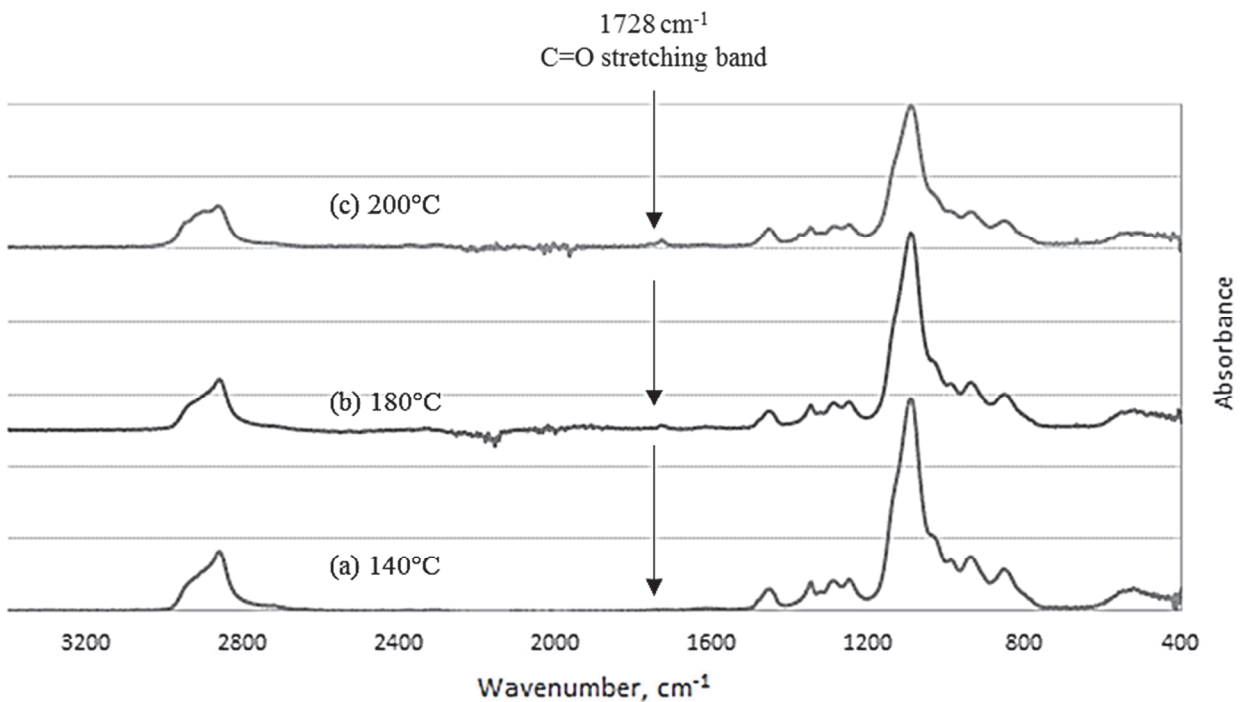


Fig. 4. Spectra FTIR of PP40%+PEG60% at 140°C (a), 180°C (b) and 200°C (c).

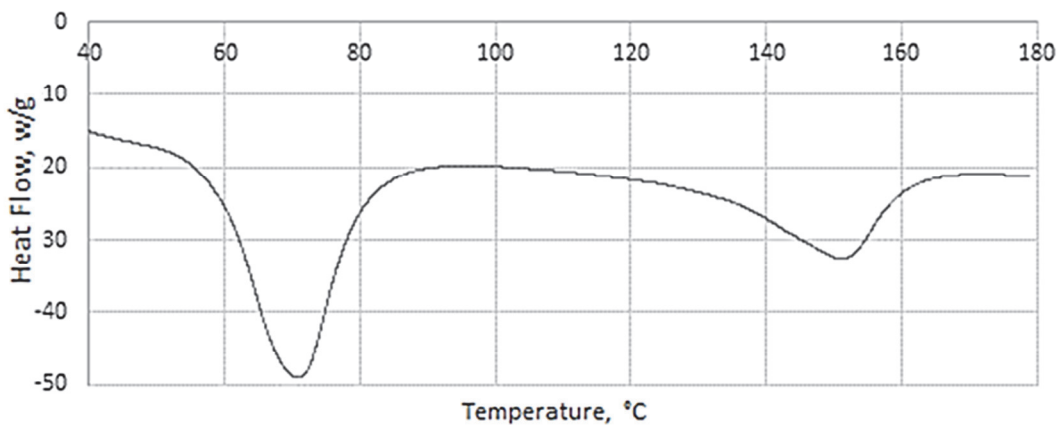


Fig. 5. DSC curve of PP40%+PEG60%.



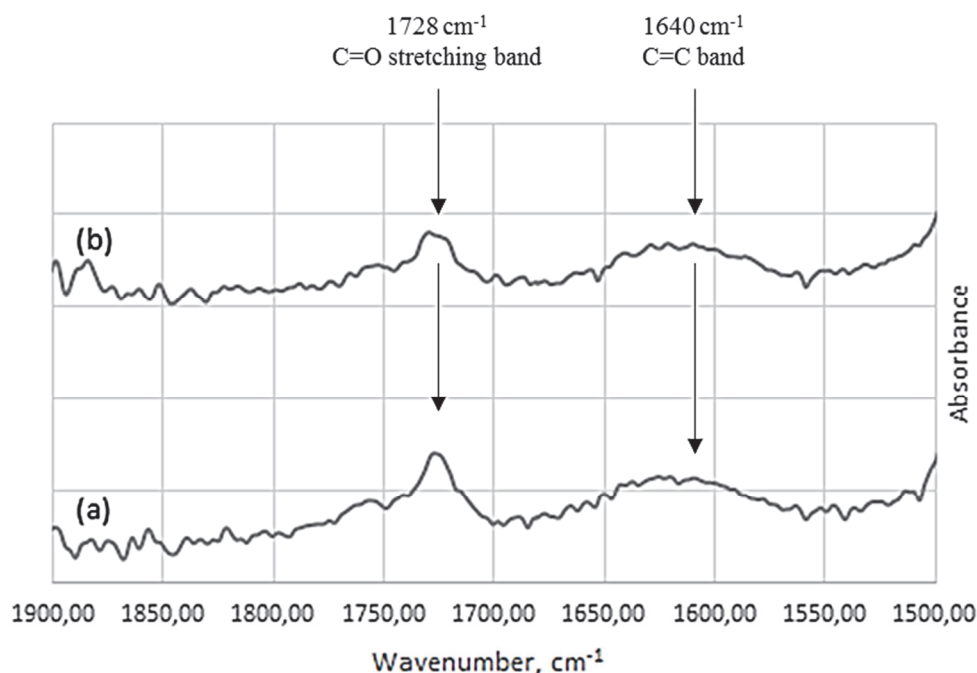


Fig. 6. Spectra of the mixture PP40%+PEG60% at 120°C after injection (a) and mixing (b).

3.4. Powder analysis

The composition of the powder is given in table 1. The Inconel 718 powder was characterized by laser granulometer and nitrogen physical absorption to determine particle size and possible porosities. Table 2 shows the results. The SEM analysis figure 7 shows the shape of the powder which is confirmed spherical. Considering this shape and with the result of the specific area the size of the powder can be calculated. The result is given in the table 2. The result of the size of the powder is confirmed by the granulometer analysis, figure 8, which shows the size distribution. The fact that the result is near shows that the powder have not porosities and a proper surface quality.

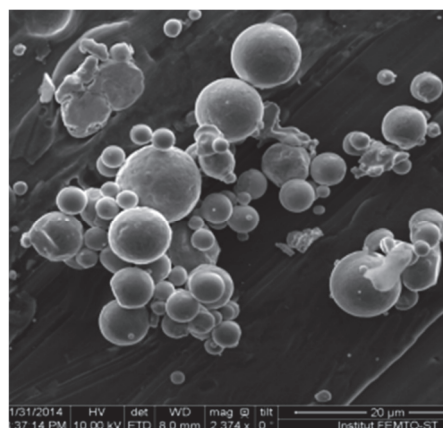


Fig. 7. SEM picture of Inconel 718 powder.

Table 1. Chemical composition of Inconel 718 powder in weight percentage.

Compound	Ni	Cr	Fe	Nb	Mo	Ti	Co	Al, Cu, C...
Percentage	50-55	17-21	Bal.	4.75-5.25	2.8-3.3.	0.65-1.15	1	<1

Table 2. Particle size of inconel 718 calculated by BET method and specific area.

Specific area, m ² /g	0,1128
Size BET, µm	6,7
d10, µm	3,5
d50, µm	5,4
d90, µm	8,2

3.5. Feedstocks behavior

One formulation has been studied in this analysis. The mix was composed with the binder formulation (55% PEG + 40% PP + 5% SA) and the Inconel powder at a rate load of 60%. The result of the FTIR analysis is given in figure 9. The spectrum shows no interactions between the powder and the binder. In the spectra of the powder no peaks are detected. In the spectra at 40°C, the result of the FTIR analysis is



the same that the binder spectra (figure 4). The peaks are not shift and no distort sign of no interactions. The thermal behavior of the component is also unchanged. In the spectra in figure 4b the peak at 1728 cm^{-1} of the decomposition of the PEG at 180°C is always present.

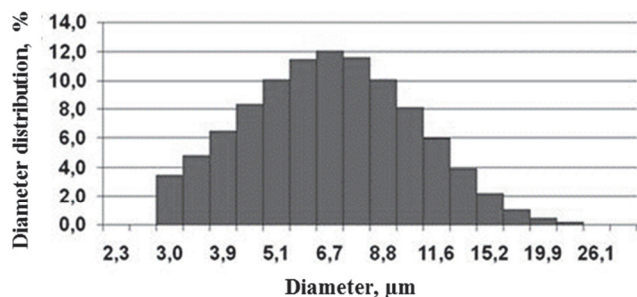


Fig. 8. Particle size distribution of Inconel 718 powder.

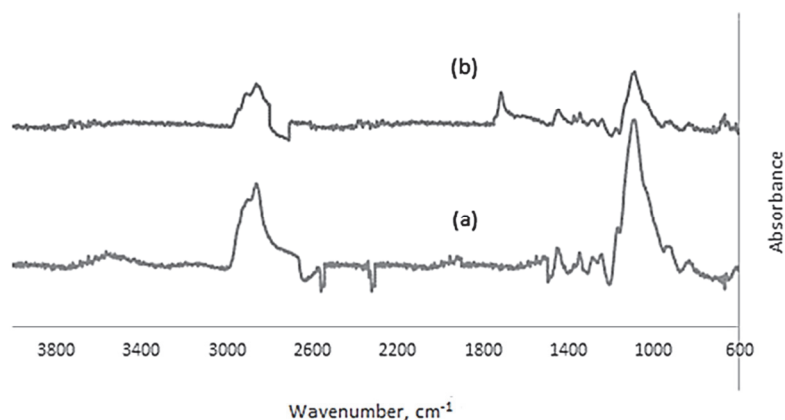


Fig. 9. Spectrum of the feedstock (60% powder volume loading, (PEG+PP+SA) binder) at 40°C (a) and at 200°C (b).

4. CONCLUSIONS

The present study has shown that the PEG is decomposed at the injection temperature in the classic MIM process conditions. The use of PP or Inconel 718 does not influence the thermal behavior of the PEG, the decomposition is always present in binder and feedstocks. These results show no chemical interactions and no influences between each component of the formulation. This fact may prove that the homogeneity of a MIM feedstock is not optimal. The PEG decomposition going on in the MIM process. The conditions of the process depend on the PP. This result shows the necessity to change the polypropylene on the formulation to conserve the characteristics of the PEG during the process. Further tests will be lead on the miscibility of the PEG with polymers and powder to improve the homogeneity and the characteristics of binders and feedstocks.

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WYKORZYSTANIE SPEKTROSKOPII W PODCZERWIENI DO CHARAKTERYSTYKI LEPI SZCZA NA BAZIE GLIKOLU POLIETYLENOWEGO I WSADU Z INCONELU 718 DO FORMOWANIA WTRYSKOWEGO PROSZKU

Streszczenie

Formowanie wtryskowe, na przestrzeni ostatniej dekady, stało się konkurencyjnym procesem stosowanym do produkcji, w dużych ilościach, małych, precyzyjnych komponentów o złożonych kształtach, których wytworzenie byłoby kosztowne przy zastosowaniu innych procesów. Formowanie wtryskowe metali (ang. MIM) łączy wszechstronność procesu wtryskiwania z wytrzymałością i integralnością innych procesów wytwarzania, na



przykład tłoczenia, stosowanych do produkcji małych, złożonych elementów. Proces MIM składa się z nadania cząstkom proszku odpowiedniego kształtu a następnie spiekania ich. Podczas fazy wtryskiwania w proszku zachodzi segregacja i w materiale, w trakcie procesu spiekania, mogą pojawić się wady. Stąd opracowywane są systemy mieszania, pozwalające na ograniczenie tego zjawiska. Systemy te opisywane są jako mieszanina różnych substancji organicznych lub nieorganicznych o wielu funkcjach. System mieszania powinien zapewniać odpowiednie własności reologiczne materiału wsadowego, potrzebne do transportu cząstek proszku do formy i zachowania spójności tzw. części „zielonej”.

W pracy przeprowadzono badania nad oddziaływaniami chemicznymi między polimerem w lepiszczu i w materiale wsadowym Inconel z wykorzystaniem spektroskopii w podczerwieni z transformacją Fouriera (ang. FTIR) oraz różnicowej kalorymetrii skaningowej (DSC). Metody te zastosowano również do badania zachowania termicznego lepiszcza w temperaturze zbliżonej do temperatury wtryskiwania. Analizy pokazały zależność między oddziaływaniami chemicznymi i mieszalnością polimeru a różnymi zachowaniami reologicznymi i mechanicznymi. Wszystkie metody nie wykazały żadnych oddziaływań pomiędzy komponentami lepiszcza a proszkiem. Otrzymane wyniki pokazały konieczność opracowania nowej, lepszej formuły dla lepiszcza w celu poprawy homogeniczności materiału wsadowego i zmniejszenia zjawiska segregacji podczas fazy wtryskiwania.

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