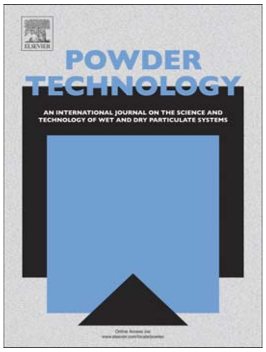


The degradation of poly(ethylene glycol) in an Inconel 718 feedstock in the metal injection moulding process

A. Royer, T. Barriere, J.C. Gelin

PII: S0032-5910(15)00564-1
DOI: doi: 10.1016/j.powtec.2015.07.032
Reference: PTEC 11149

To appear in: *Powder Technology*

Received date: 28 April 2015
Revised date: 15 July 2015
Accepted date: 18 July 2015

Please cite this article as: A. Royer, T. Barriere, J.C. Gelin, The degradation of poly(ethylene glycol) in an Inconel 718 feedstock in the metal injection moulding process, *Powder Technology* (2015), doi: 10.1016/j.powtec.2015.07.032

The degradation of poly(ethylene glycol) in an Inconel 718 feedstock in the metal injection moulding process.

A. Royer[a], *T. Barriere*[a*], *JC. Gelin*[a]

a Applied Mechanics Department at FEMTO-ST Institute, 26 Rue de l'Epitaphe, 25000, Besançon (France) alexandre.royer@femto-st.fr, thierry.barriere@univ-fcomte.fr, jean-claude.gelin@univ-fcomte.fr

* Corresponding author: FEMTO-ST Institute 26 Rue de l'Epitaphe, 25000, Besançon (France), telephone: +33381662047, e-mail: thierry.barriere@univ-fcomte.fr

Abstract

The degradation and stability of polymer binders in feedstock for metal injection moulding (MIM) has been rarely investigated. Feedstock is a mixture of polymer constituents and metallic powder and is subject to variations in temperature and the complexity of its mechanical effects. The mixture is pressed and squeezed in a mixer with two counter-rotating screws and injected into the mould cavities. This paper investigates the degradation and stability of polymer constituents under the conditions of mixing and injection. The interactions among different constituents were measured and analysed. The methods and application of the equipment are introduced with sufficient detail. The kinetics of decomposition for poly(ethylene glycol) (PEG) are studied to explain the mechanism of its degradation. The measurement of the carbonyl group resulted in a quantitative discussion of the decomposition. The effects of PEG degradation on its behaviour were also investigated and found to show benefits for the metal injection process. Moreover, it is proved that the combination of PEG and polypropylene (PP) is not favourable for a homogenous binder. Thus, other constituents should be found to use instead. The research reveals the degradation and stability of polymer binders under conditions of MIM technologies. It provides a reference for the choice and validation of MIM binder constituents.

Keywords: powder injection molding, FTIR, Inconel 718, poly (ethylene glycol).

1. Introduction

Metal injection moulding (MIM) is a technology for injecting a mixture of metallic powder and polymer binder into mould cavities to obtain desired shapes. The polymer binder should be removed from the injected part. The final step is sintering to achieve a compact metallic part in its pure state.

The binder plays the most important role in the metal injection moulding process; it must provide fluidity of the feedstock mixture for injection moulding with more than 60% of the powder loaded in the volume, and it must ensure adhesion of the powder to maintain the moulded shape [1]. Enneti, Quinard and Tam [1–3] showed that the binder must provide strength and cohesion for the moulded part, must be easily removable from the moulded part, and must be recyclable, environmentally friendly and economical. They also explained the important properties of the binder. The binder should have low viscosity with good adhesion to the powder, a low coefficient of thermal expansion, and, especially, no chemical effect on the powders. The binders are generally composed of three components [1]. To provide the necessary fluidity, PEG or waxes are generally used. Another component serves to provide the strength of the injected piece; for this, polypropylene or polyethylene is commonly employed. The last component is a surfactant such as stearic acid.

Another important aspect of MIM is an easy, proper and cost-effective way to remove the binder. There are many types of debinding technologies, including thermal, catalytic and solvent technologies [1]. Debinding by water solvent is the most attractive method. The object of the present research is to investigate the degradation and stability of the water solvent binder under the conditions of mixing and injection moulding in the MIM process. Moreover, the homogeneity of the feedstock is crucial for the MIM process and requires miscibility between the binder constituents. Thavanayagan [4] demonstrated the effect of binder properties on the homogeneity of the feedstock. Hidalgo [5] and Hausnerova [6] demonstrated that a capillary rheometer can be used to analyse the homogeneity of the feedstock.

An important research aspect in MIM technologies is the processing of Inconel superalloys. Özgün [7,8] explained the purposes of the Inconel superalloy in aviation, aerospace and nuclear power. It offers not only high resistance to corrosion and oxidation but also excellent mechanical strength at high temperatures. Inconel 718 and 625 are the grades that are currently used. The present study investigates the processing of Inconel 718 superalloy, and according to Quinard [9] and Liu [10], who demonstrated that a micro powder is well adapted for µPIM experiments, a micro powder of Inconel 718 smaller than 200 µm was chosen. The binder formulation developed by Özgün [7,8] to make MIM feedstock from the superalloys is composed of polypropylene, carnauba wax (CW), paraffin wax (PW) and stearic acid (SA). However, Hausnerova [11] demonstrated that the use of PEG instead of nonpolar waxes or polyolefins allows defect-free debinding. Moreover, the debinding of waxes requires hazardous chemical solvents, whereas PEG requires only water, which is more ecologically sound [12]. In this study, a binder formulation with PEG developed by Urterkin [13] and Checot-Moinard [14] and referenced by Enneti [1] was adopted. The composition of the binder is given in Table 1. It is composed of polypropylene to provide strength, poly(ethylene glycol) to provide fluidity and stearic acid as a surfactant. Compared to the formulation of Özgün [7,8], CW and PW are substituted with PEG because of its water solvent properties for debinding.

PEG in a pure state is well known to decompose at 180°C, and its mechanism has already been demonstrated. However, its degradation and effect on the behaviour of MIM feedstock is less understood. One of the objectives of this study is to quantify the degradation of PEG and its influence throughout the MIM process.

Hidalgo [15] used FTIR to show the chemical effects between the binders and the powder on a zircon powder with PEG and cellulose acetate butyrate at 20°C, but no explanation was provided. One of the objectives of this study is to determine possible chemical interactions between the feedstock components in order to improve the behaviour and homogeneity of the binders for the MIM process of the Inconel 718 powder. A study of the thermal behaviour and chemical interactions between the polymer constituents was performed via FTIR and other conventional methods.

2 Materials and methods

The polymers used in this study are polypropylene, polyethylene glycol and stearic acid [13,14,16]. The PEG and stearic acid are supplied by Merck KGaA. The molar weight of the PEG is 20,000 g/mol. The polypropylene is PP670Kh, supplied by Sabic. The polymer blends are made in a Brabender twin-screw mixer with the same conditions used by Checot-Moinard [14]: 180°C and 30 rpm. The mixer volume capacity is 50 cm^3. The behaviours of the polymers and the binder are further characterized by FTIR and differential scanning calorimetry (DSC). FTIR observations were taken on a Rheonaut Resultec. This device couples a Smart OMNI-Transmission Nicolet iS10 infrared spectrometer with a

Haake Mars rheometer provided by ThermoScientific. For the coupling function of the two pieces of equipment, attenuated total reflection (ATR) is used. This device allows a test temperature up to 400°C, which is suitable to study the chemical and thermal behaviour of polymers, binders and feedstock. The temperature under injection conditions is set for measurement between 180°C and 200°C. The samples were characterized by 16 scans with a resolution of 4 cm^{-1} for the FTIR analysis. The sample is put on the upper surface of the furnace, and just beneath it, there is a diamond for the function of ATR. Then, the sample is heated to the required temperature for each test. For the DSC analysis, the samples are heated in air from 30°C to 250°C at a rate of 10°C/min on a DSC92 provided by Setaram.

The powder used in the analysis is an Inconel 718 atomized by argon, which was supplied by Sandvik Ospreys Ltd. The chemical composition of the powder is given in Table 1, and its characteristics are shown in table 2. Figure 1 shows an SEM image of the powder. The morphology of the powder was characterized by a laser granulometer and nitrogen physical adsorption. The nitrogen physical adsorption was investigated using an ASAP 2020 provided by Micromeritics. The Brunauer, Emmett and Teller theory (BET) was used to determine the specific area by nitrogen physical adsorption.

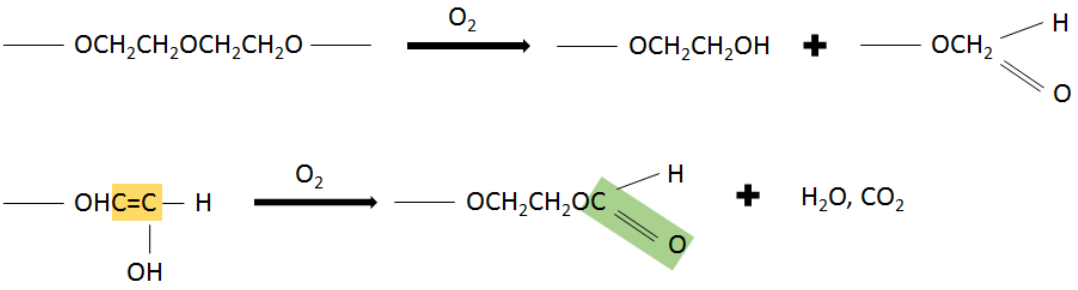
3. Experiments and results

3.1 Study of the PEG degradation

For comparison with the results of the tests, the FTIR absorption spectrum of the PEG is first recorded at 40°C, as shown in figure 2. This temperature is easily achieved on the upper surface of the furnace near the environmental temperature. This PEG spectrum shows the characteristic peaks of pure PEG, according to the explanation of Finocchio [17]. A broad band centred at 2890 cm^{-1} corresponds to the CH_2 band (stretching). The CH_2 peaks are detected at 963 cm^{-1} and 842 cm^{-1} (rocking), 1467 cm^{-1} (asymmetric deformation), 1360 cm^{-1} and 1343 cm^{-1} (wagging vibrational mode), 1280 cm^{-1} and 1242 cm^{-1} (twisting), and 1148 cm^{-1} (symmetric deformation). The other peaks correspond to the C-O-C stretching mode (1116 cm^{-1}) and the C-OH stretching mode (1060 cm^{-1}).

Finocchio [17] explained the thermal degradation of PEG 1500 until the temperature increased to 400°C. A carbonyl stretching band at 1728 cm^{-1} appears at 175°C and reaches its maximum intensity between 200°C and 250°C. The thermal decomposition of PEG was investigated by FTIR (figure 2) at increasing temperatures.

This investigation revealed the formation of decomposed products in the molten state characterized by the carbonyl stretching band at 1728 cm^{-1}. There is, in fact, confusion regarding two close peaks; the second one at 1754 cm^{-1} cannot be observed visually in the figure. This effect indicates the formation of a complex mixture with decomposed products. The low-molecular-weight fractions likely form as a result of the chain scission processes at the weak carbon-oxygen bonds in the PEG backbone. Suzuki revealed the mechanism of PEG degradation with ozone [18]. First, the PEG chains were cleaved randomly by oxygen. This produced the compounds of a terminal hydroxyl group and formic esters. Then, the oxygen attacks the double bond, which produces the formic ester plus water and carbon dioxide. The appearance of the carbonyl stretching band observed by FTIR was mentioned by Suzuki [18] in the development of his mechanism. Moreover, Han [19] proved that Suzuki's mechanism can be used to describe the decomposition of PEG in the atmosphere.



Schema of the mechanism for PEG degradation, with the appearance of carbonyl group (green) and alkene group (yellow)

3.2 Kinetics of PEG degradation

The kinetics of PEG decomposition were also studied to evaluate the evolution of the PEG behaviour throughout the mixing and injection. The PEG was tested at 180°C and 200°C for one hour. An FTIR spectrum was captured every five minutes. The results are shown in figure 3 and figure 4. In these two figures, the peak at 1640 cm^{-1} corresponds to the C=C vibration. This represents an intermediate product of the decomposition reaction. These results show that the degradation of PEG is faster at 200°C. The C=C peak at 1640 cm^{-1} disappears at 200°C. This proves that the PEG is totally degraded.

Moreover, at 180°C, the C=C peak is always present. Comparing the intensity of the two peaks to determine the quantitative content of a polymer functional group is usually a part of FTIR analysis [20]. This result is confirmed by the evolution of the peak area ratios of (C=O)/(C=C) (figure 5). To realize these curves, the peak area of the functional group is first normalized to a peak that varies as little as possible over the time period, and then they are compared. The curves show that the degradation is faster at 200°C than at 180°C with a quick increase after 30 min at 200°C. The TGA (table 3) analysis also confirmed this result. Table 3 shows the weight loss due to degassing of H_2O and CO_2 during the degradation of the PEG. This result shows a faster degradation at 200°C with a weight loss of 1.45% compared to a weight loss of 1.2% at 180°C after 1 h of experimentation.

3.3 Effects on the PEG properties

The influence of the PEG degradation on its characteristics was also investigated. A rheological study was undertaken to determine the viscosity of the PEG before and after degradation. The result is shown in figure 6. It is shown that the flow behaviour of the PEG changes and that the degradation reduces the viscosity values. The flow behaviour is Newtonian before the degradation and becomes pseudoplastic after degradation. This is probably due to the easier orientation of the degraded polymer chains in the flow.

The water solvent property is the main reason why PEG is used. Thus, the effects of the water solvent property were studied. To characterize this property, the PEG was first damaged at 200°C for 30 min and then compacted on a small tablet. The tablets are placed in water at 50°C and weighed before immersion and after different periods of time. The results are shown in table 4. The curves show better solubilization of degraded PEG. The degraded PEG solubilized 40% faster than normal PEG.

The decrease in the viscosity and the faster solubilization of the damaged PEG are beneficial results for MIM. A lower viscosity should facilitate easier injection of the feedstock and may permit a higher load rate of powder. Moreover, the weak weight loss due to the degradation does not affect the feedstock behaviour.

3.4 Binder analysis

The usual temperature for injection of the polypropylene is between 200°C and 230°C, according to the literature [21]. The PP chosen in this study permits an injection temperature between 180°C and 200°C. Thus, the temperature for the injection of the mixture should stay in this range as well. The thermal behaviour of the PP analysed by FTIR is shown in Figure 7. The spectra reveal the characteristic peaks of the polypropylene. At 40°C, the peaks at 1370 cm^{-1} and 2964 cm^{-1} correspond to the CH_3 deformation and stretching, respectively. The peaks of CH_2 are detected at 1465 cm^{-1} (asymmetric deformation), 963 cm^{-1} and 842 cm^{-1} (rocking). A broad band centred at 2890 cm^{-1} corresponds to the CH_2 band together with the peak of CH_3 at 2964 cm^{-1}. There is no visible difference between the spectrum at 40°C and the spectrum at 200°C. The peaks are not shifted or distorted. The result shows a stable behaviour of the polypropylene at this temperature.

A mixture of PEG and PP was made in the two-screw mixer at 180°C until stabilization of the mixing torque, which required at least 15 min. The FTIR spectra of the mixture after mixing and injection are shown in Figure 8. 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 PP are not shifted or distorted. This indicates no chemical change in the polymers and therefore no chemical interactive effect between these two polymers. However, the appearance of the C=O peak representing degradation of the PEG is visible on both spectra. This reveals decomposition of the PEG by the appearance of the peak for carbonyl, which means that the behaviour of the PEG is not affected by the addition of PP. Moreover, there exists a band for C=C at 1640 cm^{-1}. This means that the decomposition is not finished after the mixing process. The spectrum of the PEG after the injection process, with the peak growth for carbonyl, shows the process of decomposition during the injection phase.

The lack of any chemical interactive effect between the two polymers is due to the immiscibility between these two polymers. The nonexistence of a chemical interactive effect was confirmed by DSC analysis, as shown in figure 9. Belhaneche-Bensemra [22] used DSC analysis to study the miscibility between polyvinyl chloride and poly(methyl methacrylate). He demonstrated that the shift in the glass transition temperature depends on the percentage of polyvinyl chloride in the polymer mixture. He also explained that the presence of one glass transition temperature is a sign of miscibility of polymers. Hidalgo [23] also used the DSC characterization to determine the interactive effects between PEG and cellulose acetate butyrate. According to our observations, there are two well-defined glass transition temperatures corresponding to the pure polymers. Hence, it can be concluded that the PP and PEG used is this study are immiscible. The DSC curve also shows a melting temperature at 69°C for PEG and at 151°C for PP. These results confirm the nonexistence of chemical interaction between the constituents of the binders.

The immiscibility of the PP and PEG may result in inhomogeneity of the mixture. An optical microscopy image of the injected piece of polymer mixture is shown in figure 10. The image depicts good inhomogeneity of the polymer mixture; the PEG is transparent, and the PP is white. It also displays segregation of the polypropylene. Moreover, the capillary rheology method developed by Hidalgo [5] and Hausnerova [6] was used to characterize the homogeneity of the binder. The results are shown in figure 11. In this method, the homogeneity is evaluated by measuring the variability of the viscosity over time. This variability characterizes the homogeneity because a capillary rheometer measures finite portions of mixture and a new portion for every measure. The test was realized at 180°C with a shear rate of 10 s^{-1}. The experimentation shows some variability in the viscosity, which is proof of inhomogeneity. This inhomogeneity should induce segregation of the powder and affect the final piece geometry.

3.5 Feedstock analysis

The composition of the Inconel 718 powder is given in table 1. The powder was characterized by a laser granulometer and nitrogen physical adsorption to determine the particle size and possible porosities. The results are shown in table 2, and an SEM image of the powder is shown in figure 1.

A MIM feedstock formulation is studied in this analysis. The mixture consists of the binder (55% PEG + 40% PP + 5% SA) and Inconel 718 powder at a 60% load in the volume. The feedstock was made in a Brabender twin-screw mixer at 180°C and 30 rpm until the mixing torque was stabilized. The FTIR analysis results are given in figure 12 with the spectra of the feedstock after mixing and injection. The spectra show nonexistence of any chemical interactive effect between the powder and the binder. In the spectra of the feedstock, no different peak from the components is detected. The FTIR analysis results are the same as those of the binder system, as shown in figure 8. The peaks are not shifted or distorted. No new peak appears. This proves the lack of chemical interactions between the powder and the binder. The thermal behaviour of the PEG is also unchanged. In the spectra, the peak at 1728 cm^{-1} for decomposition of the PEG is always present in the feedstock after mixing and injection. Moreover, the intensity of the carbonyl peak is lower after mixing than after injection following the treatment owing to the presence of the carbonyl peak of the stearic acid.

The homogeneity of the feedstock was studied by the same rheological method at 180°C with a shear rate of 1000 s^{-1}. The result is shown figure 13, which shows a high variability of the viscosity versus time, a sign of inhomogeneity. This inhomogeneity can also result in segregation of the powder.

5. Conclusion

The present study has shown that PEG decomposes during the mixing and injection phases under process conditions in MIM. It is also shown that the presence of PP or Inconel 718 does not change the degradation of the PEG. Decomposition is relatively slow at 180°C but increases quickly with increasing temperature. The degradation of PEG results in decreased viscosity and faster solubilization in water. These effects should be good for the metal injection process by facilitating injection and debinding. However, this can change the load rate of the feedstock and render it unrecyclable after injection. Degassing of oxygen can also induce oxidation of the powder. Moreover, the tests demonstrated the inhomogeneity of the binder and the feedstock due to the immiscibility between the PP and the PEG. This possibly induces powder segregation during feedstock injection and affects the properties of the final piece. Because of the water solvent properties of PEG, it is the primary choice for the binder constituent. Further tests will be performed to find other suitable binder constituents that will be miscible with the PEG and will determine the characteristics of new binder systems.

ACKNOWLEDGMENTS

The authors wish to thank the FUI ProPIM project for the financial support.

REFERENCES

[1] R.K. Enneti, V.P. Onbattuvelli, S.V. Atre, 4 - Powder binder formulation and compound manufacture in metal injection molding (MIM), in: D.F. Heaney (Ed.), Handbook of Metal Injection Molding, Woodhead Publishing, 2012: pp. 64–92.

[2] K.C. Tam, S.P. Yap, M.L. Foong, N.H. Loh, Metal injection molding: effects of the vinyl acetate content on binder behavior, Journal of Materials Processing Technology. 67 (1997) 120–125.

[3] C. Quinard, J. Song, T. Barriere, J.C. Gelin, Elaboration of PIM feedstocks with 316L fine stainless steel powders for the processing of micro-components, Powder Technology. 208 (2011) 383–389.

[4] G. Thavanayagam, K.L. Pickering, J.E. Swan, P. Cao, Analysis of rheological behaviour of titanium feedstocks formulated with a water-soluble binder system for powder injection moulding, Powder Technology. 269 (2015) 227–232..

[5] J. Hidalgo, A. Jiménez-Morales, T. Barriere, J.C. Gelin, J.M. Torralba, Water soluble Invar 36 feedstock development for µPIM, Journal of Materials Processing Technology. 214 (2014) 436–444.

[6] B. Hausnerová, Rheological characterization of powder injection molding compounds, Polimery. 55 (2010) 3–11.

[7] Ö. Özgün, H. Özkan Gülsoy, R. Yilmaz, F. Findik, Injection molding of nickel based 625 superalloy: Sintering, heat treatment, microstructure and mechanical properties, Journal of Alloys and Compounds. 546 (2013) 192–207.

[8] Ö. Özgün, H.Ö. Gülsoy, R. Yılmaz, F. Fındık, Microstructural and mechanical characterization of injection molded 718 superalloy powders, Journal of Alloys and Compounds. 576 (2013) 140–153.

[9] C. Quinard, T. Barriere, J.C. Gelin, Development and property identification of 316L stainless steel feedstock for PIM and µPIM, Powder Technology. 190 (2009) 123–128.

[10] L. Liu, X.L. Ni, H.Q. Yin, X.H. Qu, Mouldability of various zirconia micro gears in micro powder injection moulding, Journal of the European Ceramic Society. 35 (2015) 171–177.

[11] B. Hausnerova, I. Kuritka, D. Bleyan, Polyolefin Backbone Substitution in Binders for Low Temperature Powder Injection Moulding Feedstocks, Molecules. 19 (2014) 2748–2760.

[12] D. Bleyan, P. Svoboda, B. Hausnerova, Specific interactions of low molecular weight analogues of carnauba wax and polyethylene glycol binders of ceramic injection moulding feedstocks, Ceramics International. 41 (2015) 3975–3982.

[13] L. Urtekin, I. Uslan, B. Tuc, Investigation of Properties of Powder Injection-Molded Steatites, Journal of Materials Engineering and Performance. 21 (2012) 358–365.

[14] D. Checot-Moinard, C. Rigollet, P. Lourdin, Powder injection moulding PIM of feedstock based on hydrosoluble binder and submicronic powder to manufacture parts having micro-details, Powder Technology. 208 (2011) 472–479.

[15] J. Hidalgo, A. Jiménez-Morales, J.M. Torralba, Thermal stability and degradation kinetics of feedstocks for powder injection moulding – A new way to determine optimal solid loading?, Polymer Degradation and Stability. 98 (2013) 1188–1195.

[16] Y. LI, X. LIU, F. LUO, J. YUE, Effects of surfactant on properties of MIM feedstock, Transactions of Nonferrous Metals Society of China. 17 (2007) 1–8.

[17] E. Finocchio, C. Cristiani, G. Dotelli, P.G. Stampino, L. Zampori, Thermal evolution of PEG-based and BRIJ-based hybrid organo-inorganic materials. FT-IR studies, Vibrational Spectroscopy. 71 (2014) 47–56.

[18] J. Suzuki, Study on ozone treatment of water-soluble polymers. I. Ozone degradation of polyethylene glycol in water, J. Appl. Polym. Sci. 20 (1976) 93–103.

[19] S. Han, C. Kim, D. Kwon, Thermal degradation of poly(ethyleneglycol), Polymer Degradation and Stability. 47 (1995) 203–208.

[20] L.T. Saw, D.N. Uy Lan, N.A.A. Rahim, A.W. Mohd Kahar, C.X. Viet, Processing degradation of polypropylene-ethylene copolymer-kaolin composites by a twin-screw extruder, Polymer Degradation and Stability. 111 (2015) 32–37.

[21] D.G.M. Wright, R. Dunk, D. Bouvart, M. Autran, The effect of crystallinity on the properties of injection moulded polypropylene and polyacetal, Polymer. 29 (1988) 793–796.

[22] N. Belhaneche-Bensemra, A. Bedda, Analyse de la relations structure-proprietes des melanges PVC-PMMA, Annales de Chimie Science Des Matériaux. 26 (2001) 79–90.

[23] J. Hidalgo, J.P. Fernández-Blázquez, A. Jiménez-Morales, T. Barriere, J.C. Gelin, J.M. Torralba, Effect of the particle size and solids volume fraction on the thermal degradation behaviour of Invar 36 feedstocks, Polymer Degradation and Stability. 98 (2013) 2546–2555.

Table captions

Table 1 Chemical composition of Inconel 718 powder in weight percentage, provided by Osprey

Table 2 Particle size of Inconel 718 determined by the BET method and the specific area obtained by nitrogen adsorption

Table 3 TGA results of PEG weight loss at 180°C constant, 190°C constant and 200°C constant after 1 hour

Table 4 Weight loss of the PEG and degraded PEG in water at 50°C

Table 1

Element (Weight %)	Ni	Cr	Ti	Mn	Mo	Si	V	C	Al	B	Fe
Percentage	50	17	2.1	0.35	2.8	0.35	0	0.08	0.2	0.006	bal.

Table 2

Specific area (m^2/g)	0.1128
Size by BET (µm)	6.7
d10 (µm)	3.2
d50 (µm)	5.7
d90 (µm)	10.9

Table 3

Temperature (°C)	180	190	200
Weight loss after 1 h (%)	1.21	1.29	1.42

Table 4

Time (min)	10	20	30	40	50	60
Weight loss of PEG (%)	26	43	55	64	81	100
Weight loss of degraded PEG (%)	52	72	83	98	100	100

Figure captions

Figure 1 SEM image of the Inconel 718 powder

Figure 2 FTIR spectra of PEG 20K at 40°C (a), 140°C (b), 180°C (c) and 200°C (d), with the appearance of the carbonyl stretching band at 1728 cm^{-1}

Figure 3 FTIR spectra of PEG 20K at 180°C after 0 min (a), 5 min (b), 15 min (c) and 25 min (d) with the appearance of the carbonyl stretching band at 1728 cm^{-1}

Figure 4 FTIR spectra of PEG 20K at 200°C after 0 min (a), 5 min (b), 15 min (c) and 25 min (d) with the appearance of the carbonyl stretching band at 1728 cm^{-1}

Figure 5 Evolution of the peak area ratios of (C=O)/(C=C) at 180°C and 200°C by FTIR

Figure 6 Viscosity at 180°C of PEG (a) and degraded PEG (b)

Figure 7 FTIR spectra of PP at 40°C (a) and 200°C (b)

Figure 8 FTIR spectra of the PP40%+PEG60% mixture after injection (a) and after mixing (b) with the appearance of the carbonyl stretching band at 1728 cm^{-1} for the decomposition of PEG

Figure 9 DSC curve at 2°C/min of PP (a), PEG (b) and mixture of PP and PEG (c) in air with the glass transitions and the melt temperature.

Figure 10 Optic microscopic image of the piece injected with mixture of PP40% (white) + PEG60% (transparent)

Figure 11 Evolution of the viscosity of a mixture with 60%PEG and 40%PP versus time at 180°C and at constant shear rate of 10 s^{-1}

Figure 12 FTIR spectra of Inconel feedstock (60% Inconel powder and 40% binder with 55% PEG, 40% PP and 5% SA) at 180°C with appearance of the carbonyl stretching band at 1728 cm^{-1} of PEG decomposition

Figure 13 Evolution of the viscosity of the feedstock (60% Inconel powder and 40% binder with 55% PEG, 40% PP and 5% SA) versus time at 180°C and at shear rate constant of 1000 s^{-1}

Figure 1

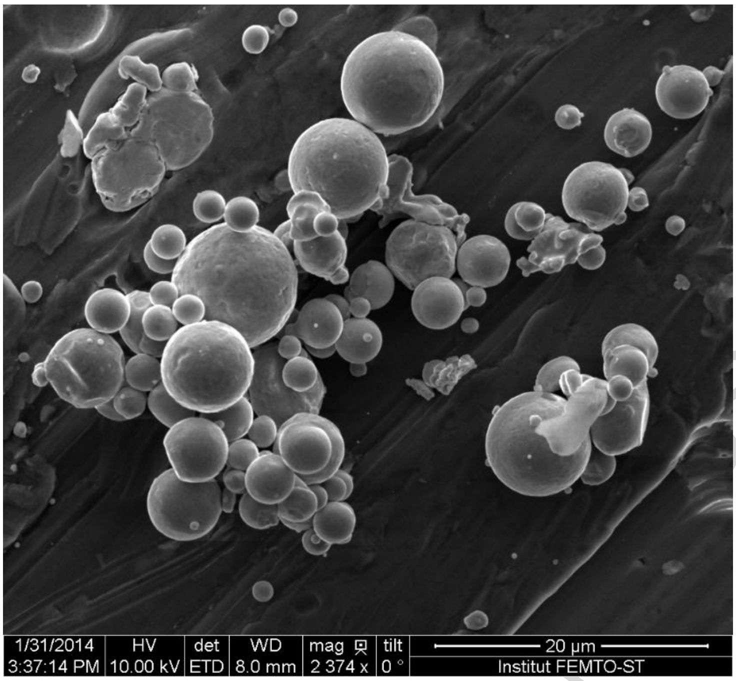

1/31/2014
3:37:14 PM
HV
10.00 kV
det
ETD
WD
8.0 mm
mag
2 374 x
tilt
0 °
20 µm
Institut FEMTO-ST

Figure 2

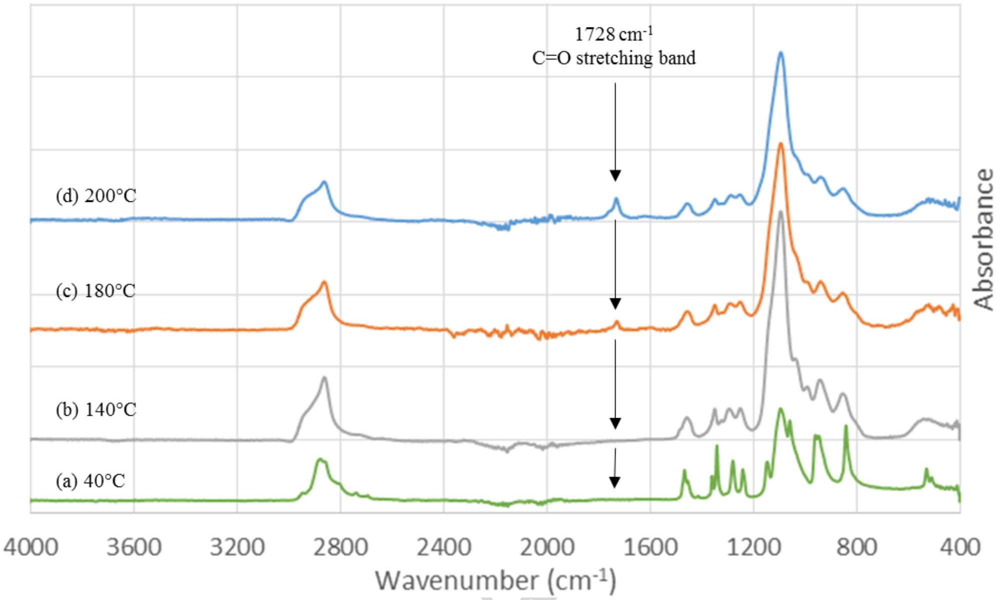

1728 cm-1
C=O stretching band
(d) 200°C
(c) 180°C
(b) 140°C
(a) 40°C
Absorbance
4000
3600
3200
2800
2400
2000
1600
1200
800
400
Wavenumber (cm-1)

Figure 3

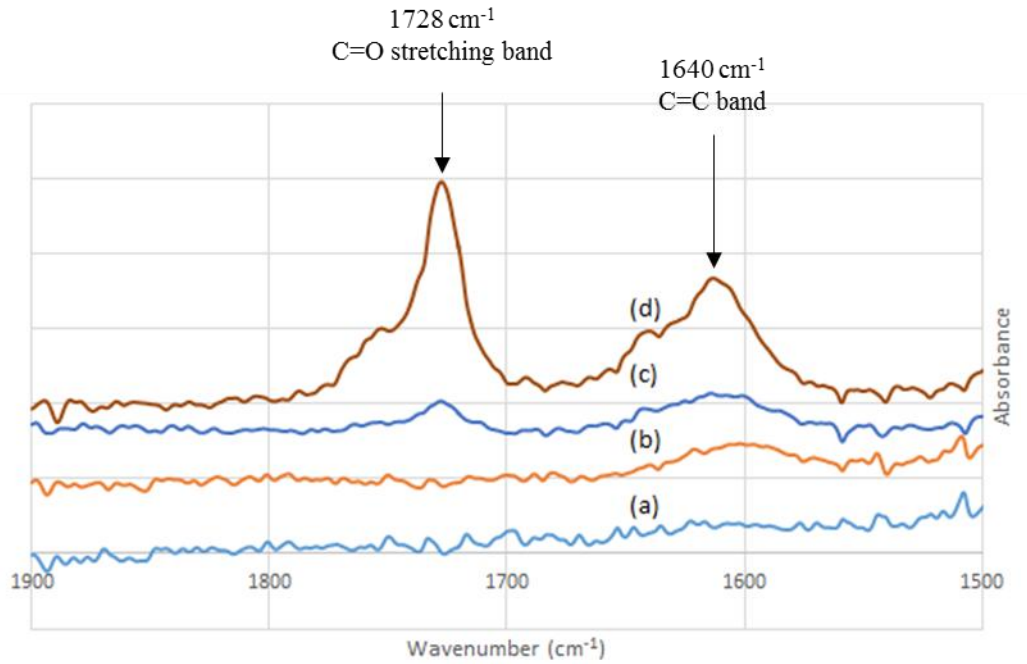

1728 cm-1
C=O stretching band
1640 cm-1
C=C band
(d)
(c)
(b)
(a)
Absorbance
1900
1800
1700
1600
1500
Wavenumber (cm-1)

Figure 4

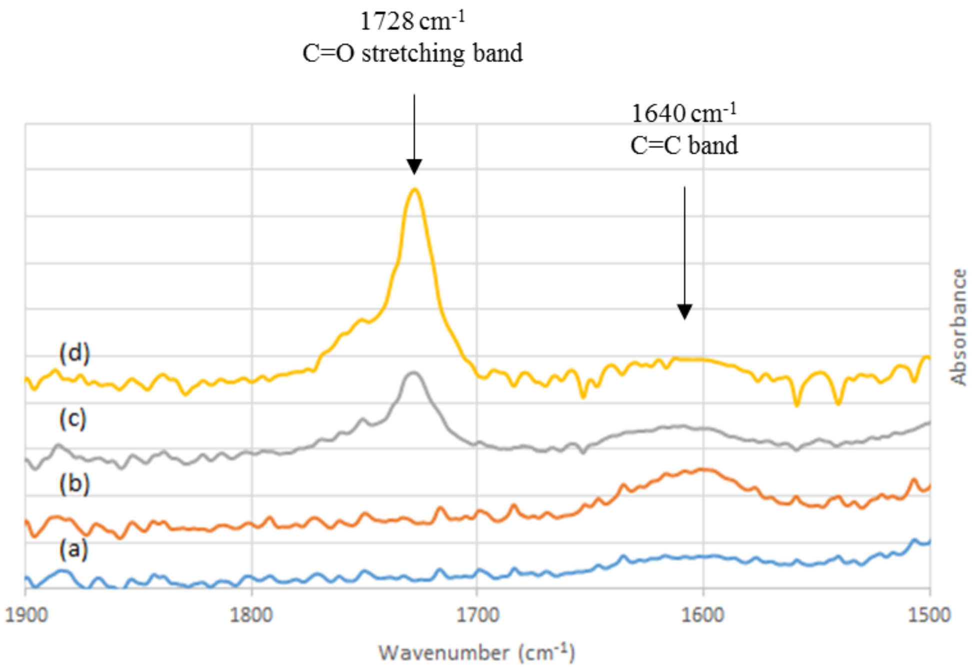

1728 cm-1
C=O stretching band
1640 cm-1
C=C band
(d)
(c)
(b)
(a)
Absorbance
1900
1800
1700
1600
1500
Wavenumber (cm-1)

Figure 5

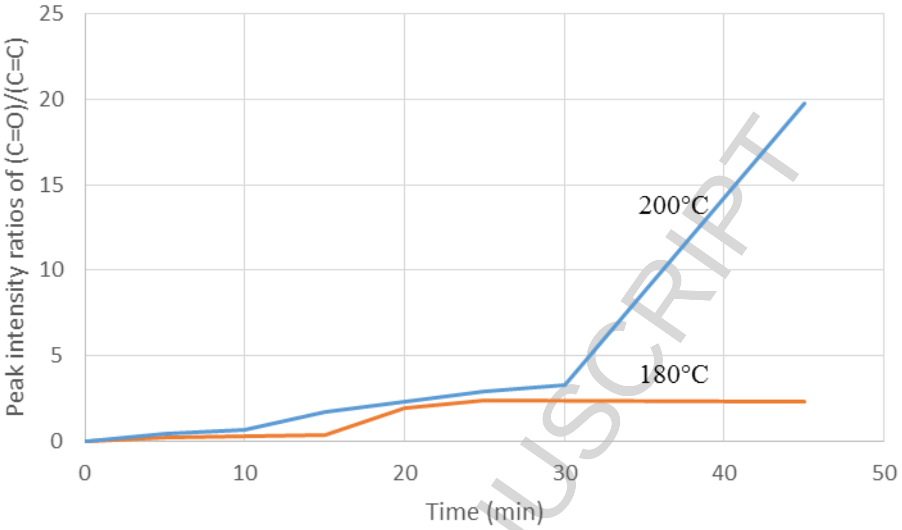

Peak intensity ratios of (C=O)/(C=C)
0
5
10
15
20
25
Time (min)
0
10
20
30
40
50
200°C
180°C

Figure 6

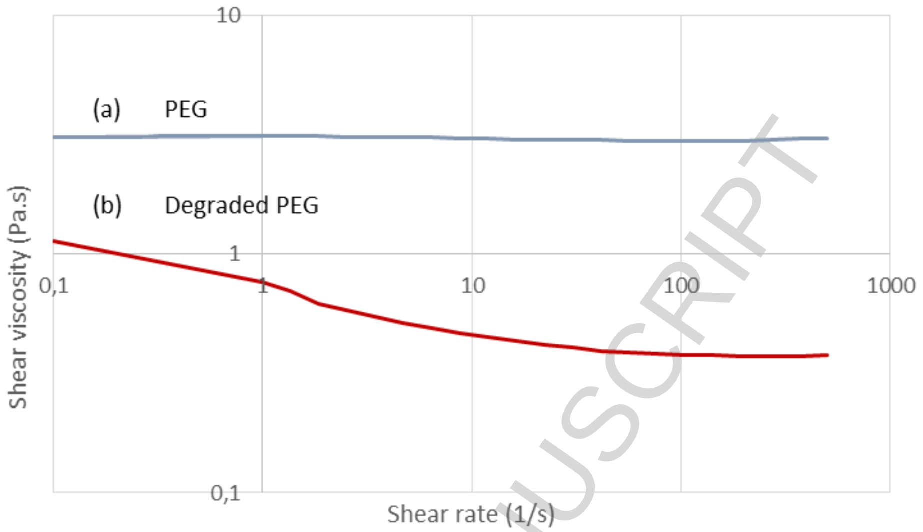

10
(a) PEG
(b) Degraded PEG
1
0,1
Shear viscosity (Pa.s)
0,1
1
10
100
1000
Shear rate (1/s)

Figure 7

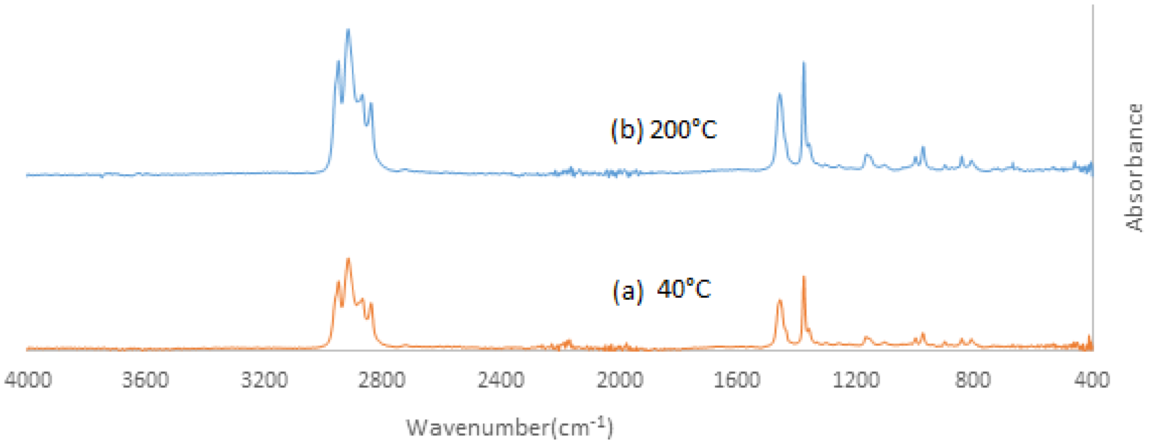

(b) 200°C
(a) 40°C
Absorbance
4000
3600
3200
2800
2400
2000
1600
1200
800
400
Wavenumber(cm^{-1})

Figure 8

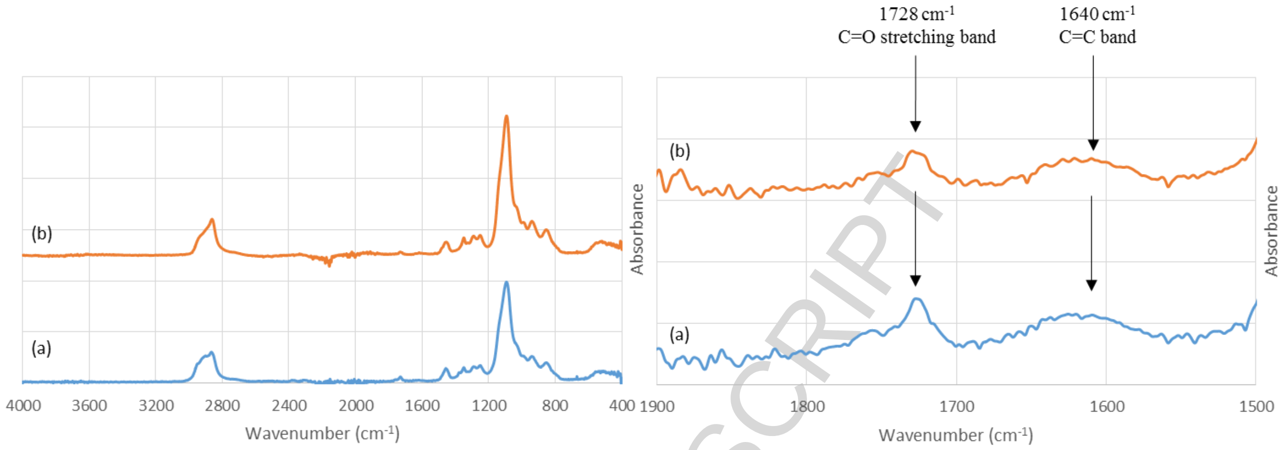

1728 cm-1
C=O stretching band
1640 cm-1
C=C band
(b)
(a)
(b)
(a)
Absorbance
Absorbance
4000
3600
3200
2800
2400
2000
1600
1200
800
400
Wavenumber (cm-1)
1900
1800
1700
1600
1500
Wavenumber (cm-1)

Figure 9

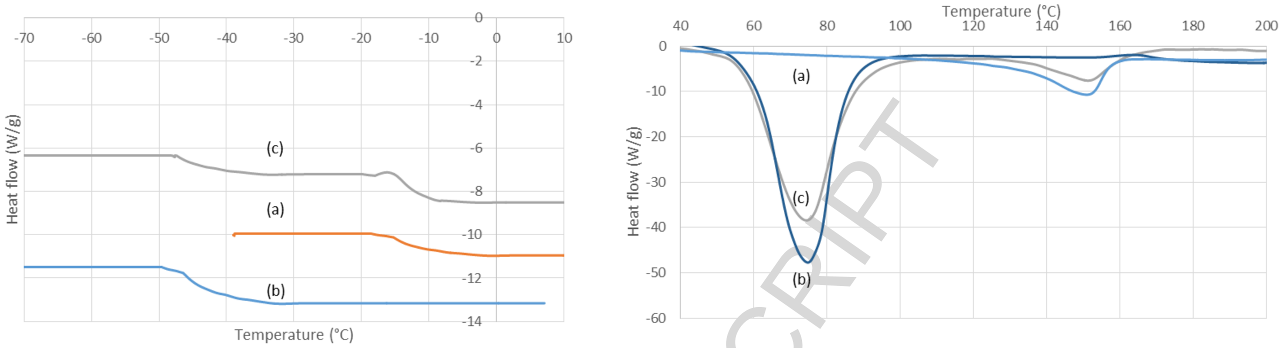

-70
-60
-50
-40
-30
-20
-10
0
10
0
-2
-4
-6
-8
-10
-12
-14
Heat flow (W/g)
Temperature (°C)
(c)
(a)
(b)
Temperature (°C)
40
60
80
100
120
140
160
180
200
0
-10
-20
-30
-40
-50
-60
Heat flow (W/g)
(a)
(c)
(b)

Figure 10

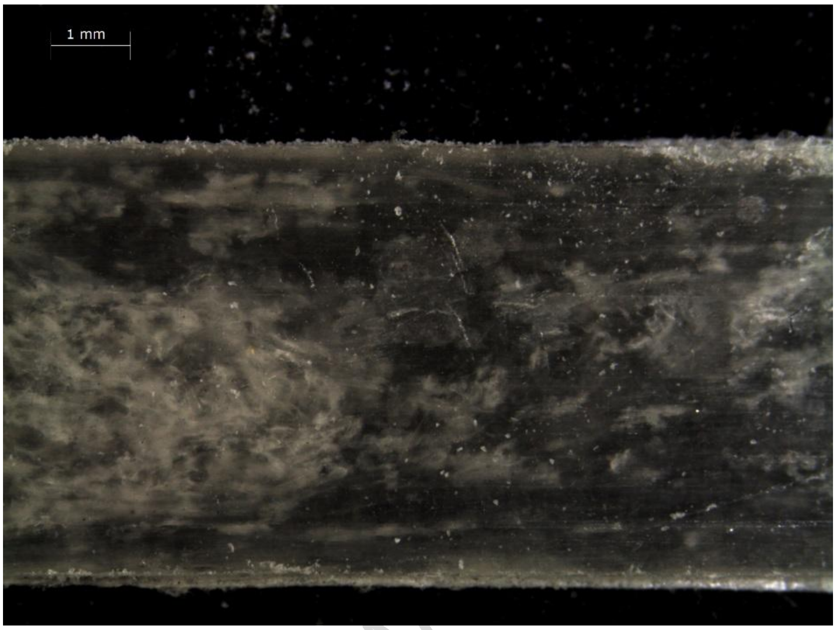


Figure 11

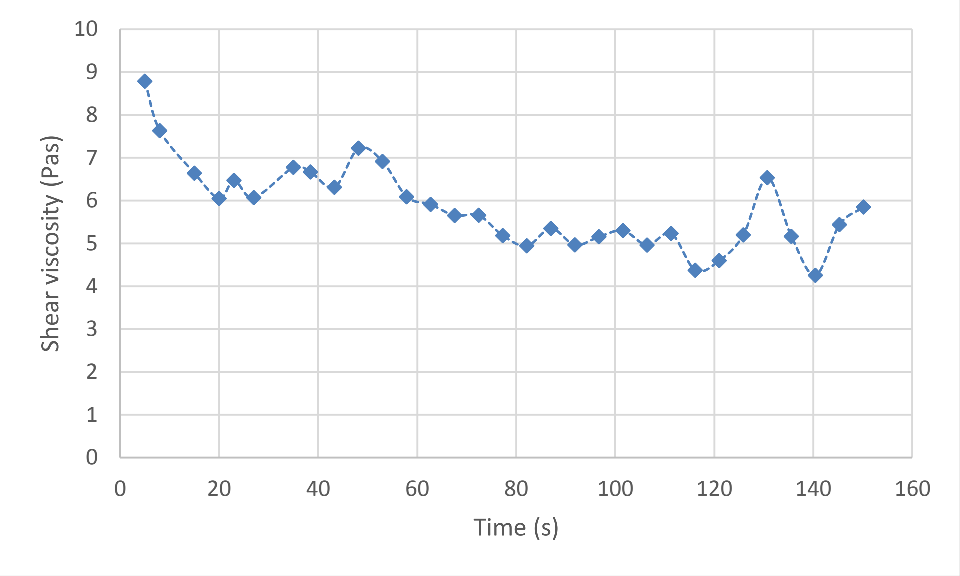

Shear viscosity (Pas)
10
9
8
7
6
5
4
3
2
1
0
0
20
40
60
80
100
120
140
160
Time (s)

Figure 12

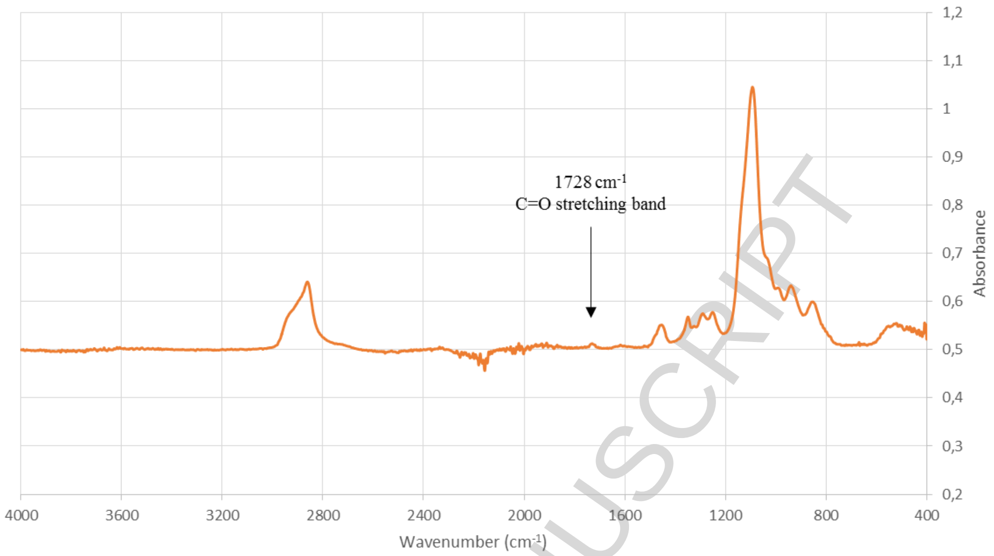
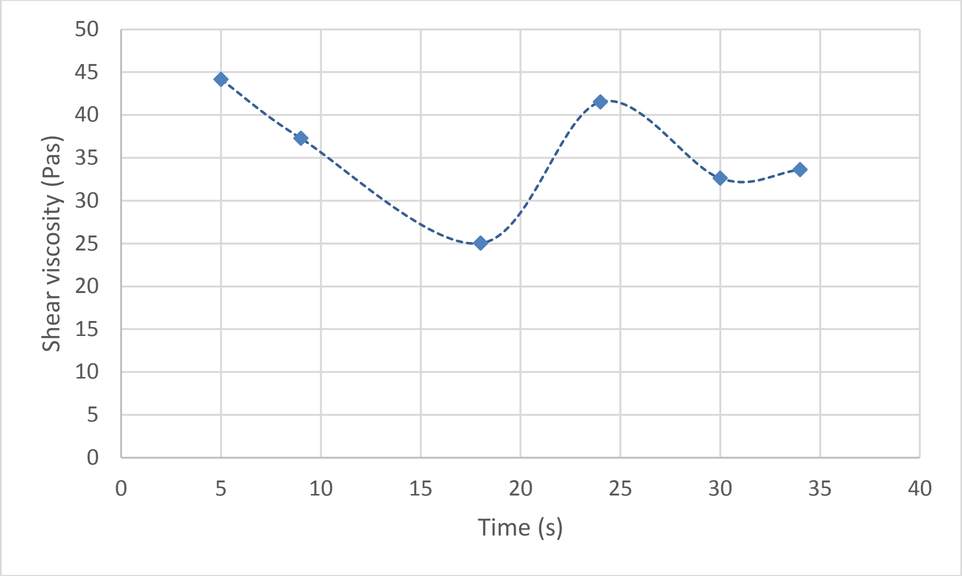
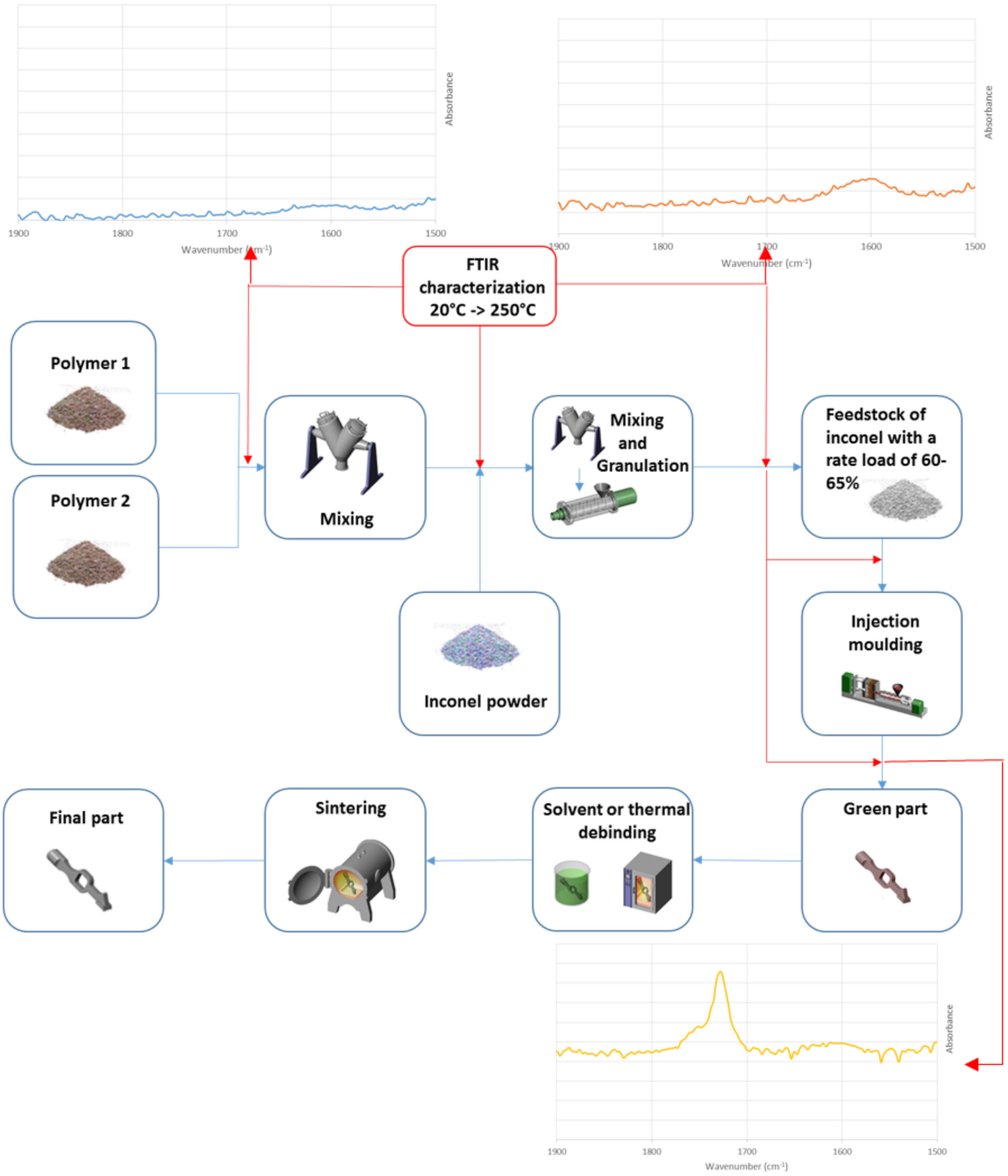

1728 cm-1
C=O stretching band
1,2
1,1
1
0,9
0,8
0,7
0,6
0,5
0,4
0,3
0,2
Absorbance
4000
3600
3200
2800
2400
2000
1600
1200
800
400
Wavenumber (cm-1)

Figure 13



Shear viscosity (Pas)
50
45
40
35
30
25
20
15
10
5
0
0
5
10
15
20
25
30
35
40
Time (s)



Graphical abstract

Highlights

- New method to characterized binder formulation by FTIR spectroscopy has been used
- The PEG is degraded throughout the mixing and injection process with PP
- Injected parts of PP/PEG binder is highly inhomogeneous