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Producing Near-Net Shape Titanium Alloy Parts By Metal Injection Moulding

A thesis
submitted in fulfilment
of the requirements for the degree
of
Doctor of Philosophy
in
Materials and Process Engineering
at
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by
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Dedication

Commit your work to the Lord, and your plans will be established

(Proverbs 16:3, NIV)

Dedicated to

Lord Jesus Christ

Who has redeemed and summoned me by name

Abstract

Metal injection moulding (MIM), is a metalworking process for producing complex parts from metal powders. It is often more cost effective to use MIM to make small, precise componentry from expensive materials such as titanium than traditional metal processes such as casting, forming, extrusion, investment casting and machining. The four processing steps in MIM are: formulating homogenous feedstock of metal powder and binders, injection moulding, removing the binder (debinding) and sintering. The binder affects feedstock rheology, allowing the required shape to be moulded. It then needs to be removed so the object can be sintered to consolidate into a near-net shaped part. As MIM has many advantages, including low wastage of material and the ability to produce intricate shapes, it is used in sophisticated applications such as biomedical instruments, in the aerospace industry, and in niche applications that use expensive materials such as titanium.

The objective of this research was to identify binders and processing methods that produced easily moulded titanium-based feedstock and final products with minimal defects. This involves understanding how factors such as binder composition, powder loading, and processing method affect feedstock rheology, homogeneity, debinding and sintering, and to develop a model for investigating feedstock rheology.

Feedstocks were manufactured by mixing different amounts of hydride-dehydride titanium alloy powder (HDH Ti-6Al-4V) with a three-component binder containing different amounts of polyethylene glycol (PEG), polyvinyl butyral (PVB) and stearic acid (SA). Most research on titanium powder metallurgy uses spherical, fine powders with mean diameters (d_{50}) between 0.3 and 19 μm . This research used HDH Ti-6Al-4V, an irregular, coarse powder with a d_{50} of 52 μm and a d_{90} of 117 μm . The effect of using different types of mixers for various mixing times was evaluated by measuring mixing torque and thermal analysis. Feedstock homogeneity was evaluated by density measurements and DTA/TGA analysis, and mouldability was evaluated by rheological properties. After mixing and extrusion, binders were removed from the formed (green) part in a two-stage process involving aqueous debinding followed by thermal debinding. The part was then sintered to remove any

remaining binder and to create the final product. Morphological characteristics of feedstocks, moulded, debound and sintered parts were assessed using optical and scanning electron microscopes.

Polyethylene glycol, PVB and SA were used as binder components because they are inexpensive and readily available. PEG is environmentally safe, easily extractable in water and reduces feedstock viscosity. The PVB is water-insoluble and provides strength to the formed (green) parts and debound (brown or grey) parts so used as a backbone component. The SA acts as a surfactant and helps wet the powder particles. Thermal characteristics were determined with DTA/TGA and rheological analyses with a capillary rheometer.

The four-stage process developed to manufacture homogeneous material suitable for titanium-MIM (Ti-MIM) involved dry-mixing irregular HDH Ti-6Al-4V powder and binder components in a planetary mixer for 30 min at room temperature, followed by 16 h further mixing at room temperature in a roller mixer rotating at 250 rpm, then melt-mixing at 125 °C for 45 min in a roller compounder. The final step involved extruding the processed feedstock in a twin-screw extruder operating with a feed-to-nozzle temperature profile of 125, 140, 135, 135, 140 °C.

Viscosity, density and mixing torque data for the PEG-PVB-SA binders indicated that the maximum (so-called critical) powder loading was 65 vol. %. Feedstocks made with 75:20:5 vol. % PEG:PVB:SA and 80:15:5 vol. % PEG:PVB:SA binders and 60 vol. % powder loading, were optimal for Ti64-MIM. This powder loading is higher than reported for spherical, fine powders. The flow behaviour index of the feedstock could be used to identify optimal powder loading and temperatures for injection moulding. A feedstock with low viscosity (<80 Pa-s), low flow activation energy (<30 kJ/mol), high mouldability index (15 – 22), high melt flow rate (up to 860 g/10 min), and high stability was selected for Ti-MIM.

Solvent debinding green parts made of 60 vol. % Ti64 powders and PEG-PVB-SA binders at 35 °C was affected by binder composition. Between 4.67 – 5.20 h, PEG removal changed from dissolution-controlled to diffusion-controlled. Increasing debinding temperature to 55 °C decreased the time at which the transition occurred.

Debinding time affected PEG removal, porosity and reaction depth to a similar extent, indicating these parameters are inter-related. The empirical relationship describing solvent debinding kinetics of Ti-MIM parts showed PEG removal (weight loss %) was linearly related to the n^{th} root of debinding time ($\sqrt[n]{t}$). This model can be used to predict optimum solvent debinding temperature and time.

The maximum relative density, tensile strength and the oxygen content of as-sintered parts were 95%, 455 MPa and 1.58 wt. % respectively. Fracture surfaces exhibited transgranular fracture. The poor mechanical properties are mainly due to porosity and high oxygen content.

New rheological models to predict feedstock flow properties, relative viscosity and critical powder loading were developed and validated. An improved model for predicting relative viscosity and critical powder loading from powder loading, surface area, shear rate, and flow behaviour index is proposed.

The Einstein relationship for relative viscosity of dilute suspensions was modified and used for MIM feedstocks, which have a much higher powder loading.

Recommendations for further work are given.

List of Publications

Journal papers

Thavanayagam, G., Pickering, K. L., Swan, J. E., Cao, P. (2014), Analysis of rheological behaviour of titanium feedstocks formulated with a water-soluble binder system for powder injection moulding. *Powder Technology*, 269, 227-232.

Thavanayagam, G., Zhang, D. L., Pickering, K. L., and Cao, P. (2013), Rheological properties of feedstock composed of titanium alloy powder and polyethylene glycol based binder system for metal injection moulding, *Wiley Online*, DOI: 10.1002/9781118792148.ch293.

Thavanayagam, G., Zhang, D. L., Pickering, K. L., and Raynova, S. (2012), A study of polyvinyl butyryl based binder system in titanium based metal injection moulding. *Key Engineering Materials*, 520, 167-173.

Conference papers and presentations

Thavanayagam, G., Pickering, K. L., Swan, J. E., Gabbittas, B (2014), Investigation of mixing methods for feedstock formulation for titanium based metal injection moulding. Oral presentation, 11th Asia-Pacific Conference on Materials Processing, 6-11 July 2014, Auckland, New Zealand.

Thavanayagam, G., Pickering, K. L., and Swan, J. (2013), A study of water debinding process in titanium based metal injection moulding. Oral presentation, International Conference on Titanium Powder Processing, Consolidation and Metallurgy, 2-4 December 2013, Hamilton, New Zealand.

Thavanayagam, G., Zhang, D. L., Pickering, K. L., and Cao, P. (2013), Rheological properties of feedstock composed of titanium alloy powder and polyethylene glycol based binder system for metal injection moulding. Oral presentation, 8th Pacific Rim International Congress on Advanced Materials and Processing, 4-9 August 2013, Waikoloa, Hawaii, USA.

Thavanayagam, G., Pickering, K. L., and Swan, J. (2013), Titanium based metal injection moulding: significance of binder formulation. Invited speaker, International Conference on Mathematical Modelling in Computer, Management & Medical Sciences, 13-15 June 2013, Tiruvalla, Kerala, India.

Thavanayagam, G., Zhang, D. L., and Pickering, K. L. (2013), Characterization of feedstock composed of titanium alloy powder and polyethylene glycol based binder system for metal injection moulding. Oral presentation, WaiCAM Symposium 2013 on Titanium Alloy Powder Metallurgy Research, Development and Commercialisation, 7 February 2013, Hamilton, New Zealand.

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Thavanayagam, G., Zhang, D. L., Pickering, K. L., and Raynova, S. (2011), A study of polyvinyl butyryl based binder system in titanium based metal injection moulding. Oral presentation, International Conference on Powder Processing, Consolidation and Metallurgy of Titanium, 5-7 December 2011, Brisbane, Australia.

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Table of Contents

Abstract.....	iii
List of publications	vii
Acknowledgements	ix
Table of Contents.....	xi
List of Figures	xv
List of Tables	xx
Nomenclature.....	xxii
 Chapter One: Introduction	 1
1.1. Manufacturing metal articles	1
1.2. Metal injection moulding.....	1
1.3. Metal injection moulding process.....	2
1.4. Titanium as a metal for MIM.....	4
1.4.1. Development of Ti-MIM.....	4
1.4.2. Development of Ti-MIM in New Zealand	5
1.5. Objectives of this research.....	5
1.6. Structure of this thesis	6
 Chapter Two: Literature Review	 7
2.1. Producing metal components.....	7
2.1.1. Powder metallurgy	9
2.2. Metal injection moulding.....	11
2.2.1. Process.....	11
2.2.2. Advantages of MIM	13
2.2.3. Materials used in MIM	14
2.2.4. Titanium metal injection moulding (Ti-MIM)	16
2.3. Binder/ feedstock formulation	17
2.3.1. Possible binders and characteristics	17
2.3.2. Binders for titanium metal injection moulding	22
2.3.3. Binder and feedstock formulations.....	25
2.4. Rheology.....	31
2.4.1. Fluid flow	31
2.4.2. Pseudoplastic flow behaviour and flow behaviour index.....	32

2.4.3.	Yield stress	35
2.4.4.	Melt flow rate and fluidity	36
2.4.5.	Flow activation energy	36
2.4.6.	General mouldability.....	38
2.4.7.	Effect of powder loading on viscosity.....	40
2.5.	Debinding and sintering.....	43
2.5.1.	Debinding.....	43
2.5.2.	Solvent debinding.....	45
2.5.3.	Solvent debinding kinetics	47
2.5.4.	Thermal debinding	49
2.5.5.	Sintering	52
2.6.	Analytical and physical methods for characterising binder and feedstock.....	54
2.7.	Intentions of this research.....	55
2.7.1.	Binder selection	56
2.7.2.	Process conditions	57
2.7.3.	Rheology.....	57
2.7.4.	Debinding and sintering.....	57
2.8.	Summary.....	58
Chapter Three: Materials and Methods		61
3.1.	Materials	61
3.2.	Manufacturing the binder systems	61
3.2.1.	Trial 1.....	61
3.2.2.	Trial 2	63
3.2.3.	Trial 3.....	63
3.2.4.	Trial 4.....	64
3.2.5.	Trial 5.....	65
3.3.	Assessing binder systems	66
3.3.1.	Morphological analysis	66
3.3.2.	Thermogravimetric analysis.....	66
3.4.	Manufacturing feedstocks.....	66
3.4.1.	Method 1	66
3.4.2.	Method 2	67
3.5.	Powder loading.....	68
3.5.1.	Bulk density	68
3.5.2.	Mixing-torque	68
3.5.3.	Viscosity.....	69

3.6.	Characteristics of Ti64 powder and feedstocks	69
3.6.1.	Particle size	69
3.6.2.	Thermogravimetric analysis	69
3.6.3.	Feedstocks density.....	69
3.6.4.	Morphology of Ti64 powder and feedstocks	69
3.7.	Rheological characteristics	70
3.8.	Injection moulding and Ti-MIM processes	70
3.8.1.	Injection moulding	71
3.8.2.	Solvent debinding.....	72
3.8.3.	Thermal debinding and sintering.....	72
3.9.	Characterising moulded, debound and sintered parts	75
Chapter Four: Results and Discussion.....		77
4.1.	Binder systems.....	77
4.1.1.	Thermal analysis	77
4.1.2.	Effect of process conditions on homogeneity	81
4.1.3.	Summary	94
4.2.	Feedstocks	94
4.2.1.	Powder loading and feedstock density	94
4.2.2.	Effect of powder loading on mixing torque	99
4.2.3.	Powder loading and feedstock relative viscosity	102
4.2.4.	Effect of powder characteristics on critical powder loading.....	107
4.2.5.	Effect of process on feedstock homogeneity.....	110
4.2.6.	Feedstock heterogeneity and powder-binder interaction.....	123
4.2.7.	Summary	128
4.3.	Rheological properties	130
4.3.1.	Shear rate and feedstock viscosity	131
4.3.2.	Powder-binder composition and yield stress.....	137
4.3.3.	Powder-binder composition and feedstock fluidity.....	140
4.3.4.	Powder-binder composition and melt flow	140
4.3.5.	MFR and flow behaviour index	143
4.3.6.	Feedstock stability.....	146
4.3.7.	Powder loading and viscosity.....	150
4.3.8.	Proposed model for determining critical powder loading from relative viscosity.....	152
4.3.9.	Model validation	155
4.3.10.	Temperature and viscosity	163

4.3.11.	Feedstock mouldability	165
4.3.12.	Summary	167
4.4.	Solvent debinding	170
4.4.1.	Effect of binder composition on solvent debinding	171
4.4.2.	Binder and inter-diffusion coefficient	173
4.4.3.	Effect of temperature on solvent debinding	177
4.4.4.	Debinding time and binder on reaction distance	180
4.4.5.	Microstructure during solvent debinding	183
4.4.6.	Summary	191
4.5.	Characterising Ti-MIM parts	193
4.5.1.	Green parts	194
4.5.2.	Brown parts	196
4.5.3.	Sintered parts	199
4.5.4.	Summary	207
Chapter Five: Conclusions and recommendations		209
5.1.	Binder components	209
5.2.	Feedstock manufacturing process	209
5.3.	Powder loading	210
5.4.	Rheology	211
5.5.	Modelling flow properties	212
5.6.	Debinding and sintering	213
5.7.	Model for solvent debinding kinetics	214
5.8.	Fracture morphology	215
5.9.	Recommendations	215
Chapter Six: References		217

List of Figures

Figure 1.1: Growth of global MIM and PIM markets.....	2
Figure 1.2: Regional influence on MIM applications.	3
Figure 2.1: Process flow for conventional and NNS production of metal parts.	9
Figure 2.2: Relationship of fabrication techniques.	11
Figure 2.3: Schematic of the stages in MIM.	12
Figure 2.4: Cost comparison of metallurgical manufacturing routes.....	14
Figure 2.5: Effect of oxygen content on elongation and ultimate tensile strength of Ti-6Al-4V MIM parts.....	17
Figure 2.6: Effect of debinding temperature under vacuum on carbon and oxygen content of parts made of Ti-6Al-4V/PW-LDPE based binder.....	24
Figure 2.7: Classification of time-independent flow behaviour.....	31
Figure 2.8: Effect of shear rate on viscosity of a melt feedstock flowing into a mould.	38
Figure 2.9: Relative viscosity versus powder loading (solids loading) for two powders. ...	40
Figure 2.10: Effect of particle size distribution on suspension viscosity.....	41
Figure 2.11: DTA/TGA curves showing thermal properties of a binder	50
Figure 2.12: Two examples of thermal debinding cycles: (a) Sotomayor <i>et al.</i> [302] and (b) Li <i>et al.</i> [272].....	51
Figure 2.13: Microstructure showing pores in as-sintered parts: (a) Li <i>et al.</i> [272] and (b) Shibo <i>et al.</i> [113].....	53
Figure 3.1: Roller compounder.	62
Figure 3.2: Mixing chamber of the roller compounder.....	63
Figure 3.3: Mechanical mixer (manufactured in-house).....	64
Figure 3.4: Thermo-Prism twin-screw extruder with an automatic feeder.	65
Figure 3.5: Schematic diagram of twin-screw extrusion.	65
Figure 3.6: Schematic diagram of a roller mixer.	68
Figure 3.7: Injection moulding machine (BOY-35A).	71
Figure 3.8: Dimension of an injection moulded test specimen.	72
Figure 3.9: Water debinding equipment (manufactured in-house).	73
Figure 3.10: ACME, GDQ S-400 high vacuum sintering furnace.....	73
Figure 3.11: Dimension of a tensile testing specimen (mm).	75
Figure 4.1: Chemical structure of (a) SA, (b) repeating unit in PEG, and (c) repeating unit in PVB (c) [186, 189].	77
Figure 4.2: Thermal analysis of (a) PEG, (b) SA and (c) PVB.....	78
Figure 4.3: DTA-TGA profile of PVB, PEG and SA showing four degradation stages.....	80
Figure 4.4: Torque at the start of mixing binder components at 175 °C and 30 rpm in the roller compounder.....	81
Figure 4.5: Torque for the complete process of mixing binder components at 175 °C and 30 rpm in the roller compounder.	82

Figure 4.6: Heterogeneous nature of the binder produced in the roller compounder at 175 °C and 30 rpm for 15 min of mixing.	82
Figure 4.7: Torque at the start of mixing binder components for 60 min at 175 °C and 30 rpm in the roller compounder.	83
Figure 4.8: Torque at the start of mixing binder components for 80 min at 175 °C and 30 rpm in the roller compounder.	84
Figure 4.9: Torque when dry mixing binder components at 175 °C and 75 rpm in the roller compounder.....	84
Figure 4.10: Optical microscope images showing the effect of mixing speed and time on microstructure of 65:30:5 vol. % PEG:PVB:SA binder at 175 °C	85
Figure 4.11: Differential thermal analysis of PEG, PVB and SA.	86
Figure 4.12: Burn-out patterns of 65:30:5 vol. % PEG:PVB:SA binder manufactured at 175 °C and 75 rpm in the roller compounder	87
Figure 4.13: Optical microscope images showing effect of mixing time on microstructure of 65:30:5 vol. % PEG:PVB:SA binder produced in a mechanical mixer at 175 °C and 300 rpm.....	89
Figure 4.14: Burn-out patterns of 65:30:5 vol. % PEG:PVB:SA binder mixed for 90 min at 175 °C and 300 rpm in the mechanical mixer.	90
Figure 4.15: Microstructure (optical microscope) of 65:30:5 vol. % PEG:PVB:SA binders produced using a twin crew extruder at 70 rpm with a feed to nozzle temperature profile of 160, 177, 170, 160, 147 °C.	91
Figure 4.16: Burn-out patterns of binder samples (PEG:PVB:SA = 65:30:5 vol. %) manufactured at 160 °C – 177 °C – 170 °C – 160 °C – 147 °C (feed to nozzle) and 70 rpm in the twin screw extruder.	92
Figure 4.17: Burn-out patterns of random samples from PEG:PVB:SA (65:30:5 vol. %) binders manufactured at 175 °C at various mixing speeds and times in three different mixers: (a) TGA and (b) DTA.	93
Figure 4.18: Effect of Ti64 volumetric powder loading on density of feedstocks made from 65:30:5 vol. % PEG:PVB:SA binder manufactured at 175 °C.	95
Figure 4.19: Schematic diagram of four possible situations of a feedstock.....	96
Figure 4.20: Effect of powder loading and binder composition on density of Ti64 binder mixes manufactured at 125 °C in method 2	97
Figure 4.21: Effect of binder composition processed at 125 °C on critical powder loading of Ti-MIM feedstocks.....	98
Figure 4.22: Mixing torque evolved as Ti64 powder was added to 65:30:5 vol. % PVB:SA binder in the roller compounder operating at 175 °C and 60 rpm.	100
Figure 4.23: Effect of adding Ti64 powder to 80:15:5 vol. % PEG:PVB:SA binder on roller compounder torque when operating at 125 °C and 60 rpm.	102
Figure 4.24: SEM images of feedstocks made from 65:30:5 vol. % PEG:PVB:SA binder and (a) 50, (b) 55 (c) 60 and (d) 63 vol. % powder loadings and manufactured at 175 °C (method 1, Section 3.4).....	104
Figure 4.25: Effect of powder loading on viscosity of 80:15:5 vol. % PEG:PVB:SA feedstock manufactured by method 2 (Section 3.4) at 145 °C.	105
Figure 4.26: SEM images of feedstocks illustrating effect of Ti64 powder loading (Φ) on feedstock made with 80:5:5 vol. % PEG:PVB:SA binder.....	105

Figure 4.27: Effect of powder loading on relative viscosity of feedstock made with 80:15:5 vol. % PEG:PVB:SA binder (method 2, Section 3.4) at 145 °C.	106
Figure 4.28: Effect of powder loading on relative viscosity of feedstock made with 75:20:5 vol. % PEG:PVB:SA binder (method 2, Section 3.4) at 145 °C.	106
Figure 4.29: SEM image of HDH Ti-6Al-4V powder used in this research.....	108
Figure 4.30: Particle size distribution of HDH Ti-6Al-4V used in this research.....	108
Figure 4.31: Burn-out patterns of samples of 60 vol. % Ti64 powder and 65:30:5 vol. % PEG:PVB:SA binder after 45 min mixing at 175 °C and 60 rpm in the roller compounder.	111
Figure 4.32: SEM images of Ti64 powder (a, b, c) and feedstock mixed for 45 min at 175 °C and 60 rpm in the roller compounder (a', b', c').	112
Figure 4.33: Effect of 60 min isothermal holding at 120 °C and 130 °C on weight loss of (a) PEG, (b) PVB and (c) SA.	114
Figure 4.34: SEM images of (a) PEG, (b) PVB, (c) SA, and (d) Ti64 powders.....	116
Figure 4.35: Burn-out patterns of samples (n=4) obtained at different stages in feedstock manufacturing (method 2, Section 3.4).	117
Figure 4.36: Torque when mixing 60 vol. % Ti64 powder and 80:15:5 vol. % PEG:PVB:SA binder at 125 °C and 60 rpm in the roller compounder.....	118
Figure 4.37: Melt mixing mechanism in (a) a roller compounder and (b) a twin screw extruder.....	119
Figure 4.38: Box and whisker plot of binder wt. % loss during stages in the process (n=4).	120
Figure 4.39: Box and whisker plot of feedstock density during stages in the process (n=5).	120
Figure 4.40: SEM images of extruded Ti64 and 80:15:5 vol. % PEG:PVB:SA binder manufactured using a four-stage process.....	122
Figure 4.41: Schematic of steric stabilization [353].	124
Figure 4.42: Interaction between Ti64 powder and SA.	124
Figure 4.43: Schematic of feedstock with mobile and immobile binders.....	125
Figure 4.44: Effect of powder loading and binder composition on mixing torque at 125 °C and 60 rpm in the roller compounder	127
Figure 4.45: Effect of powder loading and binder composition on steady state torque.....	128
Figure 4.46: Effect of shear rate and powder-binder composition on viscosity.	131
Figure 4.47: SEM images of feedstock F5575 showing the effect of shear rate.....	132
Figure 4.48: SEM images of feedstock F6075 showing the effect of shear rate on particle packing, re-arrangement and homogeneity.....	133
Figure 4.49: Effect of shear rate on feedstock viscosity.	134
Figure 4.50: Effect of powder loading on rheological behaviour of feedstock F6080 at 145 °C.....	135
Figure 4.51: Effect of temperature on flow behaviour index of feedstocks F6075 and F6080.	136
Figure 4.52: Ti64-MIM (F6080) extruded at barrel-to-nozzle temperature profiles of (a) 110 – 125 – 125 – 125 – 135 °C and (b) 125 – 140 – 135 – 135 – 140 °C.	136

Figure 4.53: Goodness of fit for yield stress of Ti64-MIM feedstocks at 145 °C using the Bingham and Casson models.	138
Figure 4.54: Effect of temperature and PEG content on yield stress of feedstocks.	139
Figure 4.55: Effect of shear rate and binder composition on fluidity of Ti65-MIM feedstocks.	141
Figure 4.56: Effect of shear rate and composition on feedstock shear stress at 145 °C. ...	142
Figure 4.57: Effect of shear stress and composition on MFR values for Ti64-MIM feedstocks at 145 °C.	143
Figure 4.58: Effect of Ti64-MIM feedstocks temperatures on flow behaviour index (n) and feedstock flow index (p).	145
Figure 4.59: Effect of shear rate on melt flow rate for various Ti64-MIM feedstocks at 145 °C.	145
Figure 4.60: Effect of shear rate, binder composition (vol. %) and powder loadings at 145 °C rate of change in Ti64-MIM feedstock viscosity.....	147
Figure 4.61: Effect of shear rate, binder composition (vol. %) and temperature on stability of Ti64-MIM feedstocks with 60 vol. % powder loading.....	149
Figure 4.62: Effect of powder loading and binder composition on relative viscosity of Ti64-MIM feedstocks at 2000 s ⁻¹ shear rate and 145 °C.	151
Figure 4.63: Comparison of experimental data for relative viscosity of feedstocks with values predicted using published models (Table 4.14).	151
Figure 4.64: Goodness of curve fitting for various m values.....	153
Figure 4.65: Effect of powder loading of Ti64-MIM feedstocks on relationship for $[1 - \eta r^{-(1/m)}]$ using m=2.5.	153
Figure 4.66: Comparison of the proposed model with the other reported models.	155
Figure 4.67: Effect of powder loading on relative viscosity of CIM powders at 100 °C and shear rate of 100 s ⁻¹ [233] using proposed model and that of Song and Evans [233].	157
Figure 4.68: Experimental data and relative viscosity predicted by the new model for different Ti64-MIM and zirconia-wax PIM feedstocks.....	158
Figure 4.69: SEM micrographs of F6080 Ti64-MIM feedstock.....	162
Figure 4.70: Effect of temperature on feedstock viscosity.	163
Figure 4.71: Effect of temperature and shear stress on viscosity of Ti64-MIM feedstocks.	164
Figure 4.72: Effect of shear rate on flow activation energy.....	165
Figure 4.73: Effect of temperature on feedstock mouldability.	166
Figure 4.74: Effect of binder composition and time on removing PEG from 60 vol. % Ti64 MIM brown parts at 35 °C.	171
Figure 4.75: SEM image of Ti64 MIM made with F6085 feedstock after 16 h solvent debinding at 35 °C.	172
Figure 4.76: Effect of binder and time on removing PEG from 60 vol. % Ti64-MIM brown parts immersed in 35 °C water	172
Figure: 4.77: Effect of binder composition on $\ln(1/F)$ and t/Ψ^2 when debinding at 35 °C.....	174

Figure 4.78: Effect of temperature and binder PVB content on PEG removal during solvent debinding.....	175
Figure 4.79: Effect of solvent debinding time at 45 °C on microstructure of Ti-MIM parts made with feedstock F6075.	176
Figure 4.80: Effect of temperature on dissolution- and diffusion-controlled removal of PEG from MIM parts.....	178
Figure 4.81: Schematic of a MIM part during solvent debinding.....	180
Figure 4.82: Effect of temperature on reaction depth when solvent debinding a MIM part	182
Figure 4.83: Effect of binder composition and debinding time at 35 °C on reaction depth	183
Figure 4.84: Effect of binder composition on porosity when solvent debinding at 35 °C...	183
Figure 4.85: Effect of binder composition on porosity when solvent debinding at 35 °C...	184
Figure 4.86: Effect of PEG content and solvent debinding time on microstructure of Ti-MIM made of (aa') 75 vol. % PEG, (bb') 80 vol. % PEG and (cc') 85vol. % PEG.	185
Figure 4.87: Effect of binder and temperature on Ti-MIM porosity.....	186
Figure 4.88: Changes in microstructure of Ti-MIM parts made with F6075 during solvent debinding at 35 °C.....	187
Figure 4.89: PEG removal, reaction depth and porosity when solvent debinding Ti-MIM parts produced with F6075.....	188
Figure 4.90: Effect of binder type and value for n to predict PEG removal (wt. %) during solvent debinding 35 °C.	189
Figure 4.91: Schematic of solvent debinding Ti-MIM parts made with PEG-PVB binder.....	191
Figure 4.92: Effect of binder composition on density at various positions of Ti-MIM part.	194
Figure 4.93: Box and Whisker plot for effect of powder loading and binder composition on Ti-MIM density (n =12).....	195
Figure 4.94: SEM images (500X and 3000X) of Ti-MIM parts made from 60 vol. % Ti64 powder and different PEG:PVB:SA binders.....	196
Figure 4.95: Thermal debinding cycle for Ti-MIM parts.	197
Figure 4.96: Effect of binder composition and solvent debinding time on Ti64-MIM microstructure after the thermal debinding stage.	198
Figure 4.97: Sintering cycle for sintering Ti-MIM parts.	199
Figure 4.98: Effect of solvent debinding temperature (a-b-c) and binder composition (a'-b'-c') on microstructure (α - β lamellar structure) of as-sintered Ti-MIM parts. ..	200
Figure 4.99: Effect of HIPping time on Ti64 microstructure [317].....	203
Figure 4.100: SEM images of as-sintered Ti-MIM parts made of 60 vol. % Ti64 powder.	203
Figure 4.101: Effect of binder composition on fracture surface of as-sintered Ti-MIM parts made with 60 vol. % Ti64 powder.....	205
Figure 4.102: Surface quality of Ti-MIM parts: (a) polished surface from this research, and (b) without and (c) with shot peening [374].	206

List of Tables

Table 2.1: Comparison of MIM and other manufacturing routes	13
Table 2.2: Cost of metals at different production stages.....	16
Table 2.3: Examples of binders used in MIM applications	19
Table 2.4: Examples of PIM binders	23
Table 2.5: Various binder/feedstock formulation methods reported in literature.	28
Table 2.6: Flow behaviour index for various feedstock formulations	34
Table 2.7: Summary of published mouldability index.....	39
Table 2.8: Published models for relative viscosity and powder loading.....	42
Table 2.9: Various debinding techniques.....	44
Table 2.10: Characteristics of various debinding processes	45
Table 2.11: Examples of proposed solvents for polymeric binders	46
Table 3.1: Details of polymeric binder components	62
Table 3.2: Ti-MIM feedstocks for rheological investigations	70
Table 3.3: Feedstock formulations used for Ti-MIM.....	71
Table 3.4: Heating profile for thermal debinding.	74
Table 3.5: Heating profile for sintering.	74
Table 4.1: DTA-TGA characteristics of binders.....	79
Table 4.2: Weight loss of binder components at different degradation stages	80
Table 4.3: Effect of binder composition on critical powder loadings at 125 °C.....	98
Table 4.4: Effect of powder loadings and shear on viscosity (Pa-s) of feedstocks made with 80:15:5 vol. % PEG:PVB:SA binder.....	103
Table 4.5: Critical (Φ_c) and optimal (Φ_o) Ti64 powder loadings obtained from density, torque and viscosity analyses.	107
Table 4.6: Powder particle size used for MIM research	109
Table 4.7: Binder component weight loss after 60 min isothermal holding	115
Table 4.8: Composition of Ti-MIM feedstocks	131
Table 4.9: Effect of powder loading and binder composition on flow behaviour index of Ti64-MIM feedstocks at 145 °C.....	134
Table 4.10: Goodness of fit of Ti64-MIM feedstocks at 145 °C to the Bingham and Casson models for yield stress (kPa).	137
Table 4.11: Effect of temperature and feedstock composition on yield stress and plastic viscosity.....	140
Table 4.12: Effect of shear rate and composition of feedstock fluidity ($10^{-3} \text{ Pa}^{-1}\text{s}^{-1}$) at 145 °C	141
Table 4.13: Effect of shear stress and composition on feedstock melt flow rate (g/10 min) at 145 °C.....	142
Table 4.14: Effect of powder loading and binder composition on feedstock flow index of Ti64-MIM feedstocks at 145 °C.....	144

Table 4.15: Effect of powder loading and binder composition on stability, expressed as <i>i</i> value, of Ti64-MIM feedstocks at 145 °C.....	150
Table 4.16: Effect of temperature on stability of Ti64-MIM feedstocks	150
Table 4.17: Effect of powder loading on relative viscosities predicted by various models.....	156
Table 4.18: Experimental critical powder loadings for zirconia-wax feedstocks [233] and values calculated using the proposed model.	156
Table 4.19: Estimating binder adsorbed layer on powder particles.	161
Table 4.20: Effect of shear stress on flow activation energy of feedstocks (kJ/mol)	165
Table 4.21: Suitability of different binders for Ti64-MIM at 60 vol. % powder loading, based on various properties where +++ is very suitable and + is least suitable.	167
Table 4.22: Effect of binder type on coefficients obtained during solvent debinding at 35 °C.	174
Table 4.23: Effect of binder composition and debinding temperature on time (h) to change from the dissolution- to the diffusion-controlled stage.	179
Table 4.24: Inter-diffusion coefficient of PEG-water, D_e ($\times 10^{-3} \text{ mm}^2\text{h}^{-1}$) for various binders and temperatures	180
Table 4.25: Effect of binder composition on physical, mechanical and oxygen content of as-sintered Ti64-MIM parts.....	201

Nomenclature

Acronyms

ASTM	American Society for Testing and Materials
CIM	Ceramic injection moulding
Diff	Diffusion-controlled
Diss	Dissolution-controlled
DTA	Differential thermal analysis
EWC	Equilibrium water content
GA	Gas atomized
HDH	Hydride-dehydride
HIP	Hot isostatic pressing
MFR/ μ	Melt flow rate
MIM	Metal injection moulding
MP	Melting point
Mw	Molecular weight
NNS	Near-net shape
PIM	Powder injection moulding
PM	Powder metallurgy
s.f	Significant figure
TGA	Thermogravimetric analysis
Ti64	Ti-6Al-4V
Ti-MIM	Titanium MIM
WA	Water atomized

Polymers

BW	Beeswax
CAB	Cellulose acetate butyrate
CW	Carnauba wax
DOP	Diocetyl phthalate
EVA	Ethylene vinyl acetate
HDPE	High density polyethylene
LDPE	Low density polyethylene
MW	Microcrystalline wax
PE	Polyethylene
PEG	Poly ethylene glycol
PEG-4000	PEG with MW of 4000
PMMA	Polymethyl methacrylate
POM	Polyoxymethylene
PP	Polypropylene
PS	Polystyrene
PVB	Polyvinyl butyral
PVOH	Poly vinyl alcohol
PW	Paraffin wax
SA	Stearic acid

Symbols

Da	Apparent interdiffusion coefficient
D, D _e	Interdiffusion coefficient of polymer and solvent
D _{eff}	Effective interdiffusion coefficient
E _a	Flow activation energy
F	Fraction of remaining soluble polymer
F _v	Fractional volume loss due to PEG removal
G	Rate of change of MFR with shear rate ($d\mu/d\dot{\gamma}$)
H	Mixing homogeneity, thickness
H _o	Initial mixing homogeneity
h	Polymer chain end-to-end length
k	Boltzmann's constant, consistency factor
m	Fluid consistency coefficient
n	Flow behaviour index
p	Rate of change of MFR with shear stress (feedstock flow index)
q	MFR as shear stress approaches unity
R	Universal gas constant, Retardation factor or radius of capillary pipe
R ²	Correlation coefficient
r	Particle radius.
S	Specific surface area
S _w	distribution slope parameter
T	Temperature
$\bar{T}$	Average temperature
t	Time
V	Volume
V ₀	Volume of moulded part
V(t)	Volume of the non-dissolved binder containing core at time, t
W _b	Weight fraction of binder in a feedstock
W _p	Weight fraction of powder in a feedstock
W _L	PEG weight loss

x	Reaction depth/distance	γ_{sv}	Interfacial tension of powder
α	Mouldability parameter	η	Viscosity
δ	Adsorbed layer thickness	η_b	Plastic viscosity
ε	Porosity	η_0	Viscosity at a reference temperature and shear rate
Φ, φ	Powder loading (Solid loading)	η_r	Relative viscosity
Φ_c	Effective critical powder loading	ν	Tortuosity
φ_b	Binder content	θ	Wetting angle
$(\varphi_b)_m$	Critical binder content	ρ	Density
φ_c	Critical powder loading	ρ_b	Binder density
φ_{eff}	Effective powder loading	ρ_f	Feedstock density
$\dot{\gamma}$	Shear rate	ρ_p	Powder density
$\bar{\gamma}$	Average shear rate	τ	Shear stress
$\dot{\gamma}_0$	Reference shear rate	τ_y	Yield stress
γ_{LV}	Interfacial tension of binder	Ψ	Modified effective length scale
γ_{SL}	Interfacial tension between powder and binder	ζ_{ss}	Steady state torque

Feedstock codes

F5580 Feedstock consists of 55 vol. % HDH Ti64 powder and 80 vol. % PEG of binder.
F6085 Feedstock consists of 60 vol. % HDH Ti64 powder and 85 vol. % PEG of binder.
F6575 Feedstock consists of 65 vol. % HDH Ti64 powder and 75 vol. % PEG of binder.

Chapter One: Introduction

1.1. Manufacturing metal articles

Metal articles were traditionally manufactured by casting, forging, extrusion or machining. Casting involves melting and pouring the metal into a mould cavity to obtain the shape required. Cast items retain properties expected of metal, such as high strength and stiffness, at elevated temperatures. Forging involves pressing to convert basic shapes into the shape required. Forged parts have excellent mechanical properties with minimum wastage. Extrusion is used to manufacture long, linear products and it is possible to produce complex cross sections. Machining involves removing material to cut a required shape. High precision parts can be produced but there is tool wear and material wastage.

Powder metallurgy (PM) is a more recently developed manufacturing approach, and encompasses many manufacturing routes including powder injection moulding (PIM). This process involves mixing powders with a suitable additive, consolidating the mixture into a required shape, and then sintering to increase the density. The major advantage of PM is that intricate shapes and near-net shape (NNS) articles can be manufactured. This reduces materials wastage and post-processing operations such as machining.

1.2. Metal injection moulding

Metal injection moulding (MIM), a major division of PIM, is widely used to produce small complex shaped parts, where a feedstock made of metallic powders and a suitable carrier is moulded (often termed the green part). After removing the binder (debinding) the compacts are sintered to produce parts that can be machined into the final products [1-3].

Metal injection moulding was developed in the late 1970s to mid-1980s to produce complex components that are difficult or impossible to manufacture using conventional powder metallurgy processing [1-4]. The advantages of MIM over other metal manufacturing techniques include: parts have higher strength than die casting; tolerances are smaller than achieved in sand or investment casting; and more complex shapes can be produced [5-6].

Because large volumes of intricate parts could be produced cheaply, the MIM industry expanded rapidly after 1995. The global market for MIM products is increasing at 14% per year [5-8]. In 2013, the US market was estimated to be US\$250 million, the European market approximately US\$350 million, and the Asian market (mainly China) was approximately US\$550 million [7]. Currently over 75% of PIM industry is MIM (Figure 1.1) [9].

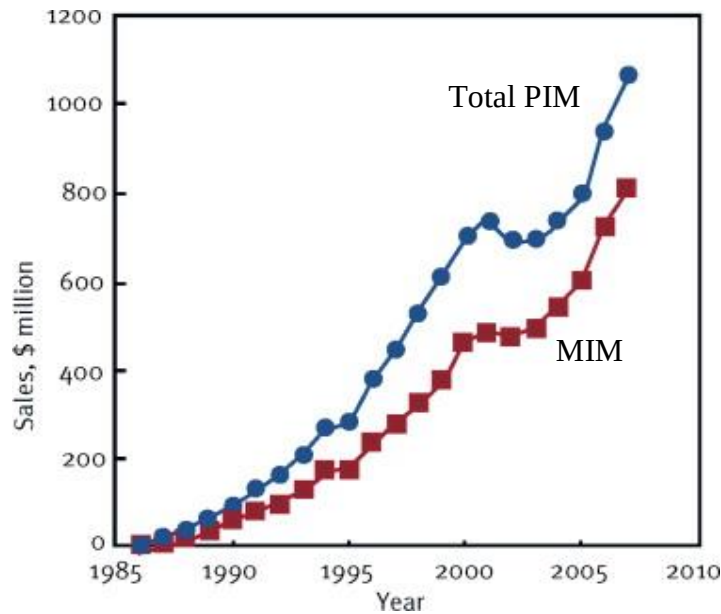


Figure 1.1: Growth of global MIM and PIM markets [9].

The MIM process is used extensively for producing automotive and consumer products, medical/dental, electronics, and firearm components [5-6, 8]. There are regional production differences (Figure 1.2). American production is mainly medical, dental and firearm applications, Asian production is mainly consumer electronics, cellular phones and computer components, whilst European production is mainly consumer products (watches, spectacle frames) and automotive applications [9].

1.3. Metal injection moulding process

There are four processing steps in MIM: feedstock formulation, injection moulding, debinding and lastly sintering. Binders control the rheological properties of the feedstock, allowing the required shape to be made (powder compact). The binders must be able to be removed easily and cheaply without affecting this shape [11]. Residual binder in the powder compact must be low and the binder must be

environmentally safe [12]. These are difficult criteria to meet and the binders are often commercial secrets.

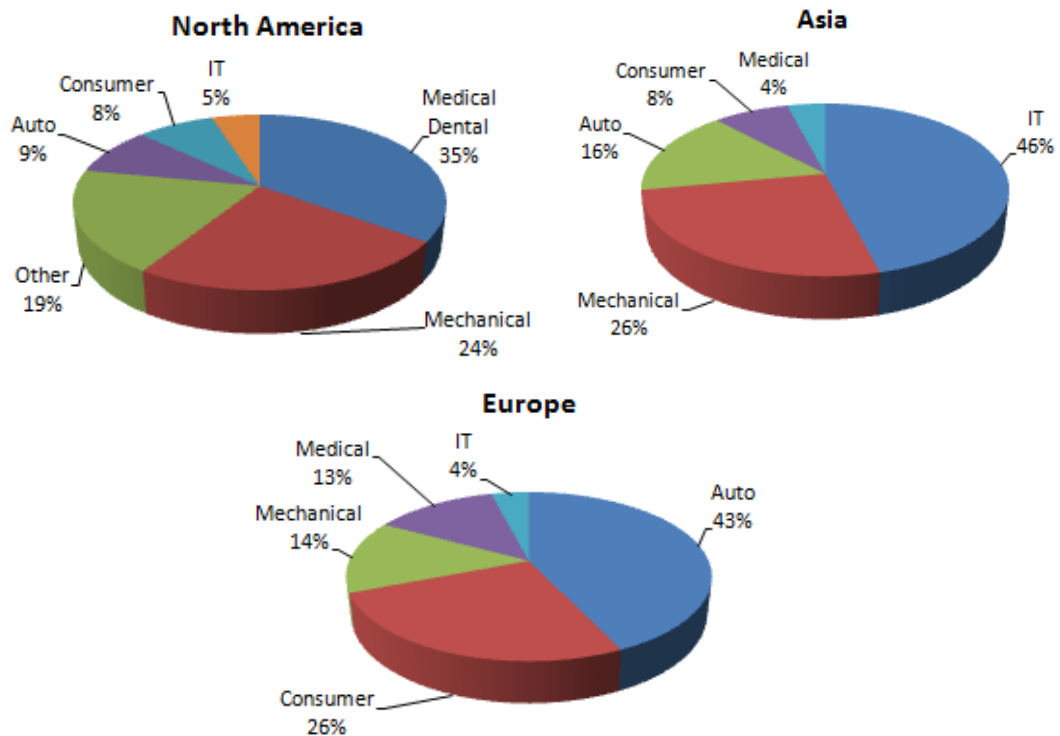


Figure 1.2: Regional influence on MIM applications (Europe and North America data is for 2010; Asia data is for 2008) [10].

Binders used in MIM include thermoplastic or thermosetting compounds (the most common), water-based systems, gelation systems and inorganics. Thermoplastic polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS) and wax are the most widely used [2].

Aluminium, stainless steel and copper powders have been successfully used in MIM since the late 1970s [4], with stainless steel making up approximately 50% of the market. This growth would otherwise have gone to investment casting. The most common materials used in MIM are stainless steel, chrome steel, hardened steel, nickel alloys and iron [13]. More recently, tungsten alloys, titanium alloys, nickel alloys and bronze have been used [9]. Titanium alloys are the most important of these materials because of their specific mechanical properties [14-15]. Titanium powders are very reactive so significant challenges need to be overcome before the full potential of titanium MIM can be realized [4].

1.4. Titanium as a metal for MIM

Many industries are looking for advanced materials. The high strength to density ratio, low modulus, high corrosion resistance and good biocompatibility of titanium and titanium alloys [16-18] make them suitable in many industries including aerospace [19], automotive [20-22], chemical and medical devices such as orthopaedic implants [23-26]. Many products such as turbine blades [27], artificial hip joints [28], fasteners [29] and landing gears [30] have been manufactured from titanium and its alloys.

Powders made from stainless steels, copper and aluminium are relatively easy to handle. The following difficulties need to be overcome when using titanium, especially powder titanium:

- Regular, spherical titanium powders are expensive and unlikely to become significantly cheaper in the near future
- Manufacturing products with excellent mechanical properties for critical applications such as dental, medical and aerospace requires high quality powders with a low oxygen content and few impurities
- Specialised binder systems are required to prevent interstitial contamination

The cost and availability of titanium powder are major problems. Titanium and titanium alloy powders used for MIM need to be cheap (<US\$44/kg), the right size (<40 μm), and have a low oxygen content (<0.2 – 0.4 wt. % depending on application) [31-33]. Spherical powders have the desired rheology for moulding and produce high sintering density, which produces high quality MIM products. However, spherical titanium powder is expensive. The cheaper, irregular shape titanium powders are often too contaminated and have poor rheological properties, making it difficult to mould MIM components to the desired precision. The ductility of titanium and its alloys decreases as oxygen content increases and they become very brittle [33]. About 45% of total titanium production is the alloy Ti-6Al-4V [32].

1.4.1. Development of Ti-MIM

Ti-MIM was first demonstrated in late 1980s and early production documented in 1992 in Japan [32]. Early difficulties in developing Ti-MIM included unavailability of suitable binders and powders and insufficient protection of the titanium during the

high temperatures used for thermal debinding and sintering. Ti-MIM parts up to 30 cm long can be made but parts over 7 to 10 cm (approximately 50 g) are uncommon because of dimensional reproducibility and chemistry [15, 33]. Recent information [33-34] indicates global Ti-MIM production of 3000–5000 kg per month. Suitable sintering furnaces are now available and titanium powders, although expensive, are available so the next challenge is identifying suitable binder systems [15, 33].

1.4.2. Development of Ti-MIM in New Zealand

In 1997, The University of Waikato began research on synthesising titanium powder, using aluminium to reduce titanium oxide ($3\text{TiO}_2 + 4\text{Al} \rightarrow 3\text{Ti} + 2\text{Al}_2\text{O}_3$) [35]. The research has reached a stage when it can support a manufacturing base for high-value products for export markets. In 2008, the opportunities, and critical technical and commercial barriers were described in a 10-year plan [36]. The Ti-MIM project is one of the six primary technologies in this research programme and aims to support a titanium applications industry in New Zealand worth \$700 million per year by 2020 and to have a one billion dollar per year titanium-based export industry before 2030 [35, 37].

1.5. Objectives of this research

Producing high-quality products by Ti-MIM requires suitable binders and processes. This research has the following broad aims:

- To identify binders that allow titanium-based feedstock to be easily and consistently moulded into required shapes using MIM, and that are easily and cost-effectively removed from the powder/binder compacts
- To understand how key factors such as powder loading, mixing condition, and binder composition affect rheological properties of the feedstock, and to identify key factors that affect solvent and thermal debinding
- To develop a model for the rheological properties of feedstocks

The following outcomes and benefits are expected from this research.

- Ability to easily and consistently injection mould feedstock made from titanium alloy powder and binder
- To obtain feedstock that has a high powder loading (≥ 60 vol. %)

- To identify cost-effective debinding and sintering processes
- To commercialize the feedstock processes and thus help develop Ti-MIM in New Zealand

1.6. Structure of this thesis

This thesis has six chapters. The MIM overall process and development of Ti-MIM in New Zealand and globally is given in Chapter 1. This chapter concludes with the broad research objectives and a description of the structure of this thesis.

Chapter 2 summarises the literature on titanium powder metallurgy, Ti-MIM and feedstock rheological properties. It gives details on issues that will be explored in the experimental work to investigate the effect of feedstock processing conditions, critical powder loading, feedstock homogeneity, rheological properties and solvent debinding kinetics on quality of Ti-MIM.

Chapter 3 describes the materials used, the testing equipment, and details of the trials done.

The effect of process conditions on binder homogeneity are discussed in Section 4.1. In Section 4.2, the effect of powder loading on feedstock properties is discussed and the critical and optimal powder loadings presented. The effect of process conditions and powder-binder interactions on feedstock homogeneity is also discussed. In Section 4.3, feedstock rheological properties such as shear thinning, fluidity, melt flow rate, flow activation energy, stability, mouldability and yield stress are presented and the relationship between melt flow rate and flow behaviour index established. The effect of powder loading on relative viscosity is used to develop a model for determining critical powder loading from relative viscosity. The effect of binder composition, temperature and debinding time on solvent debinding and solvent debinding kinetics is described in Section 4.4. The effect of binder composition and oxygen on mechanical properties of as-sintered parts is discussed in Section 4.5.

Conclusions and recommendations for further work are presented in Chapter 5. References are presented in chapter 6.

Chapter Two: Literature Review

This chapter summarises the literature on metallurgical processes, emphasising metal injection moulding (MIM) and particularly titanium MIM (Ti-MIM). The advantages and disadvantages of MIM, methods for formulating binder/metal feedstock, binder characteristics, effect of powder loading, and feedstock rheology are discussed in detail. Models explaining the behaviour of Ti-MIM feedstocks and the relationship between relative viscosity and powder loading are developed. The chapter concludes with the aims of the proposed research and methodology that will be used.

2.1. Producing metal components

Metal components can be produced by casting, forging, extrusion, machining and, more recently, injection moulding. The earliest processes for producing metal parts allowed both simple and complicated parts to be forged from a cast metal billet without special tools and with minimal wastage. Decades of developing precise tooling allowed high volumes of precision metal parts to be produced. However, tool wear can be high, further downstream machining operations may be required, materials can have variable quality, and the high cost of tooling can be only justified for large production runs. To date, there has been little interest in commercializing the many flexible forming processes developed at the laboratory scale due to their lack of precision [38].

Casting involves pouring molten metal into a mould, cooling and solidifying the metal under controlled conditions, and then removing the casting [39]. Complex shapes that would otherwise need to be assembled from separate parts can be formed. Products have the expected metal properties of high strength and stiffness and strength at elevated temperatures [40]. Limitations of casting include poor mechanical properties, poor dimensional accuracy and surface finish, and further machining is often needed. Forging, which involves hammering or pressing to convert basic shapes into a pre-determined form, produces parts with excellent properties and minimal wastage [41]. The process often involves a flat upper die hydraulically compressing an ingot against a required shaped lower die. Hot forging can reduce casting defects such as high porosity due to improper feeding or gas formation, and segregation or coarse microstructure due to long cooling times [42].

Investment casting is a multi-stage metal forming process used for complex small-to medium-sized castings. Several wax patterns are attached to a wax sprue to form a pattern tree then coated with a thin layer of refractory material to form a rigid mould. After melting and removing the wax, liquid metal is poured into the mould and allowed to solidify. The mould is broken from the finished casting, separating it from the sprue and finished by grinding [39]. This process allows complex parts with close dimensional control and good surface finish to be produced. However, investment casting is a relatively expensive multi-stage process, and takes a long time [39].

Extrusion allows long, straight semi-finished products such as bars, tubes, wires and strips to be made by compressing a solid metal slug through a die. The process can be carried out at room or higher temperatures depending on the alloy [43]. In direct extrusion, the ram moves toward the die and compresses the metal slug; in indirect extrusion, the die moves down the bore so the metal is forced through the die [44]. Compressive and shear but no tensile forces develop during extrusion so even brittle materials can be deformed without fracturing, which is not possible using other primary metalworking processes. Symmetry so the metal flows uniformly through the die is the most important factor in determining extrudability [43].

Machining, which involves cutting away material from a forged product to form the required shape, requires a cutting tool that is harder than the metal product. After the Bridgeport machining centre was invented in the 1930s, and because machining is relatively easy, machine makers developed low-cost 5-axis (or more) computer numerical control (CNC) machining centres that can convert forged metal into very high precision products at speed [38]. Disadvantages of machining include high tooling costs, tool wear and wastage (scrap).

Complex shapes with irregular curves, radial projections, eccentrics or recesses cannot be manufactured easily by casting, forging or extrusion. Significant resources are wasted in secondary operations such as turning, shaping, milling and drilling (collectively called “chipping”) to obtain the required shape. Materials scientists and industrialists realise it was important to develop near net shape (NNS) methods that minimized the cost of secondary operations [15, 45-46]. In NNS manufacturing, shaping can normally be achieved without chipping (Figure 2.1), which minimizes

secondary operations [47-48]. Investment casting and powder metallurgy (PM) can be used to produce NNS parts [46]; the latter is a low cost manufacturing method suitable for high volume production [49-50].

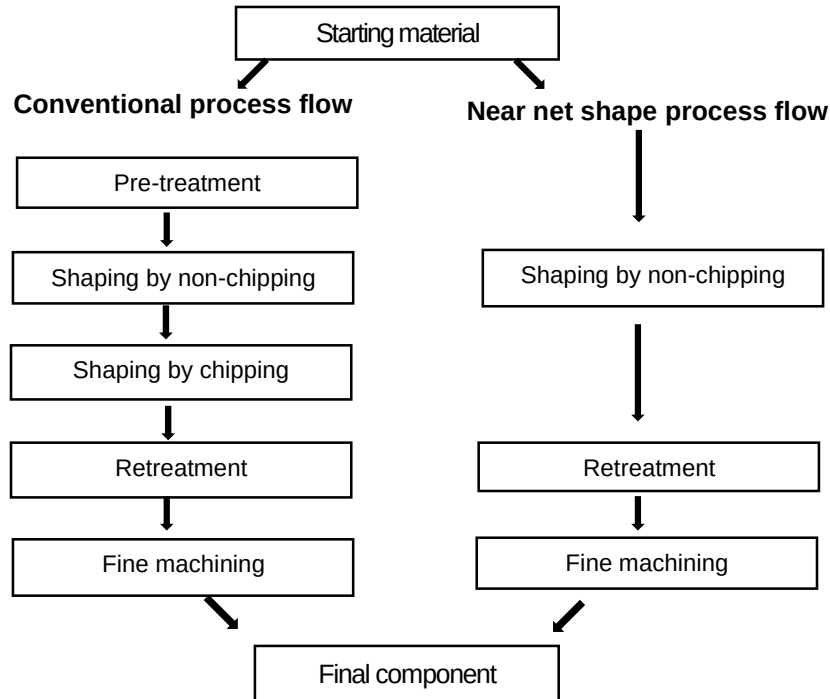


Figure 2.1: Process flow for conventional and NNS production of metal parts [46].

2.1.1. Powder metallurgy

Powder metallurgy is ideal for rapid production of parts from materials that often cannot be combined using other techniques. It is commonly used for fabricating engineering components and particulate reinforced metal matrix composites from powders rather than ingots [45-46, 51-52]. Component densification is generally done in a furnace but other sintering methods such as microwave-assisted sintering are becoming more important [53-54].

The advantages of PM are simplicity, flexibility and applicability for high volume production of a wide range of materials, lower manufacturing costs [50, 55-56], a better microstructure than casting [49], and being able to obtain the desired phase microstructure at lower temperatures [57]. The global market for PM is expected to grow to US\$32 billion by 2019 [58] as it replaces casting, forging and machining. The disadvantages of PM are often associated with joining PM parts because porosity, contamination and inclusions influence properties of a welded joint [59].

Titanium powder metallurgy

Titanium, an abundant mineral in the earth's crust (MPR, 2000), was discovered by William Gregor in 1791 and the pure form made by Hunter in 1920 [60]. Pure titanium has a melting point of 1670 °C, density of 4.4 gcm⁻³ and tensile strength of 965 MPa [61-62]. The combination of lower density, higher strength, and excellent corrosion and fatigue resistance compared to common metals such as steel makes titanium appealing to engineers and designers. However, the very high production cost limits titanium applications to aerospace, military, medical and off-shore oil drilling fields applications where performance is more important than cost [4, 15].

Titanium PM may be a cost-effective way to manufacture parts from titanium [4, 63-64]. There has been increased attention on using titanium PM to produce NNS parts with good dimensional tolerance because of greater microstructural homogeneity, less compositional segregation and no constraint in alloy composition compared with ingot metallurgy [65-68]. Various PM routes such as PIM [15, 34, 64], press and sinter, laser sintering [69-72], powder forging [73-75] and hot isostatic pressing (HIP) [76-78] have been used to manufacture titanium parts. One of the main obstacles preventing wider industrial applications of titanium and its alloys in PM is the high cost of good quality raw powders with low oxygen content [64, 79].

Powder injection moulding (a NNS method developed from plastic injection moulding) is widely used to produce small (usually below 400 g) complex parts from metal or ceramic powders and thermosetting or thermoplastic binders [3-4, 32, 34, 64]. The process is called metal injection moulding (MIM) when metal or alloy powders are used and ceramic injection moulding (CIM) when ceramics are used [13]. The Hyatt brothers patented injection moulding of pyroxyline [80] but the first recorded PIM with ceramic powder was in 1937 [81].

The advantages of PIM include high productivity, low materials wastage, ability to produce diversified geometrical complexity, enhanced product quality, more material flexibility in application, and better mechanical properties. It is therefore used in sophisticated applications such as orthodontic brackets for straightening teeth, biomedical transplants, computer hardware, and surgical tools, as well as in the niche market applications that use expensive materials such as titanium, platinum and

rhodium [2, 13]. The relationship of PM and PIM to other fabrication techniques is shown in Figure 2.2.

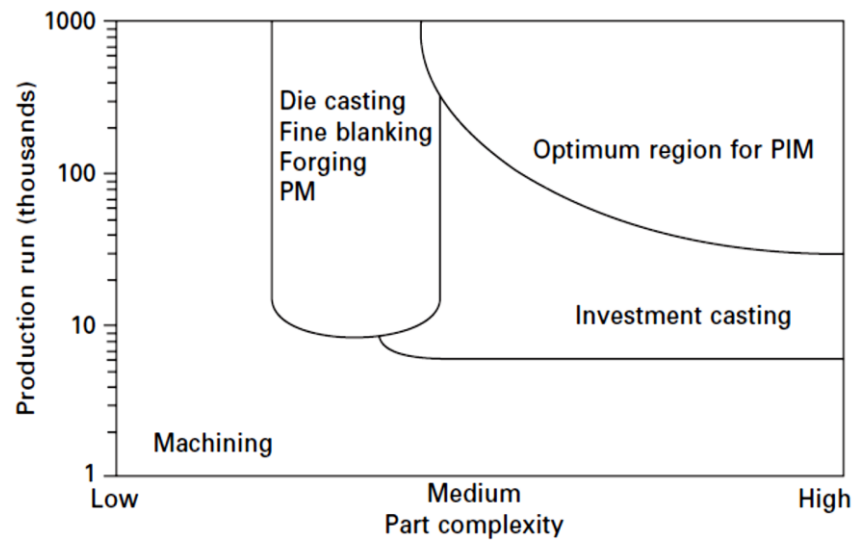


Figure 2.2: Relationship of fabrication techniques [15, 64].

2.2. Metal injection moulding

2.2.1. Process

Metal injection moulding (MIM) is a very cost-effective innovative manufacturing process for manufacturing high volumes of small (typically 30 g), complex NNS components. Although initial set-up cost is high, the large production volumes without any significant post-processing stages reduce component price [4, 82-83]. The process has four stages (Figure 2.3):

- Mixing to compound binders and metal powder into feedstock
- Injection moulding to shape the parts
- Debinding to remove the binder
- Sintering to densifying the debound parts

Materials are mixed at the appropriate temperature in a high-shear mixer. The homogeneous feedstock is then pelletized to feed the injection moulder. Process temperature (which influences viscosity) should allow feedstock to flow smoothly into the mould but be below binder decomposition temperature [2]. Injection moulding conditions such as barrel temperatures, injection pressure, injection screw speed and mould temperature must be selected to eliminate moulding defects that cannot be fixed in subsequent processes [2].

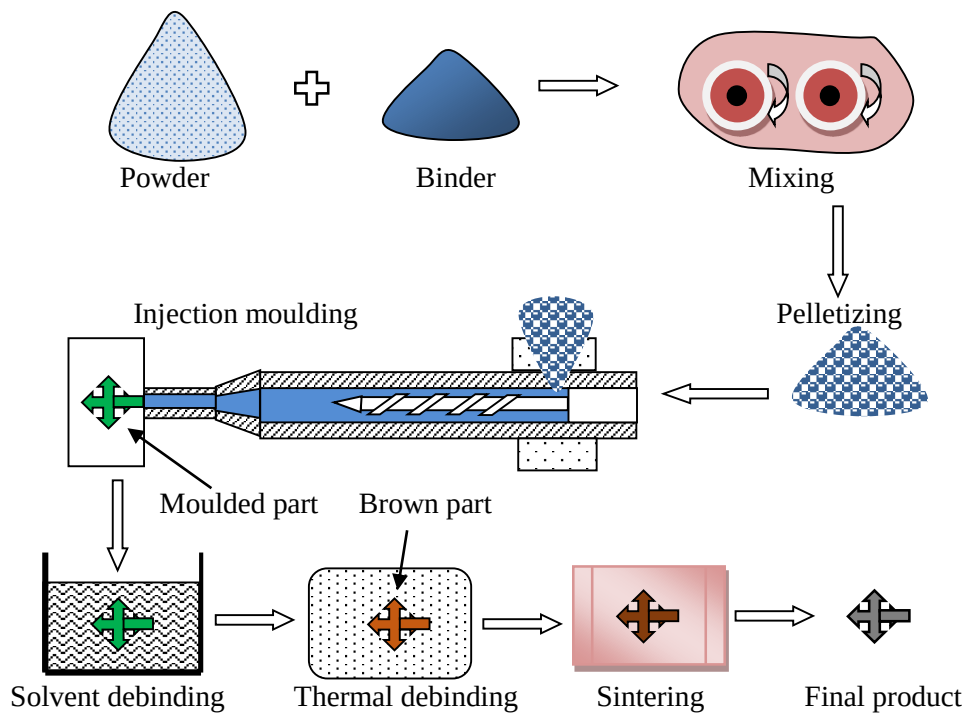


Figure 2.3: Schematic of the stages in MIM.

Debinding can be done using solvent and/or thermal processes. In solvent debinding, the green part is immersed in a solvent that dissolves at least one binder, leaving an open pore structure that is useful in the subsequent binder burnout. In thermal debinding, the solvent debound part or even the green part is heated to degrade and/or evaporate the binders. Debinding is very slow and takes several days to accomplish [2]. A key to rapid debinding is to use a multiple-component binder system; one polymer (called the backbone polymer) holds the powder particles in place and provides strength even after initial debinding. This binder degrades and/or evaporates during the preliminary stage of sintering.

Sintering, the final process, has the dual role of chemical homogenization and densification. Injection moulds are usually oversized to allow for shrinkage during sintering. The brown part is heated at elevated temperatures so powder particles can bond due to diffusion through grain boundaries and the part densifies. Further densification can be achieved by cold or hot isostatic pressing (HIP). Possible post-sintering stages include machining, drilling, reaming and heat treatment, including precipitation hardening, tempering, carburization or nitriding [2].

2.2.2. Advantages of MIM

Metal injection moulding competes with investment casting, die-casting, traditional machining and PM for making small intricate parts (Table 2.1). Parts from 2 to 50 mm and up to 1 kg can be manufactured [84] including small complex devices for minimally invasive surgery, especially laparoscopic instruments for grasping tissue, cutting and suturing [13]. Implants such as bone plates, bone screws or dental implants are good candidates for MIM [83].

Table 2.1: Comparison of MIM and other manufacturing routes [4, 64].

Method	Limitations	MIM advantages
Investment casting	Slow, labour intensive, tolerances hard to control, many secondary operations, expensive	Lower cost, high repeatability, short production cycles, excellent surface finish, minimal secondary operations
Die casting	Poor mechanical properties, rough finishes, Limited range of materials	Good mechanical properties, wide range of materials
Machining	High level of wastage, high tooling costs, design limitations, not good for intricate shapes	Virtually no material waste, excellent for intricate parts
Conventional PM	Lower densities, no complex shapes, many secondary operations	Very high densities (93-99%)

The unit cost of MIM can be up to 50% cheaper than other manufacturing routes, particularly those that involve extensive machining [4, 24]; savings increase as complexity increases (Figure 2.4). The process is suitable for manufacturing dense or porous parts [84-85]. Production volume can vary from 5000 parts per year (e.g. speciality firearms) to over 100 million parts per year (e.g. cell phone vibrator weights) [86, 87]. It is also possible to obtain energy savings at least 30% [88]. However, MIM is still not fully used for manufacturing medical devices, partly because customers and manufacturers do not know about this technology and because of difficulties with material properties. For instance, the microstructure differs from wrought materials because of residual porosity after sintering [83].

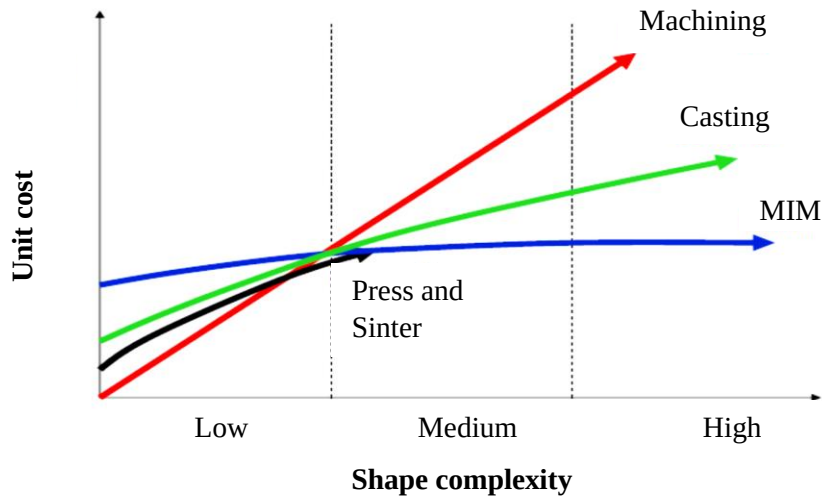


Figure 2.4: Cost comparison of metallurgical manufacturing routes [24].

2.2.3. Materials used in MIM

The primary raw materials for MIM are metal powders and thermoplastic binders. Any metal that can be made into a suitable powder can be used in MIM. However, some metals such as aluminium are difficult to process via MIM because the oxide film on the powder particles hinders sintering [89]. This oxide film has been overcome by mixing aluminium with small quantities of magnesium powder [90]. Good Ti-MIM requires powders with a low oxygen content and few impurities.

Powders for MIM need to have specific characteristics and is limited to material currently available. However, the increasing demand for MIM has motivated powder manufacturers to produce powders suitable for MIM. Manufacturing method and purity from the different powder production techniques (e.g. gas atomization (GA), water atomization (WA) and hydride-dehydride (HDH) processes) affects powder cost [89, 91]. The recommended powder characteristics for MIM are [91]:

- Nearly spherical
- Particle size between 0.1 – 20 μm with mean particle size of 2 – 8 μm
- Dense, discrete particle free of voids
- Clean particle surface

Metal injection moulded components are being manufactured from an increasing range of common and some uncommon metals and their alloys such as stainless steels, plain and low alloy steels, high-speed steels, copper base alloys, nickel and cobalt base

super alloys, titanium, intermetallics, magnetic alloys, refractory metals and hard metals (cemented carbides) [88, 92]. Fabricating parts from intermetallic compounds such as Ni₃Al [82, 93-94] and NiAl, MoSi₂ or Al₂O₃ [95-97] have been reported by many researchers. Refractory metals such as tungsten (MP 3422 °C) and molybdenum (MP 2623 °C), which have been used in high temperature applications (medical, electronic, aerospace and defence) and are difficult to melt and cast, can be used in MIM due to shaping advantage [98-101]. Fabricating refractory metal-based parts from W-Ni-Fe [102-105] and W-Cu [106-108] by MIM has been widely investigated because these materials have good ductility, corrosion resistance, high strength and density.

About 80% of global MIM powders are ferrous powders [91], with steels and stainless steels being the most common (approximately 75% of global sales). Tungsten, nickel, and iron-nickel alloys represent almost 16%, titanium and its alloys are negligible and the remainder is electronic materials, copper, and tool steel grades [5-6, 8]. Almost 4500 tonnes of copper powder, representing 10% of China and 4% of global copper production in 2012 [109], was used for manufacturing heat sinks (heat pipes) in China and Taiwan [110]. The small amount of scrap in MIM makes it particularly useful for more expensive metals where the process advantages offset the high powder cost [82, 89, 111].

There has been recent emphasis on titanium MIM because of titanium's unique properties (Section 1.4) and the cost effectiveness of MIM (Section 2.2.2). The two alloys Ti-6Al-4V and Ti-6Al-7Nb are widely used to manufacture MIM components [4, 112-113]. Other examples include titanium-hydroxyapatite (Ti-HA) composites for medical implants [114-118] and porous NiTi parts suitable for biomedical applications [119-123]. Ebel *et al.* [83] reported that Ti-6Al-4V-0.5B processed by MIM was suitable for medical implants under high loading and Chen *et al.* [85] reported that porous titanium implants made from HDH titanium powder by MIM had similar mechanical properties to spongy bone. Injection moulding has also been successful for making dental implants, medical devices including nozzles, wire and guides, optical instruments, semiconductor and microelectronics devices from various materials [13, 124].

2.2.4. Titanium metal injection moulding (Ti-MIM)

The Ti-MIM industry uses nearly 10,000 kg of titanium powder annually with estimated component sales of about \$10 million [34, 125]. Due to high production costs compared to other metals, titanium use is generally restricted by the quality and availability of suitable forms (Table 2.2). Depending on powder purity (especially low oxygen content), shape and particle size distribution, the additional stages to produce titanium powder increases cost to US\$66/kg to US\$500/kg [4, 125-126].

Table 2.2: Cost of metals at different production stages [21, 127].

Production stage	Cost (US\$ per kg)			
	Steel	Aluminium	Magnesium	Titanium
Ore	0.01	0.05	0.005	0.14
Metal	0.05	0.31	0.25	0.91
Ingot	0.07	0.32	0.27	2.05
Sheet	0.14 – 0.27	0.15 – 2.27	1.82 – 4.09	3.64 – 22.73

To expand the Ti-MIM market, powder cost needs to decrease. This may be achievable if new low-cost titanium processes currently being developed can replace expensive processes such as atomisation or milling [32-34, 125]. Qian *et al.* [128] suggest that titanium feedstock costing US\$25/kg would be sufficient to stimulate opportunities but people think powder price needs to be US\$10/kg or below [129].

Titanium is highly reactivity with interstitial elements such as oxygen, carbon and hydrogen, especially if surface area is large (small powder particles) and process temperatures higher than 260 °C. Titanium is very reactive with oxygen; consolidated Ti-MIM parts made from material with higher oxygen content have lower elongation and poorer mechanical properties (Figure 2.5). Oxygen content of the initial powder is key to meeting the ASTM specification of 2000 ppm in the final component. Unfortunately, titanium powder with oxygen below 0.2 wt. % is more expensive and seldom commercially available [112]. Oxygen can also be absorbed during Ti-MIM processes such as mixing, debinding and sintering [112]. Any binder remaining at the end of the process can react with titanium and increase carbon build-up. This build-up

can be minimized using a high debinding temperature but has the disadvantage of increasing oxygen content [113].

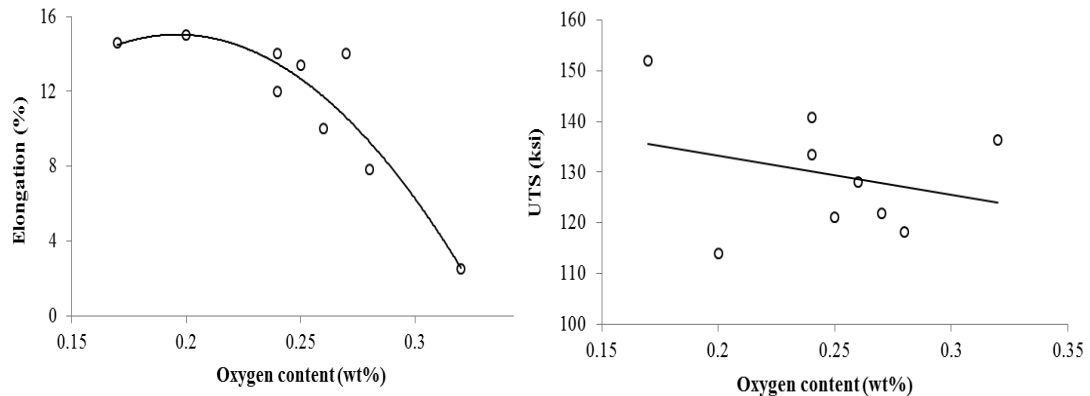


Figure 2.5: Effect of oxygen content on elongation and ultimate tensile strength of Ti-6Al-4V MIM parts [33].

Several factors affect success of the MIM process. Metal powder characteristics influence powder loading and feedstock rheology (Section 2.2.3). Binder gives the feedstock the required rheology and the moulded part the required mechanical properties [114, 11]. Powder to binder ratio determines MIM success; higher powder content can create voids in the feedstocks, making moulding difficult but lower powder content can cause debinding defects [2]. Materials must be well mixed because shortcomings cannot be fixed in subsequent processes such as injection moulding, debinding and sintering [115]. In summary, uniform powder and binder distribution (homogeneity) is essential for producing feedstock with the appropriate rheology and density to the moulded part. Feedstock rheology is very critical for success of MIM.

2.3. Binder/ feedstock formulation

2.3.1. Possible binders and characteristics

The binder used and removing this binder from the formed part are critical factors in injection moulding [130-131]. Most binders are mixes of organic compounds such as natural waxes and synthetic polymers, and many binder formulations and procedures are still proprietary [89].

The binder used depends on powder characteristics and process conditions. A good binder needs the following attributes [2, 4, 12].

- Good interaction with powders

- Able to wet the powder surface and thus assist mixing and moulding
- Provide excellent flow characteristics
- Have multiple components with differing thermal characteristics
- Have a decomposition temperature above mixing and moulding temperatures and below sintering temperature
- Have no deleterious elements that could degrade the metal
- Environmentally safe and easily disposable
- Inexpensive and available
- Easy to debind using solvent or heat without leaving residues

Binders generally have a major component that acts as a filler, lubricant and reduce feedstock viscosity, a minor component that acts as a backbone during processing, and processing aids such as surface modifiers or plasticizers [132]. Each binder components will have a different molecular weight, chemical structure and melting temperature. The backbone polymer retains the shape of a moulded part during debinding and sintering whereas a low molecular weight “filler” polymer helps decrease feedstock viscosity and is more extracted more easily than the backbone polymer during the first phase of debinding. Surface modifiers and plasticizers improve powder wetting, die lubrication, mixture viscosity, residual stress and debinding [2, 133]. In general, low molecular weight binder components are preferred because they lower residual stress in moulding and help isotropic powder packing and shrinkage [2]. The surfactant is often a low molecular weight component with a functional group that can bind to the powder surface and a chain that can extend into the binder, acting as a bridge between the binder and the powder. This improves feedstock stability [134].

The major component in binders for MIM is normally a wax and/or polymer (Table 2.3). Wax has low viscosity and excellent wetting characteristics [146]. However, disadvantages such as the tendency to distort, crack and slump can limit their use [147]. Thermoplastic polymers improve feedstock rheology and strengthen the green part [133]. Most MIM binders have long debinding times, which increases production and energy costs [148]. Defects can develop during thermal debinding so binders made from soluble polymers have been studied for MIM application [149-156].

Table 2.3: Examples of binders used in MIM applications [89].

	Binder		
	Thermoplastic binders	Polyacetal binder	Gelatine binders
Major component	Paraffin wax (PW), carnauba wax (CW), beeswax (BW), vegetable, peanut oil, acetanilide, antipyrine, naphthalene, polyethylene glycol (PEG), microcrystalline wax (MW)	Polyoxymethylene (POM)	Water
Minor component	PE, PP, PE-acrylonitrile (A), PP-A, polyamide (PA), PS, polymethyl methacrylate (PMMA), PE-vinyl acetate (VA), PMMA-ethylene-VA	Polyoxymethylene (POM)	Methyl cellulose, agar
Modifier	SA, Oleic acid, esters, phthalic acid esters	Proprietary	Glycerine, boric acid

The role of surfactants in MIM binders has been researched widely [2, 135-139]. Stearic acid (SA), one of the most popular surfactants, improves flow properties of MIM feedstock, reduces abrasion between feedstock and the machine/die walls, and reduces contact angle by lowering surface energy of the feedstock. This minimizes powder-binder separation during injection moulding and increases powder loading and homogeneity [136, 140-142]. Diffusion of SA controls removal of the low molecular weight component in a two-component binder during thermal debinding [143]. Feedstock viscosity decreased with increased SA [144] probably because the uniform packing enhanced the microstructure. Li *et al.* [145] also reported that SA decreased feedstock viscosity and increased powder loading; 5% SA was optimum for improving feedstock flow properties.

Wax-based components

Wax-based components for MIM binders have been researched and used extensively. The wax is extracted from green parts using organic solvents such as heptane and hexane. Carnauba wax (CW) and beeswax (BW) contain oxygen and are potential sources for oxygen contamination [157]. Paraffin wax (PW) is widely used in MIM. It is cheaper than other waxes, has a consistent chemical structure and hence consistent rheological properties. The commonly used backbone polymers with PW are ethylene vinyl acetate (EVA), PP, high density polyethylene (HDPE), PMMA and PE. Liu *et al.* [158] reported that reducing PW and increasing HDPE or EVA content of a multi-

component binder increased green strength and gave better shape retention during debinding.

A MIM binder based on PW and EVA with a low vinyl acetate content had the good moulding and thermal debinding performances [159]. However, severe powder-binder separation occurred in binder made of PW and PP [160], probably because the PW and PP were not compatible with the powder. As PW-EVA binder had better flow properties than PW-HDPE, Li *et al.* [160] proposed that a PW, EVA and HDPE binder would have good rheological and shape retention properties. This was also reported elsewhere [161]. These findings suggest EVA is more compatible with PW and adhere better to the powder than other polymers such as HDPE.

A study in 2002 [162] found that adding 1 to 20 wt. % microcrystalline wax (MW) to a PW-EVA-HDPE binder increased powder (carbonyl iron) loading, feedstock homogeneity and tensile strength. Two further studies [163-164] reported that adding MW, carbonate wax and Montan ester waxes increased powder loading. However, as these waxes are insoluble in methylene chloride or chloroform, these solvents could not be used for debinding [153].

Polymer-based components

Most solvents for solvent debinding are organic, flammable, carcinogenic and not environmentally friendly so water-soluble binders are preferred. Depending on the interactions between binder constituents and water, water-soluble binders can be divided into gelation-based and non-gelation based. The former include materials such as starch, cellulose and agar and solvents (usually water) are needed to formulate the feedstock whereas non-gelation based binders, such as PEG and poly vinyl alcohol (PVOH), do not need water [165]. Various types of PEGs are the most commonly-used non-gelation binder components because they are non-toxic, have a simple molecular structure $(\text{CH}_2\text{CH}_2\text{O})_n$ -, and are commonly used in foods [133, 146, 166-167] and pharmaceuticals [168-171].

Various types of PEG are used in many binders to reduce feedstock viscosity and act as a lubricant during injection moulding and de-moulding. The PEG-based binder initially developed by Polymer Solution System in 1990s has good rheology,

mouldability and shape retention. Limitations include being a long hot mixing process, low powder loadings, and not as reactive with metal powders [151]. During solvent debinding, the PEG initially removed forms pores that are helpful for extracting the backbone polymer [151, 147]. However, the amount of backbone polymer present in the binder can offset the benefits of PEG. For instance, increased HDPE content (backbone polymer) in a binder PEG, HDPE, SA, dioctyl phthalate (DOP) and proprietary polymer-W increased the viscosity and caused defects in debound parts whereas low HDPE content caused bad shape retention [151]. The effect of polymer-W in the binder is unclear and not justified by the researchers.

The viscosity of PEG increases with molecular weight (M_w), which affects feedstock rheology and debinding characteristics [146, 172]. Low to moderate M_w PEGs (500 – 4000) reduce feedstock viscosity [147-148, 151, 173-174, 175-176]. Binder made of cellulose acetate butyrate (CAB) and low M_w PEG had excellent shape retention. As the crystalline structure of PEG changes with M_w , the shape was not maintained during debinding as M_w of a PEG binder increased [133]. As crystal size increases, the area exposed to water increases, leading to poor shape retention [177-178]. Research with PEG of M_w from 1000 through to 20000 [172] showed that powder-binder separation during moulding was lower with PEG-20000 and the shapes produced had sufficient green strength. However, it took 12 h to extract 95% of the PEG [152] and cracking and poor debinding occurred [172]. When low M_w PEG was used, powder-binder separation occurred at high temperatures and shear rates [172], possibly because low M_w PEG is less viscous and tends to flow more easily from the powder under these processing conditions.

High density polyethylene and PMMA are often used as backbone polymers in MIM binders. Polyvinyl butyral (PVB) has been used as a backbone polymer in some CIM studies but seldom in MIM. Thomas and Marple [179] reported that PVB had good wetting characteristics with ceramic powders and homogenous feedstocks were produced. This component can be considered a random copolymer of vinyl butyral and vinyl alcohol units because significant amounts of unreacted vinyl alcohol units remain when manufacturing PVB [180-181]. Random copolymers tend to form miscible blends with other photopolymers because of intra-chain repulsion between different units in the copolymer [182-183] so PVB is compatible with many polymers

[180]. It is widely used in laminated safety glass, paint, adhesives, primers, sheets, surface treatments and electronic ceramics so much research on these applications is available [185-190]. Its potential as a backbone polymer for ceramic injection moulding is because strong intra-molecular interactions between the macromolecular chains make PVB very viscous and the butyral groups make it insoluble in water. The powder particles will hold together well so the shape is retained during water debinding [179]. PVB has been used as a binder component for zirconia [147, 179] and alumina [191-192] based injection moulding. Green part strength and ductility increases with PVB molecular weight and content respectively in alumina-based injection moulding [192]. However, PVB-PEG, PEG-acetal, and PEG-PMMA binders had poor wettability in cemented carbide feedstock unless suitable additives were used [184]. The high viscosity of PVB limits the amount that can be used in a binder so other backbone components such as an acetal copolymer in conjunction with PVB [193] or oxidized HDPE [179] have been investigated.

Catalytic decomposition of polyacetals, usually with nitric acid, is an established binder technology [130-131, 194]. However, expensive, sophisticated equipment is needed to handle the acid vapour and to eliminate polymer decomposition by-products [15, 33]. Environmental and economic considerations were the basis for developing an aqueous-based agar PIM binder. A 55–93 vol. % water, 4 vol. % agar and 3 vol. % glycerine binder was used with stainless steel, titanium, aluminium, zirconia and steatite [130, 195-196] to manufacture large, thick parts (1 – 2 kg) for similar costs as parts manufactured by investment casting [130]. The disadvantages of the gelation-based binder are dimensional control of the final parts and evaporation of water during feedstock formulation and moulding, which increase feedstock viscosity and hence cause difficulties in moulding.

2.3.2. Binders for titanium metal injection moulding

Special care is needed when selecting binders for Ti-MIM because titanium powder can react with the binder at elevated temperatures ($>300\text{ }^{\circ}\text{C}$) [207]. Polymers and the thermal debinding process can increase impurities by at least 1000 ppm (0.1 wt. %). Because water debinding is done at low temperatures ($<80\text{ }^{\circ}\text{C}$), powder-binder reactions are reduced and impurities increased by up to 200 ppm [32]. Examples of PIM binders are given in Table 2.4.

Table 2.4: Examples of PIM binders.

Binder	Powder	Reference
55% PW, 35% PE, 10% SA	Steatite	3
PW, isopropyl alcohol	PZT ceramic	197
PW, MW, PE wax, LDPE,	WC-Co	164
81–90 wt. % PEG, 10–15 wt. % PMMA, 0–4 wt. % SA	WC-Co	148
PW, oil, PE, SA	WC-Co	198
60% PEG, PVB, HDPE, SA, anti-oxidant, Irganox	Zirconia	179
DPE, PEG, PVB, SA	Zirconia	147
PP, PW, SA (25:70:5)	Alumina	27
65 wt. % PEG, 30 wt. % PE wax, 5 wt. % SA	Alumina	146, 166
65% PEG, 32.5% PVB, 2.5% SA	Alumina	191
PVB, DOP (10:3)	Alumina	192
50% HDPE, 46% PW, 4% SA	Alumina	142
9-20% HDPE, 47-67% PEG, 1-10% SA, 1-10% DOP, anti-oxidant, polymer-W	Iron	151
30 vol. % PP, 60 vol. %, PEG-20000, 10 vol. % PEG-4000	Strontium-ferrite	152
PW, EVA, HDPE, MW	Carbonyl Fe	162
79% PW, 10-20% EVA, 10-20% HDPE, 1% SA, 0-20% PP	Carbonyl Fe-Ni	160
Wax, oil, PE	Carbonyl Fe-Ni	153
70–80 wt. % PEG (M_w 400–1500), 20–30 wt. % PMMA	Stainless steel	174
35 wt. % CAB, 65 wt. % PEG	Stainless steel	133
PW, CW, SA, EVA	Stainless steel	199
Pan250S – commercial binder	Stainless steel	154
PW, EVA, PP, SA, BW, CW	Stainless steel	132
PMMA, PEG, SA	Stainless steel	200
73% PEG, 25% PMMA, 2% SA	stainless steel	201
HDPE, SA, PW, CW, BW (Pan250S)	Ti-6Al-4V/HA	115-117
63% PW, 12% PEG, 14% LDPE, 10% PP, 1% SA	Ti-6Al-4V	202
93% Naphthalene, 6% EVA, 1% SA	Ti-6Al-4V	63, 204, 205
PEG-1500, PMMA, SA (87:11:2)	Ti-6Al-4V	175
60 wt. % PS and 40 wt. % PE	Ti-6Al-4V	206

Binder decomposition, the inert atmosphere and rapid heating can produce carbon from the polymer. As the process temperature reaches about 450 °C, polymeric binders in the brown part enrich the carbon [114, 208]. Aromatics-based binders can be used to minimize impurities and improve debinding efficiency [63, 209]. For example, carbon content in sintered parts manufactured with an aromatics-based binder made

from naphthalene, EVA and SA did not increase significantly [114]. However, the effect of oxygen, the most important contaminant affecting mechanical properties of titanium parts, was not discussed. Nyberg *et al.* [205] report that sintered product produced by injection moulding TiH₂ powder with naphthalene-EVA-SA binder had 0.42 – 0.51 wt. % oxygen, which is much higher than the 0.2 wt. % recommended.

The PP in a PW-LDPE (low-density polyethylene) based binder can be used to minimize carbon content after debinding and sintering. An improved binder of PW, PEG, LDPE, PP and SA was proposed for Ti-MIM [202]. Parts thermally debound in argon had less carbon and more oxygen than those processed under vacuum. Carbon content decreased and oxygen content increased as debinding temperature increased (Figure 2.6). Sintering is usually done at 1200–1350 °C so carbon content may decrease further and oxygen increase further if the process were done at higher temperatures than reported in this research. It important to determine oxygen content of sintered Ti-MIM parts but researchers often do not report on this factor.

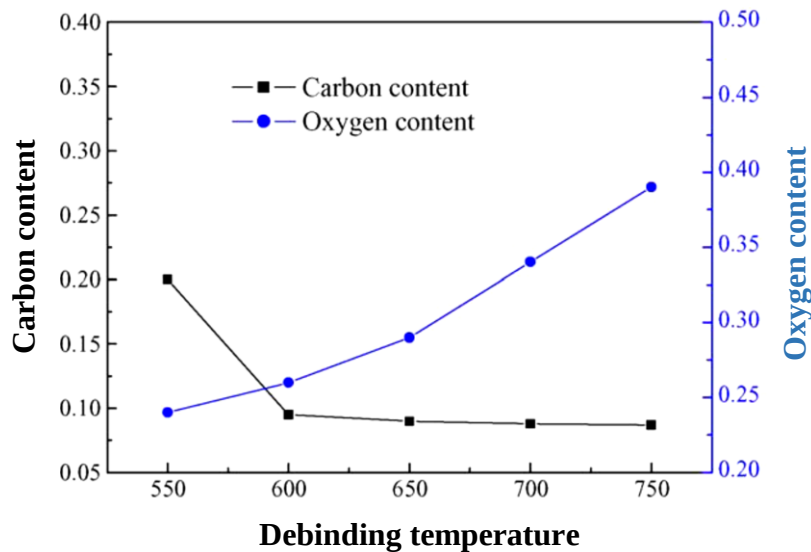


Figure 2.6: Effect of debinding temperature under vacuum on carbon and oxygen content of parts made of Ti-6Al-4V/PW-LDPE based binder [202].

Carbon increased from 0.056 to 0.2 wt. % in the initial stage of thermal debinding [202] but did not decrease significantly as temperature increased further (Figure 2.6). Calculations indicate the oxygen and carbon content of debound parts at 600 °C could be 35% and 69% higher respectively than in the initial Ti-6Al-4V powder, suggesting LDPE and PP are not suitable for minimizing carbon content in debound parts. A similar increase in oxygen content has been reported elsewhere [175].

Solid argon was proposed as a binder for Ti-MIM, based on the advantages of high purity, binder inertness and rapid debinding at room temperature [210]. However, this process was not feasible because the feedstock was heterogeneous and had unfavourable rheology, green part strength was inadequate, safety hazards, and sophisticated equipment was needed to make the binder and feedstock.

Various binders and processing methods to control impurities during Ti-MIM processing are being investigated. Some binders give satisfactory results (oxygen content <3.5 wt. %) for Ti-MIM [15, 33-34, 64] including: PP-EVA-PW-CW-DOP; PE-PW-SA; PP-PMMA-PW-SA; naphthalene-SA-EVA; PW-PEG-PE-SA; PW-copolymer-SA; Atactic PP-CW-PW-SA; and Atactic PP-EVA-PW-CW-din-butyl phthalate. Some polymer binders such as PP, PMMA, polymethyl styrene thermally depolymerise to their initial monomers at relatively low temperatures (~260 °C) and impurities are produced in the sintered Ti-MIM parts [33], making them unsuitable as Ti-MIM binders.

2.3.3. Binder and feedstock formulations

Binder composition, powder characteristics, powder loading and mixing method influence MIM feedstock attributes. Binder is typically 40 vol. % of the feedstock and metal powder particle size is usually 0.1 µm to 20 µm [2]. Very low or high powder loadings produce moulding defects such as flashing (thin layer of binder flowing between the die parts), cracking and slumping.

The powder loading when injection moulding becomes difficult is called the critical powder loading. To avoid problems during processing, loadings 2 - 5% below the critical powder loading are used. This reduces feedstock viscosity, improves mouldability and minimizes damage to processing equipment. This loading is termed the “optimal powder loading [2]. Various methods such as density, mixing torque, viscosity and melt flow can be used to identify critical powder loading [2]. Powder volume fraction affects feedstock density. Measured and theoretical feedstock densities (calculated using the rule of mixtures) are the same at low powder loadings. Voids form as powder loading increases so measured density deviates from theoretical density at the critical powder loading. Feedstock mixing torque and relative viscosity

also increase with powder loading and can be used to indicate critical powder loading [2].

Binder component compatibility and surface interactions between binder and powder affect how the binder wets the powder during mixing, adhesion between polymers and powders, feedstock rheology, and optimal powder loading. Adhesion affects binder-powder separation during injection moulding and how the part retains its shape during debinding [141, 211-212]. Identifying the appropriate temperature, mixing time and speed, and using suitable equipment help to obtain a homogeneous feedstock with an optimal rheology [2, 115, 213].

The powder must be uniformly distributed in the feedstock. A homogeneous feedstock is most effectively achieved using high shear melt mixing techniques [164]. The main mixing routes are (a) mixing binder components at a suitable temperature (usually the highest melting temperature of binder components) and then mixing in the powder, or (b) dry mixing binder components and powder[2, 215].

Various systems have been used to mix binder and powder. Martyn and James [164] used four mixing stages to formulate a feedstock. Wax-based binder components were dry ball milled for 24 h, the cemented carbide powder and binder were then wet mixed in an agitating paddle mixer for 6 h, followed by shear melt mixing for 3 h in a Torrance hydraulic paste mixer fitted with a trifol blade. The final stage involved shear melt mixing the feedstock in a Brabender Plastograph torque mixer for an unspecified time. Yang and German [184] mixed nanophase cemented carbide powders with a wax-based binder in a Teledyne Readco high shear rate mixer and a sigma-blade-batch mixer, followed by a twin-screw extruder. Allaire *et al.* [214] used two stage mixing in a Type R02 intensive mixer followed by twin-screw extrusion while Wu *et al.* [27] described five different mixing sequences.

Feedstock homogeneity can be assessed by various tests [2, 115, 140, 216-217] including mixing torque, feedstock density, binder content (burnout test), electrical conductivity and heat capacity, and porosity distribution in pre-sintered feedstock. Most published work on MIM does not report feedstock homogeneity, identify critical powder loading, or give the basis for the powder loading used. Homogeneity has been

evaluated from mixing torque, measuring feedstock density or from burn-out tests [115, 142, 154, 198-199, 216, 218-219]. Critical powder loading has been evaluated from density or mixing torque measurements [198, 202-203].

Industrial production uses powder loadings of 50 to 70 vol. % [89]. There is a lot of research on low to moderate powder loadings (45 to 55 vol. %) in various equipment and processing conditions (Table 2.5). Similar processing conditions have been used to obtain 40 and 45 vol. % powder loadings [147, 179] and 55 vol. % has been obtained under various processing conditions [151, 146, 191]. However, researchers often do not explain why they used a particular powder loading or report feedstock homogeneity. Although Thomas and Marple [179] reported two extrusion passes produced a homogenous feedstock, they did not report the degree of homogeneity. Karatas *et al.* [3] used 50 vol. % powder loading because the calculated theoretical critical powder loadings of 67 vol. % and 75 vol. % could not be achieved. They did not report on feedstock homogeneity and investigate whether the feedstock was suitable for injection moulding.

Torque values can be used to indicate feedstock homogeneity, with lower torque indicating better mixing [222]. The lowest powder loading (55 vol. % in the range 55 to 59) had the lowest torque and was claimed to be the most homogeneous feedstock and an optimal powder loading (6 in Table 2.5). However, lower torque may not necessarily mean better mixing and the claim should be validated using other evaluation methods. In this research 55 vol. % was the lowest powder loading used and the mixing torque of lower loadings was not investigated.

Hot mixing is widely used to formulate feedstocks but requires expensive equipment, can wear the machine walls, binder may degrade at high process temperatures, very viscous materials may form [12, 223] and particles may be damaged if mixed too long. An optimal powder loading of 70 vol. % was achieved by hot mixing at 155 °C for more than 2 h (7 in Table 2.5), which is surprising because only 1% of surfactant SA was used compared with the 5% recommended by Li *et al.* [145]. It is possible that the low melting point binder components (PW, PEG, SA with melting points <75 °C) would have decomposed at the temperature used.

Table 2.5: Various binder/feedstock formulation methods reported in literature.

No	Powder/ binder	Φ (vol. %)	Equipment	Time (min)	Temperature (°C)	Reference
1	Zirconia/ PEG, PVB, HDPE, SA	40, 45	Type R02 intensive mixer Twin-screw extruder	15 -	Room temp. 150 – 181	179 *
2	Zirconia/ PEG, PVB, HDPE, SA	40, 45	Twin-screw kneader	5 10	180 160	147 *†
3	Iron/ HDPE, PEG, SA, polymer-W, DOP.	55	Z-blade type mixer	120 60	145 160	151 *†
4	Alumina/ PEG, PE, SA	55	Sigma blade mixer	90	100	146 *†
5	Steatite/ PE, PW, SA	50	Turbula shaker	60	Room temp.	3 *‡
6	Alumina/ PEG, SA, PVB	55	Sigma blade mixer	30 30	180 160	191
7	Ti-6Al-4V/ PW, PEG, LDPE, PP, SA	70	Roller mixer	120 -	155 155	202
8	Zirconia/ PS-corn oil	47 – 53	Extruder	90	220	214
9	WC-Co/ PW, PE	40 – 44	Brabender W50E (roller blades)	60	130	198
10	Alumina/ PW, HDPE	58	Haake Rheocord 252p (roller rotor blades)	10 30	140 140	142
11	WC-Co/ PEG, PMMA, SA	57 – 60	-	-	-	148 *
12	Ti-6Al-4V/ naphthalene, EVA, SA	65	Haake Rheocord-90 mixer	-	90	63

No	Powder/ binder	Φ (vol. %)	Equipment	Time (min)	Temperature (°C)	Reference
13	Alumina/ PVB, DOP, wax (IRGAWAX280)	65				192
14	Stainless steel/ PEG, PMMA, SA	64	Z-blade type mixer	30	Room temp.	201, 220 ‡
			Z-blade type mixer	60	70	
15	Stainless steel/ PEG, PMMA, SA	63	Sigma blade mixer	95	-	200 †‡
16	Ti-6Al-4V/ HA, PAN-250S	60	Sigma blade mixer	120	90	115-116
17	Stainless steel/ tapioca starch, glycerol, LDPE, citric acid, water	57	Sigma blade mixer	30 -	130 140	221 *‡
18	Carbonyl iron/ PW, EVA, HDPE, MW	58	Double planetary mixer	180	130	162 *‡

Φ – Powder loading; * Feedstock homogeneity not evaluated; † critical powder loading not evaluated; ‡ injection moulding not done; - Not reported.

Adding SA before PW and PP can have a deleterious effect on feedstock properties [27] and extended mixing times cause a decrease in SA content. Decomposition of binder components may increase feedstock viscosity, thus reducing optimal powder loading. The optimal powder loading after 90 min at 220 °C (8 in Table 2.5) of 47 – 53 vol. % was relatively low. Prolonged hot mixing did not produce a homogenous feedstock and viscosity increased (>1000 Pa-s). The binder separation observed was probably due to losing the surfactant components. To avoid PW decomposition, Thomas-Vielma *et al.* [142] mixed binder and feedstock at 140 °C for 10 min and 30 min respectively and achieved an optimal powder loading of 58 vol. %.

The rheology of hardmetal feedstocks (e.g. WC-Co based powders) makes them unsuitable for obtaining higher powder loadings (>65 vol. %) [164]. The WC-Co powder particles are hollow spheres, which are not suitable for moulding. However, by using smaller particles and suitable binders, optimal powder loading could be increased to almost 55 vol. % [184]. Optimal powder loadings of 40 – 44 vol. % [198] and 57 – 60 vol. % [148] have been obtained for hardmetal feedstocks but processing conditions for achieving the higher loadings were not described. The simple, vertical plunger-type machine used for moulding is different from the widely-used, complex, horizontal screw-type injection moulding machine.

Most reported research is for low to moderate powder loadings, non-reactive metals, and done between 140 – 180 °C (1 to 9 in Table 2.5). Higher powder loadings have been achieved, usually for reactive metal between 90 – 140 °C (10 to 18 in Table 2.5). The two different process temperature regions characterize the reactive nature of powders and the need for lower process temperatures to minimize contamination. Although high powder loadings have been reported (10 to 18 in Table 2.5), feedstock homogeneity or whether it was suitable for injection moulding is not reported. Some researchers [200-201, 220-221] selected high optimal powder loading based on feedstock rheology but did not test them for injection moulding.

Predicting mouldability from rheological data is difficult. Low powder loadings and high temperatures reduce viscosity so rheological data indicate the obvious for many feedstocks and are only a basis for comparing relative feedstock behaviour [2].

2.4. Rheology

2.4.1. Fluid flow

Fluid behaviour can be classified as Newtonian and non-Newtonian. Viscosity of a Newtonian fluid is independent of shear rate or shear stress and depends only on the material, temperature and pressure. Viscosity (apparent) of a non-Newtonian fluid is not constant at a given temperature and pressure but varies with flow conditions such as shear rate and flow geometry. Many common materials such as toothpaste, tomato sauce, paint and hair gel exhibit non-Newtonian behaviour.

There are three categories of non-Newtonian fluids: time-independent (generalized Newtonian fluids), time-dependent, and viscoelastic fluids [224]. Time-independent fluid behaviour can be further categorized into pseudoplastic (shear thinning), dilatant (shear thickening) and viscoplastic fluids. Viscosity of pseudoplastic fluids decreases with increasing shear rate and viscosity of dilatant fluids increases with shear rate [191]. Viscoplastic fluids have a yield stress and can exhibit either Bingham plastic or yield-pseudoplastic behaviour (Figure 2.7). This yield stress must be exceeded before the fluid will flow. MIM feedstocks are time-independent fluids that have a yield stress at zero shear rate and may either have a linear relationship (Bingham plastic) or non-linear relationship (yield-pseudoplastic) between shear stress and shear rate [2, 172, 224].

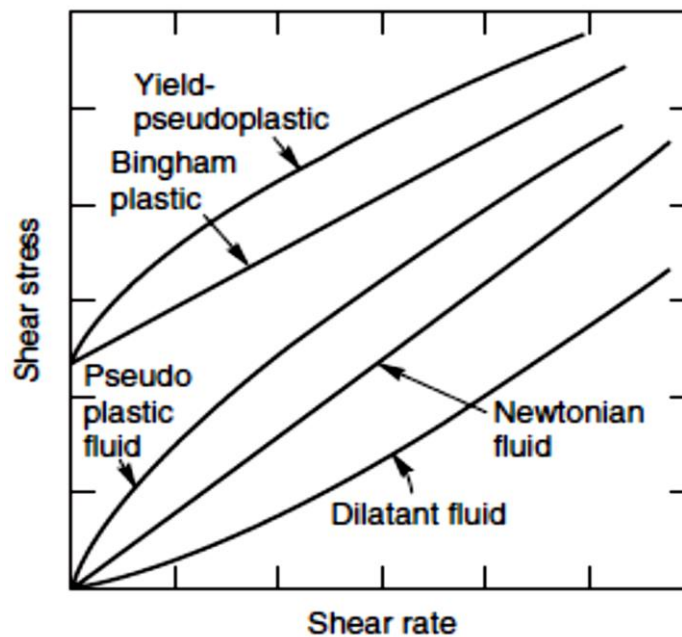


Figure 2.7: Classification of time-independent flow behaviour [224].

Rheometers measure the rheological properties of polymer/slurry systems. The three main types of rheometers (torque, dynamic rotational or oscillatory, and capillary) serve different purposes. Torque rheometers, which are basically small mixers that measure the torque on the mixing rotors/ blades, reflect the difficulty of mixing the material. Machine torque is correlated to viscosity, and is one of the primary ways for assessing a material's processability. Dynamic rotational or oscillatory rheometers operate at relatively low shear rates and are used to analyse the materials molecular structure and viscoelastic properties. A capillary rheometer heats the sample to a given temperature and then forcing it through a cylindrical barrel with a capillary die. This gives a realistic picture of flow at the high shear rate in injection moulding (up to 10^5 sec^{-1}). Capillary rheometers are good for simulating processing conditions, troubleshooting, and quality control, but expensive, being from \$30,000 at entry level to \$150,000 at advanced level [380].

2.4.2. Pseudoplastic flow behaviour and flow behaviour index

In pseudoplastic flow, increasing the shear breaks particle agglomerates, rearranges particle orientation and promotes uniform particle distribution relative to flow direction [201, 225-226]. Pseudoplastic flow can be described using mathematical models such as the power-law (also called Ostwald de Waele model), Carreau viscosity, Cross viscosity, and Ellis fluid models. Viscoplastic fluid behaviour is generally described using Bingham plastic, Herschel-Bulkley and Casson fluid models [224, 227-229]. Classification of these models is subjective because most materials exhibit several types of fluid behaviour and a model based on sound theory is yet to emerge [224].

Specific rheological properties are required for efficient mould filling in MIM. The most important is viscosity (η), which relates shear stress (τ) and shear rate ($\dot{\gamma}$):

$$\eta = \tau / \dot{\gamma} \quad 2.1$$

Shear stress is the force per unit area causing the MIM feedstock to flow over a surface (e.g. die surface) and shear rate is the change in strain (relative motion of the feedstock over the surface) with time [2]. The relationship between τ and $\dot{\gamma}$ for a power-law fluid is given by:

$$\tau = m(\dot{\gamma})^n \quad 2.2$$

where m and n are two empirical curve-fitting parameters known as fluid consistency coefficient and flow behaviour index respectively. Flow behaviours of a power-law fluid can be identified by the value of n [221, 224]. If:

$n < 1$, the fluid shows pseudoplastic fluid behaviour

$n = 1$, the fluid shows Newtonian fluid behaviour

$n > 1$, the fluid shows dilatant fluid behaviour

Pseudoplastic feedstocks are easy to mould, have minimal jetting and hold their shape. Dilatant feedstocks are unsuitable for MIM because powder-binder separation can occur under high shear rates [140, 142, 154]. Some feedstocks that exhibit pseudoplastic fluid behaviour may exhibit dilatant flow behaviour under high shear rates so rheological properties should be assessed over a wide range of shear rates [2-3, 191]. For example, a feedstock Ti-6Al-4V powder and wax-based binder was pseudoplastic below 1000 s^{-1} , but dilatant between 1000 s^{-1} and 3000 s^{-1} [115].

A feedstock is stable if variability in viscosity decreases with shear rate [230-231]. Stability of MIM feedstocks can be investigated by evaluating the ‘rate of viscosity variation’ as a function of shear rate [232]. Dihoru *et al.* [230-231] proposed the ‘instability index’, which is the standard deviation of the ‘rate of viscosity change’. A feedstock is considered unstable and subject to segregation if the instability index > 1 . Feedstocks with viscosities below $1000 \text{ Pa}\cdot\text{s}$ in the shear rate $10^2 - 10^5 \text{ s}^{-1}$ are suitable for PIM [2, 221]. Mutsuddy [215] reported shear rates varied between 100 and 1000 s^{-1} during injection moulding and viscosity must be less than $1000 \text{ Pa}\cdot\text{s}$ to produce a suitable flow. Most suspensions show power-law behaviour between 100 and 1000 s^{-1} [233].

Feedstocks made of various powders and binders exhibited pseudoplastic flow between $120 - 180 \text{ }^\circ\text{C}$ [3, 179, 181, 221, 225]. However, some research has reported dilatant flow behaviour for either increasing powder loading or decreasing molecular weight (M_w) of binders. For instance, a feedstock made of WC-Co powder and wax-based binder was pseudoplastic at low powder loadings ($\sim 50 \text{ vol. } \%$) but showed dilatant behaviour at higher powder loading ($> 62 \text{ vol. } \%$) [164]. Stainless steel-based feedstocks were pseudoplastic at $52 - 54 \text{ vol. } \%$ powder loadings ($\eta < 1000 \text{ Pa}\cdot\text{s}$), but exhibited dilatant flow behaviour when powder loading was increased to $57 \text{ vol. } \%$ (η

>1000 Pa-s) [218]. At high powder loading, friction between powder particles increases and hence viscosity increases; this may lead to powder-binder segregation. Feedstocks made from alumina powder and low M_w PEG (1000 and 1500) had dilatant flow behaviour but those made with 4000 and 20000 M_w PEG were pseudoplastic ($0.41 < n < 0.74$) between 70 and 130 °C [234]. Shear sensitivity ($n-1$) of feedstock made from titanium powder and PEG increased with M_w of PEG (M_w 1500 – 20000) [172]. These results indicate that higher M_w PEG ($4000 < M_w < 20000$) is preferable for MIM binders to avoid powder-binder segregation.

The smaller the flow behaviour index, the greater the shear thinning [142, 160, 224]. However, a low flow behaviour index sometimes produces slip flow, which causes moulding defects such as jetting and weld lines [142, 201]. The flow behaviour index of most published research is 0.12 to 0.92 (Table 2.6). Feedstocks with the lowest flow behaviour index (0.12 and 0.32; Table 2.6) were selected for MIM because they exhibit the highest shear thinning, which is necessary for efficient mould filling without defects [132, 160]. Feedstocks with a higher flow behaviour index (0.66 – 0.92; Table 2.6) exhibit dilatant flow behaviour above 10000 s⁻¹ and are not suitable for MIM [235].

Table 2.6: Flow behaviour index for various feedstock formulations.

Powder	Binder	n	Reference
Stainless steel	PW-	0.12	132
	PP-	0.27	
	EVA-	0.15	
Iron-Ni	PW-EVA-HDPE-	0.32	160
	PW-HDPE-	0.35	
	PW-EVA-	0.38	
Alumina	HDPE-PW-	0.50 – 0.56	142
Alumina	PEG-	0.41 – 0.66	146
Stainless steel	Palm stearin-PE-	0.66 – 0.92	235

The effect of powder loading and particle size on flow behaviour index is complex. It was reported that the flow behaviour index decreased as powder loading was increased for a specific particle size [236]. This may be true as long as the powder loading is below the critical limit because dilatant flow behaviour was reported either at higher

powder loading (near to critical powder loading) or higher flow behaviour indices (0.66 – 0.92; Table 2.6) [164, 218, 235]. The index increases when the powder loading is near to critical powder loading. Li *et al.* [145] reported that the flow behaviour index decreased from 0.52 to 0.42 when powder loading increased from 60 to 68 vol. % (optimal powder loading), but increased to 0.55 at 72 vol. % powder loading. In terms of shear sensitivity, higher powder loadings were preferred so these researchers selected feedstock with the lowest flow behaviour index. Data from other work [233] also supported that flow behaviour index decreased as powder loading of coarse particles increased but noted that the index increased with powder loading of fine particles. For example, the flow behaviour index of WC-Co (fine particles < 1 µm) and wax-based binder increased from 0.44 to 0.49 when powder loading was increased from 42 to 44 vol. % [198]. Such a small change in the powder loading had a large effect on the flow behaviour index because the powder loadings (42 – 44 vol. %) were near to the critical powder loading at which the flow behaviour index becomes very sensitive.

2.4.3. Yield stress

Yield stress indicates the minimum stress to make molten feedstock flow. A MIM feedstock deforms elastically below the yield stress and flows above the yield stress [224, 237]. Equation 2.3 describes this pseudoplastic rheology [3, 146, 172, 224]:

$$\tau = \tau_y + k\dot{\gamma}^n \quad 2.3$$

where τ_y is yield shear stress, k is consistency factor and n is flow behaviour index.

The yield stress of some MIM feedstocks has been reported. For example, the yield stress of zirconia and wax-based feedstocks, determined by the Casson model, increased with powder loading [233] and the yield stress of a stainless steel based feedstock increased when palm stearin binder content decreased [235]. Feedstock viscosity increases as powder loading increases and yield stress to make the molten feedstock flow also increases. A feedstock of alumina powder and PEG-wax based binder had Bingham flow behaviour; feedstock made with M_w 2000 PEG-2000 had higher yield stress than those made with PEG-1000 or 1500 PEG-1500 [146]. The latter feedstocks flowed without an induced force and were not suitable for MIM [146, 172].

2.4.4. Melt flow rate and fluidity

Melt flow rate (MFR) indicates the amount of molten feedstock flowing through an orifice in a given time (usually 10 min) under set temperature, pressure and geometrical conditions [238]. Fluidity is similar to MFR and indicates the ease of flow; the higher the MFR or fluidity, the lower the viscosity. Measuring MFR or fluidity are cost-effective ways of assessing flow properties of a feedstock.

The MFR of a steatite powder and PE-wax based feedstock decreased with powder content under constant load [3], and higher temperatures were needed to obtain good capillary flow. At constant temperature, MFR increased with load. The data could be used to set injection moulding process conditions. However, Edirisinghe and Evans [239] reported that MFR values for silicon powder-PP feedstock were unreliable so other rheological parameters need to be used to analyse the feedstock rheology.

The fluidity of MIM feedstocks with a PEG-based binder improved by increasing the temperature or shear rate [146]. However, fluidity of feedstocks with PEG-1000 and PEG-1500 became too high to hold the powder when temperature was above 90 °C and the binder and powder particles disassociated. Feedstock with PEG-20000 had lower fluidity than those made with PEG-1000, 1500 or 4000, but was selected for alumina-based injection moulding because its viscosity was below the maximum of 1000 Pas [146]. A PW-BW-SA binder, which had lower fluidity than a CW-BW binder, was proposed the most suitable for a steatite feedstock [3].

2.4.5. Flow activation energy

Feedstock temperature, which changes throughout the moulding process, can significantly affect viscosity. Understanding this effect is critical when analysing feedstock rheology. Flow activation energy is widely used to analyse temperature dependency of viscosity [3]. Feedstock viscosity usually decreases with temperature [154, 240] and can be expressed using the Arrhenius equation:

$$\eta = \eta_0 \exp\left(\frac{E_a}{RT}\right) \quad 2.4$$

where η_0 is viscosity at a reference temperature, E_a is flow activation energy, R is the universal gas constant, and T is absolute temperature [145, 160, 221, 241-242].

Flow activation energy decreases with shear rate [232] and increases with particle size [220]. The viscosity of feedstock with high flow activation energy is sensitive to temperature and pressure. As pressure increases, a feedstock becomes more viscous [2]. A small temperature change during PIM can significantly change feedstock viscosity, which can produce mould defects due to stress concentration [2, 145, 160]. Therefore, feedstocks with low flow activation energy are preferred.

The flow activation energy reported for MIM feedstocks is 3.1 to 55 kJ/mol [145, 160, 214, 221, 226]. It is affected by powder loading. For example, flow activation energy of a stainless steel-wax feedstock decreased from 33.2 to 21.9 kJ/mol as powder loading increased from 60 to 68 vol. %, then increased to 23.6 kJ/mol at 72 vol. % powder loading [145]. Feedstock with the lowest flow activation energy was used for injection moulding. The flow activation energy of a zirconia-PS-oil based feedstock increased when the powder loading increased from 47 to 57 vol. %. Adding SA reduced the flow activation energy [214].

Some feedstocks have high flow activation energy values. For example, the flow activation energy of feedstock made from WC-Co powder and wax-based binder was 139 kJ/mol, and highly temperature dependent. This feedstock solidified rapidly, preventing flow during injection moulding [164]. The flow activation energy of alumina-based feedstocks decreased from 69.2 kJ/mol for PEG-1000 to 50.2 kJ/mol for PEG-20000 [234]. The viscosity of feedstock made with PEG-1000 increased rapidly during cooling, creating uneven flow and induced internal stress so good temperature control during processing is needed. Feedstock made with PEG-20000 was used for injection moulding. Other research [172] reported that flow activation energy decreased as PEG molecular weight increased.

Binders used for feedstocks can have a higher flow activation energy than the feedstocks [3, 221]. For instance, the flow activation energy of PE-wax based binder was 25 – 99 kJ/mol whilst feedstocks made with this binder had an activation energy of 59 – 182 kJ/mol [3]. The flow activation energy of a starch-based binder was 29.2 – 30.5 kJ/mol and feedstocks made with this binder had an activation energy of 18.5 – 28.1 kJ/mol [221]. The flow activation energy can be used to identify the best binder. For example, binder made with PW-EVA-HDPE, which had a flow activation energy

of 22.0 kJ/mol, was more suitable for iron-nickel based MIM than PW-EVA binder (32.5 kJ/mol) or PW-HDPE binder (31.8 kJ/mol) [160].

2.4.6. General mouldability

Viscosity, flow behaviour index and flow activation energy data do not always indicate that a particular feedstock is best for MIM [3] so Weir [244] introduced a general mouldability parameter. He showed that feedstock viscosity changes continuously with temperature and shear rate when flowing into a mould (Figure 2.8). Average viscosity, $\bar{\eta}$, can be predicted as [244]:

$$\log \bar{\eta} = \log \eta_0 + \int_{\dot{\gamma}}^{\bar{\dot{\gamma}}} \left[\frac{\partial \log \eta}{\partial \log \dot{\gamma}} \right]_T d(\ln \dot{\gamma}) + \int_{T_0}^{\bar{T}} \left[\frac{\partial \log \eta}{\partial (\frac{1}{T})} \right]_{\dot{\gamma}} d\left(\frac{1}{T}\right) \quad 2.5$$

where, η_0 is viscosity at $\dot{\gamma} = \dot{\gamma}_0$ (reference shear rate) and $T = T_0$ (reference temperature), $\bar{\dot{\gamma}}$ is average shear rate and $\bar{T}$ is average temperature.

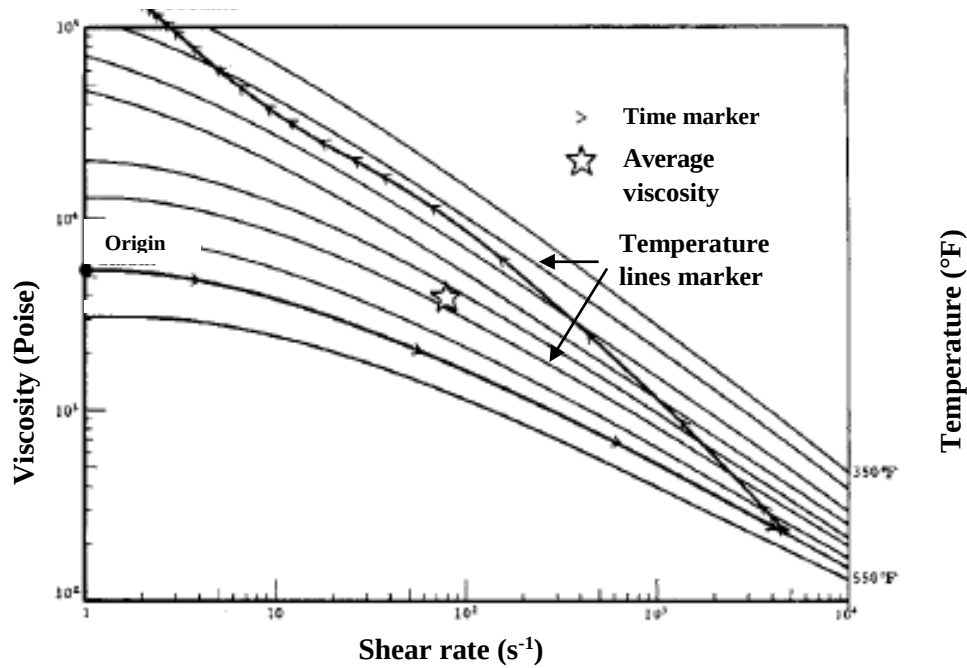


Figure 2.8: Effect of shear rate on viscosity of a melt feedstock flowing into a mould [244].

By integrating Equation 2.5 and expanding the exponentials as a power series, then approximating the first two terms, Weir [244] showed:

$$\frac{1}{\bar{\eta}} \approx K \left[\frac{1}{\eta_0} \frac{\left| \frac{\partial \log \eta}{\partial \log \dot{\gamma}} \right|}{\left(\frac{\partial \log \eta}{\partial (\frac{1}{T})} \right)} \right] \left[\frac{\ln \bar{\dot{\gamma}} / \dot{\gamma}_0}{\left(\frac{1}{\bar{T}} - \frac{1}{T_0} \right)} \right] \quad 2.6$$

or:
$$\frac{1}{\bar{\eta}} = \alpha_{STV} F(\bar{\dot{\gamma}}, \bar{T})$$

where:
$$\alpha_{STV} = \left[\frac{1}{\eta_0} \frac{\left| \frac{\partial \log \eta}{\partial \log \dot{\gamma}} \right|}{\left(\frac{\partial \log \eta}{\partial \left(\frac{1}{T} \right)} \right)} \right], \quad F(\bar{\dot{\gamma}}, \bar{T}) = K \left[\frac{\ln \bar{\dot{\gamma}} / \dot{\gamma}_0}{\left(\frac{1}{\bar{T}} - \frac{1}{T_0} \right)} \right] \text{ and } K \text{ is a constant.}$$

The mouldability index, α_{STV} (where STV = shear-temperature-viscosity) and $F(\bar{\dot{\gamma}}, \bar{T})$ depend on polymer flow properties and machine conditions respectively. The higher α_{STV} , the better the rheological properties [160].

Calculating α_{STV} is complex and done in six steps [244]. Although this index should be calculated at the reference shear rate of 10 s^{-1} , most published research uses a different shear rate (Table 2.7), probably to simplify calculating the reference viscosity (η_0). This may decrease accuracy because Weir [244] suggests η_0 should be close to zero. The α_{STV} reported by Amin *et al.* [201, 220] is arguable because the values are negative and too small (Table 2.7). Khakbiz *et al.* [232, 243] reported that the α_{STV} of composite stainless steel and TiC feedstocks increased by at least 30% for all temperatures used (60, 70 and 80 °C) when TiC was added, increasing powder mouldability.

Table 2.7: Summary of published mouldability index.

$\alpha_{STV} \times 10^7$	Reference shear rate (s^{-1})	Material	Reference
0.2 – 0.7	10	Polypropylene	244
40 – 93	1181	Iron-nickel-wax	160
0.85 – 1.94	Not reported	Steatite – HDPE	3
-0.0001 – 0.05	100 – 10000	Stainless steel-PEG	220
-0.0005 – -0.006	Not reported	Stainless steel-PEG	201
23 – 38	1000	Stainless steel-starch	221

The α_{STV} value for PE-CW and PE-PW-SA binder and feedstocks made with these binders were 10, 206, 85 and 194 respectively, indicating that PE-PW-SA binder and the resultant feedstock had better mouldability than with the other binder [3]. This agrees with fluidity but not the flow activation energy data reported by Karatas *et al.* [3], which showed the PE-CW binder was better. Similar complex relationships between mouldability and viscosity were reported by Cao *et al.* [245] for feedstocks made of polymeric binders and ceramic powders.

2.4.7. Effect of powder loading on viscosity

Feedstock viscosity increases nonlinearly with powder loading [2] and is very sensitive to powder content at high powder loading [246]. Feedstock viscosity is low at low powder loading because there is excess binder and increases with powder loading to a critical value (critical powder loading), where powder particles are tightly packed. At this powder loading, powder particles rub against each other and viscosity increases towards infinity [2, 191] (Figure 2.9).

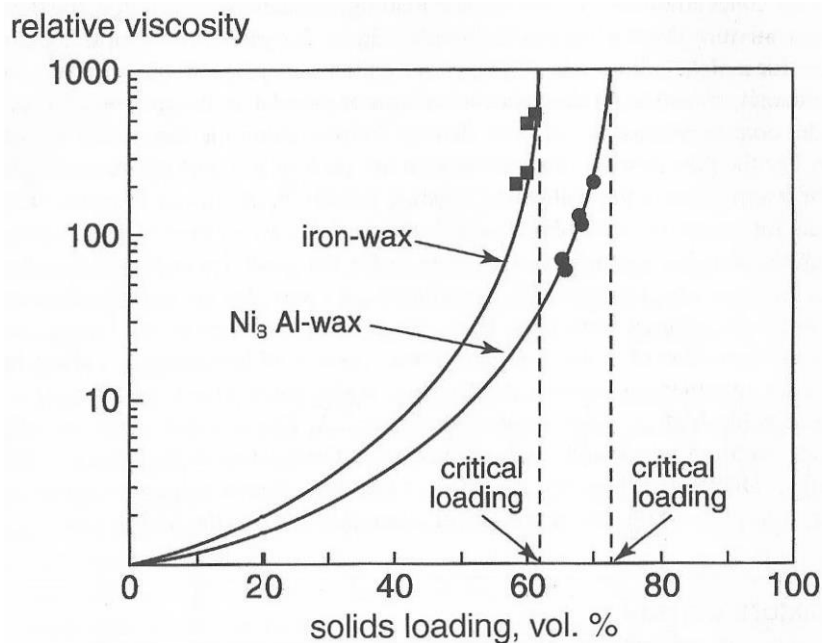


Figure 2.9: Relative viscosity versus powder loading (solids loading) for two powders [2].

Although particle shape, size and distribution affect rheological behaviour of a suspension [247] there is no accurate method to predict critical powder loading and viscosity from these characteristics. Particle distribution during shear flow depends on shear stress, so distribution under flow conditions is different from that prevailing at rest. Brownian motion of the particles allows them to revert to the equilibrium arrangement. The rheology depends on the structure at rest and the magnitude of the viscous forces relative to Brownian motion and interparticle forces [233].

Although fine powders are preferred over coarse powders for MIM, they are difficult to produce and tend to oxidise easily [207]. Spherical or near spherical powders have a high packing density, which allows a higher powder loading [89]. Systems with a wide particle distribution tend to pack better than systems with a narrow particle

distribution because the smaller particles can move into the inter-particle space between the larger particles. This allows the suspension to flow easily, reducing viscosity (Figure 2.10) and increasing powder loading.

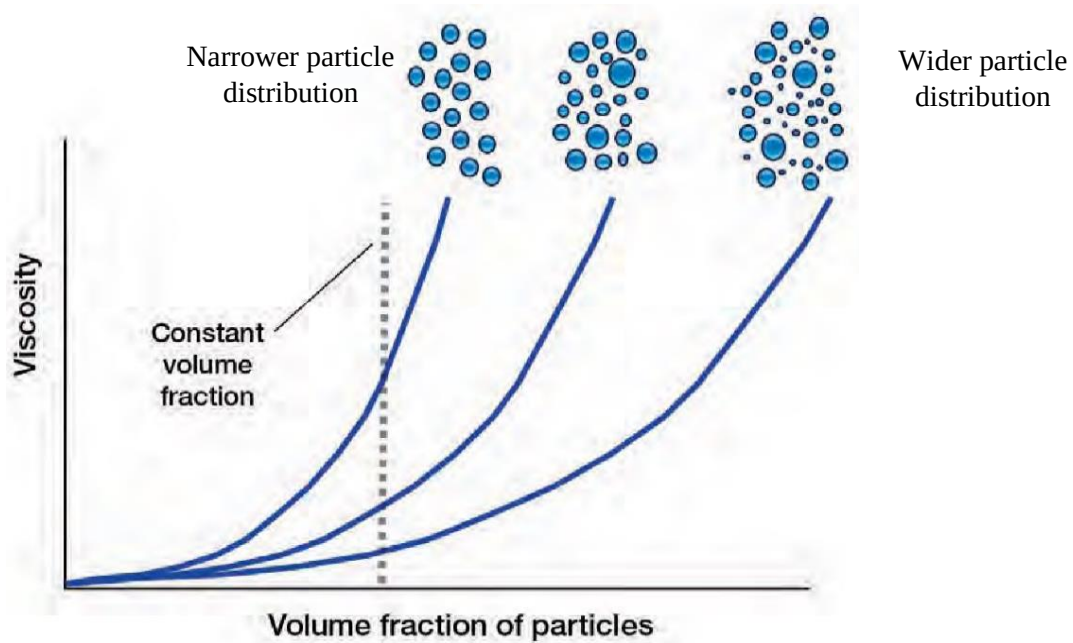


Figure 2.10: Effect of particle size distribution on suspension viscosity [248].

Much research has been done on the relationship between critical powder loading (ϕ_c) and relative viscosity (η_r) of suspensions [249-256]. Various models have been proposed to predict critical powder loading and viscosity (Table 2.8). Most models assume a spherical powder with rhombohedral packing and non-interacting rigid particles in a dilute suspension [325]. Einstein's model (Table 2.8) is for spherical, identical particles in a dilute solution ($\phi \leq 10$ vol. %) [246, 249, 256-260] and not applicable for PIM feedstocks, which have high powder concentrations (powder loadings are usually 40 to 65 vol. %), may contain non-spherical particles, and interactions may occur between binder and powder particles.

The Eilers model was developed for bitumen in a soap solution and the Chong model was developed for a bimodal mixture of glass beads in low molecular weight polyisobutylene [236, 250, 254] (Table 2.8). Both models assume a critical powder loading of 74 vol. % for rhombohedral packing of spherical particles. Chong's model agreed well with relative viscosity of silicon nitride suspensions [246]. Reddy *et al* [255]

reported that the Eilers, Chong and Mooney models did not describe feedstocks prepared using silica, alumina powders with polymer-wax based binders well.

Table 2.8: Published models for relative viscosity and powder loading.

Equation	Model	Reference
$\eta_r = 1 + 2.5\phi$	Einstein	249
$\eta_r = \left(1 + \frac{1.25\phi\phi_c}{\phi_c - \phi}\right)^2$	Eilers	250
$\eta_r = \exp\left(\frac{2.5\phi}{1 - k\phi}\right)$; k is a constant	Mooney	251
$\eta_r = \left(1 - \frac{\phi}{\phi_c}\right)^{-2}$	Maron and Pierce	252
$\eta_r = \left(1 - \frac{\phi}{\phi_c}\right)^{-[\eta]\phi_c}$	K-D (Krieger-Dougherty)	253
$\eta_r = \left(\frac{\phi_c - 0.25\phi}{\phi_c - \phi}\right)^2$	Chong	254
$\eta \phi_b = \eta(\phi_b)_m + \eta_b[1 - (\phi_b)_m]$	Reddy	255
$\eta_r = [a(\phi_c - \phi)]^{-2}$; a is a constant	Liu	256

ϕ_b = binder content, $(\phi_b)_m$ = critical binder content, η = feedstock viscosity, ϕ = powder loading

There is an exponential relationship between relative viscosity and powder loading in Mooney's model (Table 2.8), with the value 2.5 indicating the degree of agglomeration. Data from an alumina powder and EVA-based feedstock fitted the Mooney's model well at low (100 s^{-1}) shear rate [261]. However, this model predicted that the critical powder loading for a feedstock made of alumina powder and PP-MW based binder would be over 100 vol. % [135]. Other unrealistic critical powder loadings have also been reported. Zhang and Evans [246] reported 134 vol. % for feedstock made of alumina powder, isotactic PP, atactic PP and SA, and Stedman *et al.* [262] reported 120 vol. % for silicon nitride powder-PP-wax based feedstocks.

Models developed by Krieger and Dougherty [253] are similar to the common form $\eta_r = A \left(1 - \frac{\phi}{\phi_c}\right)^n$ (Table 2.8) originally developed by Maron and Pierce [252]. This model is called the Quemada's model when the exponent, n, is -2 [260, 263]. Although Reddy *et al.* [255] claimed their model (Equation 2.9) complemented other models that incorporate feedstock viscosity, binder content and a linear viscosity-powder loading relationship, it is the same as the Maron and Pierce [252] model with $n = -1$, as shown below.

$$\eta\phi_b = \eta(\phi_b)_m + \eta_b[1 - (\phi_b)_m] \quad 2.7$$

Since, $\phi_b = (1 - \phi)$ (volumetric fraction of powder), and $1 - (\phi_b)_m = \phi_c$ (critical powder loading), the Equation 2.7 can be rewritten as:

$$\eta(1 - \phi) = \eta(1 - \phi_c) + \eta_b \cdot \phi_c \quad 2.8$$

Dividing the Equation 2.8 by η_b ,

$$\eta_r(1 - \phi) = \eta_r(1 - \phi_c) + \phi_c \quad 2.9$$

where, η_r is the relative viscosity equals to η/η_b .

Rearranging the Equation 2.9 gives:

$$\eta_r = \left(\frac{\phi_c}{\phi_c - \phi} \right) = \left(\frac{1}{1 - \phi/\phi_c} \right) = \left(1 - \frac{\phi}{\phi_c} \right)^{-1} \quad 2.10$$

Therefore, critical powder loading (ϕ_c) can be determined from gradient of a plot of η_r^{-1} versus ϕ rather than the more complex $\eta\phi_b$ versus η proposed by Reddy *et al.* [255]. However, the model may not be accurate as it shows a linear relationship between relative viscosity and powder loading but relative viscosity of a feedstock is reported to increase nonlinearly with the powder loading (Figure 2.9).

2.5. Debinding and sintering

2.5.1. Debinding

Removing binder from the moulded part without disturbing the powder particles is a delicate, crucial stage in MIM. The objective is to remove binder quickly from the moulded (or green) part with the least impact. It takes longer (up to 300 h) than other stages and defects such as blistering, cracking and bloating can occur [2, 11]. Binder holds powder particles in the desired shape (now called brown part), which becomes fragile as binder is removed. The brown part must retain sufficient strength so it can be handled until sintered. As it is difficult to handle a fully debound and unsintered part, final debinding occurs during the preliminary stage of sintering [2].

The original debinding method for powder compacts involved thermal burnout. However, the carbides, hydrides and nitrides that can be produced affect composition

of the metallic parts. This contamination is unfavourable for reactive metals so solvent debinding became vital for a successful MIM [264-266]. Various debinding techniques (Table 2.9) can be used to minimize the debinding time and defects. The binder component first removed in this step must make up more than 30% (and can be up to 98%) of the binder [2]. Therefore, a suitable debinding technique needs to consider the binder components used in the green part (Table 2.10).

Table 2.9: Various debinding techniques [2].

Category	Debinding technique	Key features
Solvent	Solvent immersion	Extract major binder via dissolution by immersing in the solvent
	Supercritical extraction	Heat and pressurize fluid to dissolve binder into fluid
	Solvent vapour condensation	Hold the compact in heated vapour of solvent, allow condensation to absorb major binder, dripping off
Solvent or thermal	Catalytic depolymerisation	Heat compact in catalyst environment to continually depolymerize
Thermal	Diffusion controlled	Slow heating of compact with continual sweep gas to remove binder products
	Permeation controlled	Pass process gas over compact as it is slowly heated to give progressive degradation of binder
	Wicking	Heat compact in packed powder bed or on porous substrate that absorbs molten binder
	Oxidation	Heat compact in air continuously to burn-out binder and oxidize powder to give strength

Table 2.10: Characteristics of various debinding processes [267-268].

Binder	Debinding	Advantages	Disadvantages
Wax-PP	Thermal	Low cost, easily available, wide moulding window, good feedstock recycling	Very slow debinding, slumping, setters required.
Wax-PP	Solvent	Same as above	Waste solvent recovery, slumping, slow binding, health hazards, regulation on solvents
PEG-polymer	Water	No organic solvents	Waste water treatment, increased O ₂ in debound parts, slumping
Polyacetyl	Catalytic	Fast debinding rate, high green strength, thick parts possible	High capital expenditure, handling of acids, relatively high viscosity
Gelled water	Thermal	Fast debinding rate, thick parts possible, no special equipment	Humidity sensitivity, poor green strength, narrow moulding window
Acrylic	Thermal	Fast debinding rate, thick parts possible, no special equipment, wide moulding window	Not commercially yet

2.5.2. Solvent debinding

Defects, which are commonly produced when debinding a single-component binder, are minimized by using multi-component binders [114]. The pores created when removing the low molecular weight polymer component minimize residual stress when extracting the high molecular weight polymer [11].

Many solvents are used in solvent debinding (Table 2.11). The acids are hazardous and requiring expensive equipment so water debinding has become popular. Many researchers use PEG as the main binder component (Section 2.3.1) because it is water soluble and environmentally safe. However, other water-soluble binders such as poly(2-ethyl-2-oxaline) were also used [269].

A binder made of 70 wt. % PEG-1600 and 30 wt. % PMMA decreased debinding time and hence production cost [173]. However, mixing time was high (11 h at 150 °C), solvent debinding rate slow (90% PEG extracted in 24 h at room temperature), and moulded parts swelled. Anwar *et al.* [174] used a similar binder with 60 wt. % PEG-

400 – 1500 and 40 wt. % PMMA to extract 90% of the PEG in 2 h at 80 °C without distortion. However, they spent a significant time (>36 h) preparing the feedstock.

Solvent debinding rate increases with temperature [270]. Debinding time to extract 75 wt. % of binder decreased from 10 h to 5 h when temperature increased from 25 °C to 60 °C [271]. Solubility and diffusivity of PEG in water [166] and PW-SA binders in n-heptane [272] increased if temperature increased from 30 to 55 °C. Defects can occur at high temperatures. Cracking, slumping and sagging occurred when removing 60% of the original binder in 1 h at 55 °C but there were no visible defects for removing 68 wt. % binder in 2 h at 50 °C [272]. Defects occurred when debinding PW-LDPE from the stainless steel green part with 40 °C petroleum ether. However, there were no visible defects if the process was done at 30 °C for 6 h and 45 wt. % of the binder was extracted [273].

Table 2.11: Examples of proposed solvents for polymeric binders [286].

Binder	Proposed solvents with debinding temperatures
HDPE, LDPE, LLDPE	Aliphatic, cycloaliphatic, aromatic hydrocarbons, halogenated aliphatic, higher aliphatic esters and ketones, di-n-amyl ether (HDPE >80 °C; LDPE, LLDPE >20 – 30 °C).
PP	Atactic – Isoamyl acetate, diethyl ether, hydrocarbons and chlorinated hydrocarbons at room temperature; Isotactic – xylenes, trichlorobenzene, decahydronaphthalene (>135 °C).
EVA	Benzene, toluene, chloroform, carbon tetrachloride/ethanol, methanol, chlorobenzene, ethanol/water, n-butanol/water, allyl alcohol, glycol ethers, glycol ether esters, acetone, methyl ethyl ketone, acetic acid, 1,2,4-trichlorobenzene at 135°C.
PVB	Acetalization 70% – alcohols, cyclohexanone, ethyl acetate, ethyl glycol acetate; Acetalization 77% – methylene chloride, alcohols, acetone, methyl ethyl ketone cyclohexanone, lower esters. Acetalization 83% – methylene chloride, alcohols, ketones.

During water debinding, water diffuses into the binder and reacts with the water-soluble binder component. The hydrated binder molecules then diffuse through pores in the sample. As water has a much lower molecular weight than the water-soluble binder, it diffuses into the sample faster than binder diffuses out so debinding rate is limited by diffusion of the hydrated binder molecules rather than their dissolution [11, 150, 271, 274]. Sample thickness affects debinding rate. It took 4, 6 and 16 h at 40 °C

to extract 75 wt. % of the polyMIM binder from 2, 3 and 5-mm thick green parts respectively [271, 274] and 2 h and 16 h at 50 °C for aqueous extraction of 90 wt. % of the PEG from 2- and 6- mm thick parts respectively [179].

Debinding rate decreases with debinding time [166, 272]. Binder removal depends on the concentration gradient between the solvent and binder [276]. The diffusion distance between solvent and binder at or near the surface of a MIM part is small at the beginning of the process, giving a fast debinding rate. The pathway increases as binder is removed [166, 275]. Binder removal is affected by capillary forces and the concentration gradient until equilibrium is reached [276]. This phenomenon can be explained by mass transfer theory (similar to humidification for an open dish of water), and described using Fick's diffusion model [277-278]:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad 2.11$$

where C is the concentration of diffusing substance, t is the time, D is the interdiffusion coefficient and x is the direction normal to the section.

Binder dissolution is postulated to be a slow process occurring in two stages. Initially the solvent molecules diffuse into the binder to produce a swollen gel. If the molecular interactions are large due to cross-linking, crystallinity, or strong hydrogen bonding, the binder swells. If interactions between the polymer and solvent are larger than the polymer interactions, then the second stage of binder dissolution can occur and the gel gradually disintegrates into a true solution [166, 279]. The absorbed water content, called as the equilibrium water content (EWC), is defined as [280]:

$$EWC = \frac{\text{weight of swollen gel} - \text{weight of dry gel}}{\text{weight of swollen gel}}$$

When water concentration in PEG is greater than EWC, the PEG begins to dissolve [166, 280].

2.5.3. Solvent debinding kinetics

Solvent debinding kinetics can be analysed using parameters such as interdiffusion coefficient, reaction depth, porosity and tortuosity.

- *Interdiffusion coefficient*

The interdiffusion coefficient of polymer and solvent characterises solvent penetration, solvent-binder interactions and transport of binder molecules from the MIM part to the solvent [281]. Solvent debinding can be modelled using the modified Lin–German equation derived from Fick’s law for either one (Equation 2.12) dimensional or three (Equation 2.13) dimensional components [175, 282-283]:

$$\ln\left(\frac{1}{F}\right) = \frac{D_e \pi^2 t}{H^2} + K_1 \quad 2.12$$

$$\ln\left(\frac{1}{F}\right) = \frac{D_e \pi^2 t}{\Psi^2} + K_2 \quad 2.13$$

where F is fraction of remaining soluble polymer, t is debinding time, H is specimen thickness, K_1 and K_2 depend on the mechanism controlling debinding behaviour in a given powder-polymer system, D_e is the interdiffusion coefficient of polymer and solvent, and Ψ is the modified effective length scale (ratio of sample volume and surface area).

Temperature dependence of solvent debinding could be expressed as [2]:

$$t = \frac{H^2}{\beta} \ln\left(\frac{F}{1-\phi}\right) \exp\left(\frac{E}{kT}\right) \quad 2.14$$

where $(1 - \phi)$ is initial binder fraction, ϕ is powder loading, E is activation energy associated with binder solution into the solvent, k is the Boltzmann’s constant, T is absolute temperature and β depends on the binder solubility in the solvent.

- *Reaction depth*

Reaction depth, which is the distance from the edge of the sample to interface where the soluble binder is being removed, can be calculated by measure the binder lost if it is assumed constant binder extraction from all edges a MIM part [274]:

$$\text{Weight loss (\%)} = 100 - V_0/V_{(t)} \quad 2.15$$

where, V_0 is volume of moulded part and $V_{(t)}$ is volume of the non-dissolved binder containing core during water debinding at time (t) .

However, Equation 2.15 infers negative weight loss ($V_0 > V_{(t)}$) and must be modified when $V_0/V_{(t)} > 100\%$. As reaction depth (x) is not directly related to time (t) , Krug

[274] suggested the following parabolic relationship:

$$t = ax + ab^2x^2 \quad 2.16$$

where a and b are constants. This model could be used to analyse solvent debinding kinetics.

Porosity and tortuosity

The relationship between interdiffusion coefficient, porosity and tortuosity is [284]:

$$D_{\text{eff}} = D_e \left(\frac{\varepsilon}{v} \right) \quad 2.17$$

where D_{eff} is effective interdiffusion coefficient, ε is porosity, and v is tortuosity. As binder tends to absorb on the metal particle surface, a retardation factor R can be used [285]:

$$D_a = D_{\text{eff}}/R \quad 2.18$$

where D_a is apparent interdiffusion coefficient. Substituting D_a for D_e in Equation 2.13 [285], allows solvent debinding kinetics to be analysed using binder loss, porosity and tortuosity:

$$\ln \left(\frac{1}{F} \right) = \frac{D_e \varepsilon \pi^2}{vR} \left(\frac{t}{\psi^2} \right) + K_2 \quad 2.19$$

Various factors such as binder molecular weight, sample thickness, and temperature affect solvent debinding rate. However, powder loading did not significantly influence binder removal in a commercial feedstock made of stainless steel and nickel carbonyl iron powder [271]. This finding is debatable because high powder loadings may decrease the pores size and produce tortuous diffusion paths than for low powder loadings, inferring that powder loading should affect debinding rate.

2.5.4. Thermal debinding

Conventional thermal debinding involves one stage. The green part is kept under controlled temperature in an inert or reducing gas atmosphere [271, 274]. If thermal debinding is done rapidly, evaporation of organics can increase pressure, allowing voids to develop in the green part so defects such as bloating and cracks occur [287-290]. Therefore, stepwise binder removal is essential in thermal debinding [2].

Thermal debinding can be done in a suitable oven or furnace. It is often done using a sweep gas such as air or argon that constantly passes over the brown parts, transferring

the molten binder by-products to a venting system with special filters or other recycling system for safe disposal. During thermal debinding, lower molecular weight binders usually evaporate or wick out and higher molecular weight binders decompose by chain depolymerisation or random decomposition [114, 296]. Molten binder moves from the centre to the surface by capillary forces and is then removed by the sweep gas. A high gas flow increases binder removal from the surface.

Analyses such as differential thermal analysis (DTA) and thermogravimetric analysis (TGA) with a DTA/TGA analyser can indicate thermal properties such as melting and decomposition temperatures (Figure 2.11). These data can be used to identify suitable thermal debinding cycles [92, 142, 161, 179, 184, 272, 291-295, 300].

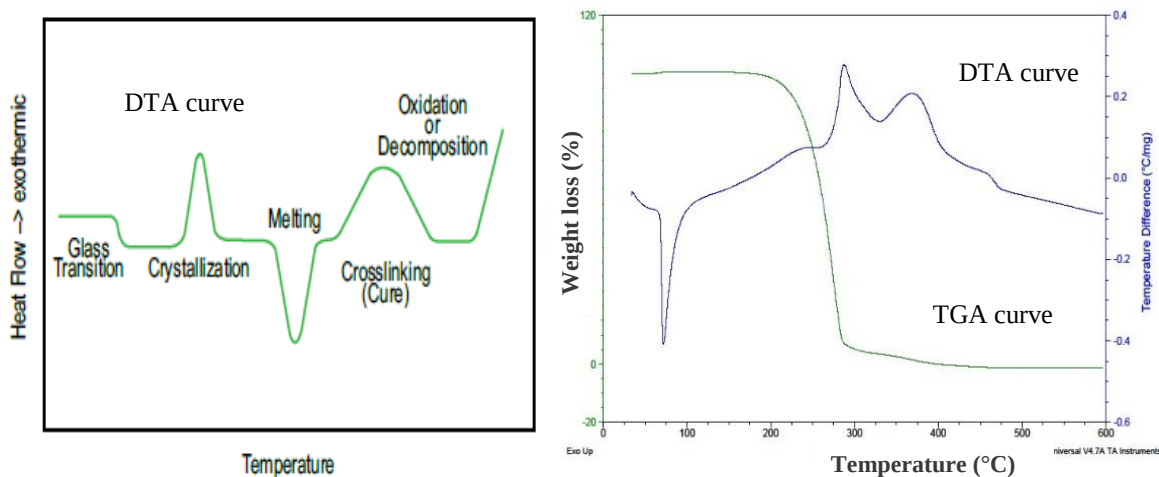


Figure 2.11: DTA/TGA curves showing thermal properties of a binder.

Thermal debinding can be divided into two stages: a low temperature region for removing low molecular weight binder, and a high temperature region for removing high molecular weight binder. Thermal debinding usually is a series of thermal stages over time. These thermal processes are typically long, energy intensive, costly, and involve component distortion.

To avoid component distortion, heating rate in the low temperature region, where most of the polymeric binders undergo phase transformation, must be sufficiently low and strictly controlled. For example, the activation energy for thermal debinding feedstock of cemented carbide powders and PW-PS based binder was almost three times lower in the low temperature region than in the high temperature region [291-292, 300].

Although a low activation energy is required for thermal rebinding, component distortion can still occur in a low temperature region.

Two-stage solvent and thermal debinding processes can take more than 10 h [295, 297-299] but some processes involve thermal debinding only. Some report heating the parts to 100 – 600 °C at 0.34 – 2 °C/min followed by further heating to 380 – 900 °C at 0.5 – 5 °C/min [114, 298-299, 301]. Heating at 1.7 °C/min for 1 h was used to thermal debind zirconia-PEG based parts [179]. Defects occurred in Ti-6Al-4V/HA parts heated at 0.58 or 0.83 °C/min but no defects were found by heating to 120 °C at 0.33 °C/min followed by heating to 380 °C at 0.5 °C/min [114]. These debinding processes take a long time (up to 2.5 days), which will increase production cost.

Some thermal debinding processes are relatively quick. For example, nearly all the PW was extracted from green parts made of stainless steel powder and 50:50 HDPE-PW in 4 h using the temperature profile shown in Figure 2.12a [302]. In comparison, it took 10 h to extract 94 wt. % of the PW using heptane at 50 °C. However, the 5 °C/min heating rate (Figure 2.12a) is much higher than the 1.7 – 2 °C/min used by other researchers for low temperature debinding so defects may occur, especially when removing large amounts of PW. The 14 h to thermally debind almost all the binder from green parts made of molybdenum powder and PW-HDPE-EVA binder (Figure 2.12b) decreased to 10.7 h if a solvent stage was done first [272]. Similarly, the 17.9 h it took to thermally debind green parts made of alumina powder and PW-HDPE-SA binder decreased to 13.7 h if a solvent stage was introduced [142].

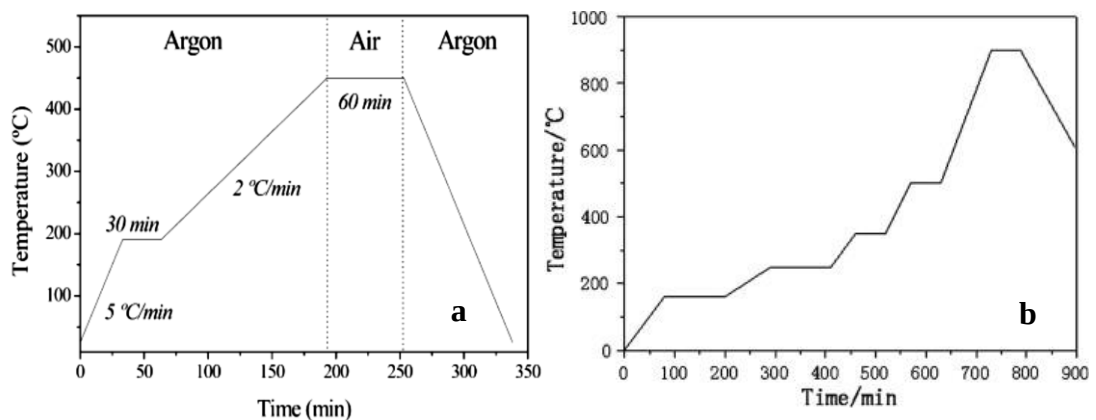


Figure 2.12: Two examples of thermal debinding cycles: (a) Sotomayor *et al.* [302] and (b) Li *et al.* [272].

Li *et al.* [151] recommended thermal or solvent debinding with ethanol to extract PEG from green parts made of iron powder and PEG-HDPE-SA binder even though PEG can be easily and economically extracted with water. Almost 50 wt. % binder was removed after the second thermal debinding stage (2 h at 300 °C), which is less than reported for solvent debinding (Section 2.5.2).

2.5.5. Sintering

Sintering minimizes or eliminates inter-particle spaces and allows bonds to be established by diffusion. The major challenge is shrinkage. If it is not uniform in all directions, distortions may occur. Several novel methods have been developed to accelerate the densification process including induction sintering [303-304], spark plasma sintering [305-307], microwave sintering [308-310], electrical resistance sintering [311-312] and overpressure sintering [313].

During sintering, the powder compact is heated to about 80% of the metal or alloy's melting temperature then held for a specific time (isothermal heating) to attain near-to-full density. Most sintering procedures use 2 h of isothermal heating to obtain the high density and better mechanical properties. For example, alumina-based parts sintered at 1600 °C for 2 h had good strength [142].

The backbone binder of the green part can affect final density and mechanical properties even though the binder is not present during sintering. Optimal backbone binder content helps powder particles to pack well. For example, the backbone polymer (HDPE) greatly influenced dimensions and mechanical properties of a sintered part [315]. Density of stainless steel-based MIM parts (63.5 vol. % powder loading) sintered at 1360 °C for 2 h increased from 92% to 95% as the PMMA (the backbone polymer) content increased from 10 to 25 wt. % [149]. However, Koikul *et al.* [314] reported that density of sintered stainless steel parts decreased as PMMA content increased from 30 to 50 vol. %. This may be because more pores development as PMMA content increased. The data indicate that a high sintered density was obtained using 25 – 35 wt. % PMMA.

The microstructure of a molybdenum part sintered at 1850 °C for 2 h had pores (Figure 2.13a). The tensile strength was 229 MPa, which is about 35% the tensile strength of

molybdenum even though the part had a sintered density of 95% [272]. Post-sintering processes such as hot-isostatic-pressing (HIP) can be used to close the pores, increase density and enhance mechanical properties. For example, Ti-6Al-4V parts sintered at 1350 °C under high (10^{-2} Pa) vacuum for 2 h had 13% more tensile strength after HIPping [83, 316]. The oxygen content in the sintered parts was 0.23 wt. %. The tensile strength of Ti-6Al-4V parts sintered at 1230 °C in vacuum (10^{-3} Pa) for 3 h (Figure 2.13b) increased by 23% after HIPping [113] and oxygen content was 0.26 wt. %. Guo *et al.* [317] also reported that HIPping enhanced microstructure of the sintered parts.

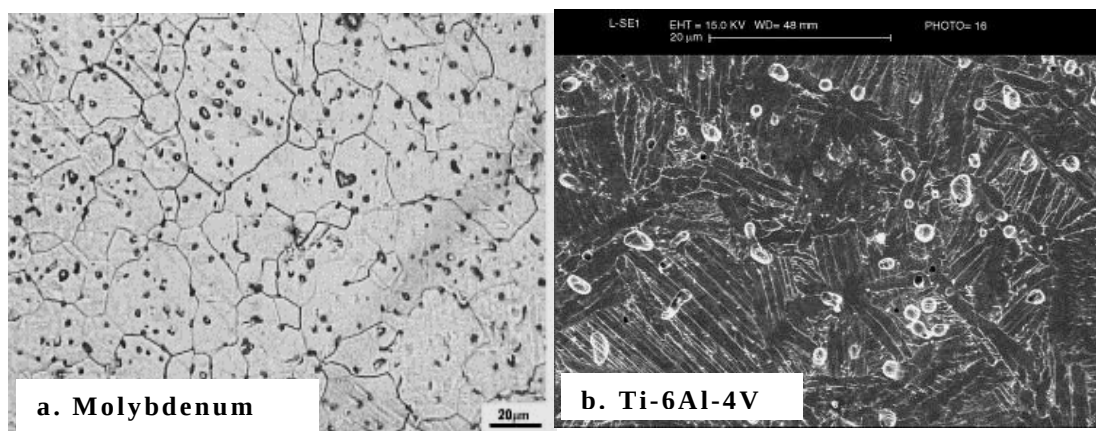


Figure 2.13: Microstructure showing pores in as-sintered parts:
(a) Li *et al.* [272] and (b) Shibo *et al.* [113].

Although sintering time was usually 2 h, longer process times can increase density and tensile strength. For instance, titanium parts made from HDH Ti-6Al-4V sintered at 1260 °C for 3 – 6 h had densities between 95.6 and 96.7%, tensile strength between 648 and 686 MPa, and elongation of less than 4% [317]. Parts made from 90% GA Ti-6Al-4V and 10% HDH Ti-6Al-4V powder that were sintered at 1260 °C for 3 – 6 h had tensile strength between 800 – 848 MPa and elongation of 7.4 – 9.5% [317]. The fine spherical GA powder (25 μm) and irregular HDH powder (45 μm) could have enhanced particle packing and sintering. However, oxygen content increased with sintering time. As oxygen content increases beyond 0.60 wt. %, the sintered parts become very brittle and fragile [317-320]. Therefore, the tray the titanium parts are on during sintering should be non-reactive. Lanthanated molybdenum trays reduce contamination for reactive metals [297].

High sintering temperatures increase density due to pore shrinkage, and enhance mechanical properties [321-322]. Shrinkage generally increases with sintering heating rate [323-324]. For example, a zirconia part had 24% shrinkage and 99% relative density when sintered at 1500 °C for 2 h in argon [179]. A novel sintering method for zirconia parts, involving heating the parts at 1500 °C for 5 min, cooling rapidly to 1300 °C; then holding at 1300 °C for 10 h produced parts with a relative density of more than 99% [301]. The shrinkage of stainless steel parts held at 1360 °C for 2 h increased from 7.8% to 15% when heating rate was increased from 5 to 15 °C/ min [323-324]. Increasing sintering temperature above 1150 °C did not increase relative density of sintered Ti-6Al-4V/HA parts [116-117].

2.6. Analytical and physical methods for characterising binder and feedstock

Feedstock homogeneity can be assessed by DTA/TGA analysis (burn-out tests), density and mixing torque [115, 142, 154, 198-199, 216, 218-219, 384-388]. Relatively expensive Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) indicate transformations such as glass transition, crystallization, melting and sublimation relative to an inert references. Data is presented as a function of temperature or time. The area under the DTA peak represents the enthalpy change of the sample and is not affected by the heat capacity of the sample.

Density of representative samples can be used to indicate homogeneity [2, 384-387]. Very accurate (up to 5 s.f) density measurements of solids, can be obtained using a gas pycnometer, which measures sample volume by gas displacement [385-386]. The torque during mixing tends to become constant as a heterogeneous feedstock becomes more homogeneous [2, 222, 388]. If a torque sensor is attached to the mixer, homogeneity can be assessed during the process.

A large change in torque when adding powder to binder can indicate the critical powder loading. Critical powder loading can be also determined from density or viscosity values [2, 198, 202, 222]. Feedstock rheology will determine the flow properties of molten feedstocks and therefore their mouldability. Rheology can be assessed by extruding feedstocks in a capillary rheometer simulates the effect of extruding feedstock in an injection moulding machine.

Both thermogravimetric analysis and density must be measured on samples obtained during the process. Density measurements are quicker, easier but more tedious than thermogravimetric analyses but the data is easier to interpret. Burn-out tests and density measurement both provide accurate results. Torque rheometers are expensive and mixture homogeneity depends on mixing geometry and shear created during mixing [331]. It is preferable to use two methods to validate homogeneity and critical powder loading.

The microstructure of samples can be evaluated with optical microscopy, scanning electron (SEM), transmission electron (TEM) and scanning transmission electron (STEM) microscopes [389-393]. An SEM micrograph provides details of the sample surface and composition whereas TEM provides information on the internal composition of samples. In terms of magnification and resolution, TEM (50 M and 0.5 Å respectively) gives greater detail than SEM (2 M and 0.4 nm) [393]. The SEM images are three dimensional and accurate representations but TEM images are two dimensional and require careful interpretation. Smaller, thinner samples (e.g. 0.3 mm³ and <100 nm respectively) are required for TEM so conclusions need to be made carefully to avoid false interpretation [392-393]. Polymers are poor electrical conductors and do not reflect electrons and more likely to be damaged by the high energy electron beam used in SEM/TEM. Therefore microstructure of a polymer is usually assessed with optical microscopes.

Oxygen content can be determined using an inert gas fusion method [394-396]. The sample is fused under a flowing inert gas (e.g. He) and combustion gases measured via infrared absorption and thermal conductivity. During this process, oxygen and carbon combine to form CO₂, and nitrogen is released as N₂ [396].

2.7. Intentions of this research

Binders help produce a homogeneous MIM feedstock. Rheology of this feedstock should ensure the green part retains its shape and helps minimise defect formation as the part progresses through the various stages of MIM process. A further aim is to maximize powder loading, which will minimize defects and shorten the time required for debinding, and hence maximize production rate and reduce manufacturing cost. Reported powder loadings are usually low to moderate (40 – 55 vol. %) although some

researchers obtained higher powder loadings (55 – 70 vol. %). Feedstock density, viscosity, melt flow or mixing torque can be used to identify optimum powder loading. However, most published research on MIM does not evaluate feedstock homogeneity, identify critical powder loading, investigate whether the feedstock is suitable for injection moulding, or give the basis for the powder loading selected. One aim of the current research is to investigate whether critical powder loading can be accurately determined using mixing torque, density or viscosity measurements. The other aims are to evaluate feedstock homogeneity using density and thermogravimetric analyses, and to develop a rheological model to predict critical powder loading and relative viscosity of Ti-MIM feedstocks. Due to the need to minimise manufacturing cost, the research will be done with irregular size HDH Ti-6Al-4V.

2.7.1. Binder selection

The main role of a binder in MIM is to help form and retain the desired shape. It then needs to be removed easily. There are currently no techniques to easily identify suitable binder formulations for Ti-MIM. The aim of this research is to develop methods that will make it easier to identify suitable binders for MIM rather than running a series of trials.

Thermal characteristics and miscibility of binder components PEG, PVB and SA will be determined. The characteristics and suitability of Ti-MIM feedstocks with different HDH Ti-6Al-4V alloy powder loading in terms of mixing, flowability (rheology), debinding and sintering will be then be investigated.

The random copolymer PVB will be used as the backbone polymer. It forms miscible blends with other binder components but is insoluble in water because of its butyral groups. This means it has potential to hold powder particles during water debinding. The main binder component influences feedstock rheology. PEG-8000 will be used as the main binder to create feedstock with rheology suitable for injection moulding but with minimum debinding defects. Surfactant enhances feedstock flow properties and reduces abrasion between feedstock and machine/die walls. The most common surfactant for MIM, SA, will be used at the recommended optimum of 5 vol. % SA.

2.7.2. Process conditions

Feedstock for MIM must be homogenous. The processing temperature for PVB is higher (MP ~185 °C) than for other binder components (PEG ~65 °C; SA ~74 °C). As PEG and SA may degrade if the temperature is too high, different binder and/or process temperature and mixing times may be required. The high viscosity of PVB may limit the amount that can be incorporated in the binder for extruding an homogenous feedstock. However, decreasing the PVB content may reduce green part strength and cause shape retention problems during debinding. The effect of PVB and PEG and changing the thermal profile during mixing, capillary extrusion and debinding will be investigated. Thermal degradation of PVB, PEG and SA in the binder is another potential problem, so processing temperature needs need to be as low as practicable. The irregular shaped HDH Ti-6Al-4V particles may affect mixing, injection moulding, debinding and sintering the titanium alloy feedstock. These difficulties may be overcome by optimizing mixing conditions, powder loading and feedstock rheology. Reactivity of titanium, especially with oxygen at 260 °C or above may decrease mechanical properties of the sintered parts. Processing under vacuum or an inert atmosphere when process temperature is >260 °C may reduce the problems. The planned outcome of the research is to identify a process to obtain homogeneous Ti-MIM feedstocks and high powder loadings and to be able to use feedstock characteristics to identify conditions for producing injection mouldable feedstocks and fast PEG extraction rates.

2.7.3. Rheology

Many MIM feedstocks have pseudoplastic flow behaviour and some exhibit dilatant flow behaviour (Section 2.4.2). It is expected feedstocks made from HDH Ti-6Al-4V powder and PEG-PEG-SA binder need the following rheological properties for injection moulding and to obtain efficient mould filling without defects: pseudoplastic flow behaviour, Flow behaviour index below unity; viscosity below 1000 Pa-s, flow activation energy between 3.1 – 55 kJ/mol, and high stability and low fluctuation in viscosity (instability index <1). A rheological model to describe rheology of Ti-MIM feedstocks will be developed.

2.7.4. Debinding and sintering

This research will use two-stage solvent and thermal debinding with the aim of

extracting at least 75 wt. % PEG in 3 – 4 h and up to 90 wt. % in 6 h of the solvent debinding stage. The optimum debinding temperature will also be investigated. The data will be used to develop a model to describe solvent debinding kinetics of Ti-MIM green parts.

2.8. Summary

This chapter reviewed metallurgical processes with an emphasis on Ti-MIM. The advantages and disadvantages of MIM, possible metals and binders and their characteristics, feedstock formulation, effect of powder loading, feedstock rheology and solvent debinding were discussed in detail. Models explaining behaviour of MIM feedstocks and the relationship between relative viscosity and powder loading were reviewed to develop an improved rheological model for Ti-MIM. The chapter ends with the aims of the research.

Titanium has a unique combination of material properties compared to other common metals such as steel and therefore attracts many metallurgists. Its high powder and production costs limit the applications to niche markets where performance is more important than cost. The distinct processing characteristics of MIM mean this may be cost-effective process for manufacturing titanium parts. Obtaining affordable titanium powders with moderate purity levels allows parts to be manufactured via MIM for non-niche market and non-load bearing applications.

GA Ti-6Al-4V powder is normally preferred for formulating titanium feedstock because the particles are spherical and it has fewer impurities, especially oxygen (<0.2 wt. %). This powder is expensive and not readily available. Most research uses this powder to obtain high powder loading and good mechanical properties. However, the reported results may not help when manufacturing inexpensive titanium products for non-niche market. This research will use HDH Ti-6Al-4V alloy powder, which is readily available and much cheaper than GA Ti-6Al-4V available. However, it contains different sized particle and has variable purity.

The literature presented in this section shows there is little published research on using MIM (an established manufacturing process) for fabricating titanium products. Ti-MIM requires special binders, good knowledge of feedstock rheology, and specific

process conditions not used for conventional MIM or polymer processing. Powder loading, binder composition, feedstock formulation, homogeneity and rheology affect success of Ti-MIM. Many researchers and industrialists have considered Ti-MIM research too difficult to resolve issues highlighted in this review. The ideal binder has not yet been identified so much research has been done to identify suitable binder combinations and appropriate process conditions. The proposed research will hopefully address some of these deficiencies.

Chapter Three: Materials and Methods

This section describes the experimental work to develop a binder system and to formulate a feasible feedstock for Ti-MIM. Methods for producing a homogeneous feedstock are investigated and various tests are used to characterise the feedstocks and injection moulded samples.

3.1. Materials

Titanium pre-alloyed Ti-6Al-4V (wt. %) powder produced by the hydride-dehydride (HDH) process and with a stated average particle size of 70 μm and oxygen content 0.50 wt. % was purchased from Xi'an Baode Powder Metallurgy Co. Ltd. (Xi'an, China). Particle size distribution was determined with a Malvern Mastersizer 2000 laser-scattering instrument and particle morphology examined by scanning electron microscopy (SEM).

Details of the polymers for the binder system are given in Table 3.1.

3.2. Manufacturing the binder systems

The effect of different mixers and processing conditions on producing a homogeneous PEG, PVB and SA binder system were investigated. Melting point and degradation temperatures of binder components were determined using a SDT-2960 DTA/ TGA analyser (TA Instruments) by heating accurately weighed samples (about 5 mg) from room temperature to 600 °C at 10 °C /min.

3.2.1 Trial 1

A roller compounder, which had been manufactured in-house (Figure 3.1), was used for mixing. The Power Flex 4M motor control unit could adjust speed up to 100 rpm and the torque was measured with process signals from the Kistler–CoMo type 4700 sensor, which sent torque, speed, power and time data to a recording system. The temperature of the mix was measured using a thermocouple located on the internal wall of the mixing chamber. The 6-mm clearance in the roller compounder between the twin roller mixing blades and chamber wall facilitates a shear zone (Figure 3.2).

Table 3.1: Details of polymeric binder components.

	Polyethylene glycol (PEG 8000)	Polyvinyl butyral (PVB)	Stearic acid (SA)
Supplier	Union Chemical Ltd., New Zealand	Sigma-Aldrich Co., New Zealand	Sigma-Aldrich Co., New Zealand
*CAS No.	25322-68-3	27360-07-2	57-11-4
Formula	$(C_2H_4O)_n \cdot H_2O$	$C_{16}H_{28}O_5$	$C_{18}H_{36}O_2$
Mw (g/mol)	7500-8800	50,000-80,000	285
Glass transition temp (°C)	-	62 – 72	-
Appearance	White powder	White, free-flowing powder	White powder, mild odour, floats on water
Density (g/cm ³)	1.1036	1.1940	0.9866
MP. (°C)	65	165 – 185	67 – 74
Solubility	Water and other organic solvents	Not water-soluble; compatible with other solvents	Slightly soluble in water, 0.1–1 g/ 100 ml at 23 °C
Hazard	No; CO ₂ and CO may form when heated	Irritating to eyes, skin and respiratory system	Irritating to eyes, skin and respiratory system, highly flammable

* CAS No: Chemical Abstracts Service registry number; - Not available.

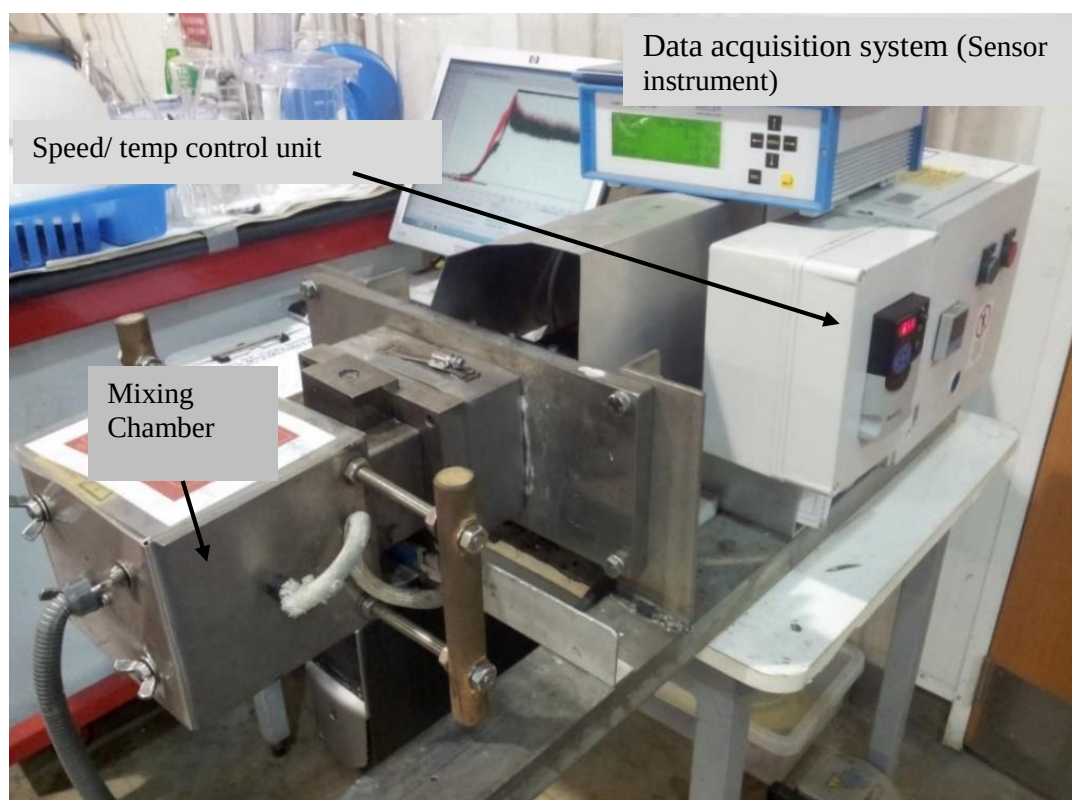


Figure 3.1: Roller compounder.

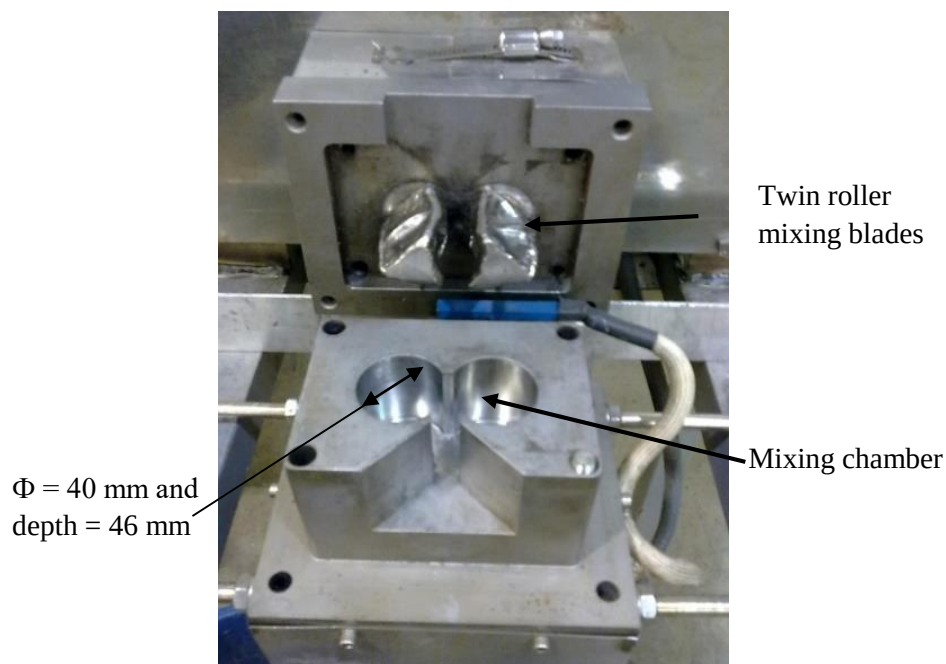


Figure 3.2: Mixing chamber of the roller compounder.

A binder system made of 65:30:5 parts by volume of PEG, PVB and SA was used. The compounder mixing-chamber was preheated to 175 °C and 21.03 g of PVB added, followed by 48.60 g PEG and 2.91 g SA. The binder system was mixed at 30 rpm for 30, 60 or 80 minutes. The mixture was then cooled to room temperature.

3.2.2. Trial 2

A known weight (72.5 g) of the 65:30:5 vol. % PEG:PVB:SA binder was dry mixed in a KM070 Kenwood planetary mixer at room temperature at 25 rpm for 15 min and then melt-mixed in the roller blade compounder at 175 °C at 75 rpm for 30 min. The mixture was then cooled to room temperature.

3.2.3. Trial 3

A large capacity (2500 cm³), high mixing speed (max. 2800 rpm) mechanical mixer (Figure 3.3), which had been manufactured in-house, was used. The mixing blade was modified (Figure 3.3b) to obtain good mixing. The mixer was heated with an IEC-N1471 bench top heater (Industrial Equipment and Control Pty Ltd., Australia) and the temperature of the mix was measured with a Cu/Con thermocouple.

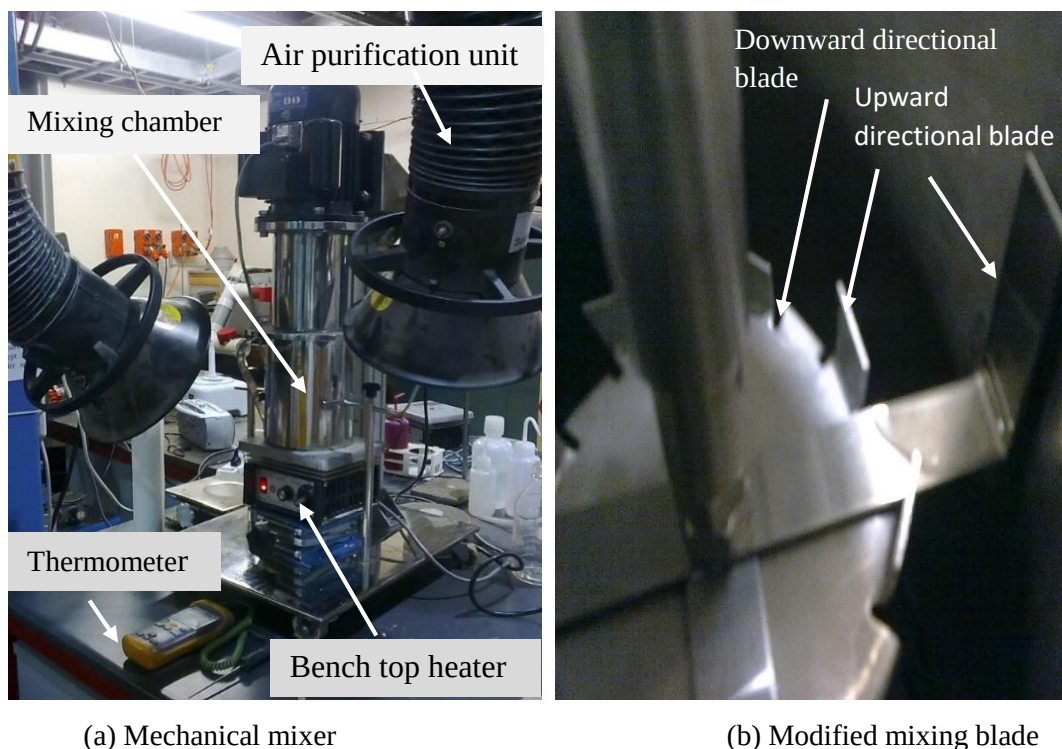


Figure 3.3: Mechanical mixer (manufactured in-house).

Known quantities (400 g) of 65:30:5 vol. % PEG:PVB:SA binder was dry mixed in the Kenwood mixer at room temperature at 25 rpm for 15 min and then melt-mixed in the mechanical mixer at 175 °C and 300 rpm for 30, 60 or 90 min. The binder system was then cooled to room temperature and granulated in a Castin granulator (CA-20VPE88, Hong Kong).

3.2.4. Trial 4

Known quantities (196 g) of the 65:30:5 vol. % PEG:PVB:SA was dry mixed in the Kenwood mixer at room temperature at 25 rpm for 15 min and then fed automatically at 25 g/min into a Thermo-Prism twin-screw extruder (Figure 3.4). The fine gap between the 15.6-mm diameter screws and 16-mm barrel provides a high-shear zone for mixing. Mixing characteristics depend on rotation (co-rotating or counter-rotating) and whether the screws intermesh. The twin screws of this extruder are counter-rotating and intermesh (Figure 3.5). Screws were operated at 70 rpm and the five heating zones along the barrel (feed to nozzle) were set at 160 °C – 177 °C – 170 °C – 160 °C – 147 °C. An extrusion-pass took approximately 10 min. The extruded mixture was cooled to room temperature and granulated. The granulated mixture was re-extruded twice to improve homogeneity.

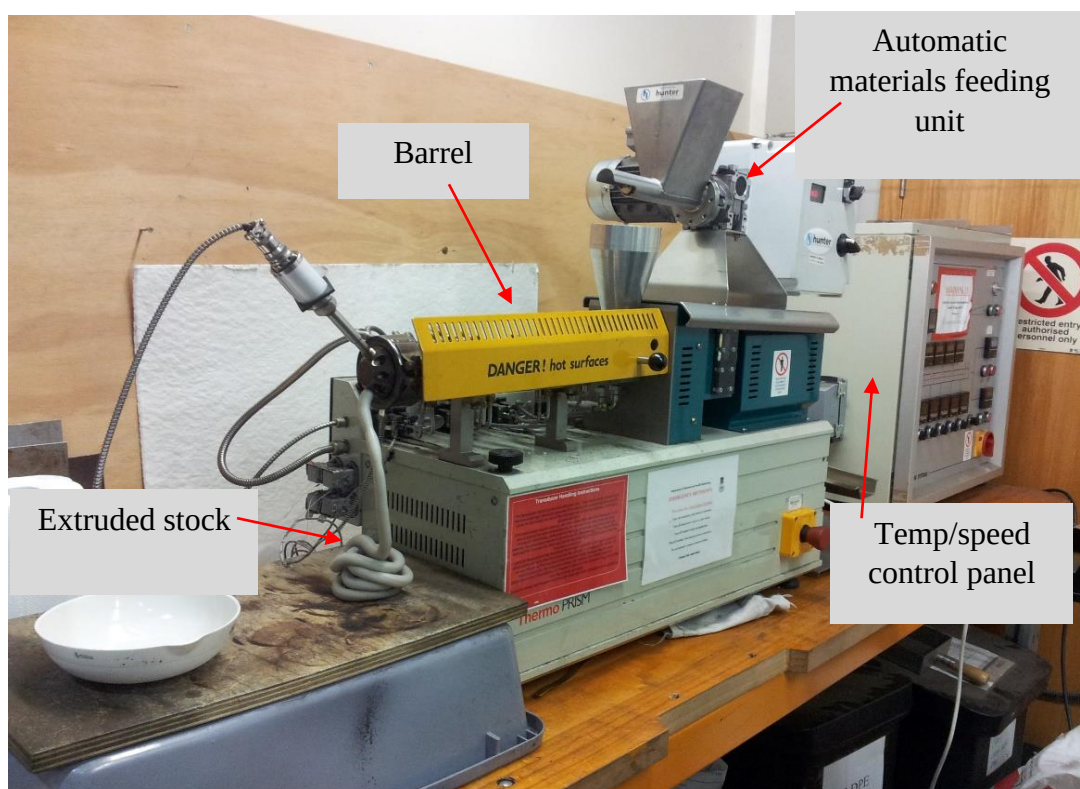


Figure 3.4: Thermo-Prism twin-screw extruder with an automatic feeder.

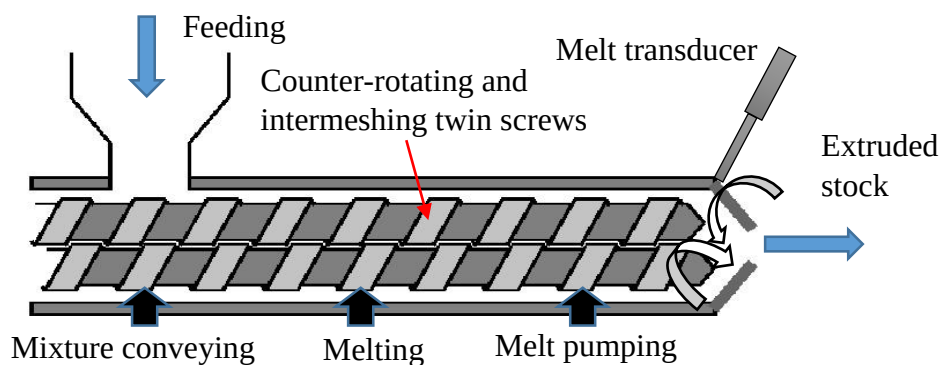


Figure 3.5: Schematic diagram of twin-screw extrusion.

3.2.5. Trial 5

To increase homogeneity, binder mix prepared by mixing in the mechanical mixer for 90 minutes (Trial-3) was extruded in the Thermo-Prism twin-screw extruder at a screw speed of 70 rpm and a temperature profile from feed to nozzle of 160 °C – 177 °C – 170 °C – 160 °C – 147 °C. The extruded mixture was cooled to room temperature and then granulated.

3.3. Assessing binder systems

3.3.1. Morphological analysis

Morphological images were obtained using an Olympus-BX60 optical microscope equipped with a digital camera. To eliminate surface contaminants and to obtain a flat surface, binder samples were processed in a Struers RotoPol-21 polisher at 150 rpm using three sequential steps with P600, P2000 and P4000 water resistant silicon carbide papers.

3.3.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) of random samples of the binder systems was done in triplicate in a SDT-2960 DTA/ TGA analyser (TA Instruments). Accurately weighed samples (about 5 mg) were heated from room temperature to 600 °C at 10 °C /min. Burn-out patterns obtained from the TGA were used to evaluate homogeneity of each binder system.

Thermogravimetric analysis of PEG was done by heating accurately weighed samples (about 5 mg) from room temperature to 120, 130, 140, 150 or 170 °C at 10 °C /min then holding them at the end temperature for one hour in a SDT-2960 DTA/ TGA analyser (TA Instruments). Thermogravimetric analysis of PVB and SA were done at 120 and 130 °C with one hour isothermal holding time at 120 and 130 °C.

3.4. Manufacturing feedstocks

Feedstocks were manufactured by dry-mixing the following combinations of pre-mixed binder with various ratios of HDH Ti-6Al-4V (Ti64) powder.

Binder systems:

PEG:PVB:SA 65:30:5, 75:20:5, 80:15:5 and 85:10:5 (vol. %)

Ti64 powder loadings 40 to 80 vol. %

A known weight (500 g) of Ti64 powder and binder components was dry-mixed in the Kenwood mixer at room temperature for 30 min at 25 rpm. The resultant dry mixture was then processed by one of two methods.

3.4.1. Method 1

In the initial trials, binder components (PEG:PVB:SA = 65:30:5 vol. %) were mixed with 40, 50, 55, 60, 65, 70 or 80 (vol. %) Ti64 powder to give a total of 500 g and

mixed in the Kenwood mixer. The mix was then divided into three approximately equal batches and manually fed at 25 g/min into the mixing chamber of the roller compounder, which had been preheated to 175 °C. After mixing for 45 min at 60 rpm, the feedstock was removed from the chamber, cooled to room temperature and granulated.

3.4.2. Method 2

28 Ti-MIM feedstocks were formulated using the following ratios of binder to powder:

PEG:PVB:SA	65:30:5, 75:20:5, 80:15:5 or 85:10:5 vol. %
Ti64 powder loadings	40, 50, 55, 60, 65, 70 or 80 (vol. %).

The feedstocks were manufactured using the following three sequential steps:

Stage 1 This stage helps increase feedstock homogeneity prior to melt mixing in the roller compounder. The dry mixture (500 g) obtained from the Kenwood mixer was placed in a plastic container containing 300, 6.3-mm stainless steel spheres (total weight 315 g). The container was placed on 100-cm long twin rollers (Figure 3.6) (the second roller was adjustable to accept different size containers) and mixed at 250 rpm for 16 hours at room temperature. Material covers on the rollers minimized slippage. After mixing, the mixture was divided into three approximately 165 – 167 g batches.

Stage 2 A batch of dry feedstock was fed into the preheated (125 °C) mixing chamber of a roller compounder and mixed at 60 rpm for 45 min at 125 °C. The batch was then removed, cooled to room temperature and granulated.

Stage 3 This stage enhanced homogeneity by melt-mixing the feedstock under extremely high shear mixing in a twin-screw extruder. Material (approx. 450 g after wastage) from stage-2 was automatically fed at 25 g/min into the Thermo-Prism twin-screw extruder operating at 150 rpm and with a barrel temperature profile (feed to nozzle) of 125 – 140 – 135 – 135 – 140 °C. Extruded feedstock was cooled to room temperature and granulated.

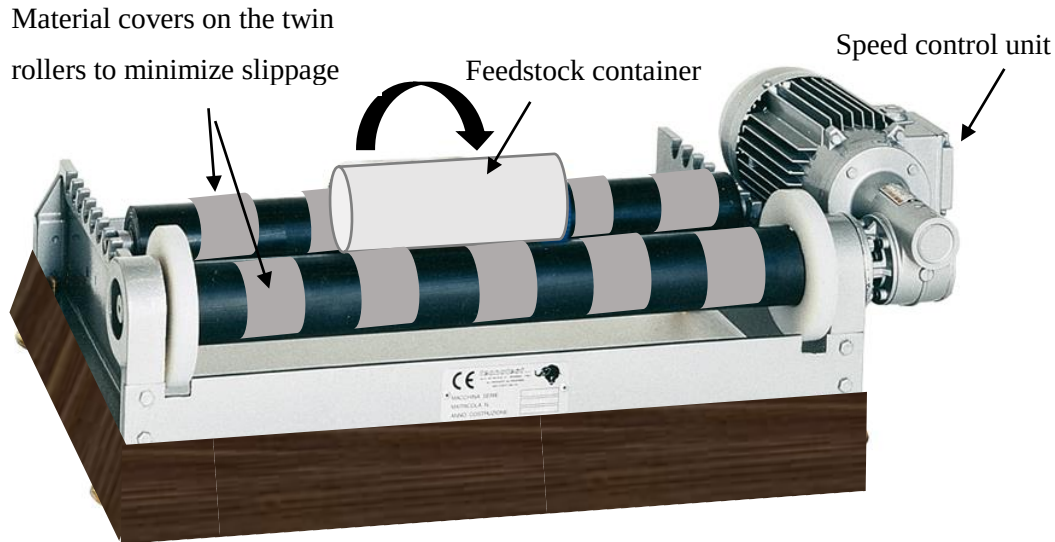


Figure 3.6: Schematic diagram of a roller mixer.

3.5. Powder loading

The effect of Ti64 powder loading on mixing-torque characteristic, density and viscosity of the Ti-MIM feedstocks were determined.

3.5.1. Bulk density

The weight of 25-mm diameter, 6-mm high disc samples of each of the Ti-MIM feedstocks manufactured using the two methods described in Section 3.4 was measured on a four decimal digital balance and density expressed as mass per unit volume. Data were expressed as the average of triplicate random samples. The deviation between measured and theoretical density was used to identify critical and optimal Ti64 powder loadings.

3.5.2. Mixing-torque

Changes in torque of the following Ti-MIM feedstocks with various Ti64 powder loadings were measured while being mixed in the roller compounder (Section 3.2, Trial-1).

65:30:5 PEG:PVB:SA from method 1

80:15:5 PEG:PVB:SA from method 2

The initial 68 g of feedstock was put into the roller compounder and mixed for 10 minutes. Further 5-g lots of Ti64 powder were then added at 10-min intervals to a total of 133 g.

3.5.3. Viscosity

The viscosity at 145 °C of the following feedstocks with various Ti64 powder loadings was determined using a Shimadzu CFT 500D capillary rheometer with a 1-mm diameter, 10-mm long capillary die.

65:30:5 PEG:PVB:SA using method-1

80:15:5 PEG:PVB:SA using method 2

3.6. Characteristics of Ti64 powder and feedstocks

3.6.1. Particle size

To measure particle size diameter distribution, 16 g of Ti64 powder were dispersed in water and analysed in a Malvern Mastersizer 2000 laser-scattering instrument with a detection range of 0.02 – 2000 µm.

3.6.2. Thermogravimetric analysis

Thermographs of the following Ti-MIM feedstocks were produced using a SDT-2960 DTA/ TGA analyser (TA Instruments). Four representative samples were taken at various stages of feedstock preparation. Each sample (about 20 mg) was heated from room temperature to 600 °C at 10 °C /min.

65:30:5 vol. % PEG:PVB:SA with 60 vol. % Ti64 powder from method 1

80:15:5 vol. % PEG:PVB:SA with 60 vol. % Ti64 powder from method 2

3.6.3. Feedstocks density

The density of five random samples of the following feedstock formulations collected at various stages in the feedstock manufacturing process were measured in an Ultra pycnometer 1000 (Quantachrome Instruments, USA).

65:30:5 vol. % PEG:PVB:SA with 60 vol. % Ti64 powder from method 1

80:15:5 vol. % PEG:PVB:SA with 60 vol. % Ti64 powder from method 2

The pycnometer cell volume was calibrated and the calibrated results were recorded automatically before measuring the density. A known weight of feedstock (about 7 g) was placed inside the sample cell and triplicate density readings taken.

3.6.4. Morphology of Ti64 powder and feedstocks

The morphology of Ti64 powder particles and following feedstock samples were

determined using a Hitachi S 4700 scanning electron microscope.

65:30:5 vol. % PEG:PVB:SA with 60 vol. % Ti64 powder from method 1

80:15:5 vol. % PEG:PVB:SA with 60 vol. % Ti64 powder from method 2

Samples were fastened with conductive carbon tape to aluminium mounts. A water-based PST carbon graphite adhesive was applied and the samples were subsequently platinum ion sputter coated.

3.7. Rheological characteristics

A Shimadzu CFT 500D capillary rheometer was used to determine the effect of different binder systems, Ti64 powder loadings and processing conditions on the rheological properties of Ti-MIM feedstocks (Table 3.2).

Table 3.2: Ti-MIM feedstocks for rheological investigations

Binder system (PEG:PVB:SA, vol. %)	65:30:5	75:20:5	80:15:5	85:10:5
Powder loading (vol. %)	55, 50	55, 60, 65	55, 60, 65	55, 60

The rheometer was operated at 20, 40, 60, 100, 160, 305 and 485 N to obtain a wide range of shear stresses and shear rates. Feedstocks were preheated for 300 seconds and readings taken between 3 mm and 7 mm. The following capillary dies were used for feedstock extrusion:

1-mm diameter x 10-mm long

2-mm diameter x 5-mm long

3-mm diameter x 3-mm long

A 3-g sample was fed into the rheometer barrel that had been preheated to 125, 145, 165 or 185 °C. A die-stopper, screwed under the capillary die to avoid losing the sample, was removed 10 seconds before extrusion. Data were reported as the average of triplicate samples.

3.8. Injection moulding and Ti-MIM processes

The following binder systems were used for injection moulding and subsequent solvent debinding, thermal debinding and sintering process to produce Ti-MIM parts:

PEG:PVB:SA 75:20:5, 80:15:5 and 85:10:5 (vol. %)

3.8.1. Injection moulding

A BOY– 35A (BOY, Germany) injection moulding machine (Figure 3.7) was used to produce test specimens from various Ti-MIM feedstocks (Table 3.3). The feed-to-nozzle temperatures were set at 125 – 130 – 135 – 140 – 145 °C and backpressure and feed length to 5 bar and 22.5 mm respectively. Feedstock (400 g) was manually fed into the machine at 20 g/min, preheated for 5 min and then injected into the mould that had been preheated to 65 °C. Test specimen dimensions are in Figure 3.8.

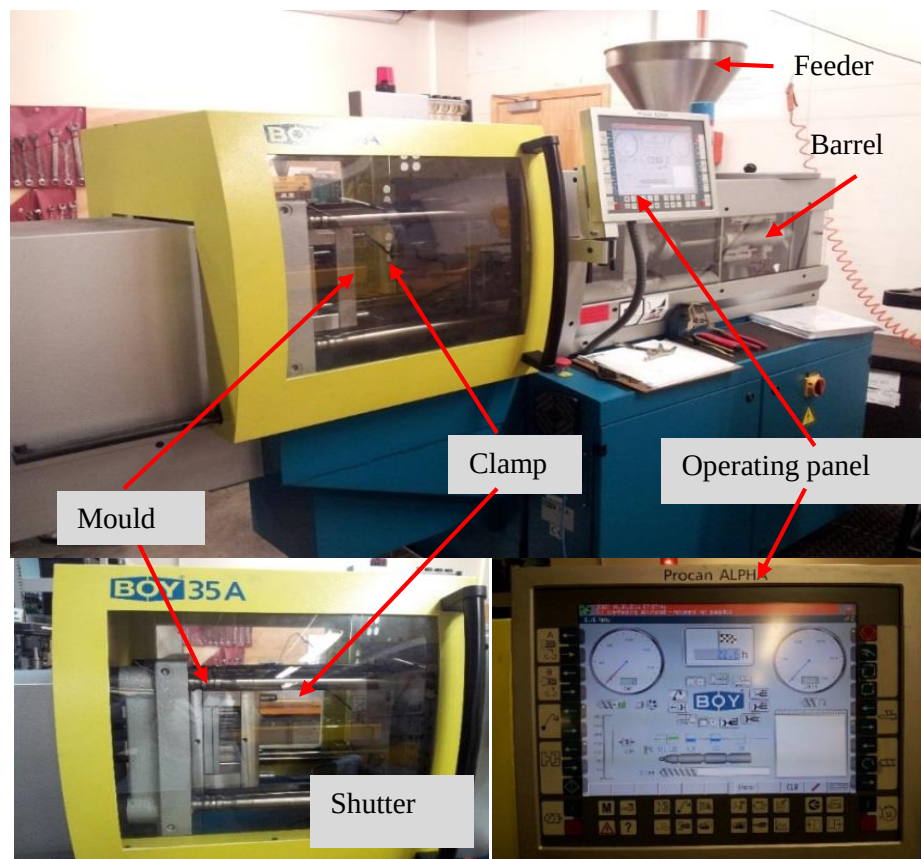


Figure 3.7: Injection moulding machine (BOY–35A).

Table 3.3: Feedstock formulations used for Ti-MIM.

PEG:PVB:SA (vol. %)	Ti64 Powder loading (vol. %)			
75:20:5	50	55	60	65
80:15:5	50	55	60	65
85:10:5	50	55	60	65

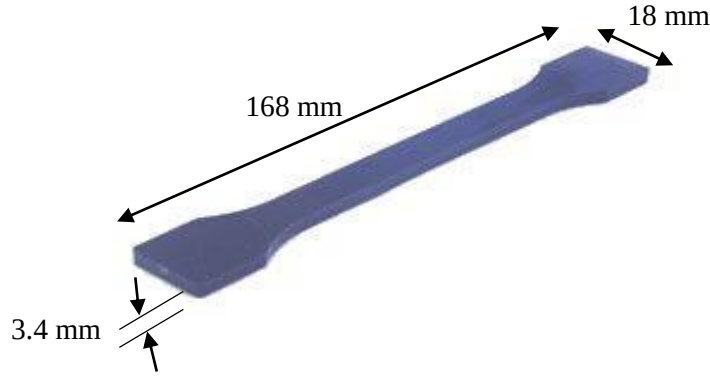


Figure 3.8: Dimension of an injection moulded test specimen.

3.8.2. Solvent debinding

The effect of temperatures and debinding time on removing the water-soluble binder component (mainly PEG, the major component) were investigated. Moulded parts were made from 60 vol. % Ti64 powder and the following binder systems, which had been identified from rheological information.

PEG:PVB:SA, vol. %: 75:20:5, 80:15:5, or 85:10:5

The 6-L solvent debinding tank, with supports to hold the samples, and a 5-L reservoir (Figure 3.9) were filled with deionized water. Samples, which had been oven dried for 5 hours at 50 °C, were placed on the sample supports. Water heated to 35, 45 or 55 °C was pumped at 1.5 L/min through the system. Triplicate samples were taken from the debinding tank at 0.5, 1, 2, 4, 6, 10, 16 and 24 hours and oven dried at 50 °C for 24 hrs. Total dissolved solids (TDS) in the water were measured with a TDS-3 digital meter (HM Digital, Inc., USA).

3.8.3. Thermal debinding and sintering

Any binder remaining in the test specimens was removed by thermal debinding and sintering to obtain the final densified metallic product.

- **Thermal debinding**

Thermal debinding and sintering was done in ACME, GDQ S-400 high-vacuum sintering furnace (Advanced Corporation for Materials and Equipment, China) with a 1000 x 500 x 450 mm chamber. It could reach 1600 °C and operate under a vacuum 10^{-3} Pa (Figure 3.10).

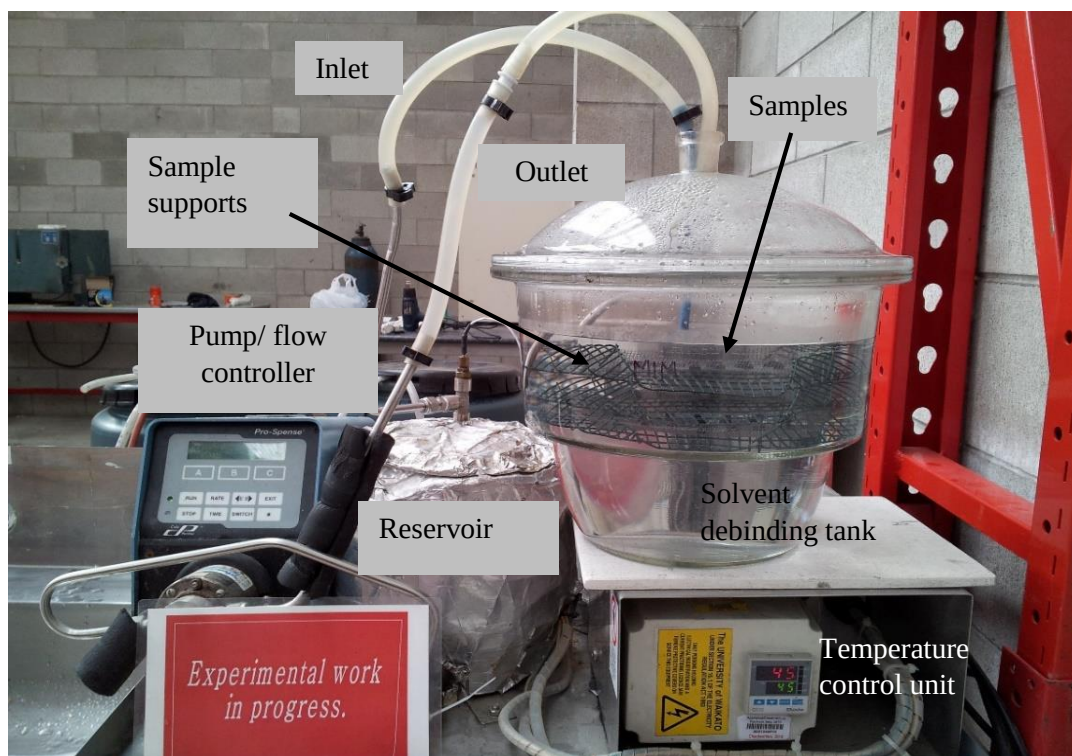


Figure 3.9: Water debinding equipment (manufactured in-house).

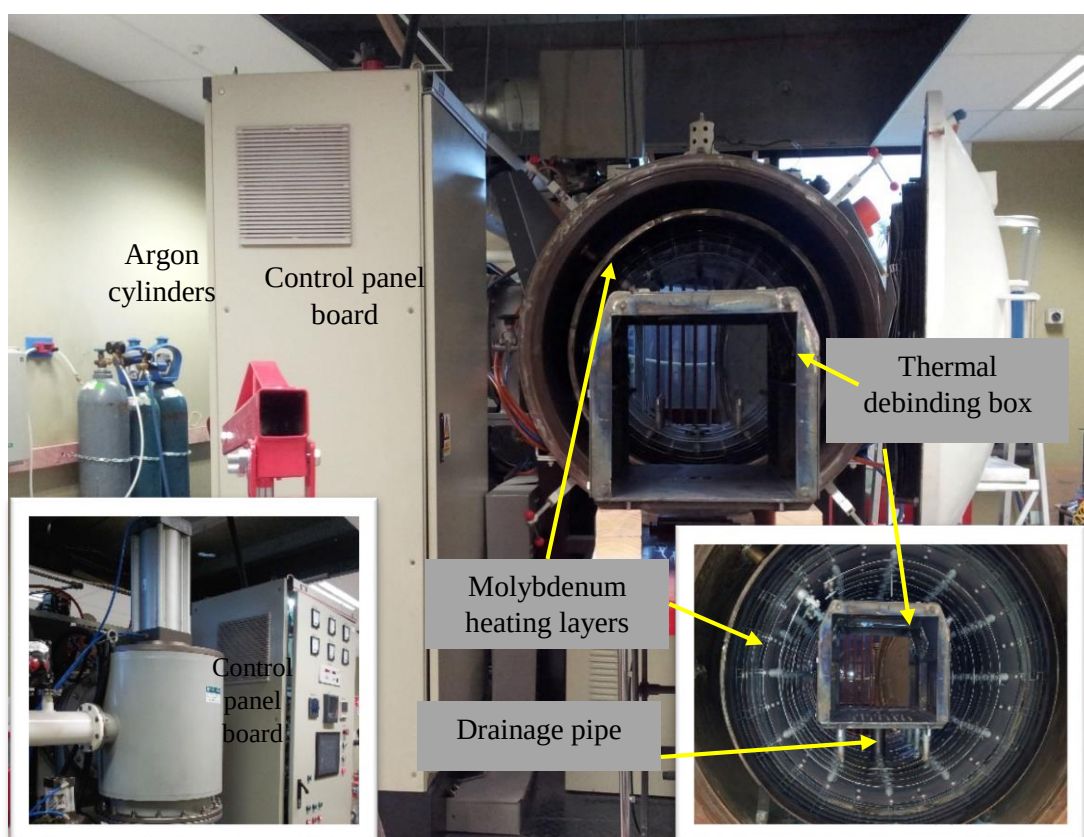


Figure 3.10: ACME, GDQ S-400 high vacuum sintering furnace.

A thermal debinding box placed inside the furnace. A pipe was connected to the furnace disposal system to safely collect the debound binders. The samples were placed inside the thermal box and closed. After closing the furnace, thermal debinding was done under argon and a specific heating profile (Table 3.4).

Table 3.4: Heating profile for thermal debinding.

Steps	Start temp. (°C)	Heating rate (°C/min)	Finish temperature (°C)	Duration (min)
1	25	2	200	88
2	200	0	200	60
3	200	3	320	40
4	320	0	320	60
5	320	5	550	46
6	550	0	550	30
7	550	5	800	50
8	800	0	800	30
9	800	-10	550	25
10	550	Cooling	25	

- **Sintering**

After thermal debinding, samples were sintered. The box and binder drain were removed from the furnace and the debound samples were carefully transferred from the box to a molybdenum sintering plate. The plate was then placed inside the furnace, the furnace was closed and 10^{-3} Pa vacuum was applied. The sintering was done under high vacuum and a specific heating profile (Table 3.5).

Table 3.5: Heating profile for sintering.

Steps	Start temp. (°C)	Heating rate (°C/min)	Finish temperature (°C)	Duration (min)
1	25	10	800	78
2	800	5	1300	100
3	1300	0	1300	180
4	1300	-15	550	50
5	550	Cooling	25	

3.9. Characterising moulded, debound and sintered parts

The density of 5 x 5 x 3.4 mm samples cut from different regions injection-moulded, debound and sintered specimens (60 vol. % Ti64 powder) were measured with a pycnometer (see Section 3.6).

The SEM images of samples of moulded, debound and sintered specimens (60 vol. % Ti64 powder) were obtained using a Hitachi S 4700 SEM. The sintered Ti64 samples were cut with an electric discharge machining (EDM) wire cutter (Sanxing Machinery and Xufeng Tec Co., Ltd., China) and mounted at room temperature onto a cylindrical sample holder using 4:1 epoxy resin and hardener. The samples were polished using a six-step sequential process with P120, P320, P600, P1200, P2000 and P4000 grit water resistant silicon carbide papers. The ground surface was then polished with a 0.3- μm particle size alumina dispersion to a ‘mirror’ finish. The samples were then etched using Kroll’s solution (2 ml HF, 6 ml HNO_3 and 92 ml distilled water).

Samples for tensile testing (Figure 3.11) were cut from the sintered specimens using an EDM wire cutter. The rough surfaces were polished using a Struers RotoPol–21 polisher. An Instron 33R4204 universal tensile testing machine with a 4.8 kN load cell was used to measure tensile test of triplicate sintered specimens from each feedstock at room temperature using a strain rate $8.3 \times 10^{-5} \text{ s}^{-1}$. Strain was recorded using a 10-mm gauge length extensometer.

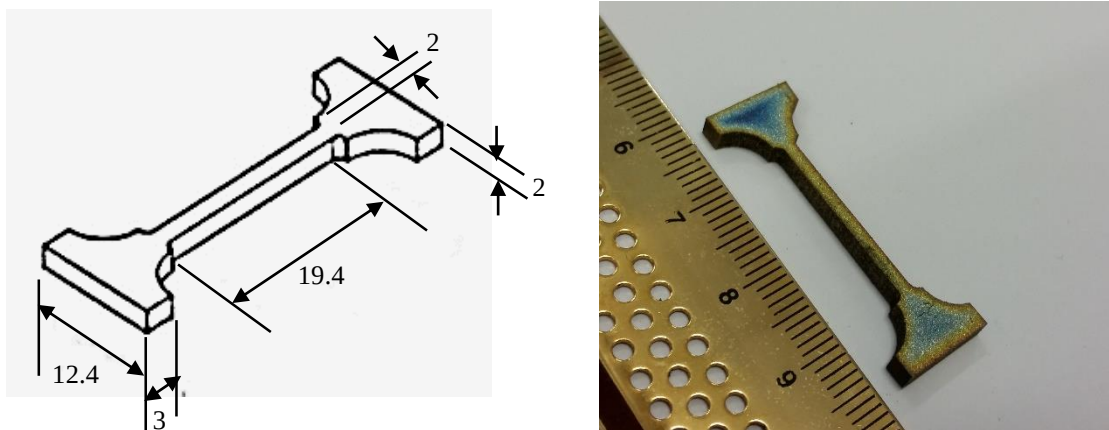


Figure 3.11: Dimension of a tensile testing specimen (mm).

The oxygen content of the following Ti64 powder, injection moulded (green) and sintered samples were determined using the LECO inert gas fusion method at Durkee Testing Laboratories, Inc. USA. Sintered specimens were cut into 10 x 10 x 3 mm rectangular prisms (weight >1 g) with an EDM wire cutter. The six sides were polished using a Struers RotoPol–21. The following samples were tested to evaluate the effectiveness of the Ti-MIM process and to find an optimised binder system:

- Ti64 starting powder
- A green and a sintered sample made from 75:20:5, 80:15:5 and 85:10:5 (vol. %) PEG:PVB:SA binder and 60 vol. % Ti64 powder

Chapter Four: Results and Discussion

This chapter discusses results obtained from the various trials to identify binder formulations and processing conditions that will produce feedstocks for Ti64-MIM that produce finished parts with minimum defects. Models are proposed for predicting suitability of binders and Ti64-MIM feedstocks.

4.1. Binder systems

Thermal properties of binder components (PEG, PVB, and SA) were studied using differential thermal analysis (DTA) and thermogravimetric analysis (TGA). Melting point profiles and thermal degradation data for each component were used to identify suitable mixing temperatures to manufacture binder used for Ti-MIM feedstocks.

4.1.1. Thermal analysis

The molecular weight of PVB (Figure 4.1) is higher (50000 – 80000 g/mol) than PEG (7500 – 8800) and SA (285).

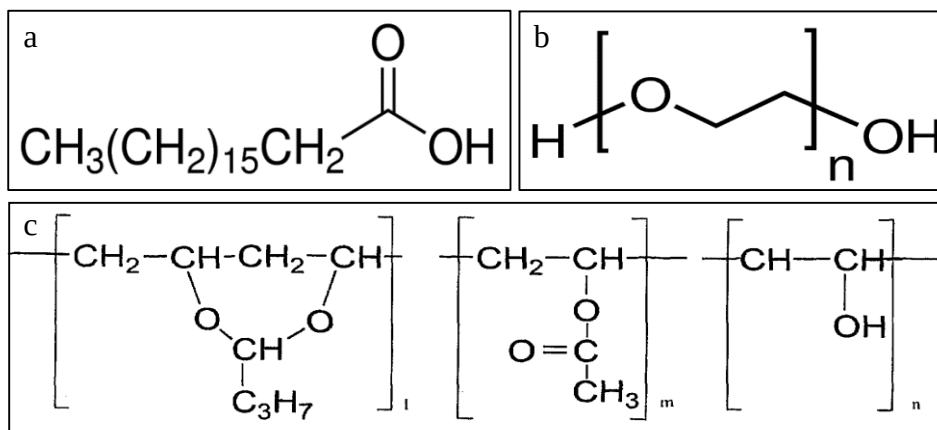


Figure 4.1: Chemical structure of (a) SA, (b) repeating unit in PEG, and (c) repeating unit in PVB [186, 189].

Thermal analysis of the components was limited to 300 °C, the temperature at which titanium starts to react with oxygen. The PEG has an endothermic peak (indicating melting) at 63.8 °C and begins to degrade at about 194 °C (Figure 4a). Weight loss was 1.23% at 194 °C and 71.2% at 300 °C. The SA has similar thermal characteristics (Figure 4.2b), melting at 71.81 °C and beginning to degrade at 190 °C with 0.63% weight loss. At 300 °C, there was 94% weight loss. In contrast, PVB has no definite

melting point (i.e. is amorphous), had lost 1.5% when it began to degrade at 205 °C and only 6% at 300 °C (Figure 4.2c). Salam *et al.* [186] reported similar thermal data for PVB.

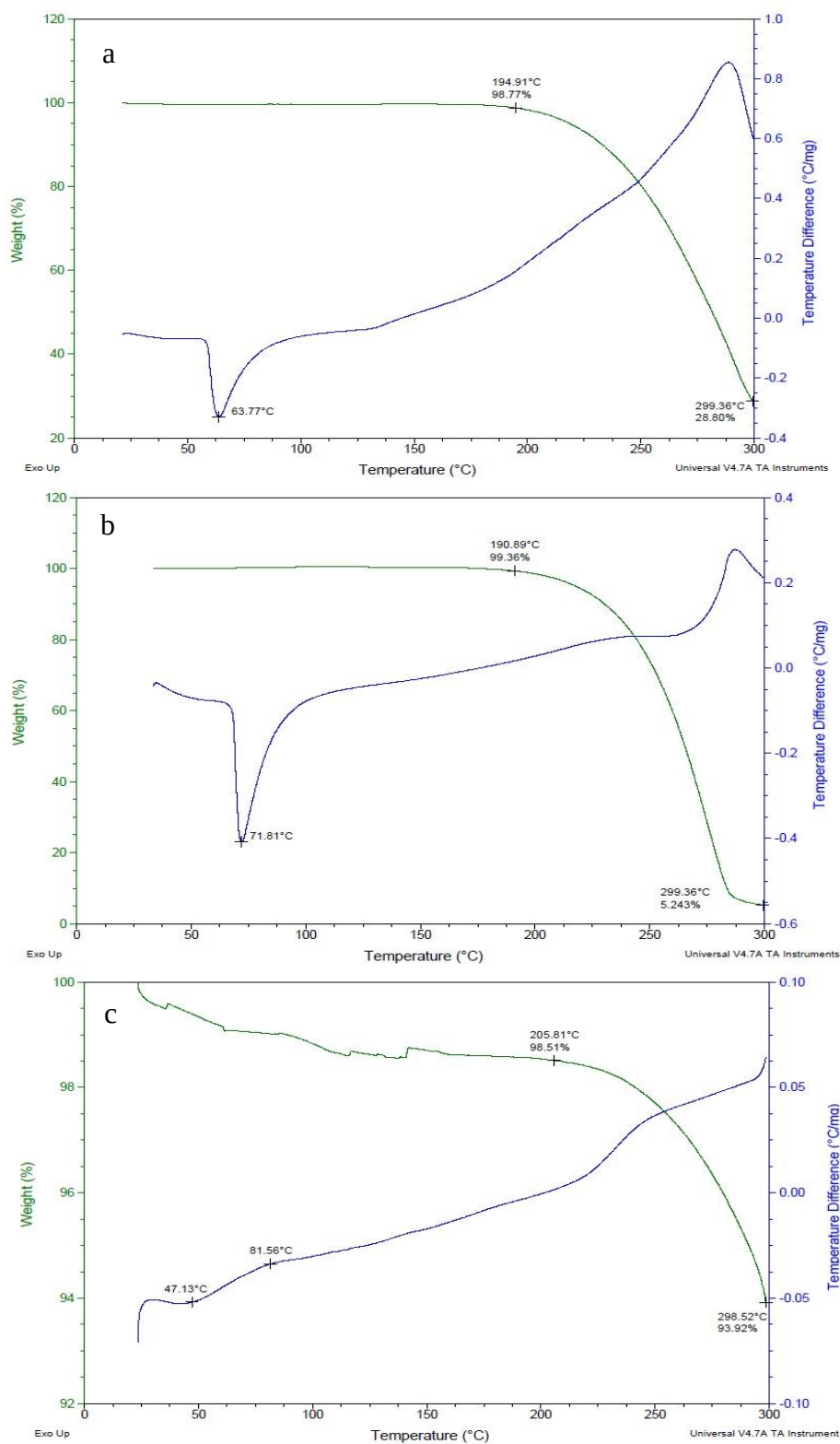


Figure 4.2: Thermal analysis of (a) PEG, (b) SA and (c) PVB.

The three binder components started degrading between 190 and 205 °C (Table 4.1) so binder should be mixed below 190 °C. PEG and SA have similar melting points (Table 4.1), indicating that a mixing temperature of about 75 °C would be suitable.

Table 4.1: DTA-TGA characteristics of binders.

	PEG	SA	PVB
Melting point (Mp/ °C)	63.8	71.8	165-185
Onset degradation temp (T _{od} / °C)	194	190	205
Degradation temperature range (°C)	194 – 425	190 – 425	205 – 525
Weight loss at T _{od} (%)	1.23	0.63	1.5
Weight loss at 300 °C (%)	71.2	94	6

Although all three binder components had lost very little weight ($\leq 1.5\%$; Table 4.1) at onset degradation temperature (T_{od}), both PEG and SA had degraded significantly when the temperature reached 300 °C. PVB, which is produced by reacting polyvinyl alcohol (PVA) with butyraldehyde, contains PVA and polyvinyl acetate (PVAc) [185-187, 189]. The low weight loss may be because any cyclic and cross-linked structures formed, break down at a higher temperature than a linear chain polymers, delaying formation of volatile products to a higher temperature [186].

The thermal data indicate the PEG and SA content of a binder made using these three components would be low at 300 °C, which could significantly increase binder and feedstock viscosity. To facilitate wetting the Ti64 powder, mixing temperature when adding the Ti64 powder must be higher than the melting point of the binder. The PEG and SA in the binder would have started to degrade at the melting point of PVB, creating problems. This phenomenon has been discussed by Thomas and Marple [179]. To balance the higher melting point of PVB and limit PEG and SA degradation, a binder with 65:30:5 vol. % PEG:PVB:SA was used in trials to investigate processing conditions at 175 °C (section 4.1.2).

Thermal degradation patterns (Figure 4.3) indicate that about 16% of the initial PEG had been lost when the temperature reached 190 – 225 °C (stage 1), 67% at 225 – 285 °C (stage 2) and 17% at 285 – 425 °C (stage 3). The SA had lost 7%, 85% and 8% at these three stages and PVB had lost 0%, 6% and 67%. The 27% of initial PVB

remaining at 425 °C will help retain the shape of the moulded part after debinding (Table 4.2). The significant weight loss of PEG (67%) and SA (85%) between 225 – 285 °C indicates mixing should not be done in this temperature range when using this binder for Ti-MIM. As only 6% of PVB was lost at this temperature it was used as the backbone polymer to give the green part mechanical strength. The PVB helps retain the shape even when the temperature reaches 425 °C (27% remaining, Table 4.2) and provides handling strength when transferring the brown parts to sintering.

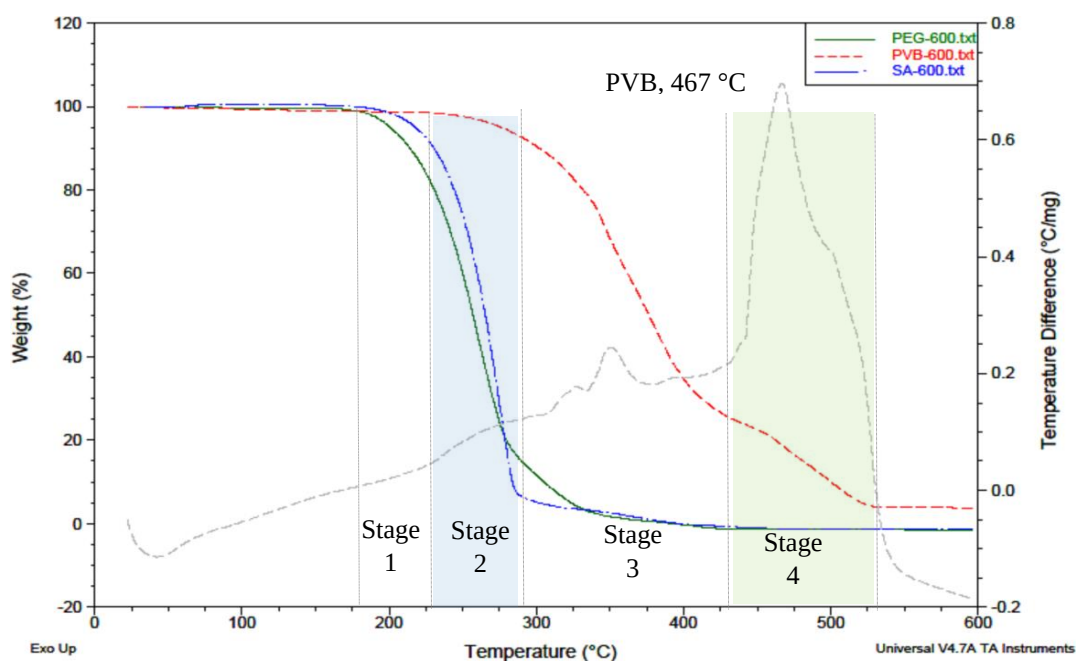


Figure 4.3: DTA-TGA profile of PVB, PEG and SA showing four degradation stages.

Table 4.2: Weight loss of binder components at different degradation stages.

Stage	Temp. (°C)	Weight loss (%)		
		PEG	PVB	SA
Stage 1	190 – 225	16	0	7
Stage 2	225 – 285	67	6	85
Stage 3	285 – 425	17	67	8
Stage 4	425 – 525	-	23	-

About 4% of PVB remained at 525 °C. The high energy (≈ 720 kJ/g mol) cyclic and cross-links in this unsaturated hydrocarbon are only broken at higher temperatures (400 – 500 °C) [329, 381]. There was a high exothermic peak at 467 °C (Figure 4.3; stage 4) after the main PVB degradation in stage 3 (285 – 425 °C), indicating oxidative

break down of the cyclic and cross-linked structures that had developed in stages 2 and 3 (Figure 4.3) and supports findings reported by Salam *et al.* [186].

The thermal analyses of the binders helped identify a system suitable for debinding and sintering. Individual binder components must burn out at different temperatures so they can be removed in sequentially stages without distorting the moulded part.

4.1.2. Effect of process conditions on homogeneity

The effect of different mixers and processing conditions to produce a homogeneous PEG, PVB and SA (65:30:5) binder was investigated. Torque measures resistance on the rotating blades and indicates degree of homogeneity [191] and decreased fluctuations in torque often indicate a mixture may be becoming more homogeneous.

(a) Binders manufactured in the roller compounder

Mixing torque increased in the first 5 min in the roller compounder operating at 175 °C and 30 rpm (Figure 4.4), indicating resistance as binder components were added, melting occurred at the surfaces, and particles coalesced into agglomerates [330].

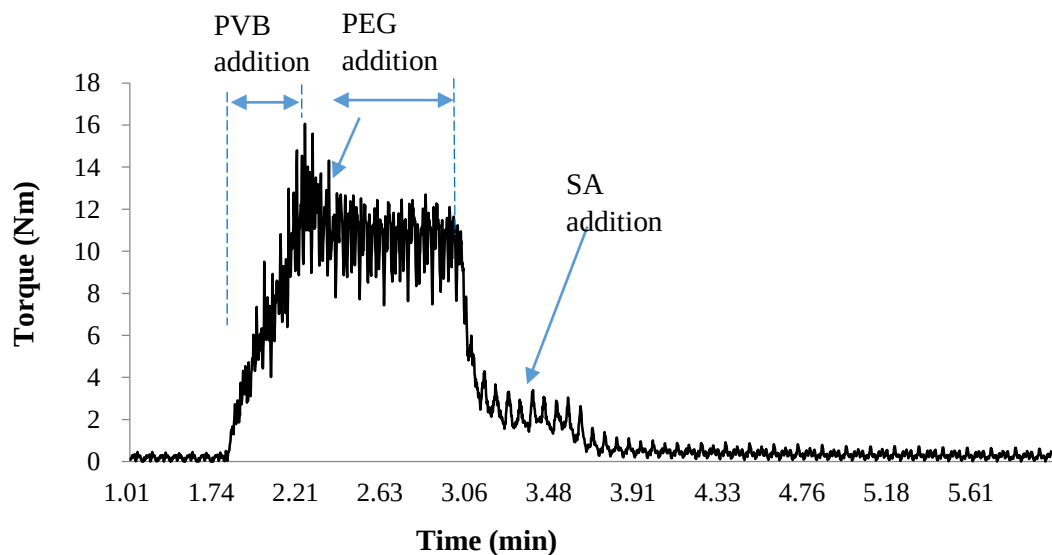


Figure 4.4: Torque at the start of mixing binder components at 175 °C and 30 rpm in the roller compounder.

After all components had been added, torque decreased with further mixing as binder agglomerates broke and binder became well mixed (Figure 4.5). The relatively

constant torque, which occurred after 5 min mixing (Figures 4.4 and 4.5), indicated increased bulk homogeneity [2]. This pattern is similar to the 3 – 15 min mixing Bousmina *et al.* [330] reported to obtain steady state (constant torque).

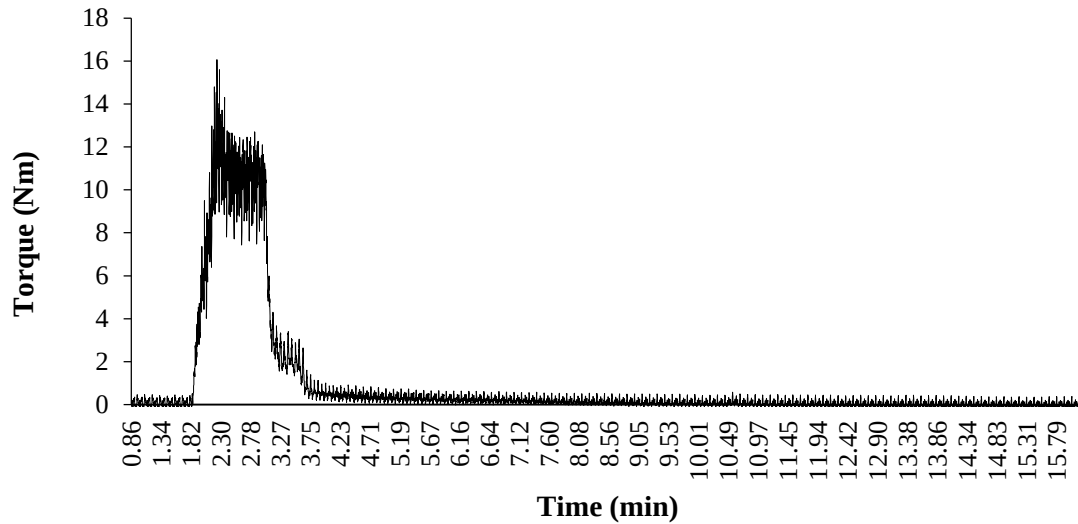


Figure 4.5: Torque for the complete process of mixing binder components at 175 °C and 30 rpm in the roller compounder.

Although the smaller fluctuation in mixing torque (Figure 4.5) suggested the binder mix was homogenous after 5 min mixing, visual inspection indicated samples had PEG and PVB regions as was heterogeneous (Figure 4.6).

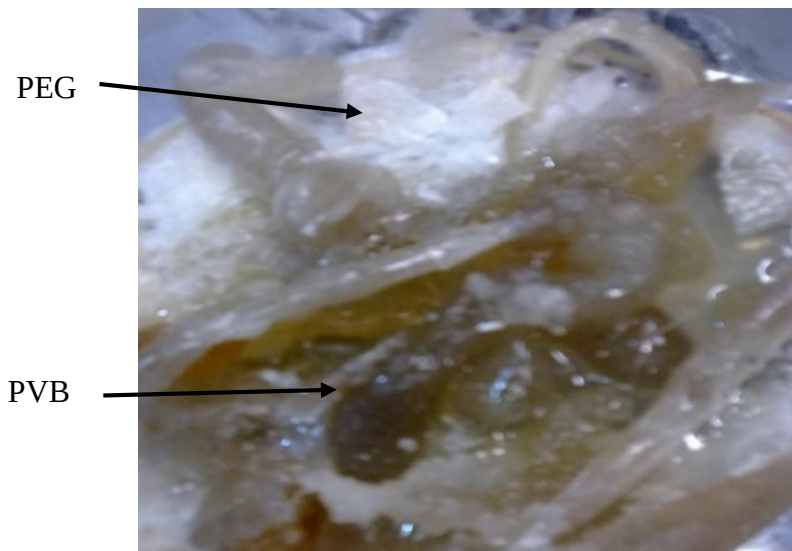


Figure 4.6: Heterogeneous nature of the binder produced in the roller compounder at 175 °C and 30 rpm for 15 min of mixing.

The heterogeneity could be due to one or more of the following reasons: (1) complexity in the thermal behaviour of PVB (explained in section 4.1.1) and its immiscibility with PEG and SA, (2) mixing geometry of the roller compounder, and/or (3) insufficient mixing. Although high shear is created as the roller blades shear the binder mixture at the mixing chamber wall, there is lower shear in other regions so only a small portion of binder mix experiences sufficient shear to break agglomerates. This effect has been reported by Todd *et al.* [331]. Mixing times reported for similar compounders vary from 30 to 120 min [3, 115-117, 202-203, 332]. Therefore, further trials were done to investigate the effect of mixing time in the roller compounder. Binder components were added sequentially, starting with PVB, the highest melting point binder (Table 3.1).

Torque data when processing for 60 (Figure 4.7) or 80 min (Figure 4.8) indicate steady state was obtained after 5 min mixing. However, torque data indicated it took 13 min to obtain steady state when dry mixing the binder before putting it in the roller compounder (Figure 4.9) even though the mixing speed was higher (75 rpm compared with 30 rpm). Mixing torque was stable until 28 min mixing then decreased slightly (which could be due to binder agglomerates breaking further). At least 30 min of mixing was required to produce a homogenous PVB-PEG binder in the roller compounder.

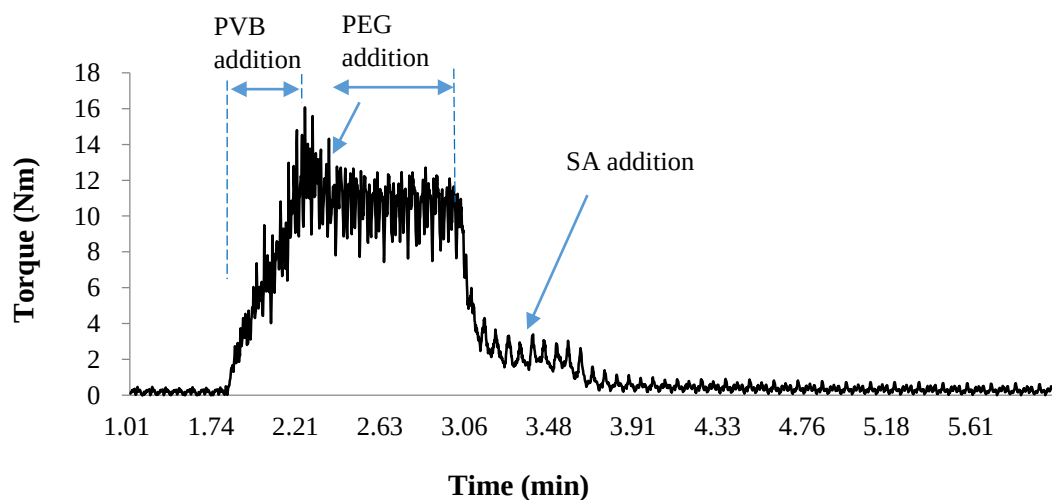


Figure 4.7: Torque at the start of mixing binder components for 60 min at 175 °C and 30 rpm in the roller compounder.

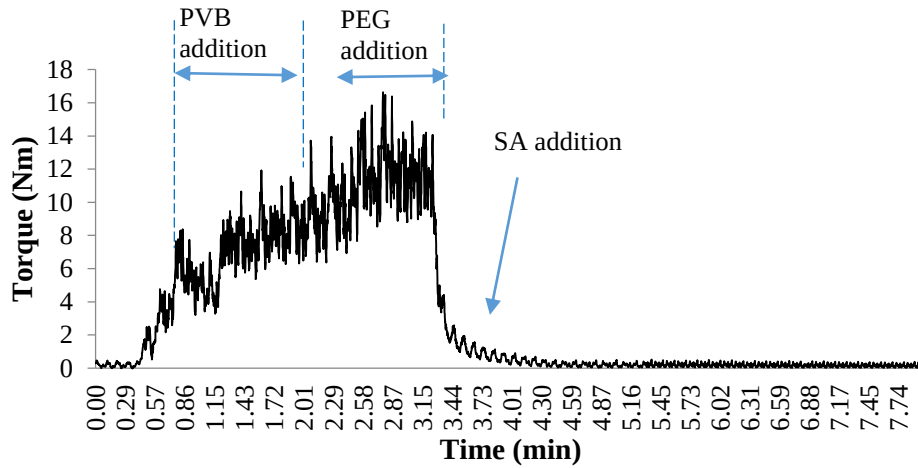


Figure 4.8: Torque at the start of mixing binder components for 80 min at 175 °C and 30 rpm in the roller compounder.

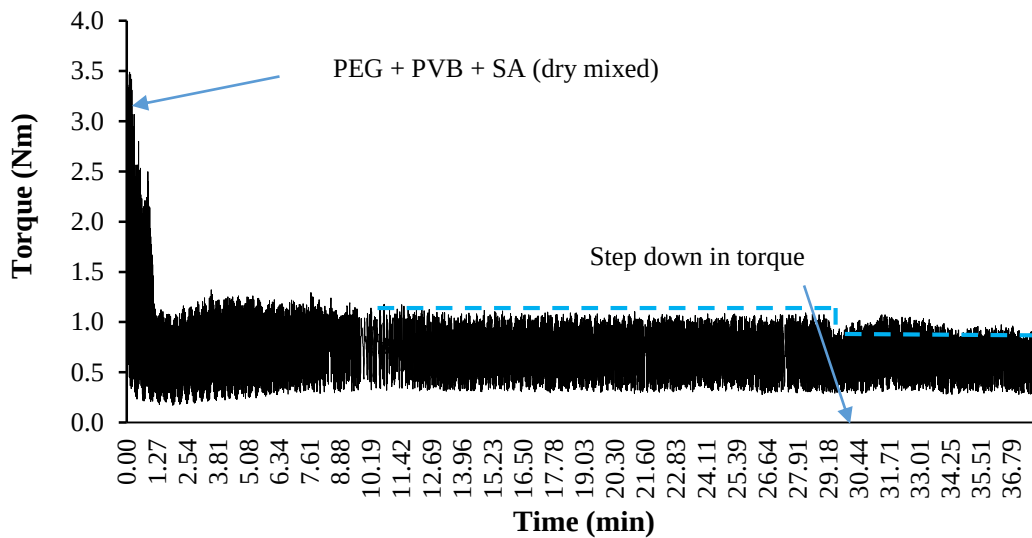


Figure 4.9: Torque when dry mixing binder components at 175 °C and 75 rpm in the roller compounder.

Optical microscope images (Figure 4.10) indicate distinct PEG and PVB regions still existed. Cracks in the PEG regions (Figure 4.10b) are due to PEG brittleness. The PVB agglomerates and particles were not uniformly distributed, especially when mixed at 30 rpm. Increasing mixing speed to 75 rpm increased homogeneity of the binder at 30 min (Figure 4.10d, d') and material could be extracted from the mixing chamber more easily. Steady state torque for data in Figures 4.5, 4.7 and 4.8 had less noise (fluctuation) than data in Figure 4.9. The noise indicates the mixture had more undispersed agglomerates (Section 4.1.2a). Therefore, torque data from a compounder or similar batch mixer with twin roller blades is not a good indicator for mixture homogeneity.

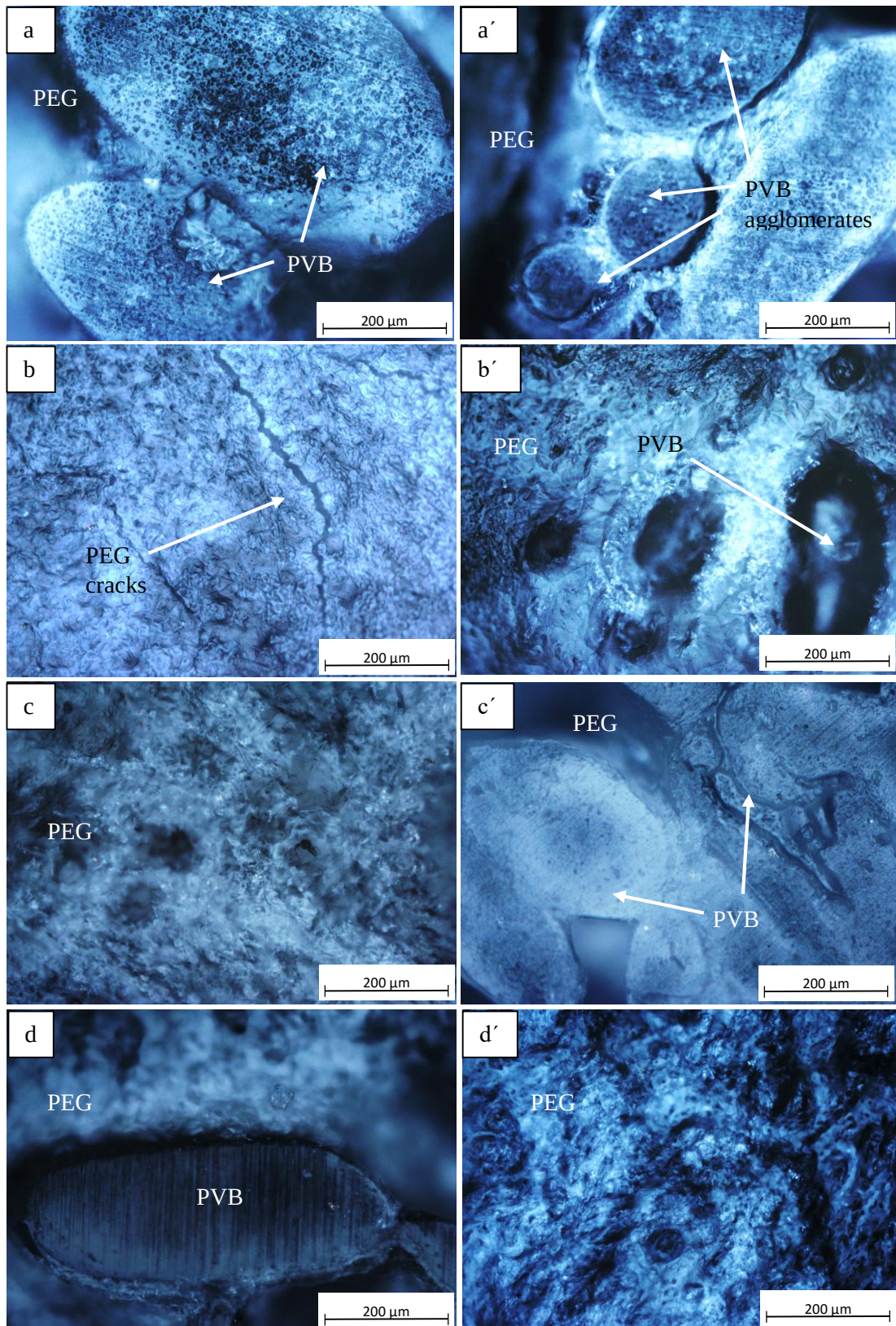


Figure 4.10: Optical microscope images showing the effect of mixing speed and time on microstructure of 65:30:5 vol. % PEG:PVB:SA binder at 175 °C: (a, a') 30 rpm, 30 min mixing; (b, b') 30 rpm, 60 min mixing; (c, c') 30 rpm, 80 min mixing; and (d, d') 75 rpm, 30 min mixing. The insoluble PVB agglomerates appear as light regions in the dark PEG matrix. Cracks in the PEG regions are due to brittleness.

The composition of polymer systems can be obtained from DTA analysis [333, 334]. Thermal characteristics are obtained by comparing temperature differences ($^{\circ}\text{C}/\text{mg}$) between the polymer and the reference pan. During an exothermic reaction, polymers release heat (positive peak). The amount of heat released depends on sample weight so exothermic peaks will indicate the amount of binder burnt out. This information allows exothermic (oxidation) peaks of binder components to be compared.

Each binder component had different thermal behaviour (Figure 4.11) caused by structural changes during heating. All binders had two exothermic peaks between 200 – 350 $^{\circ}\text{C}$ and 350 – 500 $^{\circ}\text{C}$. The first exothermic peak for PEG was higher than the second but the opposite occurred for PVB. The two exothermic peaks for SA had similar values and occurred between 200 – 400 $^{\circ}\text{C}$. These exothermic peaks indicate the binder is oxidizing at different bond energy levels [186, 329, 381].

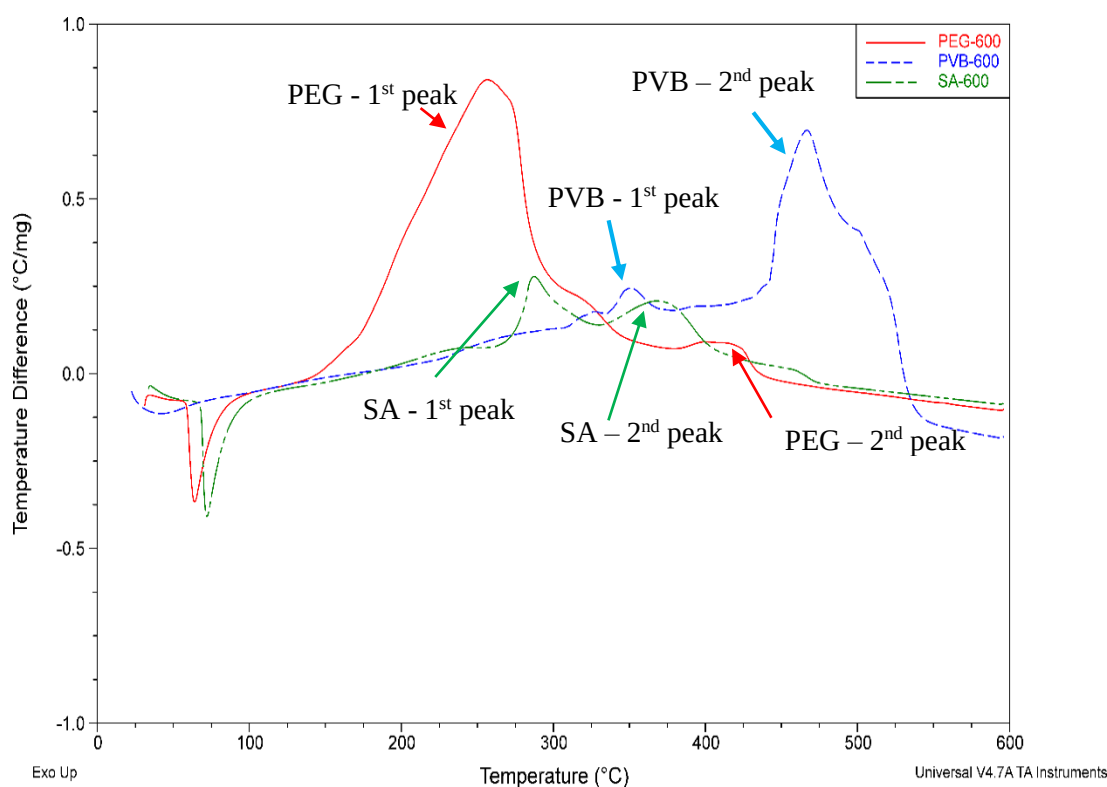


Figure 4.11: Differential thermal analysis of PEG, PVB and SA

The DTA characteristics of each component can help indicate binder homogeneity. Burn-out profiles of four randomly selected samples (Samples 1, 2, 3 and 4 in Figure 4.12) from binder manufactured at 175 $^{\circ}\text{C}$ and 75 rpm in the roller compounder were different, indicating the binder is heterogeneous. Sample 1 did not have the two

exothermic peaks (third circle in Figure 4.12b) of pure PVB (Figure 4.11), indicating that the second oxidative breakdown (section 4.1.1) of cyclic and cross-linked unsaturated hydrocarbon bonds in PVB did not occur. The profile also indicates this sample had no PVB but did contain PEG, as indicated by the prominent exothermic peak between 200 – 350 °C (Figure 4.11).

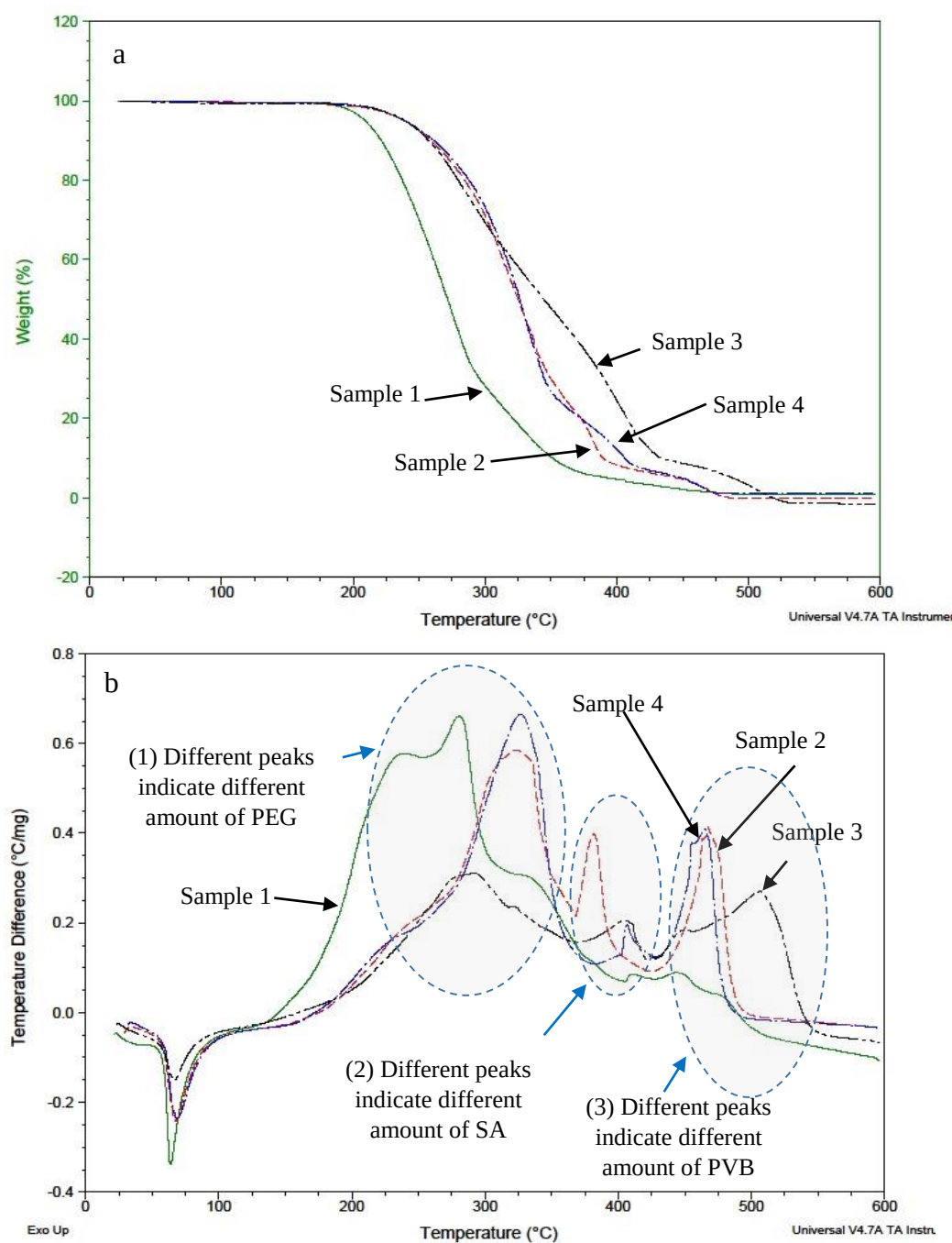


Figure 4.12: Burn-out patterns of 65:30:5 vol. % PEG:PVB:SA binder manufactured at 175 °C and 75 rpm in the roller compounder: (a) TGA and (b) DTA.

Binder manufactured at 175 °C in the roller compounder was not homogenous. The thermal data indicated that Sample 1 had less PVB than the other three random samples (third circle in Figure 4.12b) and sample 3 had less PEG than samples 1, 2 and 4 (first circle in Figure 4.12b). All four samples had different amounts of SA (second circle in Figure 4.12b).

(b) Binders manufactured at 175 °C in the mechanical mixer

As homogenous binder could not be manufactured in the roller compounder (Section 4.1.2 a), a large-capacity, high speed (2800 rpm) mechanical mixer with a modified mixing blade was used for mixing the binder. Microscope images of binder samples manufactured at 175 °C and 300 rpm in this mixer have dark (PEG) and light (PVB) regions (Figure 4.13), indicating heterogeneity. Increasing the mixing time to 90 min increased homogeneity (Figure 4.13c, c').

Burn-out tests with the SDT analyser on random triplicate samples (Samples 1, 2, and 3 in Figure 4.14) from binder mixed at 175 °C and 300 rpm for 90 min in the mechanical mixer were different, indicating different composition (as explained in Section 4.1.2a). The different PEG, SA and PVB exothermic peaks (circled regions) indicating samples had different amounts of PEG, SA and PVB and that the binder was heterogeneous.

(c) Binders manufactured in the twin screw extruder

Twin screw extrusion provides both distributive and intensive mixing [331] and can produce the intense shear stress essential for manufacturing a homogeneous mix [154, 179, 214, 331, 335-336]. However, binder produced by twin screw extrusion was heterogeneous and had PEG and PVB regions (Figure 4.15). The feed for this binder had been dry mixed so the PEG and PVB were not chemically bound. The low viscosity, low molecular weight PEG (7500 – 8800 g/mol) separated from the high viscosity, high molecular weight PVB (50000 – 80000 g/mol) under the intense shear developed during twin screw extrusion. To reduce this problem, the PEG and PVB mix must be melted before twin screw extrusion.

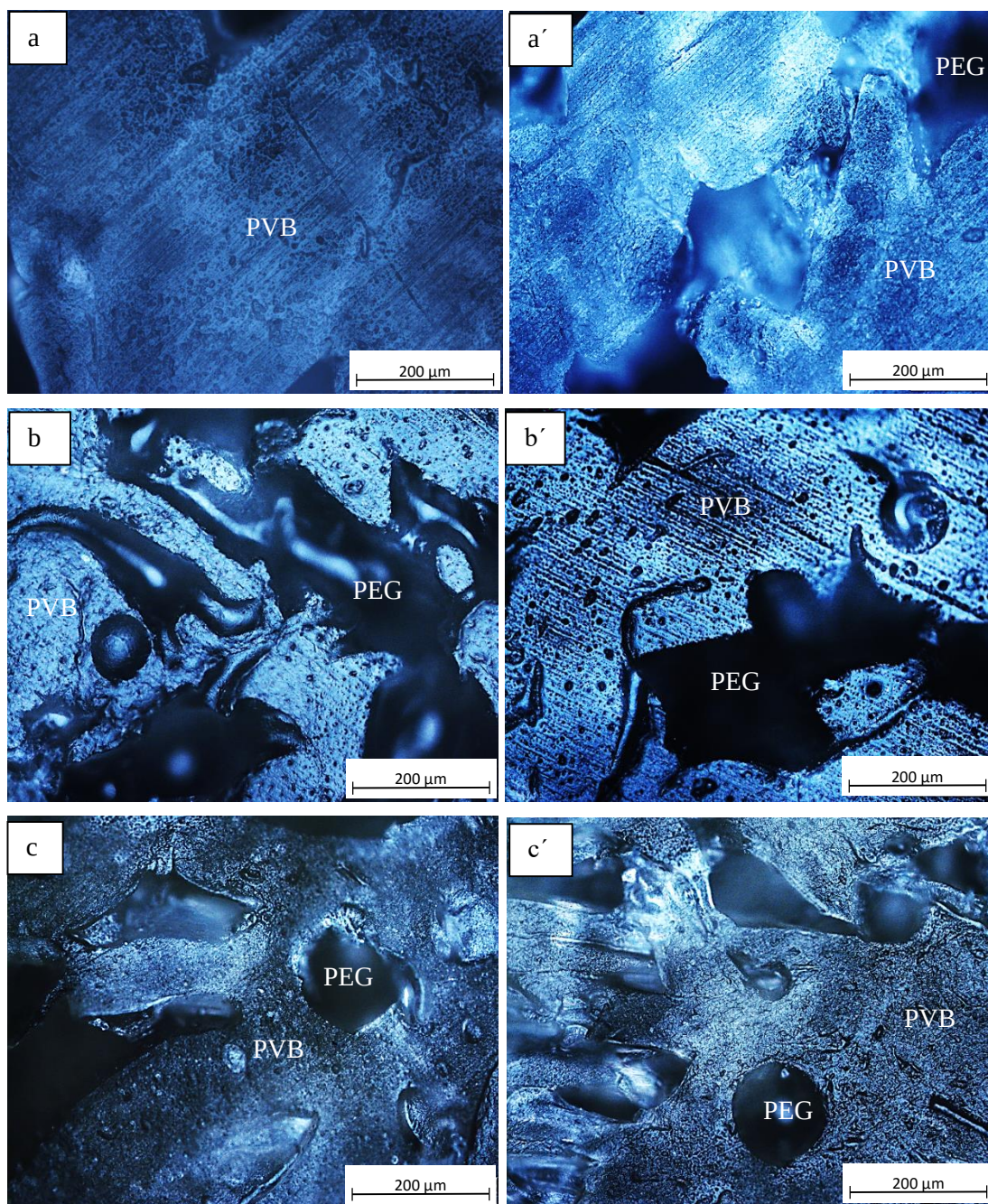


Figure 4.13: Optical microscope images showing effect of mixing time on microstructure of 65:30:5 vol. % PEG:PVB:SA binder produced in a mechanical mixer at 175 °C and 300 rpm: (a, a') 30 min mixing; (b, b') 60 min mixing; (c, c') 90 min mixing. The insoluble PVB appear as lighter regions and the PEG as dark.

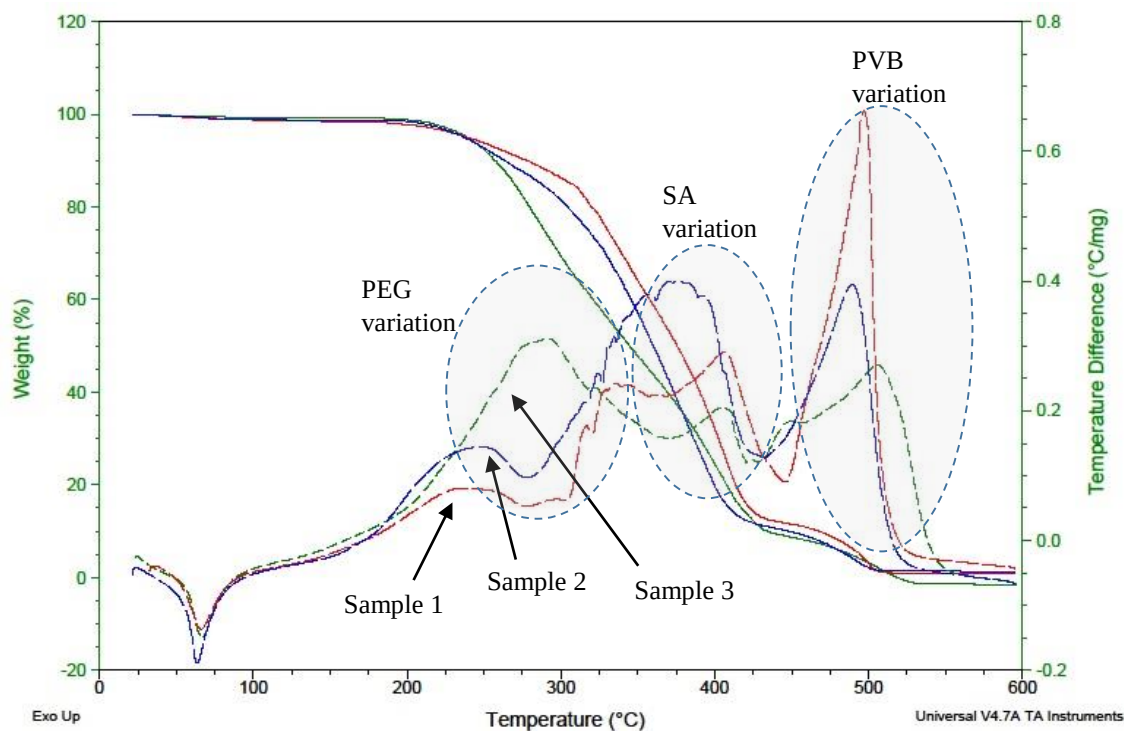


Figure 4.14: Burn-out patterns of 65:30:5 vol. % PEG:PVB:SA binder mixed for 90 min at 175 °C and 300 rpm in the mechanical mixer.

Optical microscope images showed that extruded binder that had been melt-mixed in the mechanical mixer by processing at 175 °C and 300 rpm for 90 min was more homogenous (Figure 4.15d, d') than dry mixed binders that had been direct extruded (Figure 4.15a, a', b, b' c, c'). However, the microstructure was still heterogeneous and had PEG and PVB regions (Figure 4.15).

Burn-out tests of three random samples (Samples 1, 2, and 3 in Figure 4.16) of binder manufactured at 175 °C, 300 rpm and 90 min mixing in the mechanical mixer followed by twin screw extrusion (Figure 4.15d, d') were different, indicating the binder was not homogenous.

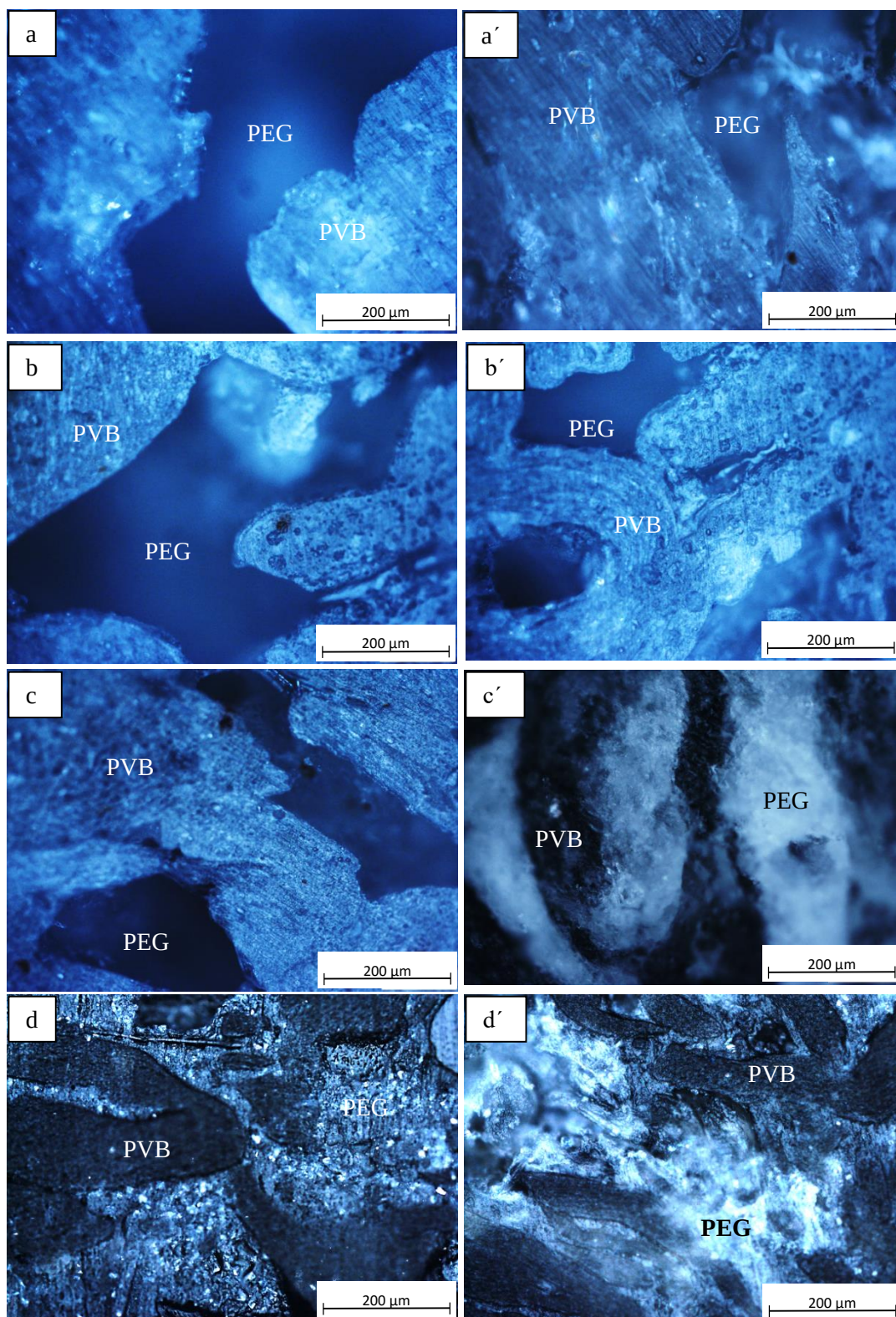


Figure 4.15: Microstructure (optical microscope) of 65:30:5 vol. % PEG:PVB:SA binders produced using a twin screw extruder at 70 rpm with a feed to nozzle temperature profile of 160, 177, 170, 160 147 °C: (a, a') first pass extrusion; (b, b') second pass extrusion; (c, c') third pass extrusion; (d, d') binder produced by 90 min mechanical mixing. The insoluble PVB are the dark regions in the lighter PEG regions.

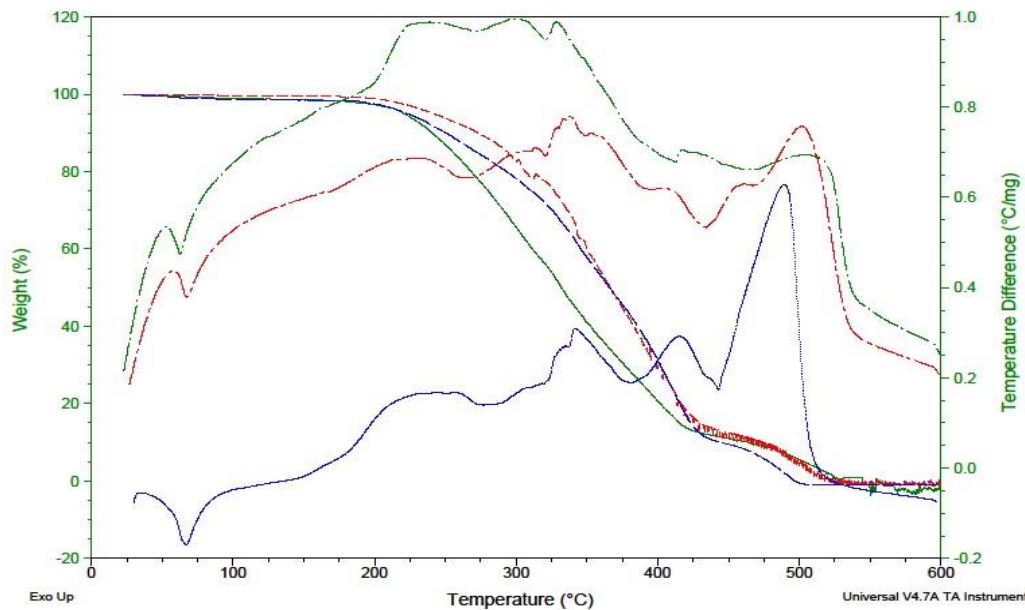


Figure 4.16: Burn-out patterns of binder samples (PEG:PVB:SA = 65:30:5 vol. %) manufactured at 160 °C – 177 °C – 170 °C – 160 °C – 147 °C (feed to nozzle) and 70 rpm in the twin screw extruder.

The DTA analysis of random samples from PEG:PVB:SA (65:30:5 vol. %) binders manufactured at 175 °C for various mixing times and speeds in three different mixers (roller compounder, mechanical mixer and twin screw extruder) had a wide range of burn-out patterns, indicating the binders were not homogenous (Figure 4.17). When the binder degraded, the first exothermic peaks for PEG (200 – 300 °C), SA (275 – 325 °C) and PVB (350 – 400 °C) (Figure 4.11) shifted to 200 – 350 °C, 300 – 450 °C and 450 – 550 °C respectively (Figure 4.17). It is assumed binder components were partially miscible in each other and hydrogen bonds were created between the binder components during mixing. Therefore, more energy was required to break molecular bonds when the components were in a binder than for pure components.

All binders made under the various process conditions investigated were heterogeneous, indicating PEG and PVB may be immiscible. The heterogeneity is shown by samples having both PEG and PVB regions in their microstructure. This heterogeneity could be due to the cohesive nature of one or more binder components, which form agglomerates due to interfacial tension and Van der Waal's forces [213, 331]. The objective was to develop a binder that would mix with Ti64 powder and produce a homogeneous feedstock for Ti-MIM. As a homogeneous binder could not be manufactured, the research focus changed to producing feedstocks for Ti-MIM by

mixing binder constituents directly with titanium alloy powder (Ti64). Titanium reacts very easily with oxygen, producing composites with poor mechanical properties. The complex oxidation mechanisms for titanium occur between 300 – 1000 °C [165, 337-339] so mixing needs to be done below 300 °C.

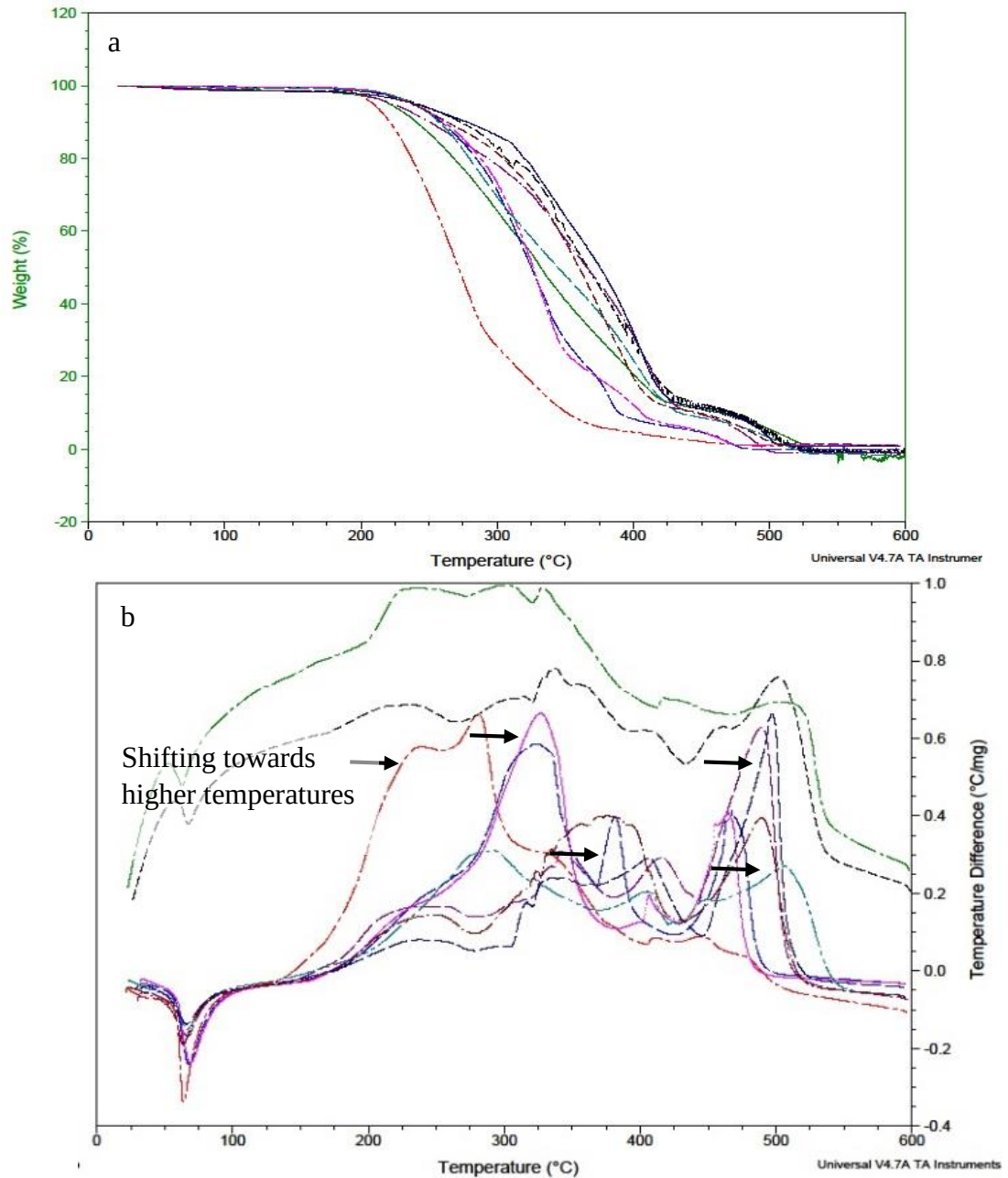


Figure 4.17: Burn-out patterns of random samples from PEG:PVB:SA (65:30:5 vol. %) binders manufactured at 175 °C at various mixing speeds and times in three different mixers: (a) TGA and (b) DTA.

4.1.3. Summary

Thermal characteristics of pure binder components (PEG, PVB and SA) and 65:30:5 vol. % PEG:PVB:SA binder produced using different process methods were determined. As the binder was for manufacturing titanium-based MIM feedstocks, thermal analysis and process temperatures were limited to 300 °C, which is when titanium starts to react with oxygen. Melting point and thermal degradation data indicated 175 °C was a suitable temperature for manufacturing the binder.

Binder morphology showed PEG and PVB regions, indicating the material was not homogenous. The DTA analyses indicated that different regions existed in the binder and that PEG and PVB were immiscible when directly melt mixed. This effect may be due to the cohesive character of PVB or PVB and PEG, which form agglomerates due to interfacial tension and Van der Waal's forces. However, PEG, SA and PVB are partially miscible, as shown by the high oxidative temperature (shift of exothermic peaks to higher temperatures) in the DTA data.

4.2. Feedstocks

As a homogeneous feedstock could not be made, mixing binder components directly with Ti64 powder was investigated. The effect of powder loadings on density, viscosity and mixing torque of various Ti-MIM feedstocks were determined to identify critical and optimal powder loadings. The effect of various process conditions on feedstock homogeneity was analysed to identify an effective feedstock manufacturing process.

4.2.1. Powder loading and feedstock density

The measured and theoretical density of 65:30:5, 75:20:5, 80:15:5 and 85:10:5 vol. % PEG:PVB:SA mixes calculated using Equations 4.1, 4.2 and 4.3 were compared [2].

$$\rho_f = \Phi \rho_p + (1 - \Phi) \rho_b \quad 4.1$$

where ρ_f is feedstock density, ρ_p is powder density, ρ_b is binder density and Φ is volumetric fraction of powder, calculated using equation 4.2.

$$\Phi = \frac{\frac{W_p}{\rho_p}}{\frac{W_p}{\rho_p} + \frac{W_b}{\rho_b}} \quad 4.2$$

where W_p and W_b are weight fraction of powder and binder respectively.

Equation 4.3 can be derived from equations 4.1 and 4.2 to convert volumetric powder loading to weight fraction.

$$W_p = \frac{\rho_p \Phi}{\rho_p \Phi + \rho_b (1 - \Phi)} \quad 4.3$$

By using density of the individual binder and Ti64 powder, a linear relationship (equation 4.4) can be developed for Ti64 volumetric powder loading (Φ) and density of the Ti64/binder mix made with 65:30:5 vol. % PEG:PVB:SA binder.

$$\rho_f = 3.3582\Phi + 1.1249 \quad 4.4$$

There was good agreement between measured and theoretical density of feedstocks manufactured at 175 °C (method 1, Section 3.4) with powder loadings of 40 – 65 vol. %. Values then diverged, with measured density at 80 vol. % powder loading being only 39% the theoretical value (Figure 4.18).

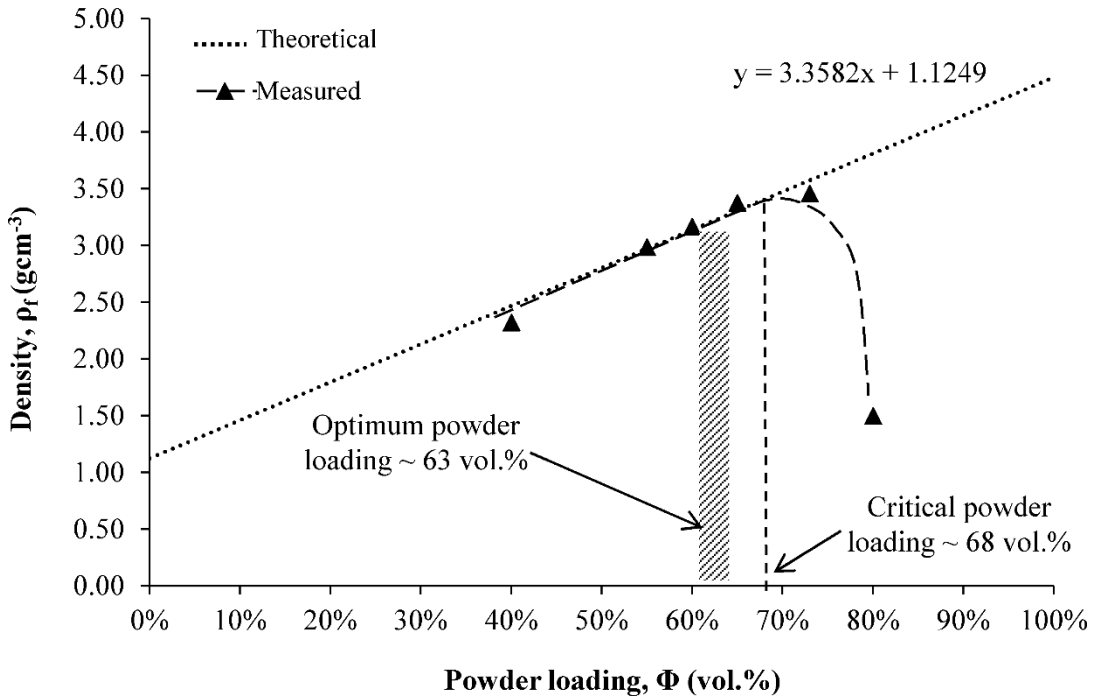


Figure 4.18: Effect of Ti64 volumetric powder loading on density of feedstocks made from 65:30:5 vol. % PEG:PVB:SA binder manufactured at 175 °C (Section 3.4).

As powder loading increases, binder per unit volume decreases (Figure 4.19a and b). At the critical loading, powder particles are packed as tightly as possible and the binder required to form a layer on these particles and fill inter-particle spaces is minimal,

leaving no voids (Figure 4.19c). If powder loading is increased further, there is insufficient binder to fill spaces between the powder particles, resulting in voids (Figure 4.19d) so measured density deviates from theoretical density. If powder loading is low (excess binder in the feedstock; Figure 4.19a), binder separation during moulding can occur. This causes heterogeneous moulded parts, slumping during debinding and significant volume shrinkage after debinding and sintering [2, 145].

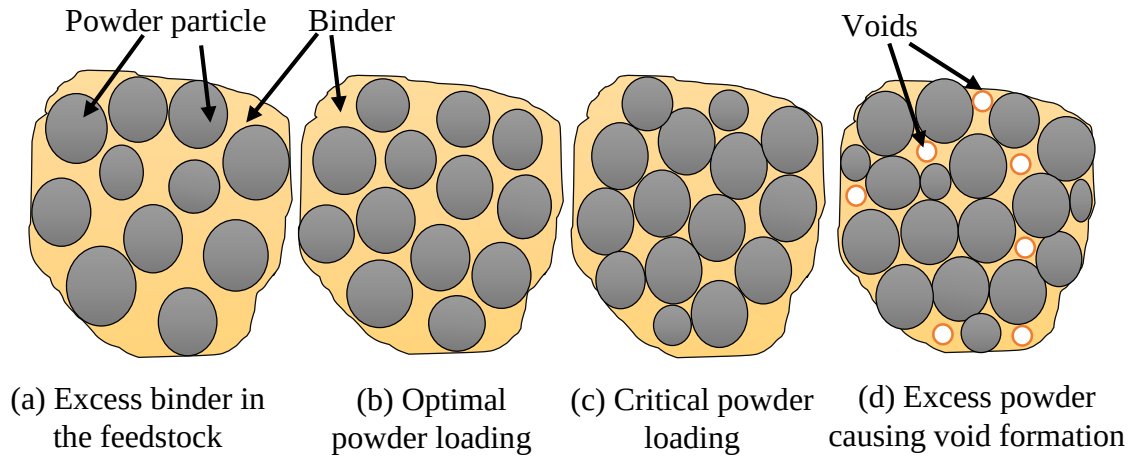


Figure 4.19: Schematic diagram of four possible situations of a feedstock.

As theoretical and measured densities diverged at about 65 vol. %, this was taken as the critical powder loading. This feedstock would be difficult to mould because of its high viscosity and low fluidity. Therefore, optimal powder loading (Figure 4.19b) that allowed maximum powder without creating processing problems was assumed to be 2 - 5 vol. % below critical value [2]. German and Bose [2] state that having additional binder improves feedstock flow. However, using slightly less than the critical powder loading does not guarantee optimal powder loading, which is also affected by particle shape and size distribution, mixing homogeneity, binder characteristics and powder-binder particle interaction. To allow for these factors, a powder loading of 63 vol. % was used as the working powder loading.

Density measurements indicated the critical Ti64 powder loading at 125 °C using 65:30:5, 75:20:5, 80:15:5 and 85:10:5 vol. % PEG:PVB:SA binder manufactured using method 2 (Section 3.4) was between 58 and 64 vol. % (Figure 4.20; Table 4.3).

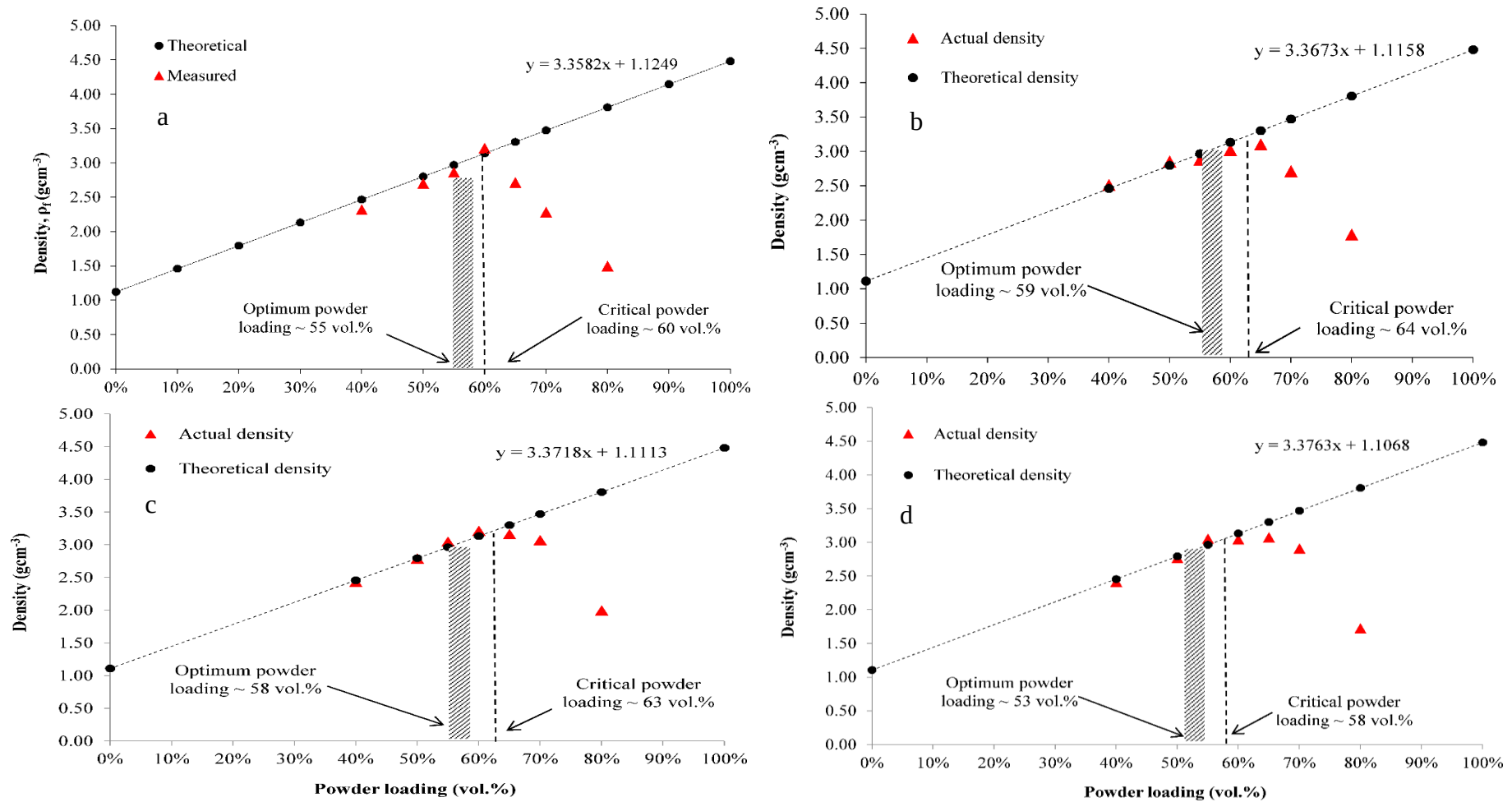


Figure 4.20: Effect of powder loading and binder composition on density of Ti64 /binder mixes manufactured at 125 °C in method 2 (Section 3.4): (a) 65:30:5, (b) 75:20:5, (c) 80:15:5 and (d) 85:10:5 vol. % PEG:PVB:SA binder.

Table 4.3: Effect of binder composition on critical powder loading at 125 °C.

PEG:PVB:SA	Critical powder loading (vol. %)	Optimal powder loading (vol. %)
65:30:5	60	55
75:20:5	64	59
80:15:5	63	58
85:10:5	58	53

The critical powder loading when PEG content in the binder increased from 65 to 85 vol. %, can be modelled as a second order polynomial ($R^2 = 0.998$), showing maximum critical powder loading at 64 vol. % (Figure 4.21). This model predicts that binder composition at the maximum critical powder loading (i.e. when dy/dx for the model is zero) is 76.7:18.3:5 vol. % PEG:PVB:SA binder and the critical powder loading is 64.1 vol. %. This is similar to the 64 vol. % for 75:20:5 vol. % PEG:PVB:SA binder obtained by density measurements (Figure 4.20b).

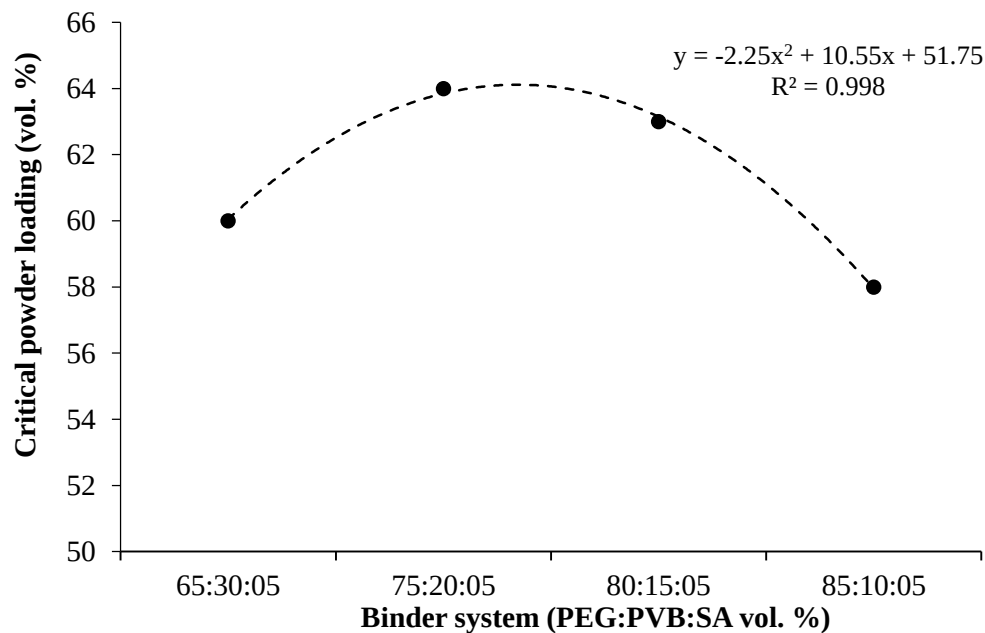


Figure 4.21: Effect of binder composition processed at 125 °C on critical powder loading of Ti-MIM feedstocks.

Voids that occur when the powder loading is above the critical value increase friction between the Ti64 powder particles. Filling these voids with a low viscosity component such as PEG may allow critical powder loading to be increased. This may explain why critical powder loading increased as PEG content in the binder increased from 65 to

75 vol. % (Figure 4.21). However, critical powder loading then decreased as PEG content increased further.

Each functional polymer in the feedstock interacts with Ti64 powder differently so more than one effect may produce the observed decrease in critical powder loading. For instance, it may be due to the increase in PEG and/or the decrease in PVB. When PEG content increases, the polymer-polymer interactions become dominant and polymer-powder interactions decrease. Therefore, powder particle mobility decreases as PEG content increases (75 – 85 vol. %) due to formation of hydrogen bonds and Van der Waals interactions between PEG and Ti64 particles. There are few reports on the effect of binder composition although Li *et al.* [151] report that PEG based binder reduces critical powder loading. However, they did not give a particular binder/powder or the reason for the decrease in powder loading.

PEG is a non-ionic polyhydroxyl polymer (Figure 4.2a) with two terminal hydroxyl groups (-OH) and many alternating ether linkages (CH₂-OH). Its molecular weight affects viscosity, surface tension, solubility and melting point [340-341]. For instance, viscosity increases exponentially with molecular weight [342]. The molecular weight of PEG used in this research (8000 g/mol) was higher than used in other MIM research. Hydrogen bonds can form between any water on the Ti64 powder surface and the electron-rich oxygen atoms in the polymer chains. The Van der Waals interactions between polymer particles and Ti64 powder particles may also increase due to the increase in PEG content, which will hinder mobility of Ti64 particles. These effects may have contributed to the decrease in critical powder loading as PEG content increased from 75 to 85 vol. % (Figure 4.21).

Further trials were done with binders that had higher critical powder loadings:

- 65:30:5 vol. % PEG:PVB:SA manufactured at 175 °C (method 1, Section 3.4),
- 80:20:5 vol. % PEG:PVB:SA manufactured at 125 °C (method 2, Section 3.4)

4.2.2. Effect of powder loading on mixing torque

The torque increased sharply ('a' in Figure 4.22) when Ti64 was added to 65:30:5 vol. % PEG:PVB:SA binder in the roller compounder operating at 175 °C and 60 rpm,

indicating feedstock particle resistance to the freely rotating mixing blades and melting of binder components in the feedstock. Torque decreases as agglomerates are broken apart and become well dispersed into the mixture.

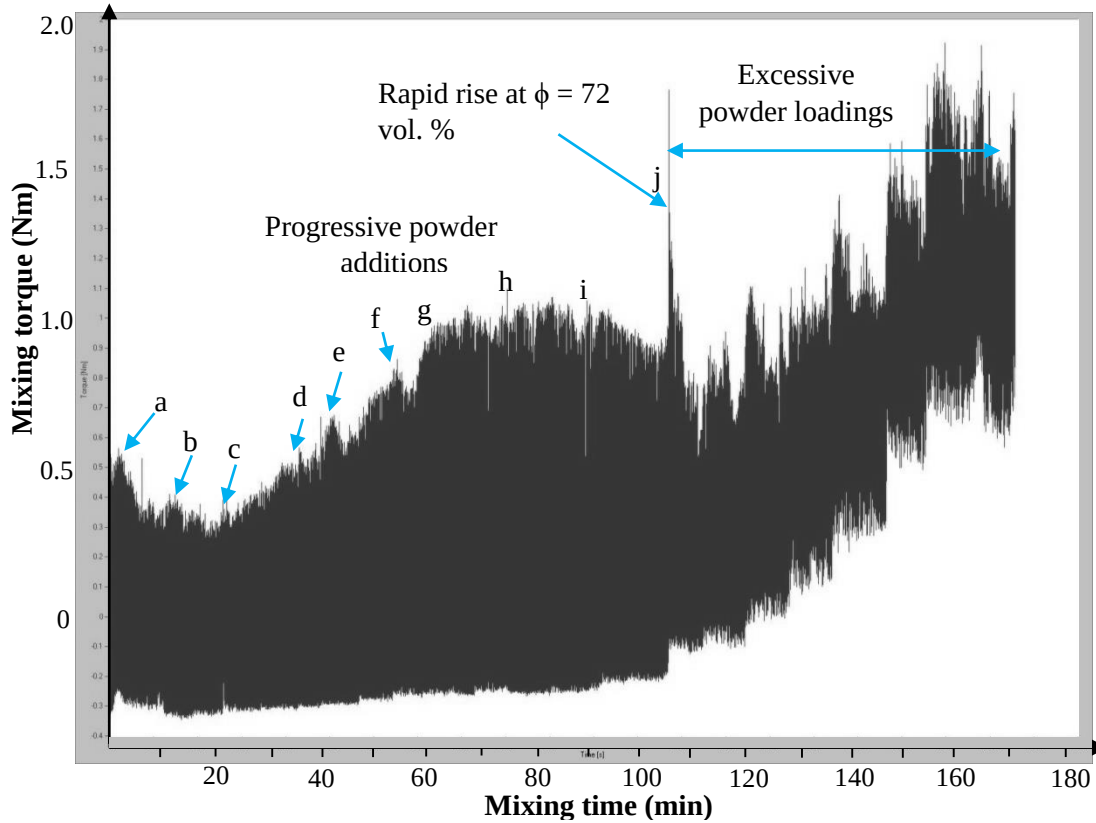


Figure 4.22: Mixing torque evolved as Ti64 powder was added to 65:30:5 vol. % PEG:PVB:SA binder in the roller compounder operating at 175 °C and 60 rpm.

At each further powder addition ('b' to 'i' in Figure 4.22), torque also increased sharply. Before the powder particles are wetted sufficiently, they are a resistance to the roller blades. This increase in torque is due to shear stress developed in the mixing chamber and indicates the work required to disperse and distribute Ti64 powder in the binder [154, 219, 302]. As powder particles become sufficiently wetted and mixed, the torque reduces [198]. After the tenth addition of powder, which represented 72 vol. % powder loading, torque increased rapidly ('j' in Figure 4.22). This was taken as the critical powder loading and occurs when feedstock viscosity is very high because there is insufficient binder and voids are formed. This phenomenon has been discussed by others [2, 191, 219]. Capillary forces oppose void formation and drag powder particles

together, increasing friction between powder particles and hence torque increases rapidly ('j' in Figure 4.22).

The critical powder loading from density (68 vol. %, Figure 4.18) and mixing torque (72 vol. %, Figure 4.22) analyses for feedstock made from 65:30:5 vol. % PEG:PVB:SA binder processed at 175 °C was similar. To allow a safety margin and minimise equipment damage, the critical loading was assumed to be 68 vol. %. This was reduced a further 5 vol. % to give lower viscosity feedstock during moulding, giving a working Ti-MIM composition of 63 vol. % (optimal powder loading).

The mixing torque of feedstocks manufactured at 125 °C and 60 rpm in the roller compounder during the first 35 minutes of operation had a similar pattern (increasing and then decreasing) as powder was added ('a' to 'f' in Figure 4.23). During processing, the mixture changed from excess binder (Figure 4.19a) to optimum powder loading (Figure 4.19b) and mixing torque increased slightly. Torque remained constant after the seventh powder addition ('g' in Figure 4.23), and increased slightly on the eighth powder addition ('h' in Figure 4.23). There was a significant increase in torque for subsequent powder additions ('i' onwards). It is deduced that the 'g', 'h' and 'i' powder additions could be related to powder loadings between "optimal" and "critical". Subsequent additions created excess powder loading conditions. Therefore, powder additions 'i' (65 vol. %) and 'g' (62 vol. %) were regarded as the critical and optimal powder loadings respectively.

The critical powder loading obtained from density analysis (63 vol. %, Figure 4.20c) and mixing torque analysis (65 vol. %, Figure 4.23) for feedstock using 80:15:5 vol. % PEG:PVB:SA binder processed at 125 °C were similar. To allow a safety margin, 63 vol. % was identified as critical loading and then reduced by 3 vol. % to decrease feedstock viscosity during moulding, to give a working Ti-MIM composition of 60 vol. % for further trials.

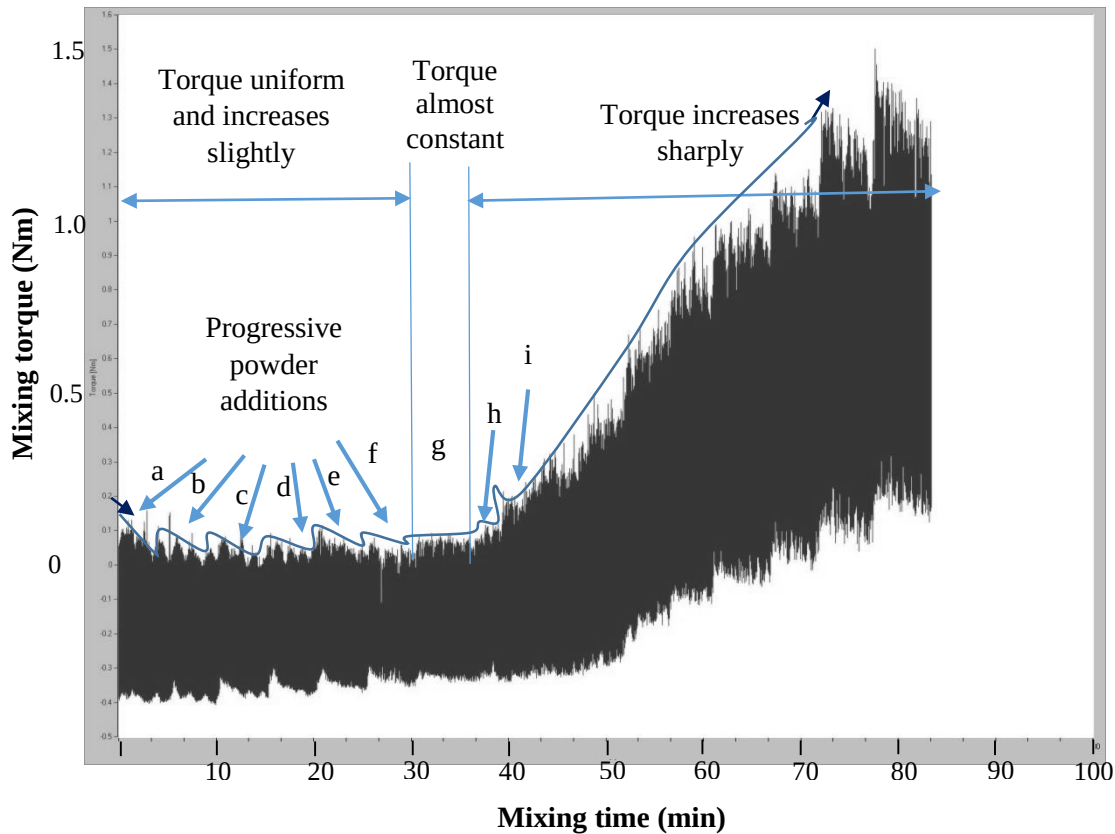


Figure 4.23: Effect of adding Ti64 powder to 80:15:5 vol. % PEG:PVB:SA binder on roller compounder torque when operating at 125 °C and 60 rpm.

Feedstock made with 65:30:5 vol. % PEG:PVB:SA binder had a higher optimal powder loading (63 vol. %) than feedstock made with 80:15:5 vol. % PEG:PVB:SA binder (60 vol. %). The optimal powder loadings obtained from density and torque analyses were consistent. However, critical powder loadings under actual moulding situations may vary. A more reliable (but expensive) method such as relative viscosity analysis is useful for validating optimal powder loadings. Viscosity analysis was done by extruding feedstocks in a capillary rheometer, which better represents the process of extruding feedstock in an injection moulding machine.

4.2.3. Powder loading and feedstock relative viscosity

Feedstocks composed of 50, 55, 60 and 63 vol. % Ti64 powder loadings with 65:30:5 vol. % PEG:PVB:SA binder could not be extruded through the 1-mm diameter (D) x 10-mm long (L) and 2-mm D x 5-mm L capillary dies at 145 °C, 165 °C or 185 °C. This indicated the feedstocks had high viscosities under these temperatures. The SEM images (Figure 4.24) showed powder particles in some regions were well coated with

binder and some were not. Inter-particle voids were observed in many regions. This indicated the feedstocks were heterogeneous and there was insufficient binder to fill all the regions between the powder particles and give the required flow.

For successful extrusion, viscosity needs to be decreased by raising processing temperature or decreasing powder loading. Extrusion temperatures above 185 °C were not tried because binder components degrade about 190 °C (Section 4.1). MIM feedstocks with low powder loadings (below 45 vol. %) can have defects and problems in subsequent MIM processes such as solvent and thermal debinding and sintering [2]. Though torque and density data showed 63 vol. %, was the optimal loading for this feedstock, the practical powder loading appeared to be below 50 vol. % due to powder characteristics, binder characteristics and rheological behaviour of the feedstock. Karatas *et al.* [3] identified a feasible powder loading of 50 vol. % even though they had found critical powder loading was 70 vol. %. Data from the trials (Section 4.1.2) showed that 65:30:5 vol. % PEG:PVB:SA binder manufactured at 175 °C (Figure 4.24) could not be used for Ti-MIM but that feedstocks made from 80:15:5 vol. % PEG:PVB:SA binder and 50 – 65 vol. % powder loadings could be successfully extruded through the 1-mm D x 10-mm L capillary die at 145 °C.

Although feedstock viscosity at shear rates of 600 s⁻¹ and 2000 s⁻¹ increased with powder loading, it was below 100 Pa-s at 50 – 60 vol. % powder loading (Table 4.4), and well below the critical limit of 1000 Pa-s for MIM [2]. However, viscosity increased considerably at 62 vol. %, and was extremely high at 65 vol. % (Table 4.4), indicating this feedstock was not suitable for MIM.

Table 4.4: Effect of powder loadings and shear on viscosity (Pa-s) of feedstocks made with 80:15:5 vol. % PEG:PVB:SA binder.

Shear rate (s ⁻¹)	Ti64 powder loading (vol. %)				
	50	55	60	62	65
600	60	65	79	1085	37900
2000	49	53	65	152	50295

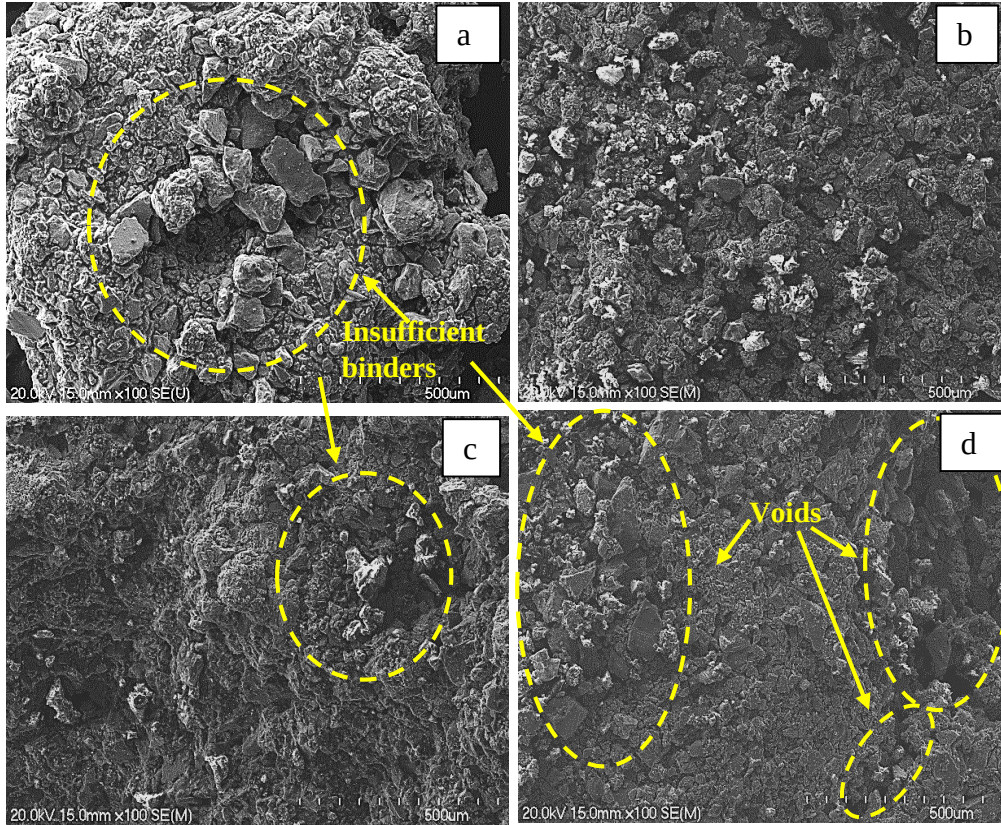


Figure 4.24: SEM images of feedstocks made from 65:30:5 vol. % PEG:PVB:SA binder and (a) 50, (b) 55 (c) 60 and (d) 63 vol. % powder loadings and manufactured at 175 °C (method 1, Section 3.4).

Viscosity at 50 and 55 vol. % powder loadings were similar (Table 4.4; Figure 4.25), indicating there was sufficient binder to coat the Ti64 particles and fill the inter-particle voids (Figure 4.26a). Although viscosity increased at 62 vol. % powder loading, there is sufficient binder to fill the inter-particle spaces between the tightly packed powder particles (Figure 4.26c). Increasing powder loading to 65 vol. % produced voids (Figure 4.26d). Viscosity increased due to inter-particle friction caused by capillary forces and was five orders higher at 65% than 62 vol. % (Figure 4.25).

Various mathematical models have been developed to describe the effect of powder loading on relative viscosity (Section 2.4.7). Relative viscosity approaches infinity as powder loading reaches the critical loading ($\Phi \rightarrow \Phi_c$). Feedstocks made of 80:15:5 vol. % PEG:PVB:SA binder had initial η_r of 50 – 80 Pa-s, rising to 38000 – 50000 Pa.s at 65 vol. % powder loading (Figure 4.27). The critical and optimal powder loadings for this feedstock were 65 vol. % and 60 vol. % respectively.

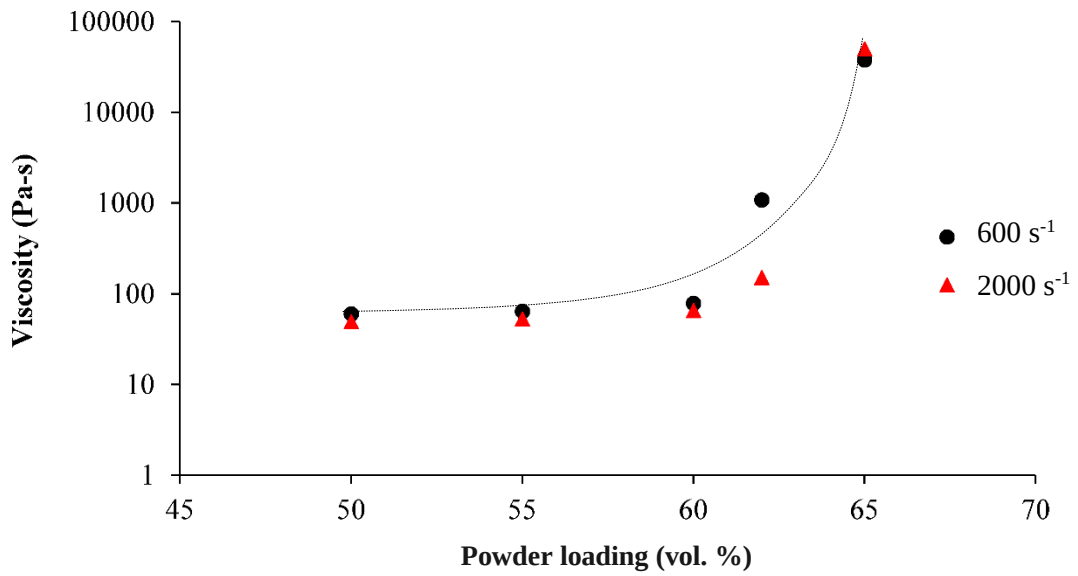


Figure 4.25: Effect of powder loading on viscosity of 80:15:5 vol. % PEG:PVB:SA feedstock manufactured by method 2 (Section 3.4) at 145 °C.

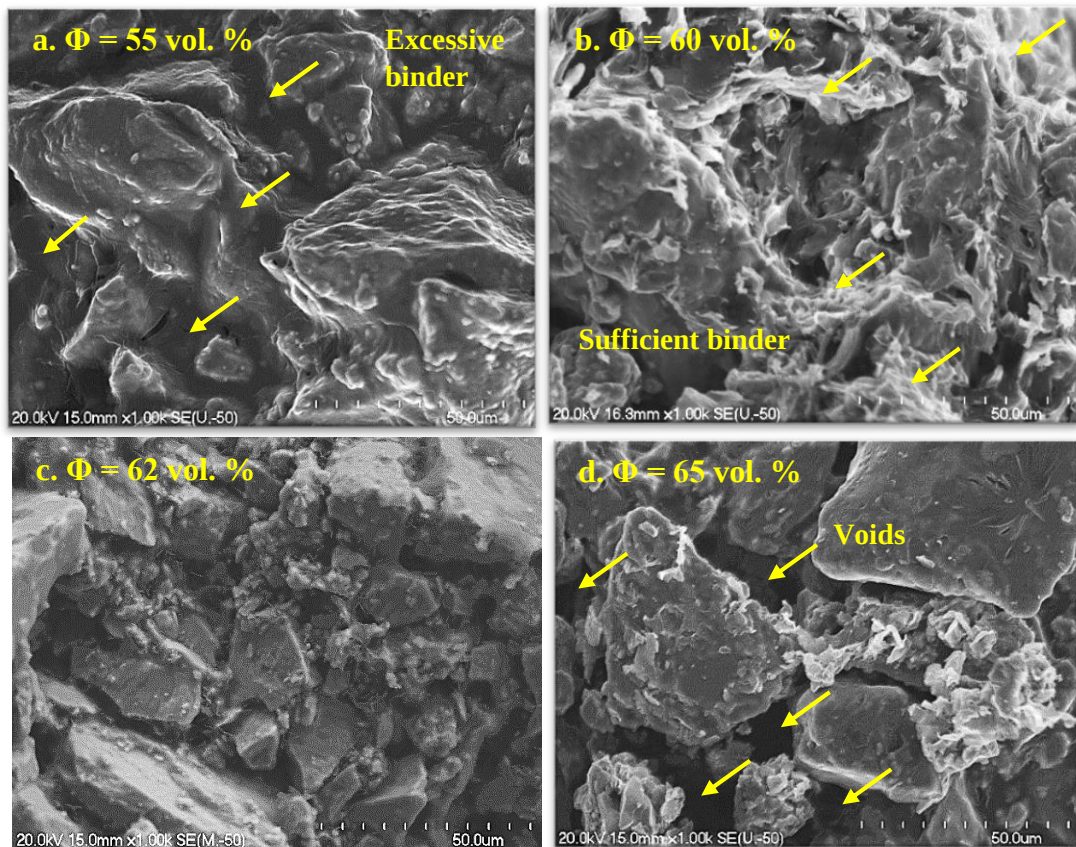


Figure 4.26: SEM images of feedstocks illustrating effect of Ti64 powder loading (Φ) on feedstock made with 80:5:5 vol. % PEG:PVB:SA binder.

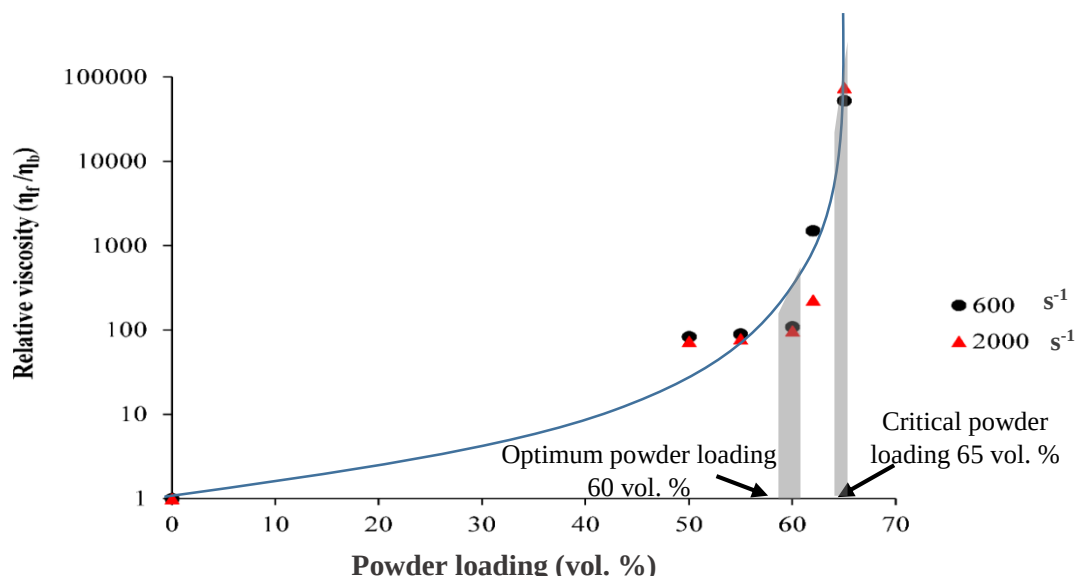


Figure 4.27: Effect of powder loading on relative viscosity of feedstock made with 80:15:5 vol. % PEG:PVB:SA binder (method 2, Section 3.4) at 145 °C.

Density analysis also showed critical powder loading for feedstock made of 75:20:5 vol. % PEG:PVB:SA binder occurred at 64 vol. % powder loading (Table 4.3) but this had not been verified using mixing torque analysis. The relative viscosity data (Figure 4.28) indicated this system had the same critical and optimal powder loadings as 80:15:5 vol. % PEG:PVB:SA binder at the three shear rates used (280, 1500 and 4500 s⁻¹). Relative viscosity analysis was not done on feedstock made from 85:10:5 vol. % PEG:PVB:SA because density analyses had shown the critical powder loading was low ($\Phi_c = 58$ vol. %).

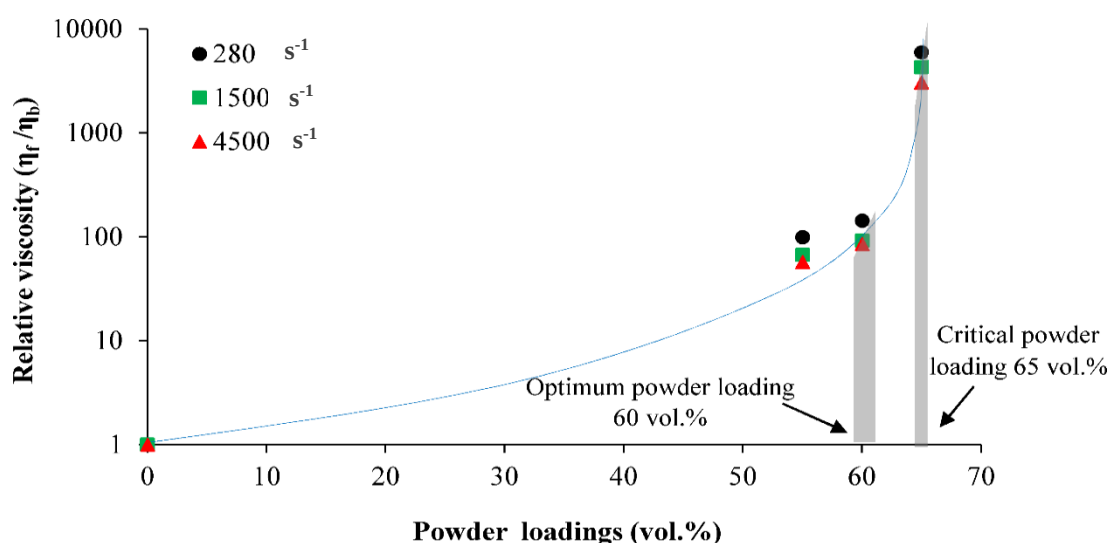


Figure 4.28: Effect of powder loading on relative viscosity of feedstock made with 75:20:5 vol. % PEG:PVB:SA binder (method 2, Section 3.4) at 145 °C.

Critical and optimal powder loadings obtained via density, mixing torque and viscosity analyses were similar (Table 4.5). Selecting the method to use depends on finance, time and skill of the operator. Density analysis is simple and inexpensive but tedious. Mixing torque and viscosity analyses need sophisticated, expensive instrumentation, such as torque and capillary rheometers. Interpreting mixing torque data is not as simple as interpreting viscosity analysis.

Table 4.5: Critical (Φ_c) and optimal (Φ_o) Ti64 powder loadings obtained from density, torque and viscosity analyses.

Analysis method	Binder (PEG:PVB:SA, vol. %)									
	65:30:5†		65:30:5*		75:20:5*		80:15:5*		85:10:5*	
	Φ_c	Φ_o	Φ_c	Φ_o	Φ_c	Φ_o	Φ_c	Φ_o	Φ_c	Φ_o
Density	68	63	60	55	64	59	63	58	58	53
Torque	72	68	-	-	-	-	63	60	-	-
Viscosity	x	x	-	-	65	60	65	60		

† Feedstock produced at 175 °C, method 1 (Section 3.4).

* Feedstock produced at 125 °C, method 2 (Section 3.4).

- Not done.

x Capillary extrusion failed.

4.2.4. Effect of powder characteristics on critical powder loading

At the optimum powder content inter-particle friction is low, which gives good mouldability in MIM [345]. The optimal Ti64 powder loadings for feedstocks made with 75:20:5 or 80:15:5 vol. % PEG:PVB:SA binder was almost 60 vol. % (Table 4.5). This is higher than reported for the smaller, spherical Ti64 powder (GA Ti-6Al-4V) preferred for manufacturing titanium feedstock (Sections 2.2.3 and 2.4.7). About one-third of the published research used powders with d_{90} between 8 – 30 μm and most of the reported MIM research has been done using spherical powders with d_{90} of 0.6 – 36 μm and d_{50} of 0.3 – 19 μm . For example, German and Bose [2] recommend 0.5 – 20 μm particles with d_{50} of 4 - 8 μm for MIM and other researchers recommend 2 – 8 μm particles for multi-component binders [218, 345]. The manufacturing process for HDH Ti64 powder used in this research [343-344] creates irregular particles (Figure 4.29) with a d_{10} , d_{50} and d_{90} of 12.8, 51.8 and 117.7 μm respectively (Figure 4.30; Table 4.6). This is much higher than the recommended values for MIM (Sections 2.2.3 and 2.4).

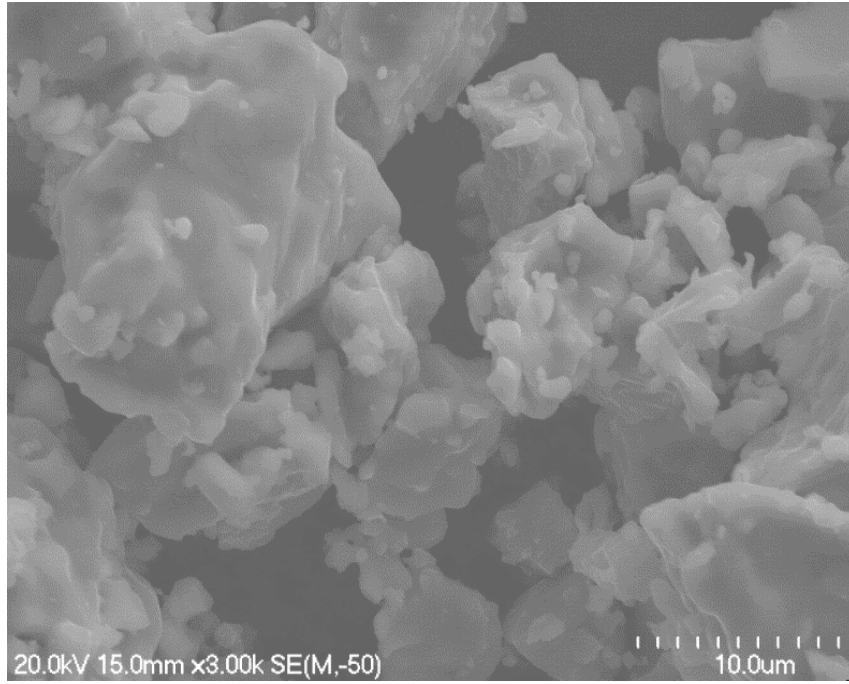


Figure 4.29: SEM image of HDH Ti-6Al-4V powder used in this research.

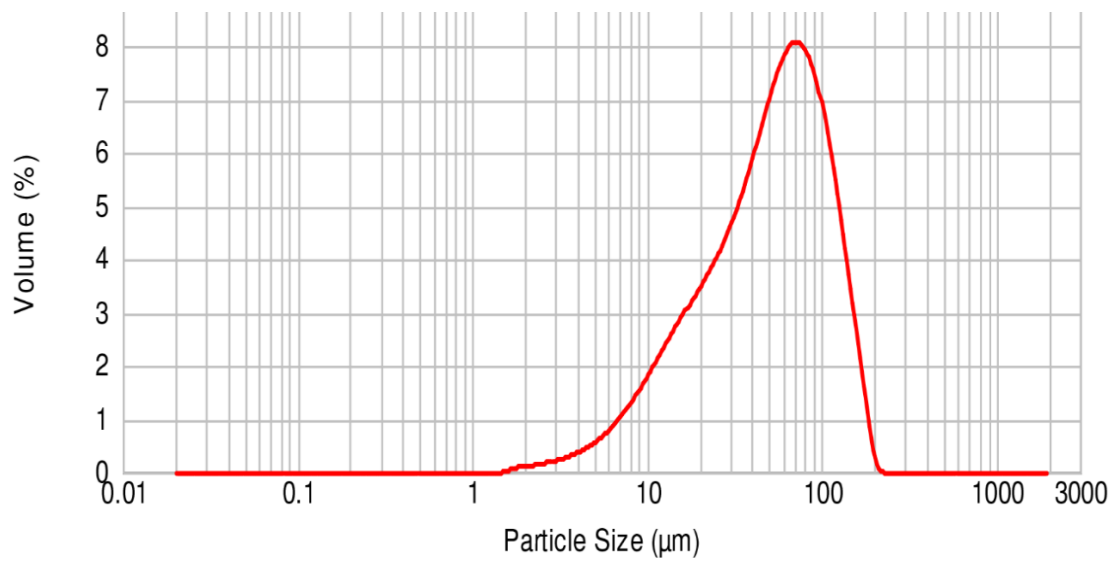


Figure 4.30: Particle size distribution of HDH Ti-6Al-4V in this research.

Although the associated optimal powder loading of 61 – 71 vol. % (Table 4.6) was higher than the 60 vol. % obtained with the Ti64 powder used in the current research, the relatively high powder loading achieved indicates feedstocks for MIM can be produced using 75:20:5 or 80:15:5 vol. % PEG:PVB:SA binder with larger particle HDH Ti-6Al-4V powders and that it is not necessary to use fine powders for MIM.

Table 4.6: Powder particle size used for MIM research.

Powder/ shape	Binder	Particle size distribution (μm)			$*S_w$	Φ_o	Reference
		d_{10}	d_{50}	d_{90}			
Zirconia/ spherical	Corn oil/polystyrene	0.1	0.3	0.6	3.29	53	[214]
Alumina	Wax/polymer	-	0.8	2.5	-	58	[142]
Tungsten carbide	Wax/polymer	-	1.6	-	-	46	[198]
Steel/ spherical	Commercial	1.2	2.4	4.0	4.90	58	[154]
Steel/ spherical	Wax/polymer	3.2	5.1	8.1	6.35	64†	[236]
Tungsten	Wax/ polymer	4.1	8.9	14.8	4.59	61†	[213]
Steel/ spherical	Wax/polymer	5	10	21	4.11	68	[302]
Steel/ spherical	Commercial	-	11	-	-	54	[218]
Steel/ spherical	Wax/polymer	5.3	11.8	26.3	3.68	71†	[236]
Steel/ spherical	Wax/polymer	5	12	22	3.98	57	[145]
Steel/ spherical	PEG/PMMA	-	12	-	-	63	[200]
Tungsten	Wax/ polymer	8.2	16.5	35.4	4.03	58†	[213]
Ti64/ Spherical	Palm stearin/ polymer	11	19	30	5.88	64	[346]
Ti64/ irregular	Polymer	12.8	51.8	117.7	2.66	60	This research

S_w - Particle size distribution gradient.

† Optimal powder loading by deducting 5 vol. % from critical powder loading.

- No published data

The distribution slope parameter (S_w) is calculated from particle size distribution (Equation 4.5); the larger the S_w value, the narrower the particle size distribution [2, 236].

$$S_w = \frac{2.56}{\log_{10}(\frac{d_{90}}{d_{10}})} \quad 4.5$$

The S_w values calculated from published size distributions were 3.29 to 6.35 (Table 4.6). The Ti64 powder used in this research had a S_w of 2.66, indicating a broad particle size distribution. This may improve powder packing as small particles can fit in voids between larger particles with sufficient binder to coat the particles and enable particle flow. Feedstocks made with powders with S_w of about 2 are easy to mould whilst powders with S_w values of 4 to 5 are difficult to mould [2, 236]. Optimal powder loading is seen to increase slightly as S_w decreased (Table 4.6).

In summary, relatively high optimal powder loadings were obtained in this research. Although particle shape and size are important for producing optimal powder loading in a standard feedstock, factors such as particle size distribution, binder, feedstock rheology, feedstock homogeneity and manufacturing process also need to be considered. The effect of process conditions on feedstock homogeneity and rheology will be discussed in Sections 4.2.5 and 4.3

4.2.5. Effect of processing on feedstock homogeneity

The effect of different mixing equipment and processing conditions for producing homogeneous feedstocks from 65:30:5 and 80:15:5 vol. % PEG:PVB:SA binders were investigated.

(a) Roller compounder (method 1, Section 3.4)

Mixing is a crucial step in MIM. Any heterogeneity in the mixture cannot be fixed in the moulding, debinding and sintering processes that follow [115-117]. Feedstock homogeneity can be evaluated from thermal data (Section 4.1.2). Four randomly selected samples from feedstock made with 60 vol. % Ti64 powder and 65:30:5 vol. % PEG:PVB:SA binder mixed for 45 min at 175 °C and 60 rpm in the roller compounder had different burn-out patterns (Figure 4.31), indicating the feedstock was not homogenous. All samples except one (sample 4 on Figure 4.31) did not have

the second exothermic peak associated with pure PVB (Figure 4.12), indicating they contained little or no PVB. Sample 2 had more PEG than the other samples.

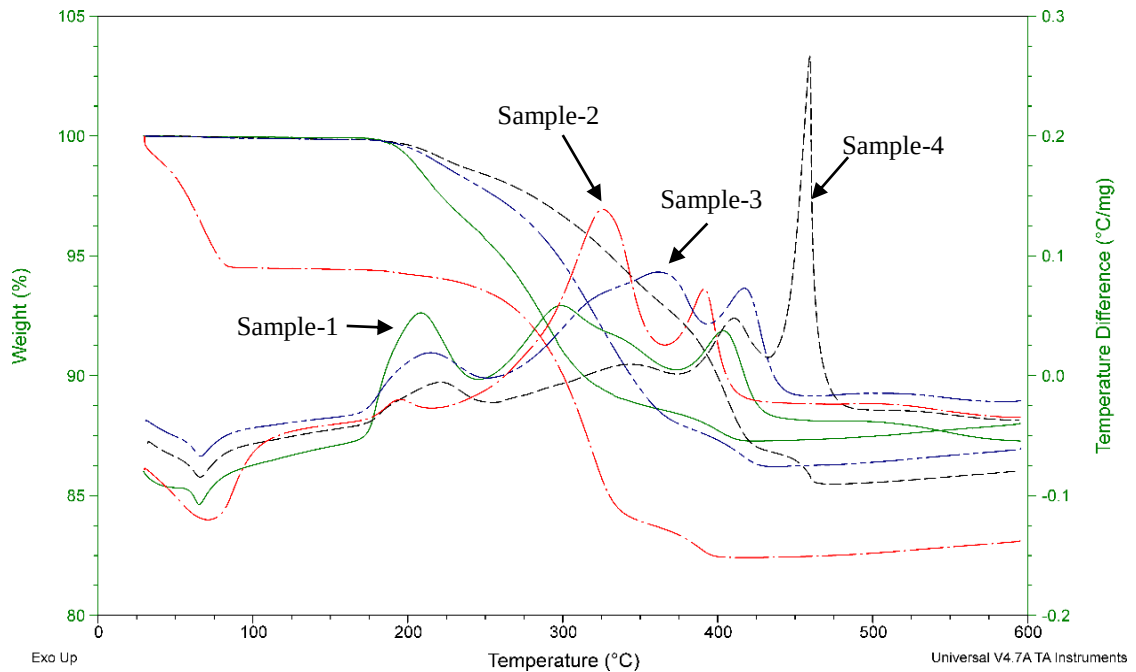


Figure 4.31: Burn-out patterns of samples of 60 vol. % Ti64 powder and 65:30:5 vol. % PEG:PVB:SA binder after 45 min mixing at 175 °C and 60 rpm in the roller compounder

Homogeneity can also be indicated by feedstock density [2, 218]. The density of five random samples was $2.76 \pm 0.37 \text{ g/cm}^3$ indicating this feedstock was not homogenous (measurement accuracy is $\pm 0.05 \text{ g/cm}^3$). The standard deviation ($8 \times 10^{-5} - 5 \times 10^{-3}$) was much higher than reported for other research on feedstock homogeneity [115-117, 142, 218, 302, 347]. SEM images also confirmed feedstock heterogeneity - in some regions powder particles were well coated with binder but other regions had voids and agglomerates (Figure 4.32a', b', c').

Hydrodynamic force ruptures agglomerates in the feedstock [213] so the presence of agglomerates in the feedstock (Figure 4.32c') indicates the roller compounder did not produce sufficient force to produce a homogenous feedstock. Song and Evans [348-349] reported that shear stress during mixing must be more than ten times agglomerate strength to ensure residues are ruptured.

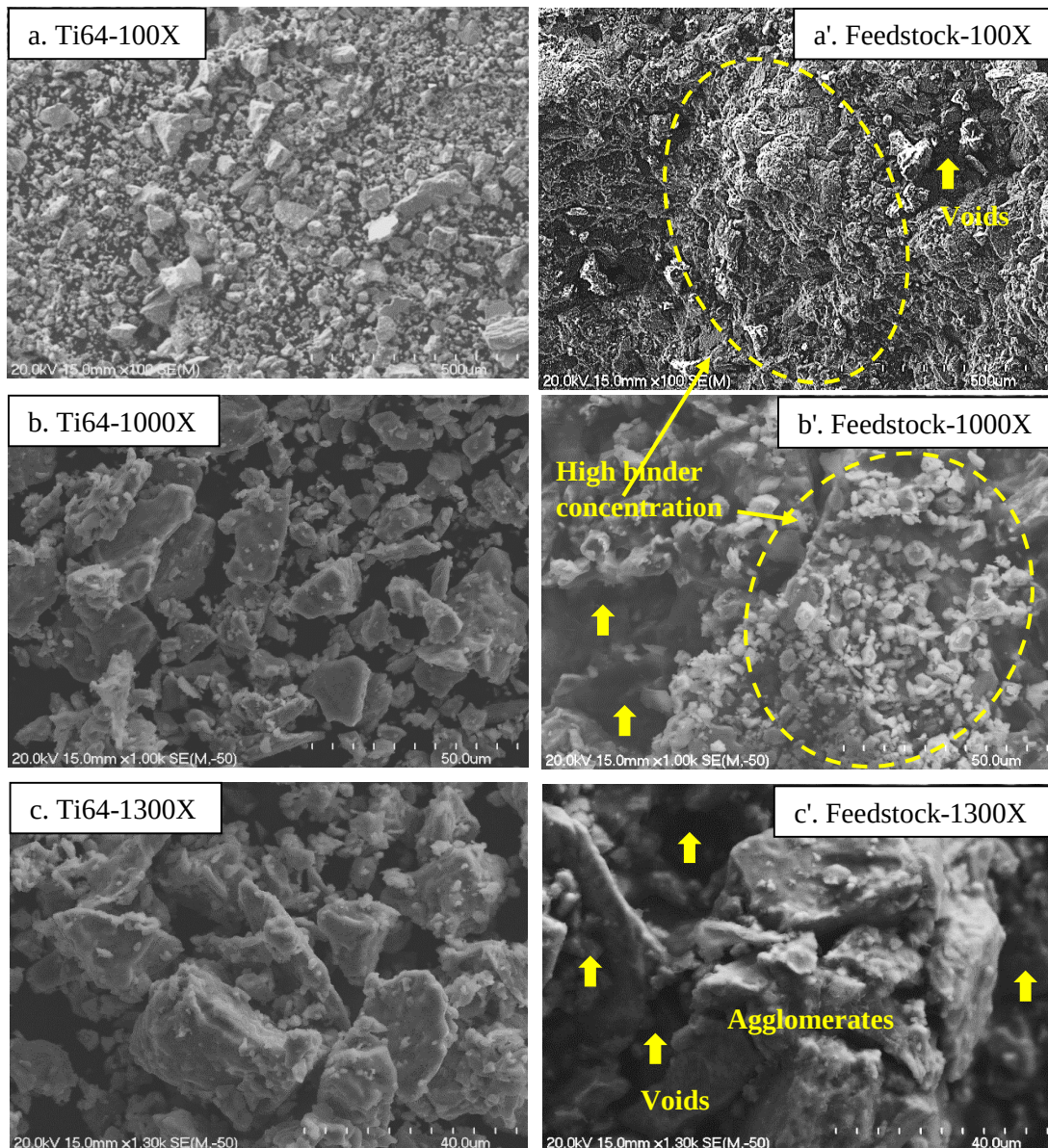


Figure 4.32: SEM images of Ti64 powder (a, b, c) and feedstock mixed for 45 min at 175 °C and 60 rpm in the roller compounder (a', b', c').

As feedstocks manufactured at 175 °C and 60 rpm in the roller compounder were heterogeneous, highly viscous and could not be extruded in the capillary rheometer, an alternative, multi-staged manufacturing method was investigated (Section 4.2.5b). German and Bose [2] proposed two feedstock-manufacturing routes: dry mixing binders and powder and then mixing in a compounder, or heating binders in the compounder and then adding the powder. They also suggested that a multi-stage mixing process may be required to obtain homogeneous feedstock. Therefore, further trials were done (Section 4.2.5b) to intensify the dry mixing step before wet mixing in the compounder. The mixing temperature (175 °C) was well below onset (190 – 205

°C) and critical (225 – 285 °C) degradation temperatures of binder components (Section 4.1.1). Weight loss due to mixing temperature and effect of isothermal holding time was reassessed using DTA. Most published MIM research uses mixing temperatures below binder degradation but there is no information on the effect of isothermal holding on binder degradation.

(b) Multi-staged process (method 2, Section 3.4)

As PEG was the main binder component (65 – 85 vol. %), the effect of 60 min isothermal holding at various temperatures (up to 170 °C) was determined. The 60-min isothermal holding time was considered an upper limit for mixing duration (45 min had been used in method-1). The most suitable mixing temperature (above the melting point and below the degradation temperature) would then be used when testing the other binder components (PVB and SA).

After 60 min isothermal holding at 120 °C, only 1 wt. % PEG had been removed; after the same isothermal holding at 170 °C, 94 wt. % PEG had been removed (Figure 4.33a, Table 4.7). If there is no isothermal holding time, only 1.23 wt. % PEG had been removed at 194 °C (the temperature, degradation starts; Table 4.1) and 67 wt. % PEG had been removed between 225 – 285 °C (Figure 4.4). Thus, isothermal holding, even at temperatures below onset of degradation, substantially increased weight loss. This infers that processing at 150 – 170 °C for long times (e.g. 60 min or more) may affect MIM.

The data indicated that the effect of both holding time and process temperature on degradation should be considered (e.g. from TGA profiles). This effect has not been previously reported even though PEG is often processed at its critical temperature for extended times. For instance, Krauss *et al.* [11, 191] mixed PEG at 160 – 180 °C for 60 min, Park *et al.* [133] mixed PEG at 150 °C for 90 min, Li *et al.* [151] mixed PEG at 160 °C for 60 min and at 145 °C for 2 h, Guo *et al.* [202-203] mixed PEG at 155 °C for 2 h, and Shibo *et al.* [113] kept PEG at 155 °C for more than 2 h.

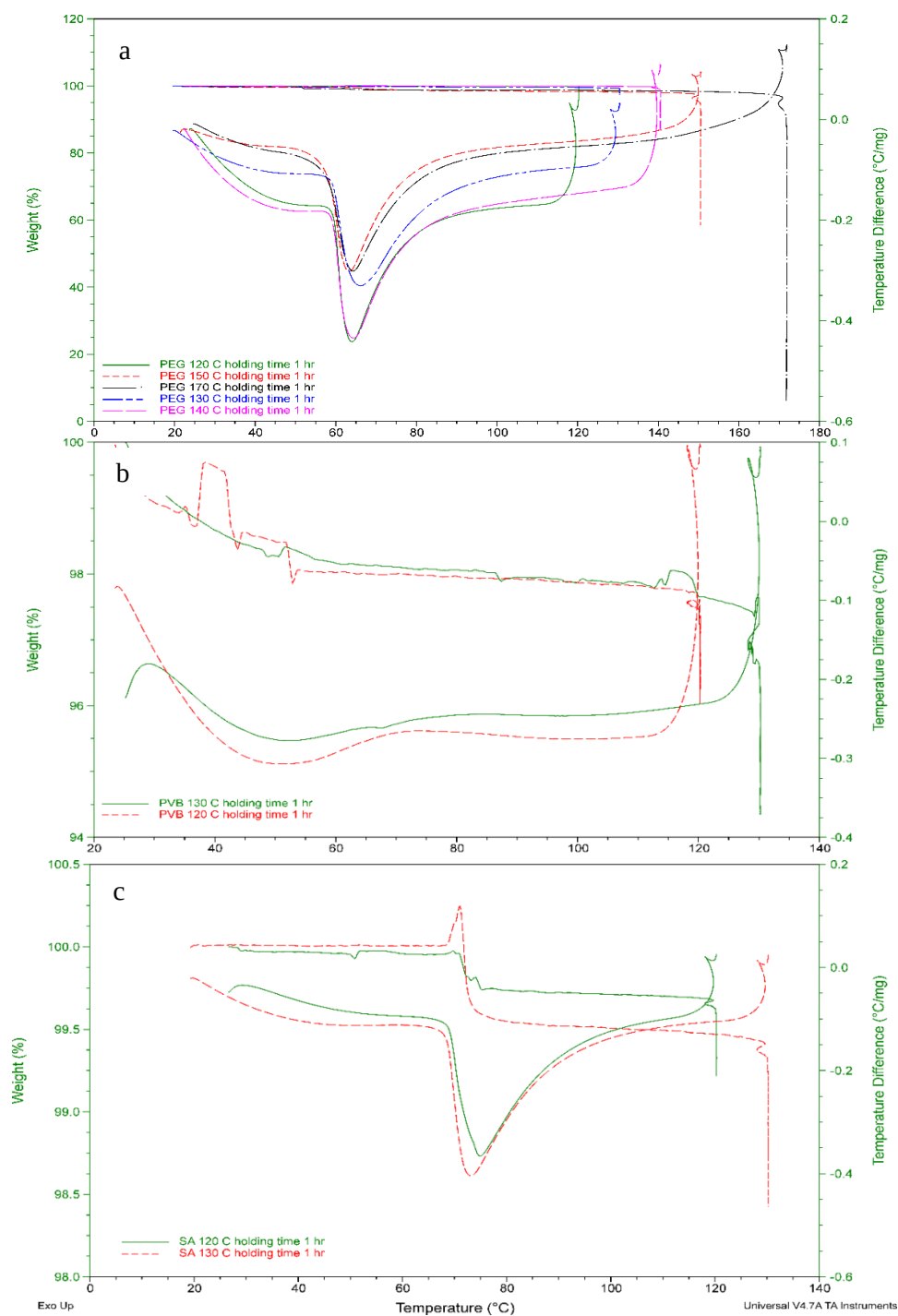


Figure 4.33: Effect of 60 min isothermal holding at 120 °C and 130 °C on weight loss of (a) PEG, (b) PVB and (c) SA.

The TGA data indicated that PEG only lost 1 – 2 wt. % between 120 and 130 °C. Therefore, this temperature range was selected as the most suitable processing temperature for PEG. Weight loss of PVB (Figure 4.33b) and SA (Figure 4.33c) after 60 min isothermal holding at 120 °C and 130 °C were also small (Table 4.7) so further trials in the roller compounder were done at 125 °C.

Table 4.7: Binder component weight loss after 60 min isothermal holding.

Temperature (°C)	Weight loss (wt. %) after 60 min isothermal heating		
	PEG	PVB	SA
120	1	4	1
130	2	6	2
140	13	*	*
150	40	*	*
170	94	*	*

* Experiments not done.

Heterogeneous feedstocks produced in the two-stage process of dry mixing Ti64 powder with binder components in the planetary mixer followed by melt mixing in a roller compounder (method 1, Section 3.4) could not be extruded (Section 4.2.5a). However, using four different mixers (planetary mixer, roller mixer, roller compounder, twin screw extruder) enhanced feedstock homogeneity. The first two stages involve dry mixing Ti64 powder and binder in a planetary and then a roller mixer at room temperature. This premix was then melt mixed in a compounder and then extruded. As the components were fine particles (Figure 4.34), a low (25 rpm) mixing speed was used. A high mixing speed would remove powders, especially Ti64 and PVB powders, from the mixing chamber (reducing the metal content), creating a heterogeneous mix. It would also be a health hazard.

Low speed mixing in a Kenwood planetary mixer was hoped would fold the 60 vol. % Ti64 powder into the 80:15:5 vol. % PEG:PVB:SA binder and increase spatial distribution of components without changing particle size. However, burn-out data (Figure 4.35a) indicated the mixture was not homogeneous and that shear during mixing was insufficient to rupture the agglomerates produced from the interfacial tension and Van der Waals forces between the particles [213, 331].

The dry-mix was then subjected to intensive distributive mixing in a roller mixer (stage 2) to increase homogeneity before melt-mixing. This stage was different to the previous melt-mix process (method 1, Section 3.4) that had produced a heterogeneous feedstock. Mixing at room temperature eliminates binder degradation during the long mixing time. The three hundred 6.3-mm diameter stainless steel spheres in the mixing

chamber rotating at 250 rpm (method 2, Section 3.4) help break the agglomerates, increase feedstock homogeneity and enhance particle packing efficiency.

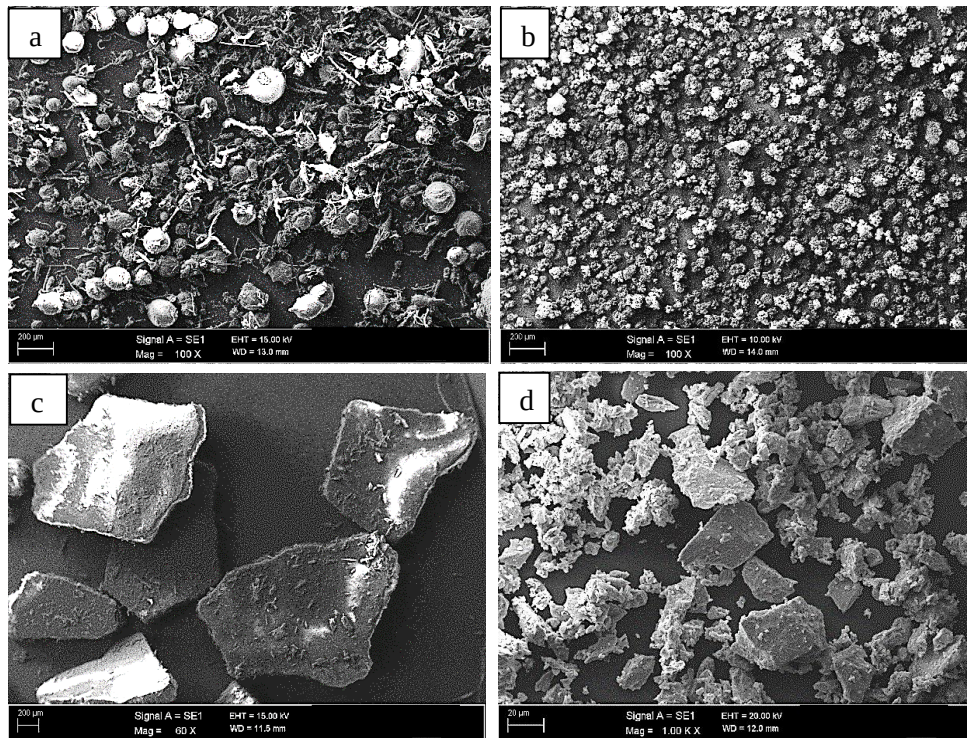


Figure 4.34: SEM images of (a) PEG, (b) PVB, (c) SA, and (d) Ti64 powders.

Burn-out data of samples after 16 hours mixing at 250 rpm in the roller mixer were similar (Figure 4.35b), indicating this dry mixture was homogenous. Roller mixing enhanced mixture homogeneity before melt mixing in the roller compounder.

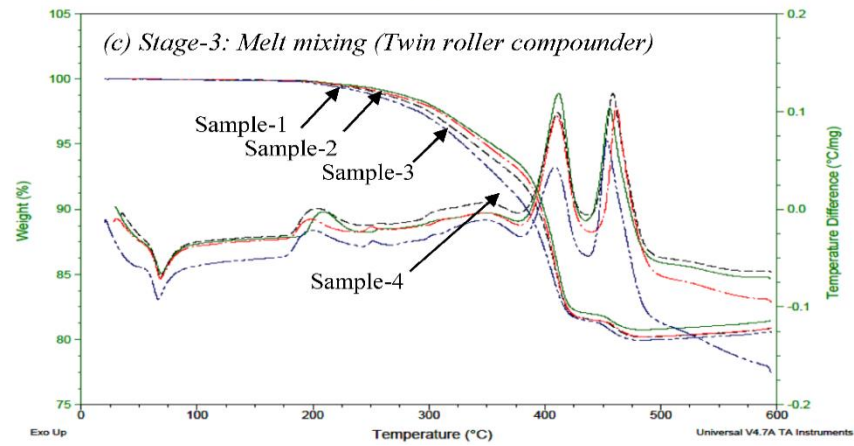
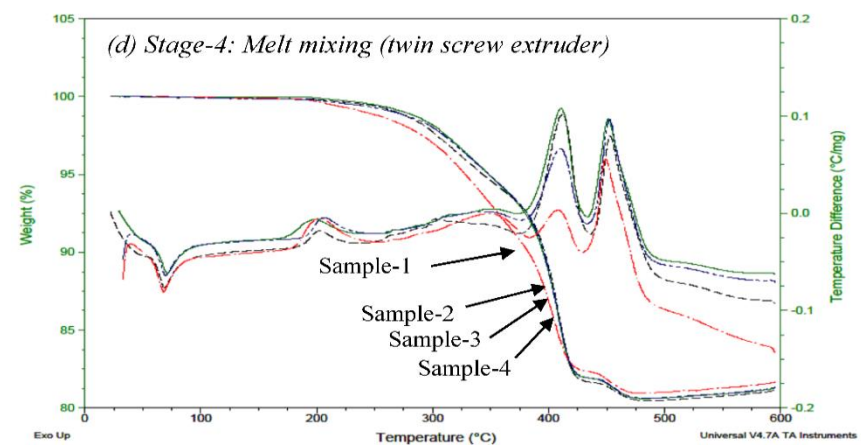
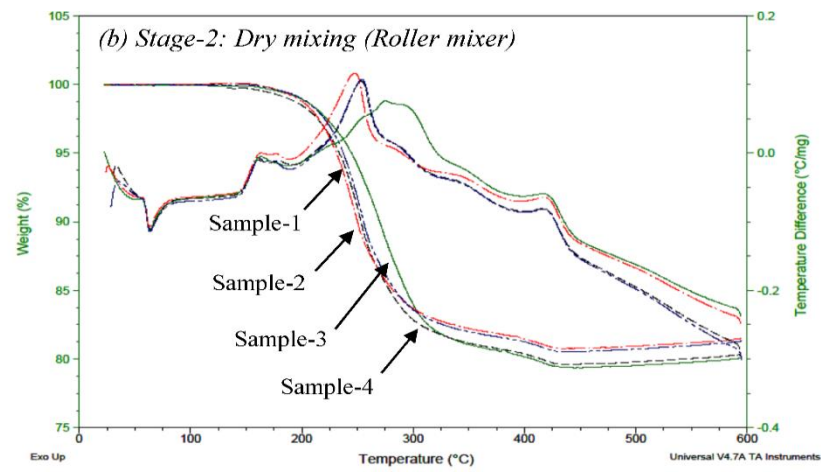
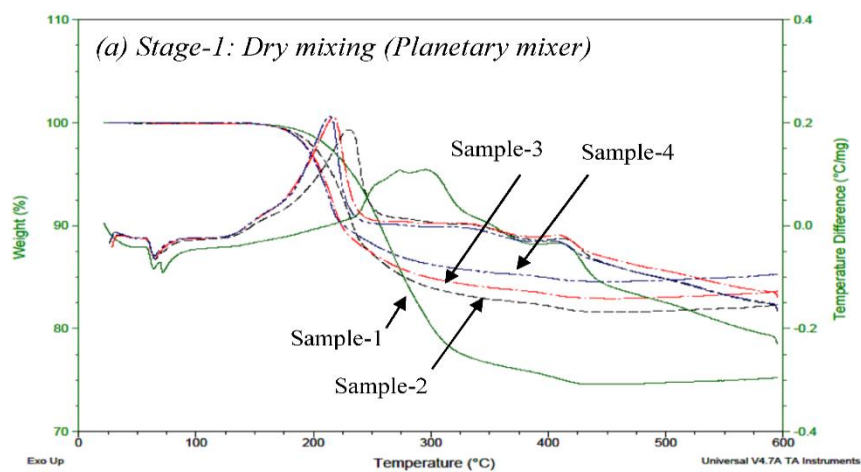


Figure 4.35: Burn-out patterns of samples (n=4) obtained at different stages in feedstock manufacturing (method 2, Section 3.4).

In stage 3, the dry mix was processed into MIM feedstock by melt-mixing in a roller compounder at 125 °C. Mixing torque increased when feedstock was added to the compounder and then became constant (Figure 4.36) as feedstock agglomerates broke and became well dispersed. Four random samples from the mix had similar burn-out patterns (Figure 4.35c), indicating homogeneity.

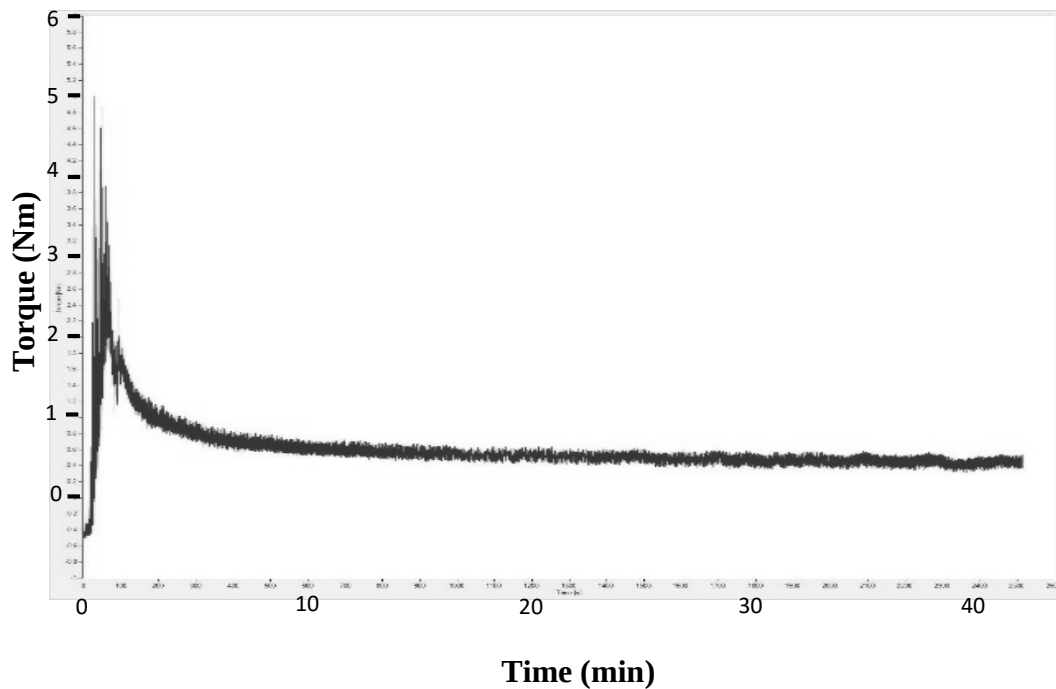


Figure 4.36: Torque when mixing 60 vol. % Ti64 powder and 80:15:5 vol. % PEG:PVB:SA binder at 125 °C and 60 rpm in the roller compounder.

In stage 4, feedstock homogeneity was further increased by dispersive mixing under high shear in a twin screw extruder. Many researchers have used twin screw extrusion to improve feedstock homogeneity [154, 179, 214, 331]. The main difference between melt mixing in a roller compounder and a twin screw extruder (Figure 4.37) is that the former uses distributive mixing to increase feedstock homogeneity whereas the latter uses dispersive mixing [335], which also increases microstructure fineness. Only some of the feedstock processed in a roller compounder experiences high shear between the wall and blades whereas feedstock in a twin screw extruder heating, shearing, and flow conditions such as conveying, compacting, melting, high pressure at the screw tips and fusing. Hydrodynamic force or shear stress developed in twin screw extrusion is sufficient to break agglomerates and help improve feedstock homogeneity.

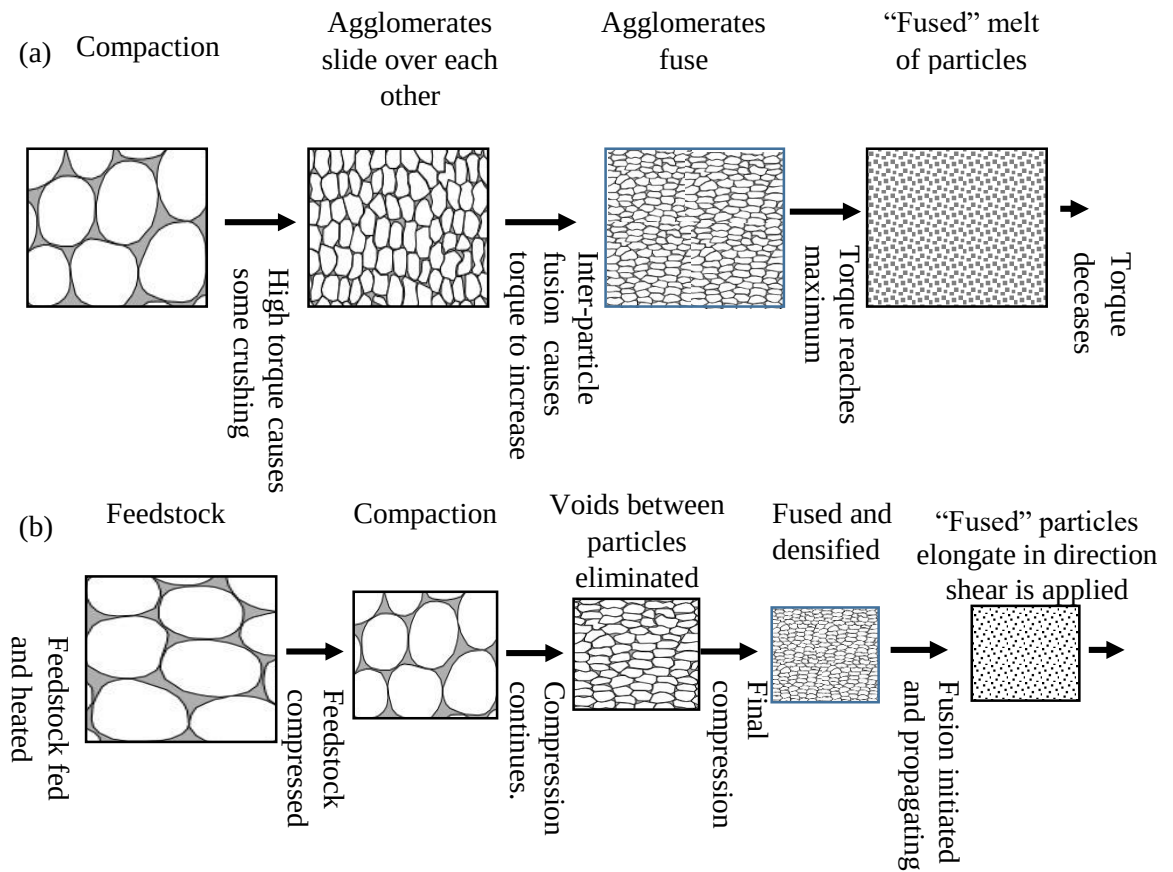


Figure 4.37: Melt mixing mechanism in (a) a roller compounder and (b) a twin screw extruder.

The burn-out pattern of four random samples from feedstock extruded in the twin screw extruder using a feed to nozzle temperature profile of 125, 140, 135, 135, 140 °C at 150 rpm were similar (Figure 4.35d), indicating it was homogeneous. On the other hand, samples manufactured in the compounder showed great variability (Figure 4.35c).

Sortino *et al.* [350] used box and whisker plots to compare data from MIM processes. The box and whisker plots of binder wt. % loss of random samples from the different mixing stages showed that process conditions affected homogeneity (Figure 4.38). A wide range (indicated by the length between two ends of a whisker) and inter-quartile range (length of the box or mid 50%) indicate high variation and inconsistency and that the feedstock is heterogeneous. During each progressive mixing stage, variability in weight loss decreased (i.e. range and interquartile range decreased), indicating

increased homogeneity. This data support work in earlier trials showing twin screw extrusion enhances feedstock homogeneity (Figure 4.37).

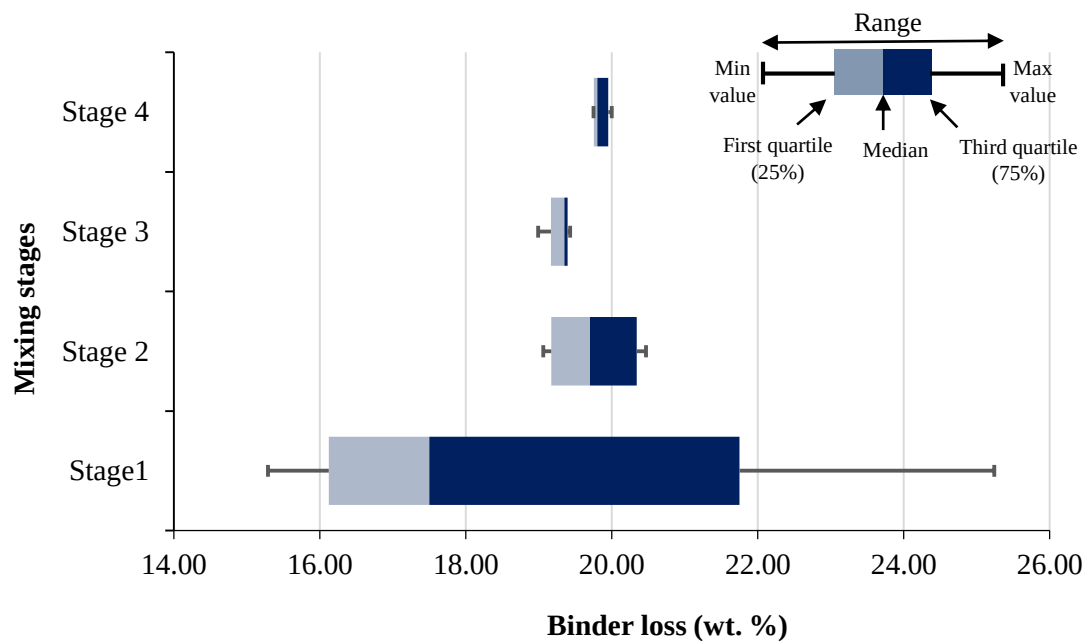


Figure 4.38: Box and whisker plot of binder wt. % loss during stages in the process (n=4).

Density of samples from each stage also indicates feedstock homogeneity increased during the process (Figure 4.39). Stage 1 samples had the highest variability, indicating feedstock produced after 30 min mixing in the planetary mixer was not homogeneous.

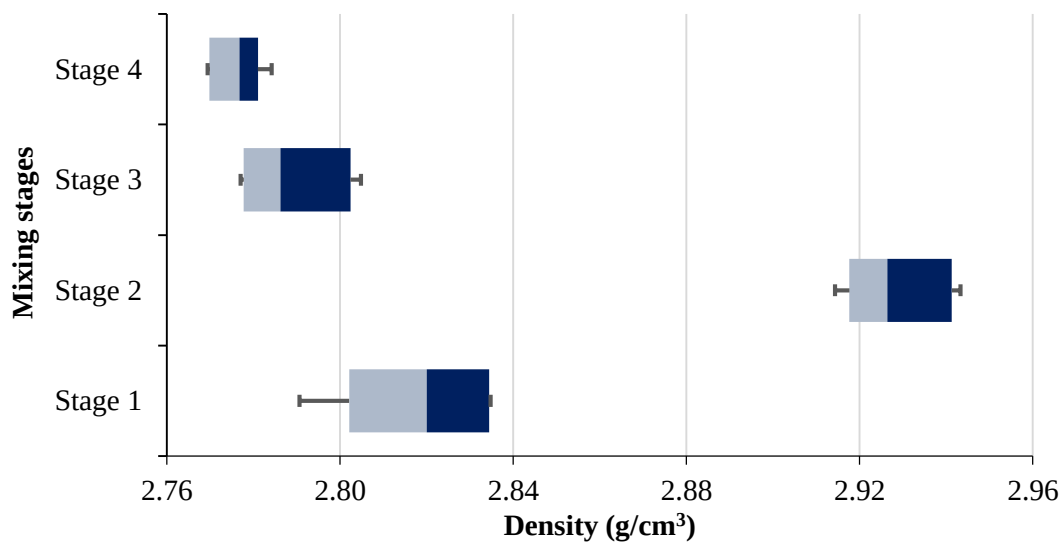


Figure 4.39: Box and whisker plot of feedstock density during stages in the process (n=5).

The range in density of stage 2 and stage 3 samples were similar but less than in stage 1, indicating dry mix homogeneity increased during roller mixing and melt mixing in the roller compounder. Feedstock density of stage 4 samples had the smallest variation, indicating twin screw extrusion increased homogeneity. The median density at stage 2 (roller mixer) was 4% higher than samples from the planetary mixer (stage 1) indicating the mix had compressed during roller mixing, probably because mechanical stress developed from the kinetic energy of 300 315-g steel balls rotating at 250 rpm for 16 hours broke the agglomerates, reduced inter-particle voids and air pockets, and hence minimised the specific volume.

The density after melt-mixing (stages 3 and 4) was lower than from dry mixing (stage 1 and 2), probably because binder components melted and coated the surface of the Ti64 powder particles and filled the inter-particles regions. Air pockets may also have developed in the feedstock during melt mixing. Loss of binder during melt mixing caused by factors that increase specific volume and thus decrease feedstock density. Median density decreased 5% between stage 2 (dry mix) to stage 3 (first melt mix stage), and then a further 0.4% in the second melt mix stage in the extruder. These values indicate that thermal expansion of molten binders filled approximately 5 % more of feedstock volume, which coated the Ti64 particles and filled the inter-particle space during melt mixing in the roller compounder. However, the binders filled only 0.4% more of the feedstock volume during twin screw extrusion, giving better binder distribution and homogeneity. Feedstock density slightly decreased (0.4%) after stage 4, probably because the extruded tubes (feedstock) expanded slightly when they flowed from a high pressure zone (inside the extrusion barrel) to low pressure zone (as they exited the extruder nozzle). Feedstock density may be effect on mass flow and geometrical arrangement of the extruder screws-barrel [397]. These factors, along with thermal expansion and further loss of binder during melt extrusion, would decrease the feedstock density by 0.4%.

Thermogravimetric and density analyses both show feedstock homogeneity increased during the four-stage process (Figures 4.35, 4.38 and 4.39) and that this is an effective process for manufacturing homogeneous Ti-MIM feedstock from Ti64 powder and a PEG:PVB:SA binder. The feedstock microstructure (Figure 4.40) showed that the Ti64 powder and binder were distributed uniformly.

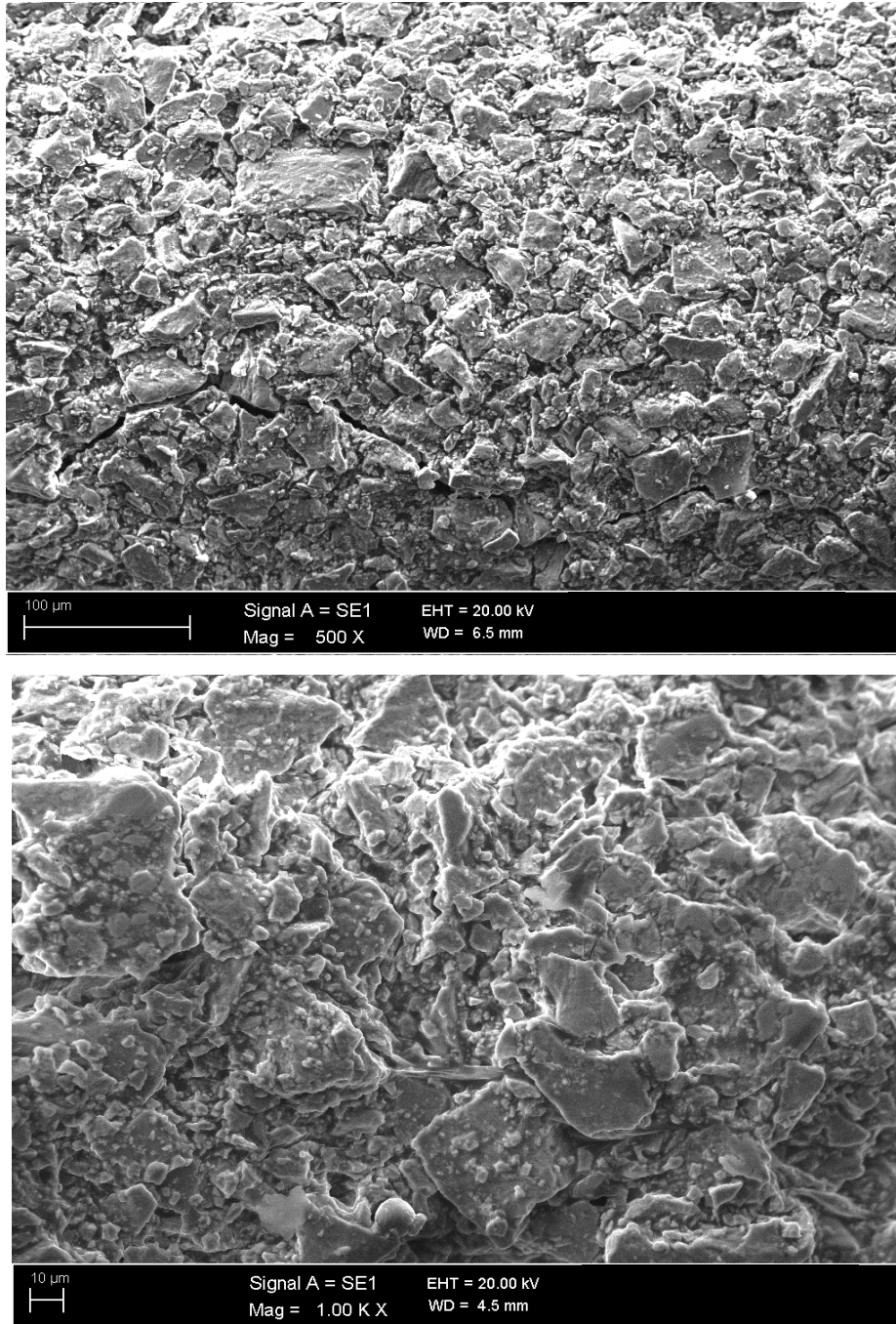


Figure 4.40: SEM images of extruded Ti64 and 80:15:5 vol. % PEG:PVB:SA binder manufactured using a four-stage process.

German and Bose [2] and German and Park [383] suggested the following expression to model feedstock homogeneity (H):

$$H = H_0 + \alpha e^{(kt + C)} \quad 4.6$$

where H_0 is initial mixing homogeneity, t is mixing time, α is mixing parameter, k is mixing rate parameter and the constants α , k , C depend on the mixer, powder

characteristics, agglomeration and powder surface conditions. This model shows that feedstock homogeneity (H) depends on initial homogeneity (H_0), mixer type and mixing time. During mixing, initial homogeneity is low but increases with mixing until a point where rate of mixing equals rate of segregation (a balance between segregation and mixing events). The homogeneity changes exponentially with mixing time and reaches an asymptotic value less than 100% [383].

Data obtained for the four-stage mixing process developed in the current research support this finding. However, as there is little research on this model, further work could be done to identify the contribution each parameter makes to homogeneity.

Density, thermal and morphological analyses showed that feedstock manufactured in the four-stage process was more homogeneous than feedstock manufactured using method 1 (Section 4.2.5a). Reasons for heterogeneity are discussed in Section 4.2.6.

4.2.6. Feedstock heterogeneity and powder-binder interaction

The functional characteristics of each binder component contribute to making a feedstock that is easily moulded, debound and sintered without defects. In the binder developed, PEG is the main polymer, lubricating the powder particles and reducing feedstock viscosity. The PVB is the backbone polymer, providing mechanical strength to the green part and handling strength when transferring the brown part to sintering. The SA is a surfactant, reducing feedstock viscosity [141, 214] and bridging powder and other binder components [27, 141, 145]. If Ti64 powder particles bind to the highly viscous PVB, they are immovable and a viscous, non-extrudable feedstock is produced. However, if powder particles bind to the low viscosity PEG, the moulded part may collapse during debinding. Therefore, it is essential that binder components are uniformly distributed to produce feedstock with the desired functionality.

The feedstock produced using method 1 had agglomerates and was not homogenous (Figures 4.31 and 4.32) due to insufficient distributive and dispersive mixing. To obtain a homogeneous feedstock, interfacial tension and Van der Waals forces between powder and binders must be minimized. Interfacial tension can be minimized by reducing the wetting-angle between binder and powder and Van der Waals forces can be minimized by introducing repulsive forces such as steric stabilization [351-352].

Polymer macromolecules attach (chemisorption) to the powder surface [351, 353] and produce steric stabilization (Figure 4.41). In this Figure, polymer 1 has strong affinity for the powder and anchors to the particle surface. Polymer 2 is more compatible with the dispersion medium and lower affinity for the particle so it extends into the dispersion medium and produces a steric barrier. In the current research, stearic acid (SA) is included in the binder for steric stabilization. Its polar carboxylate groups (COO^-) allow the SA to adsorb to the Ti64 powder surface (Figure 4.42), forming C-O-Ti- and/or C-O-Al- bonds [27]. The hydrocarbon $\text{C}_{17}\text{H}_{35}$ chain of SA extends into the binder, providing a link between powder and binder. When two powder particles with adsorbed SA layers are closer than the thickness of two polymer layers, they repel each other [351, 353], minimizing formation of agglomerates in the feedstock.

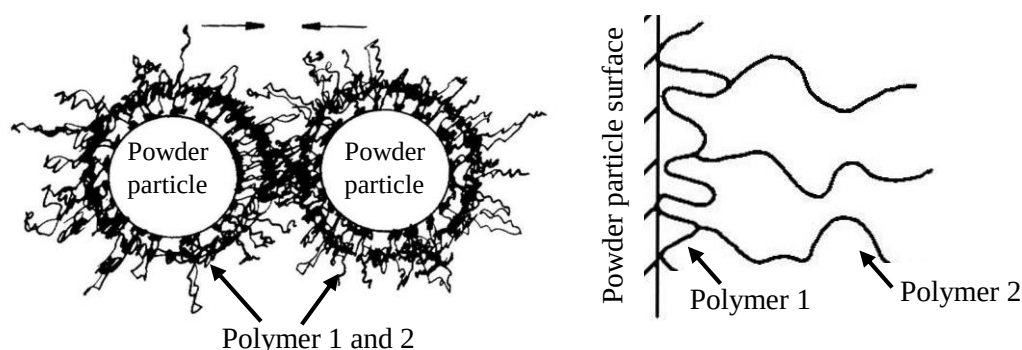


Figure 4.41: Schematic of steric stabilization [353].

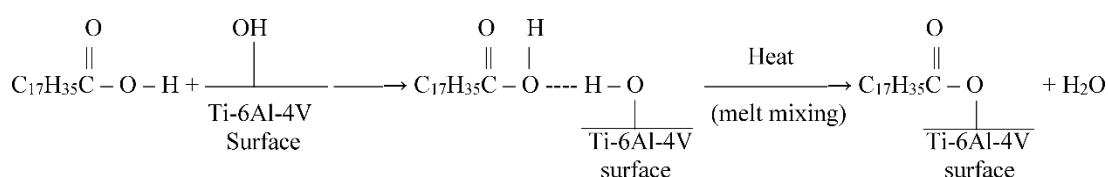


Figure 4.42: Interaction between Ti64 powder and SA.

Metal powders are usually hydrophilic; making it is difficult to coat them with binder. Surfactants enhance wettability. The SA decreases wetting angle (θ) and interfacial tension between powder and binder (γ_{SL}) (equation 4.7). Permeation pressure (ΔP , equation 4.8) caused by capillary pores attracts binder into pores in the powder agglomerates, accelerating powder dispersion [145].

$$\gamma_{SL} = \gamma_{SV} - \gamma_{LV}\cos\theta \quad 4.7$$

$$\Delta P = 2(\gamma_{SV} - \gamma_{SL})/R \quad 4.8$$

where γ_{SV} is interfacial tension of powder, γ_{LV} is interfacial tension of binder and R is radius of capillary pipe.

The SA has a key role in decreasing wetting angle and minimizing formation of agglomerates in the feedstock, thus increasing feedstock homogeneity and stability. To achieve this, SA must be uniformly distributed in the feedstock. Loss of SA and PEG when feedstock is manufactured at 175 °C in the roller compounder may also increase feedstock heterogeneity. Although onset degradation temperature for PEG was 194 °C (Table 4.1) and 67 wt. % was lost between 225 – 285 °C (Table 4.2), 60 min isothermal holding at 170 °C also produced a high loss (Figure 4.33a). The weight loss of pure PEG cannot be compared directly with loss in a compound binder but it is assumed a similar effect may occur during extended mixing at 175 °C. Similarly, although onset of SA degradation was 190 °C (Table 4.1) and it lost 85% at 225 – 285 °C (Table 4.2), SA may also be lost during extended processing times. Insufficient PEG and SA in the feedstock could contribute to agglomerates forming in the feedstock, increasing the viscosity. The viscous PVB could bind to the Ti64 particles and make the feedstock non-extrudable (Figure 4.43).

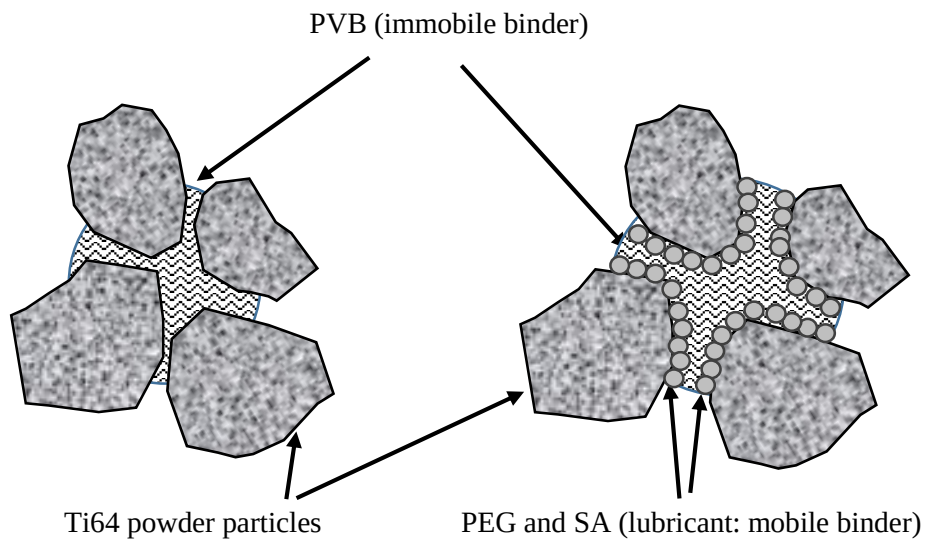


Figure 4.43: Schematic of feedstock with mobile and immobile binders.

After identifying that a homogeneous feedstock could be produced using the four-stage mixing process, several feedstock batches of Ti64 powders with 75:20:5, 80:15:5 and 85:10:5 vol. % PEG:PVB:SA binder were manufactured to investigate the effect of powder-binder composition on steady state torque (ζ_{ss}). At constant powder loadings, steady state torque decreased as PEG, the major low viscosity component in the binder increased (Figure 4.44). Steady state torque also increased with powder loading at a given binder composition.

The additional PEG in the binder fills voids between the Ti64 particles and reduces friction, reducing feedstock viscosity and the steady state torque. Torque can be related to feedstock viscosity [354]. Any increase is proportional to shear stress generated during mixing, indicating the work required to disperse and distribute Ti64 powder in the binder. Higher powder loadings infer less binder per unit volume and therefore increased friction between particles, which increases feedstock viscosity.

Steady state torque indicates feedstock homogeneity (Figure 4.44). Fluctuation (noise) in torque indicates the feedstock may contain some undispersed agglomerates, which must be broken to increase feedstock homogeneity. This was achieved in stage 4 using a twin-screw extruder (Figure 4.37). Mixing torque profiles during stage 3 mixing in the roller compounder for feedstocks with 75:20:5 and 80:15:5 vol. % PEG:PVB:SA binder had similar noise, but was less than for feedstock made with 85:10:5 vol. % PEG:PVB:SA binder (Figure 4.44). This indicated the latter feedstock was less homogenous than the former two.

The steady state torque for each binder was higher and more variable when powder loading increased from 55 to 60 vol. % (43, 86 and 120% respectively) than when it increased from 60 to 65 vol. % (20, 31 and 36% respectively) (Figure 4.45). This indicates feedstock flow properties changed more when powder loading increased from 55 to 60 vol. % than for 60 to 65 vol. %. Based on this steady state torque data, 60 vol. % was assumed to be the optimal powder loading. This is similar to the value obtained by density, mixing torque and viscosity analyses (Sections 4.2.1, 4.2.2 and 4.2.3).

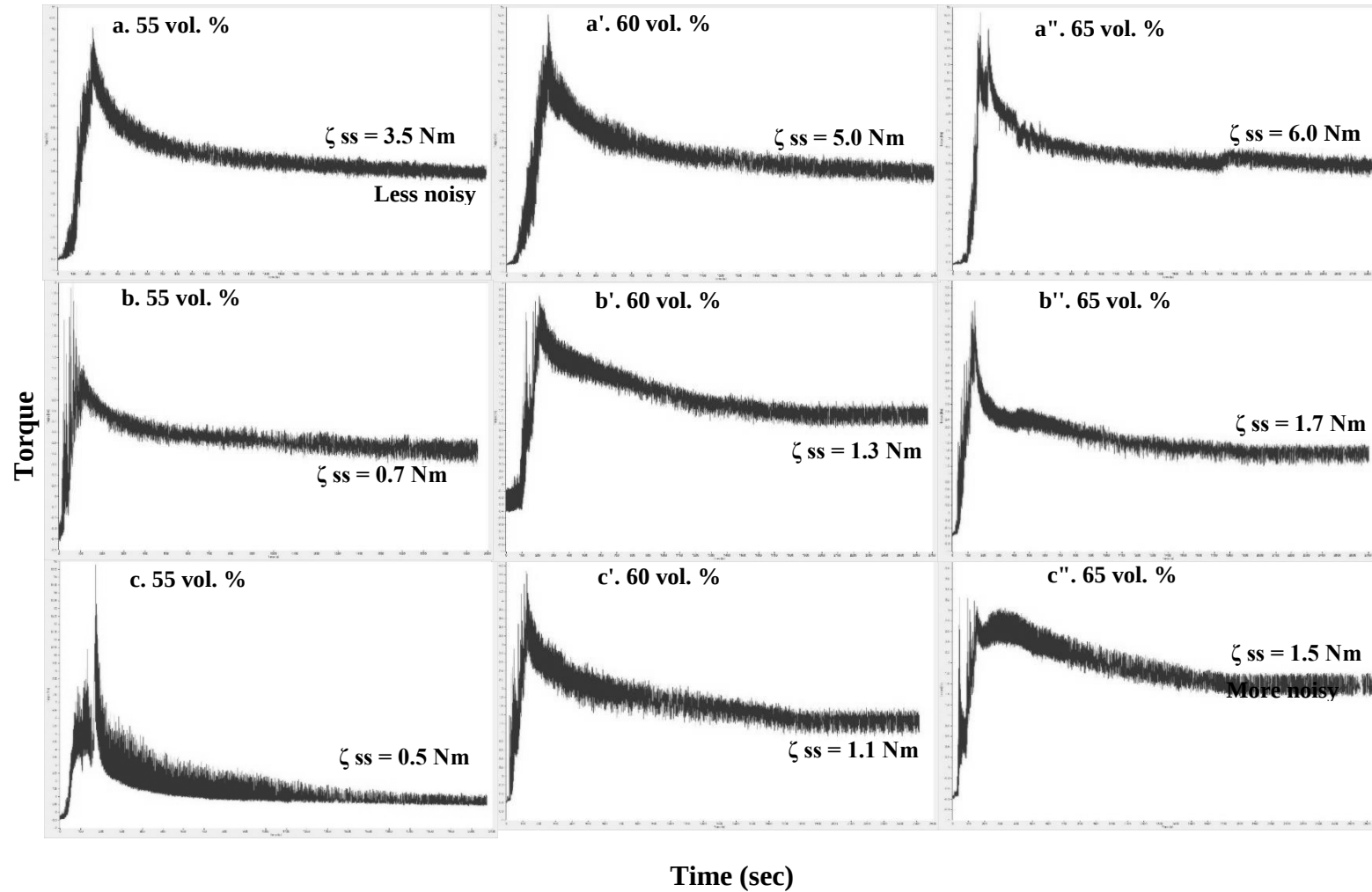


Figure 4.44: Effect of powder loading and binder composition on mixing torque at 125 °C and 60 rpm in the roller compounder: (a, a', a'') 75:20:5 vol. % PEG:PVB:SA; (b, b', b'') 80:15:5 vol. % PEG:PVB:SA; (c, c', c'') 85:10:5 vol. % PEG:PVB:SA.

The percentage decrease in steady state torque when PEG increased from 75 to 80 vol. % (and PVB decreased from 20 to 15 vol. %) was similar for all powder loadings and much higher (72%, 74% and 80%) than when PEG increased from 80 to 85 vol. % (12%, 15% and 29%) (Figure 4.45). The data indicate that feedstock flow properties were affected more when PEG increased from 75 to 80 vol. % than from 80 to 85 vol. %. This has been discussed in Section 4.2.1 (Figure 4.21). The steady state torque data indicate that a 80:15:5 vol. % PEG:PVB:SA binder would be the best binder for Ti-MIM. However, this must be validated using other methods such as rheology (Section 4.3).

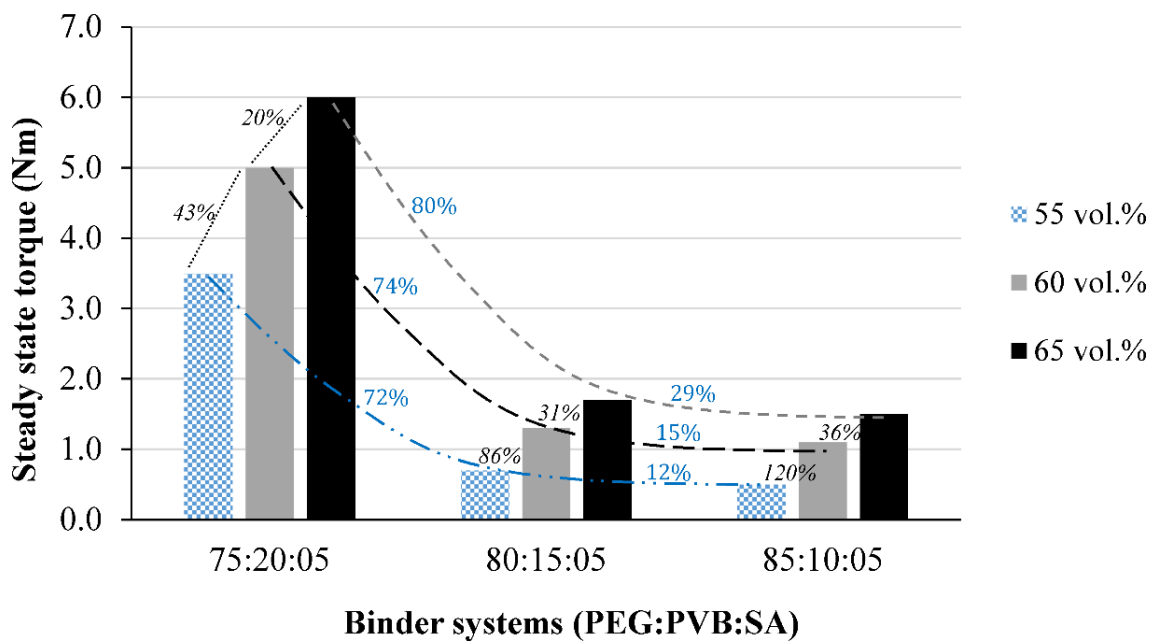


Figure 4.45: Effect of powder loading and binder composition on steady state torque.

Steady state torque data agree with data for density, mixing torque, viscosity and homogeneity analyses (Sections 4.2.1, 4.2.2, 4.2.3 and 4.2.5) and show that steady state torque can be used to characterize powder loading, and viscosity and feedstock homogeneity.

4.2.7. Summary

The effect of powder loading on density, mixing torque, viscosity and homogeneity of feedstocks manufactured using the following methods was investigated:

- Method 1: A two stage process involving dry mixing Ti64 powder with binder at room temperature for 30 min and 25 rpm in a planetary mixer followed by melt mixing at 175 °C for 45 min and 60 rpm in a roller compounder.

- Method 2: A four-stage process involving dry mixing Ti64 powder with binder at room temperature for 30 min and 25 rpm in a planetary mixer then 16 hours at 250 rpm in a roller mixer, followed by melt mixing at 125 °C for 45 min and 60 rpm in a roller compounder then extrusion in a twin screw extruder.

Critical and optimal powder loadings were determined because they influence success of subsequent MIM processes such as moulding, debinding and sintering. Binder and powder will separate if the feedstock has a low powder content, producing heterogeneous moulded parts and defects during debinding and sintering. High powder loadings are preferred because shrinkage during moulding and sintering is lower. However, these feedstocks can be difficult to mould and may damage the blades and screws in process equipment such as mixers, extruders and injection moulders, and analytical equipment such as capillary rheometers.

Critical and optimal powder loadings were determined by measuring feedstock density, mixing torque and viscosity. The PEG content in the binder influenced powder loading. The highest optimal powder loading (60 vol. %) of irregular, coarse Ti64 powder (d_{50} of 52 μm and d_{90} of 117 μm) was obtained using 75:20:5 or 80:15:5 vol. % PEG:PVB:SA binder. This is a higher loading than for the spherical, fine powders (0.5 – 20 μm) recommended in the literature. The Ti64 powder used in this research had a better particle slope parameter (2.66) than the 2.00 recommended in published research to obtain high powder loadings for powder injection moulding (Section 4.2.4). Most research uses spherical fine powders and does not investigate the effect of particle slope parameter on optimal powder loading. Although powder shape and particle size are important for producing a standard feedstock, factors such as particle slope parameter, binder system, feedstock rheology and homogeneity, as well as the manufacturing process also need to be considered.

Temperature for manufacturing the feedstock could not be identified precisely using only the TGA/DTA curve used by reported research. It was found that an appropriate isothermal holding time needs to be included to simulate the manufacturing process. Feedstock manufactured from a two-stage process (method 1) was heterogeneous and could not be extruded in a capillary rheometer. However, a new, four-stage process for manufacturing a homogeneous feedstock has been established. Burn-out tests by

TGA, density and morphological analyses showed that feedstock manufactured using the following four-stage mixing/melting process (method 2) produced homogeneous feedstock from HDH Ti-6Al-4V powder and PEG:PVB:SA binder suitable for Ti-MIM:

- Stage 1: Dry mix Ti64 powder and binder components for 30 min at room temperature in a planetary mixer operating at 25 rpm
- Stage 2: Dry mix the premix at room temperature for 16 hours in a roller mixer operating at 250 rpm
- Stage 3: Melt mix the premix at 125 °C for 45 min in the roller compounder operating at 60 rpm
- Stage 4: Extrude the feedstock using a feed to nozzle temperature profile of 125, 140, 135, 135, 140 °C in a twin-screw extruder operating at 150 rpm

For constant powder loading, steady state torque decreased when PEG content in the binder increased and increased with powder loading at constant binder composition. It was found that steady state torque values can indicate both the critical powder loading and the best binder system.

4.3. Rheological properties

The effect of powder loading, binder composition, shear rate, shear stress and temperature on the rheological properties of feedstock made from Ti64 powder and three PEG-PVB-SA binders (Table 4.8) were investigated to identify the best combination for Ti-MIM. The code for each Ti-MIM feedstock indicates the powder loading and PEG content. For instance, F5580 has 55 vol. % Ti64 powder loading and binder containing 80 vol. % PEG. Feedstocks F6065 and F6575 could not be extruded through the 1-mm diameter × 10-mm long, 2-mm × 5-mm or 3-mm × 3-mm capillary dies at 145 – 185 °C. F5565 and F6580 could be extruded through via 3-mm × 3-mm die but had viscosities (15000 – 55000 Pa·s) above the 1000 Pa·s critical limit suggested for MIM [2]. No rheological investigations were done on these four feedstocks.

Table 4.8: Composition of Ti-MIM feedstocks.

Feedstock code	PEG:PVB:SA in binder (vol. %)	Ti64 powder loading (vol. %)	Binder content in feedstock (vol. %)		
			PEG	PVB	SA
F5565	65:30:5	55	29.2	13.5	2.3
F6065	65:30:5	60	26.0	12.0	2.0
F5575	75:20:5	55	33.7	9.0	2.3
F6075	75:20:5	60	30.0	8.0	2.0
F6575	75:20:5	65	26.2	7.0	1.8
F5580	80:15:5	55	36.0	6.7	2.3
F6080	80:15:5	60	32.0	6.0	2.0
F6580	80:15:5	65	28.0	5.2	1.8
F5585	85:10:5	55	38.2	4.5	2.3
F6085	85:10:5	60	34.0	4.0	2.0

4.3.1. Shear rate and feedstock viscosity

The decrease in feedstock viscosity (η) as shear rate ($\dot{\gamma}$) increased (Figure 4.46) indicates shear thinning [224].

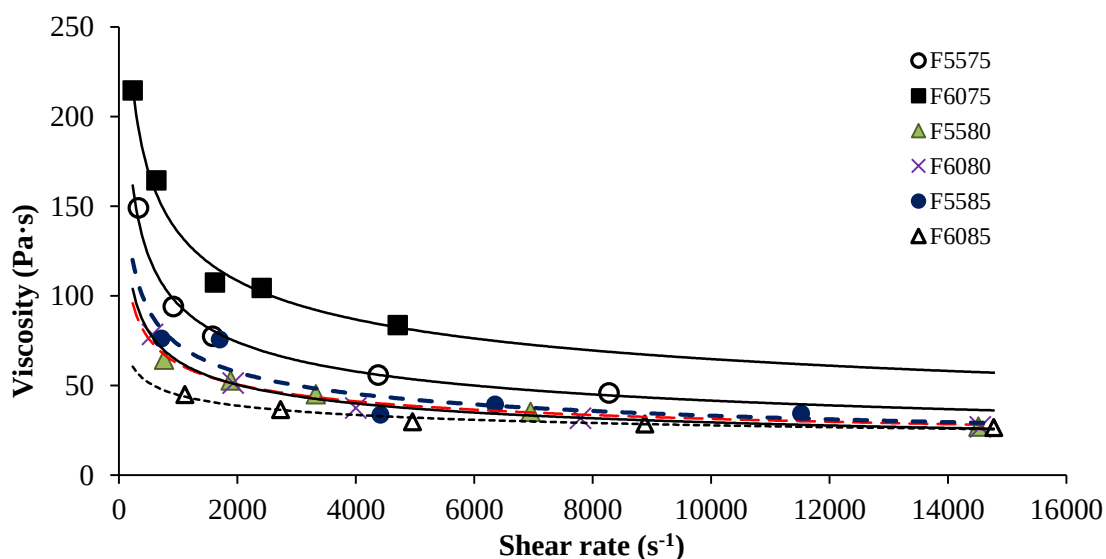


Figure 4.46: Effect of shear rate and powder-binder composition on viscosity.

In shear thinning, the hydrogen bonds and Van der Waals forces that bind the powder particles and binder are broken because the hydrodynamic force ($\eta\dot{\gamma}$) developed at high shear dominates (Sections 4.2.5 and 4.2.6). During shear thinning, the stable particle network that exists in the polymer melts at lower shear rates is broken when

shear rate increases. The Ti64 powder particles and polymeric binders in the feedstock rotate and re-arrange themselves along the flow direction, involving inter-particle motion (Figure 4.47).

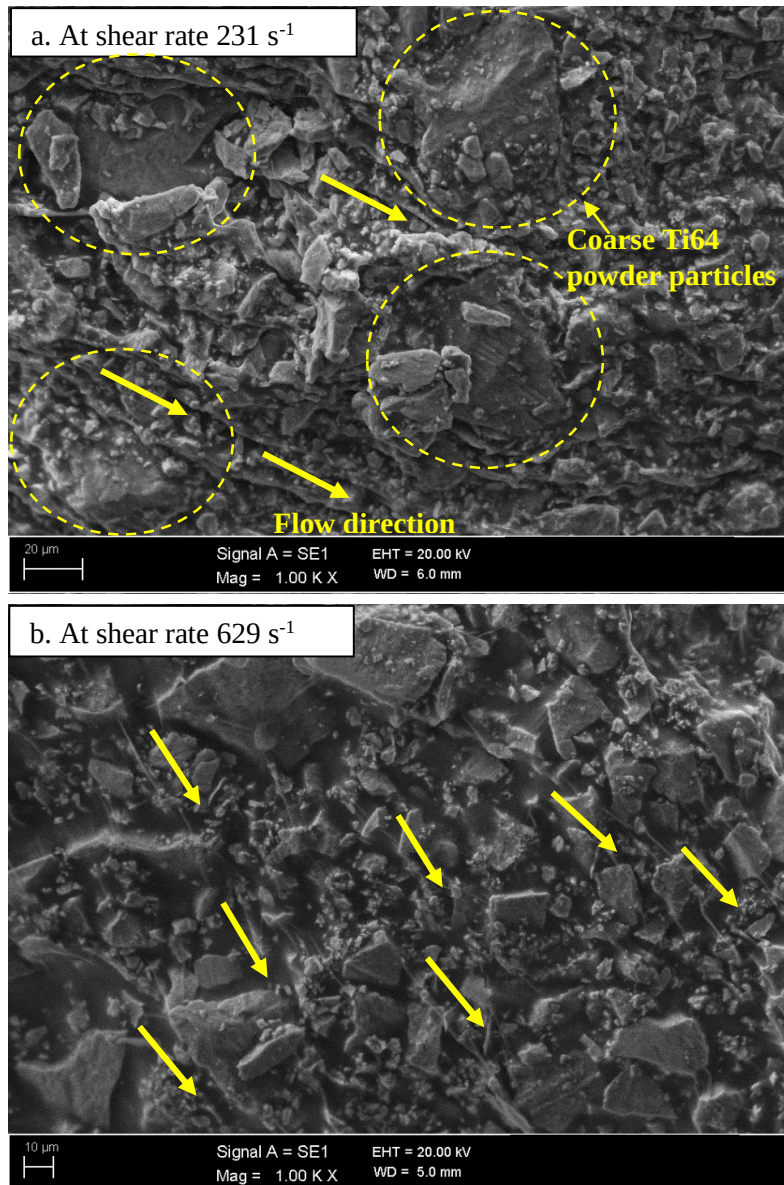


Figure 4.47: SEM images of feedstock F5575 showing effect of shear rate.

Therefore, the hydrodynamic interactions have a great influence on viscosity [352]. At 231 s⁻¹, coarse Ti64 powder particles and flow paths of molten feedstock were visible (Figure 4.47a). However, as shear rate increased to 629 s⁻¹, agglomerates and the Ti64 powder particle size reduced and particles re-arranged themselves so small particles can fit between the coarse particles along the flow direction, allowing inter-particle motion (Figure 4.47b). Hence, molten feedstock flow of 629 s⁻¹ was higher

than the initial flow of 231 s^{-1} (Figure 4.47). As hydrodynamic force during shearing becomes almost ten times greater than agglomerate strength, the agglomerates rupture [348-349], improving particle packing and feedstock homogeneity. The microstructures of feedstock F6075 showed shear thinning at 145°C (Figure 4.48).

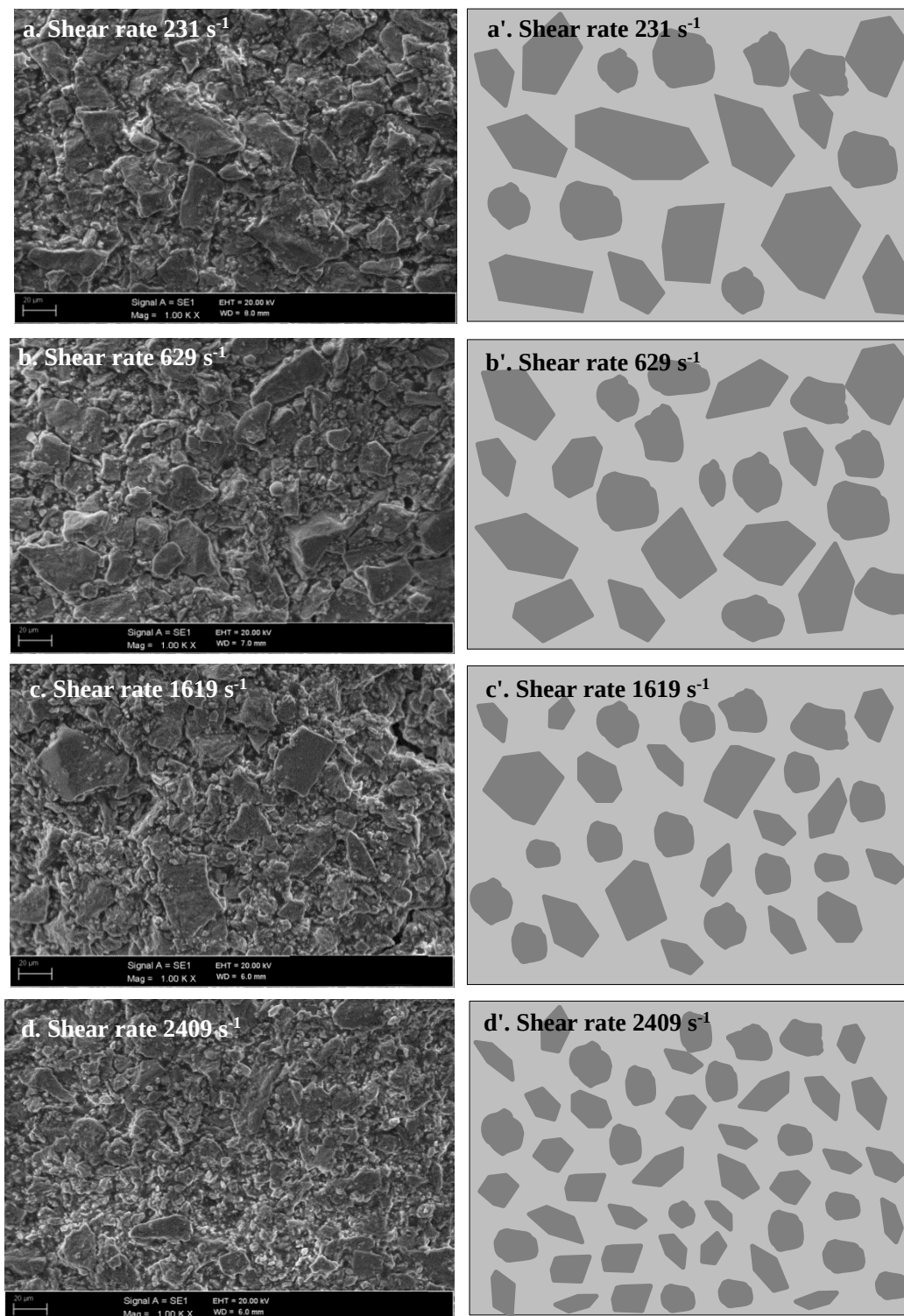


Figure 4.48: SEM images of feedstock F6075 showing the effect of shear rate on particle packing, re-arrangement and homogeneity.

Viscosity of a power law fluid can be derived from Equations 2.1 and 2.2 (Section 2.4.2):

$$\eta = \frac{\tau}{\dot{\gamma}} = m\dot{\gamma}^{n-1} \quad 4.9$$

The viscosity–shear rate data for feedstocks composed of various powder loadings and binders fitted the power law model well, with R^2 of 0.95 to 1.00 (Figure 4.49). Flow behaviour indices (n) of feedstocks are obtained by re-arranging Equation 4.9:

$$\log \eta = (n - 1) \log \dot{\gamma} + \log m \quad 4.10$$

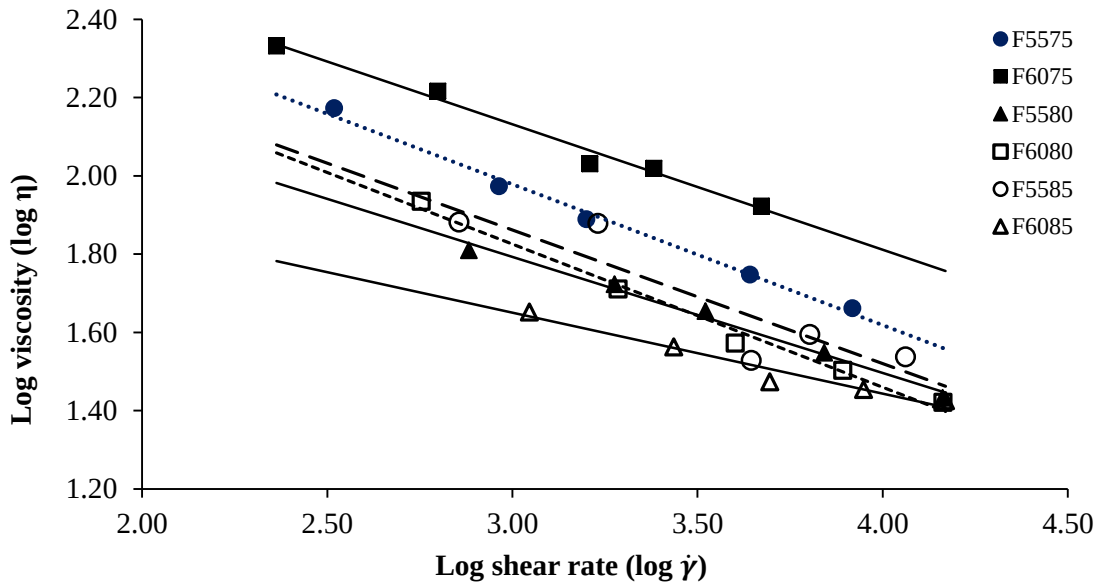


Figure 4.49: Effect of shear rate on feedstock viscosity.

All feedstocks had a flow behaviour index less than one, indicating shear thinning flow behaviour (Table 4.9). The smaller the value, the greater the shear-thinning [224] (steeper gradient). Feedstock F6080 had the lowest flow behaviour index. Other possible feedstocks for Ti-MIM, based on rheological properties, were F5575 and F6075.

Table 4.9: Effect of powder loading and binder composition on flow behaviour index of Ti64-MIM feedstocks at 145 °C.

Feedstock code	F5575	F6075	F5580	F6080	F5585	F6085
n	0.64	0.68	0.70	0.63	0.72	0.79

As well as feedstock F6080 having slightly better shear thinning flow behaviour than F5575 (Table 4.9), it also has a higher powder loading. This will minimise shrinkage and defects during debinding and sintering. Similarly, F6075 is better than F5575 because the powder loading is higher even though the lower shear thinning is less than F5575.

Further trials were done with feedstock F6080 to investigate the effect of increasing powder loading. Feedstock exhibited shear thinning at 50, 55, and 60 vol. % powder loading (Figure 4.50). At powder loading above 60 vol. %, viscosity increased significantly (Section 4.2.3) and this feedstock exhibited dilatant behaviour (Figure 4.50), which is unfavourable for MIM because powder-binder separation may occur during injection moulding. Viscosity was believed to increase because the two-dimensional layer of the particles changes to a three-dimensional form [228].

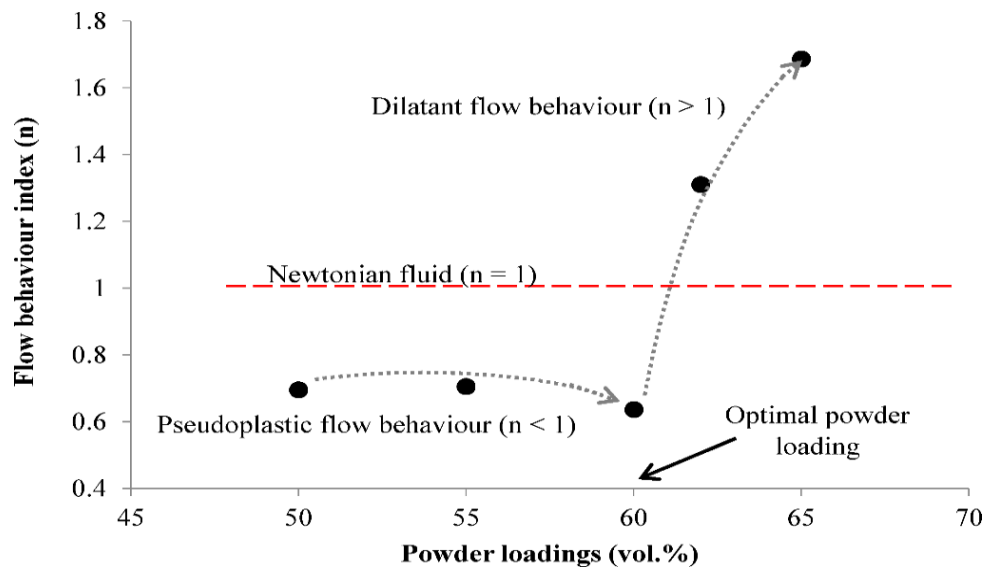


Figure 4.50: Effect of powder loading on rheological behaviour of feedstock F6080 at 145 °C.

It is proposed the flow behaviour index obtained from could be used to identify optimal powder loading of a MIM feedstock. For example, optimal powder loading could be the point where the fluid behaviour changes from pseudoplastic to dilatant (Figure 4.50). This indicated that feedstock F6080, which had the highest shear thinning of the feedstocks investigated, would be the optimal feedstock for Ti64-MIM. This powder loading supports the value identified as optimal by density, torque and viscosity analyses (Sections 4.2.1 – 4.2.3). This new method, supplements the three methods (Sections 4.2.1 – 4.2.3) given in the MIM handbook [2].

Data indicated that feedstocks F6080 and F6075 had optimal shear thinning behaviour between 125 and 165 °C with the maximum at 145 °C (Figure 4.51). This indicates the best operating temperature for injection moulding will be between 125 (when n tends to decrease) and 145 °C (optimal shear thinning temperature; n is minimum). Thus, the temperature profile (feed to nozzle) in the injection moulder should be 125 – 130 – 135 – 140 – 145 °C. This profile, which is similar to that obtained by trial and error (Method 2, Section 3.4), produced long smooth bars (Figure 4.52b) compared to the short rough bars produced when the temperature profile was lower (Figure 4.52a).

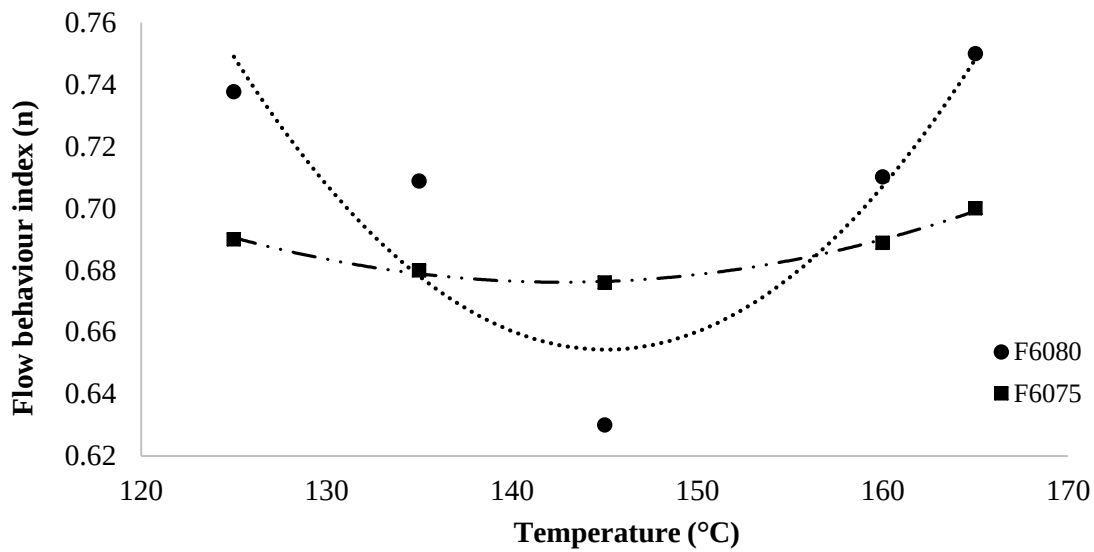


Figure 4.51: Effect of temperature on flow behaviour index of feedstocks F6075 and F6080.

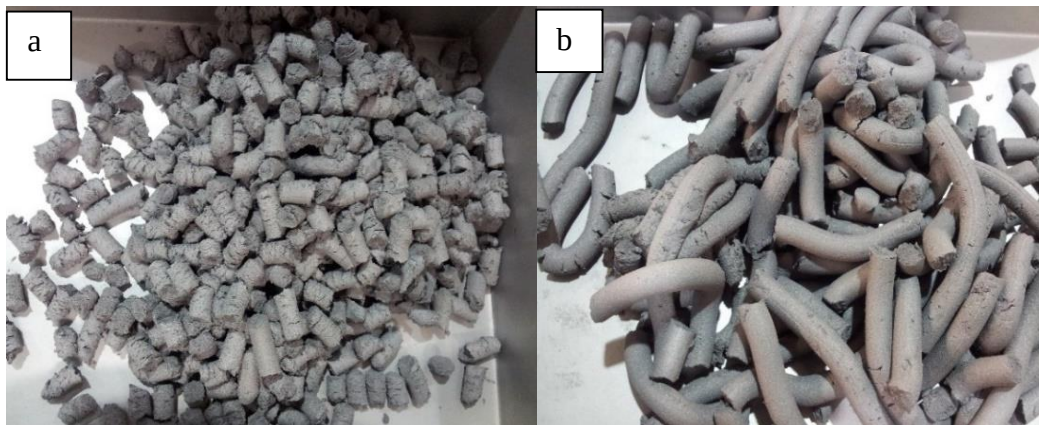


Figure 4.52: Ti64-MIM (F6080) extruded with barrel-to-nozzle temperature profiles of (a) 110 – 125 – 125 – 125 – 135 °C and (b) 125 – 140 – 135 – 135 – 140 °C.

4.3.2. Powder-binder composition and the yield stress

Yield stress is determined using either the Bingham (Equation 4.11) or Casson (Equation 4.12) models [229] and can be found from the y -intercept of these linear models.

$$\tau = \tau_y + \eta_b \dot{\gamma} \quad 4.11$$

$$\sqrt{\tau} = \sqrt{\tau_y} + \sqrt{(\eta_b \dot{\gamma})} \quad 4.12$$

where η_b is plastic viscosity.

Rheological data for feedstocks made from 55 or 60 vol. % Ti64 powder loading and 75:20:5, 80:15:5 or 85:10:5 vol. % PEG:PVB:SA binders fitted both the Bingham ($R^2 = 0.98 - 0.99$) and Casson ($R^2 = 0.99 - 1.00$) models (Table 4.10 and Figure 4.53).

Table 4.10: Goodness of fit of Ti64-MIM feedstocks at 145 °C to the Bingham and Casson models for yield stress (kPa).

Feedstock code	Bingham model			Casson model		
	Equation	R^2	τ_y	Equation	R^2	τ_y
F5575	$\tau = 0.041\dot{\gamma} + 49.2$	0.99	49.2	$\sqrt{\tau} = 0.172\sqrt{\dot{\gamma}} + 4.1$	1.00	16.5
F6075	$\tau = 0.076\dot{\gamma} + 46.4$	0.99	46.4	$\sqrt{\tau} = 0.238\sqrt{\dot{\gamma}} + 3.7$	1.00	13.4
F5580	$\tau = 0.024\dot{\gamma} + 53.3$	0.98	53.3	$\sqrt{\tau} = 0.136\sqrt{\dot{\gamma}} + 3.8$	0.99	14.8
F6080	$\tau = 0.024\dot{\gamma} + 46.9$	1.00	46.9	$\sqrt{\tau} = 0.132\sqrt{\dot{\gamma}} + 3.9$	1.00	15.6
F5585	$\tau = 0.032\dot{\gamma} + 30.9$	1.00	30.1	$\sqrt{\tau} = 0.156\sqrt{\dot{\gamma}} + 2.9$	0.93	8.3
F6085	$\tau = 0.025\dot{\gamma} + 25.0$	1.00	25.0	$\sqrt{\tau} = 0.144\sqrt{\dot{\gamma}} + 2.2$	1.00	4.9

Although the experimental data fitted both the Bingham and Casson models well, yield stresses obtained were very different (Table 4.10), with the values from the Bingham model being three to four times as large as from the Casson model. Equation 4.12 can be rewritten after squaring both sides,

$$\tau = \tau_y + \eta_b \dot{\gamma} + [2\sqrt{(\tau_y \eta_b \dot{\gamma})}] \quad 4.13$$

The additional term, $[2\sqrt{(\tau_y \eta_b \dot{\gamma})}]$ in the Casson model (Equation 4.13) compared with the Bingham model (Equation 4.11) justified the difference in the yield stresses obtained from these models (Table 4.10). However, these two models tend to converge at higher shear rates [229].

Rheological behaviour of many pseudoplastic materials fits the Casson model better than Bingham model [355-356] but the Bingham model is widely used because it is easier to obtain the yield stress at zero shear rate. Both the Casson and Bingham models indicate that yield stress of the Ti-MIM feedstock decreases as PEG content of the binder increases (Table 4.10). As PEG content increases, inter-particle voids are filled and fluidity between Ti64 particles increases, reducing friction. Therefore, lower injection pressure is required. However, excess PEG would reduce the optimal powder loading (Section 4.2.1) and cause flashing during mould filling. Yield stress decreased more quickly the higher the PEG content (Table 4.10), indicating that flashing may be more likely to occur in feedstocks F5585 and F6085.

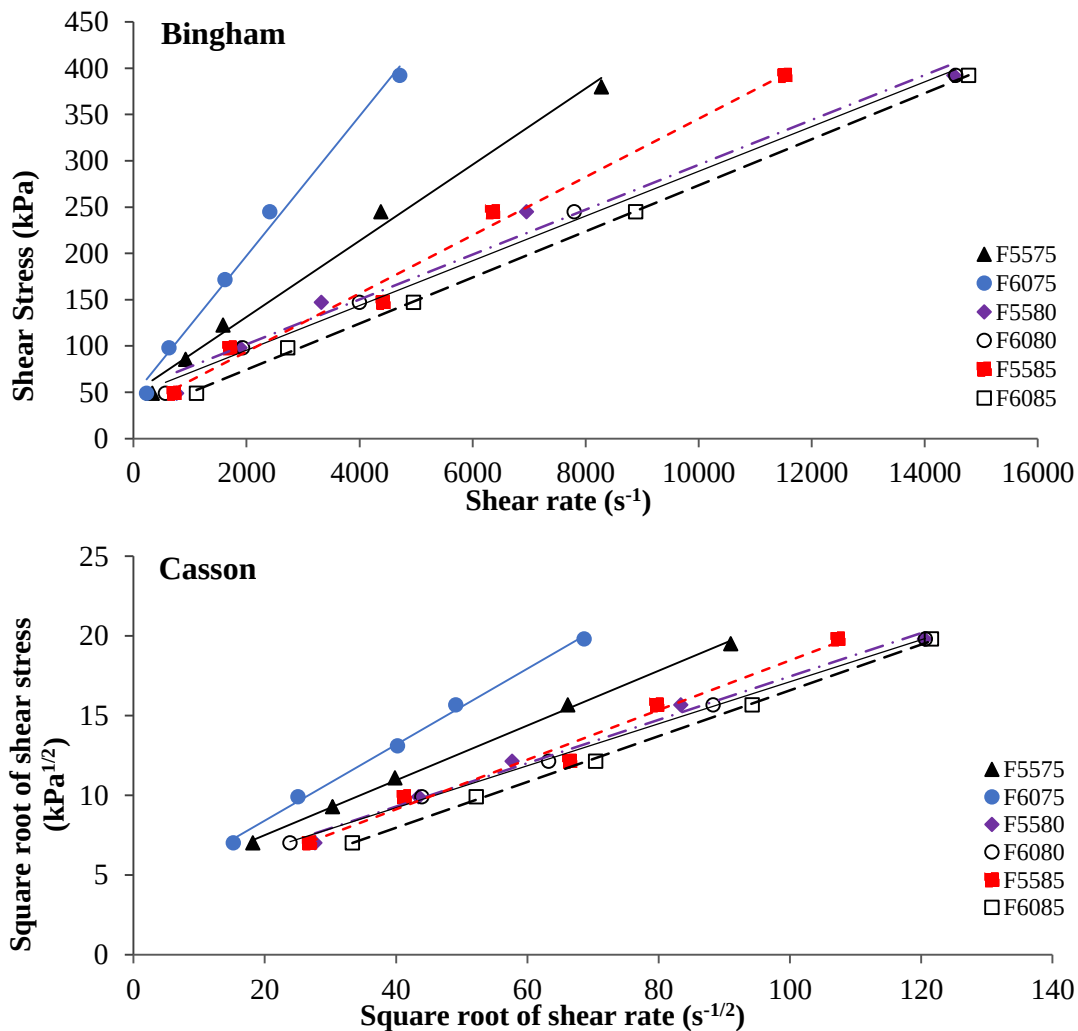


Figure 4.53: Goodness of fit for yield stress of Ti64-MIM feedstocks at 145 °C using the Bingham and Casson models.

The differences in yield stress as the powder loading increased from 55 to 60 vol. % were insignificant compare with the wide variation in yield stress exhibited by the two models (Table 4.10). Feedstocks with 60 vol. % powder loading had a lower yield stress and therefore require a lower injection pressure (Table 4.10). Yield stress data indicate feedstocks F6075 and F6080 had better flow properties and are the most promising feedstocks.

Increasing temperature or PEG content decreased plastic viscosity (gradient of Equation 4.11) of feedstocks F6075 and F6080 (Figure 4.54). The increased fluidity means lower pressure is required for injection moulding at higher processing temperatures and/or higher PEG content. Yield stress of Feedstock F6080 decreased 7% (55.9 to 51.8 kPa) when the temperature increased from 125 to 145 °C and by a further 45% (51.8 to 32.2 kPa) when the temperature was increased to 165 °C (Table 4.11). Although yield stress of feedstock F6075 was decreased 27% (55.4 to 40.3 kPa) when the temperature increased from 125 to 145 °C, the overall decrease was only 12% (55.4 to 48.6 kPa) when the temperature increased from 125 to 165 °C (Table 4.11), showing erratic yield stress fluctuation between 145 and 165 °C. This could be either due to the experimental error or feedstock instability. These data suggest that 145 to 165 °C is a vulnerable temperature during injection moulding due to high fluctuation in yield stress, which would affect the feedstock flow significantly.

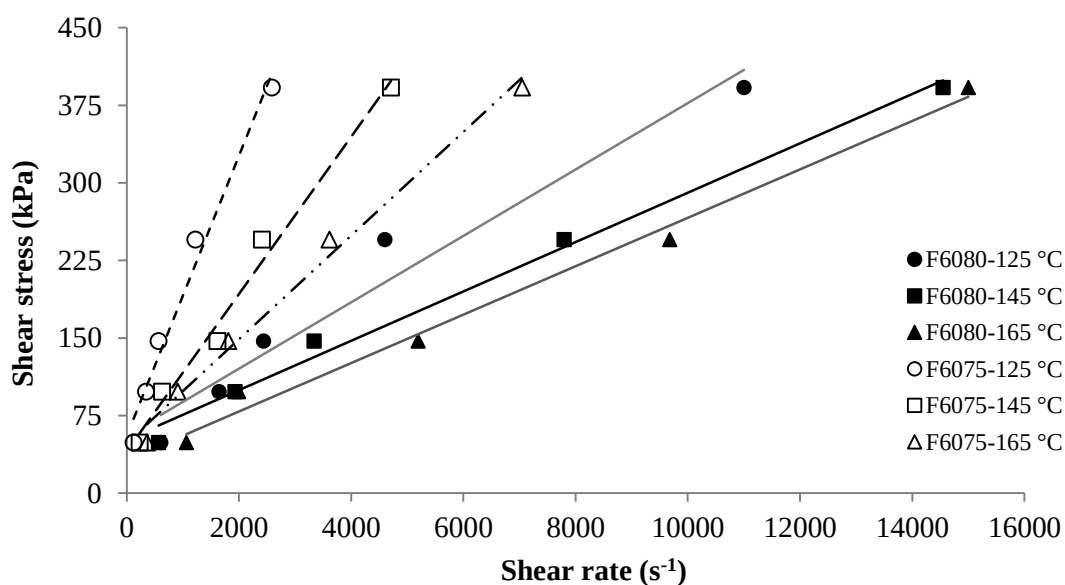


Figure 4.54: Effect of temperature and PEG content on yield stress of feedstocks.

Table 4.11: Effect of temperature and feedstock composition on yield stress and plastic viscosity.

Feedstock code – Temp (°C)	Plastic viscosity (Pa·s)	Yield stress (kPa)
F6075 – 125	0.136	55.39
F6075 – 145	0.076	40.33
F6075 – 165	0.050	48.55
F6080 – 125	0.032	55.92
F6080 – 145	0.024	51.78
F6080 – 165	0.023	32.22

4.3.3. Powder-binder composition and feedstock fluidity

Shear rates in MIM vary between 100 and 100,000 s^{-1} and feedstock viscosity at moulding temperature should be less than 1000 Pa·s [2]. Viscosities of all feedstocks produced in this research were between 214 Pa·s at 230 s^{-1} and 26 Pa·s at 14800 s^{-1} (Figure 4.46). Feedstock fluidity at 145 °C increased with shear rate, PEG content but decreased with powder loading (Figure 4.55).

Feedstocks F5580 and F6080 had similar fluidity, irrespective of shear rate, which was higher than the fluidity of F5575 and F6075 (Table 4.12). This indicates 80:15:5 vol. % PEG:PVB:SA binder is more suitable than 75:20:5 vol. % PEG:PVB:SA binder since it provides better flow properties during processing, especially mould filling as evidenced in Sections 4.4 and 4.5. However, F6085 had fluidity only above 1000 s^{-1} (Figure 4.55; Table 4.12), indicating its suitability at higher shear rates. However, the high fluidity may cause flashing if injection moulding is done at high shear rates. Based on fluidity values, F6080 appears the most promising feedstock because it had higher fluidity (Table 4.12) at wide range of shear rates, such as 560 to 14500 s^{-1} (Figure 4.55), which are likely to occur during injection moulding as discussed in the beginning of this section.

4.3.4. Powder-binder composition and melt flow

Melt flow rate (MFR) indicates the ease that molten feedstock under pressure and at a given temperature will flow through a capillary die. Feedstock MFR for a wide range of shear stress decreased with powder loading (Table 4.13). Binder concentration decreases as powder loadings increase, increasing the friction between Ti64 powder particles and binder, so feedstock melt flow rate decreases.

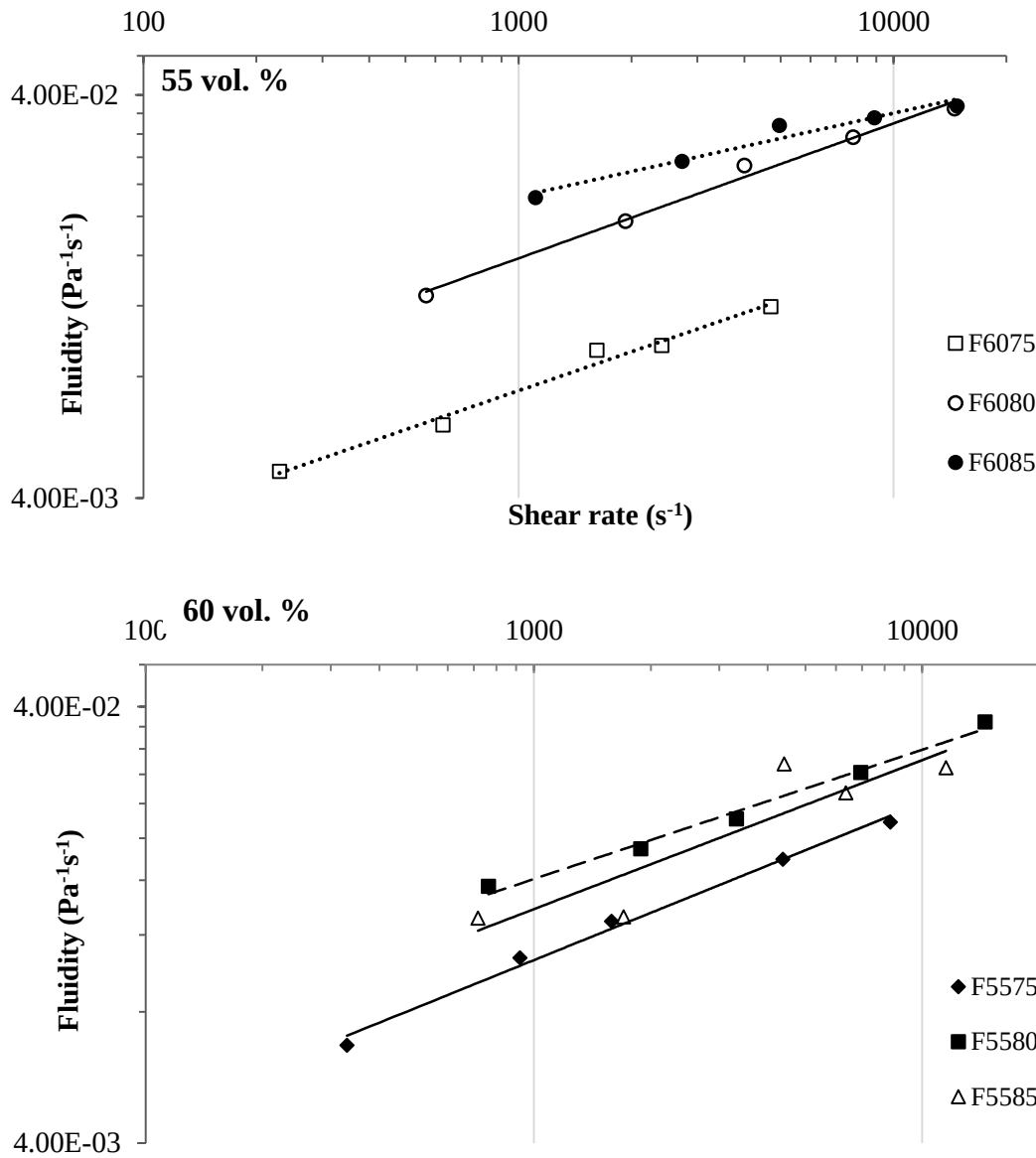


Figure 4.55: Effect of shear rate and binder composition on fluidity of Ti65-MIM feedstocks.

Table 4.12: Effect of shear rate and composition on feedstock fluidity ($10^{-3} \text{ Pa}^{-1}\text{s}^{-1}$) at 145°C .

Feedstock code	Shear rates (s^{-1})		
	800	1000	4000
F5575	9.7	10.8	17.9
F6075	6.9	7.3	11.4
F5580	15.1	16.2	24.5
F6080	14.6	16.2	25.7
F5585	12.8	13.8	22.1
F6085	-	-	29.6

- No fluidity (Figure 4.55).

Table 4.13: Effect of shear stress and composition on feedstock melt flow rate (g/10 min) at 145 °C.

Feedstock code	Shear stress (kPa)				
	49	98	147	245	392
F5575	19.5	54.2	93.3	225.6	484.9
F6075	13.6	37.0	85.3	141.9	277.4
F5580	45.0	111.1	195.8	409.5	855.1
F6080	33.4	110.6	195.6	459.1	857.0
F5585	65.5	160.7	291.9	523.2	870.3
F6085	42.3	100.2	260.0	374.1	678.7

Increasing PEG content gives a concomitant decrease in the content of high viscosity PVB in the binder, reducing feedstock bulk viscosity and increasing the MFR (Table 4.13). For all feedstock composition, MFR increases with shear stress (Table 4.13). Since (a) shear stress increases with shear rates (Figure 4.56) and (b) the increasing shear rate decreases the viscosity (Figure 4.49) and increases the fluidity, the feedstock MFR increased with the shear stress.

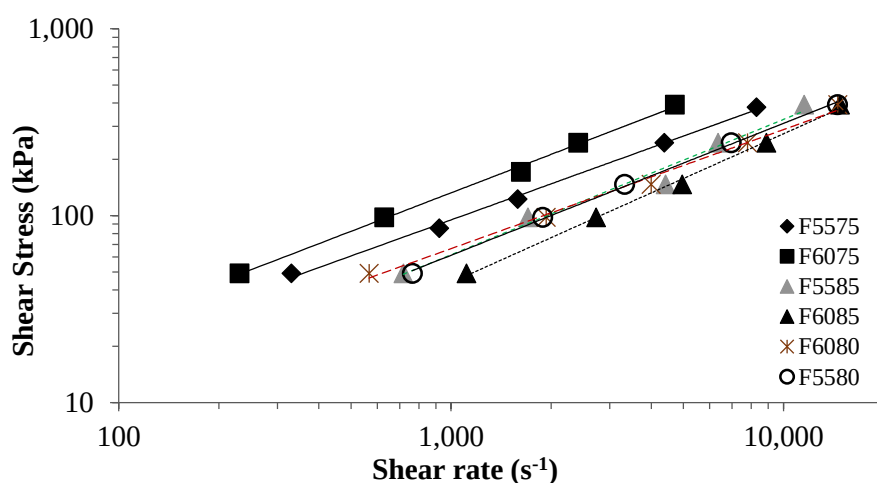


Figure 4.56: Effect of shear rate and composition on feedstock shear stress at 145 °C.

The MFR for feedstocks F5580 and F6080 were similar for all shear rates, and higher than for F5575 and F6075 (Table 4.13) indicating that 80:15:5 vol. % PEG:PVB:SA binder is more suitable for injection moulding than 75:20:5 vol. % PEG:PVB:SA binder. These results support those reported in Section 4.3.3. Feedstocks F5585 and F6085 had the highest MFR, indicating they would be more easily injected than other feedstocks. Feedstock F6085 has the added advantage of higher powder loading.

Based on MFR values, feedstocks F6085 and F6080 appeared the most promising. The MFR of feedstock F6080 was higher than F6085 at the higher shear stresses (Table 4.13) and MFR of feedstocks with 85:10:5 vol. % PEG:PVB:SA binder were more sensitive to changes in powder loading than feedstock made with 80:15:5 vol. % PEG:PVB:SA binder. This indicated the MFR of F6085 would change considerably during injection moulding if the feedstock had any heterogeneity, which would cause defects in the moulded parts. Therefore, feedstock F6080 was considered the most promising feedstock and F6085 the second choice.

4.3.5. MFR and flow behaviour index

The MFR for feedstocks made of Ti64 powder and a binder made from PEG, PVB and SA increased with shear stress and there was a good fit (R^2 of 0.98 - 1.00) for power regression trend lines (Figure 4.57). The following relationship is proposed between MFR (μ) and shear stress (τ):

$$\mu = q\tau^p \quad 4.14$$

which can be rearranged into the linear form:

$$\log \mu = p \log \tau + \log q \quad 4.15$$

where p is the rate of change of MFR with shear stress and called *feedstock flow index* from now onwards, and q is the MFR as the shear stress approaches unity; p and the q can be determined from the gradient and y-intercept respectively (Equation 4.15 and Figure 4.57).

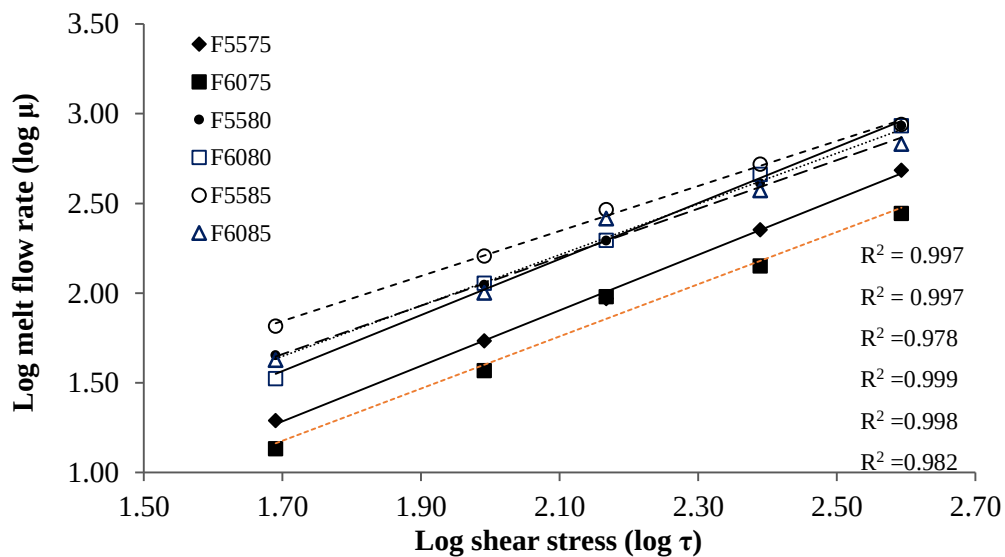


Figure 4.57: Effect of shear stress and composition on MFR values for Ti64-MIM feedstocks at 145 °C.

The relationship between $\log \mu$ and $\log \tau$ (Equation 4.15; Figure 4.57) shows the data obtained agrees with the power law model, $\log \tau = n \log \dot{\gamma} + \log m$ (Figure 4.56). The feedstock flow index for each feedstock (>1) (Table 4.14) has an inverse relationship with the flow behaviour index (<1) (Table 4.9).

Table 4.14: Effect of powder loading and binder composition on feedstock flow index of Ti64-MIM feedstocks at 145 °C.

Feedstock code	F5575	F6075	F5580	F6080	F5585	F6085
p	1.54	1.45	1.41	1.56	1.25	1.35

Feedstock flow index decreased as PEG content was increased or powder loading decreased (Table 4.14). The flow index for feedstock F6080 had the highest value, followed by that of feedstocks F5575 and F6075. The higher the feedstock flow index (or the lower the flow behaviour index) the higher the shear thinning (Section 4.3.1). The inverse relationship of feedstock flow index (p) and flow behaviour index (n) can be given as:

$$p \propto \frac{1}{n} \quad 4.16$$

i.e. $pn = k \quad 4.17$

where k is a constant for a particular feedstock formulation and depends on the correlation between feedstock flow index and flow behaviour index. The arithmetic product of experimentally obtained values for p and n satisfy the condition (Equation 4.17), where $k = 1.00 \pm 0.05$ (Figure 4.58). This gives:

$$pn = 1 \quad 4.18$$

Although flow behaviour index and feedstock flow index vary with powder loading and binder composition, their arithmetic product is constant, indicating that feedstock flow index and flow behaviour index are inversely related irrespective of powder loading, binder composition and temperature (Figure 4.58).

From Equations 2.2 (Section 2.4.2) and 4.14, the following relationship between MFR and shear rate can be obtained:

$$\mu = qm^p \dot{\gamma}^{pn} \quad 4.19$$

There were excellent linear correlations (R^2 of 0.99 - 1.00) between MFR and shear rate data for feedstocks composed of various powder and binder compositions (Figure 4.59), so:

$$\mu = G\dot{\gamma} \quad 4.20$$

where G is the rate of change of MFR with shear rate ($d\mu/d\dot{\gamma}$) for a feedstock.

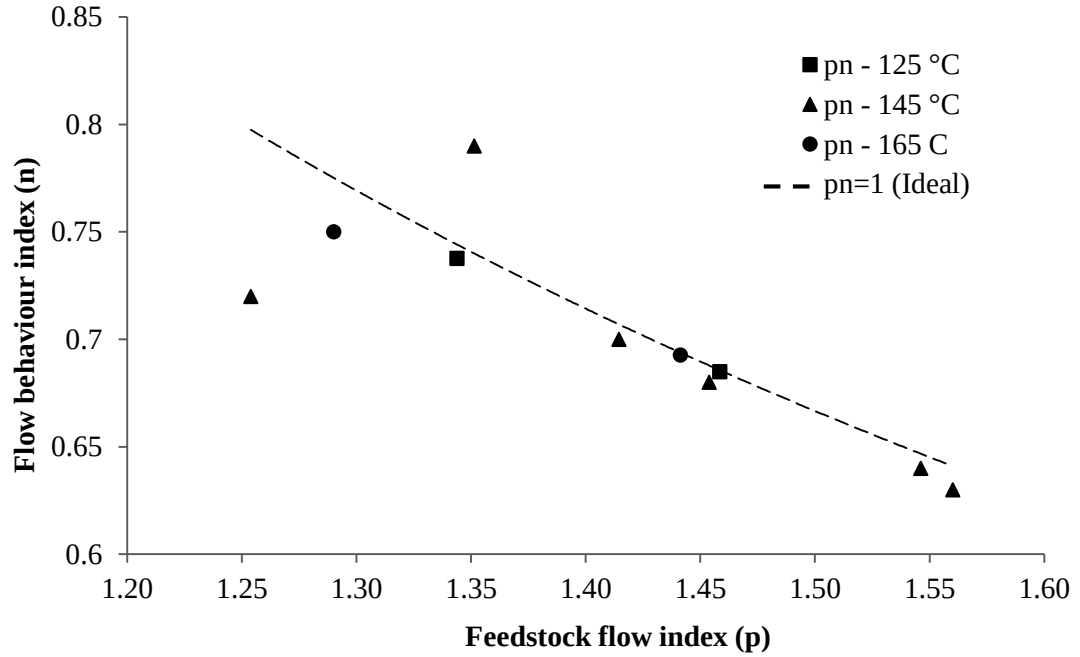


Figure 4.58: Effect of Ti64-MIM feedstocks temperatures on flow behaviour index (n) and feedstock flow index (p).

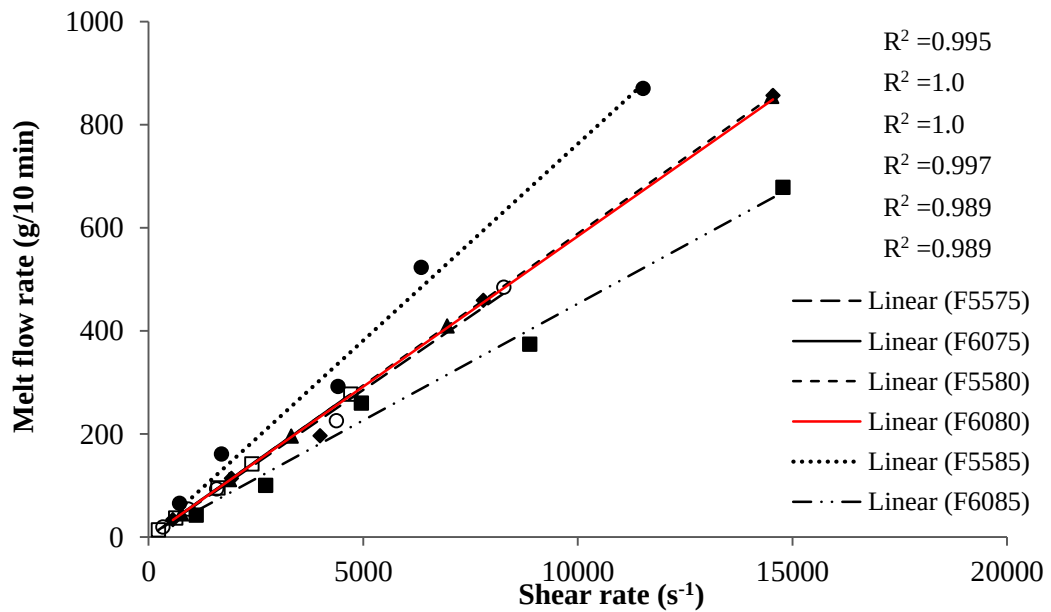


Figure 4.59: Effect of shear rate on melt flow rate for various Ti64-MIM feedstocks at 145 °C.

Shenoy *et al.* [357] reported that $\dot{\gamma}/MFR$ is constant for various polymer systems, which supports the derived relationship (Equation 4.20) for data from this research. Equations 4.19 and 4.20 are the same if the exponent (pn) of shear rate in Equation 4.19 is unity, hence supporting the previous finding (Equation 4.18).

Therefore, flow behaviour of Ti-MIM feedstock could be investigated using the following feedstock flow index, where:

$p < 1$, the fluid shows shear thickening (dilatant) flow behaviour

$p = 1$, the fluid shows Newtonian flow properties

$p > 1$, the fluid shows shear thinning (pseudoplastic) flow behaviour

Feedstocks that exhibit shear thinning ($p > 1$) are suitable and those with dilatant flow behaviour ($p < 1$) unsuitable for MIM because binder separation can occur under high shear rates (see Section 2.4.2).

The melt flow model (Equation 4.14) and the approach for identifying different flow properties, supplements the existing power law model (Sections 4.3.1) for analysing the rheological properties of a feedstock. Rheological investigation of MIM feedstocks is widely carried out using capillary rheometers, which are very expensive (around US\$ 35,000 – 50,000) than melt flow testers (US\$ 500 – 5000) that would be very useful to investigate the rheological properties in an affordable way using the melt flow model proposed in this research. Even, the flow behaviour index can be calculated from this model (Equations 4.14 and 4.18). Though capillary rheometers are highly sophisticated and provide very accurate results, melt flow testers are economic, simple and easy to use.

This following model is proposed for determining feedstock flow indices and flow behaviour indices for known MFR and shear stress. It is hoped that this model may also be applicable for MIM feedstocks composed of various metals, ceramics and binders. However, there is little research data available to validate this model for other PIM feedstocks.

4.3.6. Feedstock stability

Variation in viscosity due to changes in shear rate and processing temperature during

feedstock formulation and injection moulding is a major concern in MIM. A feedstock is more stable if variation in viscosity is minimal [230-232, 243]. The data for all feedstocks show that the rate of change of viscosity with shear rate ($d\eta/d\dot{\gamma}$) at an isothermal temperature (e.g. at 145 °C) was notable at lower shear rates but converged to zero at higher shear rates (Figure 4.60). The variation in viscosity change (Figure 4.60) was greater at higher powder loading (60 vol. %). The phenomenon of decreasing feedstock viscosity with increased shear rate was discussed in Section 4.3.1.

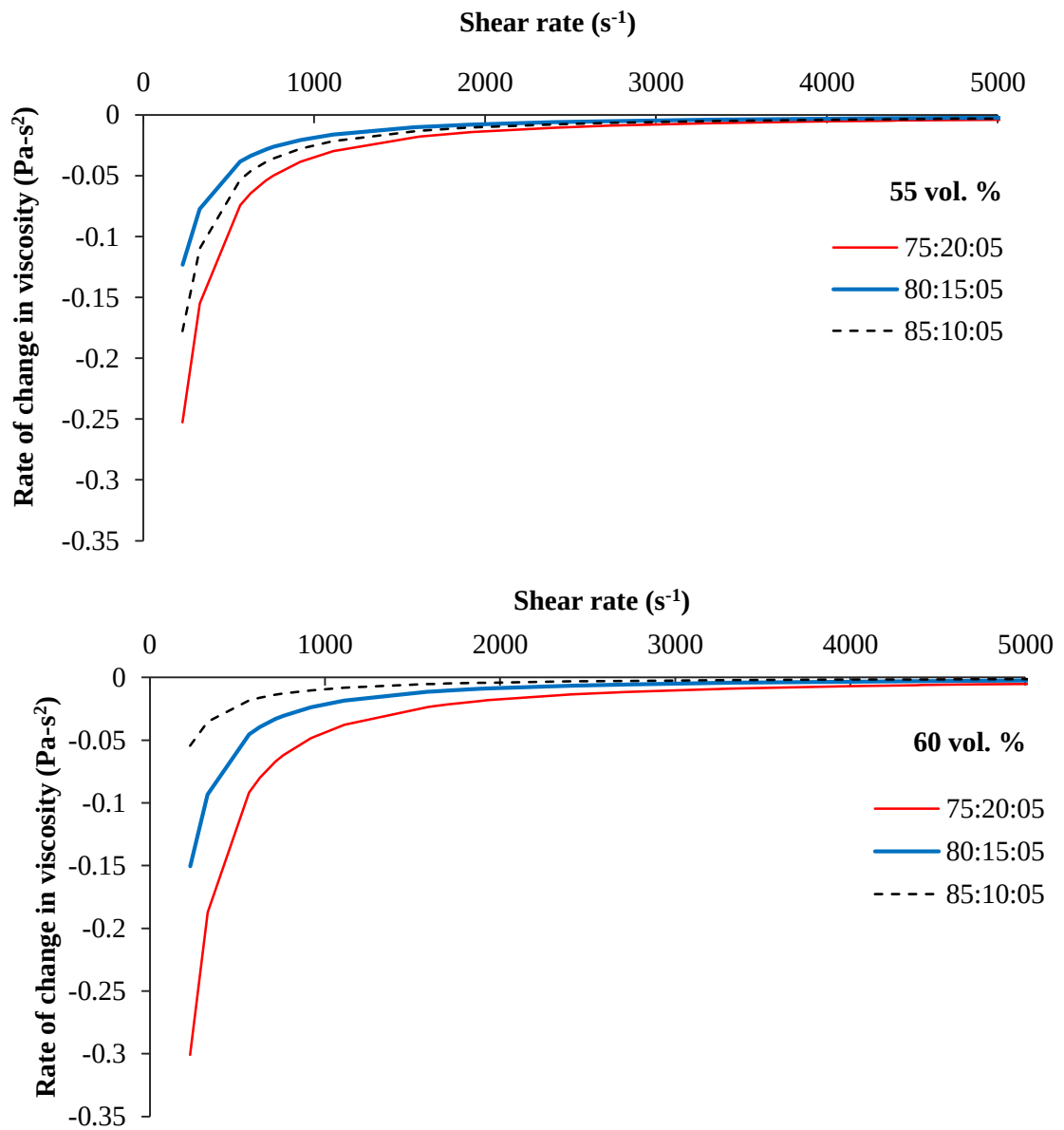


Figure 4.60: Effect of shear rate, binder composition (vol. %) and powder loadings at 145 °C on rate of change in Ti64-MIM feedstock viscosity.

Feedstocks with a 75:20:5 vol. % PEG:PVB:SA binder had the highest rate of change in viscosity at 55 and 60 vol. % powder loadings, indicating they are less stable than feedstock made with other binders (Figure 4.60). Stability of feedstocks made with 85:10:5 vol. % PEG:PVB:SA binder increased with powder loading (Figure 4.60) but there was a 69% change in stability when powder loading increased by 5 vol. % (corresponding change in stability for feedstocks with 75:20:5 and 80:15:5 vol. % PEG:PVB:SA binders were 14 and 22% respectively). This indicates the sensitivity of powder loading, hence vulnerability of the feedstock with 85:10:5 vol. % PEG:PVB:SA binder for a slight change in powder loading. However, the feedstock with 80:15:5 vol. % PEG:PVB:SA binder exhibited a consistent rate of change in viscosity at 55 and 60 vol. % (Figure 4.60). In other words, this feedstock is more stable for a slight change in homogeneity.

Feedstock stability increased with process temperature (Figure 4.61) indicating that higher temperatures will be better for injection moulding. However, binders can degrade at high process temperatures, which can increase feedstock viscosity and make moulding difficult. Feedstock with 80:15:5 vol. % PEG:PVB:SA binder was more stable than 75:20:5 vol. % PEG:PVB:SA binder (Figure 4.61), indicating that PEG-PVB concentration may influence stability. Feedstock with 75:20:5 vol. % PEG:PVB:SA binder may be more susceptible to PEG-PVB concentration in a variable shear system than feedstock with 80:15:5 vol. % PEG:PVB:SA binder. These changes in component concentration can affect viscosity and decrease stability of feedstock made with 75:20:5 vol. % PEG:PVB:SA binder.

Dihoru *et al.* [230-231] analysed stainless steel powders with wax based binders in a similar way and introduced an “instability index”, ‘*i*’, to describe the standard deviation of rate of change in viscosity. When $i > 1$, there are sufficient heterogeneous regions in the feedstock to cause variation in bulk viscosity. The higher the instability index, the greater the fluctuation in viscosity and hence instability. All feedstocks produced had an instability index less than unity, indicating they were homogeneous (Table 4.15). Feedstock stability increased with PEG content (Table 4.15), suggesting that higher PEG content is preferable. However, excess PEG is unfavourable for Ti-MIM (Section 4.2.1). At 55 vol. % powder loading, feedstock F5580 was the most stable (Table 4.15), indicating 80:15:5 vol. % PEG:PVB:SA binder would be more

suitable. At 60 vol. % powder loading, feedstock F6085 showed the highest stability (Table 4.15), which is higher than for F5580, suggesting that feedstocks with 60 vol. % powder loading are more suitable than those with 55 vol. % powder loading. However, higher powder loadings are preferable in MIM for minimizing shrinkage of moulded part during sintering.

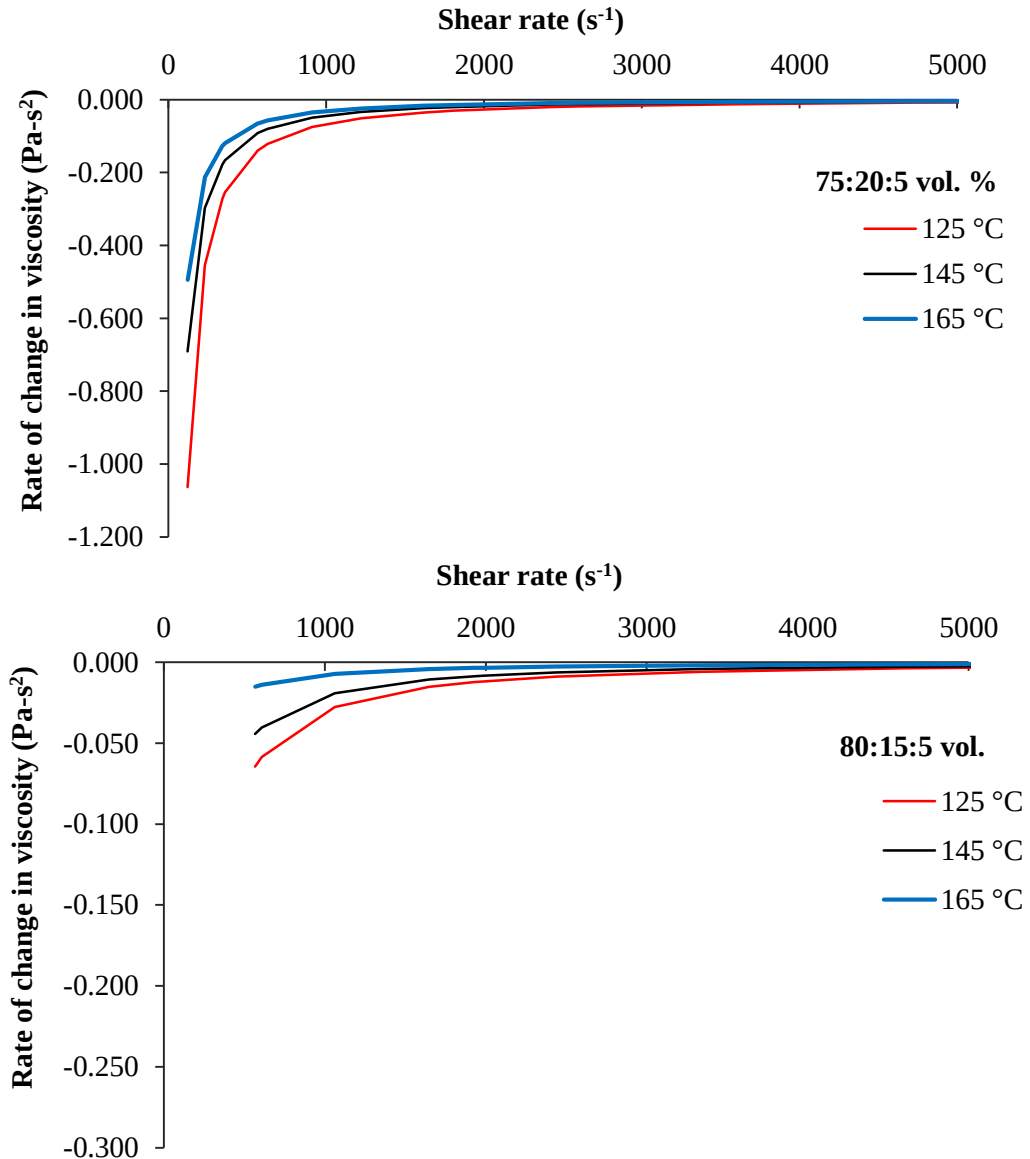


Figure 4.61: Effect of shear rate, binder composition (vol. %) and temperature on stability of Ti64-MIM feedstocks with 60 vol. % powder loading.

Feedstock stability increased with temperature and feedstocks with 80:15:5 vol. % PEG:PVB:SA binder was more stable than the feedstocks made with 75:20:5 vol. % PEG:PVB:SA binder (Table 4.16). Data indicate that feedstock F6080 exhibited the highest stability and was suitable for Ti-MIM.

Table 4.15: Effect of powder loading and binder composition on stability, expressed as i value, of Ti64-MIM feedstocks at 145 °C.

Feedstock code	F5575	F6075	F5580	F6080	F5585	F6085
i	0.06	0.12	0.01	0.02	0.02	0.003

Table 4.16: Effect of temperature on stability of Ti64-MIM feedstocks.

Temperature (°C)	Feedstock code	
	F6075	F6080
125	0.43	0.03
145	0.12	0.02
165	0.05	0.003

4.3.7. Powder loading and viscosity

The effect of powder loading on viscosity was discussed in Section 4.2.3. This section gives more detail on the effect of powder loading on rheological properties, focussing on the relationship between critical powder loading (ϕ_c) and relative viscosity (η_r) of the feedstocks. The experimental data obtained was used in the many models for this relationship and attempts made to develop models for predicting feedstock η_r and ϕ_c .

The 80:15:5 vol. % PEG:PVB:SA and 75:20:5 vol. % PEG:PVB:SA binders were selected based on their better rheological properties than other combinations (Sections 4.3.1 to 4.3.4). Relative viscosity of feedstocks made with these two binders increased dramatically with powder loading, becoming extremely high at the critical powder loading of 65 vol. % (Figure 4.62). Thus, 60 vol. % was chosen as the workable powder loading (Section 4.2.3).

There are many models describing the relationship between relative viscosity and powder loadings (ϕ) of suspensions (Section 2.4.7). The relative viscosities at 145 °C and a shear rate of 600 s⁻¹ for Ti64-MIM feedstocks made with 80:15:5 and 75:20:5 vol. % PEG:PVB:SA did not fit with published models (Figure 4.63). The relative viscosity calculated using the Mooney model is significantly higher and that calculated using the Reddy model is much lower than the experimental values (Figure 4.63). Other researchers [135, 236, 246, 255, 262, 358] also reported that the Mooney model is not a good predictor of relative viscosity. This model includes an exponential

relationship ($\eta_r = e^{2.5x}$, where x increases with the powder loading; Section 2.4.7) between relative viscosity and powder loading. Such a relationship may work only when powder loading approaches critical powder loading.

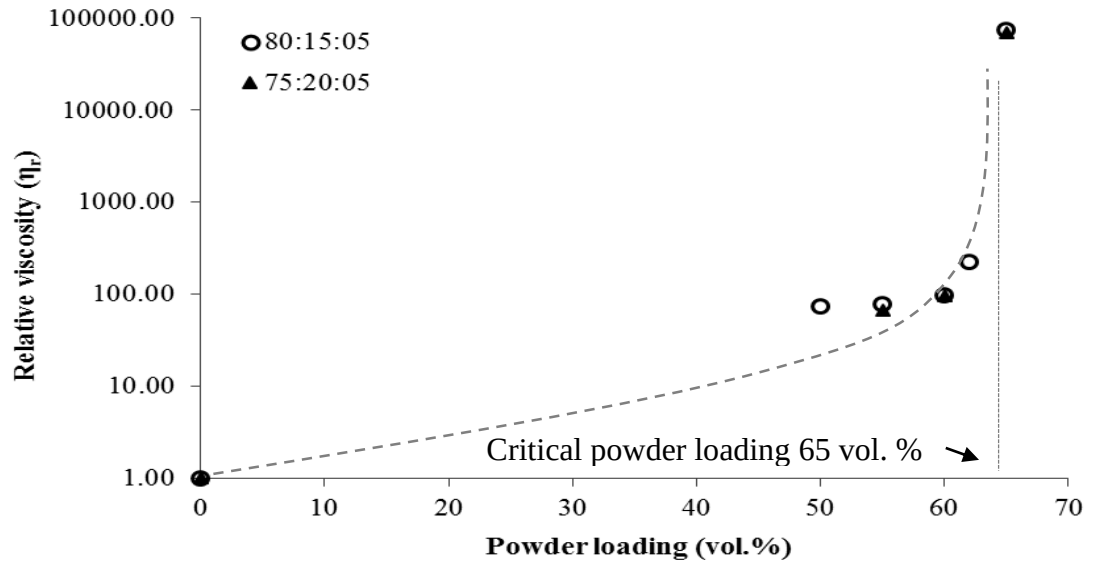


Figure 4.62: Effect of powder loading and binder composition on relative viscosity of Ti64-MIM feedstocks at 2000 s^{-1} shear rate and 145°C .

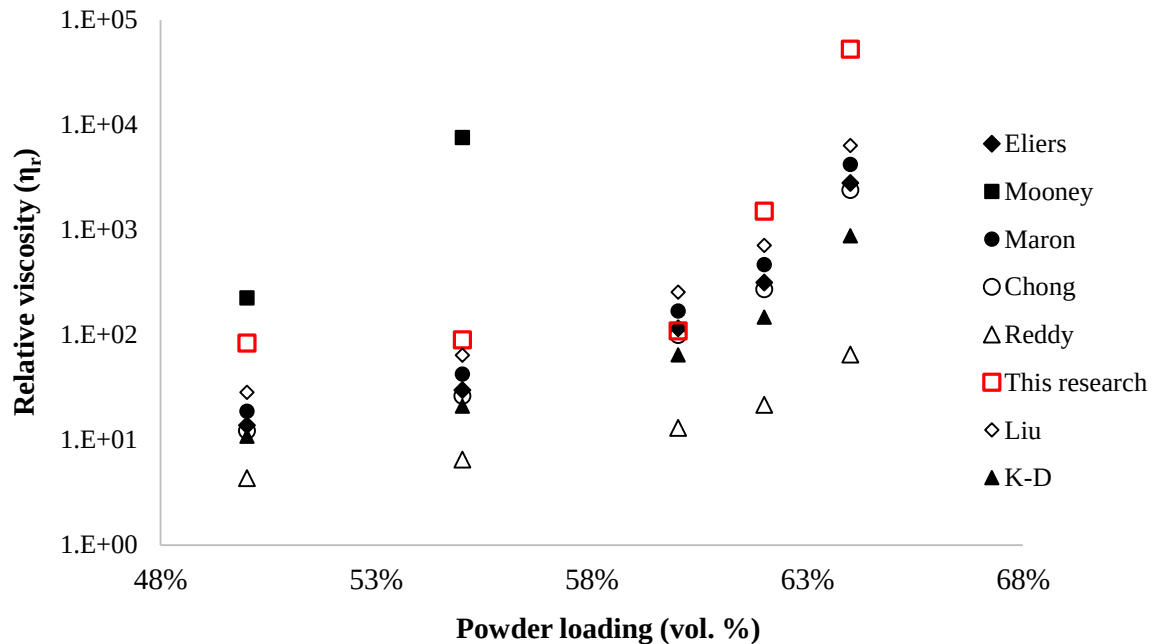


Figure 4.63: Comparison of experimental data for relative viscosity of feedstocks with values predicted using published models (Table 4.14).

The experimental data did not fit the Eilers and Chong models well because of the assumptions and constraints in these models (see Section 2.4.7). Although Wright *et*

al. [135] validated the Chong model for ceramic suspensions, Poslinski *et al.* [359] reported that their experimental relative viscosity values were higher than predicted by this model. Values predicted by the Reddy model had the greatest variance with the experimentally obtained values (Figure 4.63). This model has a linear relationship between relative viscosity and powder loading (Section 2.4.7) but data from the current research (and many other researchers; Section 2.4.7) showed that relationship was nonlinear (Figure 4.62 and Section 4.2.3). Honek *et al.* [360] also reported that the published models did not accurately predict the relative viscosity of low-density polyethylene/wax based binders with irregular, bimodal particle size metal carbide powders. Of the models investigated, only Liu's model [256] predicted values close to experimental data obtained between 55 and 60 vol. % powder loading (Figure 4.63). The Maron and Pierce model was the next most accurate model.

4.3.8. Proposed model for determining critical powder loading from relative viscosity

Any model for determining critical powder loading and relative viscosity has to satisfy two major boundary conditions:

Relative viscosity ($\eta_r = \eta/\eta_b$) becomes 1 and powder loading becomes 0 as the mix becomes pure binder (where η – mixture viscosity).

$$\lim_{\phi \rightarrow 0} (\eta_r) = 1 \quad 4.21$$

Relative viscosity tends to infinity as powder loading reaches critical powder loading (Figure 4.62).

$$\lim_{\phi \rightarrow \phi_c} (\eta_r) = \infty \quad 4.22$$

The linear form of most of the models in Table 2.8 (Section 2.4.7) is:

$$[\eta_r^{-(1/m)} - 1] = f(\phi) \quad 4.23$$

where:

$m = -1$ and -2 in the Einstein, Eilers and Chong *et al.* equations

$m = 1$ and 2 in the Reddy, Maron & Pierce and Quemada equations

$m = [\eta]\phi_c$ in the Krieger & Dougherty equation (Table 2.8).

The term '1' in Equation 4.23 satisfies boundary conditions (Equations 4.21 and 4.22).

Because

$$[\eta_r^{-(1/m)} - 1] < 0$$

4.24

the relationship between $[1 - \eta_r^{-(1/m)}]$ and ϕ was analysed for $1 < m < 5$. The best fit for the experimental data was for $m = 2.5$ (Figure 4.64).

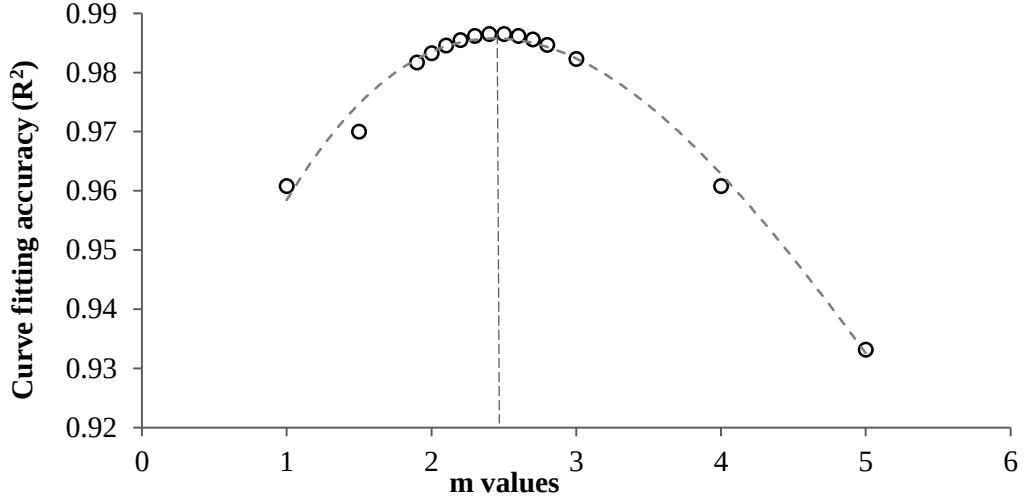


Figure 4.64: Goodness of curve fitting for various m values.

There was a good fit ($R^2 = 0.986$) when fitting experimental data to $[1 - \eta_r^{-(1/2.5)}]$ using $m = 2.5$ (Figure 4.65).

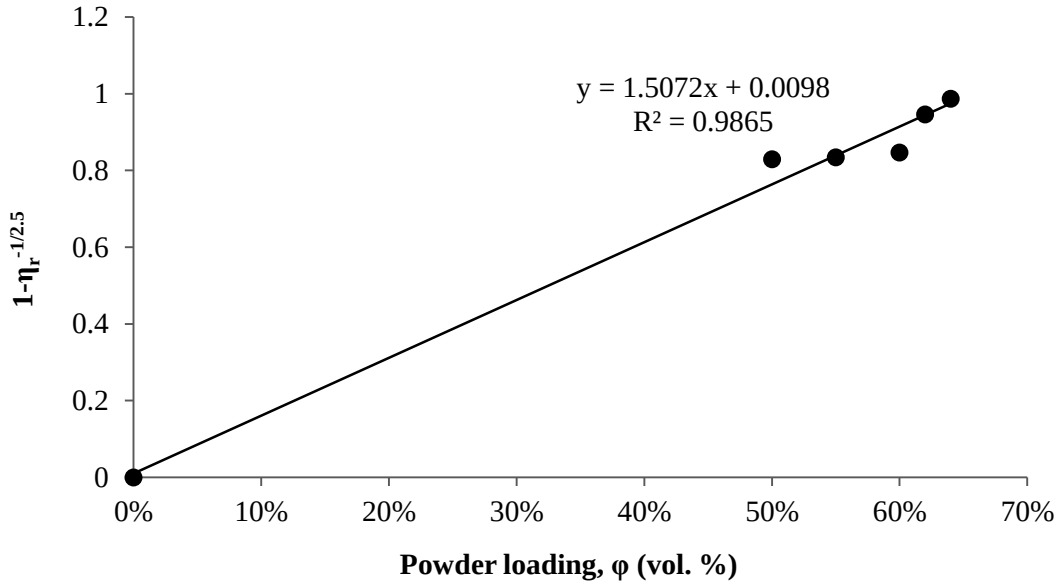


Figure 4.65: Effect of powder loading of Ti64-MIM feedstocks on relationship for $[1 - \eta_r^{-(1/m)}]$ using $m=2.5$.

Therefore:

$$[1 - \eta_r^{-(1/2.5)}] = 1.507 \phi + 0.009$$

4.25

Equation 4.25 can be generalized to:

$$[1 - \eta_r^{-(1/2.5)}] = m \varphi + c \quad 4.26$$

Where: m (gradient) = 1.507 and c (y-intercept) = 0.009.

Equation 4.26 can be rewritten as:

$$\eta_r = \left(\frac{1}{1-c-m\varphi} \right)^{2.5} \quad 4.27$$

Including the second boundary condition that relative viscosity tends to infinity as powder loading tends to the critical limit (Equation 4.22) gives:

$$(1 - c - m\varphi_c) = 0 \quad 4.28$$

Therefore, the critical powder loading can be expressed as:

$$\varphi_c = \left(\frac{1-c}{m} \right) \quad 4.29$$

This suggests the critical powder loading can be determined using the gradient and y-intercept of a linear relationship.

From Equations 4.27 and 4.29,

$$\eta_r = \left[\frac{1}{m(\varphi_c - \varphi)} \right]^{2.5} \quad 4.30$$

Equation 4.28 is then modified to satisfy the two boundary conditions (Equations 4.21 and 4.22):

$$\eta_r = 1 + \left[\frac{1}{m(\varphi_c - \varphi)} \right]^{2.5} - \left[\frac{1}{m\varphi_c} \right]^{2.5} \quad 4.31$$

The proposed model (Equation 4.31) predicts (a) the critical powder loading of feedstocks for known powder loadings and relative viscosities and (b) the relative viscosity of a feedstock for a specific powder loading and calculated critical powder loading. The ‘ m ’ in the proposed model is specific for a feedstock and depends on powder-binder characteristics.

4.3.9. Model validation

Substituting $\phi = 0$ and $\phi = \phi_c$ into Equation 4.31 gives $\eta_r = 1.0$ and $\eta_r = \infty$, showing that both boundary conditions (Equations 4.21 and 4.22) are satisfied.

- **Experimental validation**

Substituting $m = 1.507$ and $c = 0.009$ obtained from Equation 4.26 into Equation 4.29 gives $\phi_c = 0.657$ (65.7 vol. %), which is within 1% of the critical powder loading obtained experimentally (65 vol. %, Figure 4.62). The Liu model has a better fit to the experimental data than the other models (Table 2.8) but does not satisfy the first boundary condition (Equation 4.21 and Table 4.17), which is mandatory. The calculated relative viscosities fit the new model (Figure 4.66 and Table 4.17) better than all models listed in Table 2.8. Thus, it is proposed that this new model could be used to determine critical powder loading and viscosities for feedstocks made of Ti64 powders and PEG-PVB binder systems. The proposed model produces similar results to other widely used PIM models (Figure 4.66 and Table 4.17) and may be applicable to various PIM feedstocks but first needs to be validated.

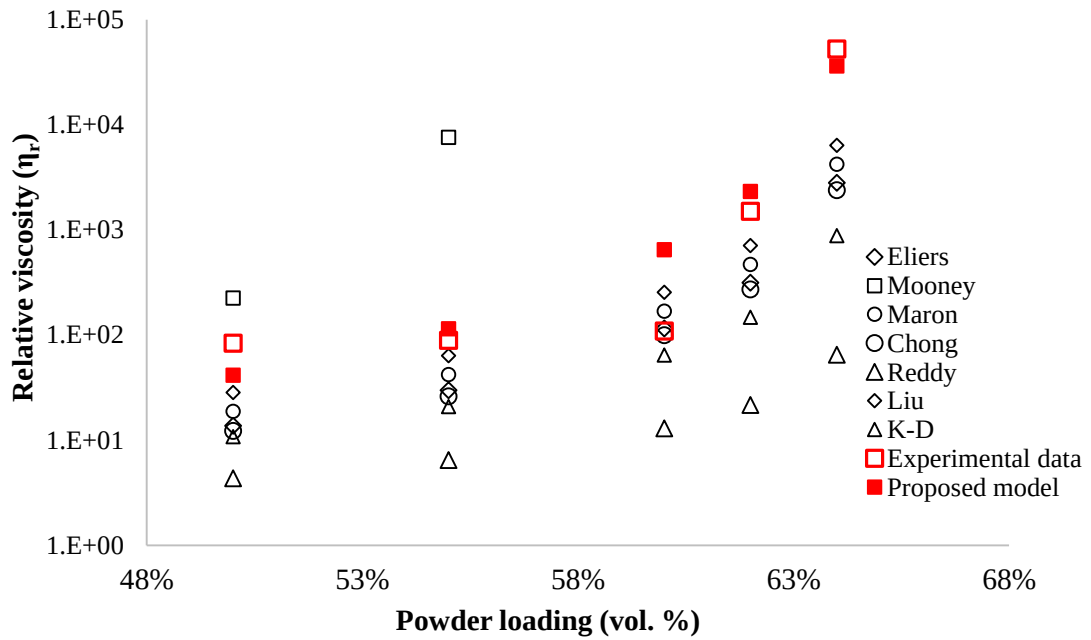


Figure 4.66: Comparison of the proposed model with the other reported models.

- **Application of the model in ceramic injection moulding**

The proposed model was tested using data [233] for ceramic injection moulding (CIM) four different zirconia-polymer-wax feedstocks (ZSH, ZKH, PSH and PKH) made with zirconia powder with average particle sizes of 70 nm, 100 nm or 1.5 μm) and

two binders (wax and polymer based) with various levels of agglomerates. The critical powder loading calculated using the proposed model agreed well (R^2 of 0.96 - 1.00) with the experimental data (Table 4.18; Figure 4.67).

Table 4.17: Effect of powder loading on relative viscosities predicted by various models.

Model	Powder loading (vol. %)					
	0	50	55	60	62	65
Experimental value	1	84	90	109	1507	52639
Eilers	1	14	30	116	317	2809
<i>Agreement*</i>	100	17	33	106	21	5
Mooney	1	225	7605	3.E+08	4.E+14	1.E+45
<i>Agreement*</i>	100	268	>1000	>1000	>1000	>1000
Chong	1	12	26	100	272	2401
<i>Agreement*</i>	100	14	29	92	18	5
Reddy	1	4	7	13	22	65
<i>Agreement*</i>	100	5	8	12	1	<0.1
K-D	1	11	21	65	148	883
<i>Agreement*</i>	100	13	23	60	10	2
Maron	1	19	42	169	469	4225
<i>Agreement*</i>	100	23	47	155	31	8
Liu	1.5	28	64	256	711	6398
<i>Agreement*</i>	150	33	71	235	47	12
Proposed model	1	42	115	649	2328	36289
<i>Agreement*</i>	100	50	128	595	154	69

*Agreement = % of experimental value

Table 4.18: Experimental critical powder loadings for zirconia-wax feedstocks [233] and values calculated using the proposed model.

Feedstocks	Reported ϕ_c (vol. %) *	Calculated ϕ_c (vol. %)
ZSH	59	59.5
ZKH	66	67.7
PSH	66	66.8
PKH	68	68.9

*Data reported to two significant figures

The proposed model worked for both Ti-MIM and CIM powders, which had different particle shape, size and distribution at different shear rates and temperatures. This

supports that the proposed model can be used to estimate critical powder loading and relative viscosities for a wide range of PIM applications.

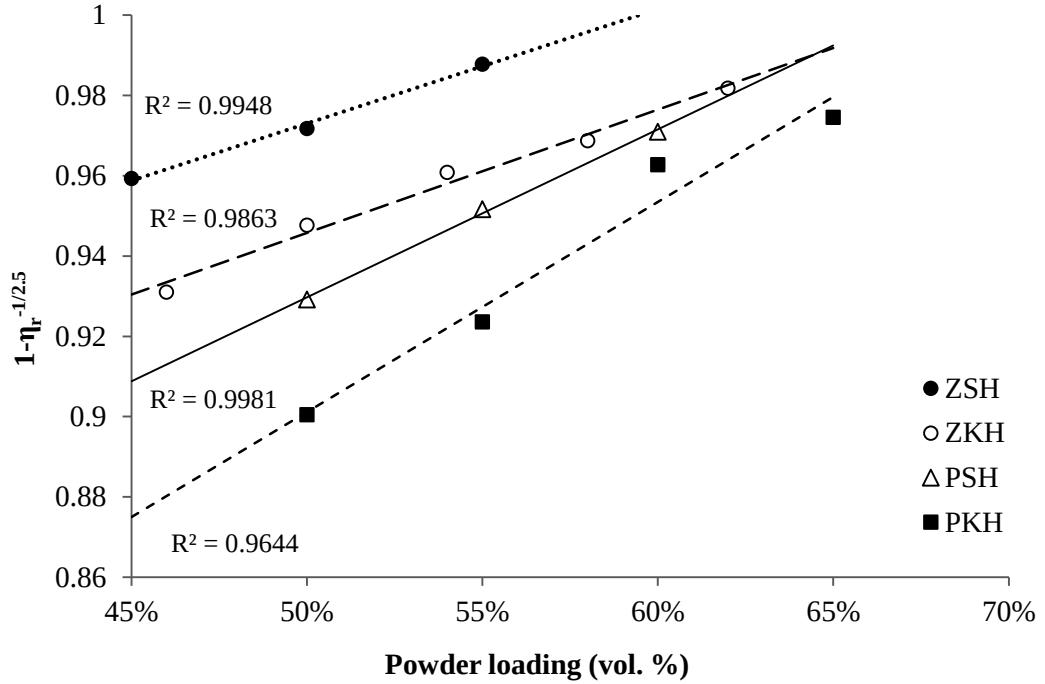


Figure 4.67: Effect of powder loading on relative viscosity of CIM powders at 100 °C and shear rate of 100 s⁻¹ [233] using proposed model and that of Song and Evans [233].

- ***Estimating relative viscosity using the proposed model***

The parameters m and ϕ_c were determined from empirical data so relative viscosity at a specific powder loading could be predicted using the proposed model. There was a good agreement ($R^2 > 0.99$) between predicted and measured relative viscosity for both F6080 Ti64 feedstock and three of the zirconia-wax CIM feedstocks [233]. Even though the correlation coefficient for the fourth CIM feedstock (PKH) was only 0.91 (Figure 4.68), the data indicate the proposed model can predict the relative viscosity of PIM feedstocks better than published models.

- ***Significance of the proposed model***

The proposed model (Equation 4.31) has two significant terms, $(\phi_c - \phi)$ and the exponent 2.5. The term $(\phi_c - \phi)$ indicates the space available for movement of particles in the feedstock. Particle size and shape influences the spatial arrangement, and therefore $(\phi_c - \phi)$. When powder loading increases, the space for particle movement decreases and inter-particle friction (and hence viscosity) increases. When $\phi \geq \phi_c$,

viscosity is very high due to higher inter-particle friction caused by capillary forces that develop from voids forming in the feedstock (Sections 4.2.1, 4.2.2, 4.2.3).

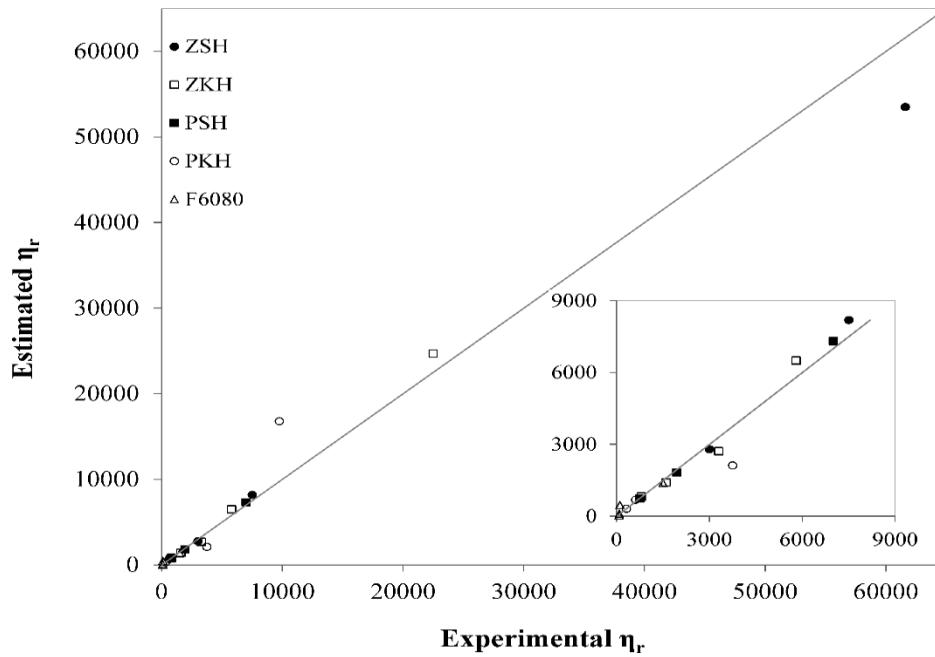


Figure 4.68: Experimental data and relative viscosity predicted by the new model for different Ti64-MIM and zirconia-wax PIM feedstocks.

Even though ϕ_c could be increased by using powder with a wider particle size distribution (Section 4.2.4), ϕ_c reflects the dynamic particle structure and the dependency on shear rate and inter-particle forces [361]. During high shear, average inter-particle distance increases perpendicular to the direction of flow and decreases along the direction of flow. This means particles move more easily, which reduces viscosity (thus increasing ϕ_c). An increase in ϕ reduces inter-particle distance, increasing inter-particle interactions and thus relative viscosity [362]. Thus, $(\phi_c - \phi)$ is a significant factor in the proposed model and improves the model by incorporating the effect of shear rate, particle size and inter-particle interactions.

The exponent 2.5 in the model is similar to the Einstein coefficient, ϕ , in the Einstein equation ($\eta_r = 1 + 2.5\phi$) [256-257, 260, 363] and indicates the degree of aggregation and size of the electro-viscous effect [257]. Einstein [249] reported that the coefficient of internal friction in a dilute suspension of very small, rigid spheres increases by 2.5 times the total volume of spheres suspended in a unit volume if total volume of spheres is small ($\phi \leq 10$ vol. %) [246, 249, 256-260, 360]. An alternative interpretation is that

feedstock relative viscosity increases 2.5 times powder loading per unit volume of a feedstock or that the first derivative of the relationship between relative viscosity and powder loading is 2.5 for pure binder [360] (Equation 4.32):

$$\lim_{\varphi \rightarrow 0} \left(\frac{d\eta_r}{d\varphi} \right) = 2.5 \quad 4.32$$

Due to restrictions in the Einstein model, it cannot be compared with the proposed model, which is for concentrated suspensions (high powder loading). However, any PIM model that describes the relationship between relative viscosity and powder loading must satisfy the Einstein condition (Equation 4.32) [360]. The Einstein coefficient is between 2.5 and 5.0 for spherical particles; the upper limit depends on the degree of particle aggregation and size of the electro-viscous effect [257].

The first derivative of the proposed model (Equation 4.31):

$$\frac{d\eta_r}{d\varphi} = \frac{2.5}{m^{2.5}(\varphi_c - \varphi)^{3.5}} \quad 4.33$$

Therefore:

$$\lim_{\varphi \rightarrow 0} \left(\frac{d\eta_r}{d\varphi} \right) = \frac{2.5}{(m\varphi_c)^{2.5}\varphi_c} = \left(\frac{2.5}{k} \right) \quad 4.34$$

where k is a constant and depends on critical powder loading. It is affected by powder particle shape, particle size and distribution, particle interactions and shear rate, which are not considered in the Einstein model (a dilute suspension of spherical, identical particles). The proposed model incorporates high powder loadings, different particle shapes, and the interactions between binder and powder particles, which explains the difference (1/k) between Equations 4.32 and 4.34.

- **Estimating k**

To meet the first boundary condition (Equation 4.21), $[1 - \eta_r^{-(1/2.5)}]$ in Equation 4.26 must approach zero and the constant, c, should be zero. Regression the experimental data (Figure 4.65) gives $c = 0.009$ (Equation 4.25), which is effectively zero. Therefore:

$$(1 - c) \approx 1$$

and Equation 4.29 becomes $m \cdot \varphi_c = 1$

Substituting $m \cdot \varphi_c = 1$ into Equation 4.34 gives:

$$\lim_{\varphi \rightarrow 0} \left(\frac{d\eta_r}{d\varphi} \right) = \frac{2.5}{\varphi_c} = \left(\frac{2.5}{k} \right) = \lambda \quad 4.35$$

Thus $k = \varphi_c$, and the model predicts a critical powder loading of 0.657 compared with 0.65 for the experimental data (Figure 4.62).

Substituting $m = 1.507$ (Equation 4.25) and $\varphi_c = 0.657$ into Equation 4.34 gives:

$$\lambda = \frac{2.5}{0.64} \quad 4.36$$

The value 0.64 obtained from the Equation 4.34 is within 1% of the 0.65 obtained from experimental data (Figure 4.62) and the 0.657 predicted in the proposed model. Thus, the Einstein coefficient could be modified by $[2.5/\varphi_c]$ for highly concentrated suspensions (i.e. high powder loadings). The value $\lambda = 3.9$ obtained in this research (Equation 4.36) is within the 3.5 and 5.6 reported for critical powder loading (45 – 70 vol. %) (Section 2.3.3) and similar to reported values [257].

In summary, the proposed model accurately predicts critical powder loading and relative viscosity for the titanium (metal) and zirconia (ceramic) PIM applications investigated. This model and the proposed modification to the Einstein coefficient for highly concentrated suspensions ($\lambda = 2.5/\varphi_c$) has not been previously reported.

• **Model refinement**

Models that accurately predict critical powder loading and relative viscosity help identify optimum PIM conditions such as workable powder loading and feedstock viscosity and help minimize the manufacturing cost of MIM components. Although many models predict critical powder loading and relative viscosity of PIM feedstocks, the effect of organic binder adsorbing to powder particles is usually not considered. This immobile, adsorbed layer of binder on the particle surface (Figure 4.43, Section 4.2.6) could be considered a solid phase, thus the effective powder loading may be slightly higher than the intended powder loading. This effective powder loading, φ_{eff} can be expressed using Equation 4.37 [246] or 4.38 [233, 364]:

$$\varphi_{\text{eff}} = \varphi (1 + k \rho S h) \quad 4.37$$

or

$$\varphi_{\text{eff}} = \varphi (1 + \delta/r)^3 \quad 4.38$$

where k is a constant ($0 < k < 1$), ρ is powder density, S is specific surface area of the powder, h is polymer chain end-to-end length, δ is adsorbed layer thickness, and r is particle radius.

For $r \gg \delta$, Equation 4.38 approximates to:

$$\varphi_{\text{eff}} = \varphi (1 + 3\delta/r) = \varphi \cdot \alpha \quad 4.39$$

where $\alpha = (1 + 3\delta/r)$.

Substituting Equation 4.39 in the proposed model (Equation 4.31) and rearranging:

$$\eta_r = 1 + \left[\frac{1}{m\alpha(\frac{\varphi_c}{\alpha} - \varphi)} \right]^{2.5} - \left[\frac{1}{m\varphi_c} \right]^{2.5} \quad 4.40$$

If $\varphi_c = \Phi_c \cdot \alpha$, Equation 4.40 becomes:

$$\eta_r = 1 + \left[\frac{1}{m\alpha(\Phi_c - \varphi)} \right]^{2.5} - \left[\frac{1}{m\alpha\Phi_c} \right]^{2.5} \quad 4.41$$

where Φ_c is the effective critical powder loading. This modification may explain why the calculated values for critical powder loading (Tables 4.18 and 4.19) were higher than the experimental values. The approximation ($r \gg \delta$) in Equation 4.39 decreases accuracy of estimating δ (Table 4.19). However, the calculated adsorbed layer thicknesses (Table 4.19) are in the range reported (5 – 100 nm) for PS on glass walls of a capillary viscometer [246, 365].

The SEM micrograph of feedstock F6080 (Figure 4.69) indicates that the adsorbed layer, which includes the immobile and mobile adsorbed layers, is about 5 μm thick, which is similar to the value predicted by the proposed model (Table 4.19).

Table 4.19: Estimating binder adsorbed layer on powder particles.

Feedstocks	Average particle size (μm)	Experimental φ_c (vol. %)	Calculated φ_c (vol. %)	Calculated adsorbed layer thickness δ (nm)
F6080	70	65	65.7	125.6
ZSH	0.07	59	59.5	0.1
ZKH	0.07	66	67.7	0.3
PSH	1.5	66	66.8	3
PKH	1.5	68	68.9	3.3

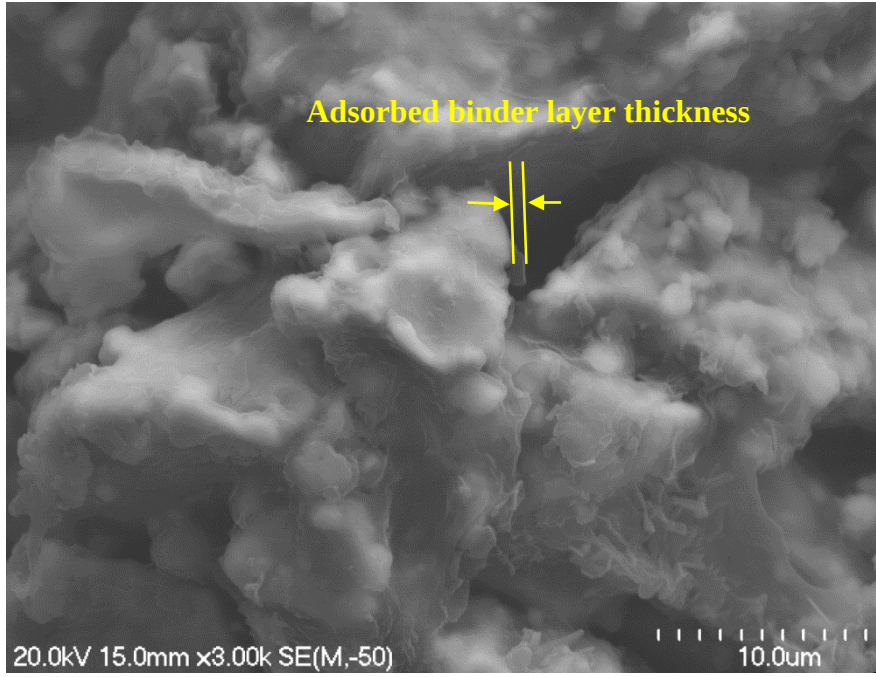


Figure 4.69: SEM micrographs of F6080 Ti64-MIM feedstock.

Shear rate ($\dot{\gamma}$) influences viscosity, relative viscosity and critical powder loading. Future models should investigate how to incorporate this factor even though model complexity increases. For instance, the Ostwald de Waele model ($\eta = m\dot{\gamma}^{n-1}$) gives:

$$\eta_r \propto \dot{\gamma}^{n-1}$$

Incorporating this into Equation 4.41 produces Equation 4.42:

$$\eta_r = 1 + K\dot{\gamma}^{n-1} \left[\left[\frac{1}{m\alpha(\Phi_c - \varphi)} \right]^{2.5} - \left[\frac{1}{m\alpha\Phi_c} \right]^{2.5} \right] \quad 4.42$$

where K is a constant and n is the flow behaviour index.

Relative viscosity increases when mean inter-particle space ($\bar{u}$) decreases [366], which can be expressed as [362]:

$$\bar{u} = 4 \left(\frac{1-\varphi}{S} \right)$$

where S is specific surface area of powder per unit volume.

The relationship between η_r and $\bar{u}$ is therefore:

$$\eta_r \propto \left[\frac{S}{4(1-\varphi)} \right] \quad 4.43$$

Combining Equation 4.43 and Equation 4.42 produces:

$$\eta_r = 1 + \frac{MS\dot{\gamma}^{n-1}}{4(1-\phi)} \left[\left[\frac{1}{m\alpha(\Phi_c - \phi)} \right]^{2.5} - \left[\frac{1}{m\alpha\Phi_c} \right]^{2.5} \right] \quad 4.44$$

where M is a constant.

Although the advanced model (Equation 4.44) incorporates most of the relevant parameters (shear rate, particle size, mean inter-particle spacing, particle surface area, adsorbed binder layer thickness, flow behaviour index) for pseudoplastic and dilatant flow behaviours, it is more complex than the initial proposed model (Equation 4.31) and was not validated. It is recommended that this advanced model be simplified and validated for a wide range of PIM applications.

4.3.10. Temperature and viscosity

Temperature affects mobility of liquid molecules. The viscosity of feedstocks F6075 and F6080 (the most promising feedstocks) decreased with temperature (Figure 4.70) due to the decrease in effective powder volume as binders expanded and the molecular chains became less tangled [2, 191]. Processing at high barrel temperature during injection moulding (as long as it is below binder degradation temperature) will improve mouldability. Data show that injection moulding temperature should be increased from 125 to 145 °C (Section 4.3.1). The viscosity of feedstock F6080 was lower than that of F6075 (Figure 4.71), indicating it was the better feedstock for Ti-MIM.

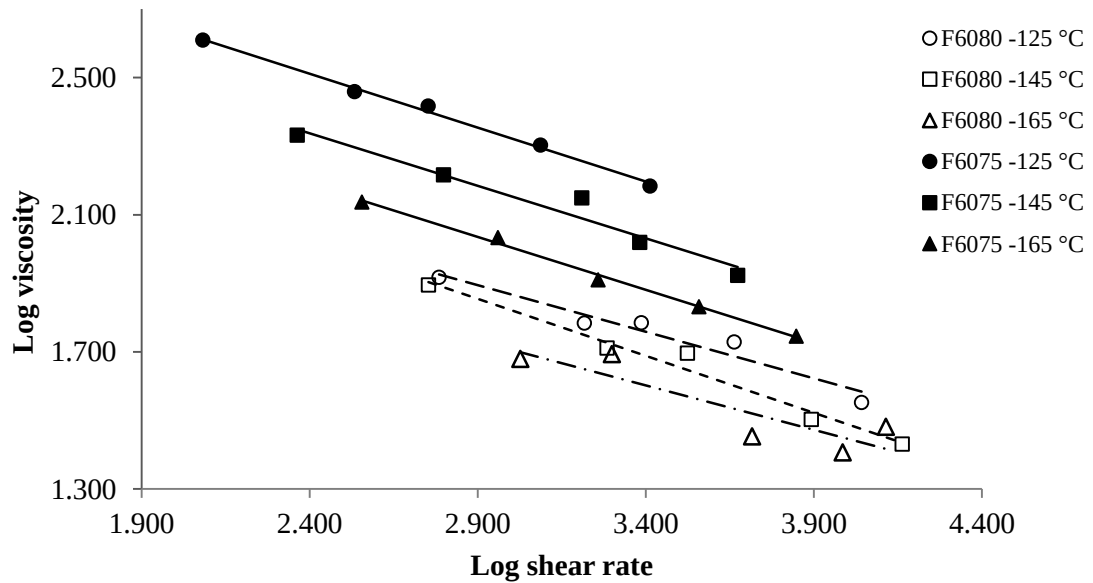


Figure 4.70: Effect of temperature on feedstock viscosity.

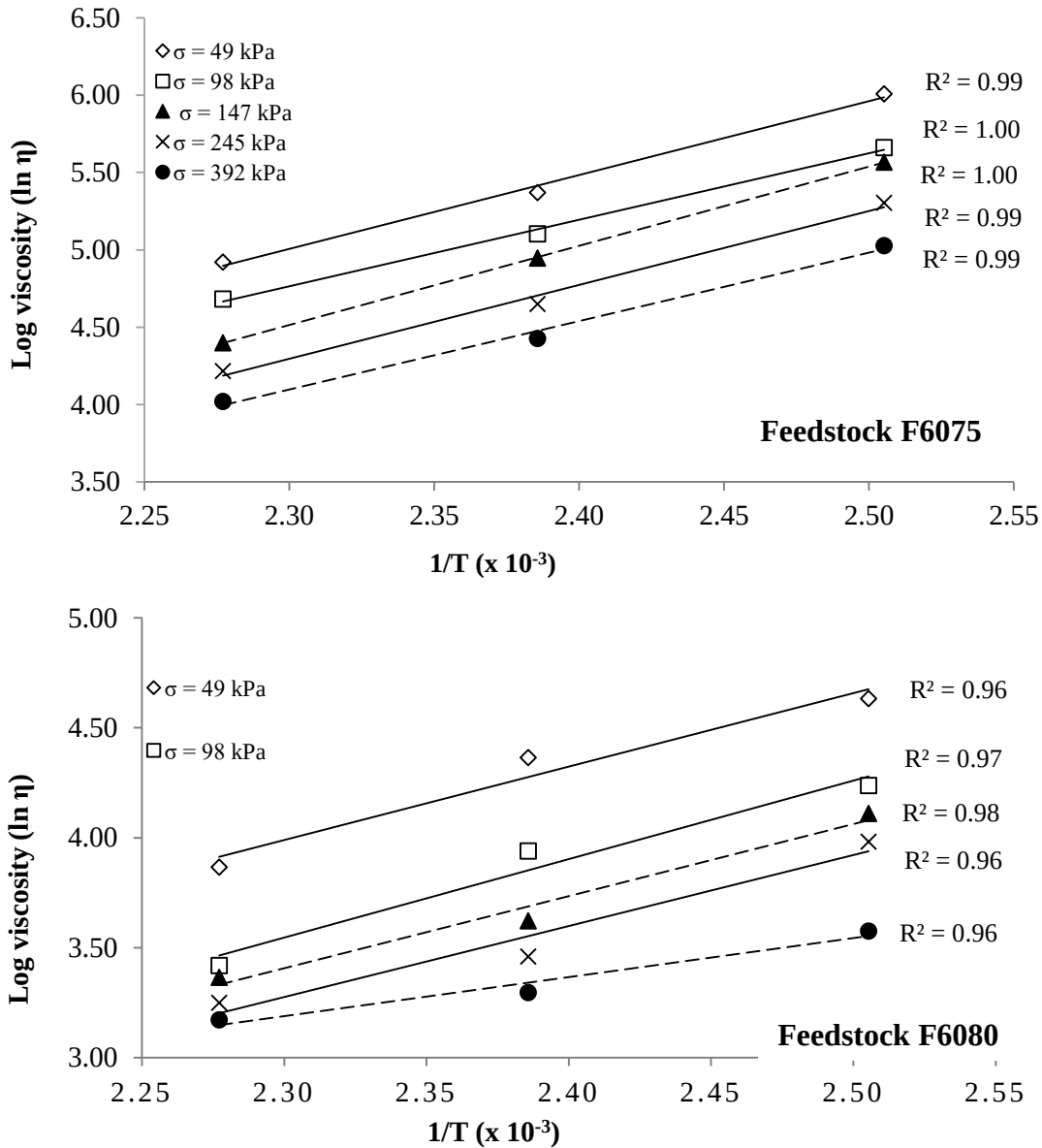


Figure 4.71: Effect of temperature and shear stress on viscosity of Ti64-MIM feedstocks.

Temperature dependency of feedstock viscosity can be expressed by rewriting the Arrhenius equation (Section 2.4.5)

$$\ln \eta = \ln \eta_0 + \left(\frac{E_a}{R}\right)\frac{1}{T} \quad 4.45$$

The data at the shear stresses (49 to 392 kPa) and temperatures used fitted this relationship well (R^2 of 0.96 to 1.00) (Figure 4.71). Feedstock F6080 had lower flow activation energy (14.8 to 29.7 kJ/mol) than that of F6075 (35.7 to 42.5 kJ/mol) (Table 4.20) indicating less energy was needed to break the barriers to flow during injection moulding. The higher PEG content of this feedstock may have reduced its activation energy.

Table 4.20: Effect of shear stress on flow activation energy of feedstocks (kJ/mol).

Feedstock	Shear stress (kPa)				
	49	98	147	245	392
F6075	39.8	35.7	42.5	39.7	36.8
F6080	27.8	29.7	27.2	26.8	14.8

If flow activation energy is high, a small change in temperature significantly affects viscosity. Therefore, temperature changes during injection moulding will change feedstock viscosity, which may produce mould defects due to undue stress concentration. Feedstock F6075 has a higher activation energy than F6080 (Figure 4.72) so injection moulding temperature needs to be controlled carefully.

Flow activation energy decreased as shear rate increased (Figure 4.72) but less for feedstock F6075 than for F6080. The results indicate it is better to have higher shear rates during injection moulding and that F6080 is the better feedstock. This effect of shear on microstructural changes was described in Section 4.3.1.

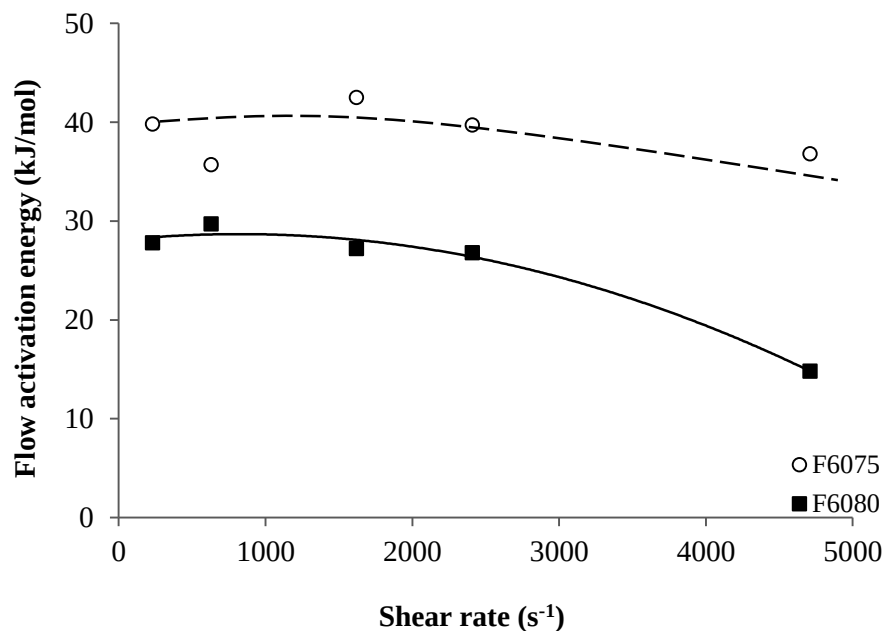


Figure 4.72: Effect of shear rate on flow activation energy.

4.3.11. Feedstock mouldability

Feedstock with high fluidity, high shear thinning (low flow behaviour index), low viscosity and low activation energy has better rheology for MIM (Sections 4.3.1 to

4.3.10). As a change in one factor may offset change in another factor, feedstock mouldability is indicated using the mouldability index (α_{STV}).

The log of rate of change of viscosity with shear rate $\left| \frac{\partial \log \eta}{\partial \log \dot{\gamma}} \right|$ is the gradient of a log-log plot of viscosity and shear rate (Figure 4.49), and gives $(n - 1)$. The term $\left(\frac{\partial \log \eta}{\partial \left(\frac{1}{T} \right)} \right)$ is the gradient of log viscosity versus $1/T$, and equals E/R (Figure 4.71). Therefore, mouldability index can be rewritten as:

$$\alpha_{STV} = \left[\frac{1}{\eta_0} \frac{|n-1|}{\left(\frac{E}{R} \right)} \right] \quad 4.46$$

Feedstocks with high α_{STV} have better rheological properties for MIM [160, 232, 243.-244]. The increase in α_{STV} with temperature indicates that moulding with F6075 and F6080 (Figure 4.73) should be done at higher temperatures. The α_{STV} for F6080 was three to five times that of F6075 (Figure 4.73), indicating it is the better feedstock for Ti-MIM.

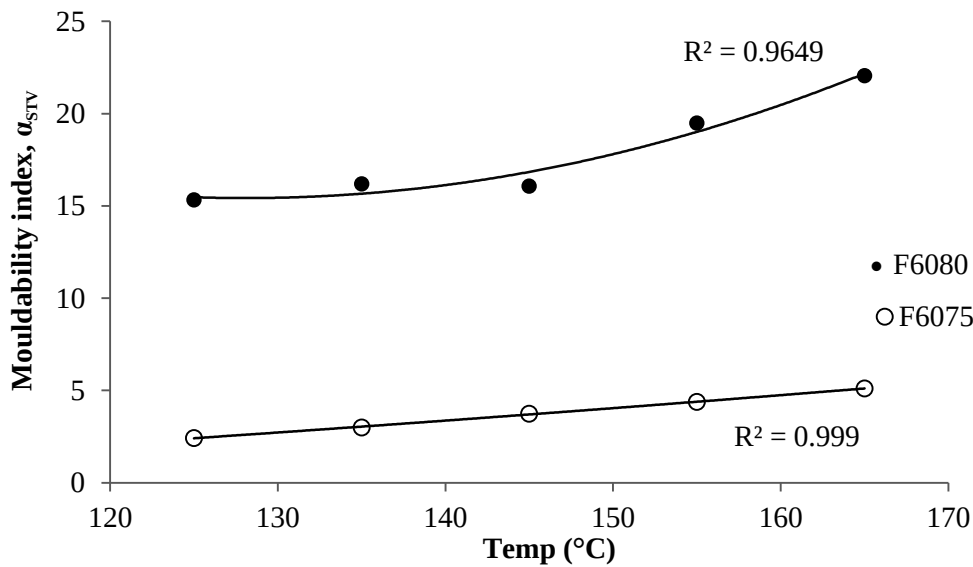


Figure 4.73: Effect of temperature on feedstock mouldability

Information on various rheological characteristics indicates that 80:15:5 vol. % PEG:PVB:SA is the most promising binder for Ti64-MIM (Table 4.21).

Table 4.21: Suitability of different binders for Ti64-MIM at 60 vol. % powder loading, based on various properties where +++ is very suitable and + is least suitable.

Factor	Binder (PEG:PVB:SA, vol. %)		
	75:20:5	80:15:5	85:10:5
Overall suitability	++	+++	+
Yield stress	+++	+++	+
Shear sensitivity (flow behaviour index)	++	+++	+
Fluidity	++	+++	+
Melt flow rate	+	+++	++
Stability index	+	+++	++
Powder loading	+++	+++	-
Flow activation energy	++	+++	-
Mouldability	++	+++	-

- Not determined.

4.3.12. Summary

The yield stress, shear sensitivity, fluidity, melt flow rate, feedstock stability, powder loading, flow activation energy and mouldability of three Ti64-MIM feedstocks were used to identify the most promising feedstock and binder for Ti-MIM. Increasing PEG content in the binder decreased feedstock yield stress and improved flowability. The substantial decrease in yield stress as PEG increased from 80 to 85 vol. % indicated that moulding defects may occur with feedstocks made with 85:10:5 vol. % PEG:PVB:SA binder. Feedstocks with 60 vol. % powder loading had lower yield stress, which is better for Ti-MIM. Yield stress decreased as temperature increases, which allows lower injection pressures to be used. However, fluctuations in yield stress were large ($> \pm 20\%$) between 145 and 165 °C, which may adversely affect injection moulding. Yield stress analysis indicated that feedstocks F6075 and F6080 would be better for Ti-MIM than F6085.

Feedstocks made with 75:20:5, 80:15:5 and 85:10:5 vol. % PEG:PVB:SA binders had the pseudoplastic flow behaviour desirable for MIM. The flow behaviour index can help identify optimal powder loading and temperatures to use in the extruder and injection moulder. Feedstock F6080 had the lowest flow behaviour index (i.e. highest shear thinning) and shear thinning of feedstocks F6080 and F6075 increased as

temperature increased from 125 to 145 °C. It is recommended that extrusion and injection moulding is done at this temperature. Shear sensitivity analysis indicated that feedstocks F6080 and F6075 were the most promising feedstocks.

Feedstock fluidity increased with shear rate and PEG content and decreased with powder loading (Figure 4.55; Table 4.12). Feedstocks made from 80:15:5 vol. % PEG:PVB:SA binder had greater fluidity than feedstocks made from 75:20:5 vol. % PEG:PVB:SA binder and were therefore considered more suitable for Ti-MIM. Feedstock F6085 showed fluidity above 1000 s^{-1} , indicating that it was not suitable for Ti-MIM at low shear rates. Fluidity values indicated that feedstock F6080 was the most promising.

Feedstock MFR increased as powder loading decreased, PEG increased and shear stress increased (Table 4.13). Feedstocks made with 80:15:5 vol. % PEG:PVB:SA binder had higher, more consistent MFR values (lower variation as powder loading increased for all shear stress) than feedstocks made with 75:20:5 or 85:10:5 vol. % PEG:PVB:SA binders. This indicates that feedstock made with F6080 would be more easily injected moulded and therefore more suitable for Ti-MIM. Feedstocks with 75:20:5 or 85:10:5 vol. % PEG:PVB:SA binder were more sensitive to powder content so feedstock F6080 was considered the best binder and F6085 was the second choice.

A new model that used MFR (μ) to predict feedstock flow properties was developed:

$$\mu = q\tau^p \quad 4.47$$

It incorporated a new flow parameter, feedstock flow index (p), which has a hyperbolic relationship with flow behaviour index (n):

$$pn = 1 \quad 4.48$$

Feedstock flow index (p) increased with the powder loading or decrease in PEG content, where:

$p < 1$, fluid has shear thickening (dilatant) flow behaviour

$p = 1$, fluid has Newtonian flow properties

$p > 1$, fluid has shear thinning (pseudoplastic) flow behaviour; the higher the flow index, the higher shear thinning.

This proposed model, which extends the existing power law model (Section 2.4.2) for analysing rheological properties of a feedstock, was validated over a narrow range of Ti-MIM conditions. Due to limited published data, it could not be validated for a wider range of PIM applications. A validated model would help predict MIM feedstock suitability and thus minimize the cost for obtaining information from rheological measurements.

Feedstock stability, measured by the rate that viscosity changes, increased with PEG content and process temperature, suggesting that PIM injection moulding can be done at higher temperatures than normally used. Feedstocks with 75:20:5 vol. % PEG:PVB:SA binder had the greatest variation in rate of viscosity change, suggesting it was an unstable feedstock for MIM. Although feedstocks with 85:10:5 vol. % PEG:PVB:SA binder had the highest stability, they were more affected by changes in powder loading. Feedstock with 80:15:5 vol. % PEG:PVB:SA binder had a consistent rate of change in viscosity at all powder loadings, indicating a more stable feedstock for MIM. In conclusion, feedstock F6080 exhibited the highest stability and suitable for Ti-MIM.

The relative viscosity of feedstocks made with 75:20:5 and 80:15:5 vol. % PEG:PVB:SA binders increased with powder loading, and became infinity at the critical powder loading (65 vol. %). These feedstocks were workable at 60 vol. % powder loading, indicating that feedstocks F6075 and F6080 were the most promising for Ti64-MIM. Many published mathematical models for predicting relative viscosity and powder loading were investigated but did not agree with the experimental data obtained. The following new model was developed and validated for metal and ceramic injection moulding:

$$\eta_r = 1 + \left[\frac{1}{m(\phi_c - \phi)} \right]^{2.5} - \left[\frac{1}{m\phi_c} \right]^{2.5} \quad 4.49$$

This model accurately predicted relative viscosity and critical powder loading for a wide range of PIM feedstocks. The Einstein viscosity coefficient (2.5), could be modified as $[2.5/\phi_c]$ for MIM feedstocks.

A method for estimating thickness of binder adsorbed on a powder particle was developed. The following model is proposed for predicting relative viscosity and critical powder loading from powder surface area, shear rate, powder loading, flow behaviour index, binder adsorbed layer thickness proposed but needs to be validated.

$$\eta_r = 1 + \frac{MS\dot{\gamma}^{n-1}}{4(1-\phi)} \left[\left[\frac{1}{m\alpha(\Phi_c - \phi)} \right]^{2.5} - \left[\frac{1}{m\alpha\Phi_c} \right]^{2.5} \right] \quad 4.50$$

Feedstock viscosity decreased as temperature increased, indicating that injection moulder barrel temperature for MIM could be increased. Feedstock F6080 had a lower viscosity than F6075 at all temperatures tested, indicating it was suitable for MIM. Flow activation energy decreased with increased shear rate, indicating feedstocks F6075 and F6080 could be injection moulding at high shear rates. Flow activation energy analysis indicated that feedstock F6080 was the most suitable feedstock for injection moulding Ti-MIM. The flow activation energy of F6075 was marginally affected by shear rate and higher than that of F60805.

The mouldability parameter for feedstocks F6075 and F6080 increased with temperature, indicating that moulding should be done at higher temperatures. Feedstock F6080 had higher mouldability values than F6075, indicating it was the most promising feedstock for Ti-MIM.

Data from various rheological investigations showed that F6080 (i.e. 60 vol. % Ti64 and 80:15:5 vol. % PEG:PVB:SA binder) was the most promising feedstock for Ti-MIM. However, the F6075 and F6085 were included in subsequent MIM trials on solvent debinding, thermal debinding, sintering and product characterization.

4.4. Solvent debinding

Solvent debinding involves dissolving the soluble component in a suitable solvent. The interconnected pores produced in the MIM part allows the remaining binder components to be removed in the thermal debinding step. Water-soluble PEG, the main component in the binder used, was extracted with deionized water and PVB (the backbone polymer) and SA were removed thermally.

4.4.1. Effect of binder composition on solvent debinding

The green parts were immersed in deionised water. After 6 h immersion at 35 °C, 92 – 96 wt. % PEG had been extracted from MIM parts made with 60 vol. % Ti64 powder, regardless of binder composition (Figure 4.74). Debinding rate then decreased and only 4 – 5 wt. % more PEG was extracted after 24 h.

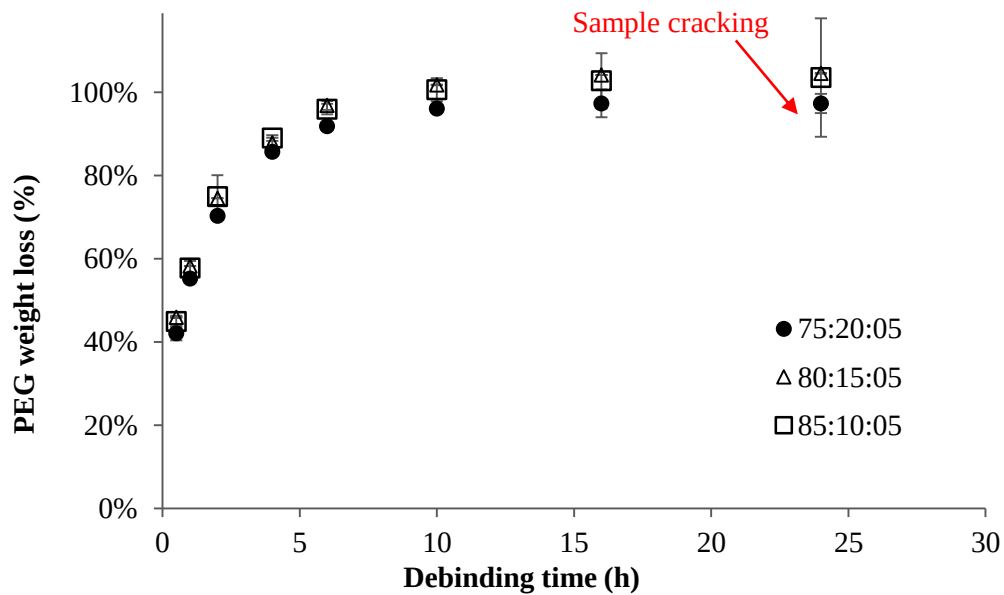


Figure 4.74: Effect of binder composition and time on removing PEG from 60 vol. % Ti64 MIM brown parts at 35 °C.

In industrial applications, 75 wt. % binder removal is considered sufficient [274] for creating the open pores required for removing other binder components in the subsequent thermal debinding and pre-sintering processes. Thomas and Marple [179] reported that removing 60 wt. % of the PEG before thermal debinding their zirconia-based ceramic injection moulding was sufficient. The 92-96 wt. % PEG removal from Ti-MIM in the first 6 h is therefore more than sufficient. Processing time could be reduced to 2 h (70 – 75 wt. % PEG removal) or 4 h 85 – 89 wt. % PEG removal). Debinding rate depends on specimen thickness [179, 274, 285]. It will take long for hydrated PEG to diffuse from the centre of thicker specimens.

The debinding pattern for all binders was similar (Figure 4.74). However, MIM parts manufactured from feedstock F6085 started to crack after 16 h solvent debinding and some Ti64 powder was lost after 24 h solvent debinding (Figure 4.75). This indicated

that the PVB content of the 85:10:5 vol. % PEG:PVB:SA binder was insufficient to hold the Ti64 particles under the debinding conditions used.

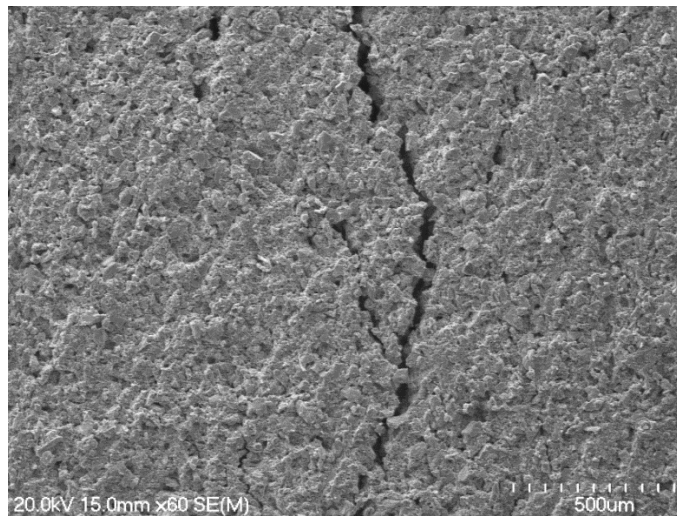


Figure 4.75: SEM image of Ti64 MIM made with F6085 feedstock after 16 h solvent debinding at 35 °C.

The marked change in debinding rate of during solvent debinding MIM parts made with 60 vol. % Ti64 powder (Figure 4.76) occurs when dissolution-controlled debinding changes to diffusion-controlled debinding.

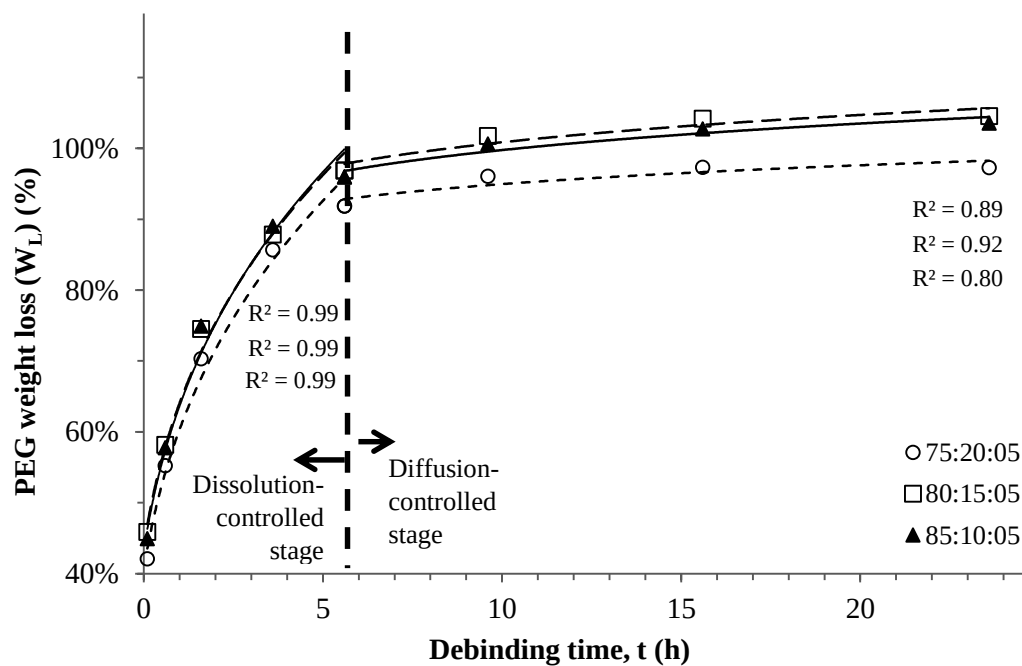


Figure 4.76: Effect of binder and time on removing PEG from 60 vol. % Ti64-MIM brown parts immersed in 35 °C water.

The high initial debinding rate is because PEG is at or near the surface so the mass transfer path is very short and the concentration gradient is high. The rate controlling step is the rate PEG can dissolve at the PEG-water interface. As debinding progresses, the PEG-water interface moves to the interior of the MIM part so PEG needs to diffuse through more tortuous pores, which decreases debinding rate (Figures 4.74; 4.76). Diffusion (i.e. transport of hydrated PEG) then becomes the rate controlling step. If water diffuses in faster than PEG diffuses out, pore volume expands and cracks occur. This occurred when MIM parts made with 85:10:5 vol. % PEG:PVB:SA binder were debound for 16 or 24 h at 35 °C (Figure 4.74; 4.75).

4.4.2. Binder and inter-diffusion coefficient

Solvent debinding data (Figure 4.76) fitted power-regression lines ($W_L = Bt^A$) well, with $R^2 = 0.99$ for the dissolution-controlled stage and $0.80 \leq R^2 \leq 0.92$ for the diffusion-controlled stage. Hence, the empirical relationship for the solvent debinding data can be represented as:

$$\ln(W_L) = A \ln(t) + \ln B \quad 4.51$$

where A is debinding rate and the constant B depends on debinding conditions.

The three-dimensional model (Equation 2.13, Section 2.5.2) was used to investigate solvent debinding kinetics. The inter-diffusion coefficient for PEG-water is obtained by plotting $\ln(1/F)$ versus t/Ψ^2 (Equation 2.13; where F is fraction of remaining soluble polymer and Ψ is the ratio of sample volume and surface area). The fit for all binders at 35 °C was high (Figure 4.77). However, parts made with 85:10:5 vol. % PEG:PVB:SA binder lost excess weight after 16 and 24 h solvent debinding so the second stage did not fit the relationship well.

The empirical model for the data (Equation 4.44) can be rewritten as:

$$\ln\left(\frac{1}{W_L}\right) = -A \ln(t) + \ln\left(\frac{1}{B}\right) \quad 4.52$$

As $W_L = (1 - F)$, and $\ln[1/(1 - F)]$ versus $\ln(t)$ has the same y-intercept and gradient (but negative) of $\ln(1/F)$ versus $\ln(t)$, Equation 4.45 can be rewritten as:

$$\ln\left(\frac{1}{F}\right) = A \ln(t) + \ln\left(\frac{1}{B}\right) \quad 4.53$$

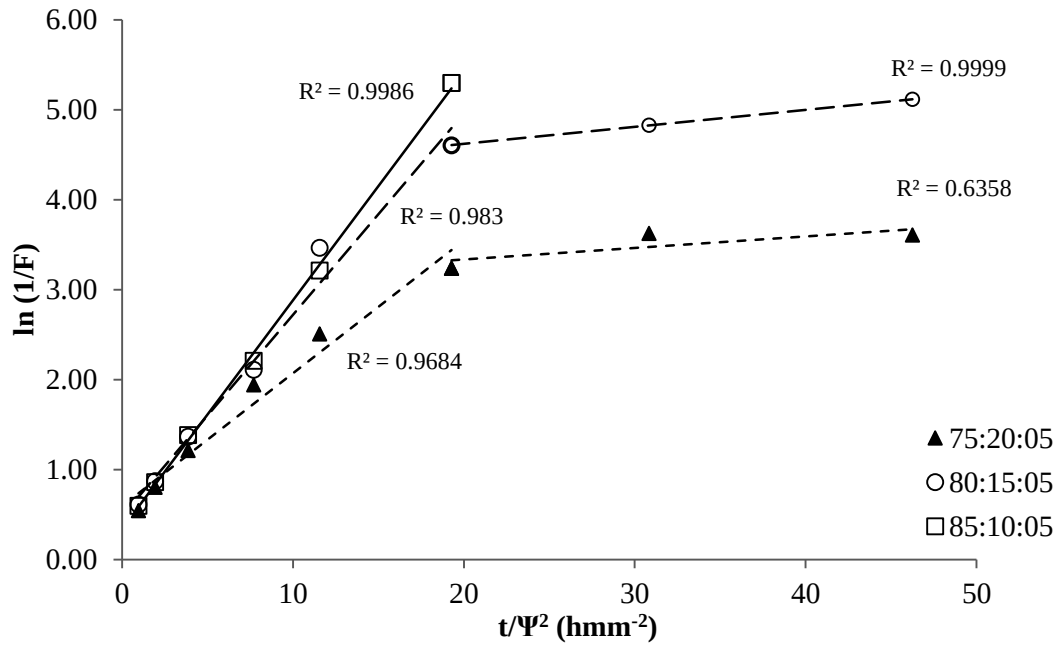


Figure 4.77: Effect of binder composition on $\ln(1/F)$ and t/Ψ^2 when debinding at 35 °C.

Equation 2.13 is the linear and Equation 4.53 is the log-log relationship between $\ln(1/F)$ and debinding time. These equations show that solvent debinding rate (A) in the proposed empirical model (Equation 4.44), is proportional to inter-diffusion coefficient between binder and solvent (D_e) and inversely proportional to Ψ^2 [179, 274, 285]. The values for T_t , the time dissolution- controlled stage (Dis. stage) changes to the diffusion-controlled stage (Diff. stage), debinding rate, and inter-diffusion coefficient (D_e) determined from data in Figures 4.76 and 4.77 are summarised in Table 4.22. The PEG and water inter-diffusion coefficient increased with PEG content in both the dissolution- and diffusion-controlled stages (Table 4.22), indicating that higher PEG content will increase mass transfer to the water.

Table 4.22: Effect of binder type on coefficients obtained during solvent debinding at 35 °C.

Binder PEG:PVB:S A vol. %	Solvent debinding rate (A) (%/ h)		T_t (h)*	T_t (h) (Empirical)	$D_e (\times 10^{-3})$ (mm ² h ⁻¹)	
	Dis. stage	Diff. stage			Dis. stage	Diff. stage
75:20:5	0.34	0.04	9.6	4.8	14.9	1.3
80:15:5	0.32	0.06	9.5	5.2	22.7	1.9
85:10:5	0.33	0.06	-	4.7	25.7	-

- Not determined

* Calculated using Lin-German [282] model (Equation 2.13)

The amount of PEG removed between 35 to 55 °C increased with PEG content (Figure 4.78). As PEG increases, PVB content (backbone polymer) decreases so resistance for diffusion also decreases because there are fewer PVB ligaments.

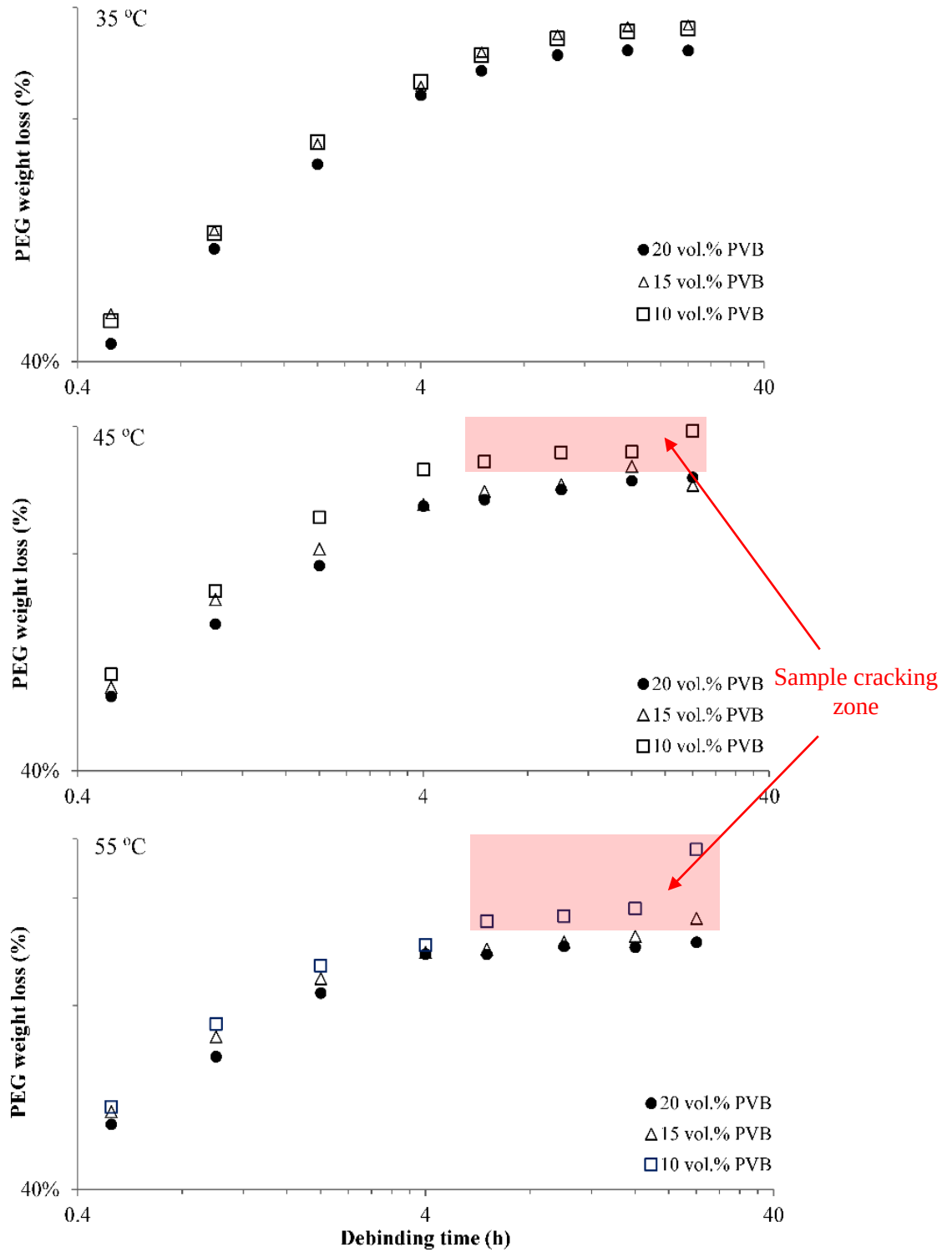


Figure 4.78: Effect of temperature and binder PVB content on PEG removal during solvent debinding.

Diffusion of PEG through the porous, tortuous channels controls solvent debinding rate. The PVB binds the Ti64 powder particles, increasing PEG diffusion resistance. After 6 h or 24 h debinding at 45 °C, Ti-MIM parts made with F6075 binder had pores where PEG had been removed and a network of porous PVB ligaments binding Ti64 particles (Figure 4.79), similar to observations for MIM parts made from stainless steel powder and PMMA binder [149]. This shows that distribution of insoluble binder in the MIM part significantly affects development of porosity during solvent debinding. The low D_e values for the diffusion-controlled stage (Table 4.22) indicates PEG content does not influence the diffusion stage, which is mainly controlled by transport of hydrated PEG through the long channels.

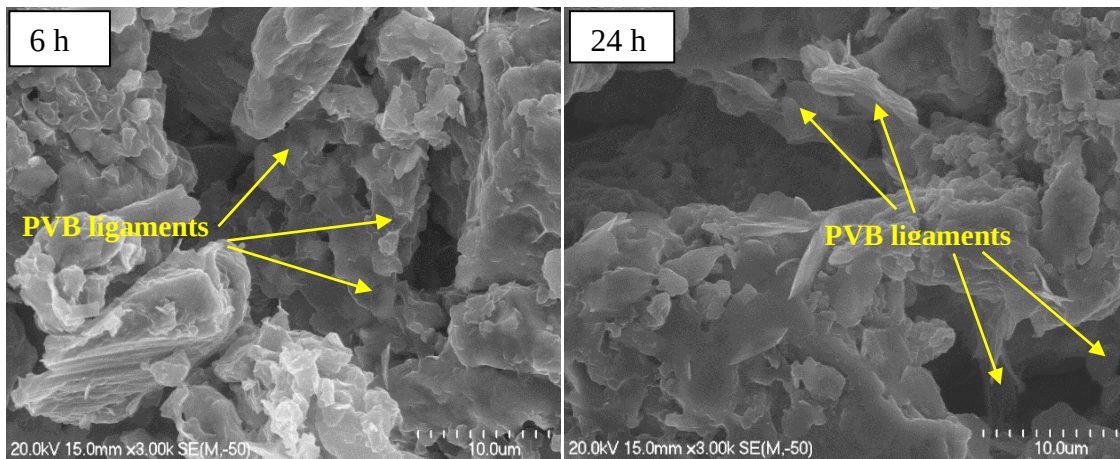


Figure 4.79: Effect of solvent debinding time at 45 °C on microstructure of Ti-MIM parts made with feedstock F6075.

The amount of PEG extracted at a given temperature and debinding time increased with initial PEG content (Figure 4.78). The PEG removal rate from MIM parts made with 80:15:5 vol. % PEG:PVB:SA binder was slightly lower in the dissolution stage than for parts made with 75:20:5 vol. % PEG:PVB:SA or 85:10:5 vol. % PEG:PVB:SA binder (Table 4.22). The 80:15:5 vol. % PEG:PVB:SA binder may give better, more uniform particle packing in the MIM part, thus producing longer diffusing paths; feedstock with this binder had the best rheology (Section 4.3.12).

The Lin-German debinding model (Equation 2.13) predicts that MIM parts made with 75:20:5 vol. % PEG:PVB:SA and 80:15:5 vol. % PEG:PVB:SA binder change from dissolution-controlled to diffusion-controlled after 9.5 h (Table 4.22). At this time,

more than 95% wt. % PEG had been removed. The transition time for MIM parts made with 85:10:5 vol. % PEG:PVB:SA binder could not be determined because of very high losses (negative value for natural logarithm, $\ln$). The debinding pattern (Figure 4.74) showed that the transition occurred between 4 and 6 h rather than at 9.5 h. By 9.5 h, debinding was already at the diffusion-controlled stage.

The empirical model (Equation 4.52) developed from the experimental data predicted that the transition would occur between 4.7 and 5.2 h (Table 4.22), which agree well with the debinding behaviour shown in Figures 4.74 and 4.76. The accuracy of the proposed model (Equation 4.45) still needs to be validated with other PIM applications. The investigations (Section 4.4.2) show that MIM parts made with 75:20:5 vol. % PEG:PVB:SA and 80:15:5 vol. % PEG:PVB:SA binder had better debinding characteristics than those made with 85:10:5 vol. % PEG:PVB:SA binder. However, binder 80:15:5 vol. % PEG:PVB:SA gave more uniform particle packing.

4.4.3. Effect of temperature on solvent debinding

For the temperatures used, solvent debinding rate increased with time irrespective of binder composition (Figure 4.80). Debinding rate increased faster between 35 °C to 45 °C than from 45 °C to 55 °C. However, the effect of temperature on debinding rate was less during the diffusion-controlled stage because debinding rate was controlled more by diffusion of hydrated PEG through the long porous channels in the MIM parts. When the debinding temperature increases, mobility of water and hence diffusivity increases [2, 274]. Water molecules penetrate the PEG molecules more quickly, increasing dissolution and transport of hydrated PEG from the moulded part to the water and hence solvent debinding rate.

The MIM samples swelled and cracked at the higher solvent temperatures (55 °C) because water molecules diffuse into PEG faster than PEG diffuses into the water, so the samples swell [166, 280], developing internal stress that cause cracking. Parts made with 85:10:5 vol. % PEG:PVB:SA binder started to crack and lose their shape after 6 h solvent debinding at 55 °C and parts made with 80:15:5 vol. % PEG:PVB:SA binder started to swell and crack after 24 h solvent debinding at 55 °C (shaded area in Figures 4.78). However, debinding temperature did not affect the integrity of parts made with 75:20:5 vol. % PEG:PVB:SA binder.

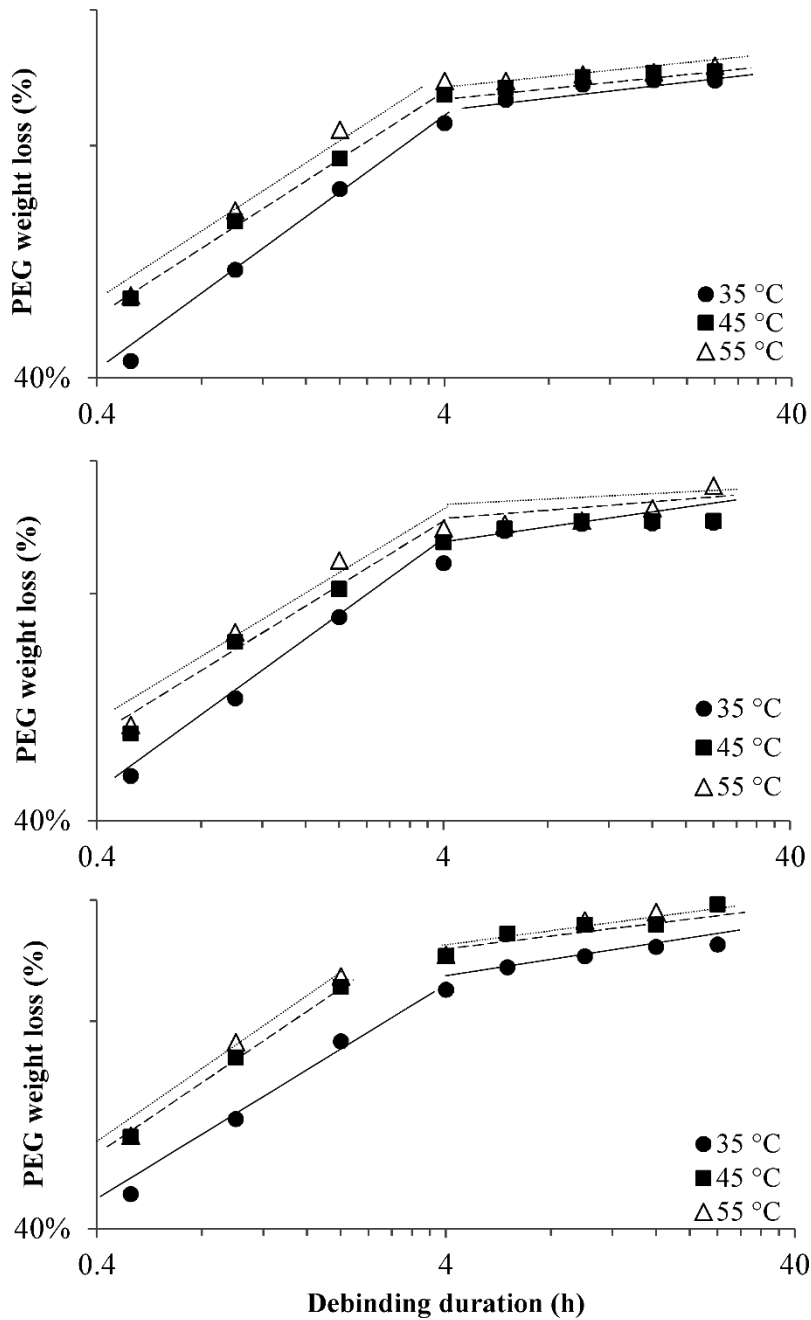


Figure 4.80: Effect of temperature on dissolution- and diffusion-controlled removal of PEG from MIM parts.

The MIM samples swelled and cracked at the higher solvent temperatures (55 °C) because water molecules diffuse into PEG faster than PEG diffuses into the water, so the samples swell [166, 280], developing internal stress that cause cracking. Parts made with 85:10:5 vol. % PEG:PVB:SA binder started to crack and lose their shape after 6 h solvent debinding at 55 °C and parts made with 80:15:5 vol. % PEG:PVB:SA binder started to swell and crack after 24 h solvent debinding at 55 °C (shaded area in

Figures 4.78). However, debinding temperature did not affect the integrity of parts made with 75:20:5 vol. % PEG:PVB:SA binder.

Irrespective of binder, the time at which the solvent debinding mechanism changed from dissolution to diffusion-controlled decreased as temperature increased (Table 4.23). However, the benefit of higher debinding rates at higher solvent temperatures (e.g. 55 °C) is offset by poor debinding performance. Debinding at 45 °C, which is 45 – 60 min faster than at 35 °C (Table 4.23) is recommended. However, debinding MIM parts made with 85:10:5 vol. % PEG:PVB:SA binder was poor at 45 °C, indicting this binder is not suitable for Ti-MIM.

Table 4.23: Effect of binder composition and debinding temperature on time (h) to change from the dissolution- to the diffusion-controlled stage.

Debinding temp (°C)	Binder (PEG:PVB:SA, vol. %)		
	75:20:5	80:15:5	85:10:5
35	4.75	5.20	4.67
45	3.99	4.29	3.54
55	3.56	2.83	2.01

Equations 2.13 and 2.14 (Section 2.5.4) can be used to obtain the inter-diffusion coefficient, D_e :

$$D_e = D \exp\left(-\frac{E}{kT}\right) \quad 4.54$$

where D is a constant indicating binder solubility in the solvent. Equation 4.54 shows that D_e is constant at a given temperature. However, experimental data (Table 4.24) show that D_e is affected by both temperature and microstructure (porosity and tortuosity) during the dissolution- and diffusion-controlled stages. For all binders, D_e for the dissolution-controlled stage was much higher than for diffusion-controlled stage at that temperature (Table 4.24), indicating faster dissolution and transportation of PEG. The value of D_e increased with temperature (Table 4.24), indicating faster molecular mobility (water and PEG) and increased diffusivity.

Table 4.24: Inter-diffusion coefficients of PEG-water, D_e ($\times 10^{-3} \text{ mm}^2\text{h}^{-1}$) for various binders and temperatures.

Debinding temp (°C)	Binder composition (PEG:PVB:SA, vol. %)					
	75:20:5		80:15:5		85:10:5	
	Dis. stage	Diff. stage	Dis. stage	Diff. stage	Dis. stage	Diff. stage
35	15	1	23	2	26	-
45	29	11	29	7	77	-
55	43	11	45	43	66	154

- Not determined.

Data indicate that solvent debinding for 5 h at 35 °C or 4 h at 45 °C is preferable. This is the time when the debinding mechanism changes (Table 4.23) and almost 90 wt. % PEG had been removed. Even if debinding times are decreased by one hour, more than 85 wt. % PEG would have been removed, which is sufficient to create channels in the green body for subsequent thermal debinding (Section 4.4.1) and will help reduce processing cost.

4.4.4. Debinding time and binder on reaction distance

The relationship between reaction distance and binder removal was investigated. Krug's [274] formula (Equation 2.15) was modified using the following assumptions: (i) homogeneous binder distribution in the MIM part, (ii) constant gradual binder removal from all sides of the MIM part, (iii) No distortion in the part during binder removal, and (iv) powder is not removed from the MIM part during solvent debinding. Water diffuses in and PEG diffuses out over a reaction distance (x , in mm) in a specific debinding time (t) at a given temperature (Figure 4.81).

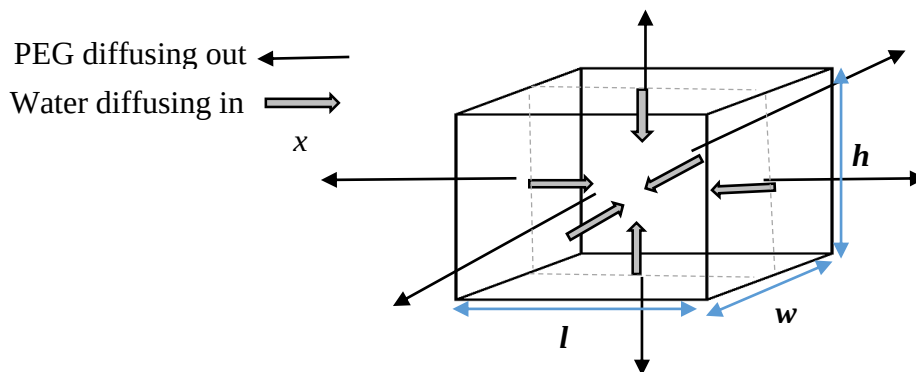


Figure 4.81: Schematic of a MIM part during solvent debinding.

The relationship between initial and final volume of the moulded part after t hours solvent debinding is:

$$\text{Initial volume } (V_0) = \text{Final volume } (V_t) + \text{Volume of PEG lost during debinding.}$$

This can be rewritten as:

$$F_v = 1 - (V_t/V_0) \quad 4.55$$

where F_v is fractional volume loss due to PEG removal, $V_t = (l - 2x)(w - 2x)(h - 2x)$ is a function of time (t), x is the associated reaction depth, and l , w and h are dimensions of a MIM part in mm (Figure 4.81).

For all binders, reaction depth increased with solvent temperature and PEG content (Figure 4.82), indicating temperature increased molecular mobility and diffusion, and PEG content helped increase homogeneity and hence reaction rate. However, reaction depth was not directly related to debinding time (Figure 4.82), indicating molecular mobility resistance across the developing porous Ti64 powder / PVB shell. Krug [274] reported a similar finding.

The non-linear relationship could be modelled as a parabolic relationship (Equation 4.56) [274, 366].

$$(t/x) = (ab^2) x + a \quad 4.56$$

There was good agreement between experimental data and the model (dashed line in Figure 4.83) in the initial debinding stage and it then deviated, indicating the model addressed the dissolution-controlled stage but not the diffusion-controlled stage of solvent debinding.

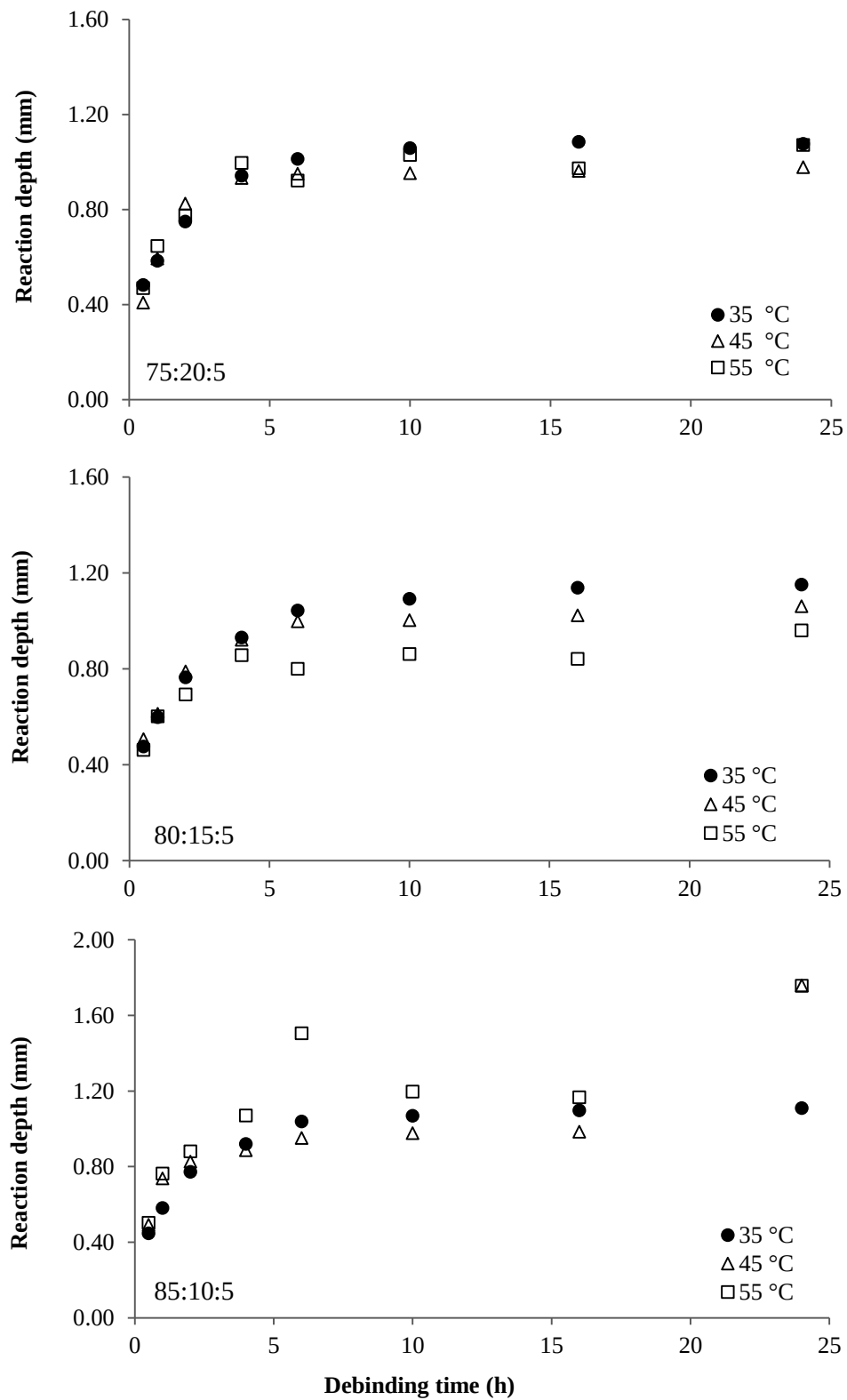


Figure 4.82: Effect of temperature on reaction depth when solvent debinding a MIM part.

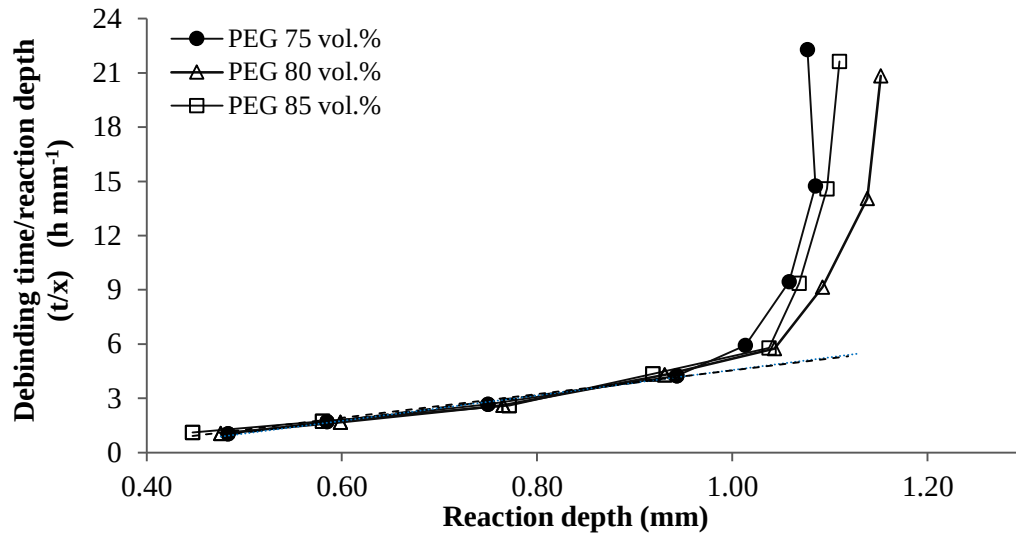


Figure 4.83: Effect of binder composition and debinding time at 35 °C on reaction depth.

4.4.5. Microstructure during solvent debinding

The decrease in apparent inter-diffusion coefficient $\left(\frac{D_e \epsilon}{\nu R}\right)$ (Equation 2.19; Section 2.5.2) when changing from dissolution-controlled to diffusion-controlled solvent debinding (Table 4.24) indicates that increase in porosity (ϵ) during solvent debinding is less than the arithmetic product of tortuosity (ν) and retardation factor (R). The diffusion paths develop interconnecting the pores during solvent debinding, so hydrated PEG needs to travel further than the sample thickness [2], which decreases the apparent inter-diffusion coefficient and therefore debinding rate. For all binders, the porosity data fitted the power regression lines (log-log scale) well (Figure 4.84).

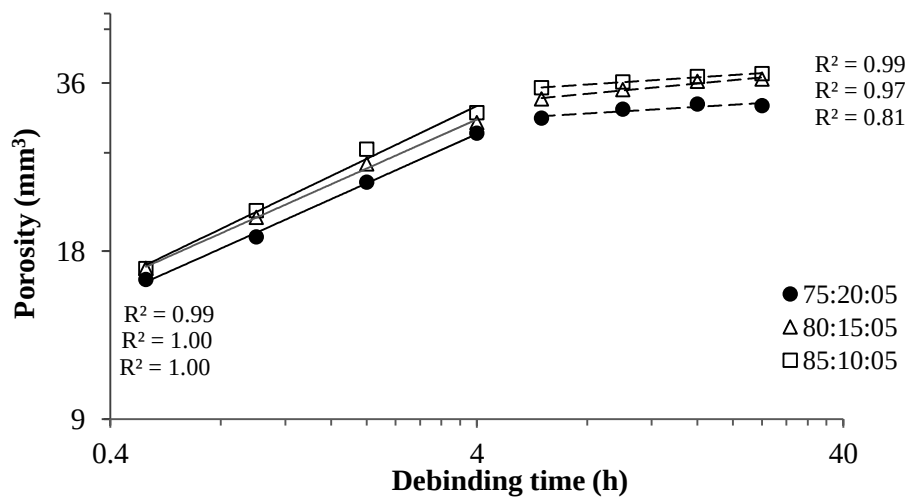


Figure 4.84: Effect of binder composition on porosity when solvent debinding at 35 °C.

The reasons the increase in porosity with debinding time and PEG content was lower in the diffusion-controlled than in the dissolution stages (Figure 4.85) was discussed in Section 4.4.2. The SEM micrographs of Ti-MIM parts showed the effect of PEG content and debinding time on porosity (Figure 4.86). Porosity increased with PEG content, which allows the PVB to be removed more easily in the thermal debinding stage. However, if porosity is too high, green part strength may decrease, there may be greater variation in density variation, and shrinkage can occur during sintering.

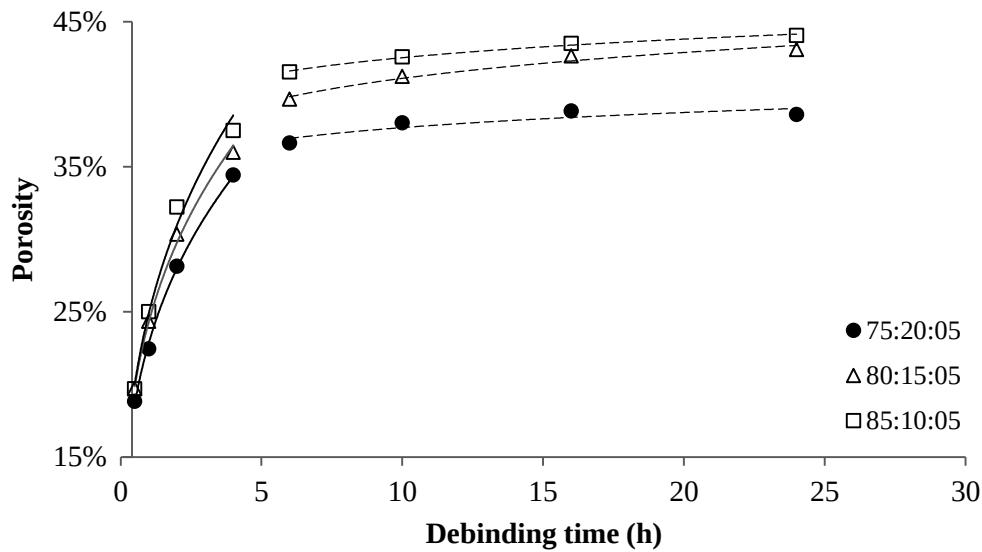


Figure 4.85: Effect of binder composition on porosity when solvent debinding at 35 °C.

Irrespective of debinding temperature, porosity approached steady state at the end of the diffusion-controlled stage (Figure 4.87), indicating the maximum amount of PEG had dissolved and diffused out. The variable porosity observed during the diffusion-controlled stage (Figure 4.87c) indicates Ti64-MIM parts with higher PEG content and/or processed at higher temperatures are more susceptible to cracking and metal powder loss, so these conditions are unsuitable for solvent debinding.

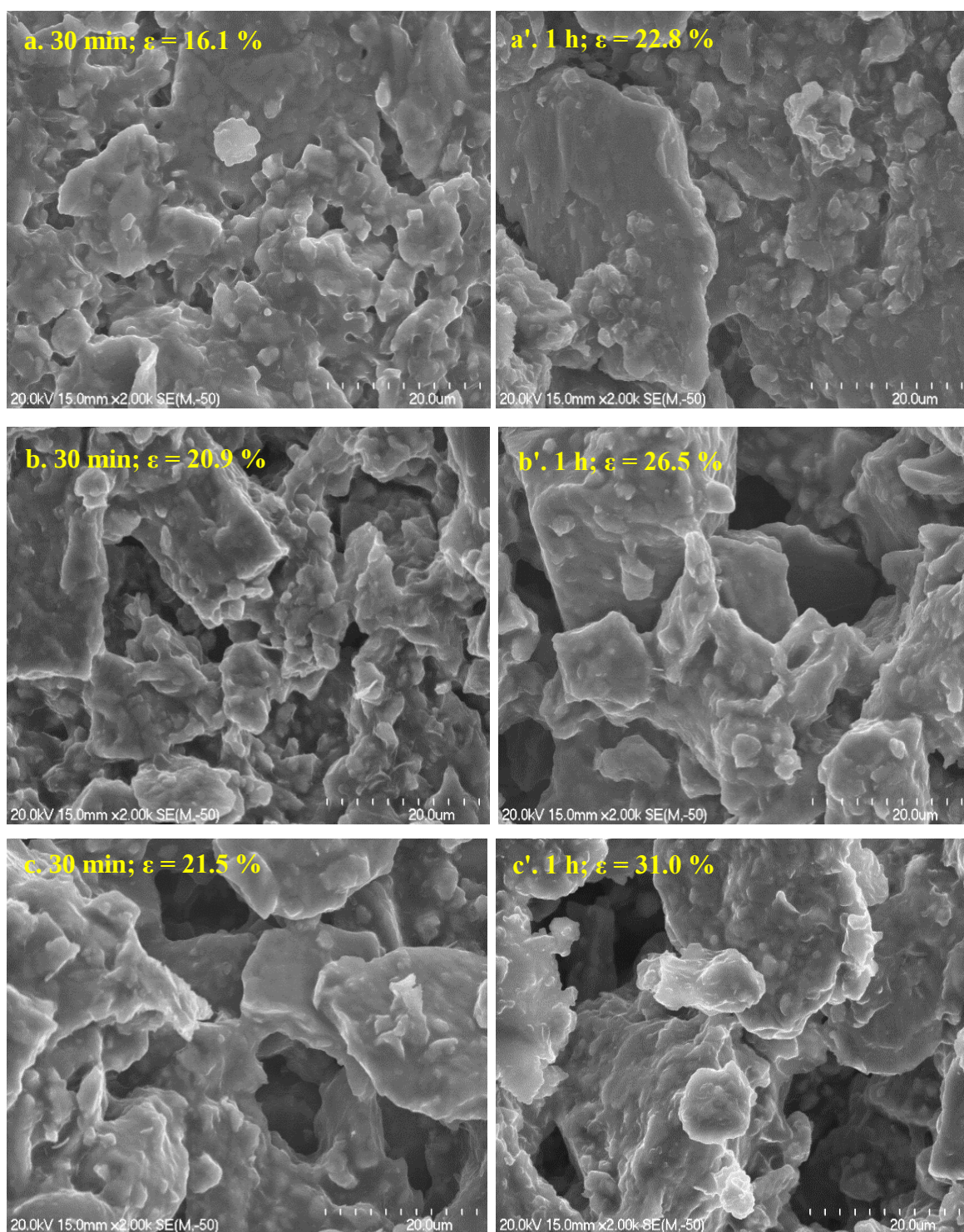


Figure 4.86: Effect of PEG content and solvent debinding time on microstructure of Ti-MIM made of (aa') 75 vol. % PEG, (bb') 80 vol. % PEG, and (cc') 85 vol. % PEG.

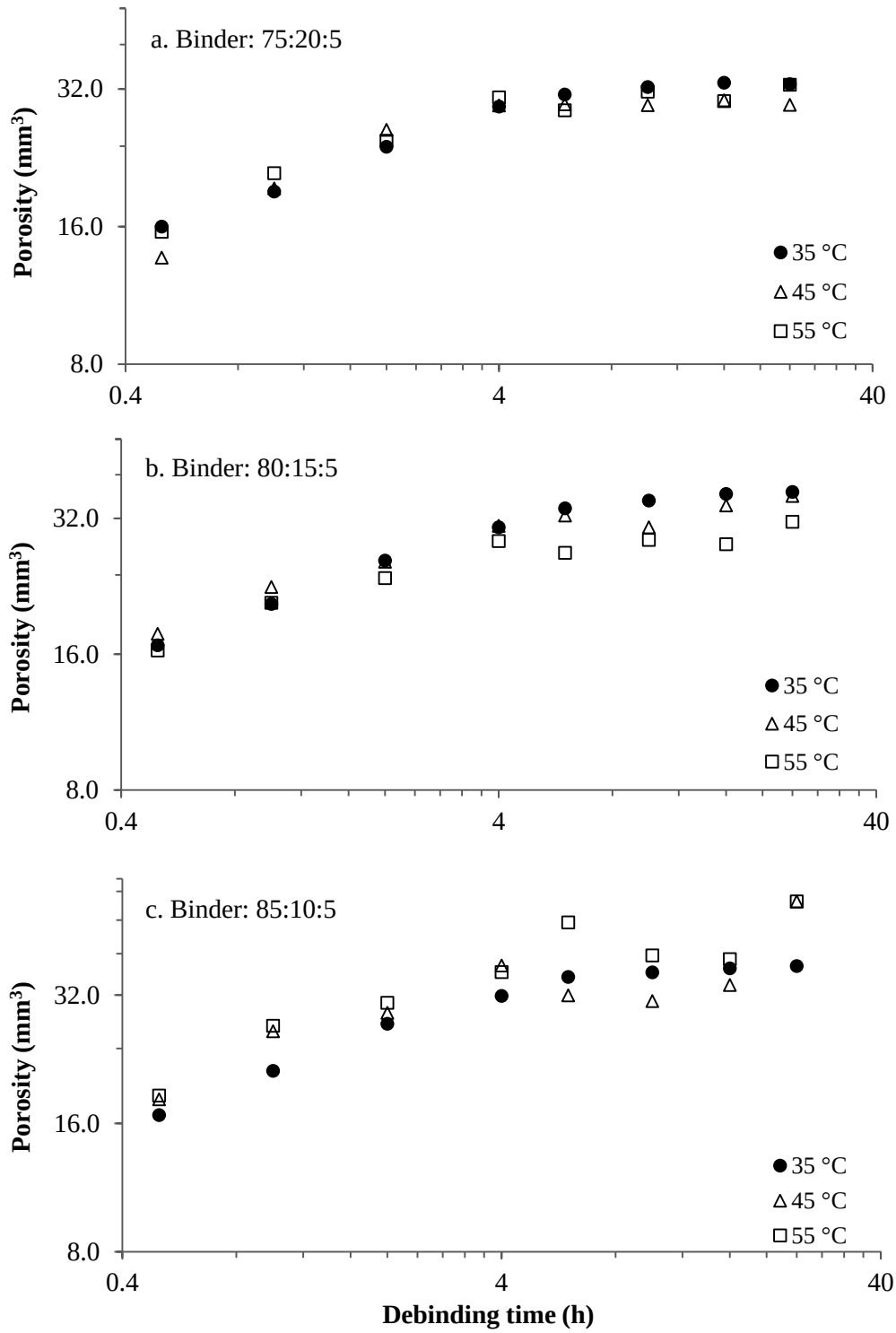


Figure 4.87: Effect of binder and temperature on Ti-MIM porosity.

By the end of dissolution-controlled stage, porosity was 30 – 35% and a further 5 % had developed by the end of the diffusion-controlled stage (Figure 4.85). Micrographs show the porosity at various stages (Figure 4.88).

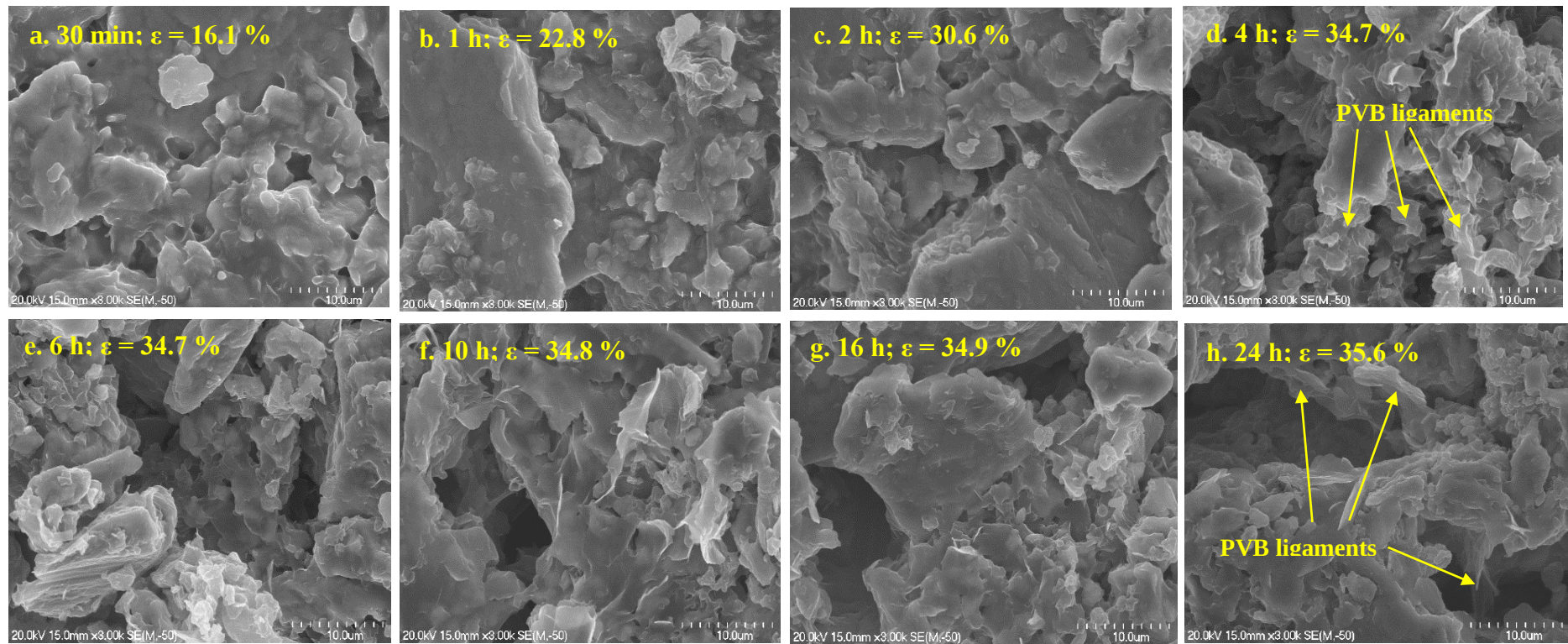


Figure 4.88: Changes in microstructure of Ti-MIM parts made with F6075 during solvent debinding at 35 °C.

Porosity analysis indicated that the MIM part had 16.1 % porosity after 30 min solvent debinding and the Ti64 powder particles were still covered with PEG (Figure 4.88a). About 51 wt. % of the PEG had been removed and reaction depth was 0.48 mm. During solvent debinding for a further 2 h, PEG removal increased to 77 wt. % and the Ti64 particles became more noticeable (Figure 4.88b, c). After 4 h solvent debinding, nearly all the PEG (93 wt. %) had been removed and the microstructure had interconnected pores and PVB ligaments (Figure 4.88d). Pore structure of samples taken between 6 and 24 h solvent debinding were similar and porosity, reaction depth and PEG removal only increased slightly (Figure 4.88e→h) during this diffusion-controlled stage. The change in microstructure occurred during the dissolution-controlled stage (30 min to 4 h debinding) is discussed further in Sections 4.5.1 and 4.5.2. The change in PEG removal, reaction depth and porosity during debinding (Figure 4.89) infer these parameters are interrelated

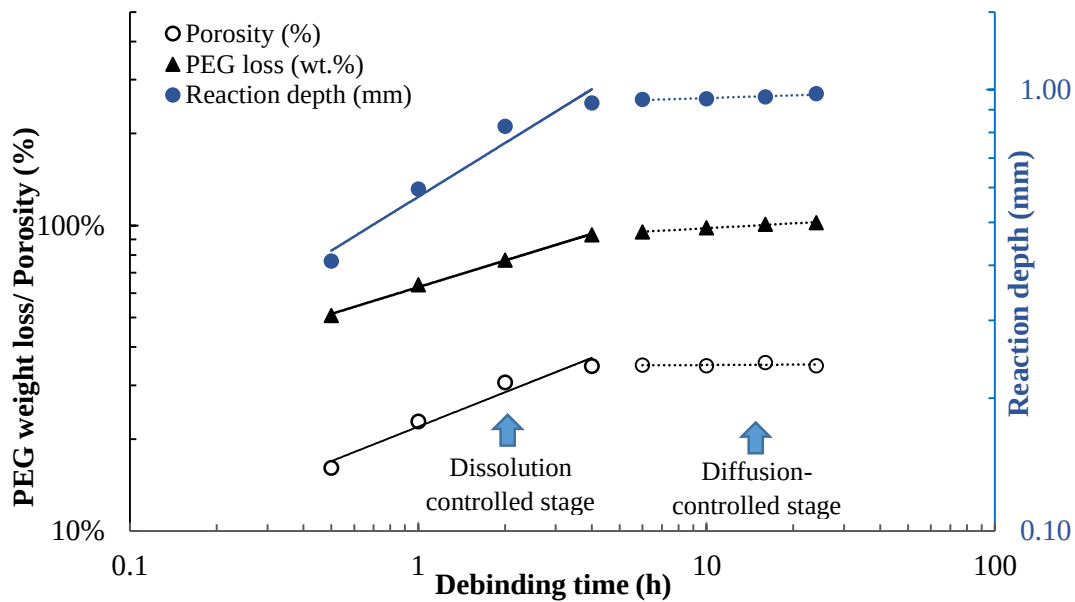


Figure 4.89: PEG removal, reaction depth and porosity when solvent debinding Ti-MIM parts produced with F6075.

By substituting $A = 1/n$, Equation 4.52 becomes:

$$W_L = Bt^{1/n} \quad 4.57$$

where n depends on powder-binder characteristics, density of MIM part and solvent debinding conditions. There was a linear relationship (Figure 4.90) between PEG removal (W_L) with n^{th} root of debinding time ($t^{1/n}$) for $2 \leq n \leq 100$ (R^2 of 0.98 – 1.00 for the dissolution-controlled stage and 0.72 – 0.92 for the diffusion-controlled stage).

Published solvent debinding models [2, 367] indicate that binder removal is proportional to square root of debinding time ($W_L = kt^{1/2}$). However, data in this study show that higher n values predict binder removal better and that the correlation coefficient, R^2 , approaches 1 as n increases to 100 (Figure 4.90).

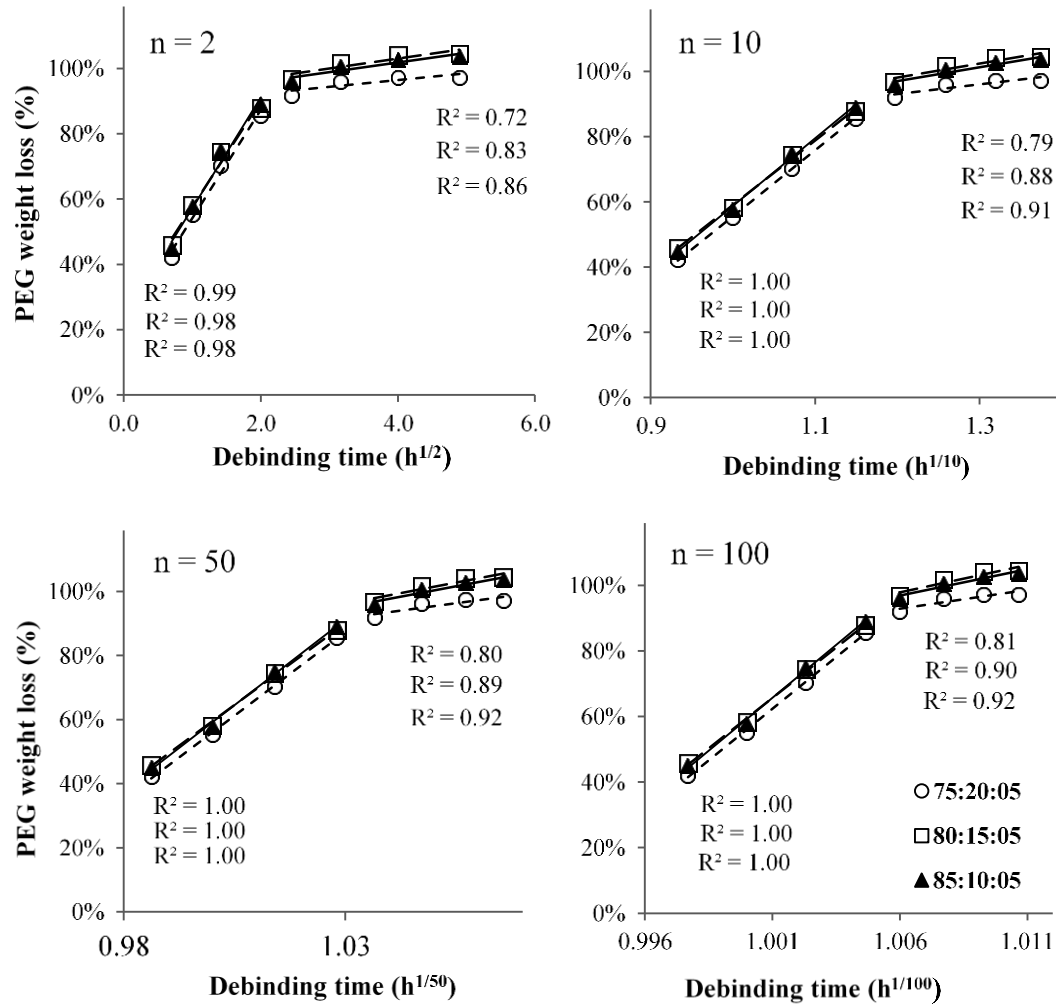


Figure 4.90: Effect of binder type and value for n to predict PEG removal (wt. %) during solvent debinding 35 °C.

The relationship of reaction depth and porosity with debinding time was similar to the relationship of PEG weight loss with debinding time and the data fitted a power regression relationship (Figures 4.84, 4.85 and 4.89). Hence, reaction depth (Equation 4.58) and porosity (Equation 4.59) could be predicted using the following empirical models:

$$x = K_r t^{1/n} \quad 4.58$$

$$\varepsilon = K_p t^{1/n} \quad 4.59$$

where the constants K_r and K_p depend on MIM density, powder-binder characteristics and solvent debinding conditions and can be found from a log-log plot of 'x' and 'ε' with debinding time. These empirical relationships can be used to predict a given binder removal, porosity or reaction depth during solvent debinding.

The following solvent debinding mechanism for Ti-MIM parts, based on PEG removal, porosity, tortuosity, reaction depth and SEM analyses, is proposed.

Initial stage

When Ti-MIM parts are immersed in water, the polar water molecule (H–O–H) dissolves PEG from the binder when water in the PEG is above the equilibrium water content (EWC) of PEG. Water diffuses into the MIM part, dissolves the PEG molecules, which then diffuse from the inter-particle spaces into the water. This reaction starts from the surface of the part (Figure 4.91a, b). Binder removal is driven by capillary forces and PEG concentration gradients between the water and dissolved binder in the MIM part until equilibrium PEG concentration is reached.

Water diffuses slowly from the exterior to the interior through the channels created when PEG is removed. Water concentration decreases with distance from edge of the Ti-MIM part. Porosity and reaction depth are less than 16% and 0.5 mm respectively at the end of the initial stage (<30 min debinding), but will depend on debinding condition and binder composition (Figure 4.82; 4.86).

Intermediate stage

As debinding progresses, water molecules gradually move into the interior of the Ti-MIM part, more PEG-water interfaces develop and debinding rate increases. The PEG-water interfaces move gradually towards the interior and new pores continue to form. Porous channel length and reaction depth continue to increase with debinding time (Figure 4.88b, c; 4.91c). At the end of the intermediate stage (~2 h debinding time), porosity and reaction depth were approximately 30% and 0.7 mm respectively. These may change with debinding condition and binder composition (Figure 4.82; 4.88).

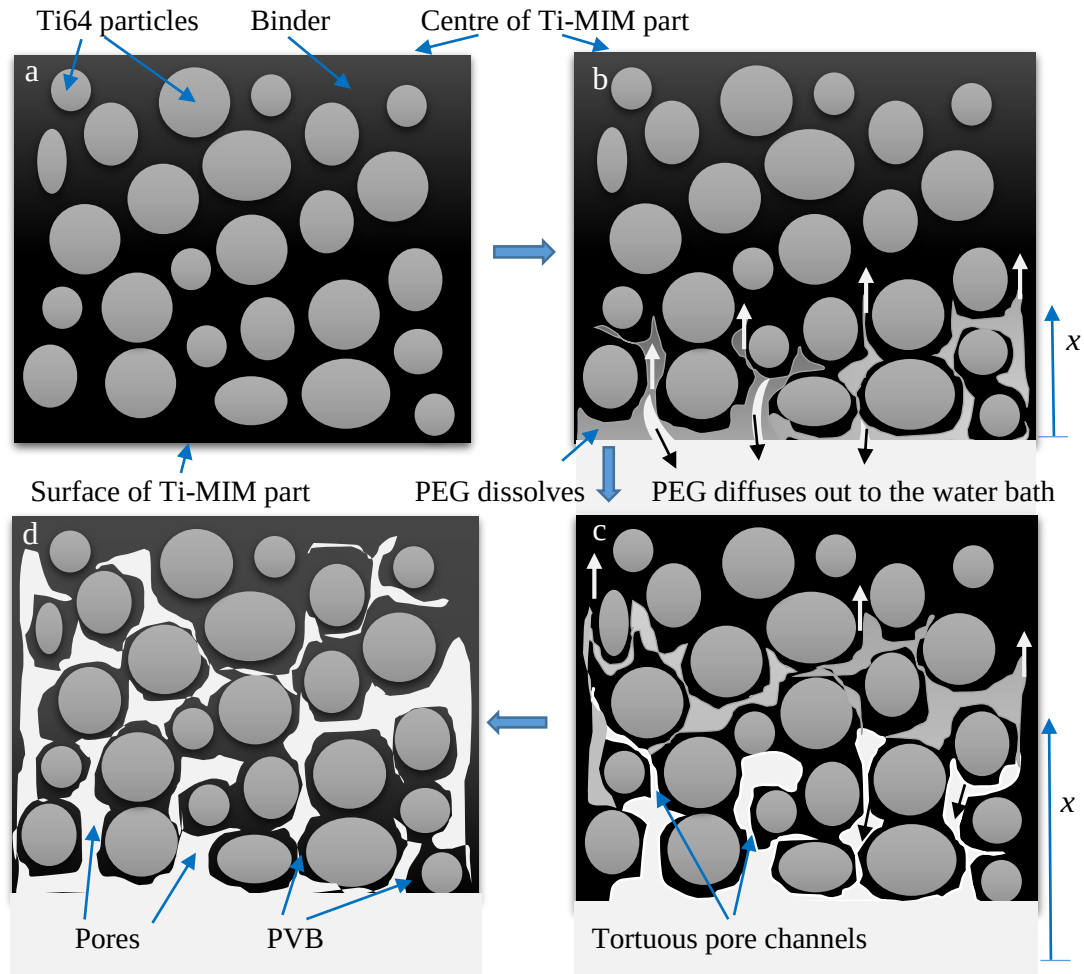


Figure 4.91: Schematic of solvent debinding Ti-MIM parts made with PEG-PVB binder.

Final stage

At solvent debinding time of 4 h or more, the debinding rate starts to slow (Figure 4.80) because the inter-diffusion distance for PEG-water has to move through is longer due to the tortuous channels to the interior of the green body (Figure 4.91d). As water molecules reach the centre of the green body, the PEG concentration gradient decreases and equilibrium is reached. This occurs in the diffusion-controlled stage of debinding. Porosity and reaction depth approach their maximum and the pore distribution broadens (Figure 4.88d→h; 4.91d). The secondary water-insoluble binder (PVB) holds the powder particles and provides strength to the green body. During this stage, porosity approaches 35–40% (Figure 4.88).

4.4.6. Summary

The effect of solvent debinding time and temperature, and binder composition on PEG removal, porosity, reaction depth, debinding rate and microstructure of Ti64-MIM

were investigated. Solvent debinding could be divided into dissolution-controlled stage and diffusion-controlled stages. Debinding rate was higher in the former because the mass transfer path between PEG at or near the surface and the solvent (water) is small. Debinding rate decreased during the diffusion-controlled stage because the dissolved PEG had to must diffuse through length porous channels. For the binders used, the transition time from dissolution-controlled stage to diffusion-controlled stage was 4.67 – 5.20 h at 35 °C and decreased as temperature increased to the upper limit used (55 °C).

The amount of PEG removed increased with PEG content, temperature and debinding time. Solvent debinding rate increased with temperature. The Ti64-MIM parts made with 80:15:5 and 85:10:5 vol. % PEG:PVB:SA binder started to crack after 16 h and 6 h of solvent debinding at 55 °C respectively, so the potential benefit of using higher solvent temperatures had the disadvantage of poor debinding performance.

The inter-diffusion PEG/water coefficient increased with PEG content and temperature, and also depends on microstructure (porosity and tortuosity) during the dissolution- and diffusion-controlled stages. The coefficient for the dissolution-controlled stage was much higher than for the diffusion-controlled stage for all binders and temperatures.

Due to increased molecular mobility and diffusion, reaction depth increased with solvent temperature. However, the relation was not linear with debinding time due to resistance for molecular mobility across the developing porous shell of Ti64 powder and backbone polymer. Although the existing parabolic model ($t = ax + ab^2x^2$) described the dissolution-controlled stage well, it did not address the diffusion-controlled stage, indicating a single model could not address both dissolution- and diffusion-controlled stages.

For all binders and temperatures used, porosity of solvent debound Ti-MIM parts increased with debinding time. However the rate of increase slowed during the diffusion-controlled stage. Porosity also increased with PEG content, indicating PEG influences porosity of the MIM part. Data for debinding at 35 °C show that 30% of

porosity had been developed at the end of dissolution-controlled stage and increased only a 5 % after the diffusion-controlled stage.

Debinding time had a similar effect on the values for PEG removal, porosity of the part and reaction depth, suggesting these parameters are inter-related. The following empirical relationships were developed to explain solvent debinding of Ti-MIM parts made with PEG-PVB binder:

$$\ln \left(\frac{1}{w_L} \right) = -\frac{1}{n} \ln t + \ln \frac{1}{B} \quad 4.60$$

$$x = K_r t^{1/n} \quad 4.61$$

$$\varepsilon = K_p t^{1/n} \quad 4.62$$

These equations indicate that binder removal is proportional to the n^{th} root of debinding time. The accuracy of predicting the amount of PEG removed in a given debinding time and processing temperature increased with n value (2→100).

All binders used exhibited similar characteristics with the debinding time. The inter-diffusion coefficient indicated that MIM part with 80:15:5 vol. % PEG:PVB:SA binder had uniform particle packing. However, defects occurred in Ti-MIM parts made with this binder when solvent debound at 55 °C. The Ti64-MIM parts made with 75:20:5 and 80:15:5 vol. % PEG:PVB:SA binder had better debinding characteristics. These results agree with results discussed in Section 4.3. It is recommended that Ti-MIM parts made with PEG-PVB binder should be solvent debound for 4 h at 35 °C or 3 h at 45 °C. Approximately 85 wt. % PEG is removed under these conditions, which is sufficient to create porous channels in the green body through which the other binder components can move during the subsequent thermal debinding. Solvent debinding at 35 °C is recommended to minimise debinding defects and energy consumption.

4.5. Characterising Ti-MIM parts

Properties of green, brown and sintered parts made with Ti64 powder and PEG:PVB:SA binder were used to identify the best binder composition for Ti-MIM. Results from previous trials (Sections 4.2 to 4.4) showed that F6080 (i.e. 60 vol. %

Ti64 and 80:15:5 vol. % PEG:PVB:SA binder) was the most promising Ti-MIM feedstock in terms of powder loading, rheology and solvent debinding kinetics. Parts were also made using other binder compositions to compare characteristics.

4.5.1. Green parts

Density analysis at 12 equidistant positions along the injected moulded part was used to evaluate homogeneity. Both powder loading and binder composition (F6075, F6080 and F6085) influenced density (Figure 4.92). Low variability in feedstock density indicates the feedstock flows better and fills the moulds uniformly. The Ti-MIM parts made with 75:20:5 or 80:15:5 vol. % PEG:PVB:SA binder had lower variation in density (0.06–0.18 and 0.05–0.13 g/cm³ respectively) than parts made with 85:10:5 vol. % PEG:PVB:SA binder (0.16–0.57 g/cm³).

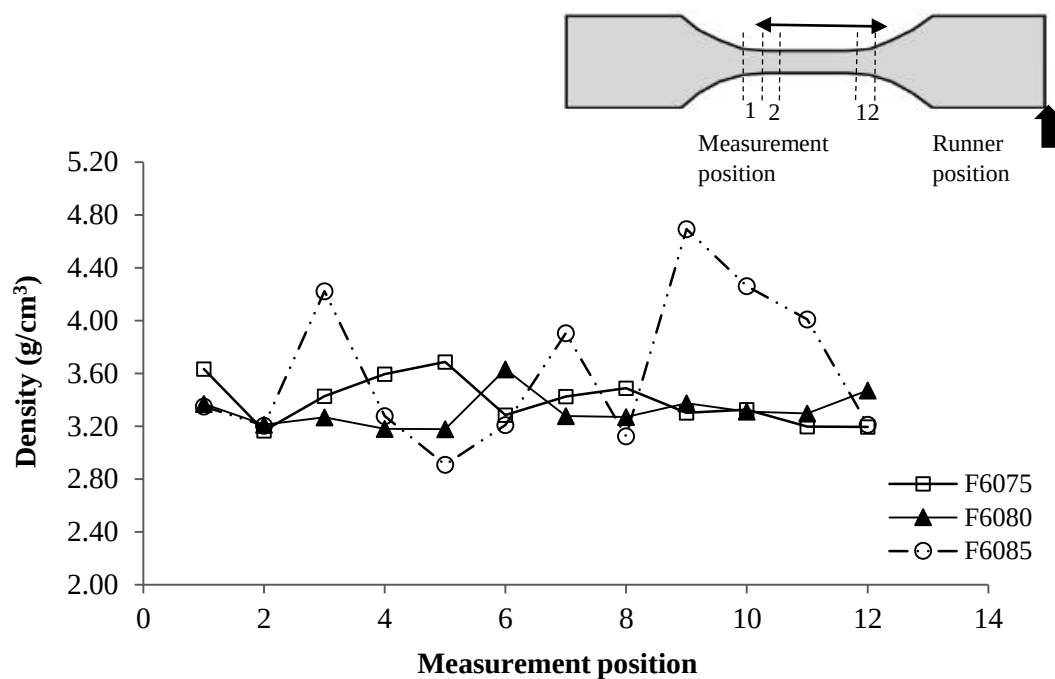


Figure 4.92: Effect of binder composition on density at various positions of the Ti-MIM part.

As Ti64 powder is more dense (4.45 g/cm³) than binder (< 1.2 g/cm³, Table 3.1), part density increased with powder loading (Figure 4.93). The MIM parts made with 80:15:5 vol. % PEG:PVB:SA binder had the lowest variability in density (narrow box and whiskers), inferring increased homogeneity and more uniform particle packing.

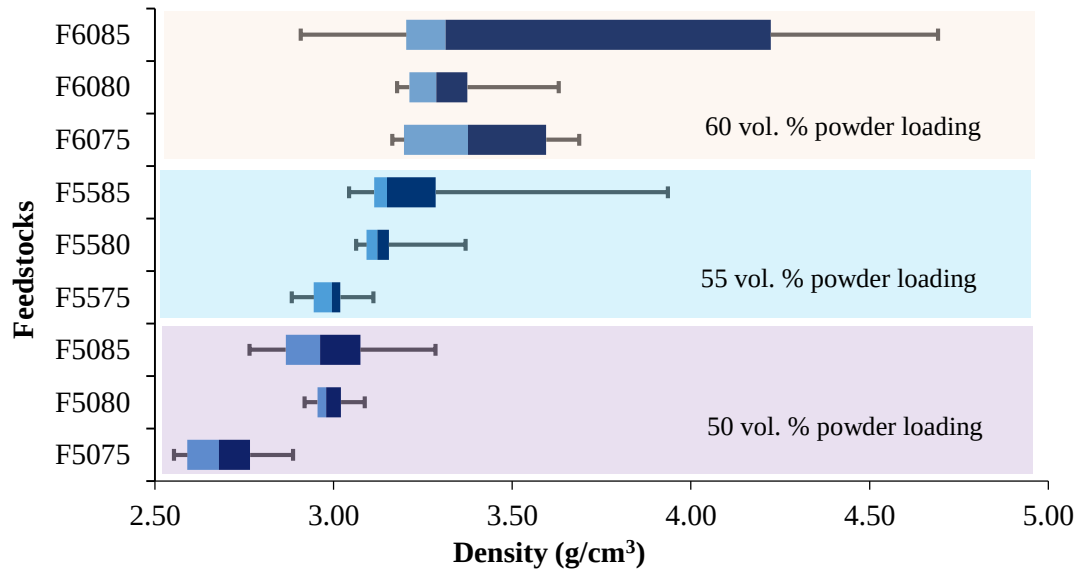


Figure 4.93: Box and Whisker plot for effect of powder loading and binder composition on Ti-MIM density (n =12).

Although moulded parts made from the feedstock F6080 had the smallest variation in density ($3.48 \pm 0.36 \text{ g/cm}^3$) (Figure 4.93), this is greater than the variation in density the F6080 feedstock ($2.78 \pm 0.01 \text{ g/cm}^3$, Stage 4, Figure 4.39). An homogenous feedstock helps produce a homogeneous MIM part but the increased variability moulded part density indicates that homogeneity decreased during moulding. This infers feedstock rheology may also affect green part homogeneity.

The MIM parts made with 75:20:5 and 85:10:5 vol. % PEG:PVB:SA binders had some pores and low packing whilst parts made with 80:15:5 vol. % PEG:PVB:SA binder had no pores and good packing (Figure 4.94), supporting data from the rheological investigations (Section 4.3).

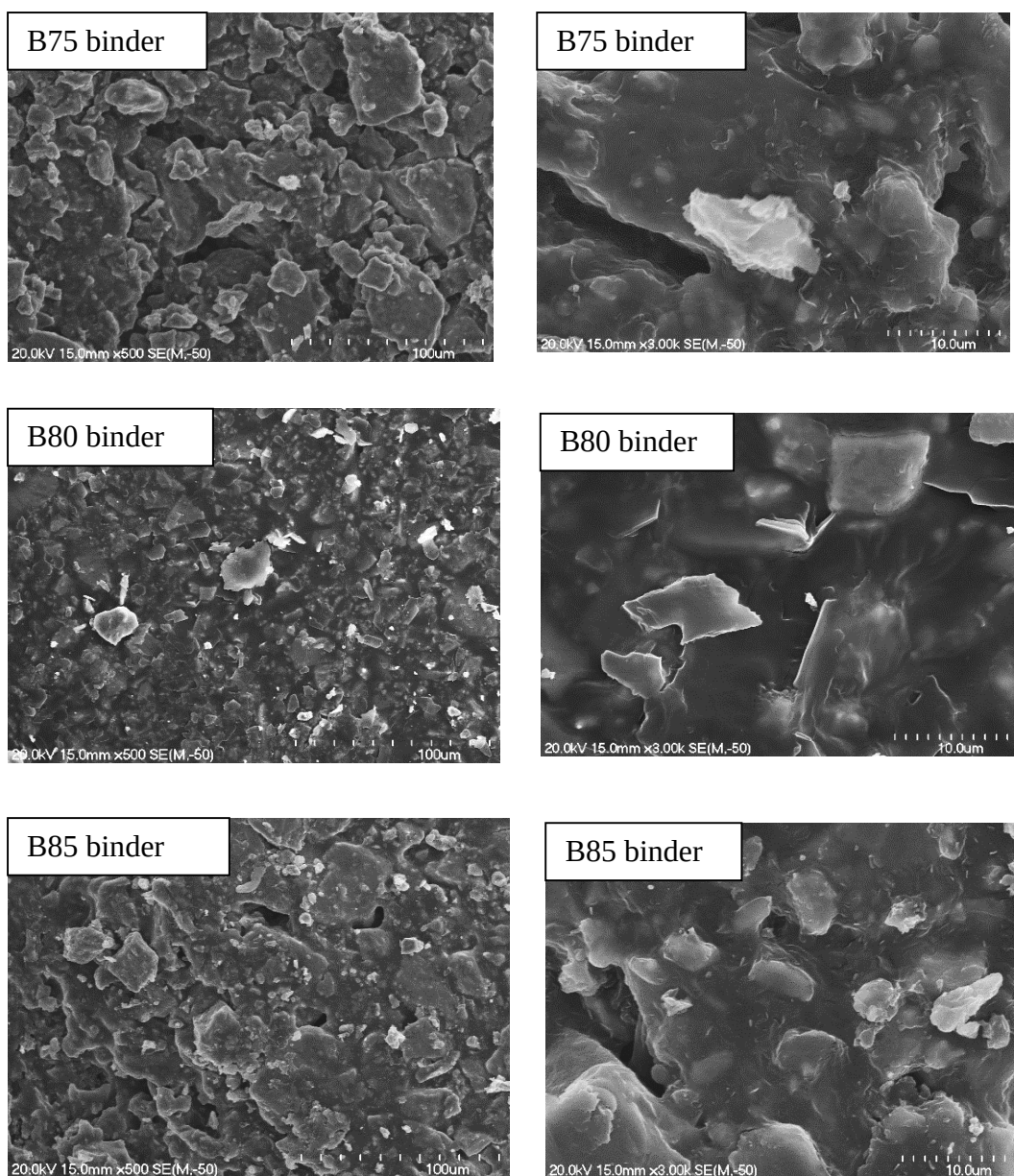


Figure 4.94: SEM images (500X and 3000X) of Ti-MIM parts made from 60 vol. % Ti64 powder and different PEG:PVB:SA binders.

4.5.2. Brown parts

The DTA/TGA data (Figure 4.3, Section 4.1.1) was used to determine the thermal debinding cycle to use (Figure 4.95). As thermal debinding-activation energy in the low temperature region is lower than that at the high temperature region, component distortion tends to occur in low temperature region [291-292, 300]. The binder components undergo phase transformation below 200 °C (Figure 4.2) and start degrading around 200 °C (Table 4.1) so a low heating rate (2 °C/ min) was used in until temperature reached 200 °C (Figure 4.95) to help increase heating uniformity.

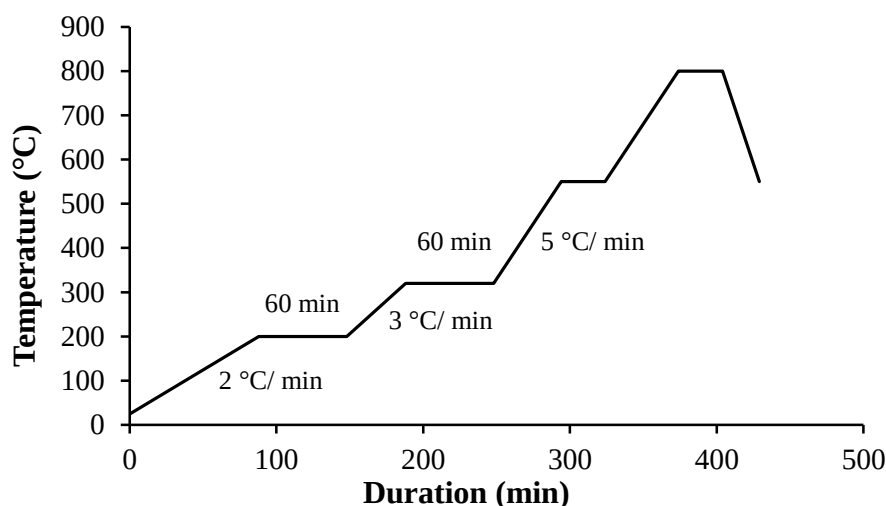


Figure 4.95: Thermal debinding cycle for Ti-MIM parts.

As 60 min of isothermal treatment had a significant effect on binder removal (Table 4.7, Section 4.2.5b), the temperature was then held at 200 °C for 60 min to as maximise binder removal (Figure 4.95). The effect of solvent debinding and low heating rate in the initial stages of thermal debinding) gave sufficient porosity so heating rates of 3 °C/ min and 5 °C/ min were used during debinding in the higher temperature region. This process extracted over 90 wt. % of the SA and PVB (Table 4.2). As it is very difficult to handle a fully debound and unsintered part, the temperature was then increased to 800 °C (Figure 4.95) to pre-sinter and also to extract the remaining SA and PVB.

Parts that had been solvent debound for 1 h or 6 h and then thermally debound had similar microstructures with no visible cracks (Figure 4.96). Thermally debound parts made with 80:15:5 vol. % PEG:PVB:SA binder had higher and more consistent porosity ($39.9 \pm 1.36\%$) than those made with 75:20:5 vol. % ($33.7 \pm 5.16\%$) or 85:10:5 vol. % PEG:PVB:SA binder ($39 \pm 4.44\%$). These data infer that feedstock made with 80:15:5 vol. % PEG:PVB:SA binder had more uniform binder distribution and favourable particle packing than using other binders, which allowed binder to be extracted more freely. Increasing solvent debinding to 3 – 4 h removes about 85 – 89 wt. % PEG (Section 4.4), which may decrease the possibility of cracks and furnace contamination if any PEG is still present.

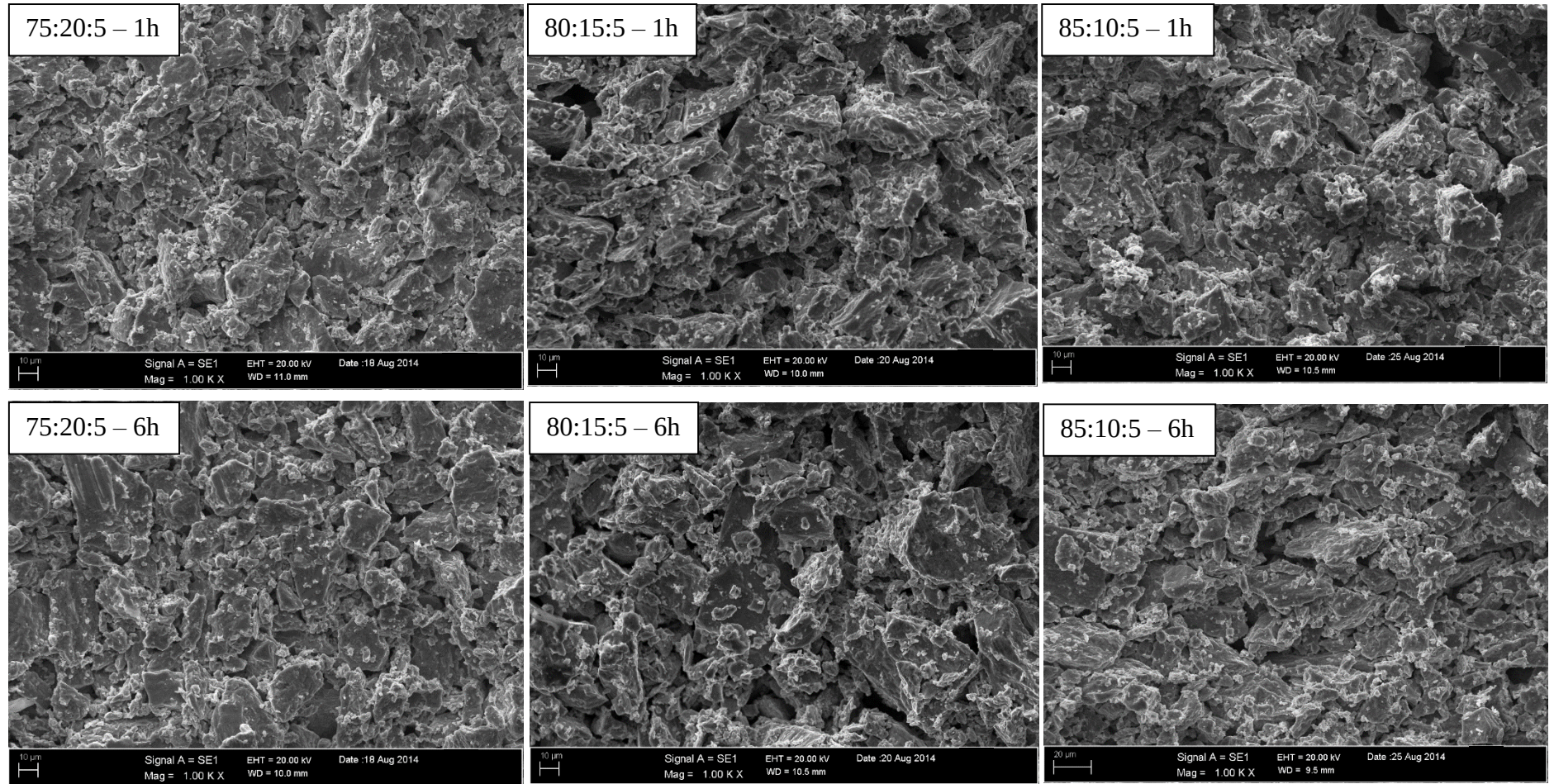


Figure 4.96: Effect of binder composition and solvent debinding time on Ti64-MIM microstructure after the thermal debinding stage.

4.5.3. Sintered parts

Defects such as warpage and cracking can occur at high heating rates of 10 °C/ min [382]. A relatively high heating rate of 5 °C/ min had been used to raise the temperature to 800 °C (Figure 4.95) in the last stage of thermal debinding so a heating rate of 10 °C/ min was used to rapidly re-heat the parts from room temperature to 800 °C. A lower heating rate (5 °C/ min) was then used to raise the temperature from 800 °C to 1300 °C during sintering (Figure 4.97) and to help minimize defects. Although sintering processes report 2 h of isothermal heating [142, 149, 272], 3 h isothermal heating was used in this research (Figure 4.96) to increase sintered density.

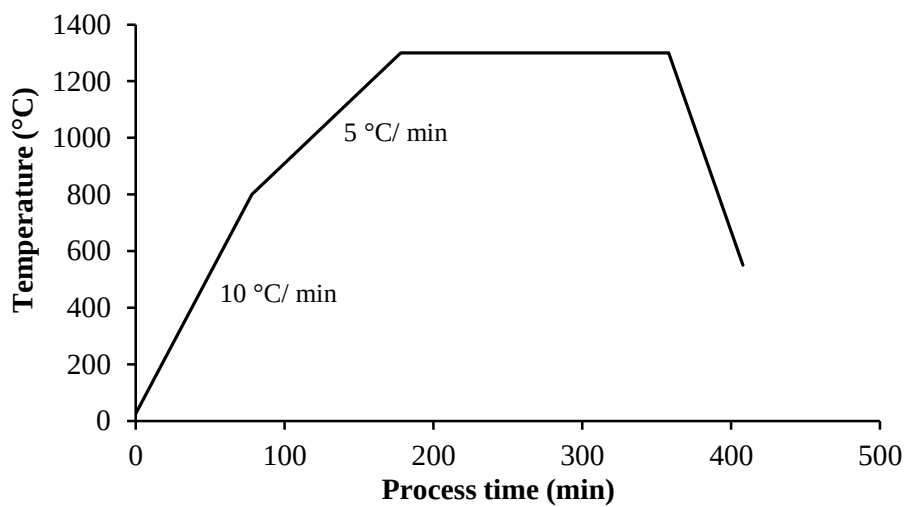


Figure 4.97: Sintering cycle for sintering Ti-MIM parts.

Relative density and porosity

The microstructure of sintered parts made with various binders and solvent debound at various temperatures had pores (Figure 4.98). The solvent debinding temperature did not affect the porosity of sintered parts made with 80:15:5 vol. % PEG:PVB:SA (Figure 4.98a-b-c). However, parts made with 85:10:5 vol. % PEG:PVB:SA binder or solvent debound at 55 °C had large pores (Figure 4.98c and 4.98c'), which will reduce density and adversely affect mechanical properties of the sintered part. These findings support results discussed in Section 4.3 and 4.4.

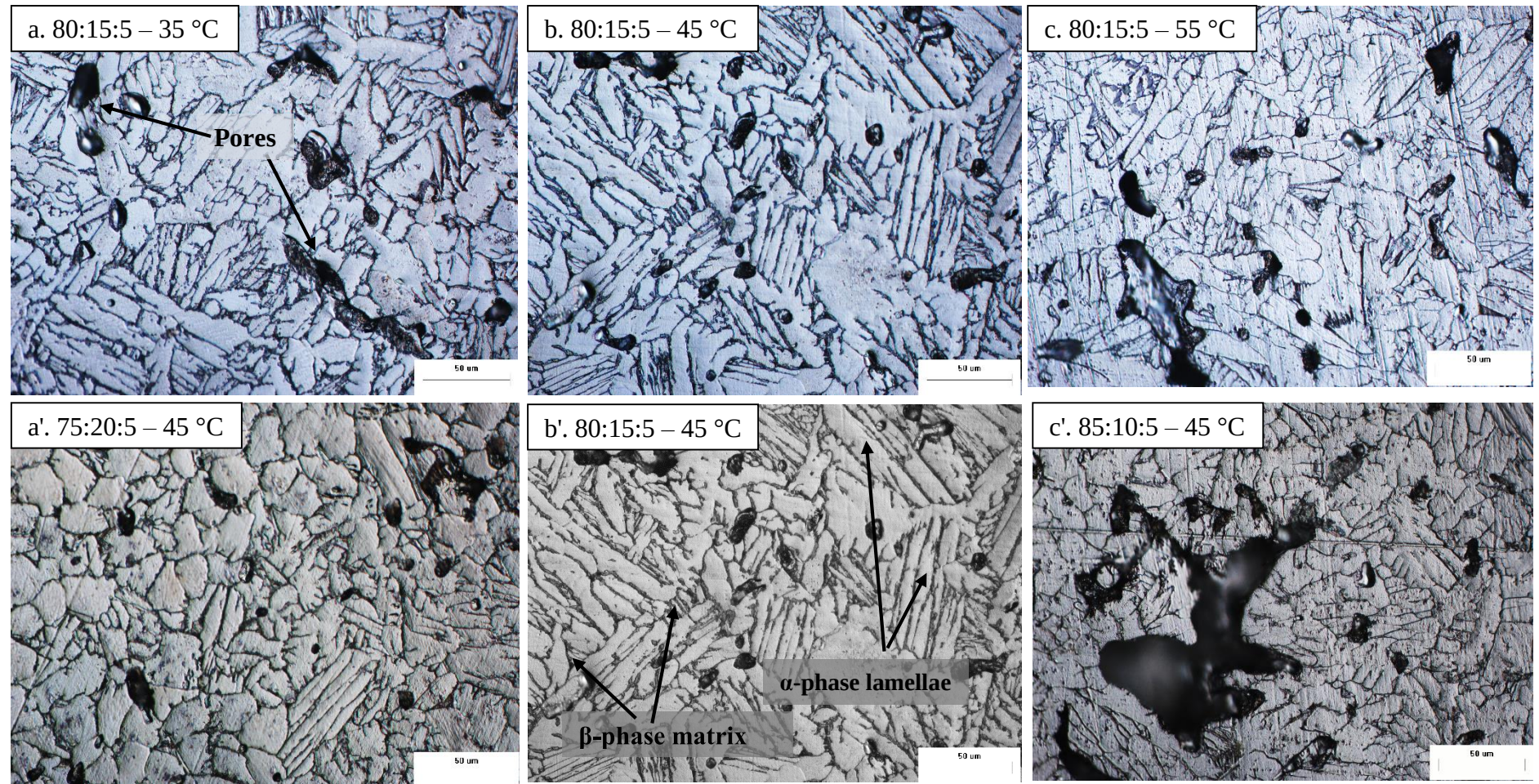


Figure 4.98: Effect of solvent debinding temperature (a-b-c) and binder composition (a'-b'-c') on microstructure (α - β lamellar structure) of as-sintered Ti-MIM parts.

Sintered parts made with 80:15:5 vol. % PEG:PVB:SA binder had the highest relative density (Table 4.25). The relative densities could be further increased by extending the isothermal holding time. For example, increasing holding time during sintering from 1 h to 10 h increased relative density of Ti64 parts from 93.2% to 96.9% [317].

Table 4.25: Effect of binder composition on physical, mechanical and oxygen content of as-sintered Ti64-MIM parts.

PEG:PVB:S A (vol. %)	Relative density (%)	Porosity (%)	Tensile strength (MPa)	Elongation (%)	Oxygen (wt. %)
75:20:5	88.5 ± 0.9	11.5 ± 0.9	172 ± 29	0.15 ± 0.10	1.58
80:15:5	93.4 ± 1.7	6.6 ± 1.7	274 ± 28	5.32 ± 2.23	0.98
85:10:5	88.2 ± 1.3	11.8 ± 1.3	225 ± 29	0.29 ± 0.27	1.39

Although there is no binder in the sintered parts, it affects particle packing in the green part and hence sintered density. An optimal PVB content may help produce favourable powder particle packing. A similar effect of the backbone polymer on sintered density has been reported for stainless steel-based MIM [149, 314-315].

Tensile strength and oxygen content

Parts manufactured with 80:15:5 vol. % PEG:PVB:SA binder had the highest tensile strength and elongation (Table 4.25). Irrespective of the binder used, the as-sintered parts had a tensile strength and elongation of less than 274 ± 28 MPa and 5.32 ± 2.23% respectively (Table 4.25). An outlier with a tensile strength of 454 MPa and 0.27% elongation has not been included in the data set. The poor mechanical properties of the sintered parts (Table 4.25) are caused by their high porosity and oxygen content compared to the maximum of 0.2 wt. % oxygen content recommended for critical load bearing applications [112]. However, the oxygen content in the sintered parts is in the range expected for parts made from Ti64 powder with an oxygen content of 0.84 wt. %.

Sintered parts made with 80:15:5 vol. % PEG:PVB:SA binder had the lowest oxygen content, inferring that this binder produced a powder packing that allowed all the binder components to be extracted easily during solvent and thermal debinding without adverse reactions with oxygen. The powder packing in sintered parts made

with the other binders may be less favourable, making binder extraction difficult; any residual binder components could react with titanium at elevated temperature and thus increase the oxygen content (Table 4.25). The 0.14 wt. % oxygen content of sintered parts made with 80:15:5 vol. % PEG:PVB:SA binder was 16% higher than the oxygen content in the Ti64 powder. This increase is similar to published values (Section 2.3.2).

Oxygen content adversely affected elongation [317 – 320] of sintered parts made with 75:20:5 and 85:10:5 vol. % PEG:PVB:SA binder (Table 4.25). Ductility, stress-corrosion resistance, crack-growth resistance and fracture toughness are better if oxygen content is low [368]. Oxygen contents above 0.6 wt. % drastically affect mechanical properties and ductile materials can become brittle [317 – 320].

Sintering time affects tensile strength. For example, increasing sintering time from 6 h to 10 h increased tensile strength of Ti64 parts by 109 – 178 MPa but reduced elongation from 7.4 – 9.5% to 1.8 – 4.2% [317]. Post-sintering process such as hot isostatic pressing (HIP) closes pores and increases the density of sintered parts [83, 113, 316-317] (Figure 4.99). For example, HIPping for 3 h at 920 °C reduced porosity of Ti64 parts from 5% to 0.02% [113] and HIPping for 4 h at 925 °C densified Ti64 parts to full density [368].

Microstructure and fractographic analyses

Ti64 sintered parts had irregular α -phase lamellae in β -phase matrix (Figure 4.98; 4.100). The sintering temperature (3 h at 1300 °C) was above the 1000 °C where the $\alpha+\beta\rightarrow\beta$ transformation occurs so sintering occurred in the pure β -region where grains grow easily [369 – 370]. During furnace cooling, the temperature drops below the β -transus temperature and α -phase is formed, producing α - β lamellar microstructure made of hexagonal close-packed (HCP) α -phase lamellae within large-body centred cubic (BCC) β -phase grains [83, 369-370]. The alternating α - β lamellae (colony) align in the same orientation (Figure 4.98; 4.100).

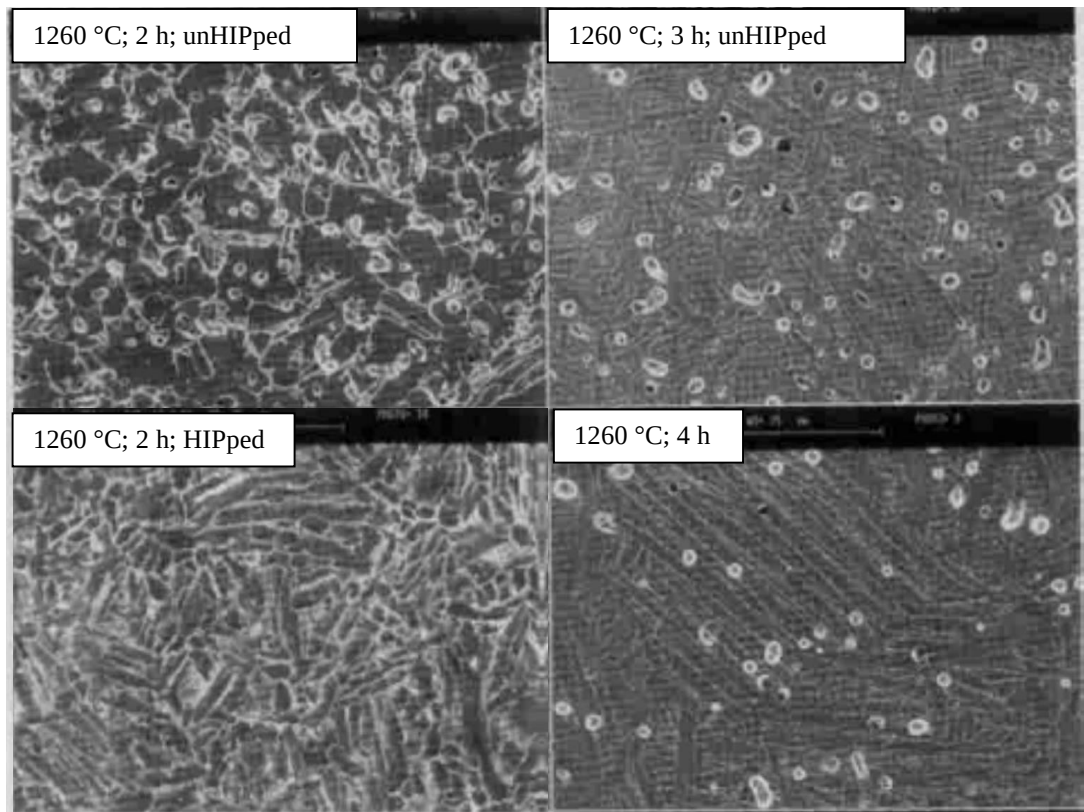


Figure 4.99: Effect of HIPping time on Ti64 microstructure (adapted from Guo et al. [317]).

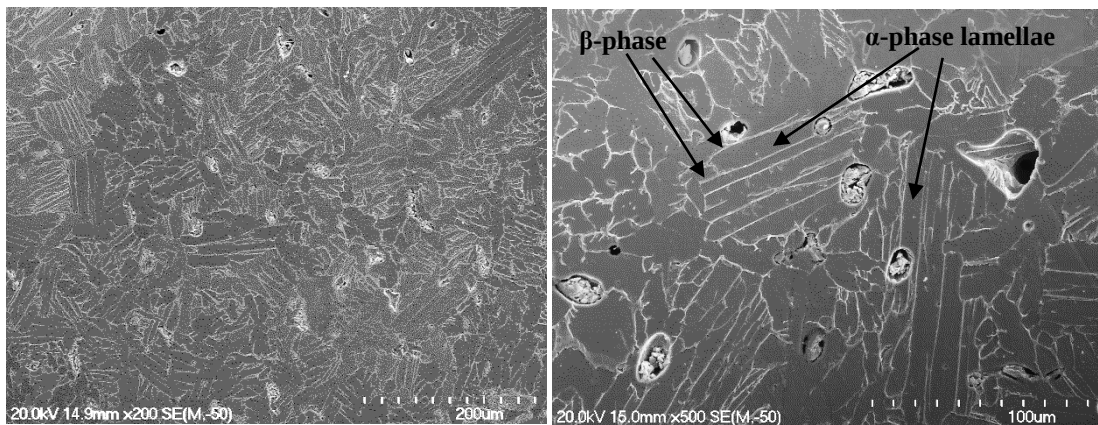


Figure 4.100: SEM images of as-sintered Ti-MIM parts made with 60 vol. % Ti64 powder.

Mechanical properties of Ti64 alloy with lamellar microstructure depend on α -phase lamellae thickness and colony diameter; tensile strength decreases with increasing α -phase lamellae width [317, 370 – 372]. The α -phase lamellae thickness, colony diameter and β -grain size of 5 – 10 μm , 50 – 60 μm and 100 – 120 μm respectively were in the reported range 3 – 11 μm , 40 – 70 μm and 120 – 350 μm respectively [317, 370 – 374]. However, porosity (5 – 12%; Table 4.25) of as-sintered parts tended to decrease tensile strength (Table 4.25). Pores in the sintered parts may act as pinning

sites and suppress grain growth [373]. Longer sintering times tend to decrease porosity and enhance grain growth, which increases tensile strength but at the cost of ductility.

All fracture surfaces had a bright, faceted, grainy appearance (Figure 4.101), due to different crystallographic planes being exposed. Fracture may have occurred by transgranular splitting of the Ti64 alloy crystal grains along HCP {0001} and BCC {100} atomic planes. Micro-cracks are primarily initiated along α lamellae at the edge of a sample and propagated along the colony and grain boundary [379]. These fracture characteristics clearly show the brittle fracture known as transgranular (also called cleavage) fracture.

However, there were fibrous regions with microvoids in the fracture surface of sintered parts made with 80:15:5 vol. % PEG:PVB:SA indicating ductile behaviour (cleavage with ductile tear ridges [377]), which produced $5.32 \pm 2.23\%$ elongation (Table 4.25). Crack initiation in α - β titanium alloys is usually associated with quasi-cleavage facets [378], where grains orientated favourably with the respect to the axis of loading, can slip and exhibit ductile behaviour. Those unfavourably oriented cannot slip and exhibit transgranular brittle behaviour [374, 378].

High oxygen content is the main cause of brittle behaviour in Ti-MIM parts (Section 2.5.5). The oxygen content of the Ti64 powder used in this research was high (0.84 wt. %), so the high oxygen content in the sintered parts, especially parts made with 80:15:5 vol. % PEG:PVB:SA binder (0.98 wt. %) was probably not due to the process or the binder.

Fracture surfaces of as-sintered Ti-MIM parts made with 75:20:5 vol. % and 85:10:5 vol. % PEG:PVB:SA binders had possible internal cracks and long pores whereas sintered parts made with 80:15:5 vol. % PEG:PVB:SA binder did not (Figure 4.101). The pores and internal cracks, which may have developed from shrinkage during sintering, caused local stress concentrations that may have initiated cracking under tensile stress. The point where a slip band meets a pore or existing internal shrinkage crack could be the site for crack initiation under tensile stress (Figure 4.101 c').

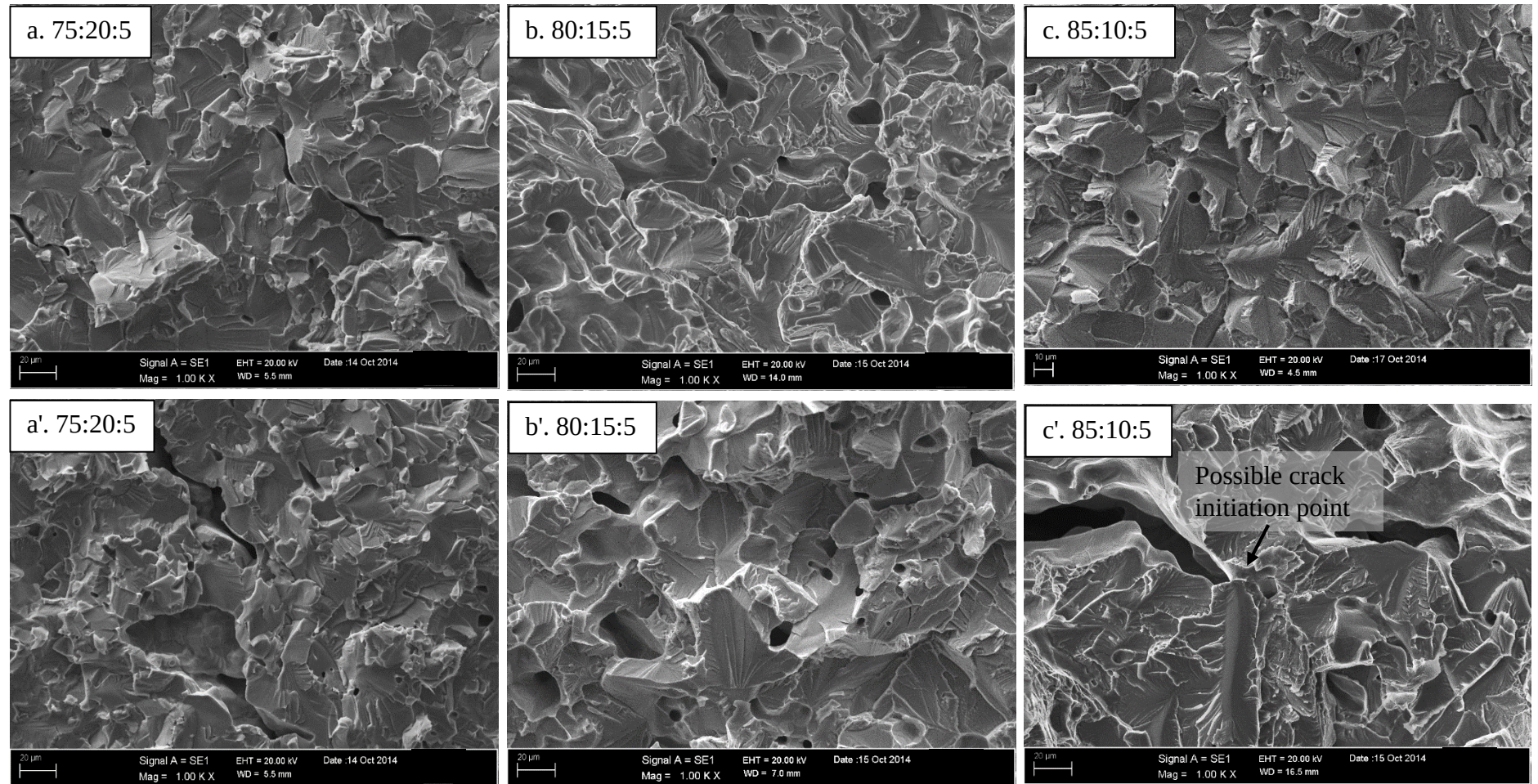


Figure 4.101: Effect of binder composition on fracture surface of as-sintered Ti-MIM parts made with 60 vol. % Ti64 powder.

Surface quality and residual stresses affect mechanical properties of engineering materials [374 – 376]. The Ti-MIM samples had been polished for the analysis but had microscopic rough surfaces (Figure 4.102a), which may have been created during the injection moulding and debinding steps in the MIM process. During injection moulding, turbulence between melted feedstock and the mould wall exposes the surface to higher shear stress than interior regions, promoting binder-powder separation [374]. Notches form when binder and any loosely adhering powder particles are removed during the debinding steps and subsequent sintering. These notches could promote crack initiation. Surface treatment (shot peening) can remove most of these notches and improve mechanical properties (Figure 4.102b, c).

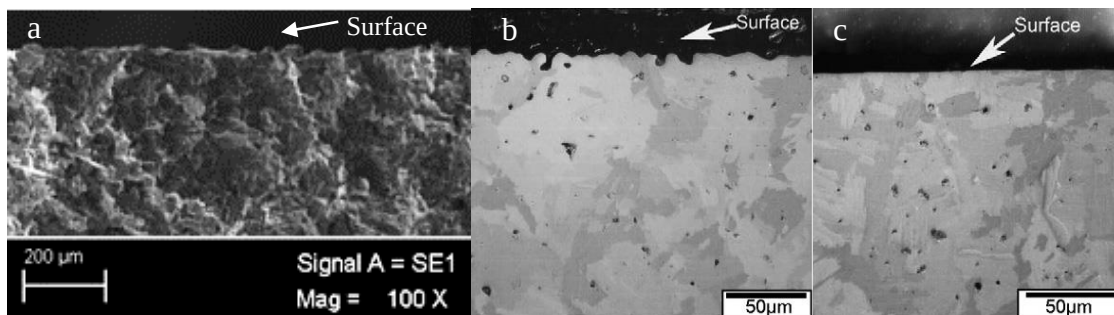


Figure 4.102: Surface quality of Ti-MIM parts: (a) polished surface from this research, and (b) without and (c) with shot peening [374].

It is proposed the following processes be further developed to make Ti-MIM parts with enhanced mechanical properties:

- Use spherical or near spherical Ti64 powders with d_{90} of 0.6 – 36 μm and d_{50} of 0.3 – 19 μm to help increase packing density and hence powder loading [89, 91, 236]. This enhances sintering and hence minimises porosity of sintered parts.
- Alternatively, use bimodal powder particle systems. Powder with a wide particle distribution tends to pack better than systems with a narrow particle distributions which helps increase powder loading and hence sintered density.
- Use Ti64 powder with low oxygen content (<0.2 wt. %), depending on the required mechanical properties and application.
- Use a post-sintering process such as HIP to close the pores, hence further densifying the sintered parts.

- Use heat treatment processes such as partial or full annealing, solution heat treatment, or ageing to further enhance the mechanical properties of sintered parts [370].
- Increase isothermal holding time, which will densify the sintered parts.

As the post-sintering processes were beyond the scope of this research and resources available, they were not investigated. Which recommendation to use would depend on the outcome desired. Mechanical properties of the final Ti-MIM product depends on whether they are being used for structural applications (exposed to stress so mechanical properties are important) or for corrosion resistant and cosmetic applications where strength is less important [33 – 34]. Titanium with lower strength (tensile strength of ~550 MPa) may be appropriate for producing MIM parts where cost is important but high strength is not required. This would allow inexpensive and/or high oxygen (≈ 0.4 wt. %) titanium powders to be used [33].

4.5.4. Summary

The effect of various binders on the characteristics of the resultant Ti64-MIM parts were investigated along with processing factors that affect mechanical properties of sintered Ti-MIM parts.

- Powder loading and binder composition influenced uniform mould-filling. Parts made with 80:15:5 vol. % PEG:PVB:SA binder was more consistent and had greater homogeneity than binders with other PEG contents.
- Sintered parts made with 80:15:5 vol. % PEG:PVB:SA binder had higher relative density ($93.4 \pm 1.7\%$) than those made with other binders. Although no binder was present in the sintered parts, it may influence particle packing and help increase sintered density. Large pores found in parts solvent debound at 55 °C or made with 85:10:5 vol. % PEG:PVB:SA binder indicate these are not suitable conditions for Ti-MIM.
- As-sintered Ti64-MIM parts exhibited poor mechanical properties, which are mainly due to the porosity (5 – 12%) and high oxygen content (0.98 – 1.58 wt. %). As-sintered parts made with 80:15:5 vol. % PEG:PVB:SA binder had the highest tensile strength (up to 454 MPa) and lowest oxygen content (0.98 wt. %).

- Fracture surface of the as-sintered Ti-MIM parts made with 75:20:5 vol. % or 85:10:5 vol. % PEG:PVB:SA binder had internal cracks and long pores that were not present in parts made with 80:15:5 vol. % PEG:PVB:SA binder. Overall, fracture surfaces showed the characteristics of a transgranular fracture; but some regions of fracture surface of the sintered parts made with 80:15:5 vol. % PEG:PVB:SA binder had the characteristic of quasi-cleavage fracture.

The following can improve the oxygen content, sintered density and mechanical properties of Ti64-MIM:

- Using fine and spherical/ near spherical Ti64 powders with bimodal particle system and low oxygen content to increase powder loading and sintered density, and decrease porosity and oxygen content.
- Increasing isothermal holding time during sintering to densify the sintered parts.
- Post-sintering process such as HIP, a heat treatment that densifies parts and enhances mechanical properties.

Chapter Five: Conclusions and Recommendations

Titanium alloys can be used where high specific strength, corrosion resistance and biocompatibility are required. Processing difficulties such as melting high MP materials and excess secondary operations including machining to fabricate complex products can be reduced by using MIM. The challenges for commercialising Ti-MIM in New Zealand include having technical expertise, process knowledge, suitable equipment, increasing customer awareness and the licensing costs.

The research reported in this thesis investigated how binder and Ti64 powder-binder composition affected the quality of the feedstocks and manufactured Ti-MIM parts. Models were developed to predict rheological characteristics of the Ti64 feedstocks and water debinding kinetics. A commercial Ti64 powder, widely used for titanium parts production, was used in this research to manufacture MIM parts. Considering the attributes of an ideal binder such as, being inexpensive and available, having good flow properties and green strength, being environmentally safe and easy to debind, binder components PEG, PVB and SA were selected. The recommended optimum level of 5 vol. % SA was used in this research. PEG of 65 – 85 vol. % was used to reduce the feedstock viscosity and cost of debinding. The backbone polymer PVB used to provide strength to green and brown parts, was restricted to 10 – 30 vol. % to reduce the feedstock viscosity.

5.1. Binder components

Data from thermal profiles (melting point and thermal degradation) indicated that PEG, PVB and SA were good binder components and that 175 °C was a suitable temperature for manufacturing the binder. These components are partially miscible in each other. Binder characterization was used to assess the efficiency of various mixing equipment and process conditions for producing a homogeneous mixture.

5.2. Feedstock manufacturing process

An appropriate temperature for manufacturing feedstock could not be identified from TGA/DTA data. Including an isothermal holding time helped simulate the manufacturing process and to identify manufacturing criteria. An homogeneous

feedstock could not be produced in a one-step mixing process so different types of mixers and process conditions were needed. A four-stage process for manufacturing a homogeneous MIM feedstock was developed. Data from burn-out tests, density measurements and morphological analyses showed that an homogenous feedstock suitable for Ti64-MIM could be made from Ti64 powder and PEG-PVB-SA binder using the following four-stage process:

- **Stage 1:** Dry mix Ti64 powder and binder components at room temperature for 30 min in a planetary mixer operating at 25 rpm
- **Stage 2:** Dry mix the premix at room temperature for 16 hours in a roller mixer operating at 250 rpm
- **Stage 3:** Melt mix the feedstock at 125 °C for 45 min in a roller compounder operating at 60 rpm
- **Stage 4:** Extrude the feedstock in a twin-screw extruder operating at 150 rpm with a feed-to-nozzle temperature profile of 125, 140, 135, 135, 140 °C.

5.3. Powder loading

Relative viscosity of feedstocks increased with powder loading, and became extremely high at the critical powder loading of 65 vol. % for 75:20:5 vol. % PEG:PVB:SA and 80:15:5 vol. % PEG:PVB:SA binder. Feedstocks F6075 (75:20:5 vol. % PEG:PVB:SA) and F6080 (80:15:5 vol. % PEG:PVB:SA), which had 60% powder loading, were workable and the most promising for Ti64-MIM. The PEG content of the binder influenced powder loading. The 60 vol. % powder loading obtained using irregular, coarse Ti64 powder ($d_{50} = 52 \mu\text{m}$; $d_{90} = 117 \mu\text{m}$) is higher than for the spherical, fine powders (0.5 – 20 μm) recommended in the literature.

Particle slope parameter, binder system, feedstock rheology and homogeneity influence critical and optimal powder loading. The Ti64 powder used in this research had a better particle slope parameter (2.66) than the 2.00 recommended in published research for obtaining high powder loadings for PIM. Critical powder loading was determined using a mixing torque, density and viscosity analysis. Viscosity analysis is expensive but more reliable than other methods. Density analysis is simple, inexpensive, but tedious. Mixing torque analysis is expensive and requires careful interpretation.

5.4. Rheology

Yield stress: Increasing process temperature or PEG content decreased feedstock yield stress and improved flowability so lower injection pressures could be used. Moulding defects may occur either with feedstocks made with 85:10:5 vol. % PEG:PVB:SA binder, or at the injection moulding temperature between 145 and 165 °C. Feedstocks with 60 vol. % powder loading had low yield stress, which is better for Ti64-MIM. Yield stress analysis indicated that feedstocks F6075 and F6080 were better for Ti64-MIM than F6085.

Pseudoplastic flow behaviour: Feedstocks made with 75:20:5, 80:15:5 and 85:10:5 vol. % PEG:PVB:SA binders had a flow behaviour index between 0.60 and 0.80 and the pseudoplastic flow behaviour required for MIM. The flow behaviour index was used to identify optimal powder loading and temperatures for injection moulding. Shear thinning of feedstocks F6080 and F6075 increased with temperature between 125 to 145 °C so injection moulding should be done in this range. Sensitivity analysis of shear indicated that feedstocks F6080 and F6075 were the most promising feedstocks for Ti-MIM, which had the viscosity below 250 Pa-s, but feedstock F6080 had the highest shear thinning.

Fluidity and melt flow rate: Feedstock fluidity and melt flow rate increased with shear stress and PEG content and decreased with powder loading. Feedstocks made from 80:15:5 vol. % PEG:PVB:SA binder had higher fluidity than feedstocks made from 75:20:5 vol. % PEG:PVB:SA binder and were therefore more suitable for Ti-MIM. The fluidity of feedstock F6085 is above 1000 s⁻¹, indicating it is unsuitable for Ti64-MIM at low shear rates. Feedstocks made with 80:15:5 vol. % PEG:PVB:SA binder had higher, more consistent MFR values than feedstocks made with 75:20:5 or 85:10:5 vol. % PEG:PVB:SA binder, indicating that feedstock F6080 would be easier to inject into a mould and therefore more suitable for Ti64-MIM. Fluidity and melt flow rate values indicated that feedstock F6080 was the most promising for Ti-MIM.

Feedstock Stability: All feedstocks produced had an instability index less than 0.50 at various temperatures, indicating they were homogeneous. Feedstock stability (minimum rate of change in viscosity with shear rate) increased with PEG content and process temperature, its viscosity decreased with temperature and its mouldability

increased with temperature, indicating that injection moulding of Ti-MIM can be done at higher temperatures than normally used for Ti-MIM in general. Feedstocks with 75:20:5 vol. % PEG:PVB:SA binder were unstable, and the feedstock with 85:10:5 vol. % PEG:PVB:SA binder was susceptible for powder loading. Feedstock with 80:15:5 vol. % PEG:PVB:SA binder had a consistent rate of change in viscosity at all powder loadings, indicating it was a more stable feedstock for Ti64-MIM.

Flow activation energy: Flow activation energy decreased with shear rate indicating feedstocks F6075 and F6080 could be injection moulded at high shear rates. The flow activation energies of feedstock F6080 (14.8 to 29.7 kJ/mol) were consistently lower than for F6075 (35.7 to 42.5 kJ/mol) suggesting less energy was required to break the barriers to flow during injection moulding. Feedstock F6080 had a lower viscosity, higher mouldability values and lower flow activation energy than F6075, indicating it was the most suitable feedstock for Ti64-MIM.

5.5. Modelling flow properties

A new model that used MFR (μ) to predict feedstock flow properties was developed:

$$\mu = q \tau^p$$

It incorporates a new flow parameter, *feedstock flow index* (p), which is related to flow behaviour index (n):

$$pn = 1$$

This model, which is a version of the existing power law model for rheological properties, was validated over a limited range of Ti64-MIM conditions. There was insufficient published data to validate it for a wider range of PIM applications.

The data obtained for powder loading and relative viscosity did not agree with published models. The following model was developed and validated for Ti-MIM and the limited published data for CIM:

$$\eta_r = 1 + \left[\frac{1}{m(\varphi_c - \varphi)} \right]^{2.5} - \left[\frac{1}{m\varphi_c} \right]^{2.5}$$

The following model, which needs to be validated, was developed for predicting relative viscosity and critical powder loading from powder surface area, shear rate, powder loading, flow behaviour index, binder adsorbed layer thickness:

$$\eta_r = 1 + \frac{GS\dot{\gamma}^{n-1}}{4(1-\varphi)} \left[\left[\frac{1}{\ln\alpha(\Phi_c - \varphi)} \right]^{2.5} - \left[\frac{1}{\ln\alpha\Phi_c} \right]^{2.5} \right]$$

The Einstein coefficient of 2.5 in this relative viscosity model for dilute suspension ($\eta_r = 1 + 2.5\varphi$) is modified as $2.5/\varphi_c$ for MIM feedstocks.

5.6. Debinding and sintering

Green parts were initially solvent-debound to remove the water-soluble binder component (PEG, the major component), and the remaining binder components were removed by thermal debinding, followed by sintering to obtain the final densified metallic part.

Solvent debinding: Solvent debinding has dissolution-controlled and diffusion-controlled stages. Debinding rate was higher in the former stage because mass transfer path for PEG from the part to solvent is small. The change from dissolution-controlled to diffusion-controlled occurred between 4.67 – 5.20 h at 35 °C and decreased as temperature increased, so high solvent temperatures are preferred for faster debinding. The published model ($t = ax + ab^2x^2$) described the dissolution-controlled stage but not the diffusion-controlled stage so a single model cannot be used for both the dissolution- and diffusion-controlled stages.

The amount of PEG removed increased with PEG content, process temperature and time. The MIM parts made with 75:20:5 and 80:15:5 vol. % PEG:PVB:SA binders had better debinding characteristics than those made with 85:10:5 vol. % PEG:PVB:SA binder. Inter-diffusion PEG/water coefficient, which increased with PEG content and temperature, and depended on microstructure, indicated that MIM parts with 80:15:5 vol. % PEG:PVB:SA binder had uniform particle packing. However, defects occurred if these parts were solvent debound for 16 h or at 55 °C so there was no benefit in using the higher solvent temperatures above 55 °C.

Porosity and reaction depth: For all binders and temperatures, porosity of solvent debound Ti64-MIM parts increased with debinding time but at a decreasing rate during the diffusion-controlled stage. Porosity increased with PEG content. At the end of dissolution-controlled stage, at 35 °C, 30% porosity had developed, which increased to 35 % after the diffusion-controlled stage. Increased molecular mobility and diffusion increased the reaction depth but decreased with debinding time as the porous shell of Ti64 powder and backbone polymer developed.

Thermal debinding and sintering: Thermal debound parts made with 80:15:5 vol. % PEG:PVB:SA binder had greater, more consistent porosity than those made with 75:20:5 vol. % and 85:10:5 vol. % PEG:PVB:SA binders. The more uniform binder distribution and favourable particle packing allowed binder to be extracted easily. Sintered parts made with 80:15:5 vol. % PEG:PVB:SA binder had the highest relative density ($93.4 \pm 1.7\%$). The large pores found in parts solvent debound at 55 °C or made with 85:10:5 vol. % PEG:PVB:SA binder indicate these are not suitable conditions for Ti-MIM.

Tensile strength and elongation of as-sintered Ti64-MIM parts were below 300 MPa and 7.6% respectively. The porosity (5 – 12%) and high oxygen content (0.98 – 1.58 wt. %) contribute to the poor mechanical properties. Sintered parts made with 80:15:5 vol. % PEG:PVB:SA binder had the highest tensile strength (up to 450 MPa) and lowest oxygen content (0.98 wt. %). The α -phase lamellae thickness, colony diameter and β -grain size were in the range reported and the low tensile strength is mainly due to higher porosity in the as-sintered parts.

5.7. Model for solvent debinding kinetics

The PEG removal, and porosity and reaction depth in the part increased with debinding time, indicating these parameters are related. The following empirical relationships were developed to explain solvent debinding of Ti64-MIM parts made with PEG-PVB-SA binder:

$$\ln\left(\frac{1}{w_L}\right) = -\frac{1}{n} \ln t + \ln \frac{1}{B}$$

$$x = K_r t^{1/n}$$

$$\varepsilon = K_p t^{1/n}$$

The accuracy of the model for predicting PEG removal increased with the n value ($2 \rightarrow 100$).

It is recommended that Ti-MIM parts made with PEG-PVB-SA binder should be solvent debound for 4 h at 35 °C or 3 h at 45 °C. About 85 wt. % PEG was removed, which created sufficient channels in the green body for other binder components to move during the subsequent thermal debinding. Solvent debinding at 35 °C minimises debinding defects and energy consumption.

5.8. Fracture morphology

Fracture surface of the as-sintered Ti-MIM parts made with 75:20:5 vol. % or 85:10:5 vol. % PEG:PVB:SA binder had internal cracks and long pores that were not present in parts made with 80:15:5 vol. % PEG:PVB:SA binder. Fracture surfaces of Ti64-MIM parts had a faceted and grainy appearance, which are the characteristics of the transgranular fracture. However, the fracture surface of sintered parts made with 80:15:5 vol. % PEG:PVB:SA had the characteristic of quasi-cleavage fracture. The brittle behaviour of Ti-MIM parts is caused by the very high oxygen content in the starting powder rather than from the process or binder. The 16% increase in oxygen in the sintered parts made with 80:15:5 vol. % PEG:PVB:SA binder is within the range reported in the literature.

Based on powder loading, rheological, solvent debinding, sintering, tensile strength and oxygen analyses, the 80:15:5 vol. % PEG:PVB:SA binder is the best binder for Ti64-MIM.

5.9. Recommendations

It is recommended that the following research be done.

- Validate the melt flow model developed ($\mu = q\tau^p$) for predicting feedstock flow index (p) and its relationship with flow behaviour index for a range of MIM and/or CIM feedstocks such as stainless steel, alumina and zirconia powders, wax-based and polymer/wax-based binders. The rheology of these various feedstock formulations must be measured using a capillary rheometer.

- Validate the proposed model for predicting relative viscosity and critical powder loading from powder surface area, shear rate, powder loading, flow behaviour index, binder adsorbed layer thickness for a range of MIM and/or CIM feedstocks.

$$\eta_r = 1 + \frac{GS\dot{\gamma}^{n-1}}{4(1-\phi)} \left[\left[\frac{1}{m\alpha(\Phi_c - \phi)} \right]^{2.5} - \left[\frac{1}{m\alpha\Phi_c} \right]^{2.5} \right]$$

- Test the following empirical relationships for solvent debinding kinetics of Ti-MIM parts made with PEG-PVB binder for other PIM applications.

$$\ln \left(\frac{1}{w_L} \right) = -\frac{1}{n} \ln t + \ln \frac{1}{B}$$

$$x = K_r t^{1/n}$$

$$\varepsilon = K_p t^{1/n}$$

- Test whether optimal powder loading can be increased above 60 vol. %, and if this affects density of as-sintered parts (>94%): Using spherical or near spherical Ti64 powders with d_{90} of 0.6 – 36 μm and d_{50} of 0.3 – 19 μm may increase packing density and enhance sintering and minimize porosity. Test whether increasing the particle size distribution can improve powder particle packing. This could be done by mixing powders such as GA Ti-6Al-4V and HDH Ti-6Al-4V powders that have different particle size distributions.
- Investigate whether the mechanical properties of sintered Ti64 parts can be enhanced by changing process conditions such as: using Ti64 powder with low oxygen content (<0.2 wt. %); using different sintering process and equipment; the effect of isothermal holding time; using post-sintering processes such as HIP to close the pores in as-sintered parts; or using heat treatment processes such as annealing, solutioning or ageing.
- Carry out quantitative studies of elemental pickup (e.g. oxygen and carbon) of Ti64 parts to identify the effects these elements have on mechanical properties of the parts. This can be done by processing GA-, HDH-Ti64 powders of different oxygen contents and processing different thermal debinding and sintering conditions.

Chapter Six: References

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