

INVESTIGATING THE PRODUCTION OF POLYPROPYLENE POWDER SUITABLE FOR PROCESSING THROUGH LASER SINTER ADDITIVE MANUFACTURING

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BLOEMFONTEIN, September 2024

Declaration of independent work

I, **JOSEPH NSENGIMANA**, student number #####, SA ID number ##### and Rwanda passport number #####, do hereby declare that this research project submitted to Central University of Technology, Free State, for the degree **DOCTOR OF ENGINEERING IN MECHANICAL ENGINEERING**, is my own independent work and complies with the Code of Academic Integrity, as well as other relevant policies, procedures, rules, and regulations of Central University of Technology, Free State; and has not been submitted before to any institution by myself or any other person in fulfilment (or partial fulfilment) of the requirements for the attainment of any qualification.

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02 September 2024
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Dedication

I dedicate this dissertation to my wife, VIRGINIE MUKANTABANA, and my sons, BOGDAN, BODGAR, and JOSHUA. To all who inspired me to leave a legacy of service to others.

List of publications arising from this work

1. Nsengimana, J., van der Walt J. G., Langner E. H. G., and de Beer, D. J., 2022, Characterization of polypropylene powder produced by precipitation for powder bed fusion additive manufacturing. *22nd Annual International RAPDASA Conference, RAPDASA 2021 Conference Proceedings*; International Convention Centre, CSIR, Pretoria, 3–5 November 2021, pp. 78–87.
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Abstract

Additive Manufacturing (AM) has become a promising technology supporting the 4th Industrial Revolution. The Laser Powder Bed Fusion (L-PBF) process is one of the AM technologies with the potential to use metallic, ceramic, and polymeric materials in powder form to produce end-usable parts. Medical, aerospace, and automobile industries are the major applications of this technology. Despite good mechanical performances obtained from laser-sintered components using polyamide powders, the high cost of these materials limits the widespread adoption of the L-PBF technology by industry. There is a need to increase the number of feedstock polymeric materials suitable for the L-PBF process to reduce the cost of producing parts through this technology.

In recent years, Polypropylene (PP) powder suitable for L-PBF has become available, but the cost is similar to that of polyamide powders. This study investigated the possibility of using PP pellets intended for the injection moulding industry supplied by South African company Sasol Limited to produce powder suitable for L-PBF.

Through experimentation, the precipitation of two isotactic PP grades, HNR100 (70%) and HTV145 (20%), mixed with talc (10%) into m-Xylene produced powder with the required particle size and morphology. A cost analysis showed that producing the new composite powder at a much-reduced cost compared to similar commercially available powder was possible.

The new PP composite powder was characterized through Differential Scanning Calorimetry (DSC), Thermogravimetry (TGA), Scanning Electron Microscope (SEM), Fourier Transform Infra-Red (FTIR), and X-ray diffraction (XRD). Results from these tests showed that the newly developed composite powder is well suited to the L-PBF process and compared well to commercial PP powder, which was acquired as a benchmark for developing the new material.

Process parameters were developed for successfully printing the newly developed composite powder on a Sintratec S1 L-PBF machine. The mechanical properties of the produced tensile test pieces showed results comparable to what could be achieved with the commercially available powder. Similarly, dimensional accuracy and surface roughness measurements showed comparable results.

It could be concluded from the study that it is worthwhile and profitable to promote the production of PP powder using locally produced PP pellets. Not only could powder suitable for L-PBF be produced that delivers

parts similar to commercially available powder but at a much-reduced cost, whilst stimulating local industry development and countering costly imported materials.

Table of Contents

Declaration of independent work	i
Acknowledgment	ii
Dedication.....	iii
List of publications arising from this work	iv
Abstract	v
Table of Contents	vii
List of Figures	xii
List of Tables	xvi
List of Abbreviations	xvii
CHAPTER 1: GENERAL INTRODUCTION	1
1.1 Background	1
1.2. Problem statement.....	2
1.3. Hypothesis.....	2
1.4. Original contribution to the field of study.....	3
1.5. Aim of the study	3
1.6. Objectives of the study	3
1.7 Methodology of the study.....	4
1.7.1. Assessment of commercially available PP powder	4
1.7.2. Production of PP powder from pellets supplied by Sasol	4
1.7.3. Characterization of the newly produced PP powder	4
1.7.4. Determining optimal process parameters for LS of newly produced PP powder and testing parts	5
1.8 Delimitation of the study	5

1.9	Layout of the thesis.....	6
CHAPTER 2: THERMO-PHYSICAL CHARACTERISTICS OF POLYMERS.....		7
2.1	Introduction to polymers	7
2.2	Thermal classification of polymeric materials.....	8
2.3	Crystallization temperature and degree of crystallinity of semi-crystalline polymers.....	11
2.4	Molecular structure of PP	15
2.5	PP in the global production market.....	18
Conclusions		20
CHAPTER 3: MELTING AND CRYSTALLIZATION PROCESS OF ISOTACTIC POLYPROPYLENE ..		22
3.1	Nucleation and growth of crystals of semi-crystalline polymers	22
3.1.1	Homogeneous and heterogeneous nucleation	22
3.1.2	Effect of shear flow on nucleation and growth of crystals	24
3.2	Polymorphism in crystallization of iPP	26
3.2.1	Formation of monoclinic phase in iPP	30
3.2.2	Formation of pseudo-hexagonal phase in iPP	31
3.2.3	Formation of mesomorphic phase	33
3.2.4	Formation of orthorhombic phase	33
3.2.5	Formation of shish kebab structures	34
Conclusions		36
CHAPTER 4: POLYPROPYLENE AND LASER POWDER BED FUSION		37
4.1	AM in the global production market	37
4.2	AM processes and technologies.....	39
4.3	Crystallization in the polymer AM processes	42
4.4	Flowability and window of sinterability of PP powder for the L-PBF process	45
4.4.1	Measurement of the powder flowability	46

4.4.2	Window of sinterability of polymeric powder for the L-PBF process	47
4.4.3	Effect of melt viscosity and crystallization activation energy	50
4.5	Effect of fillers and compatibilizers on mechanical properties and warpage control	52
4.5.1	Introduction	52
4.5.2	Use of fillers and compatibilizers for PP powder for the PBF process	52
Conclusions		55
CHAPTER 5: OVERVIEW OF TECHNIQUES FOR PRODUCTION OF POLYMERIC POWDERS FOR LASER POWDER BED FUSION		57
5.1	Cryogenic grinding of the granules	57
5.2	Spray drying	58
5.3	Fluidization in a downer reactor	60
5.4	Immiscible blends	65
5.5	Liquid-Liquid Phase Separation technique	66
Conclusions		74
General conclusion on the literature study.....		75
CHAPTER 6: PRODUCTION OF A COMPOSITE POLYPROPYLENE POWDER AND COST ANALYSIS FOR THE LASER POWDER BED FUSION PROCESS		77
6.1	Introduction.....	77
6.2	Characterization of commercially produced PP powder from Diamond Plastics.....	78
6.3	Producing PP powder from locally available pellets for IM.....	81
6.3.1	Selection of the PP grades for production of LS powder	81
6.3.2	Small-scale experimental setup	82
6.3.3	Up-scaling of experimental setup	86
6.3.4	Dissolving and precipitation of PP granules	87
6.3.5	Drying, grinding, and coating of the PP powder	90
6.4	Cost analysis for production of the new PP composite powder for the L-PBF process.....	91

Conclusions	93
CHAPTER 7: CHARACTERIZATION OF THE COMPOSITE POLYPROPYLENE POWDER FOR THE LASER POWDER BED FUSION PROCESS.....	94
7.1 Differential Scanning Calorimetry analysis	94
7.1.1 DSC through three cycles	94
7.1.2 Comparison of DSC analyses of PP in pellet and powder forms	98
7.2 Thermogravimetric analysis.....	104
7.3 Scanning Electron Microscope analysis	105
7.4 Chemical analysis.....	112
7.5 Density of the new PP powder.....	115
7.6 Particle Size Distribution.....	121
7.7 Measurement of the flowability of the powder.....	125
7.8 X-Ray Diffraction analysis.....	131
7.9 Fourier Transform Infra-Red spectrometry analysis.....	137
Conclusions	145
CHAPTER 8: LASER POWDER BED FUSION OF THE NEW POLYPROPYLENE COMPOSITE POWDER	147
8.1 Description of the machine used for the L-PBF process.....	147
8.2 L-PBF of specimens for tensile test	148
8.2.1 Tensile test and SEM analysis of fractured surfaces of specimens	148
8.2.2 Observation and interpretation of results	153
8.3 Dimensional and form accuracy of calibration block with small features	156
8.3.1 Dimensional accuracy of the protrusions	158
8.3.2 Dimensional accuracy of the top, front, and side faces	159
8.3.3 Dimensional accuracy of the height associated with upskin faces	160
8.3.4 Dimensional accuracy of depth and width of the square-shaped window	162

8.3.5	Quality of inscribed texts, edges, and corners	165
8.4	Surface roughness of tensile test specimens and features of the calibration blocks	167
8.4.1	Surface roughness of tensile test specimens	168
8.4.2	Surface roughness of the features of the calibration blocks	170
	Conclusion.....	171
	CHAPTER 9: GENERAL CONCLUSIONS AND FUTURE WORK	173
9.1	General conclusions	173
9.2	Future work.....	175
	References	177
	APPENDIX: DSC OF PP GRADES AND COMBINATIONS IN PELLET AND POWDER FORMS	199
	HNR100 in pellet form	199
	HTV145 in pellet form	200
	HNR100 in powder form	201
	HTV145 in powder form.....	202
	HNR100 + HTV145 in pellet form	203
	HNR100 + HTV145 in powder form	204
	HNR100 + HTV145 in powder form + Talc	205

List of Figures

Figure 1-1: Layout of the thesis	6
Figure 2-1: Classification of polymers.....	8
Figure 2-2: General thermal classification of plastic materials	10
Figure 2-3: Radial growth of crystalline lamellae into spherulites forming semi-crystalline polymers [32], [33]	11
Figure 2-4: Illustration of thickness and period of a crystalline lamellae of an isotactic polypropylene (iPP) as adapted from Yang <i>et al.</i> [36]	12
Figure 2-5: DSC analysis and window of sinterability of PP (a) and of PE (b) [16]	14
Figure 2-6: Chemical structure of propylene molecule.....	15
Figure 2-7: Generic chemical formula of PP	16
Figure 2-8: Tacticity and types of PP [42]	17
Figure 2-9: Molecular chain structure of homopolymer and copolymers (adapted from Wikipedia [44])	18
Figure 2-10: Predominance of PP use in Western European polymers market [26].	19
Figure 2-11: The coverage of iPP commodities for 2020 [49].	20
Figure 3-1: Homogeneous and heterogeneous nucleation	23
Figure 3-2: Illustration of FWHM of intensity distribution of X-ray diffraction (adapted from [54])	25
Figure 3-3: Vectors, edge parameters, and interaxial angles in a unit cell of a crystal lattice [56]	28
Figure 3-4: Model of the threefold helical chain conformation of iPP in crystalline state [40].	29
Figure 3-5: Cross-hatching lamellar structures in alpha and gamma phases of iPP. [60], [61].	30
Figure 3-6: Beta morphologies: early formation of face-like and flower-cup-like (a and b) [65]. Hexagonal morphology of crystallized β -iPP with pimelate β -nucleating agents (c) [38].	32
Figure 3-7: Shish kebab lamellae crystalline morphology [72]	35
Figure 4-1: Forecast revenue for all AM global market [76]	37
Figure 4-2: Global market share distribution of L-PBF of polymeric materials [82]	38
Figure 4-3: Classification of AM processes, unprocessed base materials, and related technologies	40
Figure 4-4: Layout of machine for L-PBF process	41
Figure 4-5: Interrelationships between intrinsic and extrinsic properties of powder for L-PBF [91].	44
Figure 4-6: Morphologies of powder particles [93].	46

Figure 5-1: Schematic representation of spray drying process (adapted from R. P. Patel, M. P. Patel, and Suthar [124]).....	59
Figure 5-2: A simplified illustration of the process of fluidization in a downer reactor (adapted from Cheng <i>et al.</i> [126])	61
Figure 5-3: Three-stage downer reactor for rounding irregular-shaped powder particles (adapted from Sachs <i>et al.</i> [129]).....	62
Figure 5-4: Effect of residence period on melting, coalescence, and size of powder particles [129]	63
Figure 5-5: Morphologies produced from blending of immiscible polymers	65
Figure 5-6: Effect of the PP concentration on the morphology and size of the precipitated particles [140]..	67
Figure 5-7: Effect of the quenching temperature on morphology and size of the particles: Inset pictures in (c) and (d) are the magnified pictures of the PP microsphere and the dashed region (f), respectively [140]	68
Figure 5-8: Spinodal, binodal coexistence curves and two critical points in a decomposition phase diagram [142].....	69
Figure 5-9: SEM image showing the effect of PA11 concentration on morphology and size of powder particles obtained through LLPS and precipitation [143].....	71
Figure 5-10: SEM images showing the effect of the stirring speed on particle size and morphology for 20 wt.% PA11 concentration [143]	72
Figure 6-1: Flow diagram of the experimental methodology followed in the study	78
Figure 6-2: CAD of the calibration block for assessing the dimensional accuracy	80
Figure 6-3: Quality of inscribed texts on the calibration block.....	81
Figure 6-4: Small-scale experimental setup.....	84
Figure 6-5: Two stainless steel pots (a) and stirring system (b).....	86
Figure 6-6: Experimental setup in the customized processing cabinet	87
Figure 6-7: Heating temperature versus the time of the mixture of HNR100, HTV145, and talc into m-Xylene	88
Figure 6-8: Cooling temperature versus time of the mixture of HNR100, HTV145, and talc into m-Xylene .	89
Figure 6-9: Process flow for production of a composite PP powder using HNR100 and HTV145 grades ...	90
Figure 7-1: DSC analysis of the composite PP powder for the L-PBF process.....	95
Figure 7-2: DSC analysis for HNR100 + HTV145 + talc + carbon black.....	102
Figure 7-3: DSC analysis for commercial powder PP CP75	103
Figure 7-4: TGA of the new PP composite powder.....	105

Figure 7-5: Comparison of morphologies of powder particles for commercial PP CP75 powder versus the morphology of particles of the new PP composite powder.	107
Figure 7-6: Formation of particles with smooth spherical shape	109
Figure 7-7: Formation of particles with potato and irregular shapes	110
Figure 7-8: Sizing of particles with potato and irregular shapes.....	111
Figure 7-9: Talc dispersion into PP matrix	113
Figure 7-10: EDX spectrum for points 1 and 2.....	114
Figure 7-11: Variation of the volume of the powder versus the number of the cycle.....	116
Figure 7-12: Variation of the density versus cycle number	117
Figure 7-13: Variation of the density versus the time.....	118
Figure 7-14: Variation of the total pore volume versus temperature	119
Figure 7-15: Incremental volume percentage versus particle size	123
Figure 7-16: Cumulative volume percentage versus particle size.....	124
Figure 7-17: Energy flow at fixed and variable blade tip speeds.....	127
Figure 7-18: Shear cell test for the new composite powder	129
Figure 7-19: AIF using the Mohr circle [170].....	131
Figure 7-20: XRD patterns for PP powders from separate precipitations of HNR100 and HTV145 grades.....	133
Figure 7-21: XRD patterns for (HNR100 + HTV145) and (HNR100 + HTV145 + talc) PP powders.....	134
Figure 7-22: XRD patterns of PP CP75 and (HNR100 + HTV145 + talc + carbon black) PP powders.....	136
Figure 7-23: Propagation of a sinusoidal wave of electromagnetic radiation	138
Figure 7-24: FTIR spectra for HNR100, HTV145 and (HNR100 + HTV145) in pellet form	140
Figure 7-25: FTIR spectra for HNR100, HTV145 and (HNR100 + HTV145) in powder form	141
Figure 7-26: FTIR spectra of HNR100 + HTV145 + talc, HNR100 + HTV145 + talc + carbon black and PP CP75 in powder forms.....	142
Figure 8-1: Stress-strain curve of PBF specimens.....	149
Figure 8-2: SEM images of fractured surfaces of tensile specimens 1, 2, and 3	151
Figure 8-3: SEM images of fractured surfaces of tensile specimens 4 and 5	152
Figure 8-4: Magnifications of zone 1 of specimen 1 (a), zone 2 of specimen 3 (b), and zone 4 of specimen 5 (c).	154
Figure 8-5: SEM chemical analysis of fractured surfaces	155
Figure 8-6: CAD of the calibration block with its features and nominal dimensions	157

Figure 8-7: Deviations from the nominal dimensions of edges of protrusion 1.....	158
Figure 8-8: Deviations from the nominal dimensions of edges of the protrusion 2.....	159
Figure 8-9: Deviations from overall nominal dimensions of edges of the top, front, and side faces of the block	160
Figure 8-10: Deviations from nominal height associated with the upskin faces	161
Figure 8-11: Deviations from nominal height associated with the downskin faces.....	161
Figure 8-12: Deviations from nominal dimensions of the depth and width of the windows	162
Figure 8-13: Chain of dimensions in the vertical direction of the calibration block.....	163
Figure 8-14: Quality of inscribed texts, edges, and corners	166
Figure 8-15: Typical surface finish profile generated by SURFTEST SJ-210	168
Figure 8-16: Surface roughness measurement of the tensile test specimens	169
Figure 8-17: Surface roughness of top horizontal face (x-y plane) of the tensile test specimens	169
Figure 8-18: Surface roughness of features of the calibration blocks	170

List of Tables

Table 6-1: Results of chemical and thermal analyses of LS powder PP CP75	79
Table 6-2: Thermal and mechanical properties of HNR100 and HTV145 PP grades	82
Table 6-3: Hazardous and precautional characteristics of m-Xylene	83
Table 6-4: Cost calculation for the newly produced PP composite powder	92
Table 7-1: Thermal characteristics of the new composite PP powder	96
Table 7-2: Comparison of thermal characteristics of PP in pellet and powder forms	99
Table 7-4: Chemical composition of the talc and other volatile constituents	115
Table 7-5: Summary of measured volumes and densities	120
Table 7-6: Sieves and particle size distribution of the powder	122
Table 7-7: Summary of the dynamic flow characteristics for the new PP composite powder.....	127
Table 7-8: Summary of shear cell test results.....	130
Table 7-9: Summary of wavenumbers and corresponding vibration modes of functional groups of PP in pellet and powder forms.....	143
Table 8-1: Specifications of Sintratec S1 machine.....	147
Table 8-2: Process parameter for L-PBF of tensile test specimens	148
Table 8-3: Summary of tensile test results.....	149
Table 8-4: Summary of tolerance grades obtained	164

List of Abbreviations

4IR: Fourth Industrial Revolution

ABS: Acrylonitrile Butadiene Styrene

AIF: Angle of Internal Friction

AIR: Angle of Internal Resistance

AM: Additive Manufacturing

ASTM: American Society for Testing and Materials

BCE: Before the Christian Era

BD: Bulk Density

BFE: Basic Flow Energy

CAD: Computer-Aided Design

CNT: Carbon nanotube

CRPM: Centre for Rapid Prototyping and Manufacturing

CSIR: Council for Scientific and Industrial Research

CUT: Central University of Technology, Free State

DMAC: Dimethylacetamide

DMF: Dimethylformamide

DSC: Differential Scanning Calorimetry

EAB: Elongation at Break

EDWRG: Economic Development and Well-being Research Group

EDX: Energy Dispersive X-ray

EOS: Electro-Optical Systems

FDM: Fused Deposition Modelling

FF: Flow Function

FFF: Free Form Fabrication

FRI: Flow Rate Index

FTIR: Fourier Transform Infrared

GNP: Graphene Nanoplatelets

GPC: Gel Permeation Chromatography

HDPE: High-Density Polyethylene

HPLC: High-Performance Liquid Chromatography

HR: Hauser Ratio

IM: Injection Moulding

iPP: Isotactic Polypropylene

ISO: International Standard Organization

LB: Laser Beam

LCST: Lower Critical Solution Temperature

LCST: Lower Critical Solution Temperature

LDPE: Low-Density Polyethylene

LLDPE: Linear-Low-Density Polyethylene

LLPS: Liquid-Liquid Phase Separation

L-PBF: Laser Powder Bed Fusion

LS: Laser Sintering

MAPP: Maleic anhydride polypropylene

MFR: Melt Flow Rate

MMT: Montmorillonite

MPS: Major Principal Stress

NECSA: South African Nuclear Energy Corporation

OMMTs: Montmorillonites

PA: Polyamide

PBF: Powder Bed Fusion

PBT: Polybutylene terephthalate

PC: Polycarbonate

PDI: Polydispersity Index

PE: Polyethylene

PEEK: Poly Eether Eether Kketone

PEG: Polyethylene Glycol

PEK: Poly aryl Eether Kketone

PEKK: Polyetherketoneketone

PES: Polyether-Sulphone

PET: Polyethylene Terephthalate

PLA: Polylactic Acid

PMMA: Poly (Methyl) Methacrylate

POM: Polyoxymethylene

PP: Polypropylene

PS: Polystyrene

PSD: Particle Size Distribution

PSU: Polysulfone

PTFE: Polytetrafluoroethylene

PU: Polyurethane

PVA: Polyvinyl Acetate

PVC: Polyvinyl-Chloride

RSA: Republic of South Africa

RTD: Residence Time Distribution

SA: South Africa

SE: Specific Energy

SEM: Scanning Electron Microscopy

SGF: Short Glass Fibres

SGF: Short Glass Fibres

SI: Stability Index

sPS: Syndiotactic polystyrene

TEM: Transmission Electron Microscopy

TGA: Thermogravimetry Analysis

UCST: Upper Critical Solution Temperature

UCST: Upper Critical Solution Temperature

UFS: University of the Free State

UHMWPE: Ultra-High Molecular Weight Polyethylene

UTS: Ultimate Tensile Strength

UYS: Unconfined Yield Strength

VAT: Value Added Tax

VFR: Variable Flow Rate

WAXD: Wide-Angle X-Ray Diffraction

WAXS: Wide-Angle X-Ray Scattering

XRD: X-Ray Diffraction

ZAR: South African Rand

CHAPTER 1: GENERAL INTRODUCTION

1.1 Background

Additive Manufacturing (AM), also known as 3D printing, is considered one of the most important manufacturing technologies supporting the Fourth Industrial Revolution (4IR). Different technologies are used in the production of polymer parts through AM with Laser Sintering (LS), also known as Powder Bed Fusion (PBF), which according to ISO/ASTM 52900: 2021 [1], is still considered to deliver superior results in terms of part durability and accuracy. When the source of heating energy used is a laser beam (LB) to partially melt a polymeric feedstock material, the process is specifically named PBF-LB/P or Laser Powder Bed Fusion (L-PBF) [2]. The technology is mainly applied in the medical, aerospace, and automotive industries, producing a wide range of parts. Goodridge *et al.* [3] reported that thousands of commercially available injection-moulding (IM) plastic grades are available, but only about 30 grades can be used for L-PBF. Although L-PBF can process a relatively wide range of materials, 95% of L-PBF production processes used for prototypes and functional parts based on polymers involve only nylon polyamides PA11 or PA12. However, the high cost of these commercially available nylon polyamide powders processed through L-PBF limits the large-scale uptake of this technology in industry. Poor mechanical properties of the parts and insufficient understanding of the interrelationship among processing parameters are the main reasons limiting the use of other alternative materials for the L-PBF process [4]. Polypropylene (PP), with the potential to be used in the L-PBF process [5], [6], is one of the polyolefins widely used for IM and extrusion processes. This is because of its low cost, versatility, nontoxicity, and inertness, i.e., chemical resistance against polar solvents, non-oxidizing acids, aqueous alkalis, and salt solutions. These attributes enhance PP's poor interaction with other materials and make it difficult for the polymer to be decomposed by microorganisms in the surrounding environment [7]. Furthermore, PP is characterized by improved stability over time at elevated temperatures with high melt stiffness, high-impact strength, ease of manufacturing, and not being affected by issues such as hydrolysis, moisture absorption, and oozing, which affect its counterpart plastics such as nylon, Polylactide acid (PLA) and Acrylonitrile Butadiene Styrene (ABS).[8], [9]. Petrochemical companies produce a wide range of PP grades in pellet forms, primarily used in the plastic IM and extrusion industry. If this low-cost PP can be converted to powder suitable for processing through AM laser sintering, this will result in a significant cost saving, making this AM technology more accessible to industry.

1.2. Problem statement

Goodridge *et al.* [3] reported that, although L-PBF can process a wide range of materials, 95% of L-PBF production processes of prototypes and functional parts based on polymers involve nylon polyamides PA11 or PA12. These materials in powder form have been commercialized by companies such as 3D Systems and Electro-Optical Systems (EOS) GmbH, which supply more than 95% of the current L-PBF materials market.

When writing the thesis, the imported price for PA 11 or PA12 supplied by EOS GmbH was R2 141 (South African rand) per kilogram, thus making the L-PBF process expensive. This situation has worsened significantly over recent years as a result of the weak exchange rate of the South African rand to the Euro, which deteriorated from R8.75 in 2011 to R18.91 in 2024 [10], [11], [12], [13], [14], [15]. The year-to-year increase in the cost of imported materials renders it difficult for companies to deliver a low-cost AM service through L-PBF to industry and this necessitates an investigation into alternative lower-cost materials.

The AM market lacks sufficient polymeric materials to satisfy an increasing demand for customized components for various technical and technological applications. PP is a promising polymer for the FFF market due to its high-impact strength, chemical resistance, moisture stability, and low cost. The Differential Scanning Calorimetry (DSC) analyses have shown that the sinterability window of PP grades is in the same range or sometimes even better than the window of sinterability of the polyamide (PA) references. Compared to polyethylene grades, PP grades have a wider sinterability window [16]. A wide processing window helps to delay the crystallization until the build is complete. The DSC analyses of PP grades also showed that the crystallinity of PP grades exceeds the crystallinity values of nylon grades by about 100%. This will cause a great deal of shrinkage of the laser-sintered parts because of the tendency of the parts to crystallize during the cooling process. To avoid excessive shrinkage, it was suggested that the chemical structure of PP materials should be modified to decrease the crystallinity or to fill the PP material with reinforcing fillers. While high crystallinity leads to shrinkage of the parts, the Young's modulus and the yield stress increase with an increase in the degree of crystallinity, whereas the impact strength and toughness decrease [17], [18].

1.3. Hypothesis

Research in developing materials by Drummer *et al.* [19] and Fiedler *et al.* [20] have shown semi-crystalline polymers such as PP to be suitable for processing through L-PBF. PP pellets, such as those produced by South African-based Sasol Limited for the plastic IM industry, can be converted to powder suitable for processing through L-PBF. The current PP pellets cost R33 per kg, a significantly lower cost than the

imported powder, making this AM technology more accessible to industry. Although PP powder suitable for L-PBF has become available from companies such as Diamond Plastics GmbH in recent years, the material must be imported, and the cost is similar to that supplied by EOS GmbH.

Based on existing PP grades for the IM process, such as those available from Sasol Limited, a new PP powder for L-PBF with an optimized degree of crystallinity and reinforced with fillers can be developed. The availability of an improved PP powder for L-PBF will increase the feedstock material for PBF AM, thus rendering polymer AM technology more accessible to industry.

1.4. Original contribution to the field of study

The original contribution to the research field of polymer AM can be considered to be the following: No research has been performed on the feasibility of producing powder for the L-PBF process from low-cost South African-produced PP pellets, and finding process parameters for L-PBF to produce good quality parts using the material. Although the aim of this investigation was not to replace nylon as feedstock material, the availability of these alternative materials at a lower cost will significantly decrease the cost of prototyping parts manufactured using L-PBF. This will increase the uptake of the technology in industry.

1.5. Aim of the study

The aim of the study was to produce powder suitable for the L-PBF process from locally produced PP pellets. From the newly produced PP powder, parts with comparable mechanical properties and dimensional accuracy can be produced but at a reduced cost when a commercial powder is used.

1.6. Objectives of the study

The objectives for this study were to:

- i. Acquire commercially available PP powder, determine process parameters to produce test specimens for L-PBF using the powder, and determine mechanical properties and dimensional accuracy of specimens produced.
- ii. Develop a process for producing powder suitable for L-PBF from PP pellets as supplied by Sasol Limited and determine the cost of producing the powder.
- iii. Characterize the newly developed composite powder in terms of intrinsic and extrinsic properties.

- iv. Determine process parameters for L-PBF of the newly produced PP powder, perform mechanical testing as well as dimensional accuracy and surface roughness assessment of parts produced, and compare the results to what was achieved using the commercially available PP powder.

1.7 Methodology of the study

1.7.1. Assessment of commercially available PP powder

The assessment of the commercially available PP powder consisted of the following:

- i. Obtaining a commercial PP powder from Diamond Plastics GmbH and having it analyzed at Sasol's Analytical Services for them to propose a grade with similar properties from their existing range of PP pellets.
- ii. Determining the parameters for processing the commercial powder on an EOS P380 machine at the Centre for Rapid Prototyping and Manufacturing (CRPM) at Central University of Technology (CUT), Free State.
- iii. Testing the samples produced regarding mechanical properties, dimensional accuracy, and surface finish. Results from this would serve as a benchmark for producing new powder for the L-PBF process.

1.7.2. Production of PP powder from pellets supplied by Sasol

- i. Obtaining the necessary equipment for reducing the PP grades to powder, as suggested by Sasol Limited, using a liquid-liquid phase separation technique.
- ii. Determining ratios of suggested PP grades as well as heating and cooling cycles to produce powder particles of the correct morphology to be used in the L-PBF process.
- iii. Performing a cost analysis to produce the powder and compare it to the cost of commercially available PP powder.

1.7.3. Characterization of the newly produced PP powder

To characterize the produced powder in terms of the following:

- i. Granulometry analysis: particle size distribution characterization using a laser diffraction particle analyzer and scattering method at the South Africa Nuclear Energy Corporation (NECSA).
- ii. Microscopic morphology analysis by Scanning Electron Microscope (SEM) at the University of the Free State (UFS).

- iii. Thermal analyses by Differential Scanning Calorimetry (DSC) and Thermogravimetry (TGA) at UFS.
- iv. Rheological analysis by Melt Flow Rate (MFR) at CUT and Flowability at the Council for Scientific and Industrial Research (CSIR).
- v. Crystallographic structure analysis by X-Ray Diffraction (XRD) and Fourier Transform Infra-Red (FTIR) spectrum at UFS.

1.7.4. Determining optimal process parameters for LS of newly produced PP powder and testing parts

- i. Determining process parameters for L-PBF of the powder produced on a Sintratec S1 laser-sintering machine at CRPM.
- ii. Performing mechanical testing on the test specimens and measuring dimensional accuracy and surface roughness on geometrical test pieces.
- iii. Comparing results to what was achieved with the commercially available PP CP75 powder.

1.8 Delimitation of the study

Only a sufficient amount of a new PP powder was produced in a laboratory at CUT to conclusively show that the material can be successfully processed through L-PBF. Therefore, developing equipment to produce PP powder on a large scale did not form part of this study.

1.9 Layout of the thesis

The layout of the thesis is shown in Figure 1.

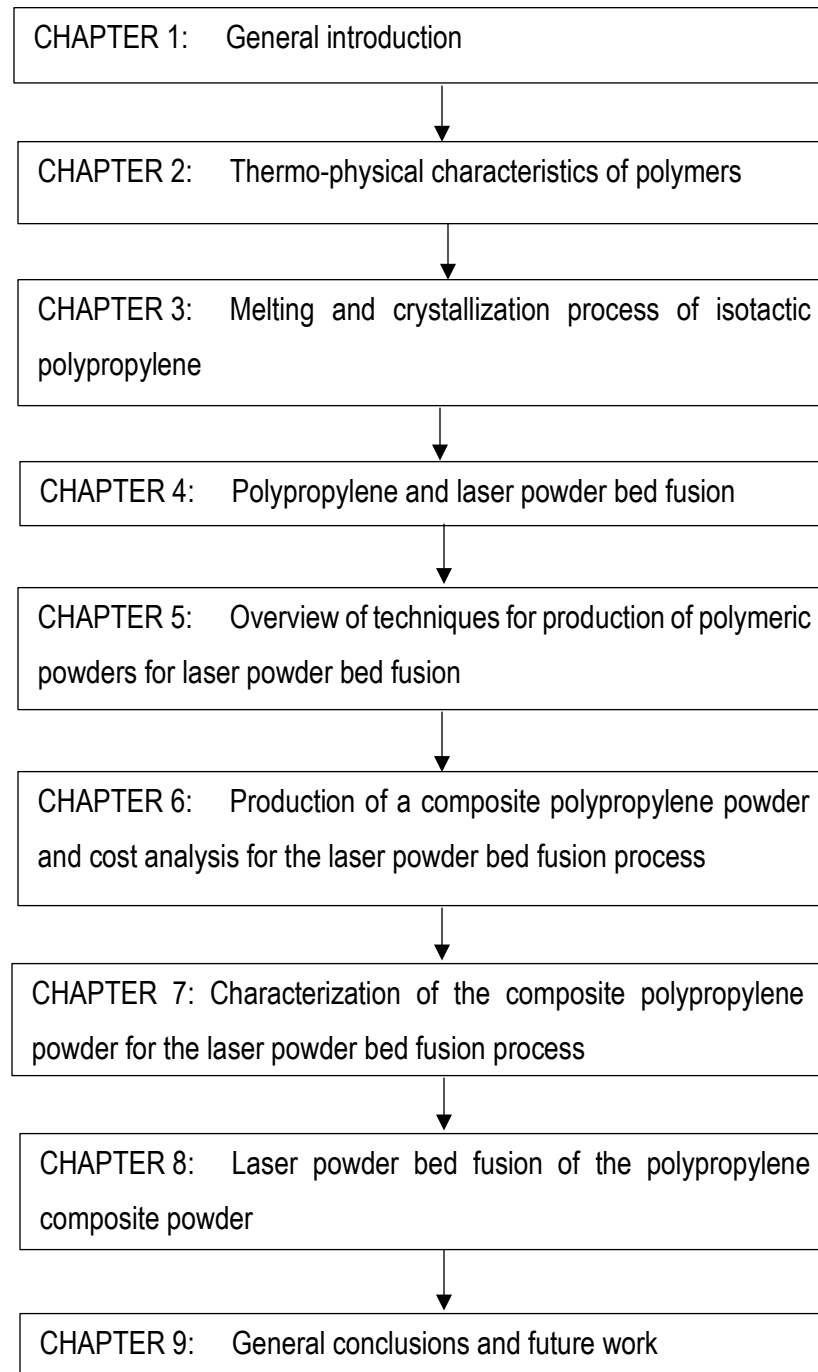


Figure 1-1: Layout of the thesis

CHAPTER 2: THERMO-PHYSICAL CHARACTERISTICS OF POLYMERS

2.1 Introduction to polymers

Polymers are materials composed of long chain molecules made primarily by carbon-to-carbon bonds forming the backbone where other pendent hydrogen atoms and groups are attached. The interlinking of many small units known as monomers results in the formation of macromolecular substances that have many applications in all areas of industry. Polymeric materials can be naturally obtained from animal and vegetable resources or chemically synthesized through polymerization processes. Plant and animal-based natural fibres, such as wood, cotton, rubber, wool, leather, and silk, have been used, especially in the textile industry, since the Stone Age (3 000–2 500 BCE). Following the work published by Carothers on polycondensation and polyaddition theory in 1929, it was only in 1930 that the first synthetic fibre based on Nylon 66 was invented and commercialized before 1940 [21]. The development of Ziegler-Natta catalysts in 1955 and contributions from Dupont and co-workers established the polymerization process for the synthesis of the most widely used and commercialized polymers such as polyamides (nylons) and polyolefins (polyethylene, polypropylene, polybutene, etc.) [22], [23]. Compared to other types of solid materials, such as metals and ceramics, polymers are lightweight and characterized by low melting points, low mechanical strength, and high toughness and ductility. Figure 2-1 shows the general classification of polymers based on the origin, type of polymerization, chemical structure, and thermal behaviour.

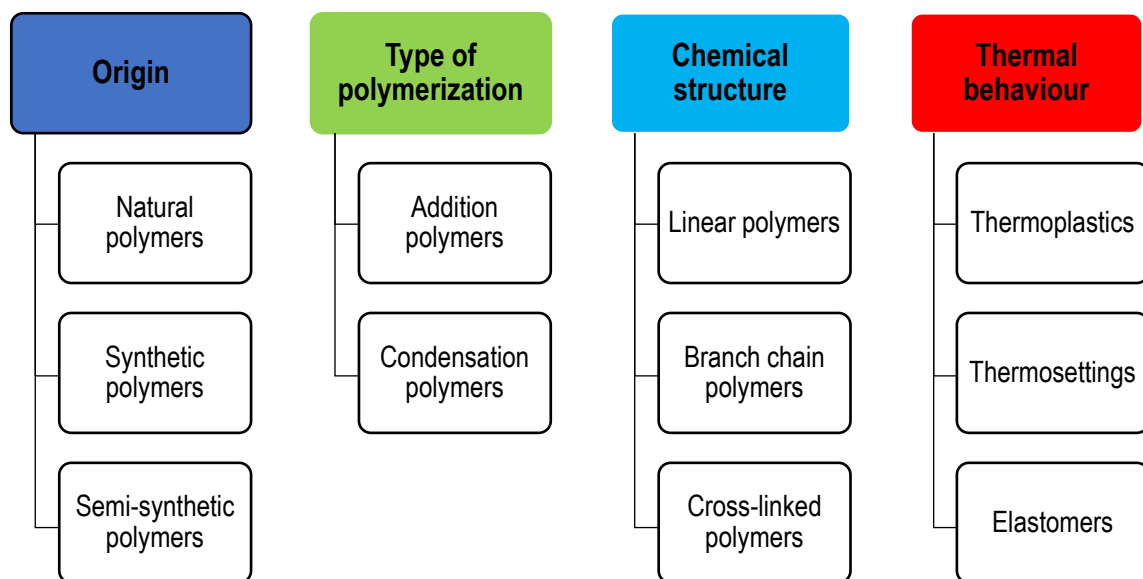


Figure 2-1: Classification of polymers

PP, Polyethylene Terephthalate (PET), High-, Low-, Linear-low Density Polyethylene (HDPE, LDPE, LLDPE), Polyvinyl Chloride (PVC), and Polystyrene (PS) occupy the most significant global market shares due to their versatility and availability. The low cost of production is associated with manufacturing of commodities, appliances, and parts based on polymeric raw materials [24], [25]. Since the mass production of polymers in 1950, the global manufacturing of plastics has grown exponentially and reached an estimated 335 to 380 million metric tons per year from 2015 to 2020. An estimated 50 million metric tons of plastic waste ended up in oceans in 2015, with an expectation for this to triple by 2025. The continuous wide usage of plastics for packaging, civil and mechanical constructions, electronic and electrical appliances, household, leisure and sport, industrial and medical applications, and other spheres of human life will result in a projected global escalation of plastic debris in disposal areas or natural environment, to 12 000 million metric tons in 2050 [24], [26].

2.2 Thermal classification of polymeric materials

The terms “polymers” and “plastics” are interchangeably used in scientific and technological literature. The word “polymer” which reflects the chemical structure of polymers, is derived from a combination of two Greek words: “poly” meaning “many” and “mer” from “meros” meaning “parts” or ‘units’. The word “plastic” or

“plastics” which reflects the technological process is derived from the Greek word “plastikos” meaning “fit for moulding” and from a Latin word “plasticus” meaning “of moulding”. Manufacturing processes of plastic parts and commodities are mainly based on the application of heat followed by cold under controlled pressure [21], [27], [28]. The melting, glass transition, crystallization, and solidification temperatures are thermal points that characterize the thermal behaviour of polymers. While the melting and solidification temperatures are explicitly defined and understood as the transition temperature from solid to liquid phase and vice versa, the glass transition and crystallization temperatures are not intrinsically defined and require more scientific and technological definition.

Thermoplastics are plastic materials that can soften when heated and harden when the temperature is lowered. The process of softening and hardening is reversible without any chemical molecular modification to the thermoplastic. When the arrangement of molecular chains in a thermoplastic is random and does not follow a well-defined order, such a plastic is known as an amorphous thermoplastic. On the other hand, a semi-crystalline thermoplastic exhibits a relatively well-organized molecular structure, forming crystalline regions separated by layers of amorphous zones.

The glass transition temperature (T_g) is a temperature associated with amorphous polymers and the amorphous phase of semi-crystalline thermoplastics, where amorphous regions undergo a transition from a rigid state to a more flexible state, thus making the border between the rigid rubber-like phases. Polymers display a similar physical behaviour at temperatures below the glass transition temperature as glassy or crystalline materials, whereas plastics behave like rubbery materials for temperatures above the glass transition temperature. From a thermodynamic point of view, an amorphous polymer can be considered as “liquid” at temperatures above its glass transition temperature. However, the viscosity of an amorphous polymer at temperatures slightly above its glass transition is practically too high, and consequently, the amorphous polymer hardly flows until reaching a specific temperature much higher than T_g . It can be said that the glass transition temperature, T_g , for amorphous plastics cannot be taken as a temperature corresponding to the melting temperature of a semi-crystalline polymer [29]. Semi-crystalline polymers have a glass transition temperature in the range of -100 to 50 °C and have a clear, distinct melting point between 100 and 400 °C, at which the solid state is abruptly changed into a liquid state involving a significant change in volume. Contrary to semi-crystalline polymers, amorphous polymers do not display a well-defined melting temperature; instead, they have a clear, distinct glass temperature around 100 °C above which the polymer changes to a leathery, rubbery, and finally, liquid phase as the temperature increases without showing any

transition [30]. The glass transition temperature represents the reversible transition in amorphous regions within amorphous or semi-crystalline polymers from a hard and relatively brittle “glassy” state into a molten or rubber-like state as a critical temperature is reached [31]. The glass transition temperature serves as a reference point for technological applications such as coatings where the material must be rigid or at a temperature below T_g [28].

The physical and mechanical properties of polymers are significantly influenced by the processing and operational temperature and pressure conditions. From the point of view of the thermal behaviour of polymers, plastic materials can be classified into thermoplastics, thermosets, and elastomers (Figure 2-2).

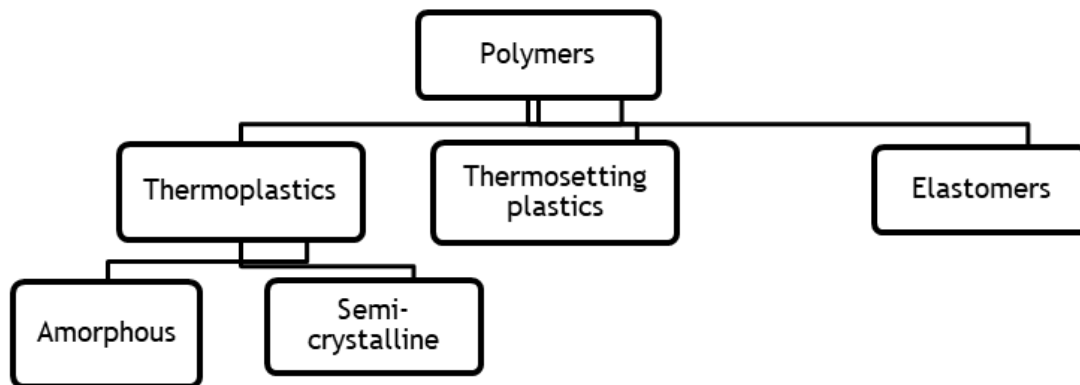


Figure 2-2: General thermal classification of plastic materials

Polymers such as ABS, Poly (Methyl) Methacrylate (PMMA), Polyvinyl-Chloride (PVC), Polycarbonate (PC), and Polystyrene (PS) are a few examples of amorphous thermoplastics. Polymers such as PP, Polyethylene (PE), Polyethylene Terephthalate (PET), Polyamides, and Polyoxymethylene (POM) are typical examples of semi-crystalline thermoplastics that are widely used in the polymer industry. Semi-crystalline polymers are denser and more prone to high shrinkage than amorphous polymers, characterized by low density and low shrinkage during cooling.

Thermosetting polymers or thermosets are polymers characterized by irreversible hardening when subjected to heat and pressure. Thermosets are produced using curing, a chemical process that induces chemical changes that render the polymer unaffected by further heating, ultraviolet light, or high pressure. The presence of cross-linking molecular chains in thermosets reduces the freedom of movement of polymer

chains under stress, resulting in thermosetting polymers being rendered more brittle than thermoplastics. Polyurethane, silicones, and epoxides are typical examples of thermosetting polymers.

Elastomers, also known as viscoelastic materials or rubbers, are polymeric materials characterized by weak intermolecular forces, rendering them highly elastic and, consequently, characterized by a high percentage of elongation at break. Elastomeric materials possess low melting temperatures compared to thermoplastics or thermosets.

2.3 Crystallization temperature and degree of crystallinity of semi-crystalline polymers

Semi-crystalline polymers cooled from melting temperature result in a crystallization process that generates a morphology of arranged regular lamellae crystalline structures separated by thin amorphous interlayers (Figure 2-3). The crystallization temperature is the temperature of occurrence of the crystalline structures in a polymer when it is cooled from the melt and can be influenced by the applied pressure and cooling rate on the melt. In the absence of a thermal gradient, the packed broad crystalline lamellae grow radially outwards in all directions, starting from point-like nuclei, resulting in spherical crystalline regions called spherulites.

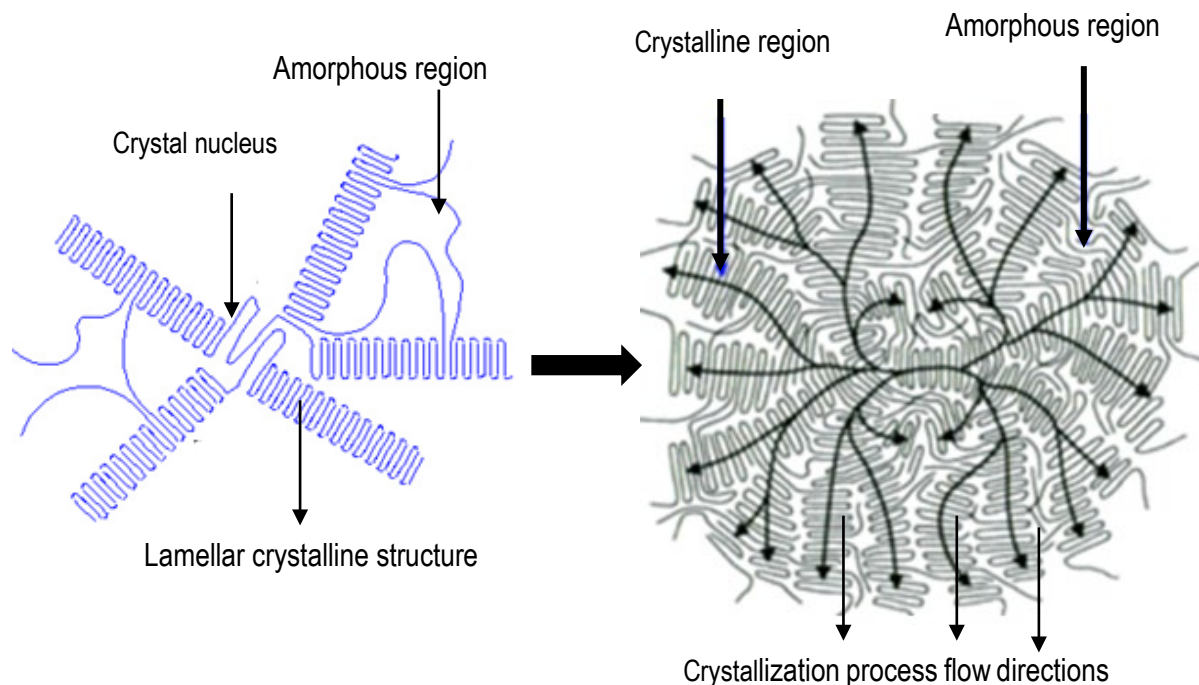


Figure 2-3: Radial growth of crystalline lamellae into spherulites forming semi-crystalline polymers [32], [33]

Spherulites can be considered the polymer analogue of grains in polycrystalline metals and ceramics. The addition of nucleating agents into the melt can change the crystallization temperature and the size of the developing spherulites. Each spherulite is composed of many different lamellar crystalline regions separated by additional channels of amorphous structures. The packing of polymer chains in crystalline regions is denser and more efficient than in amorphous parts. The nuclei grow in time depending on temperature and pressure, forming spherulites that will impinge and stop growing when complete space filling is reached [34]. It is accepted that the melting temperature of polymers within crystal modification is mainly related to the lamellae crystal thickness d_c . The lamellae thickness and the long spatial period of lamellar crystal (Figure 2-4) can increase remarkably during the heating process of semi-crystalline polymers [35].

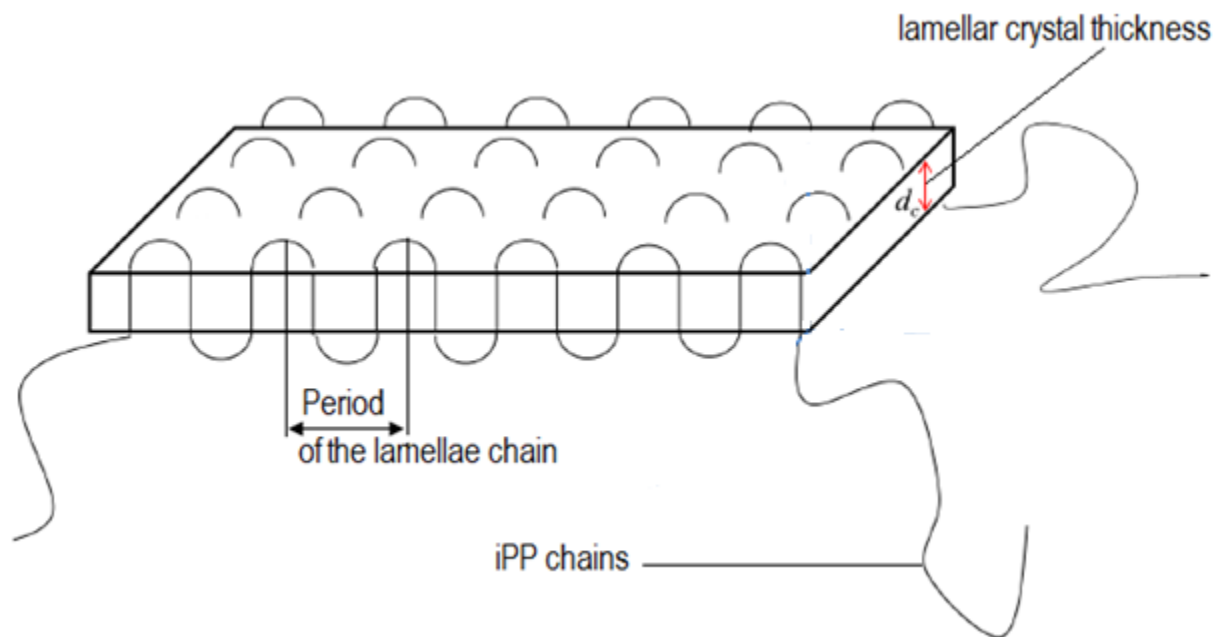


Figure 2-4: Illustration of thickness and period of a crystalline lamellae of an isotactic polypropylene (iPP) as adapted from Yang et al. [36]

The degree of crystallinity is the percentage of crystallinity, i.e., the overall level of crystalline component (or pure crystals) in relation to its amorphous component. The degree of crystallinity X_c of semi-crystalline polymers varies from 10 to 80% and can be determined as follows:

$$X_c = \frac{\Delta H_m - \Delta H_c}{\Delta H_m^0} \times 100\% \quad (\text{Eq. 1})$$

ΔH_m -is the heat (enthalpy) of melting (fusion)

ΔH_c -is the enthalpy of crystallization.

For PP, $\Delta H_m^0 = 207.1 \text{ J/g}$ is a theoretical or reference value that represents the heat of melting as if the polymer were 100% crystalline [37]. The heat of melting ΔH_m and the enthalpy of crystallization ΔH_c are determined by integrating the areas under the peaks of the heating and cooling processes as obtained during DSC experiments shown in Figure 2-5.

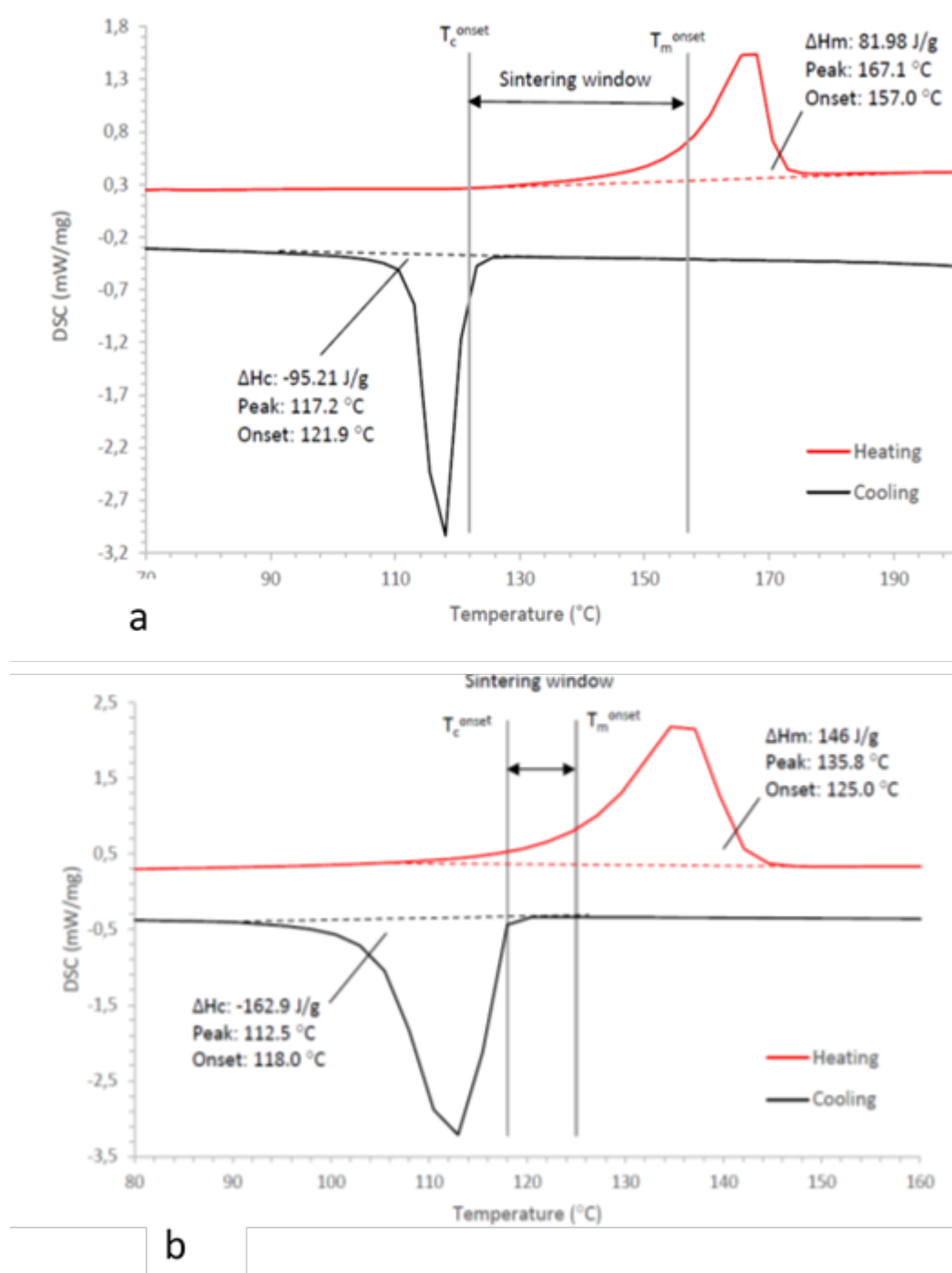


Figure 2-5: DSC analysis and window of sinterability of PP (a) and of PE (b) [16]

The degree of crystallinity is directly related to many of the key properties exhibited by a semi-crystalline polymer, such as brittleness, toughness, elastic modulus, storage modulus, loss modulus, optical clarity, creep or cold flow, permeability or barrier to resistance (ability to prevent gas transfer in or out) and long-term

stability [27], [29]. Slouf *et al.* [38] established that the microhardness of a semi-crystalline polymer is a function of the overall degree of crystallinity, average lamellae thickness, and the stiffness of the amorphous phase of the polymer. The cooling rate and addition of nucleating agents can influence the degree of crystallinity. Rhoades *et al.* [39] investigated the effect of cooling rates on non-nucleated and nucleated isotactic polypropylene (iPP) with γ -quinacridrone used as a β -nucleating agent with concentrations of 1, 4, and 500 ppm. They found that for slow cooling rates not exceeding $100\text{--}200\text{ Ks}^{-1}$, the maximum enthalpy of crystallization obtained at 105 J/g was independent of the concentration of nucleating agents. In contrast, for higher cooling rates up to 1000 Ks^{-1} , the degree of crystallinity rapidly decreased for non-nucleated and nucleated samples. Such a pronounced decrease in crystallinity was evidenced for the sample containing 500 ppm for cooling rates beyond 1000 Ks^{-1} .

2.4 Molecular structure of PP

Propylene is a monomer with a molecular structure obtained from natural carbon sources such as crude oil and gas and is made up of alternating pendent hydrogen (H) atoms and methyl (CH_3) side groups attached to its carbon (C) backbone to form C_3H_6 propylene monomer (Figure 2-6).

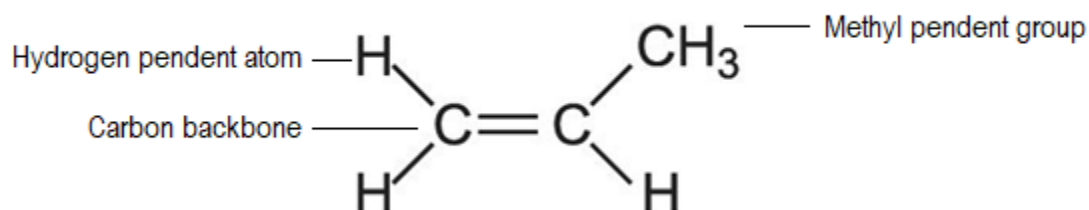


Figure 2-6: Chemical structure of propylene molecule

Polymerization is a chemical process that combines many monomers to form a long-chain molecule known as a polymer. At the beginning of 1954, Ziegler-Natta [40] catalysts could polymerize propylene into a highly crystalline linear polymer. PP is a polyolefin thermoplastic semi-crystalline polymer obtained by polymerization into a long chain of propylene molecules. Figure 2-7 illustrates such a combination of a number n of propylene monomers to form a molecular chain known as polypropylene (PP).

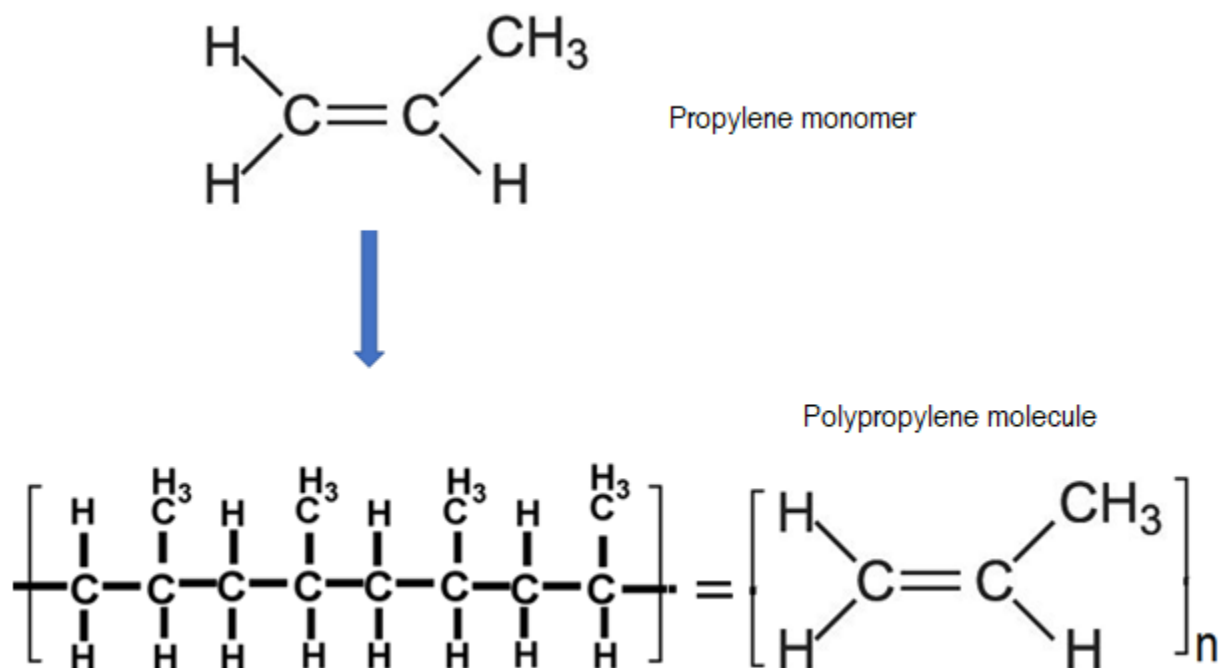


Figure 2-7: Generic chemical formula of PP

Tacticity is a concept that characterizes the way the pendent groups are relatively arranged to the backbone of the polymer. Depending on the location of the methyl group CH_3 in the PP molecule, the polymerization process can produce three types of PP molecular chain structures, namely isotactic, syndiotactic, and atactic polypropylenes (Figure 2-8). In December 1954, Natta, an expert in structural and catalytic chemistry, announced the discovery of processes leading to the production of polymers with extraordinary regularity from the points of chemical constitution and configuration of the successive monomeric units along the chain of each macromolecule. The regular succession of propylene monomeric units with the same steric configuration was named isotactic polypropylene (iPP). The methyl groups are located on the same side of the backbone for an iPP. In practice, it is never possible to produce 100% iPP as residual stereospecific and regional defects always exist [41]. For syndiotactic PP, the methyl groups are positioned on alternating sides of the backbone, while for atactic PP, methyl groups are arranged randomly.

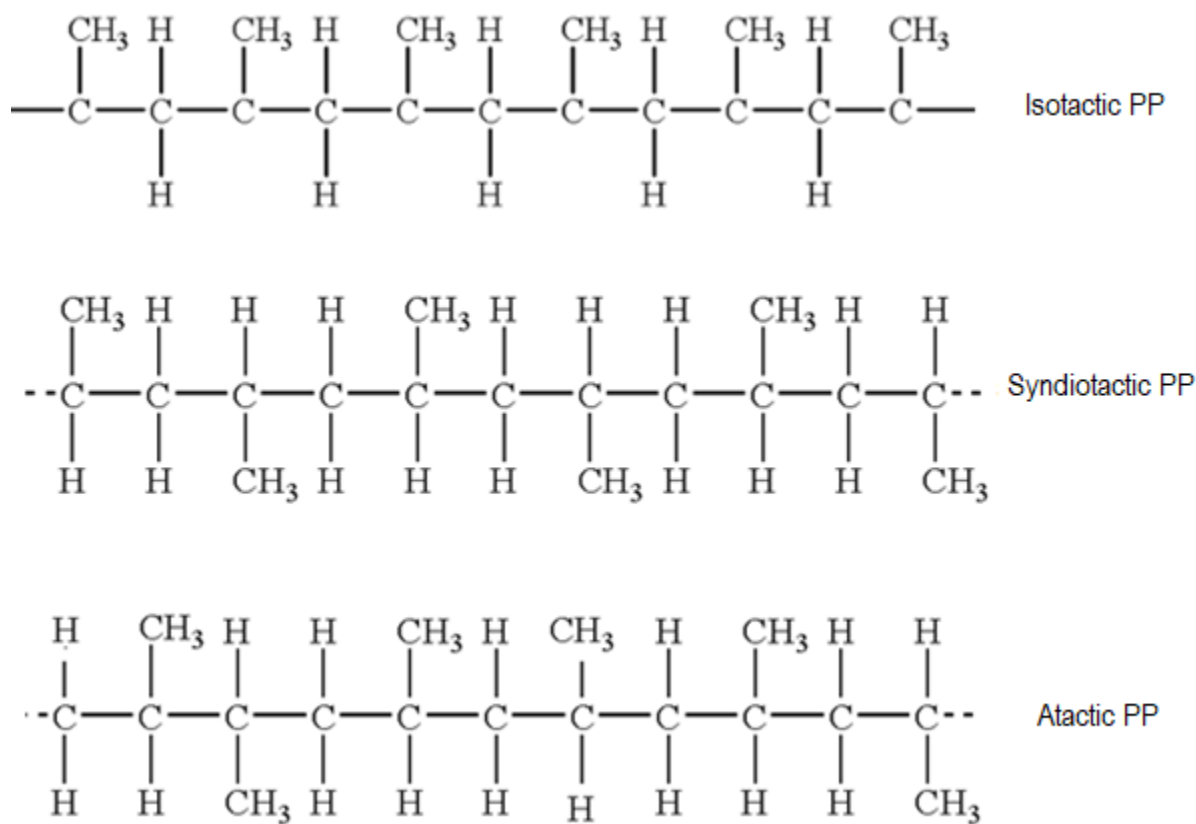


Figure 2-8: Tacticity and types of PP [42]

The control of metallocene and/or other new-generation catalysts in Ziegler-Natta catalyst technology allows the polymerization into isotactic, syndiotactic, or atactic PP [40], [42]. Isotacticity is a key parameter that has significant effects on crystallinity, polymorphism and crystallization temperature of a polymer [18]. With the increase of isotacticity, the degree of crystallinity increases as spherulites become more densely packed, and the strength and stiffness increase. The degree of crystallinity of PP can be changed by modifying the chain structure, i.e., branching, tacticity of the backbone, or by mixing low and high isotactic PPs [17], [43].

Depending on the homogeneity of the combination of propylene monomers, polymerization can form PP homopolymer and PP copolymer (Figure 2-9). When the molecular chain consists of a combination of only one type of monomer that may contain irregularities, especially at the end of the chains and at junctions leading to branches, the PP is known as a homopolymer. A copolymer is obtained through polymerization of more than one type of monomer arranged in a more or less irregular sequence. PP and non-polypropylene monomers combined to form a copolymer can be arranged in alternating or random order, grouped in blocks or monomer blocks grafted to a homopolymer.

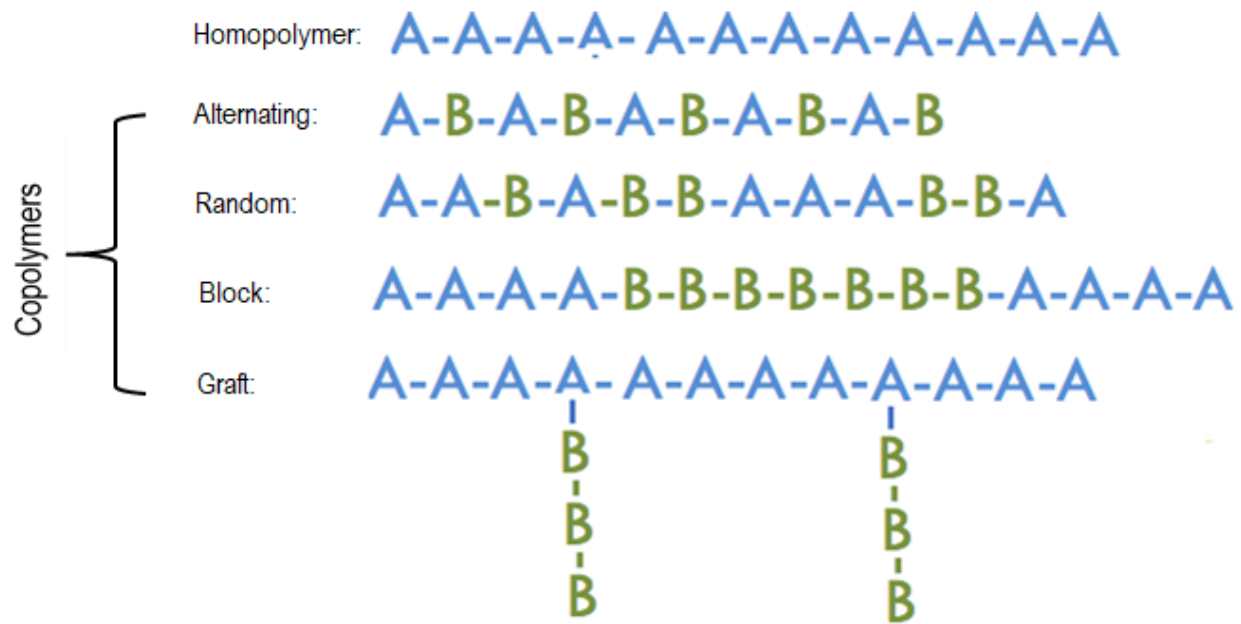


Figure 2-9: Molecular chain structure of homopolymer and copolymers (adapted from Wikipedia [44])

An example of a PP copolymer is the combination of propylene and ethylene units where up to 6% of ethylene is introduced in PP chains to improve the flexibility and optical properties suitable for products requiring a transparent appearance. When the mass of ethylene is raised to 15%, a tougher, stronger, and less brittle polymer is obtained for industrial applications. Impact copolymer is another class of PP obtained through PP homopolymer randomly co-mixed with a copolymer phase that contains 45 to 65% ethylene. Such impact copolymers are used in packaging, automobile components, houseware utensils, pipelines, and the electrical industry, where resistance to impact loading is one of the leading criteria for selecting suitable engineering materials.

2.5 PP in the global production market

Nowadays, PP is one of the most inexpensive, versatile semi-crystalline polymers commonly used in both short and long-term applications due to its tunability under various processing conditions. This enables the modification of its thermomechanical history up to solidification by changing the particular organization of crystallites and thus influencing material properties such as geometrical dimensions, strength, hardness, permeability, surface texture, and transparency. Figure 2-10 shows PP's predominance consumption market demand for 2019 and 2020 in Western Europe, compared with other most used polymeric materials

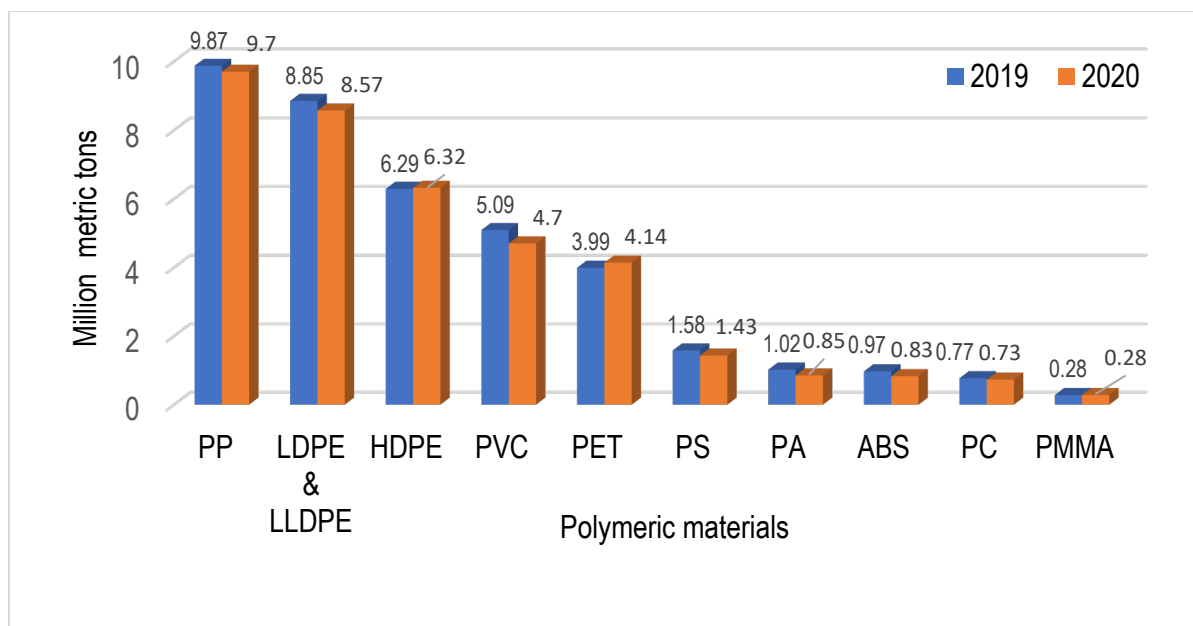


Figure 2-10: Predominance of PP use in Western European polymers market [26]

Most PP products manufactured through IM and extrusion processes offer a good combination of physical, chemical, mechanical, thermal, and electrical properties with a good strength-to-weight ratio. The PP products are lightweight (with a density varying from 0.89 to 0.92 g/cm³), have good resistance to staining from oils and chemicals, and do not absorb moisture. Injection-moulded PP has been found to have a wide range of applications, including beer crates, luggage and automobile panels and trims, and internal hinges because of its fatigue resistance. A thermal resistance above 100 °C allows the sterilization of parts produced from PP, while a negligible water absorption that varies from 0.02 to 0.04% at 23 °C facilitates the easy storage of PP products at ambient temperature [45]. However, PP absorbs non-polar solvents such as chlorinated solvents and hydrocarbons, and oxidizing agents such as nitric and sulfuric acids and halogens chemically degrade PP products [43].

Isotactic polypropylene (iPP) is one of the most important and widely used semi-crystalline thermoplastic polymers that occupy the second position in worldwide consumption of polymers [46] and has been investigated since the 1960s [35] due to its relatively low cost, versatility, recyclability, and good mechanical performances in engineering and medical applications. The properties of iPP can be varied within a wide range by rearranging its crystalline structure [47]. Low impact strength, especially at low temperatures, low toughness, and notch sensitivity, can limit the range of its engineering applications [48]. The advantages of iPP compared to syndiotactic and atactic PP arise from its high degree of crystallinity that ranges from 40 to 70%. Despite the dimensional inaccuracy that such a high degree of crystallinity will cause, the resulting

polymer has a high melting point (160–180 °C), high density, exceptionally high mechanical properties, and low permeability to vapour and solvents relative to syndiotactic and atactic types [9]. iPP is used for non-structural applications (disposal products and non-woven fabrics) and semi-structural applications, including automotive parts, construction materials, and some electrical appliance components. Figure 2-11 shows the global market of 62.3 million metric tons of iPP achieved in 2020 at US\$ 93.5 billion. The market was expected to grow by 4.6% annually [49].

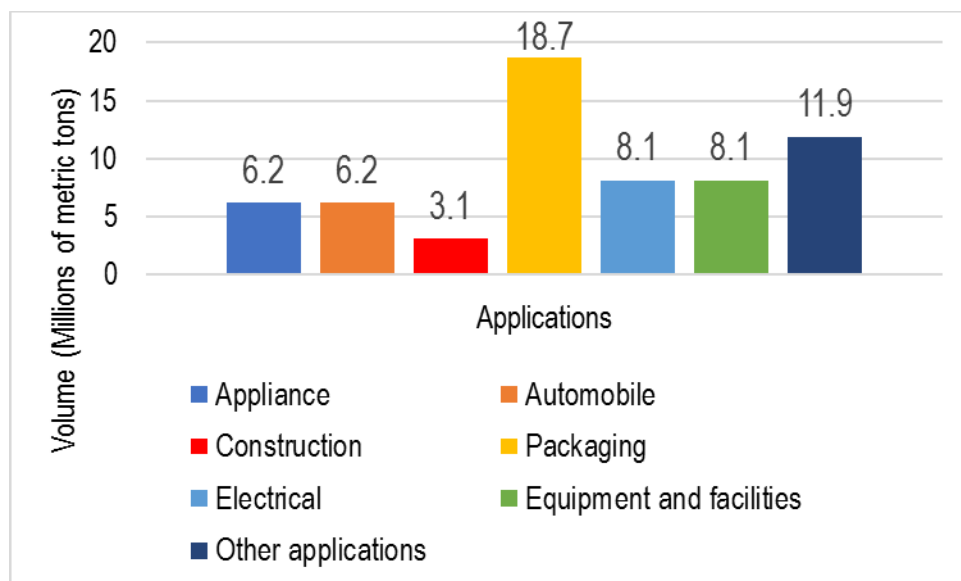


Figure 2-11: The coverage of iPP commodities for 2020 [49]

Due to its superior properties, such as a high heat deflection temperature (107–120°C), suitable flexibility, and rigidity, iPP is often used for a variety of food packaging commodities ranging from cold chain to heat-treated food products, including microwaveable cooking utensils available in either flexible or rigid plastic packaging [50].

Conclusions

1. This chapter introduced the role of natural polymeric materials in human history and the subsequent development that resulted in polymer synthesis for broad application in the plastic industry due to the discovery of catalysts for polymerization processes.

2. Glass transition, melting, and crystallization temperatures constitute the main thermal characteristics of polymers, which influence their technological industrial processability and usage as final products.
3. PP is a semi-crystalline polymer widely used in the global polymer market, where PP has been leading in terms of the total volume of industrial applications and commodities. Traditional manufacturing processes such as IM, rotational moulding, blow moulding, and extrusion have been used in mass production for many years. The use of PP for AM processes has the potential to continue the growth of the global plastic market.

CHAPTER 3: MELTING AND CRYSTALLIZATION PROCESS OF ISOTACTIC POLYPROPYLENE

3.1 Nucleation and growth of crystals of semi-crystalline polymers

The crystallization process occurs when a polymer sample cools down from the melt to temperatures ranging from about 10 °C below the melting point and 30 °C above the glass transition temperature [51]. The crystallization of polymers is often characterized by multiple mechanisms of the birth and growth of crystals. According to the classical crystallization theory, the liquid-crystal phase transition requires, in the first step, the formation of nuclei of supercritical size, which then grow by attachment of chain segments. The initial formation of the nucleus, which ultimately is needed to overcome an energy barrier to create a stable boundary between the amorphous phase and the ordered or crystallized domains, is called primary nucleation. If an additional energy barrier is needed for the attachment of chain segments during crystal growth, the process is called secondary nucleation. If this secondary barrier is molar-mass dependent, it is more precisely known as molecular nucleation [52].

3.1.1 Homogeneous and heterogeneous nucleation

Nucleation is a self-organizing process that leads to a new thermodynamic phase or a self-assembled structure, where the formation of a nucleus requires several molecules to come together spontaneously. Nucleation is affected by the level of impurities or foreign substances in a system that can provide the surfaces for supporting the structure. With respect to the absence or presence of foreign surfaces, homogeneous or heterogeneous nucleation can occur (Figure 3-1). Heterogeneous nucleation occurs at a pre-existent surface, and the energy barrier to form a stable nucleus is typically lower than the energy barrier in the case of homogeneous nucleation, where the organization of structures takes place away from a surface. A homogeneous nucleation process is determined by the competition between bulk and surface free energy changes ΔG_b and ΔG_s , respectively. Bulk free energy change should overcome surface free energy change to generate stable nuclei. However, due to the presence of contaminants, catalyst residues, and dormant precursors that provide extra surface free energy change ΔG_s , thus lowering nucleation barriers, pure homogeneous nucleation rarely happens. Moreover, the application of flow as an important unavoidable processing factor raises the total free energy by decreasing the bulk energy change ΔG_b and consequently promoting the heterogeneous nucleation process.

The homogeneous nucleation of crystallization, typically observed only at a sizeable supercooling rate leading to lower temperatures, in contrast, results in the formation of mesophase, presumably due to the large number of nuclei. Mesophase growth is non-spherulitic and ultimately results in the appearance of non-lamellar, nodular nanometer-sized objects [52].

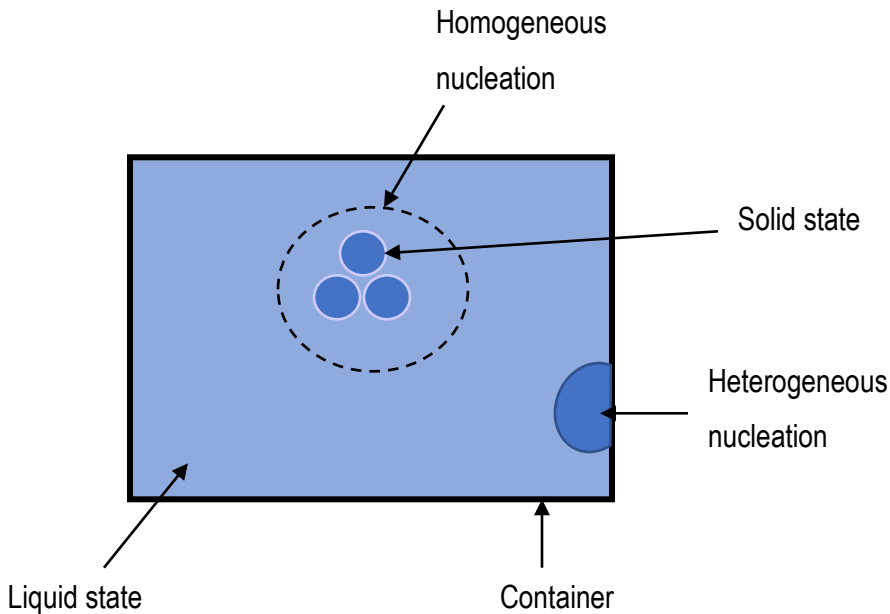


Figure 3-1: Homogeneous and heterogeneous nucleation

At the initial stage, the crystallization rate is very low, and after an induction period, the process accelerates to a maximum crystallization rate and then slows down again as it approaches its final equilibrium state. If the equilibrium degree of crystallinity is not reached due to a low crystallization rate, semi-crystalline polymers continue to gradually increase in their crystalline percentage content until the final equilibrium level is attained even at room temperature.

In Classical Nucleation Theory (CNT), the nucleus is characterized either by the total number of crystal monomers (1D-characterization approach) or by the length and diameter (2D-characterization approach) of the nucleus [41]. Mileva *et al.* [52] investigated the kinetics of crystallization of an iPP with a molar mass of 373 g/mol and polydispersity index of 6.2. It was found that there was a need for modification of the classical crystallization theory, which restricts the crystallization process within a range of temperatures between the equilibrium melting and glass transition temperatures. Differential Fast Scanning Chip (DFSC) analysis revealed the nucleation and growth of small mesophase particles of perhaps sub-nanometer sizes in a glassy

state of iPP, suggesting that cooperative, large amplitude mobility of unrestrained molecule segment chains is not a requirement for partial ordering of macromolecules as assumed in the classical theory. It was concluded that non-cooperative local large amplitude mobility of chain segments was sufficient to form ordered structures even at temperatures below the glass transition temperature, and this agreed with early findings on crystallization of Poly (ϵ -Capro-Lactone) (PCL).

3.1.2 Effect of shear flow on nucleation and growth of crystals

The flow influences the nucleation and growth process by increasing the equilibrium melting temperature. The effect of the flow process on nucleation can be determined directly by counting the resulting crystallites when they become large enough to be identified with a microscope. The nucleation rate can be determined by considering the number of spherulites composing the populations before and after the polymer is subjected to a specific process and dividing the difference by the time taken by the process. The growth rate is measured by monitoring the radius of spherulites during the time and slope of the plot, reporting the radius of the spherulite versus the time taken to attain that radius constitutes the growth rate. It is reported that the growth rates of iPP homopolymers are similar for different grades, while the nucleation density is always unique due to residuals and catalysts remaining from industrial synthesis [34].

To bridge the gap between the nuclei and the resulting crystalline structures, Ma *et al.* [53] investigated the formation of crystalline structures during and after flow using synchrotron radiation X-ray with a wavelength of 1.033 Å for Small Angle X-Ray Scattering (SAXS) and Wide Angle X-Ray Diffraction (WAXD) measurements. The Full Width Half Maximum (FWHM) is a characteristic of a function, or a graph curve, that describes the extent to which the data distribution is wide. For a periodic function, the FWHM indicates the difference between two extreme values of the independent variable at which the dependent variable equals half of the maximum value of the dependent variable (Figure 3-2). Using the criterion of FWHM on one-dimensional WAXD curves, the influence of different nuclei on the degree of orientation of the crystallites was explored and evaluated.

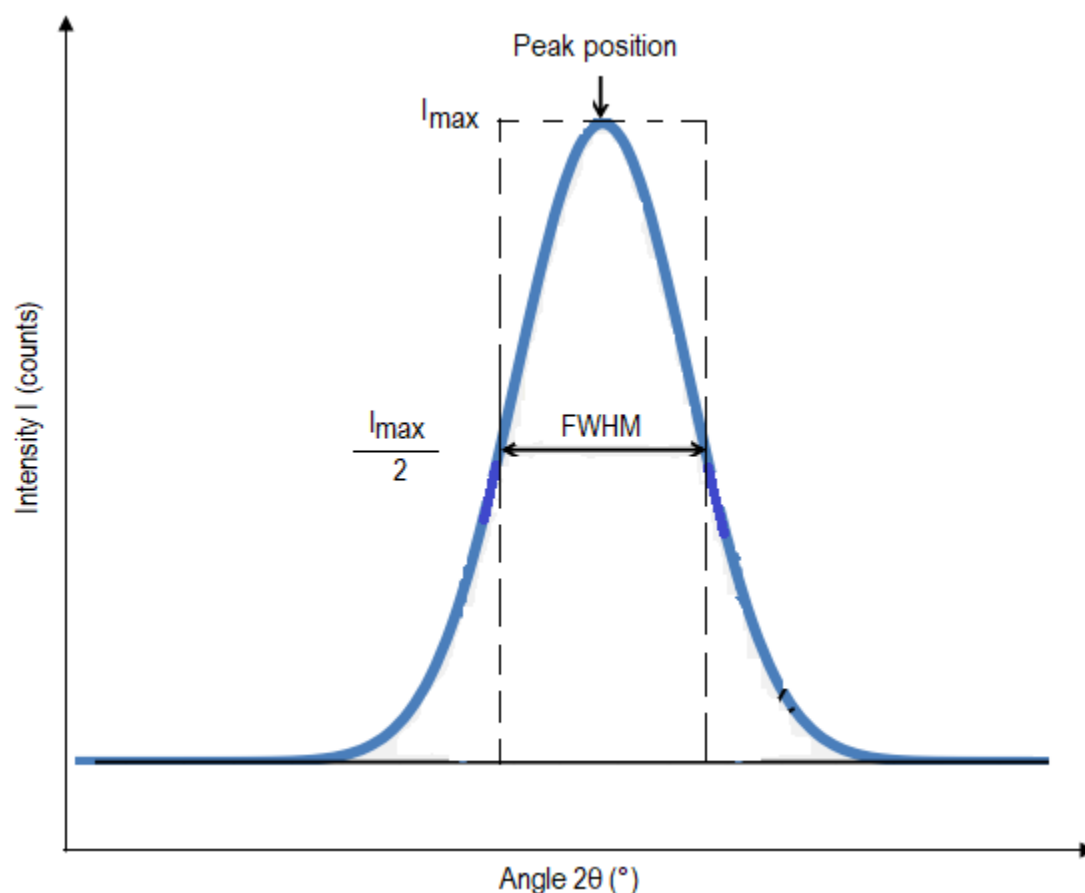


Figure 3-2: Illustration of FWHM of intensity distribution of X-ray diffraction (adapted from [54])

A narrow FWHM value corresponds to a higher average lamellae orientation, implying a higher degree of crystallinity, while a wide value indicates a low degree of crystal orientation. For a weaker flow of shear rate ranging from 80 to 160 s⁻¹, the time to start crystallization increased, and birefringence measurements were used to characterize the behaviour of X-ray invisible precursors during and just after the flow. For a shear rate of 160 s⁻¹, during flow, the birefringence showed an unusual upswing that was called “threadlike”. The identified threadlike birefringence consisted of oriented molecular segments that did not completely relax or disappear after the cessation of flow. It was hypothesized that the stretched and oriented segments are arranged in locally ordered aggregations that promote nucleation. For the flow with a shear rate of 80 s⁻¹, the accelerated kinetics and orientation of crystalline structures could not be revealed, as the flow-induced ordering was below the detection limit of birefringence. Adopted from the Arabic word for roasted meat, the shish-kebab is a term used to name one of the crystalline structures obtained under flow. The long central core fiber known as shish is surrounded by lamellar crystalline structure known as kebab (Figure 3-7). For high shear rates ranging from 320 to 560 s⁻¹, a narrow FWHM around 4° confirmed that both shish precursors

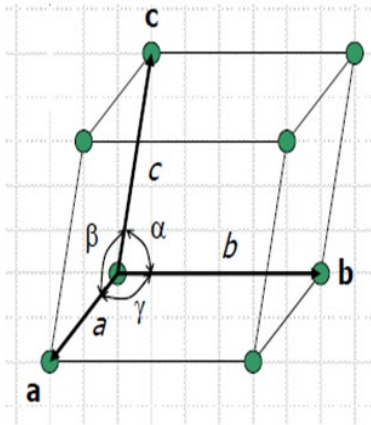
and shish possessed a high orientation with respect to the flow direction. A narrow value of 6° for FWHM was obtained for a shear rate of 160 s^{-1} , demonstrating that the threadlikes were also highly oriented and consistently proved by the birefringence signals. However, as the crystallization proceeded, the FWHM value increased to 9.6° , 11° , and 14.5° for high shear rates 400, 320, and 240 s^{-1} , respectively, showing a low orientation of lamellar structures, thus lowering the degree of crystallinity. For relatively low shear rates of 160 and 80 s^{-1} , the overlapping of daughter and parent lamellae contributed to the lowering of the orientation to the extent that very wide values of 40° and 50° for FWHM were measured. It was concluded that the orientation of the ultimate structure depends on both the orientation of initial nuclei or precursors and the imperfect growth during crystallization. The contribution of curving and twisting to the low average orientation depends on the available lateral space for growth, which is associated with the nucleation density. For higher nucleation density, the average distance between neighbouring nuclei is smaller, leaving less space for lateral growth and, consequently, limiting the possibility for change in lamellar orientation. On the other hand, in the case of a low nucleation density, imperfect lamellar growth may lead to a drastic decrease in the orientation because of significant curving and twisting of lamellar structure [53].

3.2 Polymorphism in crystallization of iPP

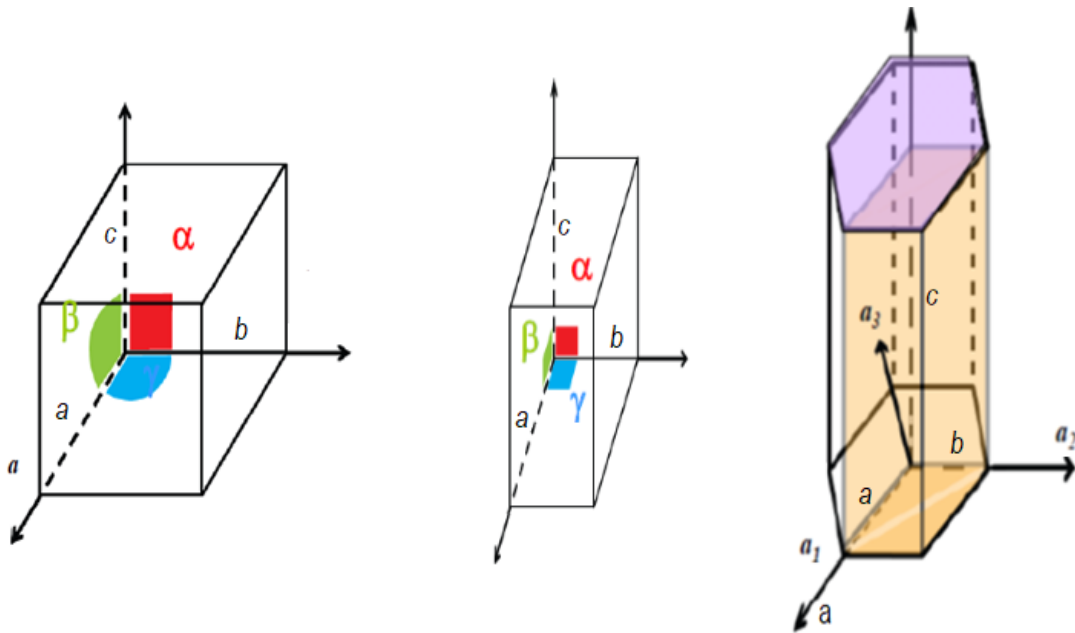
Polymorphism is defined as the ability of a substance to exist in more than one structural form or crystal and is common in semi-crystalline polymers [55]. To optimize the processing conditions for manufacturing products with acceptable physical and mechanical properties, it is crucial to understand the mechanism that governs nucleation and crystal growth in semi-crystalline polymers. Researchers found that polymorphism may be the first reason for the complex melting behaviour of crystalline polymers. Since most semi-crystalline polymers are polymorphic, their thermal and micromechanical properties vary and respond very sensitively to modifying the crystalline structure [38]. Moreover, it was found that the crystallization and annealing temperatures, heating rate, nucleating agent, and other factors could influence the melting temperature of semi-crystalline polymers. The cooling rate influences the crystallization temperature, which, in turn, affects the formation of a specific crystalline morphology. In normal circumstances, a low supercooling rate results in the growth of spherulites with thicker and more perfect lamellar structures that melt at a higher temperature than ones grown at a high supercooling rate.

A three-dimensional (3D) structural arrangement of molecules as points inside the crystal forms a crystal lattice. A unit cell is the smallest repeating 3D structure in a crystal lattice and can be described by the interrelationships between its three edges, a , b , and c , and the relative particular orientation of the edges

characterized by angles α , β , and γ . Depending on external specific conditions such as thermal kinetics, pressure, shearing forces, and addition of nucleating agents, iPP exhibits three main crystalline structures (phases), namely monoclinic-alpha (α), pseudo-hexagonal-beta (β) and triclinic or orthorhombic-gamma (γ). Figure 3-3 shows the geometrical interrelations between linear and angular parameters for the three main crystalline structures of iPP.



A unit cell of a lattice



Monoclinic:

$$a \neq b \neq c$$

$$\alpha = \gamma = 90^\circ; \beta \neq 90^\circ$$

Orthorhombic:

$$a \neq b \neq c$$

$$\alpha = \beta = \gamma = 90^\circ$$

Hexagonal:

$$a = b \neq c$$

$$\alpha = \beta = 90^\circ; \gamma = 120^\circ$$

Figure 3-3: Vectors, edge parameters, and interaxial angles in a unit cell of a crystal lattice [56]

The mesomorphic phase is an intermediate structure between amorphous and crystalline forms, and shish-kebab morphology can also be developed under specific conditions. All the crystalline forms of iPP are

characterized by the same stable helical conformation [55], including three monomeric units in one turn with a periodicity $c = 6.5 \text{ \AA}$ (Figure 3-4).

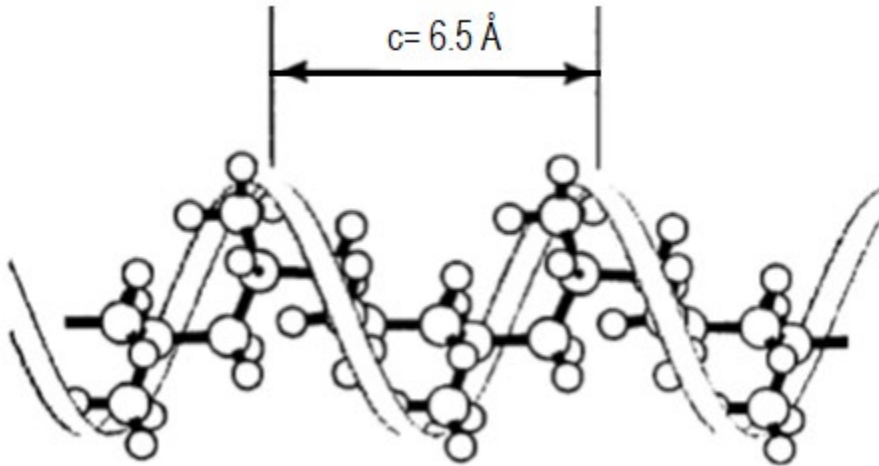


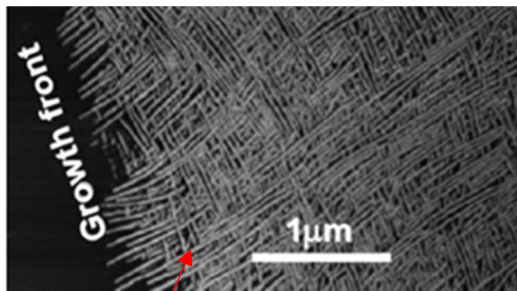
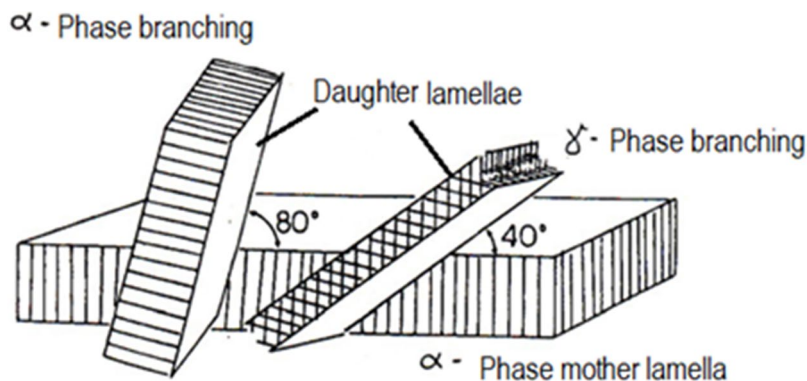
Figure 3-4: Model of the threefold helical chain conformation of iPP in crystalline state [40]

The crystallographic forms characterized by chains with identical conformation packed in different unit cells and/or space group symmetries are known as packing polymorphism [57]. The form of packing determines the nature of the spherulites, which induce the physical and mechanical behaviour of the semi-crystalline polymer at a macroscopic level. In an investigation done by Coulon *et al.* [58] on plasticity and damage mechanisms of iPP spherulites under simple shear, Parenteau *et al.* [59] found the α -spherulites to be brittle, while β -spherulites were ductile up to large strain. Slouf *et al.* [38] established that the microhardness, Young's modulus, storage modulus and yield stress of α -iPP, β -iPP and γ -iPP increased linearly with the overall degree of crystallinity and average lamellae thickness of the semi-crystalline polymer.

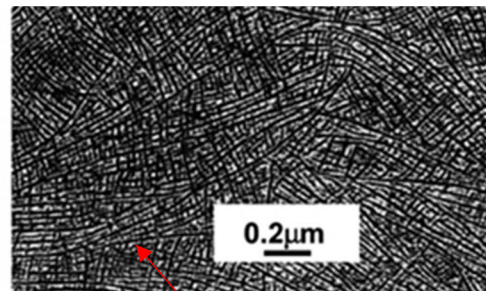
Wide-Angle X-Ray Diffraction or Scattering (WAXD or WAXS) is the most used technique to provide information on the crystallographic structure, atomic position, sizes in a unit cell, and, to some extent, the chemical composition of reactants. The method specifically consists of an analysis of Bragg's peaks scattered to a wide angle 2θ , testifying to the presence of nano-sized crystalline structures.

3.2.1 Formation of monoclinic phase in iPP

The monoclinic α -phase for isotactic PP (α -iPP) is the most common phase with the most thermodynamically stable crystals with the best packing and the highest melting temperature around 165°C. A cross-hatched morphology (Figure 3-5) resulting from initially parent lamellae and late-formed branching daughter lamellae at angles varying from 80 to 90° are distinctive characteristics of α -phase [9], [35], [55], [42].



Cross-hatching lamellar structures of iPP isothermally crystallized at 146 °C



Cross-hatching lamellar structure in a solution cast iPP film at 110 °C

Figure 3-5: Cross-hatching lamellar structures in alpha and gamma phases of iPP. [60], [61].

The structure of α -crystals is maintained at a slow heating rate, and the ambient temperature increases their stability. The spherulites obtained while solidifying iPP in quiescent conditions at a moderate cooling rate are roughly 50% α -crystals crystals and 50% amorphous phase. If the cooling rate is low enough, the resulting spherulites are richer in α -crystals at about 60%, while the amorphous content of spherulite will be lowered

to around 40% [62]. When a non-nucleated iPP is slowly heated to reach a temperature of about 350 °K, the mesophase is transformed into α -crystals with a low enthalpy, thus indicating that the mesophase can be considered as a precursor for α -crystals formation.

The study on the crystallization of iPP showed that heterogeneous nucleation, which dominates at temperatures higher than 320-330 °K was connected to the formation of monoclinic lamellar crystals and the growth of spherulites. Elevated chamber temperature promoted the increase in the size of the spherulites, thus reducing the nucleation growth rate, whereas the low chamber temperature contributed to the small size of the spherulites, consequently promoting more nuclei sites to take place [9].

3.2.2 Formation of pseudo-hexagonal phase in iPP

The application of shear forces, increase of cooling rate, and/ or the addition of β -nucleating agents to the melt of homopolymers causes small changes in the arrangement of α -crystals lattice. Under such conditions, the polymer chains do not have enough time to form the thermodynamically stable α -phase; instead, the formation of a hexagonal β -crystalline phase will result. The morphology precursors of iPP with β -nucleating agents are hexagonites (Figure 3-6c), and two immature structures named “flower-cup-like” and “face-like” (Figure 3-6a and b) are developed at the early stage before a clear spherulite is formed. Hexagonal β -phase crystal is characterized by a low density of packing comparatively to the packing density of α -phase crystals and under specific temperature gradient conditions, β -modification can be considered as one of the stages leading to α -phase formation [63]. The predominance of β -crystals over α -crystals contributes to increasing the elongation at break and impact strength at the expense of reducing the tensile strength and the Young's modulus [64].

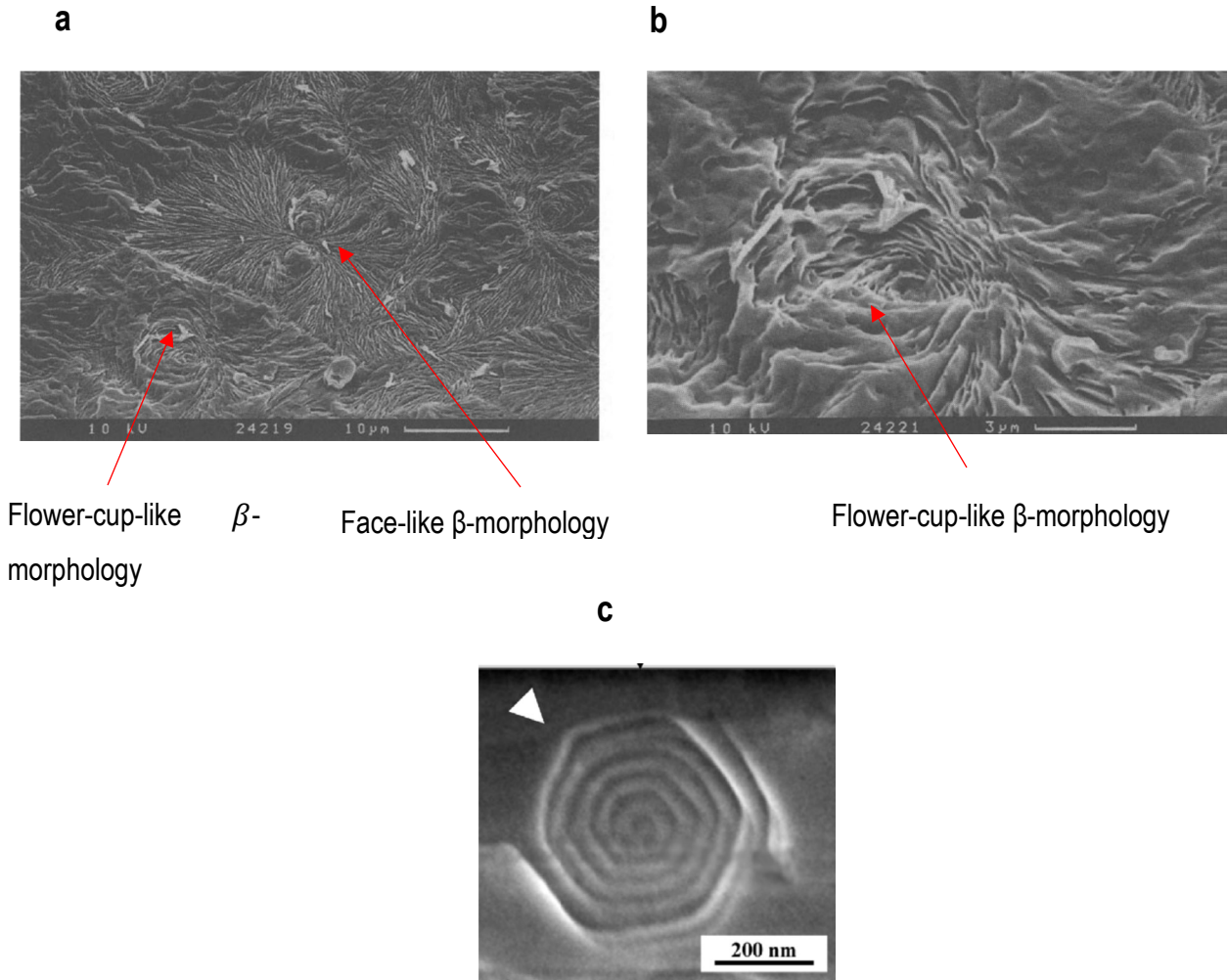


Figure 3-6: Beta morphologies: early formation of face-like and flower-cup-like (a and b) [65]. Hexagonal morphology of crystallized β -iPP with pimelate β -nucleating agents (c) [38]

It has been established that between 105 and 140°C, the growth rate of β -crystals is higher than the α -crystals while formation of the latter morphology is predominant at temperatures below 105°C and above 140°C [42], [66]. The fraction of β -phase in a crystallized mixture from a melt also containing α -phase, depends on the concentration and ability of the nucleating agent to solely induce the growth of β -phase. Contrary to the extrusion process, where sheets of almost pure β -iPP could be successfully formed, based on the previous study [66], Varga and Ehrenstein [65] confirmed that the IM process cannot form pure β -iPP. Bisodium salt of o-phthalic acid, aluminium salt of 6-quinizarin sulfonic acid, isophthalic and terephthalic acids, calcium carboxylates, N, N-dicyclohexyl-2,6-naphthalene dicarboxamide, trans γ -quinacridone, wollastonite,

and calcium pimelate are typical examples of additives that can be used as β -nucleating agents [38], [39], [65], [67].

3.2.3 Formation of mesomorphic phase

The mesomorphic crystalline structure in iPP is a phase with intermediate features to those of crystalline and amorphous states and is obtained when the sample is cooled from a melt at a high cooling rate and formed from about 77 down to 7°C. The rapid cooling prevents the formation of large crystallites, thus reducing the crystalline region, which results in poor alignment of individual crystallites. Due to the high crystallinity of iPP in α , β , or γ phase, the polymer is typically opaque, while the relatively low crystallinity of mesomorphic iPP results in a transparent polymer. The mesophase is metastable at ambient temperature and transformed upon heating into α -crystals while at the same time keeping its initial non-spherulitic superstructure and nodular geometry [39], [68]. The absence of crystallization at a low supercooling rate below 100°Cs⁻¹ is the prerequisite for mesophase formation. It is known that for unmodified iPP, i.e., iPP without any additives, at slow heating at rates lower than about 30°Cs⁻¹, with phase transition beginning at temperatures of about 77–87°C, by local chain organization/removal of helix reversals, the mesophase converts to α -crystals. For standard DSC that applies slow heating rates typically less than 1.0°Cs⁻¹, the mesophase reorganization into crystals appears connected with exothermic heat flow at 87–107°C [52]. Further heating finally leads to the melting of α -crystals starting around 147°C to complete at about 157°C. In the case of unmodified iPP, the cooling rate can be adjusted such that relatively slow crystallization at temperatures higher than 77°C can be suppressed but still permit mesophase formation at high supercooling. On the other hand, for iPP containing a nucleating agent, the suppression of crystallization at higher temperatures due to fast cooling is inevitably connected with the suppression of mesophase formation at low temperatures if the crystallization and ordering time characteristics are closed. Mollova *et al.* [69] concluded that the reorganization of mesophase, which has never been detected before in iPP containing a β -nucleating agent, is not affected by the presence of a β -nucleating agent in iPP melt.

3.2.4 Formation of orthorhombic phase

Unfractionated orthorhombic γ -crystals can be formed in isothermal conditions at elevated pressures and crystallization temperatures or high pressure with low cooling rates (such as 0.1°Cs⁻¹) in copolymers [31, 37, 49]. The γ -structure is the least commonly observed, meaning that is the least understood and develops in low molar mass fractions of polydisperse iPP, in random copolymers with shortened isotactic sequences, or in the presence of high pressure, particularly in the shear region near the gate in IM processes [70]. The γ -

phase is typically formed in conjunction with mixed α -phase spherulites and its predominance depends on molar mass of the polymer and the applied crystallization method. Mollova *et al.* [69] found that the crystallization of iPP into the α - and γ -phases led to a simultaneous occurrence of radially and tangentially aligned lamellae forming a net birefringence of spherulites lower than that of β -crystals that were easily identified by polarizing optical microscopy. The daughter lamellar structures containing γ -phase are known to nucleate and grow upon parent α -phase by epitaxial mechanism, following a specific angle of 40° (Figure 3-5) with respect to the orientation of mother (parent) lamellae. The crystallization of iPP at a high pressure of 300 MPa and kept at 200°C for four hours, followed by cooling to 50°C with a cooling rate of $8^\circ\text{C}/\text{min}$, resulted in the area of γ -lamellae branching at a 40° direction from α -lamellae (Figure 3-5) and zones of non-cross-hatched structures of γ -phase [38].

3.2.5 Formation of shish kebab structures

The application of shear flow enhances crystallization by breaking the kinetic barrier, thus providing extra nucleation sites. The shear flow, which is ever-present in most of the traditional industrial processes of polymers, causes the polymer chains to lose some of their conformation freedom, creating elongated oriented templates that will induce anisotropic lamellar growth. Varga and Karger-Kocsis [71] reported that the shear induced to iPP-row nuclei created by means of fibre pulling could induce crystal modification by initiating the growth of α - and β -phases. The effect of flow on nucleation and growth rates was attributed to an increase of equilibrium melting temperature due to flow. Strong induced flow rate changes the spherulite morphology into fibrillar highly aligned crystalline structures known as shish kebabs [64]. A highly oriented threadlike core composed of extended chains (shish) is first formed and, thereafter, provides a template for the formation and growth of oriented chain folded lamellae (kebabs) [70]. The length per unit volume of shish is assumed to be constant after cessation of the flow. The kebabs, known as parent lamellae, grow radially outward from the shish lamellae backbone. Another type of lamellae, known as daughters, can nucleate and grow on the lateral surface of the parent lamellae. Figure 3-7 illustrates the crystallographic morphology of the parent shish kebabs and the possible development of daughter kebabs.

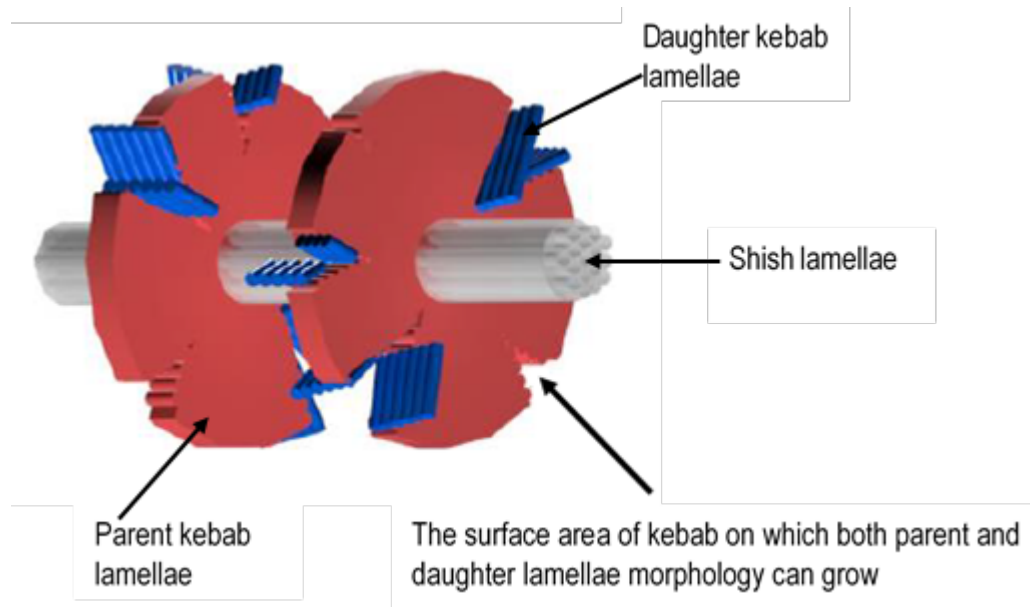


Figure 3-7: Shish kebab lamellae crystalline morphology [72]

Isothermal crystallization consists of a quick cooling of the polymer sample from the molten state to a temperature of measurement followed by the measurement of the development of crystallinity at a constant temperature. For a quiescent isothermal crystallization, the ratio between parent and daughter lamellae in iPP depends on crystallization temperature: few daughter lamellae are formed with increasing crystallization temperature [66]. Contrary to the previous explanations on the dependency of parent/daughter ratio in iPP, suggesting that the growth of parent lamellae is preferential during flow, this study could show that the amount of parent lamellae formed during the flow is too little to vary the final ratio significantly. The different growth rates of parent and daughter lamellae are conditioned by the fact that the two lamellae experience different molecular orientations.

The radius of the shish is about 10 nm, while the radius of the shish kebab can grow up to about 100 nm [72]. More significant flow-induced effects can be attained by raising the temperature to just below or even slightly above the nominal crystal melting temperature [41]. The combined effect of strong shear flow and pressure leads to the formation of a shish-kebab crystalline structure composed of both α - and γ -phases. Under flow, the strained segments crystallize forming an extended chain of shish backbone of α -phase, while the less oriented γ -phase chains crystallize into parent kebabs growing perpendicular to the surface of the shish. The parent kebabs are oriented parallel to the flow direction while the daughter lamellae grow epitaxially on the developed parent lamellae being oriented at an angle varying from 80 to 100° relatively to the direction of the induced shear flow [55].

Conclusions

1. Semi-crystalline polymers are characterized by the crystallization process, which consists of multiple mechanisms of the birth (nucleation) and growth of crystals when the polymer melt is subjected to cooling.
2. Heterogeneous nucleation, which often happens, is promoted by the pre-existence of foreign substances (additives, contaminants, catalyst residues, and dormant precursors) and foreign surfaces.
3. The homogeneous nucleation, which rarely occurs, is governed by the competition between bulk- and surface-free energy changes ΔG_b and ΔG_s , respectively. The bulk-free energy change should overcome the surface-free energy change to generate stable nuclei.
4. The cooling rate, pressure, and shear flow applied on the polymer melt determine the crystalline morphology resulting from the crystallization process. The crystallization of iPP can lead to five crystalline morphologies: monoclinic α , pseudo-hexagonal β , orthorhombic γ , mesomorphic, and shish kebab phases.
5. The position and role of PP in polymer AM, specifically in the L-PBF technological process, will be the focus of the next chapter.

CHAPTER 4: POLYPROPYLENE AND LASER POWDER BED FUSION

4.1 AM in the global production market

The Fourth Industrial Revolution (IR 4.0 or 4-IR) represents the integration of cyber and physical systems focusing on digitalization leading to intelligent automation for smart sustainable manufacturing industry. AM with its capability to digitalize and automate the manufacturing of physical functional mechanical parts is one of the vital components of 4-IR [73], [74]. The worldwide market for AM products and services grew exponentially to the extent that a global market value of more than US\$ 21 billion was expected for 2020 [75]. However, the COVID-19 global pandemic also negatively impacted this industry, resulting in an estimated average value of US\$ 12.6 billion (Figure 4-1) by 2020. A Compound Annual Growth Rate (CAGR) of 17% is expected, likely resulting in a global market value of US\$ 37.2 billion by 2026 [76].

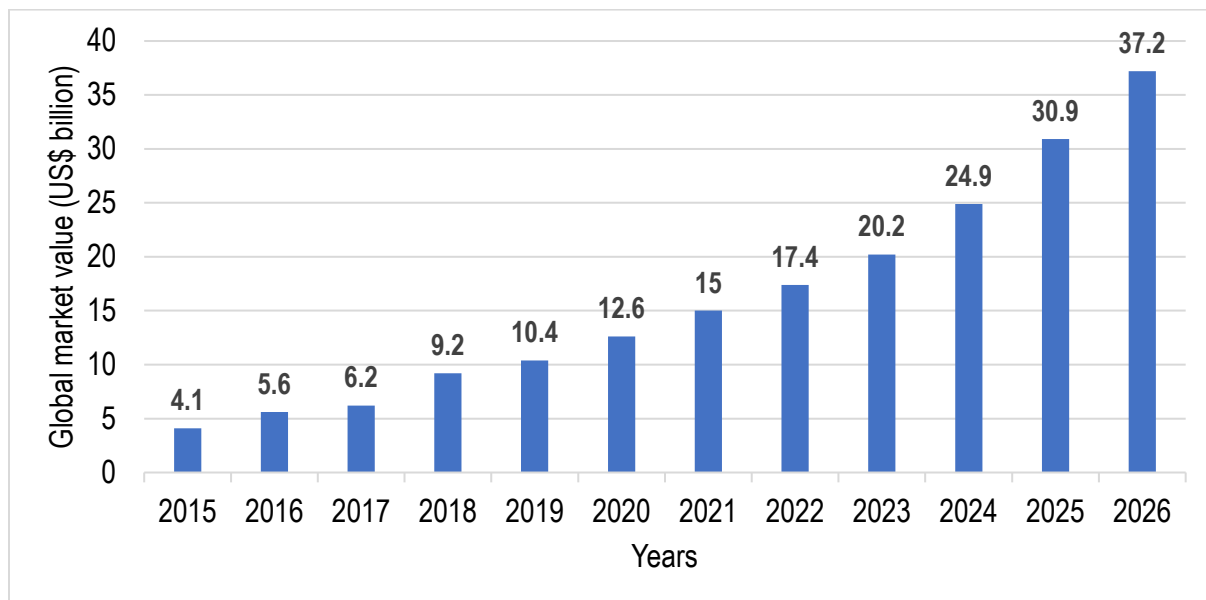


Figure 4-1: Forecast revenue for all AM global market [76]

Polymers, ceramics, and metals are used in AM technologies, and it is projected that polymeric materials, representing the largest share of 82% of the total 3D printing market, will continue to lead through 2023 [77], [78]. On the other hand, there is a significant gap between the sold volume of polymeric powder for AM processes and the sold volume of polymers for conventional manufacturing. Schmid and Wegener [79]

reported that the global market of polymeric powder for the L-PBF process consisted of a small share of 1900 tons per year, contrasting to an annual high volume of about 290×10^6 tons of the global total consumption of plastics. Each kilogram of marketed polymeric powder for the L-PBF process was estimated to correspond to 200 tons of plastic materials involved in conventional manufacturing [80]. Tan *et al.* [81] mentioned that a significant share, estimated to be 90% of the global polymer market, is used for commodities, whereas only a small portion of less than 5% of the product is produced through L-PBF. Kusoglu *et al.* [82] conducted quantitative research on the L-PBF of polymers and linked the polymer feedstock and their frequency (number) of occurrence over a period ranging from 2009 to 2019, as published works or cited articles in scientific journals and/or conference proceedings (Figure 4-2).

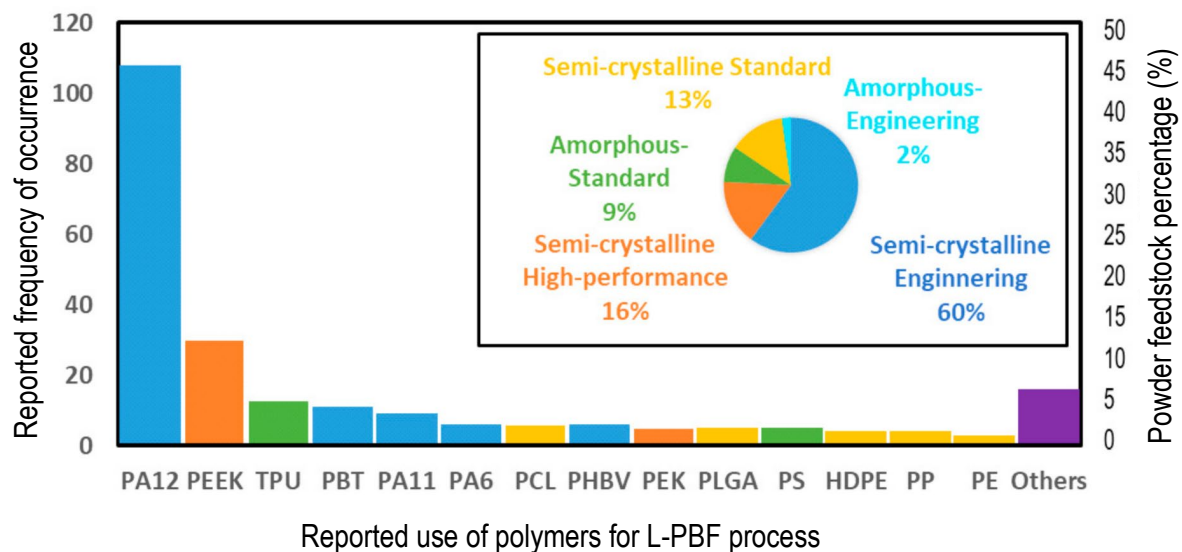


Figure 4-2: Global market share distribution of L-PBF of polymeric materials [82]

Other reported polymers included Polyoxymethylene (POM), Polyurethane (PU), Polyamide 12-Polyethylene glycol (PA12-PEG) blend, Polyamide 12-Polyvinyl acetate (PA12-PVA) blend, Polyetherketoneketone (PEKK), Poly (Methyl) Methacrylate (PMMA), cellulose-acetate and starch-cellulose. It can be observed that the number of published articles together with the number of citations for PA12 was around 110 times, whereas for PP, only around five publications together with citations could be recorded. On the other hand, the powder feedstock produced for PA12 could take a share of about 45%, contrasting with a very small share of about 2% for PP.

4.2 AM processes and technologies

Traditional fabrication methods use subtractive manufacturing and/or formative processes to obtain the desired component geometry. Subtractive manufacturing processes remove unwanted materials through the relative motion between the raw material and a cutting tool. The formative processes involve the filling of the material into cavities defined by moulds such as IM or the deformation of the raw material through the application of thermal and mechanical loads to obtain the final desired shape of the product, such as blow moulding.

AM, also known as 3D printing, consists of processes and technologies that create the desired geometry of a solid component from 3D model data. This is usually achieved by gradually adding and joining 2D layers one atop each other, as opposed to subtractive and formative methodologies until the building of the entire part is completed. Historically, terminologies such as additive fabrication, additive process, additive technique, additive layer manufacturing, layer manufacturing, solid freeform fabrication, and freeform fabrication have been interchangeably used to signify AM equally [1], [83]. Figure 4-3 shows seven categories [84], [85] of AM processes as classified by the technical committee F42 of the American Society for Testing and Materials (ASTM International).

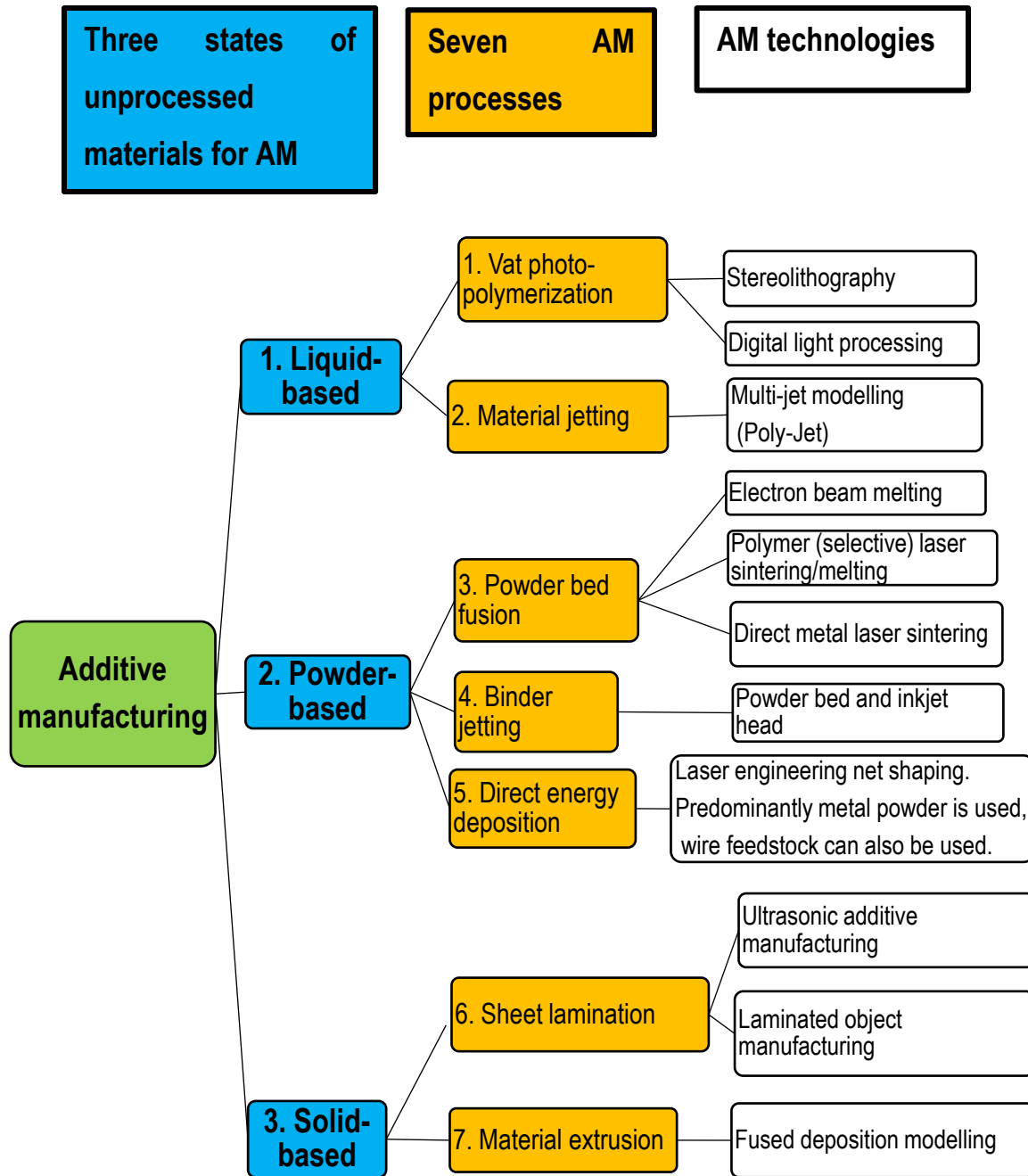


Figure 4-3: Classification of AM processes, unprocessed base materials, and related technologies

In this study, the focus will be on PBF, specifically L-PBF. According to ASTM/ISO 52900 [1], PBF is defined as an AM process in which thermal energy fuses regions of a powder bed. The L-PBF of polymer feedstock

is defined as an AM process that leads to the fabrication of polymer parts using a laser beam to sinter the powder [82].

The L-PBF process of polymers is described by four main steps as follows:

1. **Modelling and slicing of the parts:** The 3D model of the part is designed using engineering computer-aided design (CAD) software such as SolidWorks, Pro-engineer, or Catia. The CAD model is converted into standard tessellation language (STL) format, which allows the slicing of the 3D model into 2D layers.
2. **Fabrication of the parts:** The powder stored in the supply bins is delivered to the recoater (Figure 4-4). The to-and-fro horizontal movement of the recoater delivers and facilitates the even spreading of the powder to form the first 2D layer of a defined thickness on the platform of the building chamber.

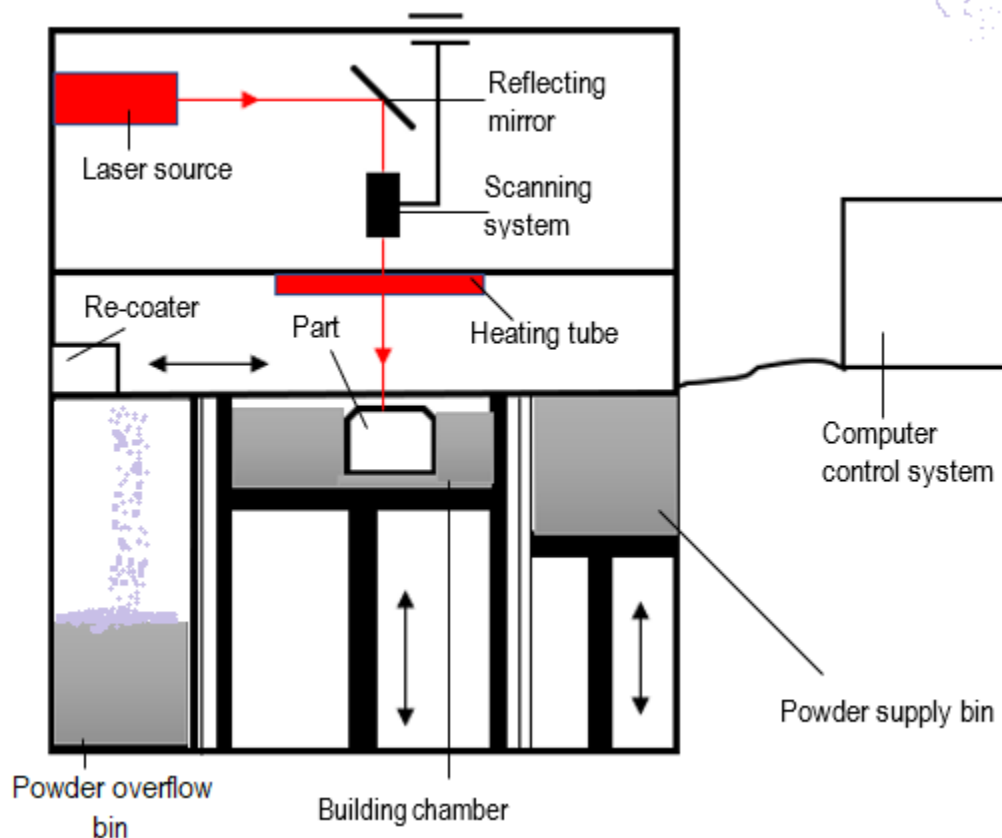


Figure 4-4: Layout of machine for L-PBF process

For semi-crystalline polymers, the building chamber is preheated for a period extending to one hour or more to a temperature above crystallization temperature and just below their melting point. The preheating is required to reduce the temperature gradient during the heating and cooling of each deposited layer to minimize the residual stresses in the sintered powder, thus avoiding curling or warping of the built part. Warping or plastic deformation of the sintered part occurs when the residual stresses exceed the yield stresses of the material of the powder, whereas cracking may result if the residual stresses are greater than the local ultimate tensile strength of the material [86]. In some L-PBF processes, infrared heaters or built-in resistive heaters in the build platform are used to maintain the temperature of the powder just below the glass transition temperature, which is an advantage in reducing the amount of laser energy required for fusion of the powder [87]. The spread powder forming the top layer is also preheated on the platform before being selectively fused or sintered by the laser energy according to digital data of the cross-section of the sliced CAD model. When the required preheating temperature of the top layer powder is attained, the computer control system controls the movement of the laser to sinter the surface powder, followed by the solidification of the fused powder [88]. After the sintering of each layer, the building platform is lowered through a height distance equal to the layer thickness to allow the deposition of a new layer. The process of depositing one layer atop another, followed by their subsequent fusion, is repeated until a 3D physical part is additively manufactured.

3. **Cooling of the built part:** After the fabrication is finished, the solidified part and the surrounding supporting cake powder are allowed to cool down to room temperature in a controlled manner to prevent curling and warping of the part.
4. **Removing, cleaning, and post-processing:** The part is removed from the building chamber and cleaned from the cake powder. The cleaned part may be subjected to post-processing techniques to improve the surface finish, dimensional accuracy, and mechanical properties.

4.3 Crystallization in the polymer AM processes

Crystallization can be defined as a process where the polymeric melt partially solidifies under cooling, thus resulting in a specific spatial arrangement of molecular chains in the polymer. At the beginning of crystallization, the polymer remains viscous. During crystal growth, molecular mobility is prevented since the crystallized area reduces the chain movement, and the material can be considered viscoelastic solid as opposed to viscoelastic fluid. The transition temperature between the two states, also known as the cross-

over point, serves as a reference temperature below which the viscoelastic behaviour is dominated by the elastic behaviour of the material. The polymer in a viscoelastic solid state is characterized by an incomplete and progressing crystallization process [89].

Material extrusion, commercially known as Fused Deposition Modelling (FDM), is an extrusion AM technology that uses polymeric filament to produce parts with mechanical properties comparable to their counterparts obtained through IM. Amorphous polymers such as ABS, PLA, PC, and Polystyrene PS are frequently used for FDM and are not often processed through L-PBF due to associated difficulties in producing suitable powder. Amorphous polymers are characterized by a low degree of crystallinity and low coefficient of thermal expansion, which makes their AM processability easy, thus producing parts with low shrinkage and warpage defects during the solidification process upon cooling. However, their main drawbacks are their relative brittleness, a high tendency to degrade in chemically aggressive environments, and a narrow temperature range of their application for engineering purposes. In contrast, semi-crystalline polymers such as LDPE, LLDPE, HDPE, Ultra-High Molecular Weight Polyethylene (UHMWPE), Polyoxymethylene homopolymer, Polytetrafluoroethylene (PTFE), and PP possess better physical and chemical resisting properties. Semicrystalline polymers are characterized by a high degree of crystallinity greater than 40%, thus rendering their AM processability difficult through L-PBF, which is prone to produce parts with high shrinkage, warpage, and distortion [9], [42].

In addition to processing parameters, the quality of laser-sintered polymeric parts is influenced by intrinsic and extrinsic material properties. The intrinsic polymer properties are defined by the choice of the polymer grade or preferably by a customized formulation of the polymer chains and architecture via chemistry. The extrinsic properties of the material are associated with the mechanisms used to obtain the shape and size of the powder particles. Adapted from Schmid, Amado, and Wegener [90], Kleijnen, Schmid, and Wegener [91] showed interrelations of components involving intrinsic and extrinsic properties of the powder for laser sintering, as illustrated by Figure 4-5.

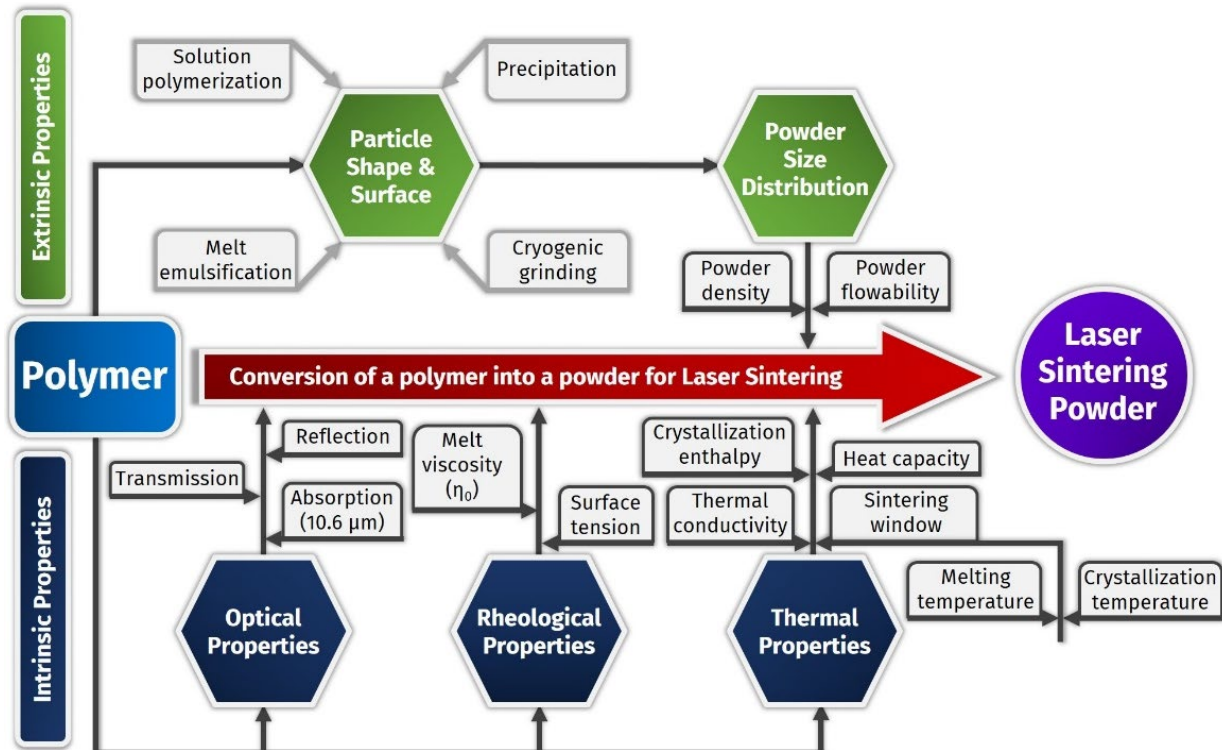


Figure 4-5: Interrelationships between intrinsic and extrinsic properties of powder for L-PBF [91]

The degree of crystallinity is an intrinsic property of the material that significantly affects the level of shrinkage and warpage of semi-crystalline polymers during AM processes. As the molten polymer is below its melting temperature, the nucleation and growth of polymer crystals are initiated with a subsequent formation of zones of ordered oriented molecular chains. The repeated rapid heating and cooling of the layers through the movement of the recoater induces complex temperature conditions during L-PBF. The printed part is exposed to a rather inhomogeneous temperature distribution, resulting in internal stresses occurring in the growing of crystals, which can cause part deformation. Therefore, the temperature variation during L-PBF of PP powder does not only define the interfusion depth with implications on mechanical properties through the raising of thermally induced residual stresses but also influences the growth of different crystalline morphologies influencing the warpage and shrinkage behaviour of the printed part. The higher the processing or melting temperature, the longer time is required to cool down the polymer, thus lowering the cooling rate and consequently enhancing the formation of a crystalline structure during processing, making the parts produced less vulnerable to post-building deformation. A prolonged cooling period under a slow cooling rate at the end of L-PBF promotes more growth of crystals compared to the IM process, where the melted polymer is quickly

cooled inside the mould before it is ejected. For PBF processes with semi-crystalline polymers, the preheating of the polymeric powder inside the processing chamber to a temperature slightly below its melting point and maintaining it for a period extending to two hours is the practice used to minimize the level of warpage and shrinkage of laser-sintered parts. The preheating reduces the temperature differences, thus improving the thermal conductivity of the powder [30].

Hämäläinen [43] found that during FDM of PE and PP with the same deposition temperature, the additional heat supplied from the build platform and build chamber reduced the cooling rate, thus keeping the average temperature of the part higher, allowing crystallization during processing. Furthermore, the tensile test conducted on both materials showed that the slow cooling rate led to an improved degree of necking for PE compared to PP specimens due to the melting point of PE, which is 30 °C lower than that of PP. On the other hand, a high cooling rate eliminates the crystallization process by shifting the crystallization onset temperature towards a lower temperature, thus lowering the degree of crystallinity, making the parts less prone to post-building shrinkage and warping. For the FDM process, it was reported that additional cooling during deposition suppresses the crystallization and can lead to parts with metastable morphology with higher specific volumes [43].

Comparing experimental and mathematical modelling results in the prediction of residual stress and part warpage in the FDM process applied to PP copolymer, Watanabe *et al.* [92] found in both cases that the temperature of the first layer decayed exponentially and could only stabilize after a fraction of a second. Though the variation of the deposition temperature did not significantly influence the amount of warpage, it was revealed that with lower deposition speed, a longer time was required to complete one layer, thus leading to a large temperature gradient within the layer and, therefore, high warpage. On the other hand, with high deposition speed, a shorter time is needed to complete the layer, causing a slight temperature gradient and, therefore, decreasing the amount of the warpage of the printed part [92].

4.4 Flowability and window of sinterability of PP powder for the L-PBF process

An ideal powder for L-PBF should have particles of high sphericity to facilitate the flow of the powder during the recoating process and to reduce the surface-area-to-volume ratio, which improves the packing efficiency. Poor flowability and low bulk density are detrimental factors for the L-PBF process. They can cause inhomogeneous deposition of the powder during the recoating stage, thus resulting in parts with high levels of porosity, poor surface finish, dimensional inaccuracy, and reduced mechanical properties. Spherical,

potato, and irregular shapes (Figure 4-6) are three primary morphologies of powder particles identified by Schmid *et al.* [90] while investigating the flowability of nylon and PP powders for LS.

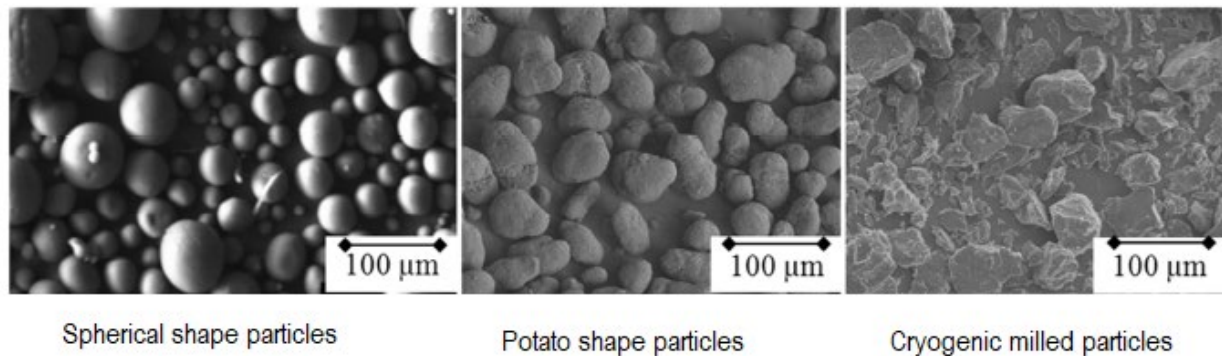


Figure 4-6: Morphologies of powder particles [93].

Commercialized PA12 powder for L-PBF, obtained by precipitation, is a typical example of potato-shaped morphology. Particles with irregular shapes obtained from cryogenic grinding and solid-state shear pulverization of granules can also be used despite the difficulties of easy flow during powder recoating [5].

4.4.1 Measurement of the powder flowability

The Hausner Ratio (HR) is one of the methods used to measure the powder flowability or the level of interparticle interaction. More significant interparticle interaction characterizes a poor-flowing powder, while the interparticle interaction will be less significant for a free-flowing powder. The HR, a ratio between the tapped (or packed) density and the bulk free-flowing untapped density of the powder, is evaluated following the ASTM D748 standard. The HR is not an absolute property of the material as it may depend on the number of taps, filling procedure, used volume, or geometry of the device. It is adopted that a powder with an HR less than 1.25 is expected to have good flowability, while a powder with an HR value greater than 1.4 is considered to be cohesive with very poor flowability [91], [94]. For good flowability and acceptable mechanical properties, powders of spherical shape and an average particle size of around 50 µm are desirable for the polymer PBF processes. Laser sintering of powders with large particle sizes may result in parts of low mechanical properties due to the increased number of large pores and high surface roughness, which can require additional surface finish post-processing techniques. On the other hand, if a significant portion of powder is dominated by particles of very small size, less than 15 µm in diameter, good flowability is prevented by the tendency of the small particles to stick together. Such behaviour leads to difficulties in dispensing the new layer on the top of the previously sintered layer, thus causing fissures and gashes in the top surface of the

part as high friction among extremely small particles results in big in-plane shear forces. Moreover, under the same thermal processing conditions, unwanted sintering of too small particles is expected as such particles sinter to each other at a higher rate comparatively to the sintering rate of relatively large particles. Unwanted sintering of ultrafine particles make it difficult to remove the built part from the cake powder. This leads to possible loss of definition and resolution of the laser-sintered parts in terms of dimensional accuracy and surface finish, especially for sharp edges, corners, and small features. A non-uniform spreading of the powder and incorrect setting of the build chamber temperature will lead to a premature curling of the part, causing the recoater to dislodge the affected parts from the powder bed. In such cases, the building process must be stopped and restarted again with adjusted process parameters settings. The action of the recoater blade can also introduce electrostatic charges to the powder, thus favouring the agglomerations of powder particles which hinders a uniform flow of the powder. The addition of anti-static agents such as carbon black, graphene nanotube, glassy oxides, fluoroplastics, metallic stearates or silica to reduce the contact areas between powder particles, thus limiting interparticle attractive forces is recommended to achieve an even spreading of the powder. The possibility of lowering the mechanical properties of the laser-sintered parts is the main drawback of adding the flow and/or antistatic agents to the powder; hence, their volume fraction should be limited from 0.05 to 0.5% [3], [95].

4.4.2 Window of sinterability of polymeric powder for the L-PBF process

The window of sinterability, also commonly known as the processing window (as described in Section 2.3), is defined as the difference between the onset melting (T_m -onset) and the initial onset crystallization (T_c -onset) temperatures [80]. In L-PBF of semi-crystalline polymers, for a full coalescence of polymer particles in the top powder layer as well as its adhesion with previous sintered layers, the crystallization temperature should be inhibited during processing as far as possible, at least for several sintered layers, meaning that the processing temperature must be controlled within the processing window. If the bed sintering temperature is too low or close to peak crystallization temperature, curling due to premature crystallization is induced, resulting in the accumulation of residual stresses in the parts, leading to their distortion after release from the surrounding powder bed. On the other hand, a high bed processing temperature too close to the peak melting temperature will lead to powder caking, resulting in a loss of the exact definition of the small features of the parts. The powder particles, located in the direct neighbourhood of the laser, stick on the molten surfaces and prevent the desired resolution of the part topography [79], [81].

The concept of a window of sinterability cannot be applied to amorphous polymers as they do not experience a suddenly defined melting point or undergo a crystallization process. Amorphous polymers are laser sintered by heating the powder at temperatures higher than their glass transition temperature [3]. The absence of the window of sinterability in three semi-crystalline commercial polymeric powders, namely poly aryl ether ketone (PEK) HP3, poly ether ether ketone (PEEK) 150PF, and PEEK 450PF, was reported by Berretta *et al.* [96]. For such semi-crystalline polymers, a very narrow processing window or a practical absence of a window of sinterability is caused by the lack of a practical difference between the onset melting and the initial onset crystallization temperatures when the polymer is subjected to continuous heating beyond its melting point followed by cooling to room temperature. Despite the difficulties in controlling the processing temperature within a too-narrow range, a trial-and-error approach can still be taken for the L-PBF of these semi-crystalline and amorphous polymers [96].

The melting and cooling process of semi-crystalline polymers presents two sharp peaks representing the endothermic melting and exothermic crystallization phases of the materials. The presence of the two distinct temperature peaks promotes an efficient control of the processing temperature during the L-PBF process. In contrast, the melting and cooling process of amorphous polymers does not show distinct transitions, which renders their temperature control during PBF more complex [97].

DSC (as described in Section 2.3) is a thermal analysis method that measures the difference between the rate of heat flow into a specimen and a reference specimen as a function of temperature and/or time. Since the main stages in LS of polymers involve heating of the material from ambient temperature to just below the melting temperature to allow sintering and then cooling back down to room temperature for consolidation of the part, DSC is used to determine the window of sinterability of polymeric powders for L-PBF. The building of the part through L-PBF of the powder is considered a quasi-isothermal process. Therefore, under nitrogen atmosphere, according to DIN EN ISO 11357 standard as used in [98], the heating and cooling rate of 10°C/min. or 10°K/min. can be used to generate DSC curves to determine the suitable sinterability window [31]. The powder is heated and then cooled to a bed temperature maintained within the sintering window for a relatively long period, varying from two to three hours. However, as the crystallization temperature depends on the cooling rates used, crystallization may take place even if the bed temperature is set above the onset standard crystallization temperature, meaning that through trial and error, the bed processing temperature

must be customized to the particular powder used, machine and surrounding environmental thermal conditions.

Using DSC analysis, Fiedler *et al.* [99] conducted a comparative study on the window of sinterability and the degree of crystallinity of nylon PA grades and a series of homopolymer and copolymer PP grades. It was found that the window of sinterability of all considered PP grades was in the same range or sometimes even better than the window of sinterability of the PA references. On the other hand, the DSC analysis of PP grades showed that the degree of crystallinity exceeded the values degree of crystallinity of PA grades by about 100%, resulting in a high degree of shrinkage of the laser-sintered PP parts. To avoid excessive shrinkage, it was suggested that the chemical structure of PP materials should be modified to decrease the crystallinity or to fill the PP material with reinforcing fillers. DSC analysis conducted on commercial PP and Polyethylene (PE) grades showed that the sintering window of PP can cover a range of as much as 35.1°C, while a too-narrow sintering window of only 7°C for PE grade was measured. The DSC analysis conducted by Ituarte, Wiikinkoski, and Jansson [80] on a neat PP Coathylene®, mechanically mixed with 0.25 wt.% nano-SiO₂ fillers, showed a sinterability window of 35.1°C for the composite with a melting peak of 167.1°C and a degree of crystallinity of 39.58%.

Wudy *et al.* [98] investigated the water adsorption of specimens obtained through L-PBF of PP coathylene PD0580 powder of irregular shape with an average particle size of 62 µm, filled with the spherical shape of 15 µm size obtained through spray agglomerated zeolite particles in a matrix of polyvinyl alcohol binder. They found a processing window within a range of 127 and 156°C, meaning a sinterability window equal to 29°C with the bed temperature set at 155°C. Considering three weight ratios of PP/zeolite, i.e., 70/30, 60/40, and 50/50, the DSC analysis showed that the filling of zeolite into a PP matrix resulted in the appearance of second endothermic peaks at 78.4, 84.4, and 86.2°C, respectively, while the melting peak for all three composites was almost the same at 163°C. The second peak that shifted to a higher temperature with the increase in the fraction of zeolite was caused by the evaporation of absorbed water from the zeolite phase. During the second heating process, it could be concluded that the zeolite concentration had no significant influence on the recorded crystallization temperature of around 123°C for the pure PP in all three mixtures. Fang, Wang, and Xu [100] used the dissolution-precipitation method to produce PP powder by dissolving PP resin in Xylene. Spherical-shaped powder with an average size of about 42.7 µm was obtained, and DSC analysis showed a sintering window of 19.5°C. The processing parameters for the laser-sintered

specimens were optimized, and the tensile strength and impact strength of 27.9 MPa and 6.3 kJ/m², respectively, were very close to the tensile and impact strength of 28.7 MPa and 6.5 kJ/m² obtained for their counterparts processed through IM.

Tan *et al.* [81] carried out a comparative study between L-PBF and IM of three semi-crystalline polymeric powders, namely, iPP homopolymer, propylene-ethylene random copolymer (CoPP), and polyamide 12 (PA12) commercially designated as PP CP 20, PP CP 60 and PA2200, respectively. Polypropylene powders PP CP 20 and PP CP 60 were supplied by Diamond Plastics GmbH, while the polyamide 12 (PA12) powder was purchased from EOS GmbH. The flowability of the powders evaluated using HR measurements were 1.28, 1.22, and 1.13 for iPP homopolymer, CoPP, and PA12, respectively, indicating that PA12 would flow better than CoPP, which, in turn, is improved compared to iPP homopolymer. During the printing process, the flowability of iPP powder was significantly poorer than that of CoPP, to the extent that the iPP powder could not easily flow from the hopper, which resulted in a visibly rougher surface of laser-sintered powder. The processability of powders was further characterized using thermal analyses such as DSC and thermogravimetry (TG). To determine the window of sinterability and the suitable bed temperature, using different sets of four isothermal crystallization temperatures for each polymeric powder, DSC analyses found 26.3°C, 2.2°C, and 25.8°C as processing windows for iPP, CoPP, and PA12, respectively, corresponding to suitable bed temperature greater than 146°C, 123°C and 170°C. These findings suggest that, despite a low HR of 1.22, less than 1.25, the processing of propylene-ethylene random copolymer (CoPP) powder with a very narrow sinterability window of 2.2°C will be difficult compared to iPP and PA12 with a similar wide processing window that can be approximated to 26°C.

4.4.3 Effect of melt viscosity and crystallization activation energy

The Melt Flow Rate (MFR) is another measurement that reflects the easy flow of the molten polymer and depends mainly on molecular weight, molecular weight distribution, and branching characteristics such as the degree of branching and its distribution frequency in the polymer chains. A polymer with a high molecular weight exhibits a high melt viscosity and a low MFR, while a polymer with a low molecular weight is characterized by a low melt viscosity, implying a high MFR. Abbas-Abadi, Haghighi, and Yaganeh [144] found that PP and PE grades with medium or low MFR required more activation energy for their thermal degradation, thus resulting in greater thermal stability.

A good coalescence of particles, which leads to good interlayer adhesion, is influenced by the melt viscosity of the polymeric powder. A low viscosity promotes good coalescence, resulting in quick sintering of particles,

causing the filling of inter-particle gaps [101] and parts built with reduced mechanical properties and prone to warpage and shrinkage. On the other hand, the high melt viscosity of high molecular weight polymer hinders a good coalescence, thus slowing the sintering of the powder, promoting the building of parts with enhanced mechanical performances and dimensional accuracy [96]. While the good coalescence for PA12 was in agreement with its wide sintering window and measured melt viscosity of about 400 Pa.s, Tan *et al.* [81] observed a poor coalescence with PBF of iPP as a result of poor flowability rather than the effect of viscosity. At 25°C above their respective melting temperature, iPP, with a lower melt viscosity of 237 Pa.s, was expected to show better coalescence than CoPP, with a higher melt viscosity of 1481.3 Pa.s. However, it was likely, that the measured HR of 1.28, greater than 1.25, was the main contributing factor to the poor flowability of the iPP powder.

Besides the sintering window, the crystallization activation energy E_A is another factor that governs the level of warpage for laser-sintered parts. The crystallization activation energy determines the sensitivity and dependence of the crystallization rates (or nucleation rates) of a polymer on temperature variations. Polymers with higher amounts of activation energy are prone to fast nucleation - even at temperatures below their theoretical crystallization temperature, thus rendering them difficult to process using L-PBF with the expectation of producing warped parts [81], [102]. Activation energies were evaluated to be 300.7 kJ/mol, 306 kJ/mol, and 501.0 kJ/mol for iPP, CoPP, and PA12, respectively, implying the temperature variations in proximity of the crystallization temperature will less affect iPP and CoPP. In contrast, for PA12, such variations will be accompanied by adverse effects of greater magnitude. With the exception of laser-sintered CoPP specimens, where XRD showed the predominance of γ -phase mainly due to the presence of ethylene as revealed by FTIR analysis, XRD showed that α -phase was predominant in iPP and CoPP powders, injection-moulded iPP and CoPP specimens, and in iPP laser-sintered specimens.

The process parameters for L-PBF were optimized to achieve energy densities of 0.167 J/mm³ and 0.138 J/mm³ for iPP and CoPP, respectively. The optimal values for Ultimate Tensile Strength (UTS) and Elongation at Break (EAB) were 14.9 MPa and 1%, and 19.5 MPa and 207% for iPP and CoPP, respectively. On the other hand, the injection-moulded specimens displayed better average values for UTS and EAB at 38 MPa and 11.3%, and 31 MPa and 951% for iPP and CoPP, respectively. The decrease of the EAB for laser-sintered specimens is explained by the promotion of the formation of larger crystals due to slow cooling instead of rapid cooling, which characterizes the IM process. Despite the relatively weak mechanical properties of laser-sintered specimens, it was concluded that LS is an alternative to produce PP parts with

γ -crystals, which is not easily achieved under typical IM conditions, especially when using PP powder that presents high structural irregularities.

4.5 Effect of fillers and compatibilizers on mechanical properties and warpage control

4.5.1 Introduction

As long as the temperature is above the glass transition point, the free volume between the molecular chains and the vibrational volume decreases when the polymer melts and cools down. The combined effect of both linear volumetric and crystallization shrinkages controls the total shrinkage of semicrystalline polymers when cooled down for solidification. Shrinkage and warpage are well-known as the main drawbacks of using PP in traditional manufacturing and AM processes due to its high level of crystallinity, especially when the fraction of α -crystals is high in neat, unmodified PP [9]. The failure to attain an equilibrium crystalline state due to a low crystallization rate may induce post-shrinkage that can last several weeks at room temperature before the part reaches its final dimensional stability [8], [9], [43], [103], [92], [104]. The use of fillers and compatibilizers is one of the strategies to reduce the amount of chain orientation and consequently decrease the shrinkage and warpage of parts produced in PP. Glass, mica, calcium carbonate, silicates, cellulose, cellulose nanofibrils, thermotropic liquid crystalline fibrils, bamboo fibrils, hemp, harakeke fibres, ash, mineral fibres, short glass fibres, perlites, inorganic soda lime glass, talc, wollastonite, carbon black, and carbon nanotubes (CNT) are widely used as reinforcing fillers in commercialized thermoplastics to enhance their physical and mechanical properties. Adding fillers such as graphite, carbon black, CNT, and carbon fibres to insulating polymers induces thermal and electrical conductivity in the resulting polymer composites [105].

4.5.2 Use of fillers and compatibilizers for PP powder for the PBF process

In heterogeneous polymeric mixtures, compatibilization is a technological process to enhance the blend properties while improving adhesion between phases. The use of compatibilizers allows a decrease in interfacial tension between the phases through the facilitation of the formation and stability of co-continuous structures, thus decreasing the mobility of the interface, also called the Marangoni effect [106], [107], [108]. Maleic anhydride polypropylene (MAPP) with a density of 0.91 g/cm³ and Melt Flow Index (MFI) of 115 g/10 min. (190 °C, 2.16 kg) is a compatibilizer and a nucleating agent for iPP. MAPP is known to improve the compatibility between iPP and the fillers by creating a better distribution of the fillers into the PP matrix during the FDM AM process [46].

To produce solid, dense parts, Greiner *et al.* [109] recommended the use of compatibilizers in the powder of a partially miscible blend of Polybutylene terephthalate (PBT) and PC prepared for L-PBF [109]. Drummer *et al.* [110] also realized that the mechanical properties of parts produced through L-PBF of the powder obtained by mixing two immiscible polymers, i.e., PA12 and PP, could have been improved by adding MAPP compatibilizer to the blend. For the L-PBF process, Jiang *et al.* [111] prepared a composite powder based on Polyether-Sulphone (PES) filled with PP, wood flour particles and compatibilized by MAPP. The addition of PP grafting maleic anhydride acted as a coupling agent to form stronger chemical bonds between the wood flour, PES, and PP. This combination resulted in laser sintering of parts with improved dimensional accuracy with a relative warpage rate of 0.26%, tensile strength of 0.014 MPa, and impact strength of 0.954 kJ/m². A SEM analysis of the parts showed an even, dense distribution of wood flour fibres and PP particles within the PES matrix.

When the powder bed temperature is too low or the laser power is too high during L-PBF, the corners and edges of the laser-sintered layers undergo a detrimental phenomenon known as curling [3]. In a study on the usability of zeolite particles filled into a PP coathylene powder for L-PBF of heat exchangers for refrigeration systems, Wudy *et al.* [98] found that the increase of the fraction ratio of zeolite/PP (30/70, 40/60, and 50/50) reduced the curling effect of the first layers. For all considered mixtures, the exposure of the first layer with three levels of energy densities, i.e., 0.11, 0.18, and 0.25 J/mm², showed that, with the increase of energy density, the layer changed colour from beige to brown, also followed by an increase in the layer thickness. When higher energy density was applied, TGA confirmed that the colour change was due to degradation at an onset temperature of 254 °C of the polyvinyl alcohol binder used to obtain agglomeration of zeolite particles. An improved water adsorption, which increased with the increase of the zeolite content, required the conservation of the crystal structure characteristics. XRD analysis showed that the crystal morphology of zeolite particles was not affected by the L-PBF process, thus making L-PBF of PP/zeolite polymeric composite, a viable manufacturing technology for improvement of heat transfer in heat exchangers. Furthermore, diffused reflectance spectrometry indicated that the increase in the zeolite content resulted in a decrease in diffused reflectance. Consequently, the absorption capacity of the CO₂ laser by the composite powder is improved, thus leading to a low demand of sintering energy comparatively to energy requirement for sintering of pure PP powder.

Montmorillonite (MMT) is a type of natural clay commonly used for the preparation of composites due to its fine particles, and MMT is usually modified with surfactants such as alkylammonium salts to obtain organically

modified montmorillonites (OMMTs). Tan, Zhu, and Zhou [77] prepared a composite powder made of a mixture of OMMTs and a commercial laser-sintering powder, PP CP20, produced by Diamond Plastics GmbH. The mechanically mixed powder designated as ME-OMMT/PP was subjected to a thermally induced phase separation (TIPS) process. Though OMMTs could act as nucleating agents, thus enhancing the growth of nucleation sites, they could not avoid the agglomeration of particles, and the addition of 1-hexanol was important to produce the desirable shape and size of the composite powder. It was reported that the window of sinterability of non-modified PP CP20 powder was improved from 26.3 to 32.2°C for the new composite powder. The addition of the nano-sized OMMT fragments contributed to hindering the diffusion of polymer chain melt during the TIPS process.

Gong *et al.* [112] investigated the thermal treatment method using a mixture solvent system (TTMS) to produce PP powder with a wide sintering window well-suited to the L-PBF process. A cryogenically ground PP powder was dispersed into a mixture of glycerin and silicon oil solvents. The simultaneous actions of heating and stirring of the mixture produced a homogeneous solution to be quenched in ice water for the precipitation of PP. The filtering and washing with ethyl acetate, followed by drying in a vacuum oven, resulted in PP powder. DSC analysis showed that the window of sinterability of non-modified raw PP powder was improved from 15 to 51 °C for the new composite powder TTMS-PP with a reduced degree of crystallinity, which was evident by the presence of low-intensity α -crystals. Compared to CAD sizes of a rectangular layer of 40 x 50 mm², the dimensional accuracy of one single layer processed through L-PBF was improved from 84% for non-treated PP to 98% for TTMS-PP. This showed that the thermally treated PP powder was less prone to shrinkage and warpage during L-PBF.

Sillani *et al.* [2] investigated the influence of adding wollastonite and short carbon fibres to PA12 and iCoPP powders, respectively, to be used in the L-PBF process. The two non-modified powders were characterized by a similar thermal conductivity of approximately 200 mWm⁻¹K⁻¹ in a solid state. Depending on the packing density of the composite powder, it was found that the filling of 11% wollastonite with a thermal conductivity of 2700 mWm⁻¹K⁻¹ into PA12 powder led to a drastic increase of thermal conductivity ranging from 60 to 80 mWm⁻¹K⁻¹. On the other hand, depending on the packing density, 10% short carbon fibres with 6000 mWm⁻¹K⁻¹ of thermal conductivity filled into iCoPP powder resulted in a modest increase ranging from 50 to 150 mWm⁻¹K⁻¹ thermal conductivity. Contrary to the increase of flowability upon the addition of fillers reported by Ituarte, Wiikinkoski, and Jansson [82], the flowability of the two newly formed composite powders was found to decrease with the addition of elongated short carbon fibres into iCoPP or wollastonite with

acicular shape into PA12 powder, as non-sphericity of the fillers negatively affected the rheological behaviour of the initial powders.

Ram, Kalaitzidou, and Das measured an increase in the electrical conductivity of parts obtained through the L-PBF of PA12 powder filled with 4 wt.% carbon black [105]. The electrical conductivity of $1 \times 10^{-4} \text{ s/cm}$ for the new laser-sintered composite polymeric part was measured, which was five times greater than for the neat PA12 part produced through L-PBF. On the other hand, adding carbon black contributed to a decrease in the maximum flexural modulus from 1750 to 1450 MPa. A SEM analysis showed that the highly segregated structure led to poor adhesion between the polymer particles and reinforcing carbon black, which resulted in a weaker part as some crystallites could remain unmelted and dispersed in the final laser-sintered part.

Lanzl and Drummer [113] investigated the effect of filling PA12 powder with Short Glass Fibres (SGF) in terms of the optical and thermal properties of the powder during PBF. An increase of 10, 30, and 50 wt.% in SGF resulted in a decrease in diffuse reflection from 2% for the neat PA12 powder to 0.76, 0.6, and 0.4%, respectively, thus enhancing the absorption of the laser energy by the powder. On the other hand, the increase of filling content weight linearly reduced the specific heat capacity of the powder. The capacity of the filled powder to store thermal energy was reduced, which contributed to increasing the melting temperature of the composite polymeric powder.

Conclusions

1. L-PBF is one AM process that supports the Fourth Industrial Revolution (4-IR). Though PP has shown potential as a candidate material for L-PBF processing, the use of PP powder is still very low compared to volumes achieved with traditional manufacturing methods. To satisfy the market demand for customized PP products, PP powder must meet the intrinsic and extrinsic properties required for laser sintering parts with acceptable physical and mechanical properties.
2. The shrinkage, warpage, and curling of L-PBF parts can be overcome by preventing crystallization during the process. DSC analysis of the powder is required to establish the window of sinterability.
3. The addition of fillers and compatibilizers to polymeric powder for L-PBF leads to the reduction of shrinkage, warpage, and curling of laser-sintered components. Adding fillers with nearly spherical particles improves the flowability of the powder, whereas acicular or elongated shapes such as carbon and glass fibres may reduce the flowability of the neat polymeric powder.

4. Besides the effects of fillers on mechanical properties and shrinkage and warpage control of laser-sintered parts, the addition of fillers to neat feedstock polymeric material can improve thermal and electrical conductivity. The addition of fillers also reduces the linear thermal expansion associated with the reduced crystallinity of the neat polymer. Mineral fillers such as carbon black change the pigmentation of the neat PP, thus enhancing laser absorption during L-PBF.
5. Within a wide range of PP grades in the form of pellets or granules, research work is being carried out to find a particular PP grade to produce a powder for L-PBF with a reduced degree of crystallinity, wide sintering window, good flowability, and melt viscosity.
6. The focus of the next chapter is a thorough investigation into techniques available for producing polymeric powder, especially PP powder, suitable for L-PBF.

CHAPTER 5: OVERVIEW OF TECHNIQUES FOR PRODUCTION OF POLYMERIC POWDERS FOR LASER POWDER BED FUSION

An ideal powder for PBF should have particles of high sphericity to facilitate the flow, reduce the surface area to volume ratio, and improve the packing efficiency. The powder should also have a size distribution between 1 and 100 μm and a mean diameter bigger than 10 μm [5]. Grinding of granules (pellets), spray drying, fluidization in a downer reactor, immiscible blends, supercritical fluid, and physicochemical techniques are methods used to produce powder particles of various shapes and sizes.

5.1 Cryogenic grinding of the granules

Generating spherical particles directly from polymerization is not possible with all types of plastics. Cryogenic grinding is a well-established method for bio-analytical, biotechnological, and pharmaceutical purposes. Grinding is a proven mechanical process for reducing plastic solid materials in the form of pellets or granules to a smaller particle of average size ranging from 50 to 125 μm suitable for L-PBF [114]. At ambient temperature, the viscous flow or elastic-plastic behaviour characterizing the polymeric materials causes the polymer to resist highly applied mechanical forces. For grinding of plastic materials, a cryogenic gas, mostly liquid nitrogen cooled at -196°C or dry ice at -78°C , is used to cool down a thermoplastic material which becomes brittle, usually at temperatures below the glass transition [115], [116]. The pellets are cooled down to a temperature lower than the glass transition temperature and fed into a counter-rotating pinned disc mill that uses the impact crusher principle to reduce the size of the pellets. The used cooling gas from the grinding system is removed by a centrifugal pump, channelled to a storage container, recirculated, and reused. The powder is sieved, screened and separated to a desired particle diameter using the air classification technological method. A drawback of the process is that a significant amount of wastage results from non-fractionated material to a desired shape and particle size, thus reducing the productivity of the process [31], [115]. Moreover, it is time-consuming and costly to grind the polymeric pellets into a powder of particle size below 100 μm as such a particle size range can only be achieved through a series of multiple grinding stages that can lead to discolouration as evidence of enhanced polymer degradation.

To obtain a free-flowing powder, Mys *et al.* [31] conducted a comparative study on the characterization of Polysulfone (PSU) powder produced via rotor milling, ball milling, and spray-drying techniques. Through three successive grinding stages, the rotor milling of PSU pellets produced powders of 500, 120, and 80 μm particle size, and after the sieving of the last product, the powder was re-fed and reground to finally produce

a suitable powder for L-PBF, having a spherical shape with a mean particle size of $51.8\ \mu\text{m}$ and a relatively large standard deviation of $15.2\ \mu\text{m}$. The rotor milling was more effective compared to ball milling, which produced very irregularly shaped small particles with a mean diameter of $1.7\ \mu\text{m}$ and a wide standard deviation of $1.5\ \mu\text{m}$. Moreover, contrary to the powder obtained through rotor milling, DSC analysis indicated a change in the glass transition temperature from 189 to $196\ ^\circ\text{C}$, while XRD showed unexpected sharp peaks, indicating the presence of ordered crystalline structures. It was concluded that the contamination from the ceramic cups of the ball milling machine led to a significant degradation of the original PSU, thus making the ball milling less suitable than rotor milling.

Using cryogenic grinding, Diamond Plastics GmbH produces and commercializes PP powders CP2, CP20, CP22, CP50, CP60, and CP75 for L-PBF [117], [118], [77], [119], [120], [121]. Particles of irregular shapes characterize these powders with an average size of $\pm 60\ \mu\text{m}$. Nsengimana *et al.* [117] obtained an acceptable surface finish of $R_a=12.5\ \mu\text{m}$ and dimensional accuracy of $\pm 16\%$ for thin walls of $0.75\ \text{mm}$ thickness when PP CP75 powder was processed on an EOS P380 L-PBF machine at optimal scanning speeds ranging from 1481 to $1600\ \text{mm/s}$. By maintaining a relatively high degradation temperature of 457.3°C , Mwanja, Maringa, and Van der Walt [119] found that a single re-use of PP CP60 powder increased the sintering window from 21.04 to 26.95°C , while the degree of crystallinity was reduced from 13.92 to 12.12% .

5.2 Spray drying

Spray drying is a physicochemical technique that consists of atomizing or forming small droplets of emulsion using a rotary spraying nozzle. (Figure 5-1). The atomization is followed by continuous spraying of the feed (solution, suspension, dispersion, or emulsion) into a hot drying medium to enable the transformation from a fluid state into dried solid particulate in the form of powders, granules, or agglomerates. This technique has been used from the 1870s through the early 1900s until today in micro-encapsulation of food ingredients and pharmaceutical products [122], [123]. Nearly spherical and usually hollow particles can be produced with feed rates ranging from a few kilograms to over $100\ \text{tons per hour}$ [5], [124].

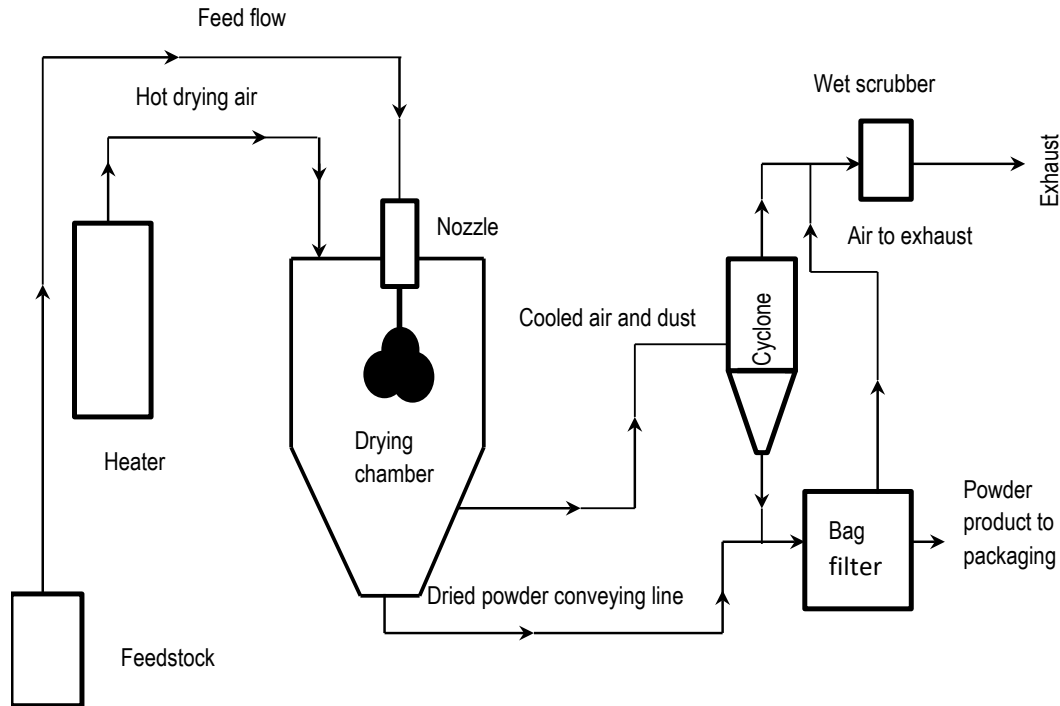


Figure 5-1: Schematic representation of spray drying process (adapted from R. P. Patel, M. P. Patel, and Suthar [124])

Using acrylate or styrene-based amorphous homopolymer or copolymer as raw materials with a glass transition temperature in the range of 30 to 100 °C, McAlea *et al.* [114] patented the spray drying production of spherical-shaped particles of powder with an average size varying from 20 to 50 μm with less than 5% fraction of particles of less than 15 μm and less than 1% particle fraction of higher than 75 μm in diameter. The powder could be used for L-PBF parts with sufficient pores, which is an advantage to preventing cracks in moulds in the investment casting of metals. However, a low tensile strength of 6.9 MPa in the x-direction and 5.5 MPa in the y- and z-directions, with a surface finish varying from 3.8 to 9 μm , were recorded. Though spray drying has the advantage of good powder productivity, due to the presence of hollow particles, the density of laser-sintered parts can drop to a range of 55 to 75% compared to the density of the original raw polymeric material.

Polyamides with a glass transition temperature of 35–60 °C are established as semi-crystalline polymers for laser sintering, and average tensile strength and Young's modulus of 45 MPa and 1700 MPa, respectively, can be achieved. For broadening the range of polymers to be used as powder for L-PBF, in addition to ball

milling and rotor milling, Mys *et al.* [31] used spray drying of PSU as an amorphous polymer with thermal and mechanical properties significantly different from the properties of the frequently used conventional polyamides for L-PBF. PSU has a tensile strength and Young's modulus of 72 MPa and 2.5 GPa, respectively, and a glass transition temperature of 189 °C. Mixed with N,N-Dimethylformamide (DMF) as a suitable solvent, the spray drying resulted in powder characterized by the predominance of spherical-shaped morphology mixed with a negligible fraction of string-like structures. The spherical particles were of a small mean diameter size of 26.1 μm and a wide standard deviation of 12.8 μm with particle size distribution skewed to the higher diameter ranges. Similar results were obtained by Mys *et al.* [125] when a spray-drying technique was performed on a syndiotactic polystyrene (sPS). The process resulted in a powder with spherical-shaped particles, however, characterized by a small mean diameter of 20.7 μm and a wide standard deviation of 13.1 μm . A possible increase in particle size for the powder suitable for L-PBF was conditioned to optimize the process further, using a bigger nozzle diameter and operating in a larger drying chamber. Gel Permeation Chromatography (GPC), also known as gel filtration or size exclusion chromatography, is a technique in which the separation of the solution components is based on the difference in their molecular weights or sizes. A component with large size and/or spherical shape and/or high molecular weight will flow to pass (elute) through the fixed column being unhindered without penetrating the gel matrix, whereas a component with a small size and/or irregular shape and/or a low molecular weight is retarded and consequently penetrates the gel matrix. The GPC measurements showed no substantial difference in elution peaks for the virgin and spray-dried PSU samples, though the change in polydispersity index from 2.01 to 2.02 was an indicator of a slight degradation that might be caused by subjecting the pellets to two successive heat treatments, namely dissolving by reflux and the spray-drying process to obtain the PSU powder.

5.3 Fluidization in a downer reactor

Fluidization in a downer reactor (Figure 5-2) is a process in which a gas and solids move downwards concurrently in a downer reactor, and the back-mixing of phases is effectively reduced due to gravitational forces. The working principle of a downer reactor lies in the gravitational force assisting the downflow streams so that uniform flow structures and narrow Residence Time Distributions (RTDs) are achieved for both solid and gaseous phases. The very fast reaction between the gas and solid phases, where the uniform short contact time is generally from milliseconds to seconds, is essential to prevent over-reaction and to ensure good flowability [126]. In a downer reactor, using the surface tension effect, the free surface energy is reduced by decreasing the overall surface area, and spherical powder particles can be formed [127].

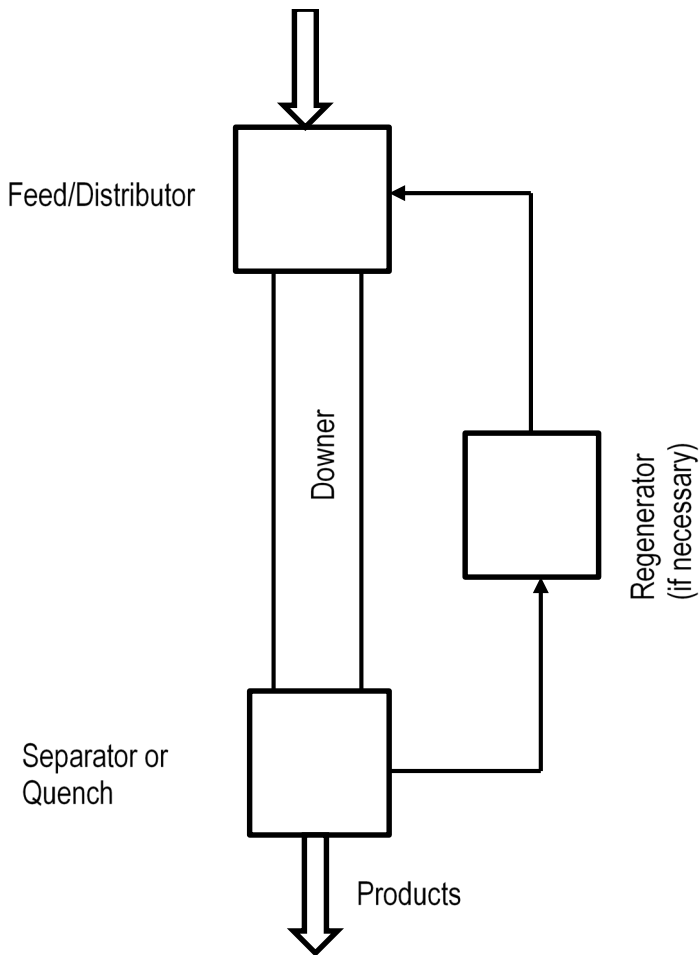


Figure 5-2: A simplified illustration of the process of fluidization in a downer reactor (adapted from Cheng *et al.* [126])

Polymer particles produced through grinding often require shape modification to render the powder more suitable for L-PBF. Based on the work done by Schmidt *et al.* [128], Sachs *et al.* [129] used the downer reactor, which had a height of 1.6 m and an inner diameter of 25 mm to round the irregular shape of PS obtained after a wet grinding with a ball milling machine. For a residence period ranging from 0.6 to 2.7 seconds, a downer reactor equipped with a three-stage heating system (Figure 5-3) produced PS powder with spherical-shaped particles. The dispersion of the particles to create an aerosol of PS particles was achieved by using a PALAS RGB powder disperser with a brush. The aerosol consisting of the PS particles enters the reactor in the centre of its cross-section via a tube with a diameter of 10 mm. This primary gas flow was surrounded by a secondary gas (nitrogen gas) flow, which can be described as a sheath gas flow, necessary to minimize

further the contact of molten polymer materials and the hot reactor wall to avoid the loss, oxidation, and degradation of the PS powder. The temperature is lowered stepwise for the solidification of the spherical particles, and the powder is cooled in the zone of the downer reactor exposed to ambient temperature. Schmidt *et al.* [128] found that the level of sphericity of the particles depended on the residence period of the powder in the downer reactor, where the melting and coalescence processes are made perfect with the increase in the residence time (Figure 5-4).

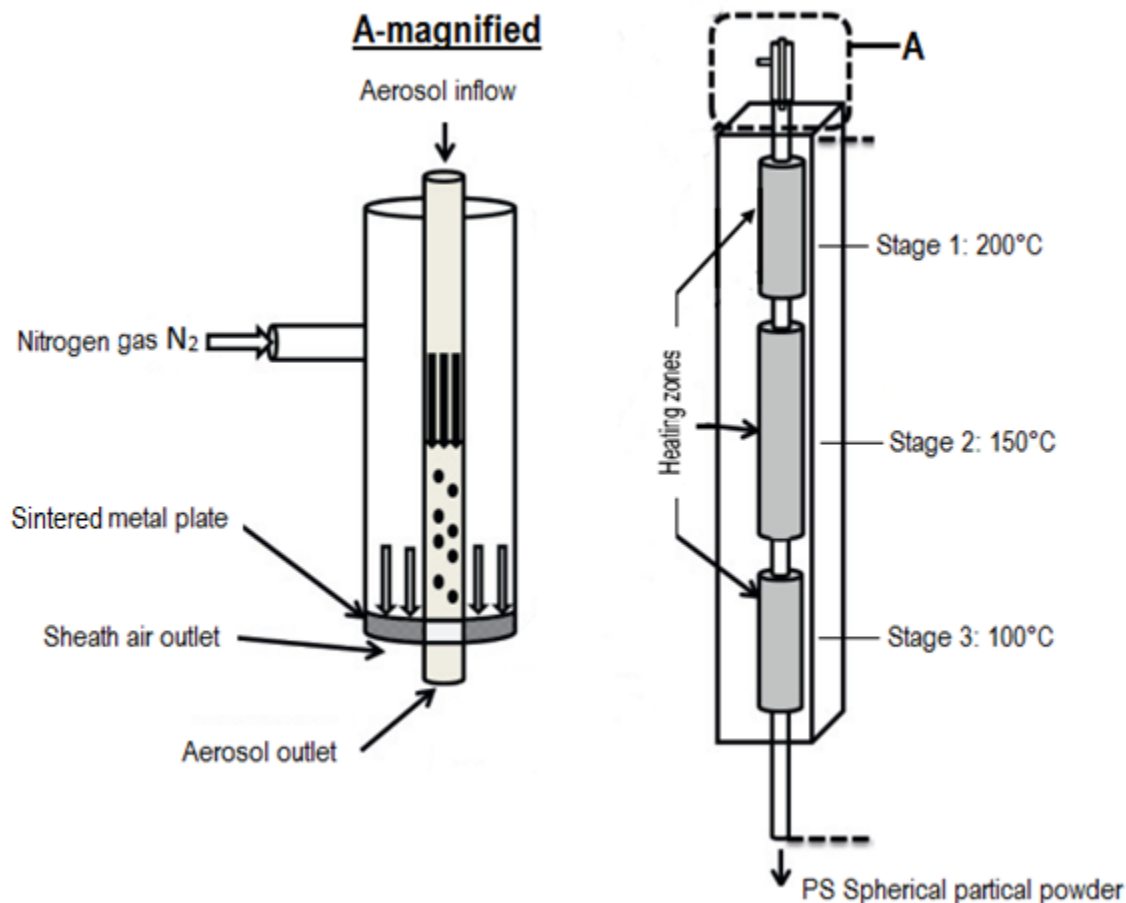


Figure 5-3: Three-stage downer reactor for rounding irregular-shaped powder particles (adapted from Sachs *et al.* [129])

It was found that a residence time of 2.7 s was enough to produce spherical particles with sizes ranging from 10 to 50 μm in diameter in the downer reactor. The particle size measurements taken using SEM showed

that rounding in the downer reactor did not change the particle size of the powder, proving that the agglomeration of powder particles in the molten state was avoided.

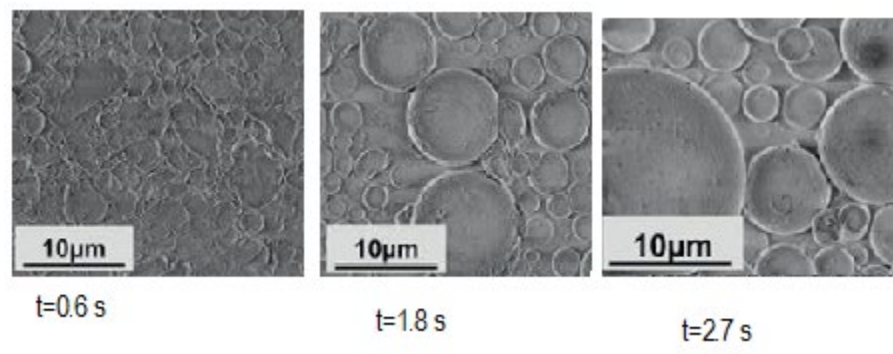


Figure 5-4: Effect of residence period on melting, coalescence, and size of powder particles [129]

Sachs *et al.* [127] studied the characteristics of a downer reactor with a 100 mm diameter and an overall length of 6 m, designed for rounding irregular-shaped particles obtained from a wet grinding of PBT granules. They found that agglomeration and sintering effects due to contact between particles in the molten state could not be eliminated. Such agglomeration, which is also influenced by the concentration of the particles in the carrier gas flow, was confirmed by SEM, which showed rounded particles with a 100 μm diameter. Moreover, the turbulence regime that mainly occurs within the first 0.2 m after the inlet leads to the back-mixing of gas and particles and their subsequent attachment to the reactor walls. After reducing the turbulence phenomenon in the inlet zone, particle size distribution could be observed in a radial direction of the reactor. Despite a visible free zone to prevent contact between the particles and the reactor walls, a class of particle size ranging from 20 to 50 μm was predominant in the region close to the reactor walls. Powder with particle sizes ranging from 60 to 70 μm appeared in a radial direction towards the center, while powder with the smallest particle sizes ranging from 1 to 20 μm was found in the region near the center of the reactor. In an early study conducted by Schmidt *et al.* [130], a procedure of wet grinding of PBT granules of less than 500 μm diameter, followed by rounding in a downer reactor, and finally, performing a dry coating with fumed nano-silica particles was investigated. This process was found to be a suitable method for optimizing the flowability of a very fine PBT powder for PBF. DSC analysis found that the rounding in a downer reactor of particles of sizes less than 10 μm obtained through wet grinding resulted in an increase in the melting temperature from 227.3 to 230.2°C and a slight decrease of the degree of crystallinity from 35 to 32.1%. The

XRD analysis showed that the presence of α -PBT crystalline structures was common for both fed granules and wet ground powder, while both α - and β -polymorphs were observed in the thermally rounded particles in a downer reactor. The amount of β -crystals formed, presumably caused by the solidification of the polymer melt upon fast cooling, was found to be reduced in the laser-sintered part when rounded dry coated powder was used.

Bonilla *et al.* [131] investigated the characteristics of thermally rounded particles of High-Density Polyethylene (HDPE) after being subjected to direct and indirect heating in a downer reactor with a diameter of 100 mm and a total length of 1.2 m. The direct heating consisted of setting the sheath gas to a temperature of 140 °C, which resulted in a direct transfer of the heat to particles, thus also creating the maximum temperatures at the central zones of the downer reactor, while the zones near the wall experienced the minimum temperatures. On the other hand, the indirect heating approach consisted of using electric elements to directly heat the reactor wall to a temperature of 250 °C and the heat was indirectly transferred by convection, conduction, and radiation to finally achieve a temperature of 140 °C for the gas phase mixed with solid particles (aerosol). In both cases, the aerosol was fed at an inlet temperature of 120°C, and the temperature could be reduced below the onset melting temperature in vertical sections through independent temperature control to allow the solidification of the particles at the outlet. A considerable increase in the particle size to reach an average diameter of 85 μm was observed when particles were rounded by applying indirect heating. Despite the complete melting of the raw particles of irregular shapes resulting in the formation of particles with smooth spherical surfaces, the indirect heating caused the agglomeration of spherical particles, resulting in the formation of larger-sized elongated structures with rounded edges. The ratio between the mass of the outlet powder with rounded particles and the mass of the raw HDPE powder, as fed into the reactor, was $32 \pm 6\%$. The remaining 68% of the feed material was deposited on the reactor walls, leading to a further requirement of a high temperature for cleaning after each experiment. On the other hand, compared to indirect heating, with a reduced agglomeration of spherical particles, the direct heating approach produced rounded spherical particles with an average size of 63 μm , characterized by a variety of completely melted, partially melted, and unmodified particles. Compared to indirect heating, the reduced risk of partially molten powder particles sticking on the colder walls significantly improved the productivity ratio up to $85 \pm 10\%$, thus making the direct heating approach more beneficial in yield and powder flowability.

5.4 Immiscible blends

Blending of polymers is an effective method to develop new materials with improved properties [132]. Most of the time, when two polymers are mixed and melted together in solvents and non-solvents, phase-separated heterogeneous mixtures are obtained. The produced system is commonly known as an immiscible blend of two or more polymers. Depending on the proportion weights of the mixed polymeric components, the polymer with the highest proportion of component is called the major component, while the other polymer is known as the minor component of the immiscible blend. The melting and mixing process can generate morphologies ranging from dispersed spherical drops to fibres, lamella, and co-continuous structures (Figure 5-5). The generated morphology of spheres or spheroids dispersed in a polymeric matrix can be used to produce powder particles with a spherical shape.

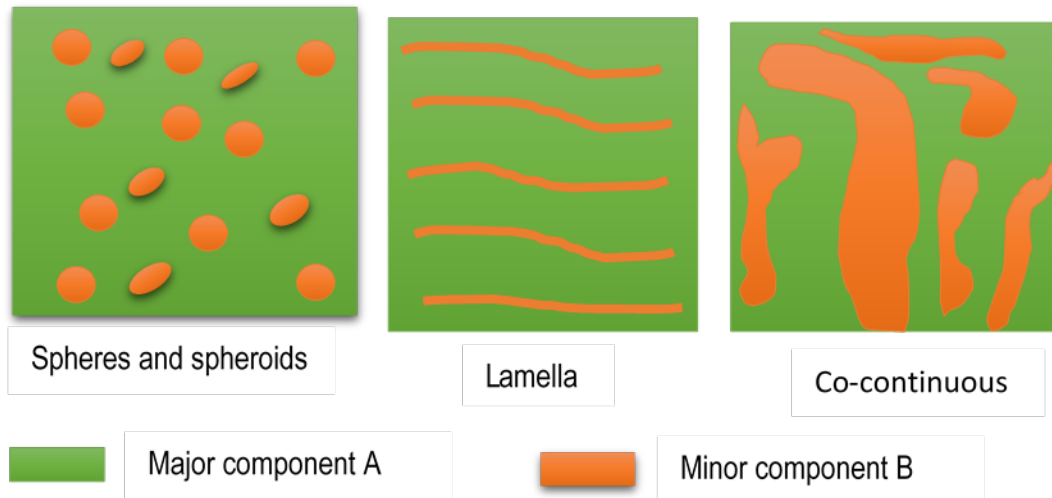


Figure 5-5: Morphologies produced from blending of immiscible polymers

The produced polymeric powder is in the form of fine solidified droplets obtained by the subsequent removal of the solvent. The interfacial tension, rheological properties, and the complex strain field of the mixer mainly control the size and shape of the dispersed phase. In many situations, the droplet shape is very close to an ellipsoid.

From the works done by Schreiber and Olguin [133], Karger-Kocsis, Kallo and Kuleznev [134], and Favis [135], Scott and Macosko [136] reported no significant changes of morphologies of PS or PC dispersed into

PP matrices. The variation of mixing time from one to ten minutes could generate dispersed spherical shape particles with very small diameters, varying from 0.3 to 3 μm , which is not recommended for L-PBF. The literature [5], [29], [137], [138] could show that the immiscible blend was an attractive technique for producing polymeric powder with ellipsoidal and nearly spherical shape particles. However, the powders were not suitable for L-PBF. Ellipsoidal-shaped particles in small quantities dispersed into a continuous polymer matrix could be produced and were characterized with very small diameters varying from nano-size to 20 μm , thus leading to agglomeration and poor powder flowability.

5.5 Liquid-Liquid Phase Separation technique

Liquid-Liquid Phase Separation (LLPS) is a physicochemical technique that consists of heating, under continuous stirring, of a polymer in the form of granules or pellets together with a suitable solvent until complete dissolution is obtained. Under quiescent conditions, the homogeneous system is cooled to form a liquid-liquid dispersed system. The size and morphology of the formed particles are influenced mainly by the polymer concentration, cooling rate, and chemical interaction between the polymer and the solvent used. After the cooling process, the solvent is removed from the mixture by filtration to produce a gel that is dried in sunny open air to obtain agglomerates of powder particles suitable for L-PBF. Mechanical breaking of agglomerates, followed by sieving, is performed on the dried powder to enhance good flowability and particle size distribution.

Korsgen *et al.* [139] produced a patent on the process of producing PP powders using a physicochemical technique. The patent elaborated on dissolving PP material in a solvent or a mixture of solvent and non-solvent at a temperature varying from 120 to 140°C. A ratio of 1 kg of solid material dissolved into 10 to 15 liters of liquid was recommended. The solution was subjected to cooling under quiescent conditions to a temperature below 80°C. The quiescent cooling process allowed the formation of a gel, which was centrifuged to separate the solid material from the liquid until the residual solvent content was about 10%. The PP particles, with an average sizes below 74 μm , precipitated in the form of agglomeration. The agglomerated PP particles were dried to contain less than 2% residual moisture. Finally, the powder with more than 90% of the particles sized below 74 μm was obtained by mechanical comminution in conventional grinding assemblies such as beater mills, ball mills, pin mills, or in a simple high-speed domestic mixer for relatively small quantities. The patent did not specify the chemical formulation of PP granules that respond efficiently to obtain spherical shape particles with the desirable sizes suitable for L-PBF.

Wang *et al.* [140] established the role of LLPS and crystallization during the preparation of PP microsphere particles for L-PBF. Among five possible solvents, namely, n-Heptane, Isoamyl acetate, Xylene, Diphenyl ether, and Methyl salicylate, xylene was found to be the best solvent for generating PP spherical particles with PSD within the range of 20 to 80 μm . They used iPP with an MFR of 3.0 g/10 min. with an isotactic index of 94.5%. After dissolving the PP into xylene at 145°C, the stirring was stopped, and the solution was kept quiescent for 30 minutes to ensure a homogeneous solution was formed. This was followed by quenching to a specific temperature for 60 minutes to allow the precipitation of iPP. Finally, the xylene was removed from the precipitated PP through several washing cycles with ethanol and evaporation through vacuum drying. When the quenching temperature was fixed to 0°C and varying the concentration of PP into xylene was from 3.0 to 13.0 wt.% (Figure 5-6b-e), the diameter of the particles was found to increase from 24 to 40 μm .

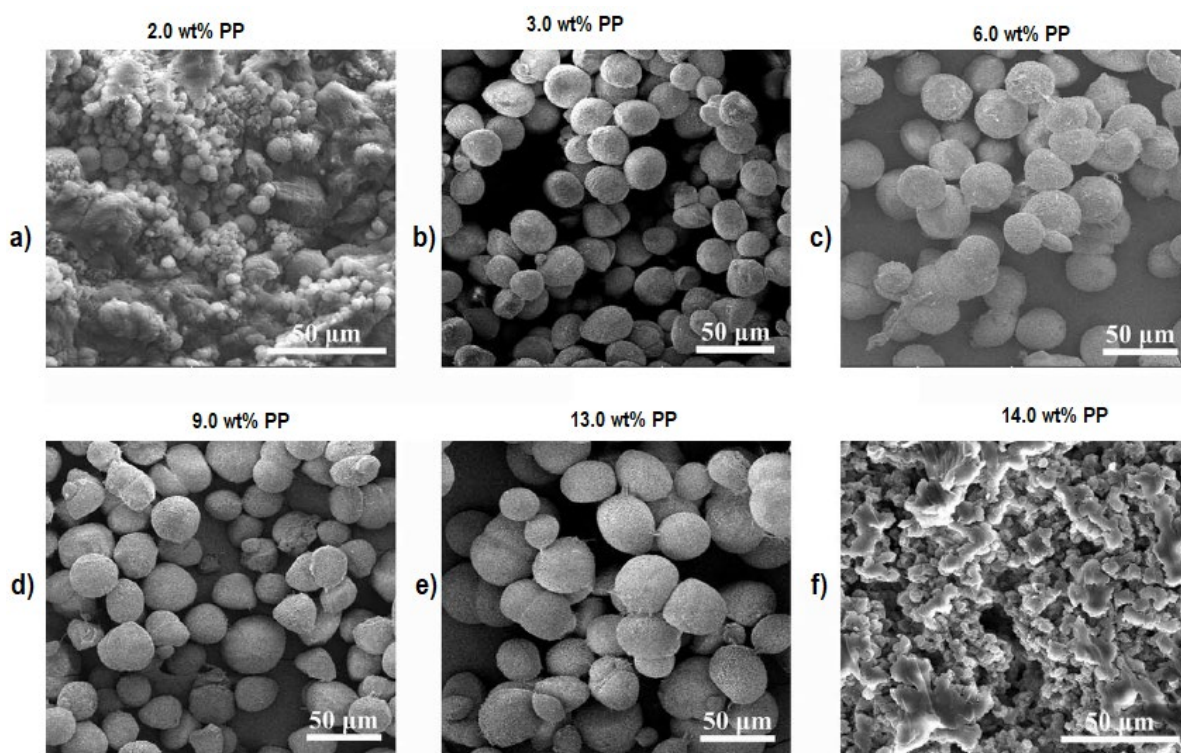


Figure 5-6: Effect of the PP concentration on the morphology and size of the precipitated particles [140]

Assuming the polymer-rich phase remained constant, the following relationship was established:

$$\frac{d_2^3}{d_1^3} = \frac{c_2}{c_1} \quad (\text{Eq. 2})$$

d_1 and d_2 are particle size diameters obtained at a concentration c_1 and c_2 respectively.

A DSC study on quenching PP showed only one endothermic peak at 165°C that occurred during the first heating, thus indicating the presence of α -phase only as if the quenching process could not promote the formation of β -crystals. To produce PP powder for L-PBF, the DSC curve obtained at a heating and cooling rate of 10°C/min. revealed that the chamber temperature must be controlled within a range of 124 to 155°C. It was found that for quenching temperatures (T_q) below 50°C, smooth and large microsphere particles with some attached filaments could be produced contrary (Figure 5-7a-c) to rougher and smaller particles made of the stacks of small lamellae that were obtained when the quenching temperatures were raised to 50 up to 80°C (Figure 5-7d-f).

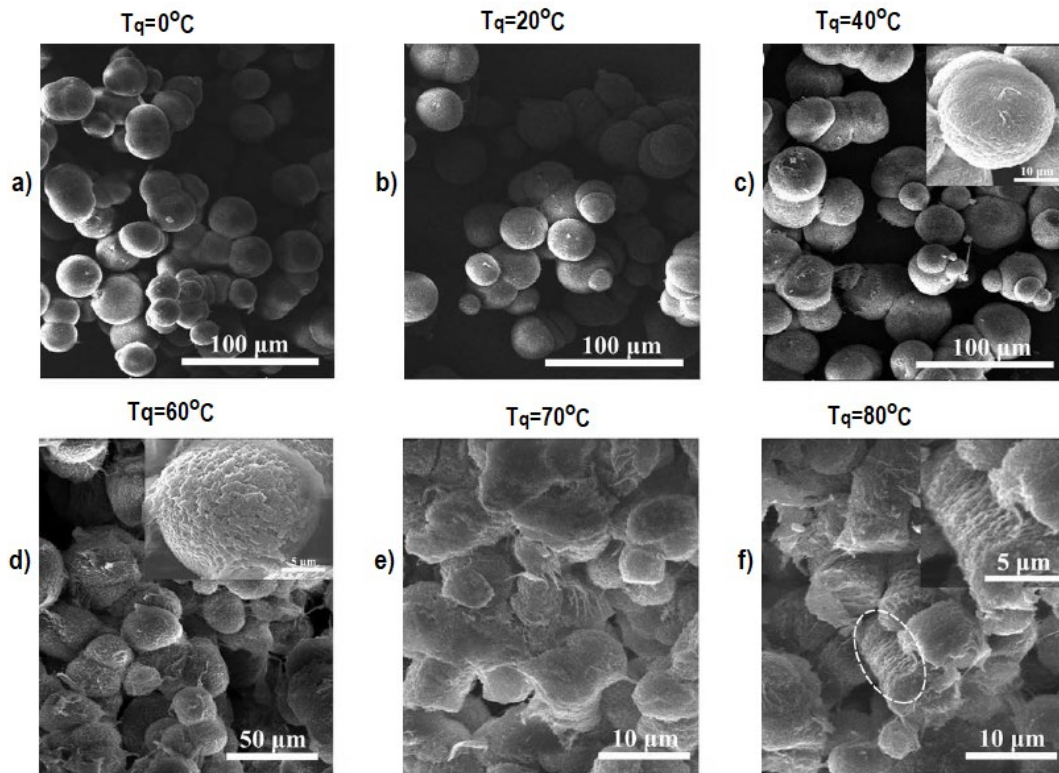


Figure 5-7: Effect of the quenching temperature on morphology and size of the particles: Inset pictures in (c) and (d) are the magnified pictures of the PP microsphere and the dashed region (f), respectively [140]

The irregular shape of such particles was more pronounced when the quenching temperature was above 80°C, rendering the lamellae inside the microspheres larger with higher ordering while the very small lamellae on the boundary disappeared.

In a phase diagram, for a series of temperatures, the locus of the free energy minima, as a function of a temperature decomposition of the phase constituents, defines the phase boundary known as the spinodal curve (Figure 5-8). When a system has crossed this locus, phase separation occurs spontaneously in the absence of nucleation and growth of crystals. This process, known as a spinodal decomposition and characterized by a high interconnectivity between the two phases, occurs when the homogeneous phase becomes thermodynamically unstable, thus implying the presence of a maximum free energy. On the other hand, nucleation and growth leading to crystallization occur when the homogeneous phase becomes stable (metastable) with minimum free energy in the solution [141].

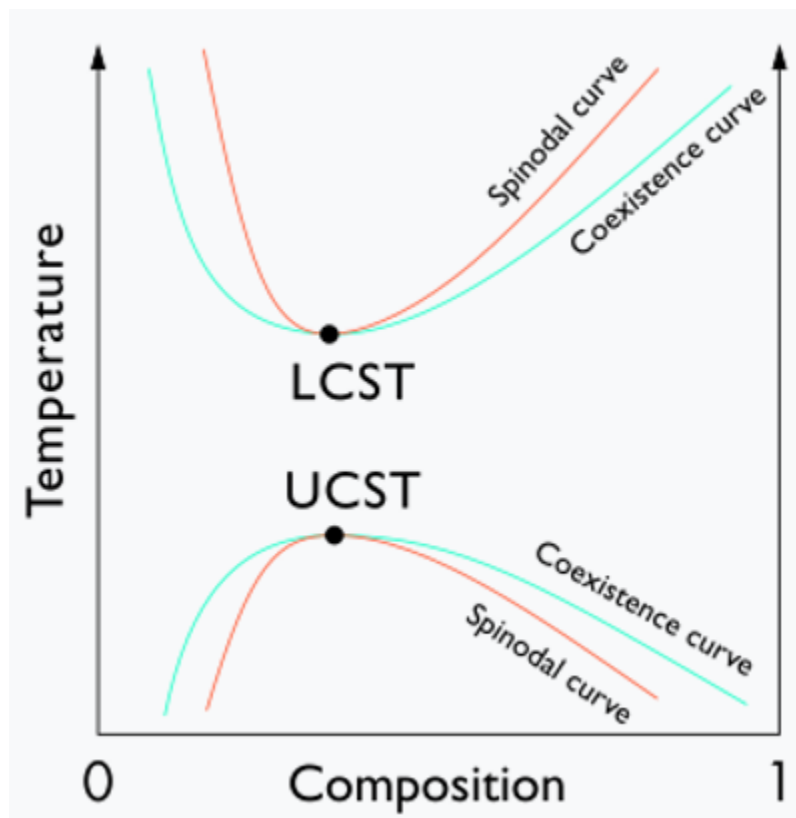


Figure 5-8: Spinodal, binodal coexistence curves and two critical points in a decomposition phase diagram [142]

The binodal curve, also known as the coexistence curve, indicates the conditions in which the chemical potential for all components of the solution is equal in each phase. As the free energy of mixing changes with temperature and concentration, the binodal and spinodal curves meet at their extremum at points known as Upper Critical Solution Temperature (UCST) and Lower Critical Solution Temperature (LCST). The LLPS in the PP and xylene solution is induced upon the removal of thermal energy by cooling or quenching the solution below the UCST point.

This investigation found that the formation of PP microspheres was driven by the competition between the LLPS and crystallization processes that occur when the quenching temperature was below the binodal curve within the temperature range of 50 to 60°C. In general, increasing the quenching temperature or applying less undercooling slowed the crystallization rate and provided a longer time for the coarsening process and growth of the polymer-rich phase, thus leading to the increase in the diameter of the formed microspheres. However, increasing the quenching temperature towards the proximity of the binodal line promoted the crystallization of PP, resulting in pure crystallization that starts taking place inside the polymer-rich phase because of the high polymer concentration. Consequently, LLPS-induced crystallization along the LLPS interface and pure crystallization inside the polymer-rich phase occurred simultaneously, thus causing the formation of the inwards-bent tiny lamellae on the surface of the PP microspheres with a reduced diameter due to the further inwards bending of the grown lamellae. A further rise in quenching temperature above the binodal curve did not lead to LLPS. Instead, it enhanced pure crystallization as high temperatures provided sufficient freedom for the ordering of PP chains, thus promoting the formation of PP particles with irregular shapes.

Using the method of LLPS and precipitation, Dechet *et al.* [143] produced Polyamide 11 (PA11) powder for L-PBF. Granules of PA11 were dissolved in ethanol using an autoclave heated to 190°C, and the mixture was constantly stirred by magnetic bars. The solution was kept at 190°C for 15 minutes and then cooled below 50°C with cooling rates ranging from 0.5 to 3°K/min. The effects of polymer concentration, stirring speed, and temperature regime on the shape and particle size distribution were investigated. The consideration of 5, 10, and 20 wt.% concentrations of PA11 resulted in particle size distributions $X_{50,3} = 30 \mu\text{m}$; $X_{50,3} = 83 \mu\text{m}$ and $X_{50,3} = 134 \mu\text{m}$, respectively, meaning that the higher the weight fraction of the polymer, larger particles with smoother surfaces were obtained as opposed to the occurrence of small particles of about 10 μm size with coarse structured surfaces for low polymer concentration (Figure 5-9).

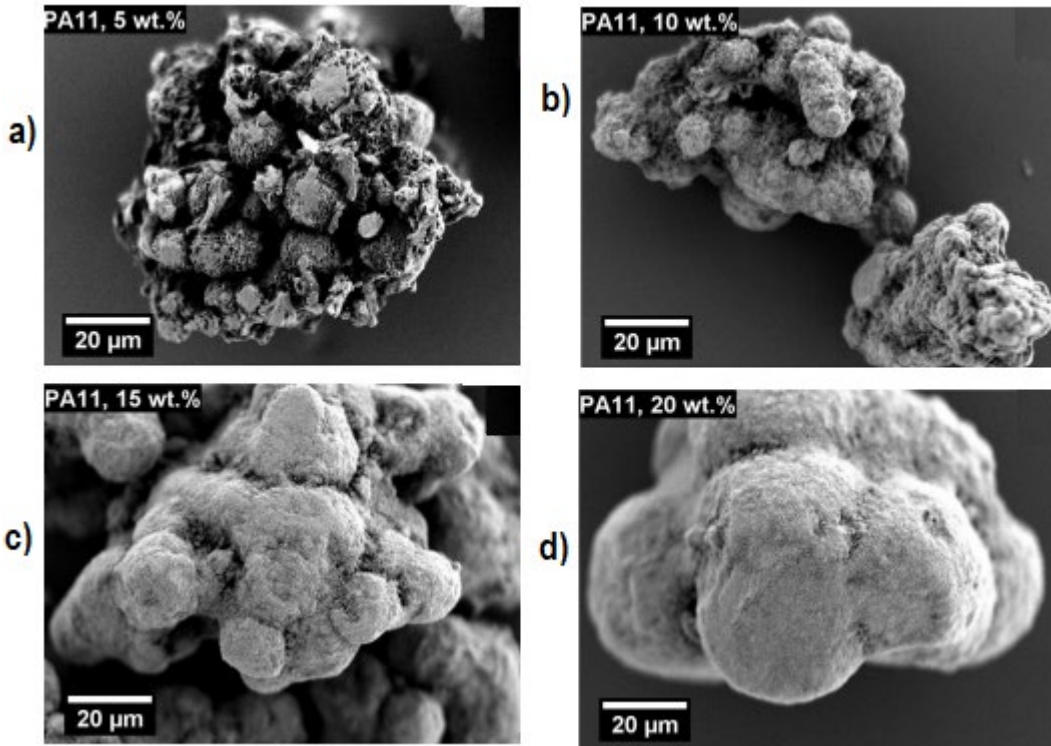


Figure 5-9: SEM image showing the effect of PA11 concentration on morphology and size of powder particles obtained through LLPS and precipitation [143].

An earlier study by McGuire *et al.* [144], as cited by Dechet *et al.* [143], showed a similar trend of a proportional growth of particle size with the polymer weight concentration when a range of 0.005 to 0.1 wt.% of PP diluted in diphenyl ether was investigated. On the other hand, Matsuyama *et al.* [145], as cited in Dechet *et al.* [143], with the same system, found an opposite trend for a higher range of 10 to 20 wt.% of PP concentration where 10 wt.% resulted in the largest particle size. The experiment was carried out at stirring speeds of 100, 300, 600, and 1200 rpm while maintaining the weight concentration of the PA11 as a constant. Though the coalescence effect may contribute to the generation of large particles at higher stirring speeds, Dechet *et al.* [143] established that the increase in the stirring speed led to a decrease in the particle size distribution since higher speeds enhance the breaking up of the formed droplets leading to the formation of small particles with coarse surfaces (Figure 5-10).

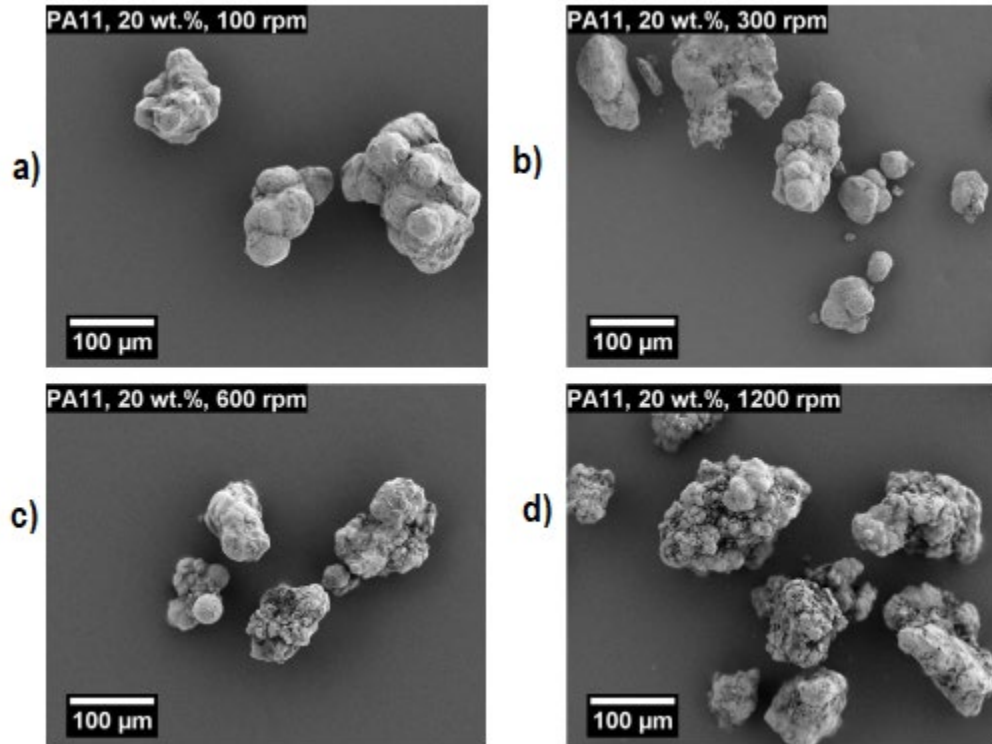


Figure 5-10: SEM images showing the effect of the stirring speed on particle size and morphology for 20 wt.% PA11 concentration [143]

Under continuous cooling rates in the range of 1.5 to 2°K/min., subjected to PA11-ethanol solution with a polymer concentration of 20 wt.%, the experiments showed that higher isothermal precipitation temperatures led to powder with a smaller particle size distribution, and the solution precipitated at 110°C resulted in the largest particle size. A solid density varying from 1.08 to 1.111 g/cm³ for the precipitated PA11 was slightly higher than that of 1.03 g/cm³ for the feed commercial granules. An XRD analysis was performed on both raw and precipitated polymers and showed similar patterns with reflexes for $C_{uK\alpha 1}$ radiation at $2\theta = 7.50^\circ$, 19.92° and 23.74° for the feed PA11 granules against $2\theta = 7.56^\circ$, 19.95° and 23.73° for the isothermally precipitated PA11. The broader reflexes for precipitated PA11 compared to those for the commercial PA11 feed granules indicate that the precipitated PA11 appeared to have smaller crystallites with a wider distribution of α crystals of varying size and perfection, implying a polymer with a higher degree of crystallinity. This behaviour was confirmed by DSC analysis where a second peak appeared during the second heating, leading to higher calculated degrees of crystallinity of 55.7, 64.3, and 61.5% for the continued cooled sample, and the isothermally precipitated samples for 30 min., at 120 and 130°C, respectively. The

PA11 feed granules and PA1101 commercial powder obtained by grinding showed opposite behaviours, with an appearance of one single peak and lower calculated degrees of crystallinity of 25.3 and 46.5%, respectively.

With a 20 wt.% polymer concentration, the isothermally precipitated PA11 particles at 120°C for 30 min. were optimal for L-PBF due to the narrow PSD with a mean size of 90 μm and fewer very small particles with diameter size below 20 μm . Despite a wide processing window of 19.1 °C, the precipitated powder showed a high degree of crystallinity of 64.3%, thus requiring an improvement of its flowability and additional measures to reduce the level of shrinkage and warpage. The dry coating with 0.5 wt.% hydrophobic fumed silica was performed on the powder to obtain a free-flowing and anti-caking characteristic during L-PBF. Furthermore, the ability of the precipitated powder to build dense parts was assessed by measuring the viscosity characteristics of the powder. The melt viscosity determines the extent to which the particles of the new layer can infiltrate the molten polymer. The zero-shear flow and the viscosity number can be used as measurements for the free flow of the polymer melt under LS process conditions. Due to low viscosity, the pores close very well, resulting in a dense inner structure without non-sintered particles. By comparing the fed PA11 granules and reference powder PA1101 supplied by EOS, it was found that the precipitation of PA11 resulted in reduced viscosity number and zero shear flow, leading to a 20% decrease in the molecular weight, also promoted by the depletion, and washing of the stabilizing agents with ethanol. The LS showed that the precipitated and coated powder was sensitive to temperature change, which required optimizing the process parameters to manufacture sintered parts with acceptable curling. A building chamber temperature of 170°C and energy density of 0.6 J/mm³ were found to produce dense dumbbell tensile test specimens free of curling.

Su *et al.* [146] used the mixture of a polar solvent N, N-dimethylacetamide (DMAC), and polyethylene glycol 400 (PEG400) as a second solvent for the LLPS method to produce PA12 powder for L-PBF. The gradual increase in DMAC content in ratios of 65, 70, 75, 80, and 85 wt.% resulted in an improvement in the morphology from irregular to spherical-shaped powder particles, however, decreasing the average particle size D_{50} to 443.80, 81.52, 55.20, 51.08, and 41.93 μm , respectively. On the other hand, the PA12 pellet could not be completely dissolved when the content of PEG400 exceeded 35 wt.%. A powder with an average size of $D_{50} = 55.2 \mu\text{m}$ with a higher sintering window of 29°C compared to 19.1 °C for EOS commercial powder PA2200, with a higher degree of crystallinity of 39% compared to 24% for PA12 in pellet form, was obtained when the process was optimized for a solvent mixture of 75 and 25 wt.% for DMAC and PEG400, respectively.

EOS GmbH is a worldwide commercial company based in Germany that, through the LLPS process, produces PA11 and PA12 powders dominated mainly by particles with potato shapes with average size distribution ranging from 50 to 70 μm . Despite the big market of nylon powders for the L-PBF process supplied by EOS GmbH, the use of aggressive solvents such as ethanol at high temperatures and pressure for dissolving nylon pellets into powder [146] requires strict safety measures to be imposed, thus limiting the wide spread of easy application of this technology. PA12 has been widely used and is a proven semi-crystalline polymeric material from which LS powder is produced for L-PBF to manufacture dense parts for various industrial applications. The MFR for the PA12 virgin commercial powder is reported to be in the range of 45 to 50 g/10 min [95]. It was reported that nylon PA12 powder for L-PBF, with a lower MFR, produced parts characterized by a poor, rough surface finish known as an “orange peel” texture and a higher level of shrinkage. The consideration of an MFR not lower than 18 g/10 min, and preferably higher than (25 to 27) g/10 min when mixing and blending the used and new PA12 powders to produce parts with acceptable surface finish without “orange peel” texture was recommended [147], [148].

Conclusions

1. A polymeric powder obtained through mechanical comminution, usually by cryogenic grinding, is not well-suited for L-PBF due to the generalized irregular shape of the powder particles. Moreover, multiple stages are required to reduce the particles to the desired size, and a long grinding process is required, which can change the original crystalline structure of the polymer. The presence of non-spherical particles that need extra post-grinding treatments, such as rounding in a downer reactor and dry coating, constitute additional limitations to adopting the grinding techniques to produce a polymeric powder for the L-PBF process.
2. Though the spray drying technique can produce a considerable volume of powder with particle size in the range of 20 to 50 μm favourable for good flowability during the L-PBF process, the hollowed nature of the spherical particles increases the porosity, thus reducing mechanical properties of the LS parts.
3. The rounding of the irregular-shaped powder in a downer reactor is a quick process requiring a thorough control of the short residence time and high temperatures at various stages of the process. The heat involved in the fluidization of the polymer can result in modification of the crystalline structure of the original fed material, thus generating powder with slight changes in thermal properties. Despite the low productivity due to a significant amount of raw or half-melted fed powder

deposited on the reactor's walls, desirable powder particle sizes for L-PBF can be obtained. The agglomeration of very small particles with sizes less than 20 μm leads to a non-freely flowing powder that is difficult to process through L-PBF.

4. The mixing and melting of two or more polymers in solvent and non-solvent to make a blend can generate particles with spherical, continuous, and co-continuous morphologies. Continuous and co-continuous shapes can be characterized as fibrillar forms, which are not suitable particle shapes for L-PBF. The spherical or spheroidal particles are characterized by predominating diameter sizes ranging from 2 to 10 μm , which is not advantageous for L-PBF.
5. The LLPS and precipitation technique can be applied to PP, PA, and POM pellets to generate spherical particles suitable for L-PBF. Depending on the concentration of basic polymer within the used solvents, powder particles of average size, varying from 20 to 444 μm , can be obtained, thus rendering the LLPS process more suitable to produce polymeric powders for L-PBF.

General conclusion on the literature study

The scarcity of polymeric materials suitable for the L-PBF AM process has been one of the major challenges to overcome to satisfy the market demand for products manufactured using this process. The polymer powder most widely used for L-PBF is PA12, produced by EOS, with an estimated 1900 tons delivered annually. The cost of the imported powder for L-PBF, as supplied by commercial companies such as EOS GmbH and Diamond Plastics GmbH, both based in Germany, is expensive at about 65 times the cost of their counterpart raw materials in the form of granules or pellets intended for IM. For instance, the cost of PP CP75 LS powder supplied by Diamond Plastics GmbH is €71 per kg, equivalent to R1420 per kg, with the cost of shipping included. The cost is subject to the continuous fluctuation of exchange rates between the South African rand and the euro. The cost of producing AM parts through L-PBF, which uses PP as feedstock material, can be significantly reduced by investigating the possibility of producing PP powder using locally available PP grades in pellet form. The LLPS technique is efficient in terms of productivity as the total mass of the polymer is dissolved and transformed into powder, and the solvent can be reused for a new production cycle. A simplified experimental setup can be designed to control and optimize the polymer/solvent ratio, stirring speed, and cooling rate to produce a wet gel of agglomerated spherical particles. The gel can be easily dried and subjected to mechanical grinding at ambient temperature to obtain loose powder to be sieved. The classified powder can be dry coated or filled with antistatic agents to remediate the possible increase in the degree of crystallinity of the precipitated powder and, at the same time, improve the flowability of the powder. The

development of an LLPS technique applicable to PP homopolymer grades supplied by a locally based South African company, SASOL Ltd, to produce PP powder suitable for PBF is the focus of the following chapters of this study.

CHAPTER 6: PRODUCTION OF A COMPOSITE POLYPROPYLENE POWDER AND COST ANALYSIS FOR THE LASER POWDER BED FUSION PROCESS

6.1 Introduction

As explained in the conclusion of the literature review, the main reason for the slow uptake of the polymer L-PBF manufacturing process by industry is the high cost of the powder used in the process. It was proposed, in this study, to investigate the feasibility of using a polymer commonly used in the IM industry as a feedstock for the L-PBF process since it is available at a low cost. Although nylon PA12 delivers excellent results for L-PBF, it is not easy to reduce the pellet material to a powder form suitable for the process. As mentioned in Section 5.5, aggressive solvents are required to produce powder through the LLPS process, which must be done under strict safety protocols. This is especially true if the process is upscaled to produce large quantities of powder for the commercial market. Reducing nylon pellets through cryogenic grinding may require other agents, such as boron nitride, to facilitate the breaking of the pellets into smaller particles. The process also does not deliver good results regarding the flowability of the powder produced because of the irregular shape of the particles, and additives such as nano-silica (SiO_2) must be added to improve the flowability of the powder [149]. PP powder suitable for L-PBF can be produced through cryogenic grinding. However, the liquid nitrogen used in the process is expensive, thus making the end product expensive. Grinding of PP also produces irregular particle shapes, which reduces the flowability of the powder. Therefore, producing PP powder using the LLPS process was proposed for this study. In 2022, PP pellets for IM were available from local suppliers at about R33 per kg. Since there is no locally manufactured PP powder in South Africa, the powder must be imported from an international supplier, such as Diamond Plastics GmbH (Germany), but by 2024, the estimated cost is still high at about R1309 per kg.

The steps followed to investigate the LLPS process for producing powder suitable for L-PBF in this study are illustrated through a flow diagram in Figure 6-1.

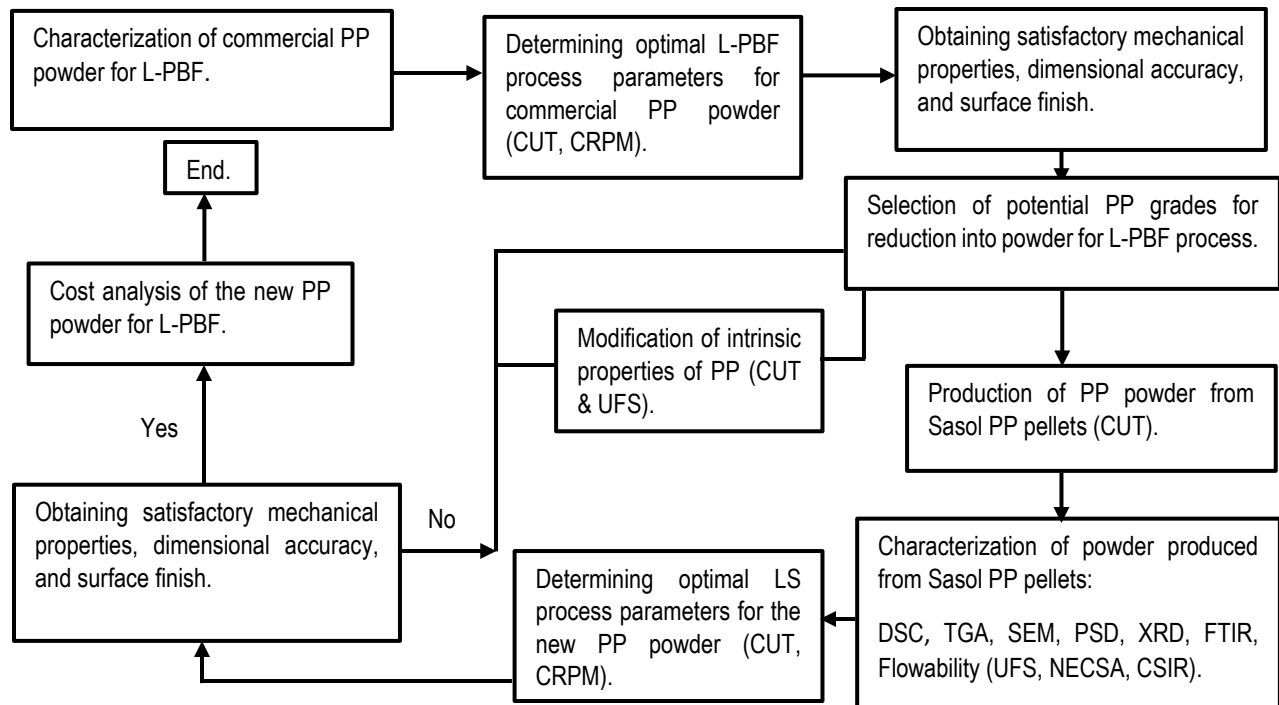


Figure 6-1: Flow diagram of the experimental methodology followed in the study

6.2 Characterization of commercially produced PP powder from Diamond Plastics

A commercial PP powder PP CP75 for L-PBF was acquired from Diamond Plastics GmbH (Germany) to serve as benchmark against the powder produced in this study could be compared. A powder sample was sent to Sasol Limited, an integrated energy and chemical company based in Sandton, South Africa, for chemical and thermal analyses. As the producer of a range of polymers, Sasol could then propose a grade with similar properties to their existing range of PP pellets. FTIR and High-Performance Liquid Chromatography (HPLC) tests were used to analyze the chemical composition, while DSC was applied to determine the thermal behaviour of the powder. Table 6-1 summarizes the characteristic findings from the chemical and thermal analyses.

Table 6-1: Results of chemical and thermal analyses of LS powder PP CP75

Chemical analysis	Characteristic findings
FTIR	PP powder containing 10.7% talc evidenced by peaks at 668, 1012, and 3675 cm^{-1} wave numbers
HPLC	PP powder containing stabilizing antioxidant additives: 95 ppm of Irganox 1010, 254 ppm of Irgafos, and 849 ppm of Glyceril monostearate (GMS)
Thermal analysis: DSC analysis	Onset, peak and final melting temperatures were at 157.9, 163.1 and 167.1°C, respectively. Starting, peak, and final crystallization temperatures were at 130.2, 124.9, and 119.4°C, respectively. Degree of crystallinity of 43.4%

A parallel investigation was carried out on optimal process parameters applicable to PP CP75 powder when processed on an EOS P380 L-PBF machine in terms of mechanical properties, dimensional accuracy, and surface finish of the parts produced [117]. Based on recommendations from the powder supplier, six process parameters, namely, layer thickness, scanning speed, hatch distance, laser power, and building and removal chamber temperatures, were determined by experimenting with the processing of the commercial PP CP75 powder. The scanning speed was optimized when the building and removal chamber temperatures were fixed at 158 °C and 100 °C, respectively, with a layer thickness of 0.150 mm, hatching distance of 0.250 mm, and laser power of 10 W [117]. The tensile test pieces produced were characterized with the highest tensile strengths of 18.5, 12, and 7 MPa and moduli of elasticity of 2264, 2308, and 1729 MPa obtained in x-, y- and z-directions, respectively, for an optimal scanning speed of 1740 mm/s. The surface roughness of tensile specimens built in the x-direction was generally found to increase with the increase of the scanning speed. When the scanning speed was increased from 1481 to 2105 mm/s, the R_a value increased from 12.9 to 15.8 μm .

A calibration block (Figure 6-2) was designed to assess the dimensional accuracy and the quality of the inscribed texts.

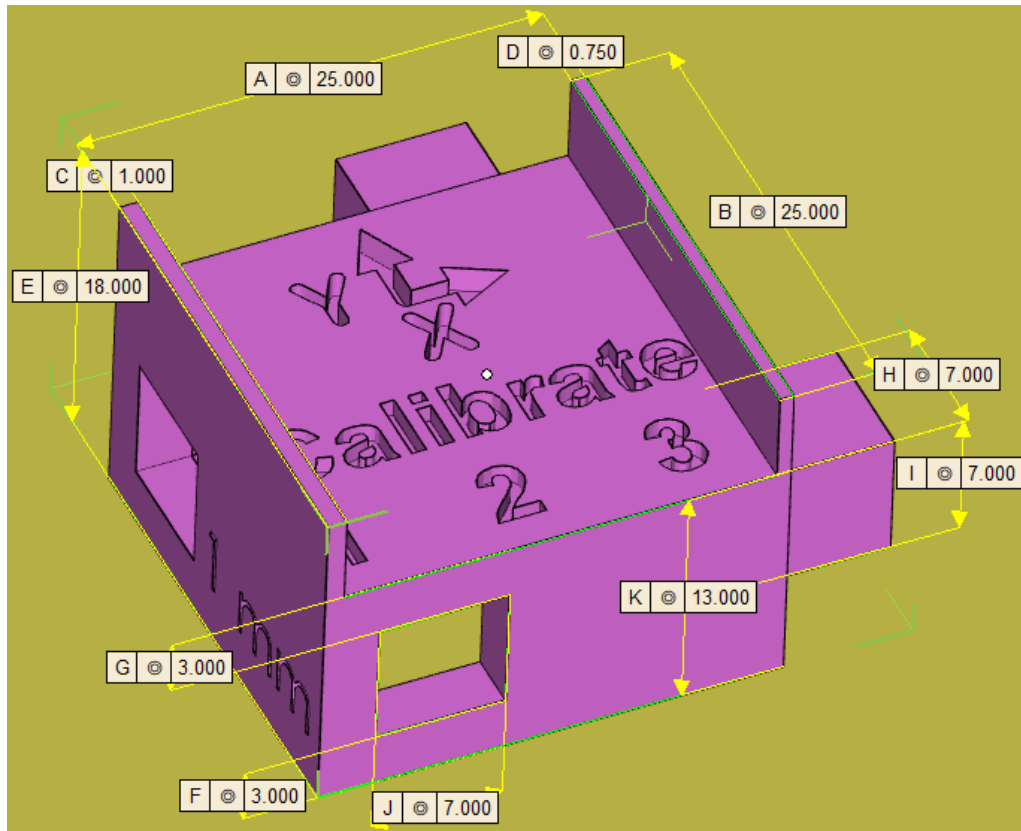


Figure 6-2: CAD of the calibration block for assessing the dimensional accuracy

The dimensional deviations from the nominal size of 25 mm of the calibration block in the x-direction and deviations from nominal thicknesses increased with the increase in the scanning speed. The deviations from nominal dimensions associated with the upskin and downskin surfaces showed either neutral or decreasing trends with the increase in the scanning speed. The accuracy of the formation of walls thinner than 0.75 mm required a scanning speed lower than 1481 mm/s.

Various texts (Figure 6-3) were purposely designed on the test block to assess the quality of printing of aesthetic features.

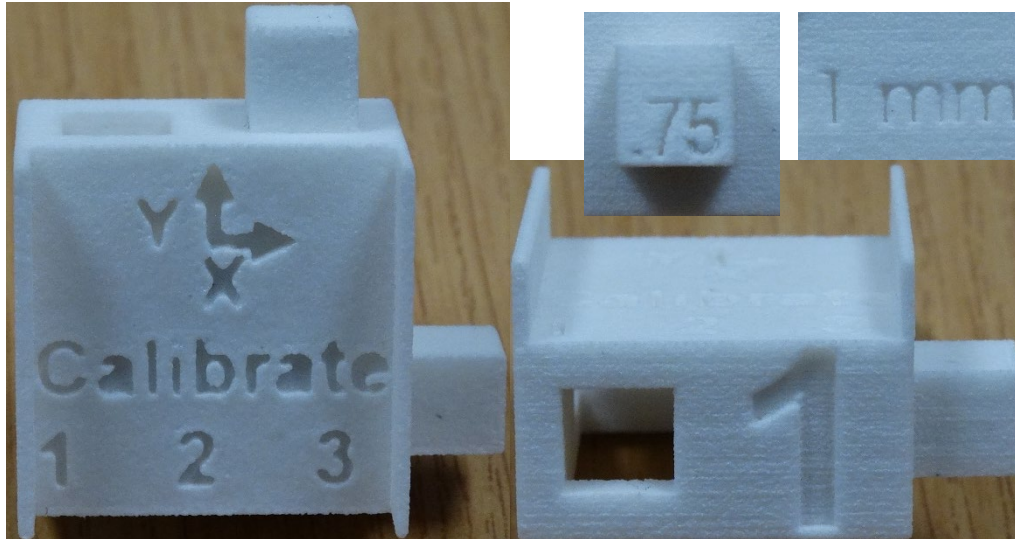


Figure 6-3: Quality of inscribed texts on the calibration block

Visual inspection could not establish a significant effect of the scanning speed on the quality of the texts inscribed on the calibration block or tensile test pieces. Accurate texts with very good readability were produced for all investigated text fonts and sizes for all considered scanning speeds.

6.3 Producing PP powder from locally available pellets for IM

6.3.1 Selection of the PP grades for production of LS powder

The aim of this study was to investigate the production of PP powder suitable for L-PBF to reduce the overall cost of end-use components produced through the process. As mentioned in Section 2.4, PP is a semi-crystalline polymer with more than 20 varieties of grades, which can be mainly classified into homopolymer or copolymer categories. Depending on the chemical formulation, which also dictates the intended application in science and technology, homopolymers are diversified into grades characterized by different thermal, rheological, mechanical, and technological properties. Sasol Limited produces a wide range of homopolymer and copolymer PP grades. For this study, the investigation was limited to available homopolymers. HNR100 grade was chosen as pure PP without any nucleating agents added. It has an MFR of 12 g/10 min, which is slightly lower than the MFR of 20 g/10 min of PP CP75 supplied by Diamond Plastics GmbH [150]. Initial testing on HNR100, which was available to the researchers [151], showed promising results in producing powder using the LLPS process described in Section 5.5. The HTV145 grade was also chosen because of its MFR value of 50 g/10 min, which is close to that of virgin PA12 powder from EOS and known to perform well with L-PBF.

Compared to syndiotactic or atactic forms of PP, 90% of commercial PP components are produced in isotactic PP form due to their desirable forming characteristics, low density, and satisfactory mechanical properties [152]. The granules of both isotactic homopolymer grades, HNR100 and HTV145, are widely used in the traditional plastic manufacturing industry, the former for IM and the latter for extrusion-coating. Table 6-2 summarizes the thermal and mechanical properties of HNR100 and HTV145 grades.

Table 6-2: Thermal and mechanical properties of HNR100 and HTV145 PP grades

Grades	Melt Flow Rate (230 °C/ 2.16 kg), g/10 min.	Tensile stress at yield, MPa	Tensile strain at yield, %	Tensile modulus of elasticity, MPa	Flexural modulus, MPa	Charpy notched impact strength at 23 °C, kJ/m ²	Melting temperature, °C	Application
HNR100	12	34	8.5	1550	1500	2.8	163	Injection moulding
HTV145	50	35	8.5	1650	1600	2.5	163	Extrusion- coating
Standards	ISO 1133	ISO 527			ISO 178	ISO 179	ISO 11357	

Table 6-2 shows that the PP grades, HNR100 and HTV145, have similar ranges of mechanical properties and melting temperatures. The significant difference in their MFR associated with their average molecular weights (261500 for HNR100 with a polydispersity index (PDI) of 6.25 and 165800 for HTV145 with a PDI of 4.85) can be a deterministic property that affects the intrinsic and extrinsic properties of the resulting powder for L-PBF.

6.3.2 Small-scale experimental setup

The LLPS technique described in the patent by Korsgen *et al.* [128] (see Section 5.5) was chosen to reduce the selected PP pellets to powder. Xylene is an established efficient solvent for PP, especially in polymer

recycling technology aimed at sustainable environmental development [153], [154]. The liquid m-Xylene supplied by Merck (Pty) Ltd, South Africa, with a chemical formula C_8H_{10} and a boiling temperature of $139.1^{\circ}C$, was used as a dissolving medium in the current study. The hazardous and precautional information on the m-Xylene retrieved from the safety data sheet of the product [155] is summarized in Table 6-3.

Table 6-3: Hazardous and precautional characteristics of m-Xylene

Code of hazard or precautionary statement	Category	Hazard or precautionary statement
H226	3	Flammable liquid and vapour
H304	1	May be fatal if swallowed and enters the airways
H312	4	Harmful in contact with skin
H315	2	Causes skin irritation
H319	2A	Causes serious eye irritation
H332	4	Harmful if inhaled
P210		Keep away from heat/sparks/ open flames/ hot surfaces. No smoking
P271		Use only outdoors or in a well-ventilated area
P273		Avoid release into the environment

Considering the level of hazard and precautions for handling m-Xylene, PP granules were dissolved and precipitated into heated xylene in a custom-designed processing cabinet, shown in Figure 6-4. Initial small-scale testing was performed to determine the suitability of the process for the PP. A quantity of 50 g of HNR100 was dissolved in 400 ml of m-Xylene in a 1-liter isolated glass beaker on an FMH instruments Model STR-MH 180 magnetic stirrer hotplate.

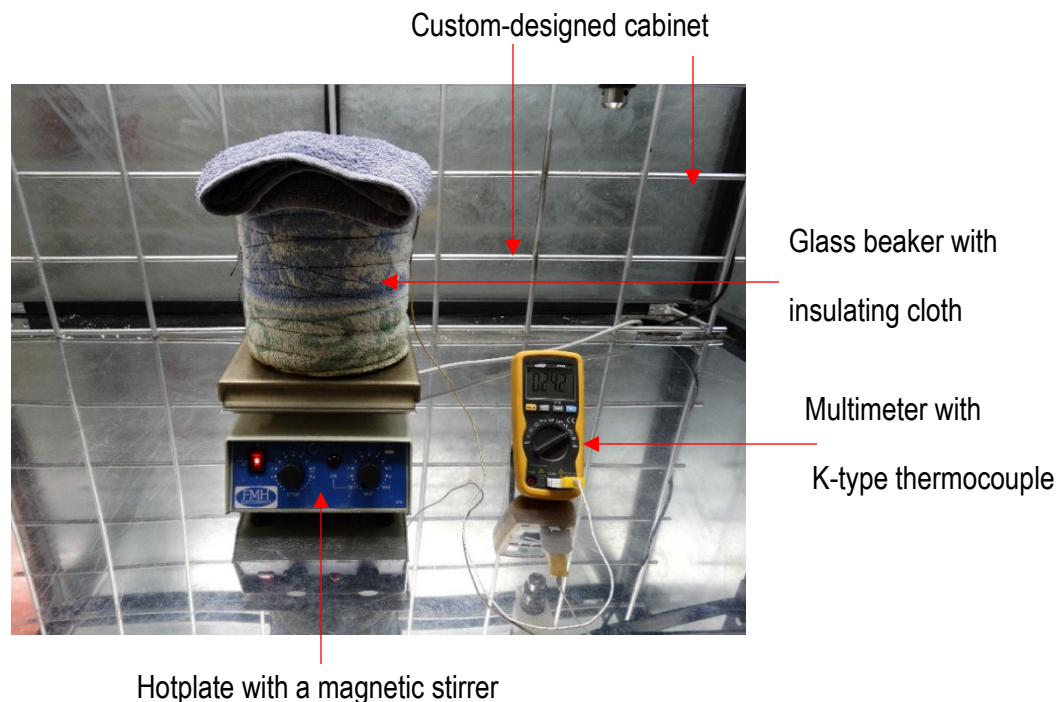


Figure 6-4: Small-scale experimental setup

The temperature of the mixture was slowly raised at a heating rate of about $1^{\circ}\text{C}/\text{min}$ while stirring till the boiling point was reached. A Major Tech MT24 multimeter with a K-type thermocouple was used to measure the temperature. Complete dissolution of the PP was attained at a temperature of 134°C , which is below the m-Xylene's boiling point of 139.1°C . The hotplate and stirrer were switched off, and the mixture was allowed to cool on the hotplate to a room temperature of 25°C under quiescent conditions. Spherical particles of HNR100 were formed and settled to the bottom of the beaker. The m-Xylene was poured off, and the PP particles were dried in sunlight. Some clumping of the particles took place while drying, but it was easy to separate by just rubbing between fingers. Inspection of the particles under an optical microscope showed sizes ranging from 100 to 200 μm . Particles with such big sizes are unsuitable for L-PBF, which requires particle sizes ranging from 20 to 100 μm [2]. The experiment was repeated, but the beaker was removed from the hotplate after heating, and the isolation material was removed. This resulted in a much more rapid cooling of the solution and caused particles smaller than 10 μm to form. Although the cooling rate can be used to control the size of particles that form, this is difficult to control since it depends on ambient temperature, which can vary widely if not controlled.

To overcome the drawbacks encountered with the dissolution and precipitation of HNR100, the investigation continued with HTV145, a PP homopolymer containing nucleating additives characterized by MFR of 50 g/10 min. Following a similar process of dissolution, precipitation, drying, and grinding as used for HNR100, the powder obtained through heating the HTV145 granules in m-Xylene up to 134 °C in an isolated beaker and left to cool slowly to room temperature resulted in precipitation of small spherical particles with sizes ranging from 10 to 30 µm. Contrary to the findings of Fang, Wang, and Xu [100], where it was expected to obtain bigger-sized particles when a PP grade with higher MFR is used, the current investigation found an opposite trend. The two opposite behaviours in terms of the particle size from the dissolution and precipitation of the two grades when processed separately suggested that their mixture in well-defined proportions could lead to powder with desirable particle sizes for L-PBF. Experiments with different weight ratios of HNR100 and HTV145 were found to alter the particle size of the L-PBF powder. The results were also found to be repeatable when the mixture was slowly cooled in an isolated beaker to eliminate the effect of the ambient temperature on the cooling rate.

The effect of the weight ratio between solvent and non-solvent was mentioned as a means to influence only the size of the powder particles, with no effect on the intrinsic properties of the product from the dissolution and precipitation process. Himma, Wardani, and Wenten [152] reported the effect of non-solvents on increasing the surface roughness and porosity of a PP membrane dissolved in Xylene with non-solvents added. The m-Xylene was used alone as a solvent without adding a non-solvent to avoid any possible increase in surface roughness and porosity of the powder particles that would form. The addition of a non-solvent could not only increase the production cost but also affect the integrity of m-Xylene as it was recycled and reused to produce new batches of PP powder. A ratio of 80% HNR100 to 20% HTV145 was found to produce powder particles with sizes around 60 µm.

The characterization of PP CP75 from Diamond Plastics GmbH by Sasol Ltd. showed that 10.7% talc was added to the powder to reduce the crystallinity of the polymer. The ratio of polymer to talc that was finally decided upon through experimentation was 280 g HNR100 (70%) to 80 g HTV145 (20%) with 40 g of talc (10%) added. The addition of talc did not change the size of the particles significantly.

Sufficient data was gained from the small-scale testing to show that it was possible to produce PP particles using a combination of HNR100 and HTV145 grades supplied by Sasol Ltd. Since it was only possible to

produce small quantities of powder, which was insufficient to test for processability through the L-PBF process, it was decided to up-scale the experimental setup.

6.3.3 Up-scaling of experimental setup

Two concentric stainless steel pots (Figure 6-5a) with internal diameters of 240 mm and 315 mm and heights of 190 mm and 215 mm, respectively, were used. The larger pot had a ferrous metal base for heating on a Snappy Chef model SM-CO2D industrial induction plate. Stirring was made possible by using a simple Ryobi model PD-650 hand drill attached to a two-bladed stirrer that passed through the lids of the two pots when one was concentrically placed inside the other (Figure 6-5b).

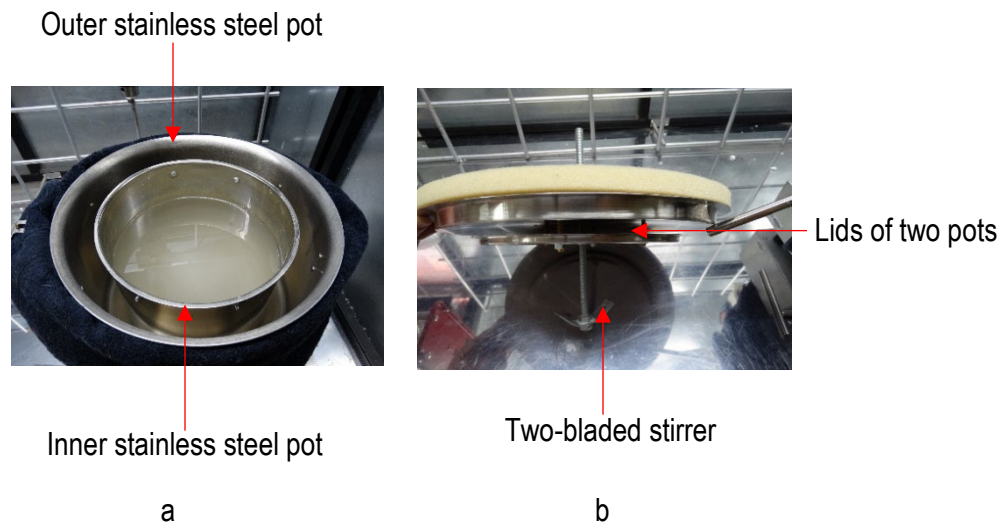


Figure 6-5: Two stainless steel pots (a) and stirring system (b)

Four holes specified by numbers 1, 2, 3, and 4 and circumferentially positioned at 90° to one another were drilled at distances of 50, 80, 120, and 120 mm, respectively, from the center of the two lids. The holes accommodated the passing through of four K-type thermocouples corresponding to channels 1, 2, 3, and 4, respectively. From the surface of the lids, the endpoints of thermocouples corresponding to channels 1, 2, 3, and 4 were immersed into the solution in the inner pot at depths of 40, 75, 125, and 160 mm, respectively. For monitoring the temperature of the solution at four locations, the thermocouples were connected to an 8-channel Pico® Technology TC-08 data logger. Isolation of the double-walled pot was achieved by wrapping a thick towel around the outer pot and cutting a piece of polyurethane foam to fit on top of the lid of the outer pot. The setup was placed inside the flow cabinet that was also used for the small-scale setup to safely heat the m-Xylene, as shown in Figure 6-6.

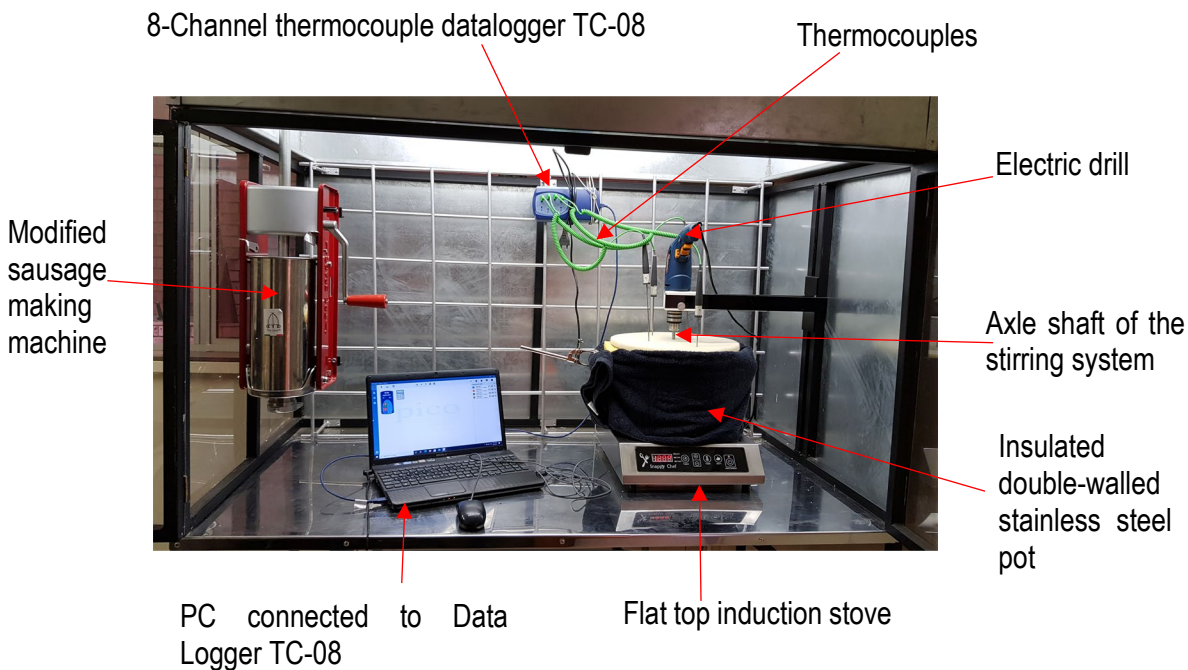


Figure 6-6: Experimental setup in the customized processing cabinet

6.3.4 Dissolving and precipitation of PP granules

The larger experimental setup allowed for 400 g of HNR100 (280 g), HTV145 (80 g) PP pellets, and talc (40 g) to be dissolved into 5.5 litres of m-Xylene. The mixture was heated from room temperature of 20°C to 133.48°C at an average heating rate of 1.656°C/min (Figure 6-7) while continuously stirring at 50 rpm until the PP was wholly dissolved into the m-Xylene.

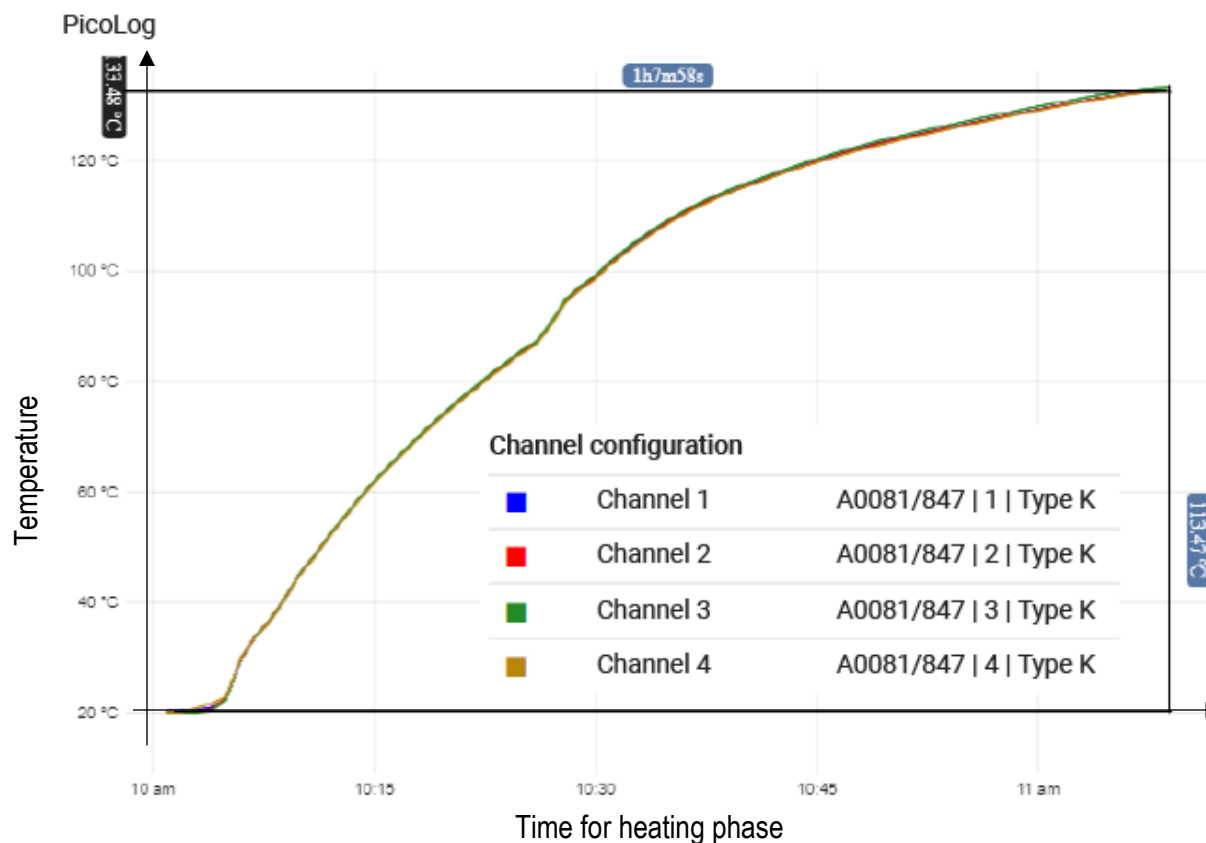


Figure 6-7: Heating temperature versus the time of the mixture of HNR100, HTV145, and talc into m-Xylene

Figure 6-7 shows the effectiveness of the stirring system, where the temperature of the mixture, through heating, was uniformly distributed and homogeneously recorded at the four different locations by the thermocouples.

Once complete dissolution was achieved, the stirring and heating were stopped, and the solution was left to cool down to room temperature at an average cooling rate of 0.287 °C/min (Figure 6-8). This allowed the precipitation of the dissolved PP mixture through the nucleation and growth of PP crystals for the formation of spherical microscopic particles in the form of a gel.

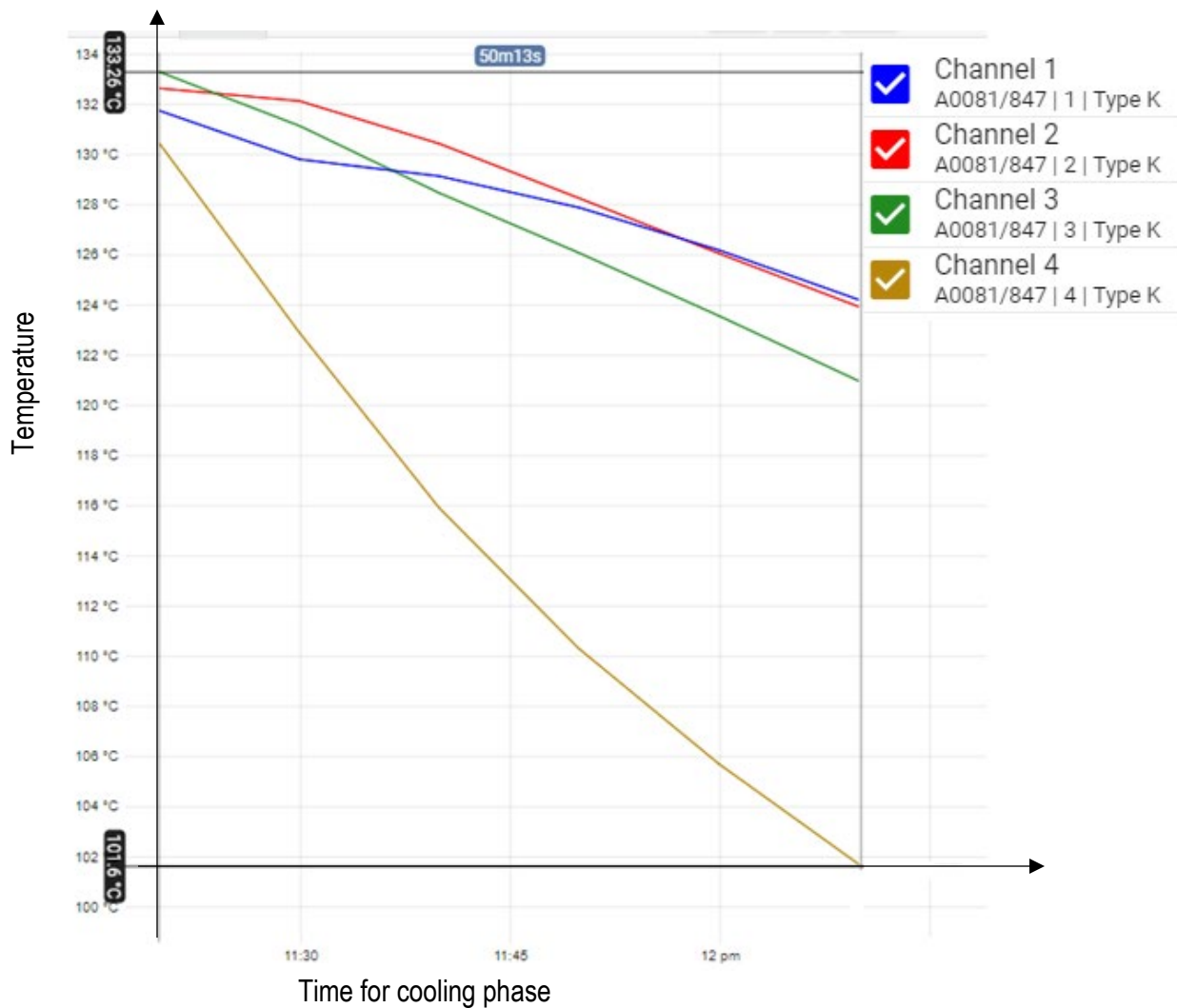


Figure 6-8: Cooling temperature versus time of the mixture of HNR100, HTV145, and talc into *m*-Xylene

Figure 6-8 shows that the four locations were subjected to different average cooling rates of 0.151, 0.176, 0.246, and 0.574 °C/min, respectively, corresponding to channels 1, 2, 3, and 4. The temperature of the mixture was not uniformly distributed and decreased from the upper to lower layers of the solution. Since the double-walled pot was left on the induction plate to cool, which was not thermally isolated similar to the rest of the pot, cooling took place more rapidly from the bottom of the solution upwards.

6.3.5 Drying, grinding, and coating of the PP powder

Using a modified TRE SPADE sausage filler machine, most of the m-Xylene was removed from the precipitated PP gel (Figure 6-9). The gel was introduced into the machine's stainless steel barrel and compressed by hand cranking a rack-and-pinion mechanism connected to a piston.

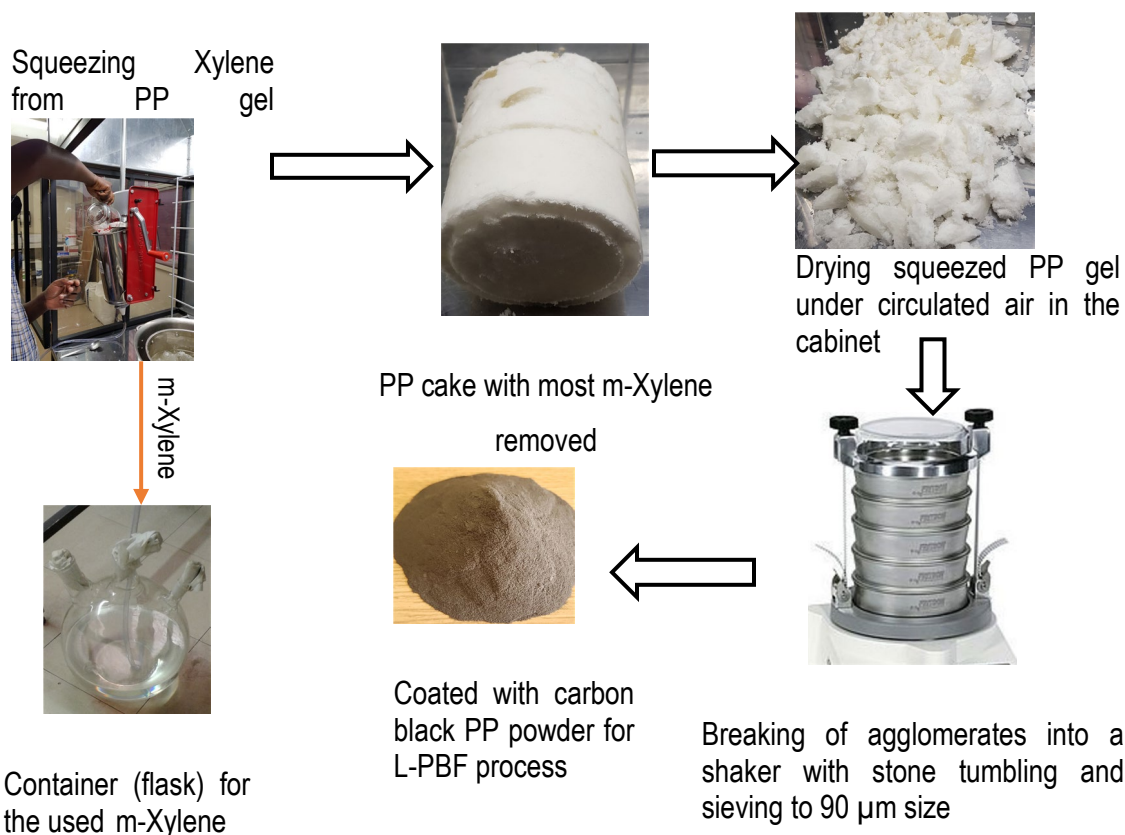


Figure 6-9: Process flow for production of a composite PP powder using HNR100 and HTV145 grades

The press-squeezing action forced the liquid m-Xylene through a stainless-steel filter at the bottom of the barrel, from where it flowed through a flexible pipe to a storage container for future re-use. The PP cake was removed from the barrel, weighed, and found to be 1257 g. The weight of the m-Xylene remaining in the cake was, therefore the difference between 1275 g and 400 g (of PP grades and talc), which was equal to 875 g. The volume of the m-Xylene removed after the experiment was 4310 ml. The loss of m-Xylene was thus 1190 ml, considering that the experiment was started with 5500 ml of xylene. Considering the density of 0.860 g/ml for m-Xylene at 25°C, the volume of the 1190 ml, therefore, equates to 1023.4 g of m-Xylene. This is more than the 875 g of m-Xylene that was determined to have remained in the cake; the difference of

148.4 g could be ascribed to the evaporation of the m-Xylene in the cabinet to be eliminated through the centralized ventilation of the room during the heating process to dissolve the PP.

The squeezed PP cake was spread on aluminum trays inside the flow cabinet, and the residual m-Xylene was allowed to evaporate for 48 hours. The weight of the dried powder was 394 g, which was 6 g less than the input of 400 g of both PP grades and talc that the experiment started with. Since the metal sieve filter in the sausage filler used for squeezing out, the m-Xylene was coarse at 200 μm , a negligible quantity of the polymer particles could have ended up in the m-Xylene drained out for future re-use.

The dried powder particles were clumped together and needed to be separated to improve the flowability of the powder. This was achieved by using a Fritsch Analysette three-sieve shaker machine. The powder was introduced into the machine's stainless steel bowl with stone tumbling media. Continuous shaking for one hour at a frequency of 50 Hz with an amplitude of 2 mm effectively separated the powder particles.

Inspection of the powder particles under a microscope showed particles with average diameter of 60 μm comparable to particle size achieved with the small-scale experimental setup. Again, the talc did not influence the particle size, and the talc could be seen as separate particles intermixed with the PP particles.

Since the powder would have been processed using a Sintratec S1 laser-sintering machine with a low-power diode laser, the white PP powder needed to be coloured dark grey. Grey nylon powder supplied with the machine was used as a reference to determine how much carbon black needed to be added to the PP for sufficient laser power absorption. One gram of carbon black added to every 400 g batch of dried powder was found to be sufficient. The carbon black would also act as an antistatic agent to improve the flowability of the powder during L-PBF on the Sintratec S1 machine.

6.4 Cost analysis for production of the new PP composite powder for the L-PBF process

A simplified cost for the production of 1 kg of the new composite PP powder was calculated and compared to the cost of the PP CP75 supplied by Diamond Plastics in 2022. Table 6-4 summarizes the cost to produce the new PP composite powder in the laboratory environment. The experimental procedure described in Section 6.3.4 was to produce 400 g of the new composite powder. To produce 1 kg of the powder, the quantities of PP pellets and talc must be scaled up 2.5 times. The quantity of m-Xylene indicated in the table was also based on the 1190 ml lost in producing the 400 g of powder, and this will also have to be scaled up

by the same amount. Recovering the m-Xylene by only compressing the PP cake was not effective, and it should be possible to recover significantly more of the solvent by using a centrifuge. The carbon black used to produce the new composite was received as a donation, and since such a small amount was required to colour the powder grey, the cost of it was not included in the calculation.

Table 6-4: Cost calculation for the newly produced PP composite powder

Item	Sell quantity	Price	Required quantity for 1 kg of new PP composite powder	Price
HNR100 pellets	25 kg	R825,00	700 g	R23,10
HTV45 pellets	25 kg	R825,00	200 g	R6,60
Talc	25 kg	R212,00	100 g	R0,85
Carbon black	-	-	2.5 g	0
m-Xylene	25 litres	R2267,80	2,975 litres	R270,00
Electrical power for the heating phase	4,5 kWh	R2,26	4,5	R11,70
Total cost				R312.25

The cost calculation did not include the cost of labour as the powder was produced for research purposes in a laboratory environment. The equipment used in producing the powder was also not included in the cost calculation because it can also be used for other research studies. Compared to the cost of R2141 for 1 kg of imported commercial PP CP75, it can be concluded that it should be worthwhile and profitable to promote the production of PP powder using locally produced PP pellets. The cost of 1 kg of the new composite PP powder was estimated at R312.25, which is 6.86 times cheaper than the cost of the PP CP75 imported commercial powder with comparable suitability for L-PBF. Upscaling the process to deliver powder on a commercial scale will require factors such as labour cost, depreciation of equipment, overheads with renting of a building, electricity consumption etc. to be taken into consideration. This however fell outside the scope of the current study. Upscaling the process into an industrial process should yield significant economies-of-scale which will bring the cost of producing the powder down again.

Conclusions

1. To produce suitable powder for L-PBF process, two PP grades, namely HNR100 and HTV145, locally supplied by Sasol Ltd were selected to be dissolved through LLPS process using m-Xylene solvent.
2. The weight ratios of 70% for HNR100 and 20% for HTV145 with 10% talc added could generate spherical particles with an average size diameter of 60 μm . A negligible amount of carbon black (2 g) was particularly added to enhance the laser absorption on the Sintratec laser sintering machine.
3. A simplified cost analysis showed that the cost of the newly produced PP powder was 6.86 times cheaper than the cost of the PP CP75 imported commercial powder with comparable suitability for L-PBF.
4. For sustainable future use, the development of the current study continues with the characterization of the newly produced PP powder through TGA, DSC, SEM, PSD, XRD, FTIR, chemical analyses; density and flowability measurements.

CHAPTER 7: CHARACTERIZATION OF THE COMPOSITE POLYPROPYLENE POWDER FOR THE LASER POWDER BED FUSION PROCESS

The characterization of the PP powder for laser sintering was performed through DSC, TGA, SEM analysis, chemical composition analysis, powder density, PSD, flowability, WAXRD, and FTIR spectroscopy.

7.1 Differential Scanning Calorimetry analysis

DSC is a thermal analysis method based on the principle of measuring the difference of the heat flow rates as a function of temperature and/or time into a specimen under investigation and another material known as a reference. The DSC apparatus measures the energy required to maintain both the reference and the sample at the same temperature. The difference in heat flow between the sample and reference constitutes a quantitative measure of absorbed or released heat during thermal transitions of the sample. The curves produced through DSC analysis provide the possibility for a correct understanding of the thermal behaviour of the polymeric sample when it absorbs energy during heating, leading to its melting, or when the sample releases its latent energy due to cooling, resulting in nucleation and growth of crystals. Since the main stages in the L-PBF process involve heating the powder from ambient temperature to just below the melting temperature to allow sintering of the powder and then cooling down to room temperature for consolidation of the part, the DSC analysis is used to investigate the thermal characteristics such as degree of crystallinity and window of sinterability of polymeric powders for L- PBF.

7.1.1 DSC through three cycles

To investigate the thermal behaviour of the new PP/talc/carbon black powder, a sample of 5 mg of powder was subjected to DSC analysis using a Mettler Toledo DSC 822e machine at the Department of Chemistry at the UFS. The sample was subjected to three cycles of heating and cooling at a standard rate of 10°C/min under a nitrogen atmosphere, and the resulting experimental DSC curves are shown in Figure 7-1.

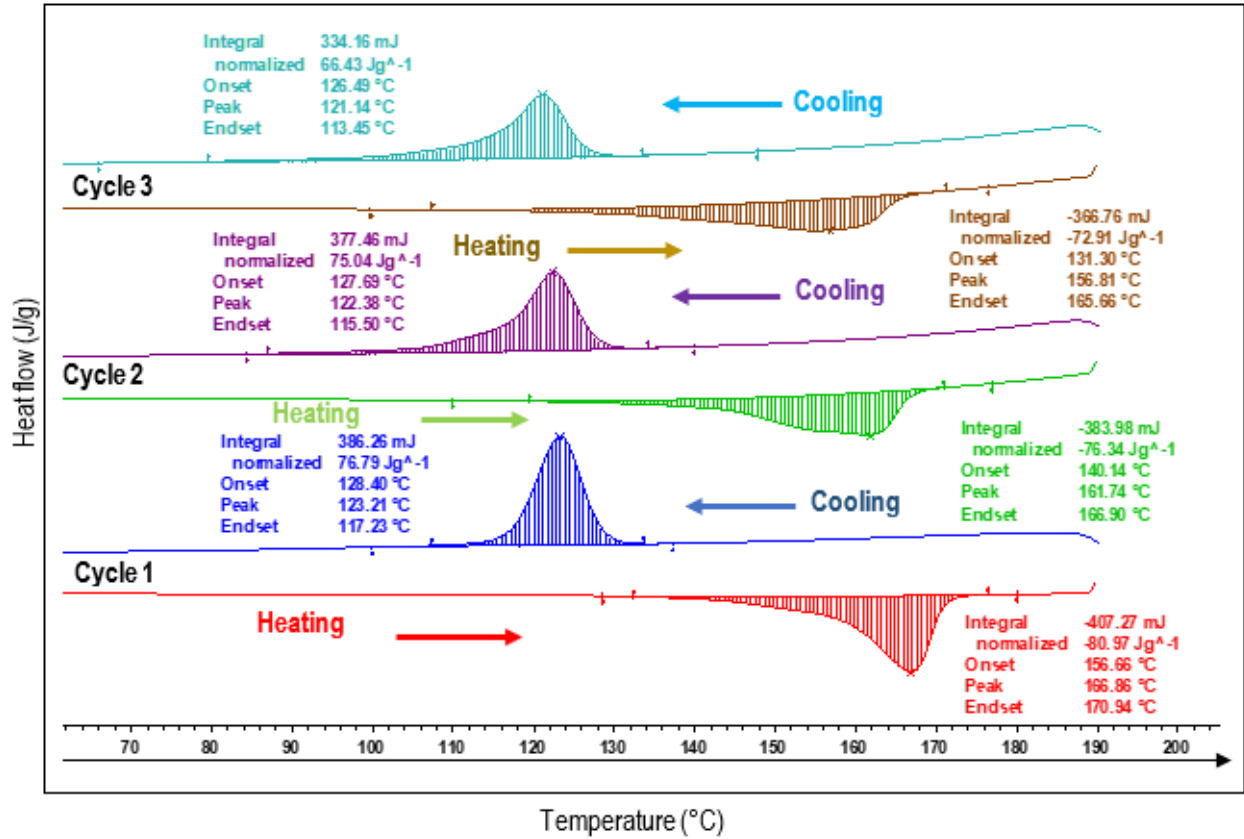


Figure 7-1: DSC analysis of the composite PP powder for the L-PBF process

Each cycle consisted of heating the sample from 25 to 190°C, followed by cooling from 190 to 25°C. It was observed that after the cooling of the first cycle, the powder sample was transformed into a bulk solid, with the talc and carbon black components already dispersed in the polymer matrix. To investigate the thermal behaviour of the solid bulk material, the second and third cycles were run, and Table 7-1 summarizes the results. The percentage degree of crystallinity X_c was calculated by applying the method used by Wang *et al.* [46] as follows:

$$X_c = \frac{\Delta H_m}{\Delta H_f \times \phi} \times 100\% \quad (\text{Eq. 3})$$

ΔH_m -is the melting enthalpy of the investigated isotactic PP,

ΔH_f -is the fusion (melting) enthalpy of an isotactic PP with 100% degree of crystallinity, and the corresponding theoretical melting enthalpy is considered to be 209 J/g [46],

ϕ is the fraction of the polymer in the composite, estimated to be 90% for the new PP powder with 10% talc, ignoring the small percentage of carbon black.

Table 7-1: Thermal characteristics of the new composite PP powder

	First cycle	Second cycle	Third cycle
Melting properties			
Starting melting temperature (T_{ms}), °C	144.7	134.4	130.5
Final melting temperature (T_{mf}), °C	173.7	171.8	168.7
Peak melting temperature (T_{mp}), °C	166.9	161.7	158.7
Onset melting temperature ($T_{m-onset}$), °C	156.7	140.1	131.3
End-set melting temperature ($T_{m-end-set}$), °C	170.9	166.9	165.7
Heat of melting (J/g)	81	76.3	72.9
Degree of crystallinity (%)	43	40.6	38.8
Crystallization properties			
Starting crystallization temperature (T_{cs}), °C	132	131.7	132
Onset crystallization temperature ($T_{c-onset}$), °C	128.4	127	126.5
End-set crystallization temperature ($T_{c-end-set}$), °C	117.2	115.5	113.5
Peak crystallization temperature (T_{cp}), °C	123.2	122.4	121.1
Final crystallization temperature (T_{cf}), °C	106.2	101.4	97.1
Heat of crystallization (J/g)	76.8	75	66.4
Supercooling temperature $T_{mf}-T_{cs}$, °C	41.7	40.1	36.6
Range of LS processing temperatures [$T_{c-onset}$, $T_{m-onset}$] and, °C	From 128.4 to 156.7	From 127.0 to 140.1	From 126.5 to 131.3
Sinterability window, $T_{m-onset} - T_{c-onset}$, °C	28.3	13.1	4.8
Degradation properties			
Range of degradation temperature, °C	385 to 494		
Mass loss, (%)	88		

Therefore, for the first cycle, the percentage degree of crystallinity was obtained as follows:

$$X_c = \frac{\Delta H_m}{\Delta H_f \times \phi} \times 100\% = \frac{80.97}{209 \times 0.9} \times 100\% = 43\%$$

The percentages of the degree of crystallinity of the new PP powder for the second and third cycles were calculated similarly, and the results are shown in Table 7-1.

The degree of crystallinity of semi-crystalline polymers varies from 10 to 80% [37], and it ranges from 40 to 70% for isotactic PP [42], [48]. Under moderate conditions, the spherulites obtained while solidifying iPP in

quiescent conditions at a moderate cooling rate are roughly made up of 50% α -phase crystals and 50% amorphous phase. If the cooling rate is low enough (less than 3°C/s), the resulting spherulites are richer in α -phase at about 60%, while the amorphous content of spherulite will be lowered to around 40% [62]. The melting and crystallization behaviour of the sample during the three cycles can be used to determine the degree of crystallinity and the sintering parameters of the powder. From Figure 7-1 and Table 7-1, earlier onset of melting temperatures, as well as the lowering of the degree of crystallinity, are observed during the second and third DSC cycles. The dispersion of the talc and carbon black in the polymer matrix seen after the first DSC analysis cycle could be the cause of significant shifts in the onset melting temperatures from 157 to 140°C for the second cycle and from 140 to 131°C for the third cycle. On the other hand, slight decreases in onset crystallization temperatures from 128.4 to 127°C and from 127 to 126.5°C were recorded during the transitions from first to second and from second to third cycles. Such decreases in onset melting temperature resulted in a significant narrowing of the sinterability window from 28.26 to 13.14°C and 13.1 to 4.8°C , respectively. During the first cycle, the window of sinterability of 28.3°C , i.e., allowing sintering within a range from 128.4 to 156.7°C (Table 7-1), is greater and comparable to a window of sinterability of 25.8°C obtained by Fang, Wang, and Xu [100]. A slight progressive decrease in the degree of crystallinity from 43 to 40.6 and 38.8% is also observed, meaning that a better dispersion of the talc and carbon black into the polymer matrix is achieved after each heating and cooling cycle. The resulting degree of crystallinity of 43% is close to that of 43.4% (Table 7-1) of the DSC analysis of PP CP75 powder from Diamond Plastics. This indicates that the filling with talc and coating with carbon black would lead to levels of shrinkage and warpage comparable to those experienced during L-PBF of the commercial powder PP CP75.

The window of melting region can be defined as the difference between the final and starting melting temperatures. A narrow melting region is desirable during L-PBF to avoid the high laser energy consumption to melt the powder particles. Higher laser energy will promote the degradation of laser-sintered powder, thus limiting the number of possible recycling for future usage [3]. The DSC analysis showed an increase in the window of melting region from 29°C for the first cycle to 37.3°C for the second cycle. From the second to the third cycle, a slight increase in the window of melting from 37.3 to 38.1°C was recorded. Such an increase in the window of melting region from one heating cycle to another testified to the possible degradation of laser-sintered powder, and thermogravimetry analysis would be used for deeper investigation.

7.1.2 Comparison of DSC analyses of PP in pellet and powder forms

The desirable average size and PSD of powder particles, good flowability, and efficient laser energy absorption are required for L-PBF. Further investigation was carried out to find the extent to which the precipitation process followed by the mechanical comminution of agglomerates and the addition of talc and carbon black into the sieved powder could affect the thermal behaviour of the original pellets.

DSC analyses were performed at the UFS on a TA Instruments DSC 2500 machine under a nitrogen atmosphere. The heating and cooling temperature cycle varied between 25°C and 200°C with a heating and cooling rate of 10°C/min. Experiments were conducted on nine PP samples of 5 g each, which consisted of the following:

- HNR 100 and HTV145 pellets were melted individually, and solid samples were taken.
- HNR100 (75%) and HTV145 (25%) were melted together and a solid sample was taken.
- Powder was produced from HNR100 and HTV145 individually through the LLPS process, and a powder sample was taken of each.
- Powder was produced from a mix of HNR100 (75%) and HTV145 (25%) using the LLPS process, and a powder sample was taken.
- Powder was produced from a mix of HNR100 (70%), HTV145 (20%), and talc (10%) through the LLPS process, and a powder sample was taken.
- Powder was produced from a mix of HNR100 (70%), HTV145 (20%), and talc (10%) using the LLPS process to which carbon black (1 g/400 g) was added, and a powder sample was taken.
- A powder sample was taken from a batch of PP CP75 supplied by Diamond Plastics.

Typical DCS graphs were obtained from all the samples, and the results are summarized in Table 7-2. Instrument-integrated TRIOS software was used for data acquisition and preliminary analyses.

Table 7-2: Comparison of thermal characteristics of PP in pellet and powder forms

	Pellet form			Powder form					
	HNR100	HTV145	HNR100 + HTV145	HNR100	HTV145	HNR100 + HTV145	HNR100 + HTV145 + Talc	HNR100 + HTV145 + Talc + Carbon Black	PP CP75
Melting properties									
Starting melting temperature (T_{ms}), °C	142	141	133	141	143	142	140	138	143
Final melting temperature (T_{mf}), °C	177	173	173	172	172	171	171	171	171
Peak melting temperature (T_{mp}), °C	167.7	165.3	163.3	162.6	164.8	163.2	164.2	165.3	162.6
Onset melting temperature ($T_{m-onset}$), °C	156.4	157	156.1	158.6	159.4	158.9	160.2	160.3	158.6
End-set melting temperature ($T_{m-end-set}$), °C	172	171	171	170	170	168	167	169	169
Heat of melting (J/g)	78.4	77.8	87.5	82.1	78	83	74.7	78	81
Crystallization properties									
Degree of crystallinity (%)	37.5	37.2	42	39.3	37.3	39.8	35.7	37.3	38.7
Starting crystallization temperature (T_{cs}), °C	123	126	125	124	128	126	132	133	126
Onset crystallization temperature, ($T_{c-onset}$), °C	115.5	123.4	120.6	120.7	124.4	122.7	126.9	129.2	120.7
End-set crystallization temperature, ($T_{c-end-set}$), °C	105	113	108	112	115	112	117	119	112
Peak crystallization temperature (T_{cp}), °C	111.5	119.6	115.5	116.3	120.3	118.7	122.5	124.5	116.3
Final crystallization temperature (T_{cf}), °C	98	108	103	108	108	108	110	113	108
Heat of crystallization (J/g)	98.7	98.7	99.6	98.6	100.1	101.5	91.1	90.2	97.9
Supercooling temperature, $T_{mf}-T_{cs}$, °C	54	47	48	48	44	45	39	38	45
Range of LS processing temperatures [$T_{c-onset}$, $T_{m-onset}$] and, °C	115.5 to 156.4	123.4 to 157	120.6 to 156.1	120.7 to 158.6	124.4 to 159.4	122.7 to 158.9	126.9 to 160.2	From 129.2 to 160.3	From 120.7 to 158.7
Sinterability window, $T_{m-onset} - T_{c-onset}$, °C	40.9	33.6	35.5	37.9	35	36.2	33.3	31.1	38

The HNR100 and HTV145 in pellet form started melting almost at the same temperature, around 141°C, while the starting melting temperature of the two grades mixed together was significantly reduced to 133°C. The possible breaking of molecular chains while mixing the two grades at elevated temperatures may explain this behaviour appearing at the start and peak of the melting process. While onset melting temperatures were almost maintained around 156°C for the three grades in pellet form, the peak melting point for the combined HNR100 + HTV145 was reduced to 163.3°C compared to 167.7 and 165.3°C for HNR100 and HTV145, respectively. On the other hand, there were no significant differences in the melting behaviour of HNR100, HTV145, and the combined HNR100 + HTV145 in powder forms. The melting characteristics of HNR100 + HTV145 appeared to be averaged values of those of HNR100 and HTV145. This shows that the well-defined weight ratios of the two grades, leading to a desirable powder particle size during the precipitation process, had no significant influence on the melting characteristics of the mixture. The addition of talc to the combined grade HNR100 + HTV145 in powder form slightly lowered the starting melting temperature from 142 to 140°C, which was again reduced to 138°C when the carbon black was added. The presence of talc and carbon black facilitated the easy heat transfer, which triggered the early start of the melting of the PP composite PP. A slight increase of approximately 1°C in the peak melting temperatures from 163 to 164°C and to 165°C, respectively, is observed with the addition of talc and carbon black to the HNR100 + HTV145 powder. While the addition of talc shifted the onset melting temperature from 159 to 160°C, further addition of carbon black did not significantly change the onset melting point.

For both pellet and powder forms, it could be observed that both the heat of melting and heat of crystallization of the mixture HNR100 + HTV145 was slightly higher than the heat of melting or crystallization of each separate component HNR100 or HTV145. Such an increase in melting enthalpy implies a slight increase in the degree of crystallinity for the processed mixture. This was unexpected behaviour as a low crystalline polymer HTV145, when mixed with a high crystalline polymer HNR100, could result in a polymer with an averaged degree of crystallinity. On the other hand, other crystallization characteristics of the mixture HNR100 + HTV145 were found to be closer and falling between those of HNR100 and HTV145. The addition of fillers promotes crystallization and leads to a higher crystallization temperature, as the addition of a second phase results in heterogeneous nucleation, which is quicker and requires less activation energy than homogeneous nucleation [156]. The addition of talc accelerates the crystallization process, which appeared at high temperatures compared to crystallization temperatures for pure HNR100 + HTV145. The addition of talc could cause an increase in crystallization characteristics ranging from 2 to 6°C, while the further addition of carbon black resulted in a further increase ranging from 1 to 3°C. Similar behaviour was found by Guerra,

Wan, and McNally [157], where the addition of Graphene Nanoplatelets (GNP) to iPP during the extrusion process led to an increase in the crystallization temperature from 116°C for neat iPP to 126 °C for iPP with added GNP. The current investigation indicates that while talc and carbon black could improve the flowability of the powder during the recoating process, the two additives could act as nucleating agents during the crystallization process. With talc and carbon black being thermally conductive while PP is a thermal insulator, the two additives induced a faster crystallization of the neighbouring PP crystals, reducing the degree of crystallinity of the composite PP powder. Such an increase in crystallization temperatures while melting temperatures remained unaffected, led to significant narrowing of the sintering window from 36 to 33 and 31°C for pure HNR100 + HTV145, HNR100 + HTV145 + talc, and HNR100 + HTV145 + talc + carbon black. It is worth noting that even with such a decrease, the final sinterability window of 31°C is wide enough for a successful L-PBF process.

A commercial powder PP CP75, supplied by Diamond Plastics, was identified to benchmark the newly produced HNR100 + HTV145 + talc + carbon black powder. The DSC analyses could show that the thermal properties and L-PBF processing characteristics for the newly produced powder (Figure 7-2) are comparable to the thermal properties and L-PBF processing characteristics of the commercial powder (Figure 7-3). For a successful L-PBF process of polymers, the laser energy absorbed by the powder must overcome the melting enthalpy (heat) of the material [158]. The melting enthalpy of the newly produced powder was found to be 78.033 J/g, which is lower than the melting enthalpy of 80.96 J/g recorded for the commercial powder PP CP75. Though the difference is not very significant, this implies that less laser energy would be required for the sintering of the newly produced powder, which could contribute to energy savings in the long run. The degree of crystallinity of the newly produced powder was found to be 37.34% versus 38.74% for the commercial powder PP CP75. It was observed that the thermal characteristics of pure HNR100 + HTV145 are closer to those of PP CP75, implying pronounced differences in thermal characteristics of HNR100 + HTV145 + talc + carbon black compared to PP CP75. Comparable sintering windows of 36 and 38°C for pure HNR100 + HTV145 and PP CP75 were recorded, while the sintering window narrowed to 31°C due to higher temperature crystallization characteristics when talc and carbon black were added. The sintering window can be increased to 33°C if the powder without carbon black is used on another L-PBF machine with improved laser absorption capacity. The carbon black was added to provide a dark pigmentation to the powder, thus enabling the absorption of the laser energy of the 5 W diode laser in the Sintratec S1 machine that was used for determining the sinterability of the newly developed powder.

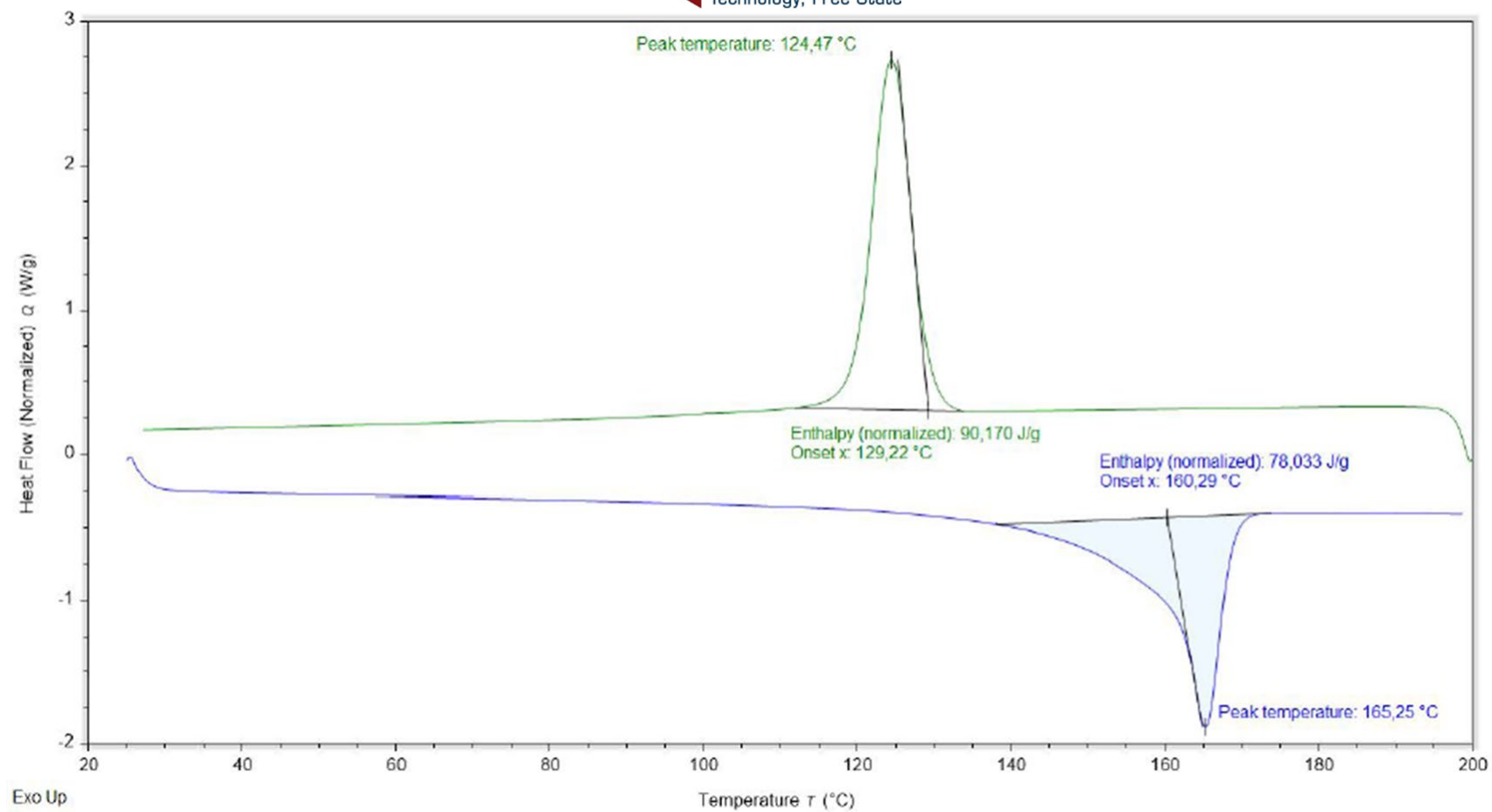


Figure 7-2: DSC analysis for HNR100 + HTV145 + talc + carbon black

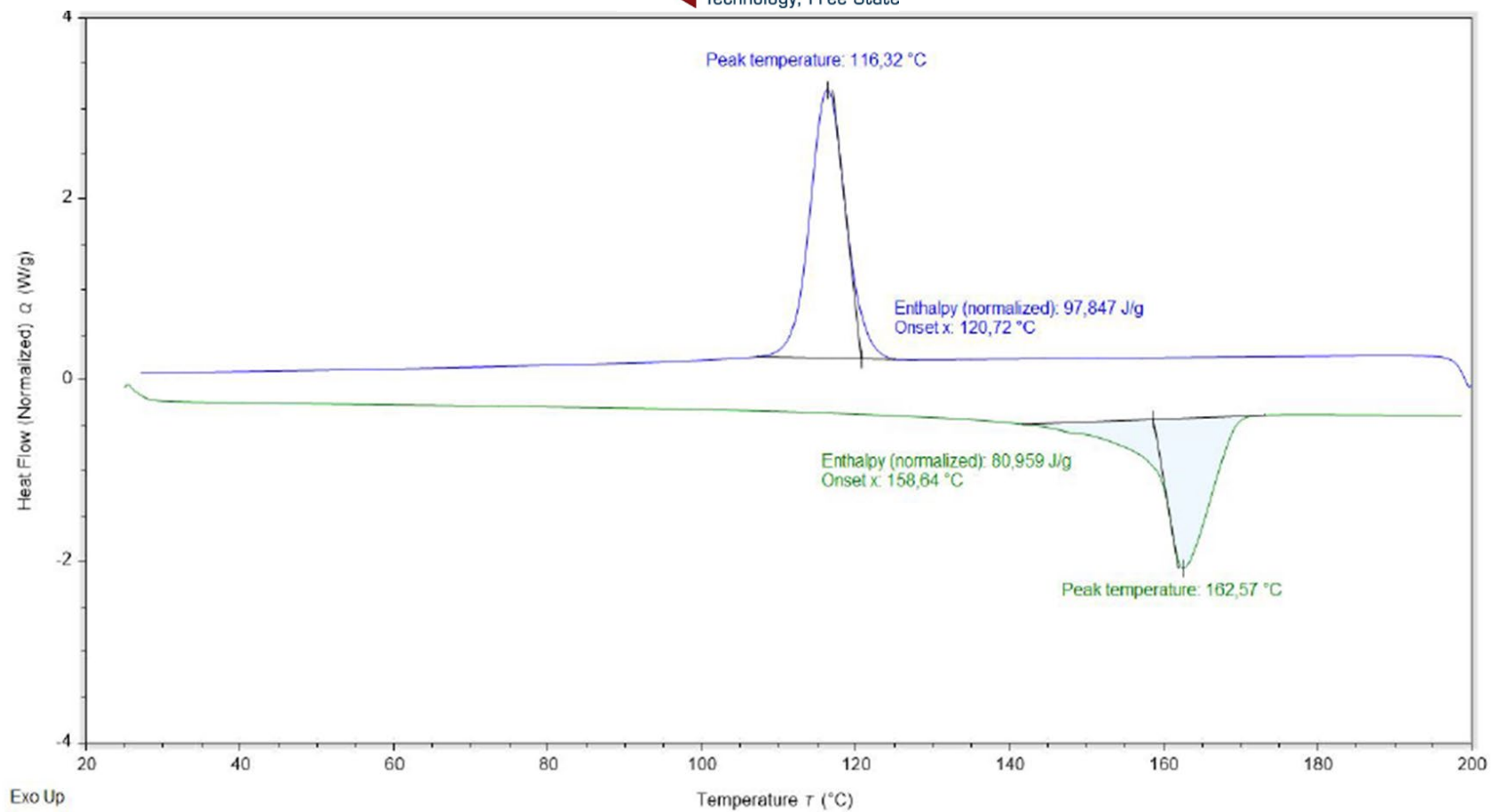


Figure 7-3: DSC analysis for commercial powder PP CP75

Figure 7-2 and Figure 7-3 typically represent all DSC curves presenting single melting and crystallization peak points for all the analyzed samples, thus indicating that the two PP formulations (HNR100 and HTV145) formed a homogeneous mixture.

7.2 Thermogravimetric analysis

TGA is an experimental technique used to evaluate the thermal or oxidative (in an oxidizing atmosphere) stability of a material when subjected to a variation in temperatures. The mass of a substance is continuously investigated as a function of a controlled variation of temperature or time. Although building a part during the L-PBF process occurs at a quasi-static temperature, the surrounding supporting powder is exposed to relatively high temperatures that deteriorate its future re-use. The cross-linking of hydrocarbon chains is one of the modes of changing the original structure of the polymer chains and can be caused by a long exposure of the polymer to high temperatures [45], [159]. The cross-linking leads to an increase in the molecular weight of the polymer and, subsequently, increases its melt viscosity, thus reducing the MFR, which has a detrimental effect on the good flowability of the powder for L-PBF.

To investigate the mass loss of the newly developed PP composite as a function of heating temperature, a TGA was conducted using a Mettler Toledo TGA/SDTA 851e machine at the UFS. A mass of 6.03 mg was subject to continuous heating up to 600°C with a constant heating rate of 10°C/min under a nitrogen atmosphere. The mass of the sample as the temperature increased was recorded, as shown in Figure 7-4.

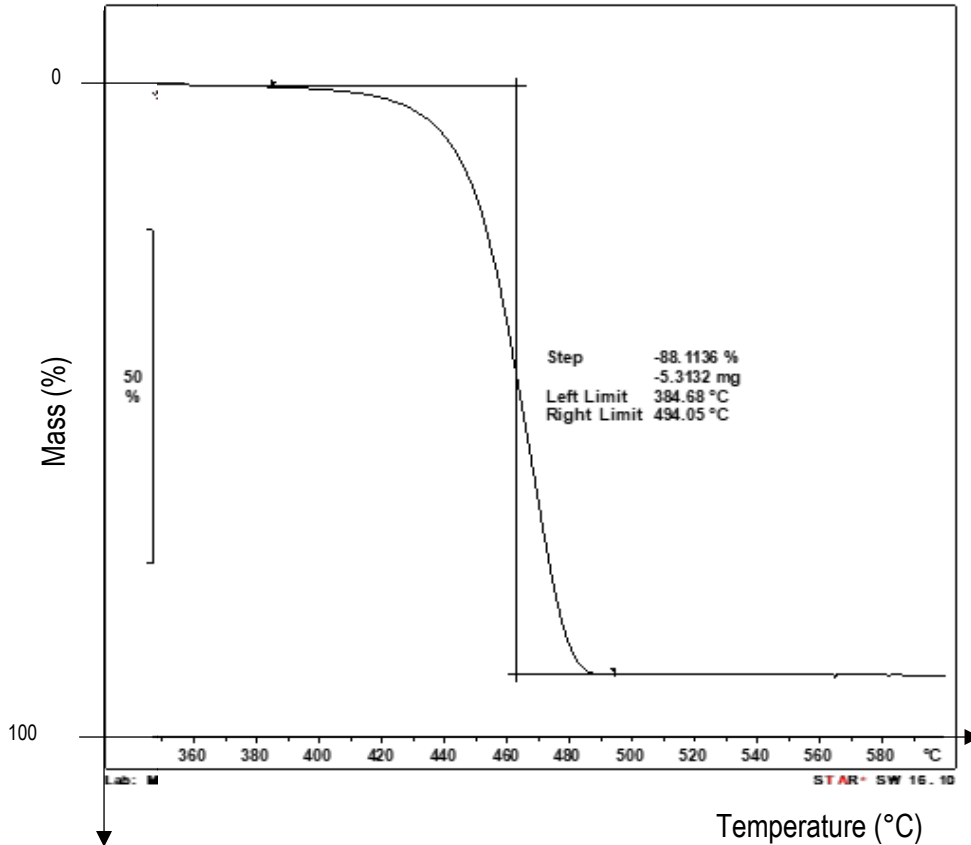


Figure 7-4: TGA of the new PP composite powder

The degradation of the PP sample starts at 385°C and terminates at 495°C, implying a degradation range of 110°C, where 88% of the mass of the polymer and its moisture content was completely lost. As the powder contains 10% talc and a negligible mass of carbon black, the 12% that was determined not to have degraded represents the 10% talc and 0.25% carbon black for which the applied temperatures were insufficient to cause degradation, and 1.75% of the remaining residue from PP after being burnt out. The degradation at such high temperatures, ranging from 385 to 495°C, confirms that the relatively lower operational temperatures for L-PBF should not lead to the degradation of the newly produced PP composite powder. Therefore, the unsintered powder surrounding the laser-sintered parts can be reused in the L-PBF process.

7.3 Scanning Electron Microscope analysis

As described in this research, an investigation of the size and morphology of the particles of the composite PP powder was conducted at the Department of Geology at the UFS. Samples of the powder were scanned on a JEOL JSM 6610 SEM at an accelerating voltage of 20 kV. The particle sizes and morphology of the

newly produced powder were compared to those of PP CP75 from Diamond Plastics GmbH. Polymeric samples are usually coated with gold or carbon in a vacuum environment to enhance electrical conductivity before being subjected to SEM analysis. A sputter coater turbo evaporator, model Quorum Q150TE, was used to deposit a carbon film on the surfaces of both polymeric powder samples, which were fixed on inserts to be fitted into the SEM machine. The morphologies of the PP CP75 powder particles (Figure 7-5a, c, e, g) were compared at different magnifications to morphologies of particles for the newly produced composite PP powder (Figure 7-5b, d, f, h).

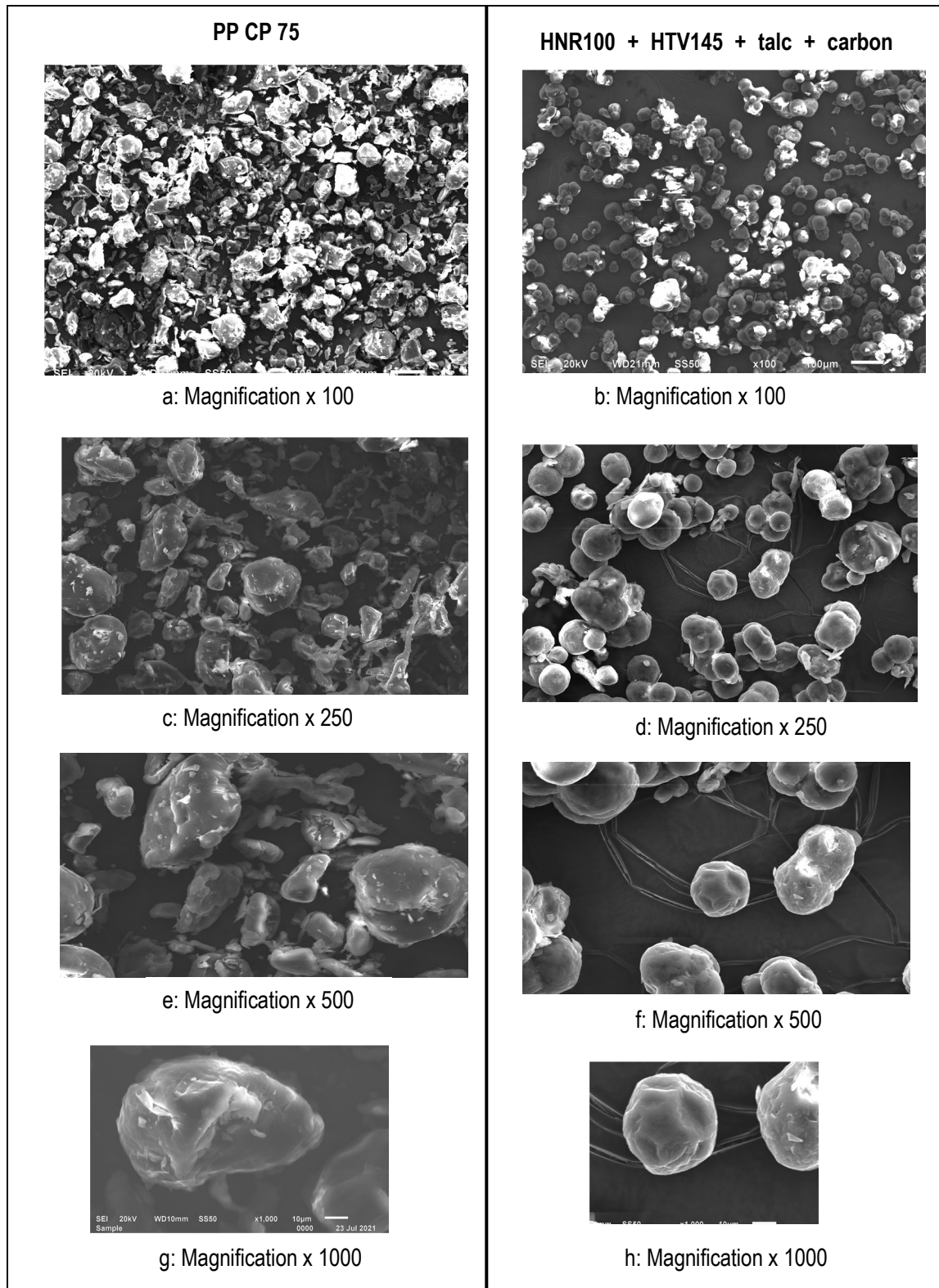


Figure 7-5: Comparison of morphologies of powder particles for commercial PP CP75 powder versus the morphology of particles of the new PP composite powder.

To facilitate the flow of the powder during the recoating process and to reduce the surface-area-to-volume ratio (thus enhancing the packing efficiency), it is proved that an ideal powder for L-PBF should contain particles of high sphericity. Powder particles with irregular or potato shapes cause poor flowability and low bulk density, leading to inhomogeneous deposition of the powder during the recoating stage. This results in parts with high levels of porosity, poor surface finish, poor dimensional accuracy, and reduced mechanical properties.

The particles of CP75 are generally characterized by irregular and potato shapes, while the particles of the newly produced powder are mostly spherical (Figure 7-5a, c, e, and g). Furthermore, the CP75 powder has a significant number of very small, dispersed fractioned particles, or they are attached to relatively bigger particles. In contrast, the particles of the new powder are easily separately identifiable or attached to other particles with almost equal diameters. The small particles attached to the surfaces of big particles of CP75 powder will result in a rough surface topography contrary to the expected smoother surface when the newly produced PP composite powder is sintered. The diameter sizes of particles with nearly spherical shapes, dimensions of agglomerates, and the overall dimensions of particles with potato or irregular shapes were measured as shown in Figure 7-6, Figure 7-7, and Figure 7-8. The diameters of particles with nearly spherical shapes range from 29 to 100 μm with an average diameter of approximately 60 μm and a standard deviation of 5.4 μm .

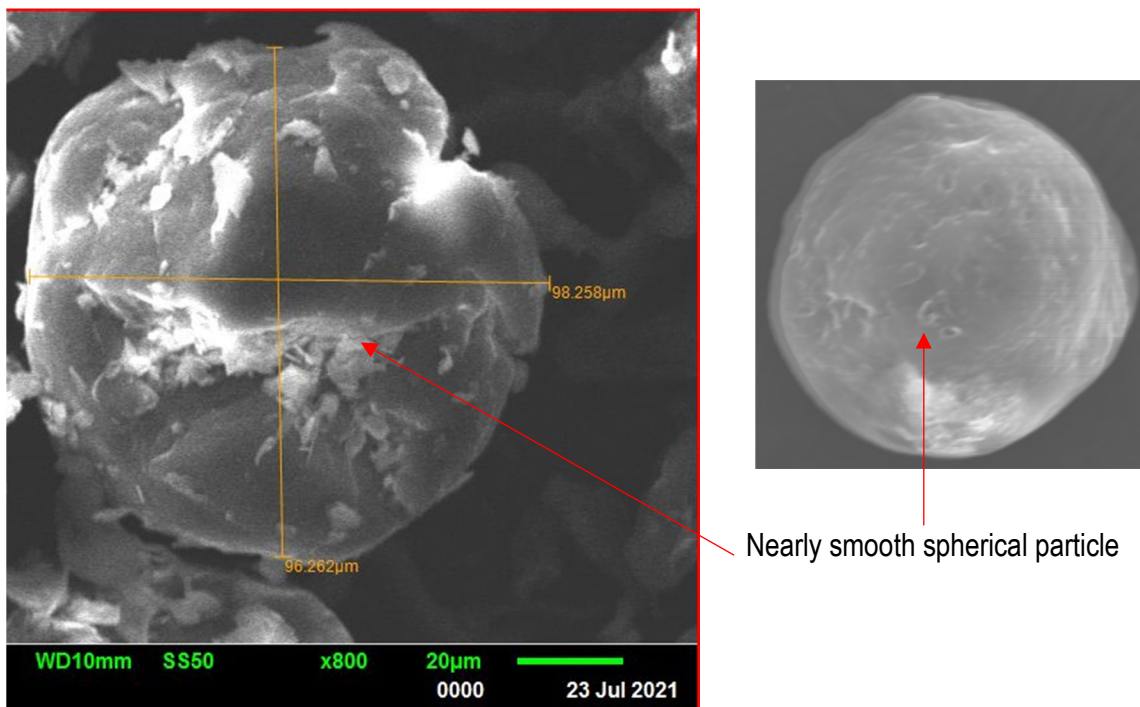
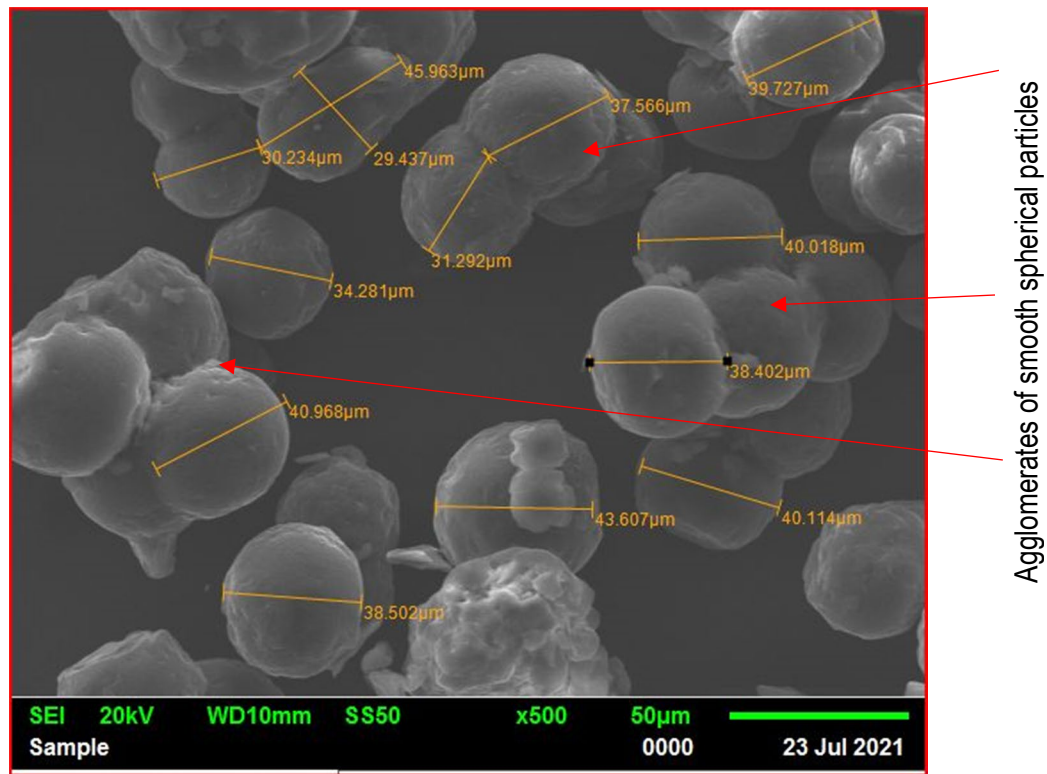
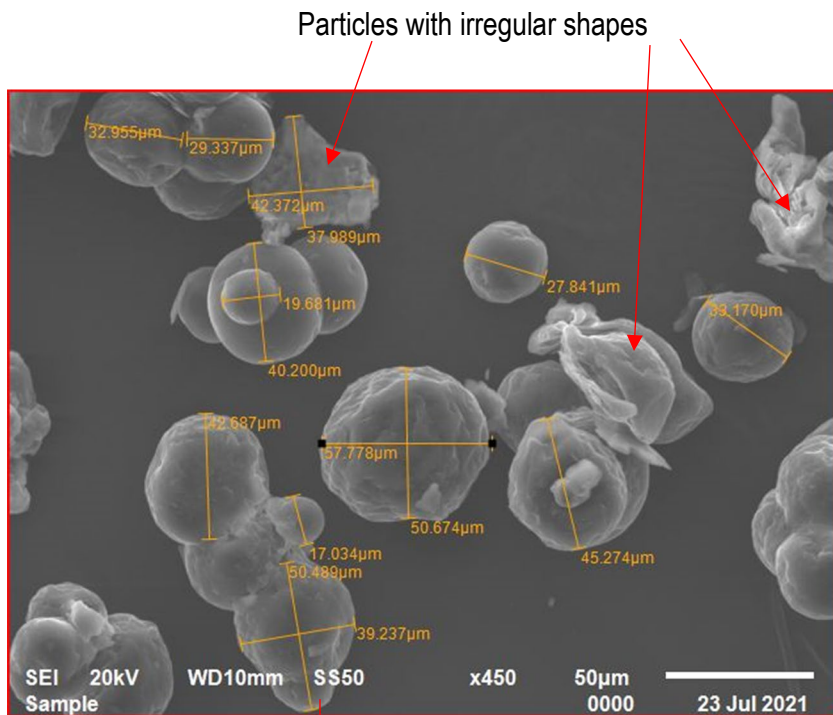


Figure 7-6: Formation of particles with smooth spherical shape

The presence of a negligible number of particles with irregular and potato shapes is evident in Figure 7-7.



A particle with a potato shape

Figure 7-7: Formation of particles with potato and irregular shapes

The sizes of a few particles with potato or irregular shapes could range from 13.6 to 88 μm with aspect ratios ranging from 1.2 to 1.9, thus confirming the absence of fibrous particles (Figure 7-8).

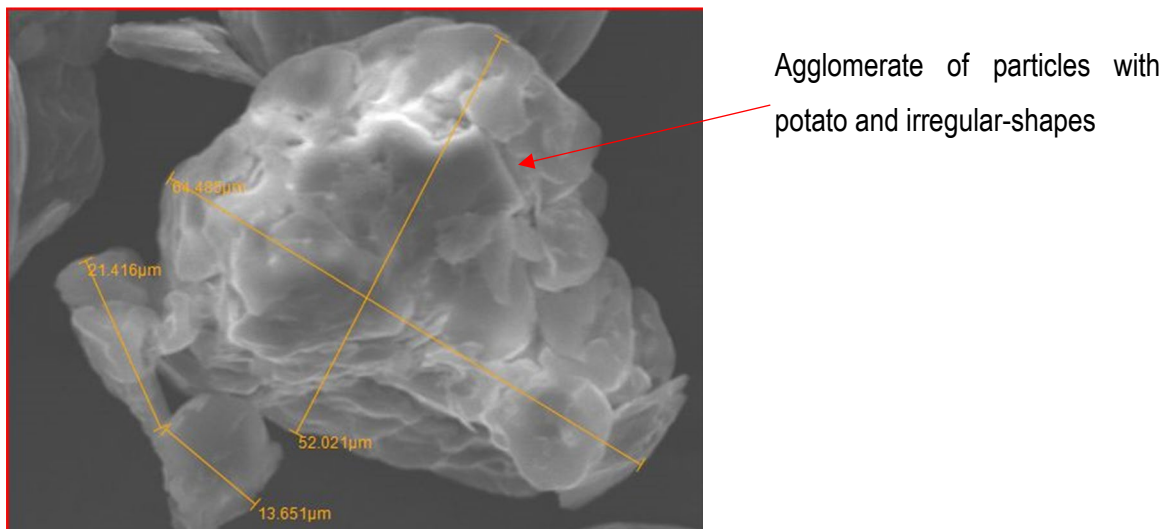
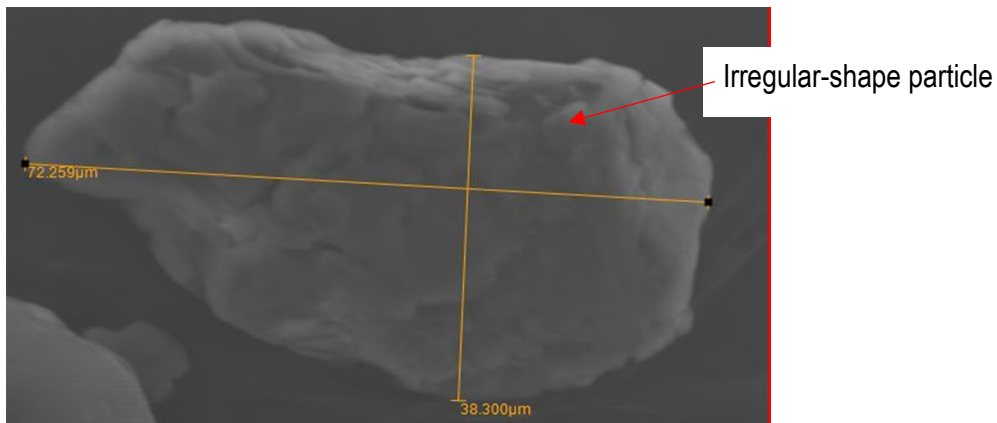
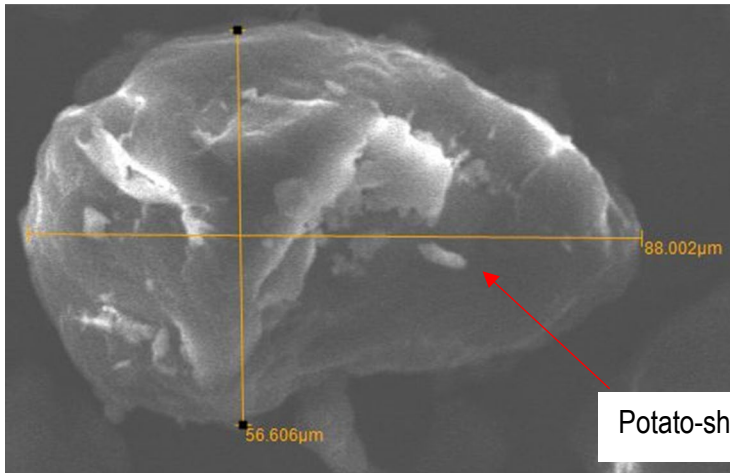


Figure 7-8: Sizing of particles with potato and irregular shapes

The formation of powder particles with spherical shapes and smooth surfaces was general when HNR100 and HTV145 were dissolved and precipitated into m-Xylene. There was a negligible number of malformed particles, probably due to heterogeneous nucleation in the proximity of the walls of the pot and/ or caused by non-uniform temperature distribution during the cooling process, thus leading to the formation of particles with potato or irregular shapes. While enhancing the flowability of the powder, the small portion of 10% talc powder also contributed to the share of irregular-shaped particles within the newly produced PP composite powder. The grinding process could easily break the predominance of well-identifiable particles with spherical shapes that formed agglomerates. The agglomerates in the range of 60 to 100 μm made up of small particles did not require the particles to be broken up since the agglomerates were roughly spherical and free-flowing, which would allow the sintering of parts with acceptable surface finish and dimensional accuracy.

7.4 Chemical analysis

SEM is a non-destructive technique for characterizing individual particles of powder in terms of size, shape, and chemical composition. The Backscattered Secondary Electron (BSE) imaging in SEM could identify the presence of two main phases in the new composite powder as contrasted by the appearance of the white-coloured spots dispersed within the predominant dark-coloured matrix. In a composite structure, regions of higher average atomic numbers emit more backscattered secondary electrons, leading to a brighter colour, while regions with lower average atomic numbers are prone to a dark appearance. It could be concluded that the regions of white spots constituted the portion of the talc which could not form a homogeneous mixture, with the dark zones representing the dissolved PP matrix composed of hydrogen and carbon atoms with lower atomic numbers. Under an accelerating voltage of 20 kV, a chemical analysis was performed on the five identified white spot zones (Figure 7-9).

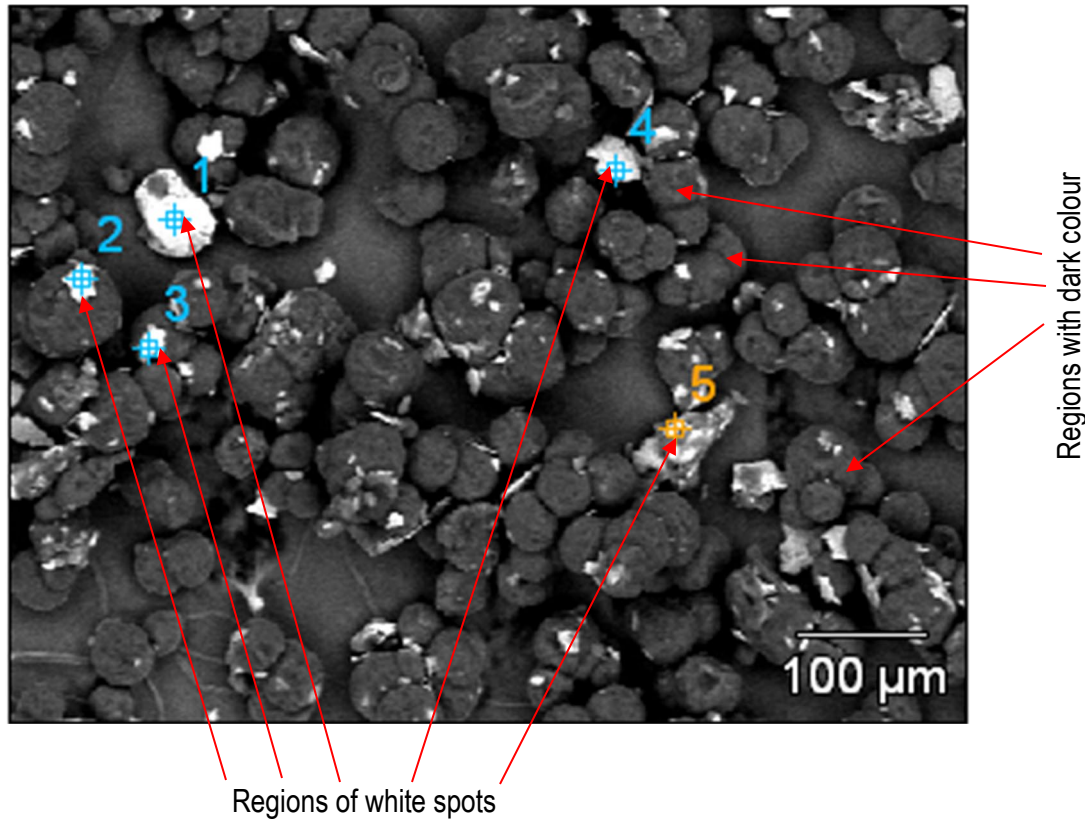


Figure 7-9: Talc dispersion into PP matrix

In conjunction with SEM, the quantitative analysis of the chemical composition of the identified zones was performed using the Energy Dispersive X-ray (EDX) spectroscopy method. Upon emission of electrons from the source, a beam of electrons is channelled through an accelerating anode and directed into a series of condensing and objective lenses, which allow the incident beam to be focused on the specimen. The interaction between the primary incident electrons (electromagnetic radiation) and atoms and electrons of the analyzed specimen results in the change in direction of primary electrons from their original paths, thus causing the emission of secondary electrons and a spectrum of scattered X-rays. The generated and emitted X-rays from a specific specimen location are detected and counted according to their emission energy [160].

Each chemical element has a unique atomic structure, allowing specific X-rays that are characteristic of the atomic structure of the element to be uniquely identified from other chemical elements. The characteristic X-rays attributed to specific chemical elements and the corresponding caused energy states were produced for all five considered points, and the EDX spectrum results for points 1 and 2 are graphically reported in Figure

7-10. The characteristic X-ray peaks confirmed the presence of silicon dioxide (SiO_2) and magnesium oxide (MgO), which are the main components of talc. It can be understood that the talc remains heterogeneously suspended within the dissolved polypropylene in m-Xylene, and during the drying and grinding stages of the mixture, the talc particles are deposited on the surfaces of the PP particles. The silicon dioxide or silica is known to act as an antistatic agent to improve the flowability of the powder during L-PBF.

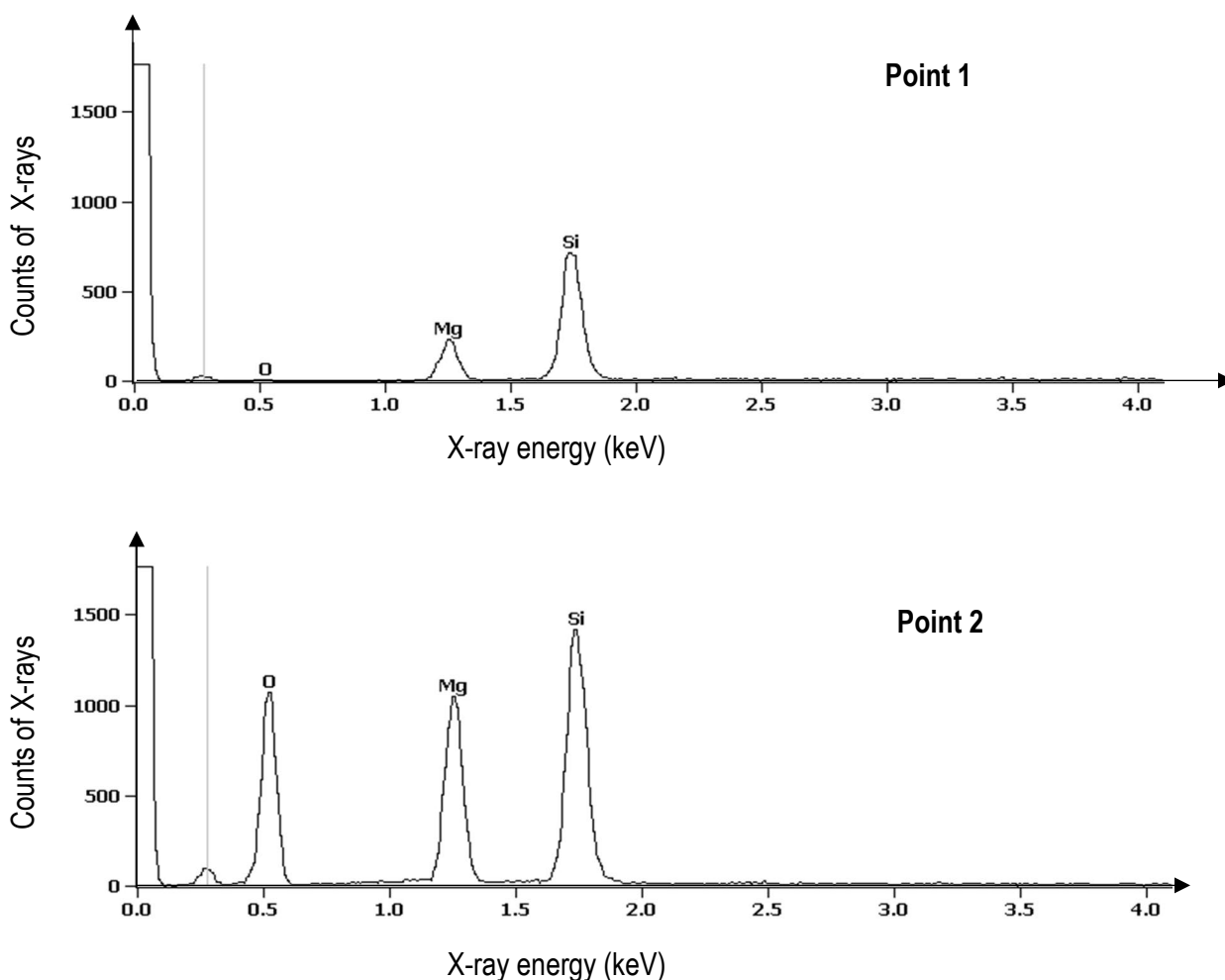


Figure 7-10: EDX spectrum for points 1 and 2

Table 7-3 summarizes the qualitative and quantitative chemical composition of the talc at five points.

Table 7-3: Chemical composition of the talc and other volatile constituents

Points	Chemical composition (%)			
	SiO ₂	MgO	Al ₂ O ₃	Fe ₂ O ₃
1	83.01	16.99	0	0
2	69.52	30.48	0	0
3	69.22	30.78	0	0
4	85.67	14.33	0	0
5	49.23	34.49	14.88	1.40

The analysis performed in the zone shown in point 5 indicates the presence of aluminium oxide (Al₂O₃) and an insignificant percentage of ferric oxide (Fe₂O₃), which could result from local powder contamination. During the drying process, the powder was spread out in aluminium trays and placed inside the flow cabinet, where the airflow evaporated the remaining xylene.

7.5 Density of the new PP powder

The true density of the new PP powder was analyzed at the South Africa Nuclear Energy Corporation (NECSA) using an AccuPyc II model 1340 V. 1.07 pycnometer from Micromeritics® Instrument Corporation. Contrary to the bulk or apparent density, which includes the volume of all open and closed pores within the sample, the true or skeletal density considers only the volume of the solid material and excludes the volume of all open pores [161]. Following the test methods described in the ASTM D-6226 Standard, the AccuPyc II model 1340 pycnometer applies helium gas as a displacement medium. The sole solid phase of the sample displaces the gas while the gas molecules fill the small pores of approximately one Angstrom (0.1 nm) diameter size. The volume and the true density of the powder sample are automatically determined simultaneously during the filling process.

Using an insert chamber of 3.5 cm³ placed in a cell chamber of 5.7729 cm³ and allowing the gas to expand within a volume of 8.4989 cm³, a sample with a mass of 0.8217 g was analyzed at a set and stabilized temperature of 17.98°C. The drying of the sample was achieved by performing three purges to eliminate any

possible moisture content. With three cycles at a relative equilibration pressure rate of 0.05 psig/min, the analysis of volume was recorded as a function of the cycle number, and the results are reported in Figure 7-11.

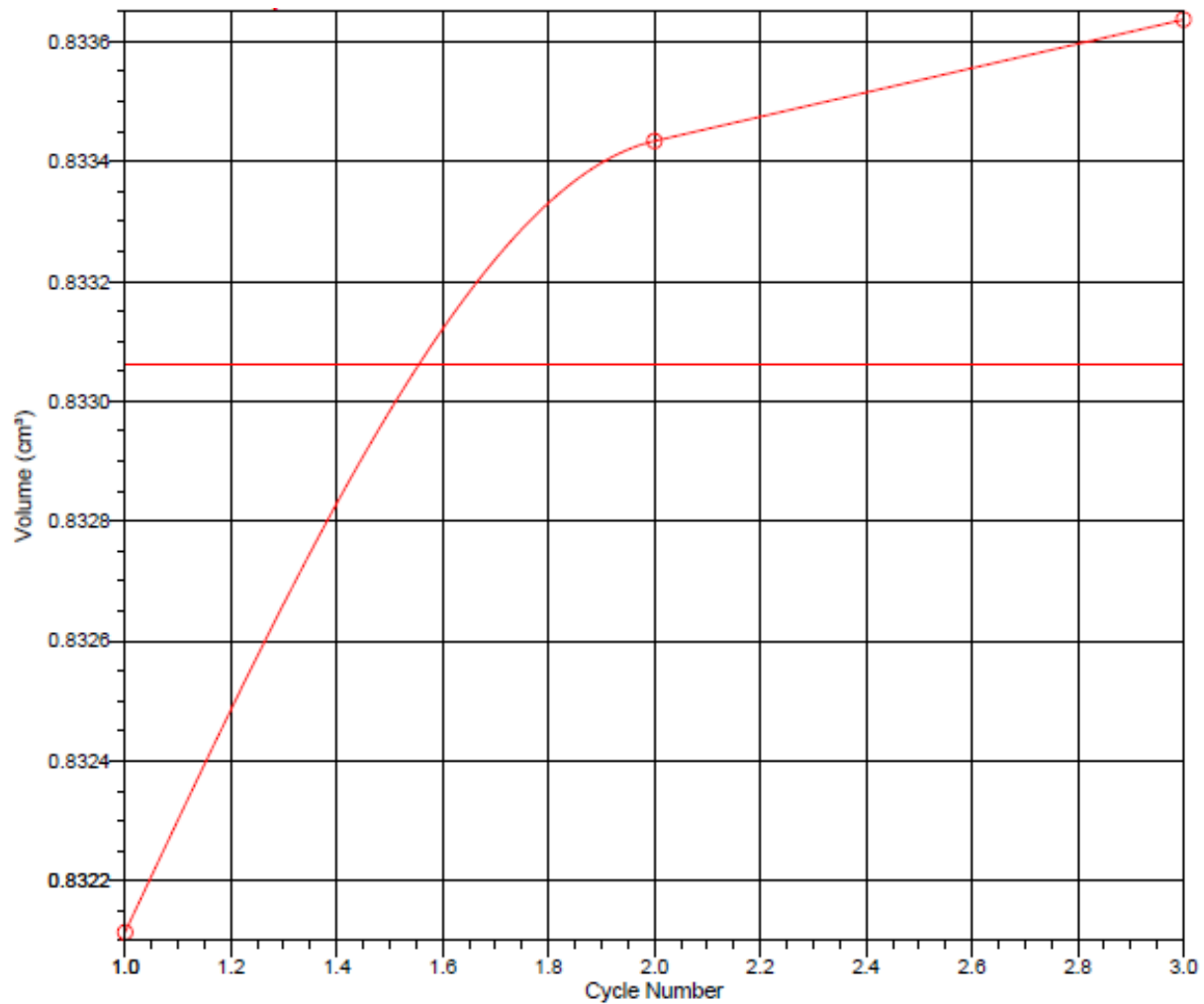


Figure 7-11: Variation of the volume of the powder versus the number of the cycle

The corresponding variation of density versus cycle number is shown in Figure 7-12.

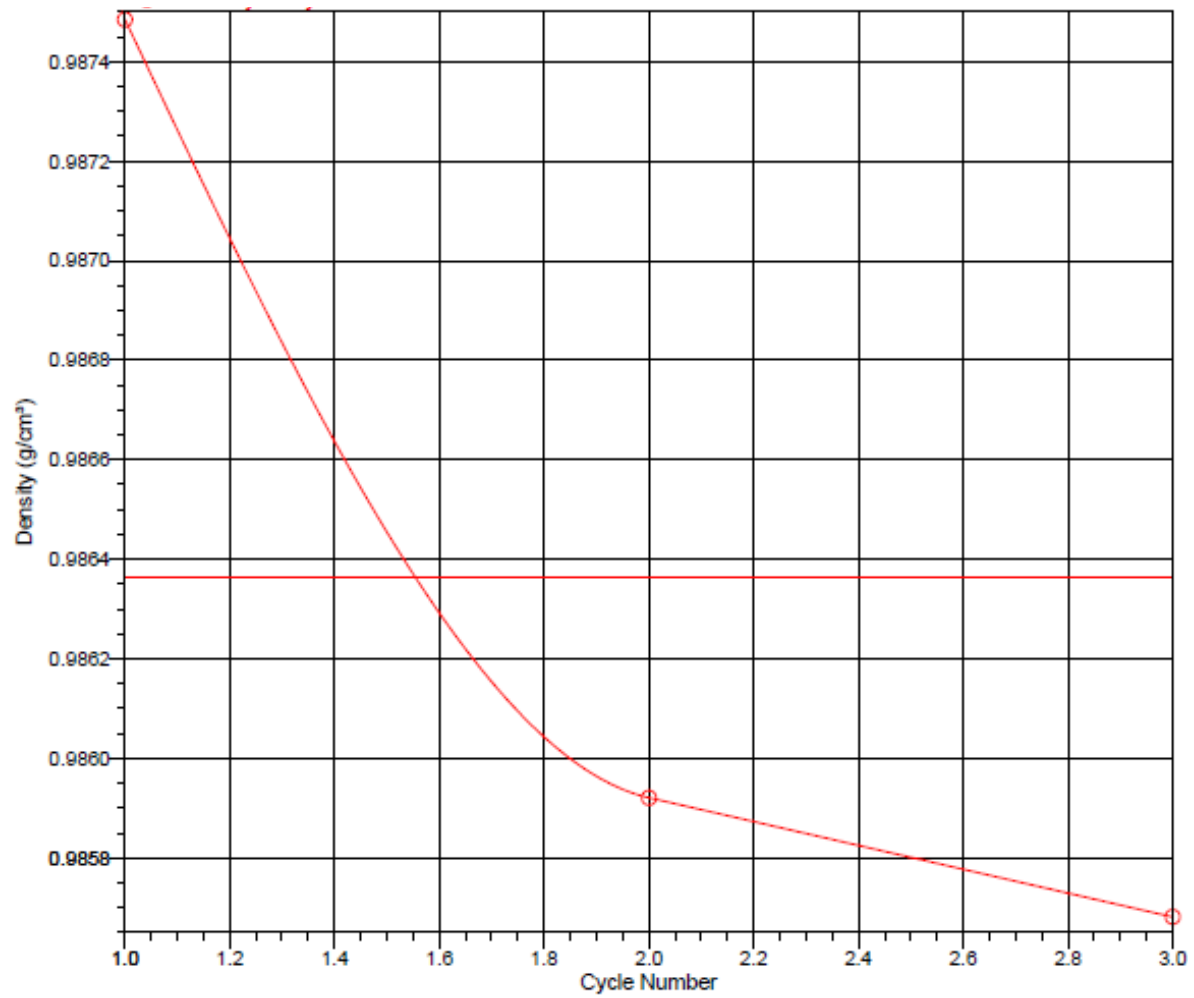


Figure 7-12: Variation of the density versus cycle number

The variation of the density versus the testing period is shown in Figure 7-13.

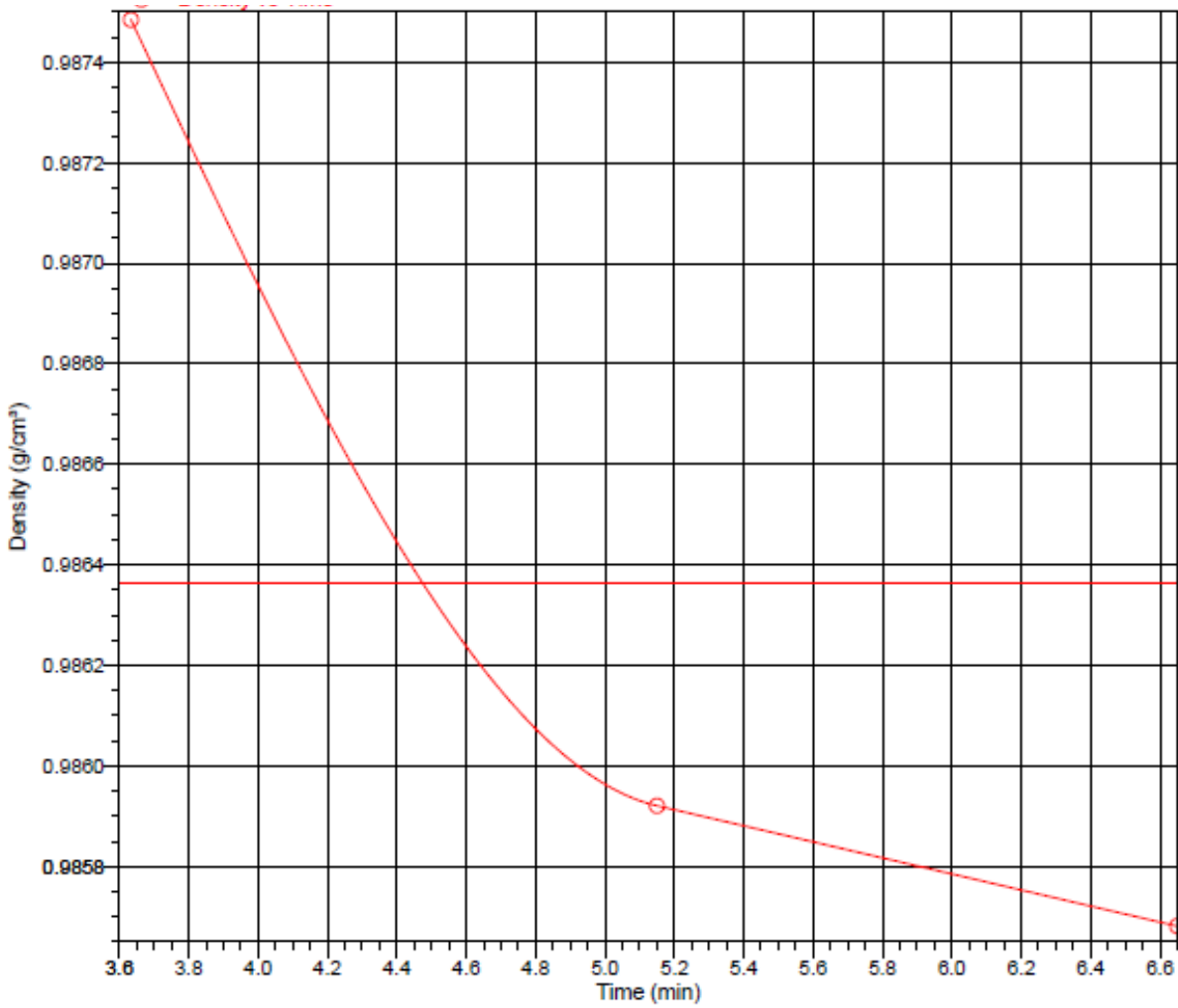


Figure 7-13: Variation of the density versus the time

The variation of the total pore volume against the temperature is shown in Figure 7-14.

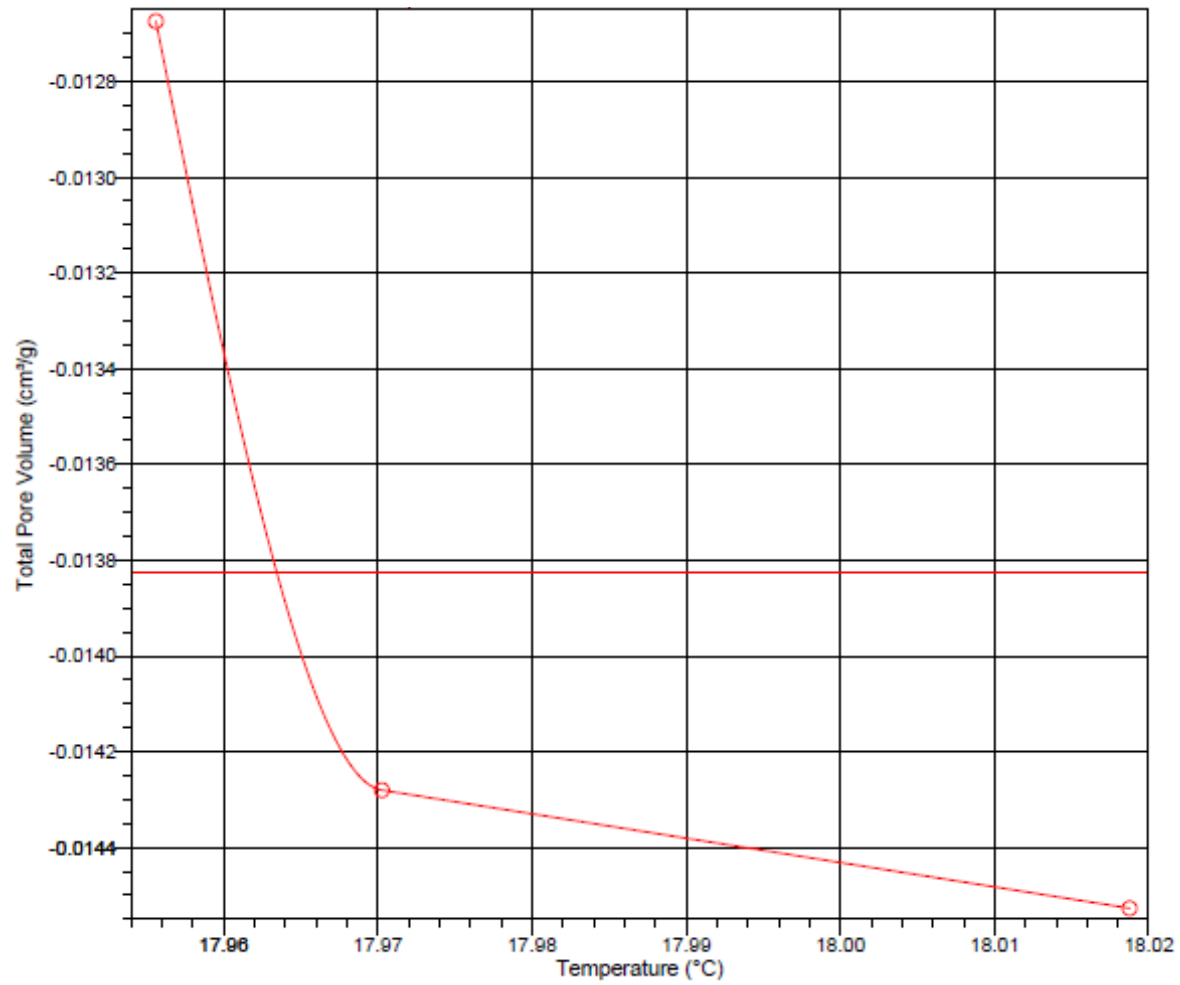


Figure 7-14: Variation of the total pore volume versus temperature

Table 7-4 summarizes the results from the analysis of the volume, density, and total pore volume of the new PP powder sample.

Table 7-4: Summary of measured volumes and densities

Cycles	Initial filling pressure (psig)	Final pressure after expansion (psig)	Sample volume (cm ³)	Density (g/cm ³)	Total pore volume (cm ³ /g)
1	19.803	7.280	0.8321	0.9875	-0.0127
2	19.813	7.283	0.8334	0.9859	-0.0143
3	19.745	7.257	0.8336	0.9857	-0.0145
Average			0.8331	0.9864	-0.0138
Standard deviation			0.0007	0.0008	0.0008

The evaluated density based on the average volume of the sample (Figure 7-11) was obtained as follows:

$$\rho = \frac{\text{Mass of the sample}}{\text{Average volume}} = \frac{0.822}{0.833} = \frac{0.986 \text{ g}}{\text{cm}^3}$$

The reported average true density of 0.986 g/cm³ (Figure 7-12, Figure 7-13, and Table 7-4) is in complete agreement with the calculated true density and is greater than the commonly reported density of iPP, varying from 0.910 to 0.930 g/cm³ [42], [150]. With an equal amorphous density of 0.858 g/cm³ for both α -iPP and β -iPP, the crystal densities of 0.936 and 0.921 g/cm³ for α -iPP and β -iPP, respectively, have been reported by Varga and Ehrenstein [65]. A density of 0.938 g/cm³ was recorded for γ -iPP crystallized at 185.8 °C at a high pressure of 200 MPa, while under atmospheric pressure, the density was 0.935 g/cm³. A crystallization carried out under atmospheric pressure at low temperature produced a density of 0.951 g/cm³ [38], [162]. The new composite PP powder contains 10% talc with a true density of 2.7 g/cm³, while carbon black has a density varying from 1.8 to 2.1 g/cm³. Both denser additives contributed to raising the density to 0.986 g/cm³. Such a high density suggests the predominance of α -iPP phase in the polymer sample, which was confirmed by XRD analysis.

Sillani *et al.* [2] investigated the effect of the packing density and fillers on the thermal conductivity and flowability of four polymeric powders for L-PBF. Three commercial powders, namely pure PA12, PA12 filled with 10% wollastonite (PA12-MF), pure polypropylene iCoPP, and one research grade iCoPP-CF which is iCoPP filled with 10% carbon fibres, were considered. It was found that the increase in packing density increased the thermal conductivity for all samples, and it was more influential in PA12, where a variation of a packing density from 0.42 to 0.51 g/cm³ resulted in a linear dependence on a thermal conductivity from 90 to 130 mWm⁻¹K⁻¹. The PA12-MF filled with wollastonite was denser than the pure PA12, where with a variation of packing densities ranging from 0.43 to 0.65 g/cm³, a linear trend on the increase of thermal conductivity from 140 to 180 mWm⁻¹K⁻¹ was recorded. The thermal conductivity for the pure iCoPP powder was around 130 mWm⁻¹K⁻¹, meaning that the variation of packing density did not significantly influence the thermal conductivity of the neat PP powder. The filling of iCoPP with carbon fibres increased the thermal conductivity from the lowest level of 175 mWm⁻¹K⁻¹ to the highest value of 270 mWm⁻¹K⁻¹, corresponding to packing densities of 0.38 and 0.455 g/cm³, respectively. In optimizing the process parameters for L-PBF of polymeric powders reinforced with fillers, an increase in thermal conductivity and a decrease in flowability of the initial powder are to be expected. It was also found that the presence of reinforcing fillers with elongated non-spherical irregular morphology, such as carbon fibres, reduced the flowability of the initial powder by increasing the HR from 1.15 (good flowability) to 1.33 (transitional or passable flowability).

Using a Hall flowmeter funnel according to ASTM 212B, 9.92 g of the new PP composite powder was loaded in a cup with a volume of 25 cm³. The resulting packing density of 0.397 g/cm³, which can be approximated to 0.4 g/cm³, is close to a packing density of 0.38 g/cm³ for iCoPP, as reported by Sillani *et al.* [2] and also within a range from 0.32 to 0.4 g/cm³ packing density of a typical polymeric powder, as mentioned by Paul [163].

7.6 Particle Size Distribution

PSD is influenced by the particle shape, which varies from regular symmetrical (nearly spherical) to asymmetrical (uneven irregular) shape. The size of a nearly spherical-shaped particle can be described by an equivalent diameter of an imaginary sphere with the same diameter, surface area, weight, or volume as the actual physical particle. The PSD defines the range of particle sizes in a specific powder sample based on the mass or volume of the particles falling in that range [164]. During L-PBF, the PSD affects the flowability of the powder and, consequently, the level of porosity present in the laser-sintered part. The D-values are a

convenient specification to describe the PSD for cases where most of the particles in a sample are relatively close to spherical shape. A D-value is a specific diameter size of particles that divides the total mass of the sample into two defined percentages when all particles are arranged in order of ascending mass or volume. The new PP composite powder was sieved three times with four mesh sizes of 300, 125, 53, and 20 μm , and Table 7-5 summarizes the PSD of the powder.

Table 7-5: Sieves and particle size distribution of the powder

Designation of the sieve	Size of the aperture (μm)	Cumulative volume (%)	Incremental volume (%)	Standard deviation of cumulative volume
Nº 50	300.0	100.0	0.0	0.0
Nº 120	125.0	99.2	0.8	0.1
Nº 270	53.0	41.1	58.1	2.8
Nº 635	20.0	5.5	35.7	0.7

The laser light scattering technique was also used to characterize the PSD for the newly produced PP powder. The diffraction angle is inversely proportional to the particle size, while the intensity of light scattered is directly proportional to the particle size. For repeatability of the results, three consecutive test runs with a time spacing of six minutes apart were conducted using the Saturn DigiSizer II model 520 laser light scattering particle size analyzer 5 at NECSA. The deconvolution of the data was carried out using a sample reflecting index of 1.540/0.0001 in a smoothing water medium of a density of 1.331 g/cm^3 . Figure 7-15 shows the incremental volume percentage obtained versus the particle sizes.

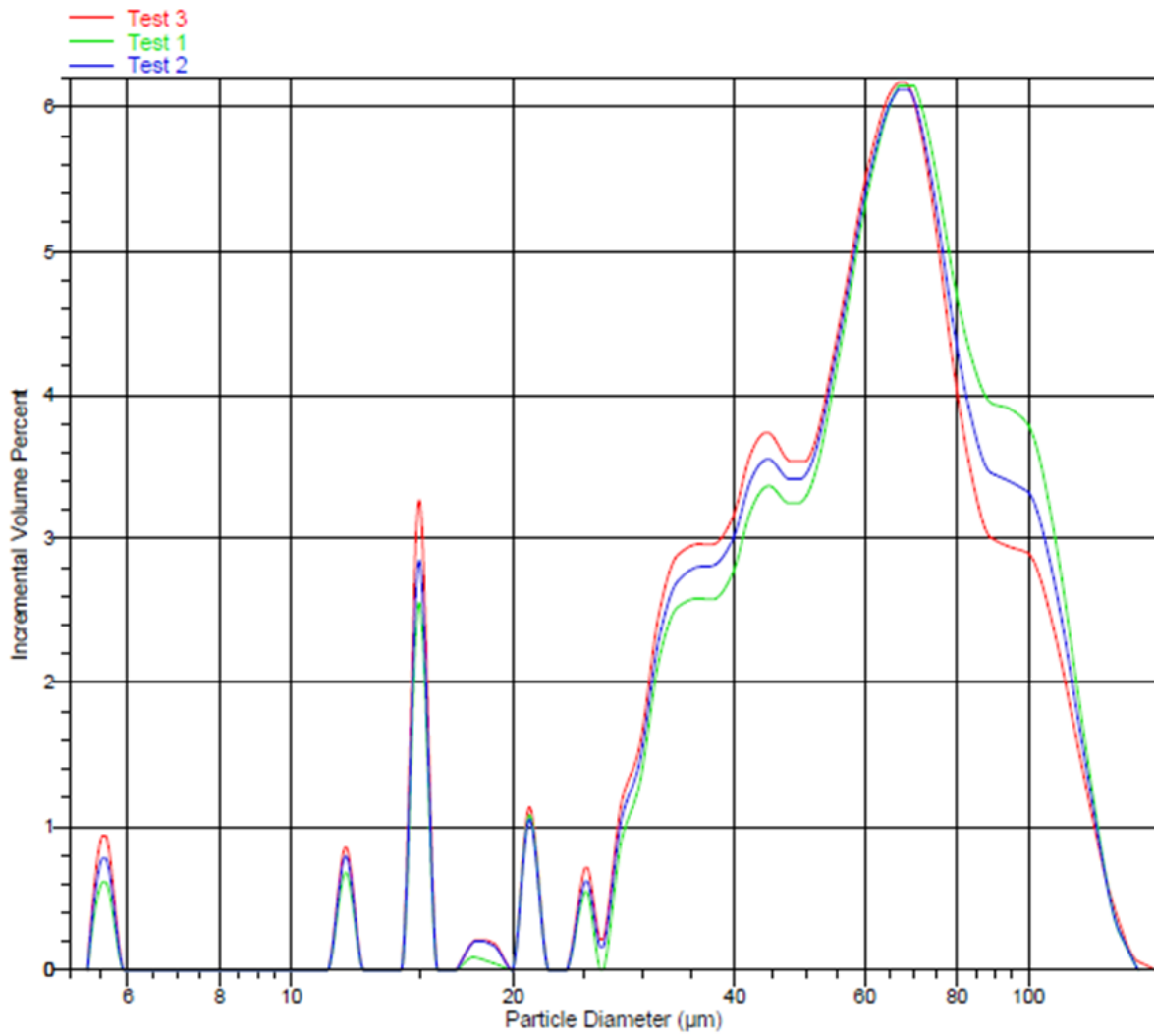


Figure 7-15: Incremental volume percentage versus particle size

Figure 7-16 shows the corresponding cumulative volume percentage versus the particle size.

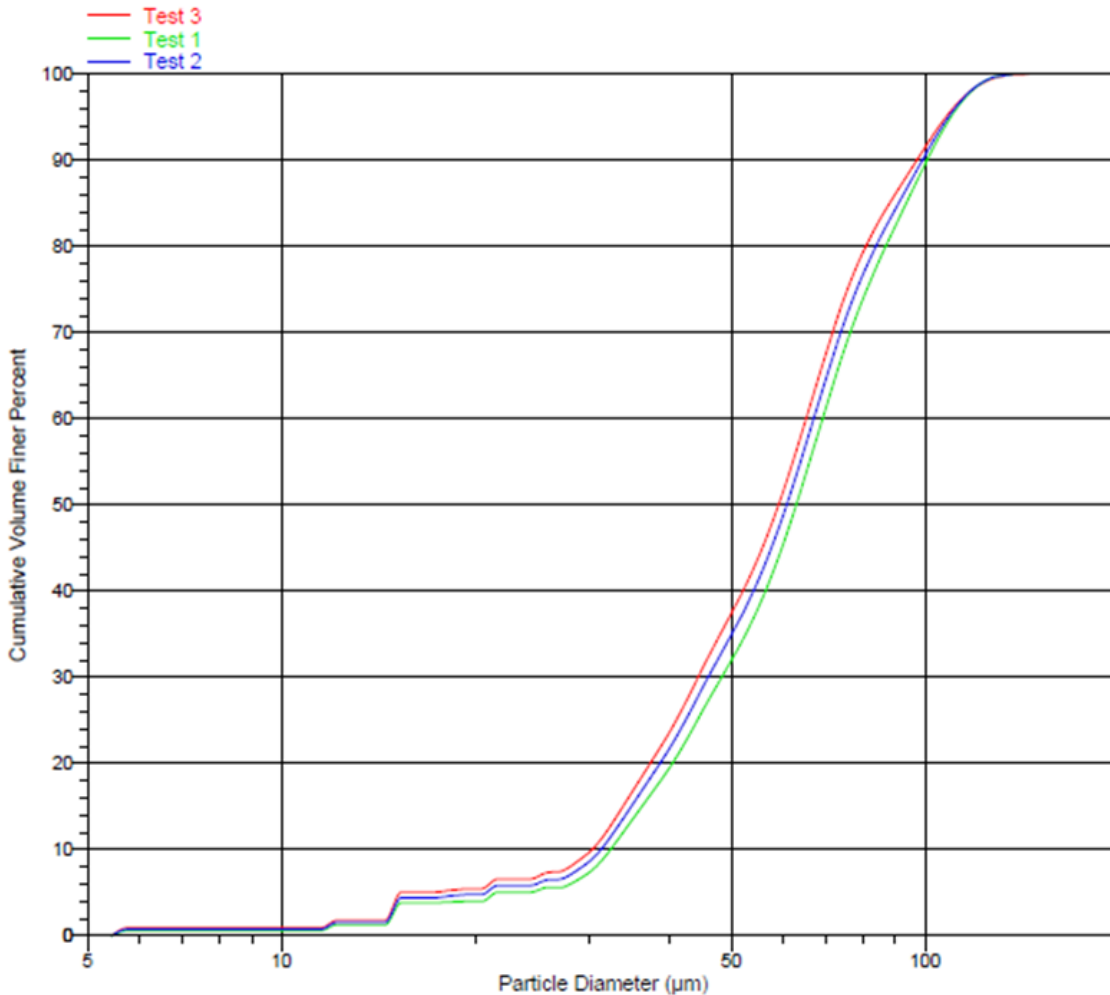


Figure 7-16: Cumulative volume percentage versus particle size

The PSD for the newly produced PP powder can be described using three commonly applicable D-values, namely D_{10} , D_{50} , and D_{90} [82]. A fraction of 10% of the volume of the sample was made up of particles with a diameter size of less than 30 μm or $D_{10} = 30 \mu\text{m}$. Half, i.e., 50% of the volume of the sample, was constituted by particles less than 60 μm or $D_{50} = 60 \mu\text{m}$, while 90% of the sample volume was made up of particles with size less than 100 μm or $D_{90} = 100 \mu\text{m}$. Only 30% of the total powder volume was composed of particles of an average size of less than 50 μm . During L-PBF, sufficient energy is required to ensure that the powder fusion is caused by direct contact between the laser and the particle instead of relying on particle-particle heat conduction. Berreta, Ghita, and Evans [165] mentioned that direct contact between the laser and particles

can be achieved when layer thickness is at least twice the average size of the particles. Commercial laser-sintering machines such as EOS P380 and Sintratec S1 operate with a layer thickness varying from 100 to 150 μm . The newly produced composite PP powder was characterized by particles with an average size of 60 μm , which is less than half of the available maximum layer thickness, thus ensuring an efficient powder fusion. Fang, Wang, and Xu [100] found that increasing the dissolution temperatures in the range of 160 to 185°C resulted in a decrease in the average size of the powder particles from 98 to 26 μm . This trend was explained by the fact that at low dissolution temperatures, polymer particles are partially dissolved, initiating the generation of large particles, while the remaining undissolved part acts as a nucleating agent during the crystallization process. For this study, the dissolution temperature was fixed at a relatively low temperature around 130°C, slightly lower than the boiling temperature of 139.1 °C for m-Xylene, as the PP mixture was completely dissolved while maintaining the quantity of evaporated m-Xylene vapour at a low level. It was found that the size of the particles was dependent on the weight ratio between the HNR100 and HTV145 grades. Maintaining the HNR100 grade with low MFR of 12 g/10 min. as a major component and the HTV145 grade with a high MFR of 50 g/10 min. as a minor component, the new PP composite powder with nearly spherical shape and size suitable for L-PBF could be produced.

7.7 Measurement of the flowability of the powder

The efficiency of L-PBF requires the use of a powder with a high level of flowability to uniformly lay down each newly deposited layer to facilitate the building of parts with good surface finish and dimensional accuracy. The flowability is affected by the size, PSD, morphology, and smoothness of the powder particles. Very small powder particles tend to agglomerate and are generally cohesive, preventing a smooth powder flow due to strong inter-particulate Van der Waals and dispersion forces. The Housner Ratio (HR) is used as a quantitative measurement for characterization of the rheological (flowability) behaviour of the powder in its solid state and is calculated as follows:

$$HR = \frac{\rho_T}{\rho_A} \quad (\text{Eq. 4})$$

where ρ_T and ρ_A are the tap and apparent (bulk) density of the powder, respectively.

According to Ludwig *et al.* [94], a cohesive powder with poor flowability is characterized by an HR greater than 1.4, while a transitional powder is identified by $1.25 < H_R < 1.4$. A good loose-flowing powder, designated as aeratable, is characterized by an HR of less than 1.25. The apparent (bulk) and tap densities of the new composite PP powder were measured to be $0.398 \pm 0.004 \text{ g/cm}^3$ and $0.504 \pm 0.001 \text{ g/cm}^3$, implying $H_R = 1.266 \pm 0.013$, thus obtaining transitional characteristics that are very close to good loose flowing aeratable powder.

A Freeman Technology FT4 Rheometer® at the CSIR was used to characterize the new composite PP powder. This is a flow-measuring instrument capable of evaluating the powder's flowability in a dynamic regime. The flow resistance of the powder is calculated based on the flow energy, which is equivalent to the summation of the translational and rotational works required to move the rotating impeller of the FT4 Rheometer® through a certain distance into a powder bed [94], [166], [167]. Using a newly reconditioned sample powder each time to remove any stress history, the test for repeatability and stability, the Variable Flow Rate (VFR), was performed three times using a glass vessel with a diameter of 25 mm. To measure the powder's resistance against the blade's constant rotation, it was subjected to a constant tip speed of 100 mm/s during the first eight tests. For assessment of the dependence of the powder resistance on the blade speed, the following three tests were performed at variable tip speeds of 70, 40, and 10 mm/s. Figure 7-17 shows the recorded energy to make the powder flow around the blade subjected to constant and variable rotation speeds.

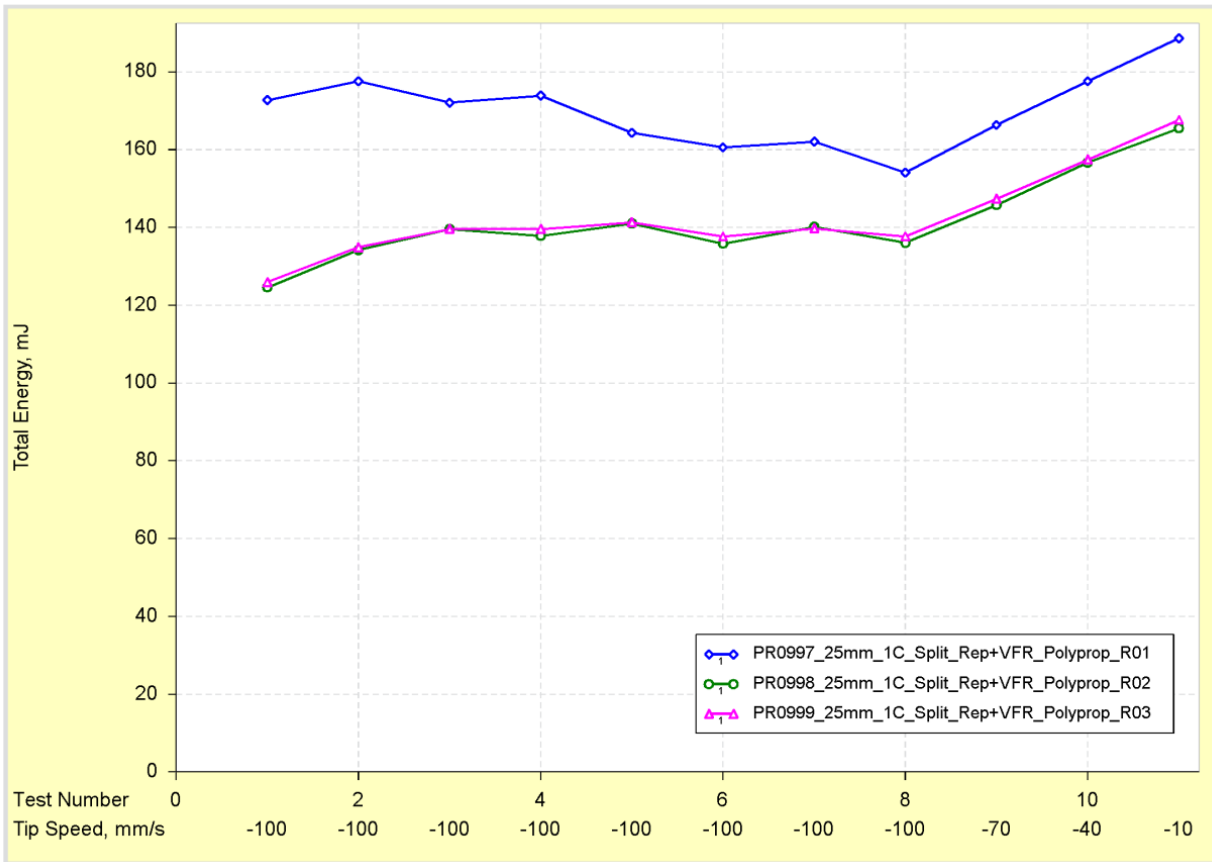


Figure 7-17: Energy flow at fixed and variable blade tip speeds

Table 7-6 summarizes the dynamic characteristics of stability and VFR of the PP composite powder.

Table 7-6: Summary of the dynamic flow characteristics for the new PP composite powder

Designation of the PP sample	Basic Flow Energy (BFE), (mJ)	Specific Energy (SE), (mJ/g)	Stability Index (SI)	Flow Rate Index (FRI)	Conditioned Bulk Density (CBD) (g/ml)
Polyprop_R01	162.15	7.45	0.94	1.22	0.42
Polyprop_R02	140.22	6.92	1.12	1.22	0.42
Polyprop_R03	139.80	6.73	1.11	1.22	0.42

The Basic Flow Energy (BFE) is the energy required to move the blade downwards in cycle 7, while the Specific Energy (SE) is the average energy required to move the blade upwards in cycles 6 and 7. The free-flowing powder is characterized by an SE less than 5, while an SE greater than 10 indicates a cohesive powder. The decreasing order of SE values 7.45, 6.9, and 6.73, within the limiting range from 5 to 10, indicated a transitional powder characterized by a trend of moving from a cohesive towards a free-flowing powder after each conditioning. The dynamic testing agreed with the measured HR of 1.266, indicating that the new PP composite powder was characterized as a transitional flowing powder.

The stability Index (SI) is the ratio between the flow energies of cycles 7 and 1 and indicates the extent to which repeated testing affects particle size distribution. The increase in particle size is characterized by an SI value significantly greater than 1, while an overall decrease in particle size, which is associated with powder caking before the test, is indicated by an SI value significantly less than 1 [167]. Generally, powders with a stability index between 0.9 and 1.1 can be considered normal stable powders [168]. The closeness to 1 of the recorded SI values 0.92, 1.12, and 1.11, respectively, corresponding to tests 1, 2, and 3, indicated no significant change in PSD from one test to another. Despite the possible thermal degradation of the powder, the stability indices obtained showed that the translational movement of the recoater during L-PBF will not significantly affect the particle size distribution of the new composite PP powder, thus allowing the powder to be reused for several cycles. The effect of reducing the blade rotation speed is assessed by the Flow Rate Index (FRI), which is the ratio between the flow energies during the downward cycle 11 and cycle 8, respectively, corresponding to 10 and 100 mm/s tip speeds. For the three tests performed, a repeatable constant FRI of 1.22 characterized the flow behaviour of the powder, thus indicating the stability of flow properties through a series of dynamic tests.

The ease of beginning to flow for a consolidated powder that was previously at rest can be evaluated by the shear properties of the powder. The shear cell head, an integral part of the FT4 Powder Rheometer®, makes contact with the top of the powder and induces a normal stress σ . The powder sample was subjected to a compressive normal stress established at 9 kPa. The shear stresses were induced through the gradual increase of the rotation speed of the shear head until a constant shear stress was reached, leading to the powder bed failure at the maximum shear stress τ_{max} . This is referred to as pre-shearing and was used to place the powder in a critical state, which was incorporated to increase the repeatability between tests [169]. By repeating the pre-shearing process and measuring the shear stress at five additional lower normal stresses of 3, 4, 5, 6, and 7 kPa, the corresponding shear stresses τ were obtained to produce the yield

locus. The cohesion values were obtained by extrapolating the yield loci to zero normal stress $\sigma = 0$ (Figure 7-18).

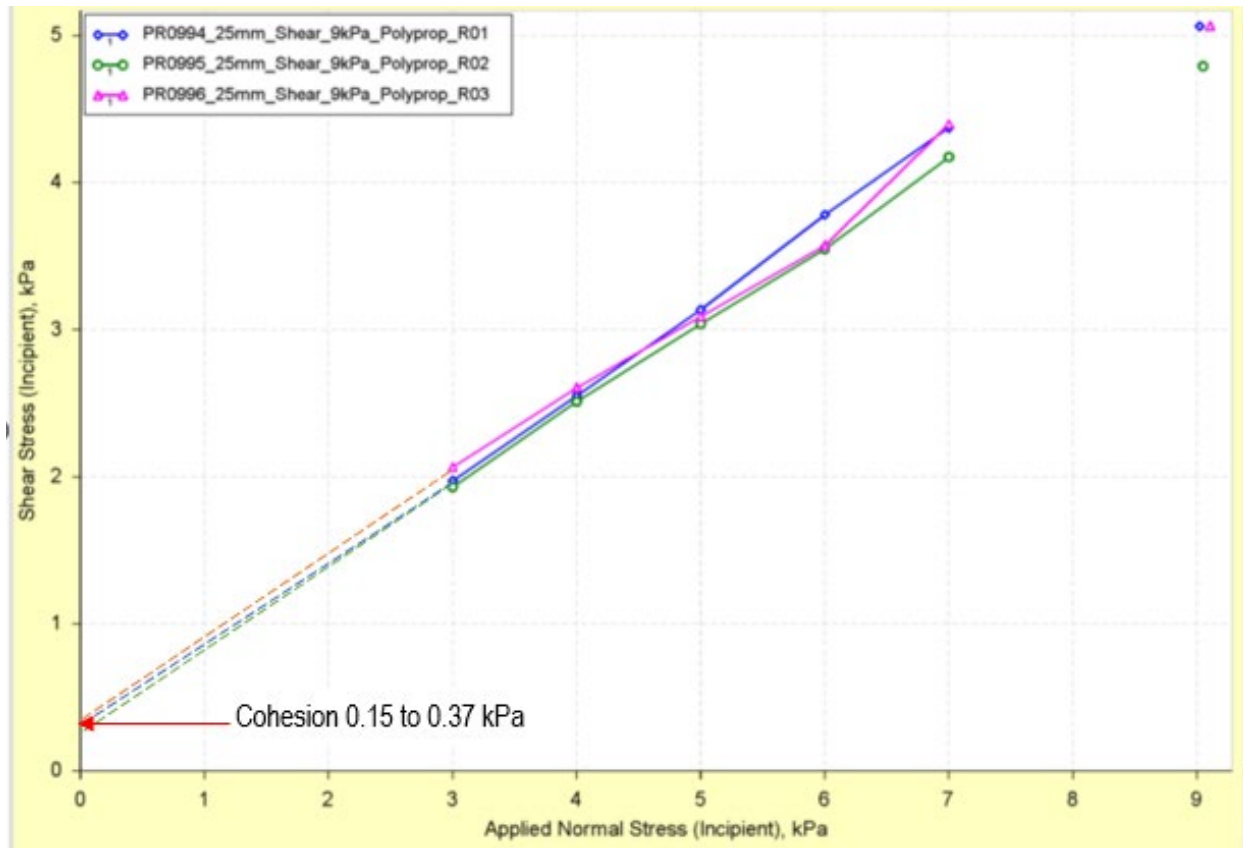


Figure 7-18: Shear cell test for the new composite powder

Three tests were performed to evaluate the cohesion, Unconfined Yield Strength (UYS), Major Principal Stress (MPS), Flow Function (FF), Angle of Internal Friction (AIF), also known as Angle of Internal Resistance (AIR), and bulk density (BD) of the new composite PP powder. Table 7-7 summarizes the results obtained from the shear cell test.

Table 7-7: Summary of shear cell test results

	Cohesion, kPa	UYS, kPa	MPS, kPa	FF	AIF, °	BD, g/ml
Test 1	0.15	0.53	14.74	27.64	31.08	0.46
Test 2	0.28	0.96	14.25	14.80	28.89	0.45
Test 3	0.37	1.25	15.02	12.05	29.07	0.45

The FF is the ratio between the MPS and UYS and is used to classify the flowability of different materials. For this study, FF was used to compare the shear strength of the new composite powder when subjected to three shear cell tests. Cohesive powder with poor flowability is characterized by significant cohesion forces or considerable shear stress with a small FF value. On the other hand, a non-cohesive free-flowing powder displays small cohesion resisting forces or small shear stress and possesses a greater FF value. Despite insignificant differences in the cohesion and FF values, the three shear cell tests produced nearly overlapping yield loci, thus indicating a high level of repeatability of the results. A free-flowing powder is characterized by an FF function greater than 10 [167], and all calculated FF values of 27.64, 14.80, and 12.05 for the three tests satisfied the free-flowing powder requirements. The progressive increase in cohesion from 0.15 to 0.28 kPa and from 0.28 to 0.37 kPa indicated a slight reduction of flowability of the powder when it was reused despite the conditioning process between any two consecutive tests.

The AIF (δ) or AIR, also known as angle of shear resistance (Figure 7-19) is defined as the theoretical angle between the axis of normal stress σ and the tangent to the Mohr envelope at a point representing a given failure-stress condition for the powder. In an initially static powder, the flow occurs when a critical maximum macroscopic shear stress is attained, above which particles start to slide against each other.

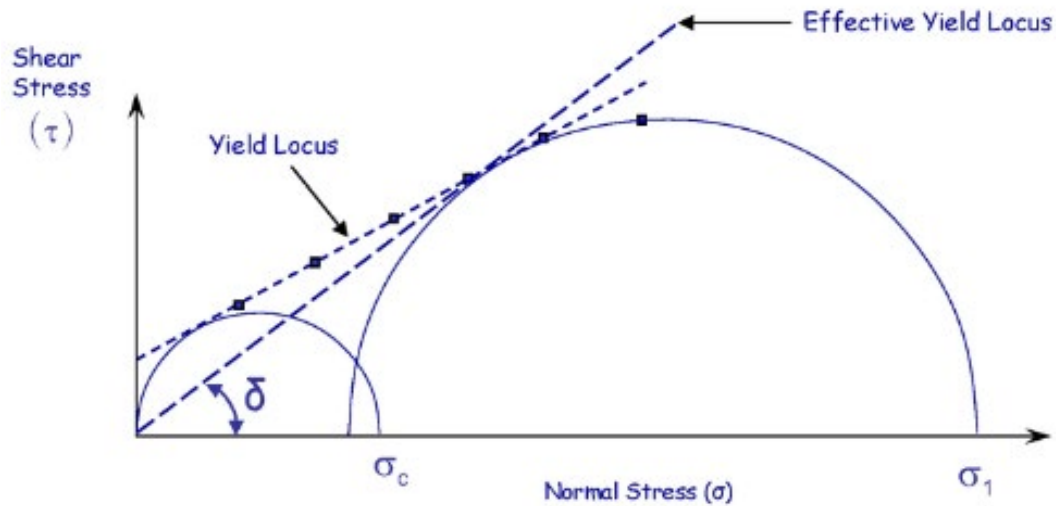


Figure 7-19: AIF using the Mohr circle [170]

In addition to the shear yield stress that must be overcome for easy flow of the powder, the friction force between the powder and the wall surface of the container must also be exceeded or conquered. A small AIF characterizes easy-flowing powder, while a big angle of internal friction must be exceeded for a cohesive powder. In modelling the AIF of powder particles and supported with experimental work on spherical particles of NaCl salt, Zegzulka *et al.* [171] found that with the same probability of all particle displacements, the mean probable AIF of the powder was found to be 39.2° . For this study, the values of 31.08° , 28.89° , and 29.07° , which were smaller than 39.2° , indicated good flowability of the new PP composite powder. The differences between the values of AIF for the three tests were not significant, indicating that the reproducibility of flow results can be extended to AIF. The measured bulk density was also repeatable, around 0.45 g/ml. However, it was greater than the bulk density of 0.389 g/ml, measured in a static regime.

7.8 X-Ray Diffraction analysis

WAXD or WAXS are the most used techniques to provide information on the crystallographic structure and degree of crystallinity, micro-distortion of a lattice and dislocation in a structure, atomic position, sizes in a unit cell, and, to some extent, the chemical composition of a crystalline material. The method relies on analyses of Bragg's peaks generated from the scattered X-ray waves due to the energy loss of ionizing radiation when waves pass through a sample. The detector is moved around a circular path through an

increment of an angular displacement 2θ , and the number of scattered X-rays observed in terms of intensity or number of counts are recorded. Bragg's curves can be produced with peaks for specific 2θ angles, implying the presence of nano-sized structures or crystals arranged in a particular plane defining the type of crystallographic phase. Each crystalline material possesses a unique atomic structure, which causes the diffracting X-ray beam to generate a distinct characteristic pattern. In general, the smaller the crystallite size, the broader the diffraction peak. The larger the crystallite size, the sharper the peak appears, implying an increase in the degree of crystallinity. The degree of crystallinity can be determined based on the intensity of the peaks corresponding to specific repeating structures [42], [161].

A comparative investigation of XRD patterns for the powder-form samples was conducted on a Bruker D2 Phaser X-ray diffractometer at the UFS. With a flat plate sample holder at a temperature of 25 °C, copper radiation ($K\alpha$ Cu) with a wavelength $\lambda = 1.5406 \text{ \AA}$ was used as an X-ray source. The diffraction patterns were collected in the angular range for 2θ varying from 5 to 70°, with a step size of 0.1° and time per step equal to two seconds. The extent to which crystalline structures are prevalent in samples was analyzed using the FWHM criterion or sharpness of the Bragg's peaks within the corresponding diffraction angular positions.

The XRD spectrum patterns for HNR100 and HTV145 PP powders produced separately using the precipitation process are shown in Figure 7-20.

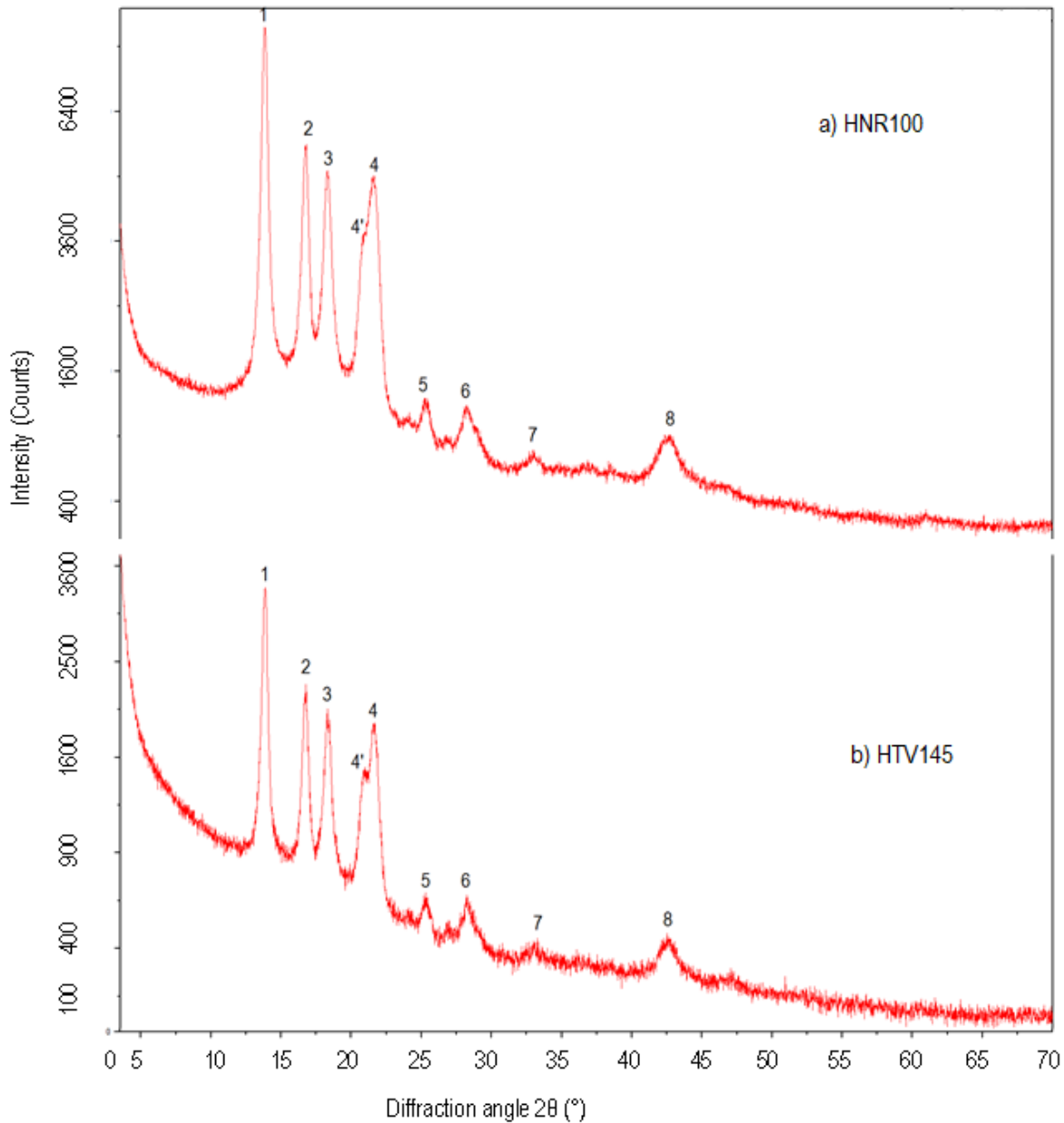


Figure 7-20: XRD patterns for PP powders from separate precipitations of HNR100 and HTV145 grades

It could be observed that the appearance of the sharp peaks 1, 2, 3, and 4 at diffraction angle 2θ in positions 13.75° , 16.67° , 18.33° , and 21.67° , respectively, were identical for both grades HNR100 and HTV145. The similarities of the patterns reveal how strong the two grades are similar in terms of crystallographic structure despite the vast difference in their MFIs. Such patterns are evidence of the presence of crystals arranged in a particular plane defining the type of the crystallographic phase. From the angular positions 2θ equal or greater than 25.42° , the sharpness of peaks 5, 6, 7, and 8 (Figure 7-20a & b) is significantly reduced, thus

increasing the FWHM of the patterns from approximately 2.5° to 5° which implies the presence of amorphous phase with less oriented lamellae in the PP powder samples.

The XRD spectra for the PP powder obtained from the precipitated mixture of HNR100 + HTV145, as compared to the patterns resulting from the same mixture with added talc (HNR100 + HTV145 + talc), are shown in Figure 7-21.

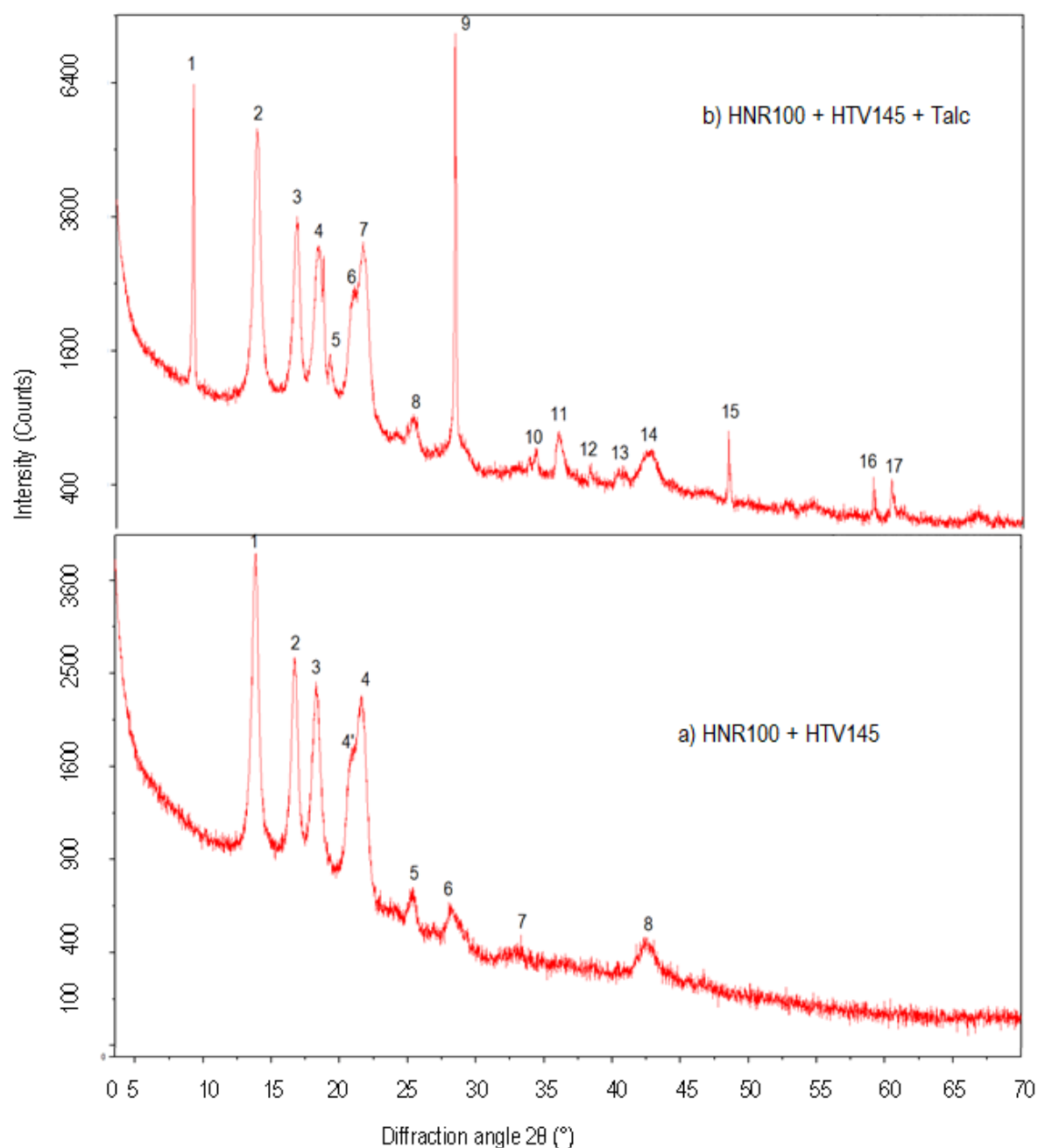


Figure 7-21: XRD patterns for (HNR100 + HTV145) and (HNR100 + HTV145 + talc) PP powders

It could be observed that the precipitation of the mixture of the two grades did not affect the XRD patterns resulting from the separate precipitation of each grade. This implies that the mixing and precipitation of the two grades produced a powder with equally important degrees of crystallinity and crystallographic structure as those of the constituent grades. The addition of talc changed the XRD patterns by the occurrence of three additional well-pronounced sharp peaks at angular positions 2θ of 9.17° , 28.33° , and 48.33° . The new XRD patterns with additional sharp peaks and broader, less sharp Bragg's peaks indicate the possible rearrangement of crystals to form additional crystallographic beta (β)-phase as talc may act as a nucleating agent. The competition of alpha (α) and beta phases may cause a slight decrease in the degree of crystallinity from 39.8 to 35.72%, as the DSC analyses have shown.

The comparative analyses of XRD spectra for the newly produced PP powder HNR100 + HTV145 + talc + carbon black and the commercial PP CP75 are shown in Figure 7-22. Adding carbon black to the HNR100 + HTV145 + talc (Figure 7-21b) slightly modified the location of the Bragg's peaks. The sharp peak, which appeared at diffraction angles 2θ of 9.17° and 28.33° , shifted to 8.88° and 25.83° , respectively, while the sharp peak at angular position 2θ of 48.33° completely disappeared. The Bragg's peaks 2, 3, 4, and 6 (Figure 7-22b) are precisely the fingerprint of PP crystallographic peaks which occurred at diffraction angle 2θ in positions 13.75° , 16.67° , 18.33° , and 21.67° in other analyzed samples, i.e., HNR100, HTV145, HNR100 + HTV145 and HNR100 + HTV145 + talc. A similar pattern was observed by Karacan and Benli [152], where the predominance of alpha phase in oriented crystallographic planes of 110, 040, and 130 was found at scattering angle 2θ of 14.16° , 15.71° , and 18.57° together with less oriented crystals in planes 060, 200, and 220 at scattering angle 2θ of 25.54° , 27.11° , and 28.36° , respectively. It is evident that peak 1 (Figure 7-22b) at the scattering angle 2θ of 8.88° results from additives such as talc and/or carbon black. The peak 8 at the angular position 2θ of 25.83° with a little shift due to the type of process applied to the polymer or the nature of the X-ray used, as mentioned by Guerra, Wan, and McNally [157], could be an overlapping of alpha and beta phases of iPP in 111 and 301 crystallographic planes as a result of the effect of nucleating agents to form β -phase.

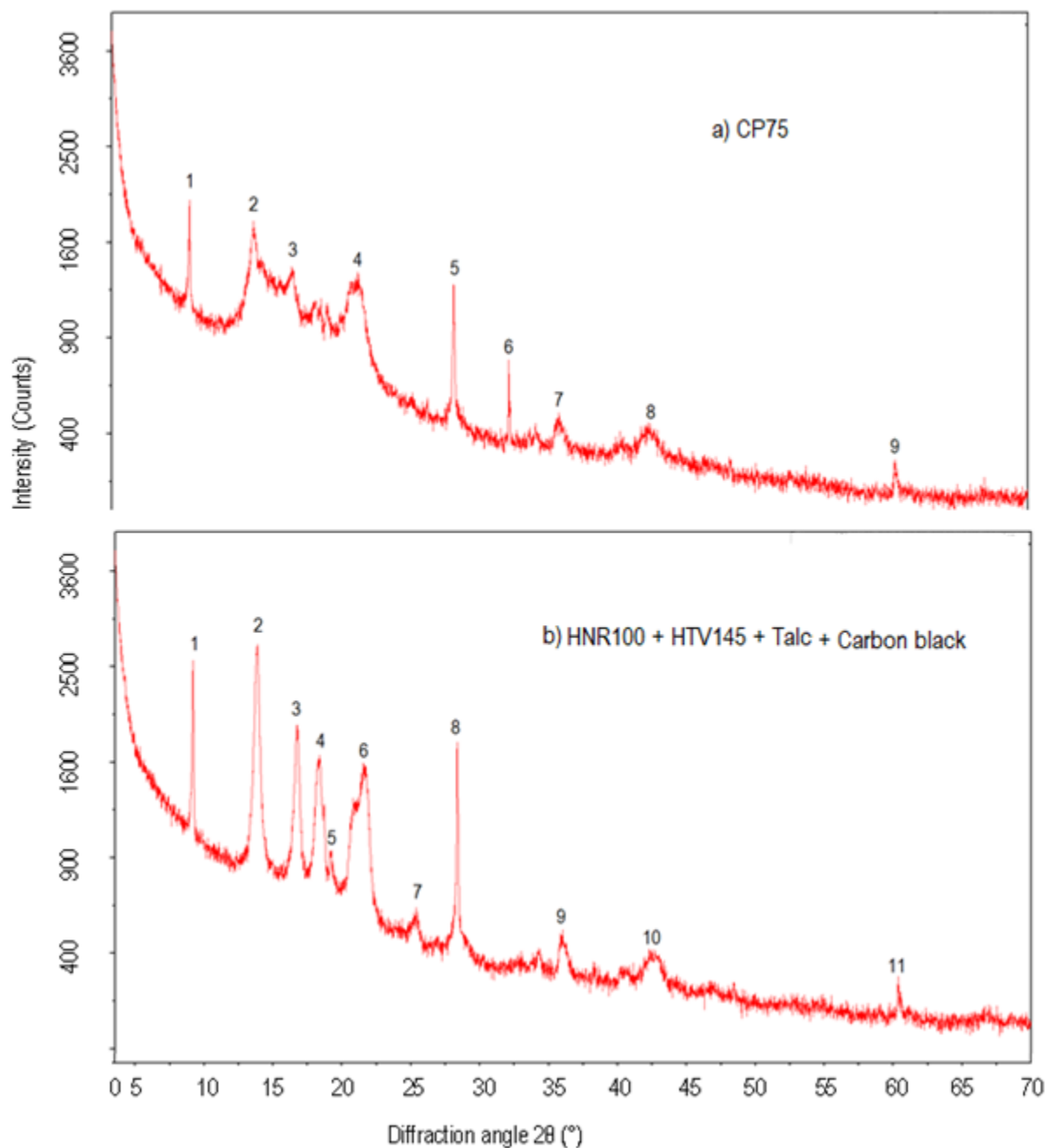


Figure 7-22: XRD patterns of PP CP75 and (HNR100 + HTV145 + talc + carbon black) PP powders

Regarding the sharpness of diffraction peaks, the patterns obtained from the XRD analysis of commercial powder PP CP75 (Figure 7-22a) displayed significant deviations from the spectra of other PP samples based on HNR100 and HTV145 grades. Though the peaks 2, 3, and 4 at angular positions 13.75° , 16.67° , and 21.67° , respectively, reflect the scattering angle of a typical PP, the sharpness of the peaks is noticeably reduced, testifying to a polymer with less oriented crystalline structure of the alpha phase. The published

work by Nsengimana *et al.* [117] indicated that PP CP75 powder was filled with wollastonite, while it was also found that the powder contained a high level of additives, including talc and 10.07% ash. As a similar understanding was applied to HNR100 + HTV145 + talc + carbon black powder, peak 1 (Figure 7-22a) at an angular position 2θ of 10° appeared due to mineral additives in the PP CP75 powder. The sharp peaks 5 and 6 could also indicate the presence of β -phase resulting from the nucleating action of the mineral additives.

7.9 Fourier Transform Infra-Red spectrometry analysis

FTIR spectrometry is a technique that uses electromagnetic properties of light to produce the infrared spectrum of absorption, emission, and photoconductivity of a solid, liquid, or gaseous sample [172]. When a sample is exposed to infrared radiation, some infrared radiation is absorbed by the sample while other radiation is passed through the sample and transmitted. While the dispersive instruments or techniques use only radiation energy with a well-defined narrow range of wavelengths to interact with the sample, the FTIR technique can use interference waves to measure all the infrared radiation simultaneously over a wide range of frequencies. This constitutes a significant advantage over dispersive spectrometers, which measure intensity over a narrow range of wavelengths [25]. The electromagnetic radiations are associated with the functional chemical groups or bonds in the analyzed sample. Chemical bonds and molecular structures vibrate at characteristic frequencies, and when exposed to infrared radiation, they absorb the radiation at frequencies corresponding with their vibration modes [173]. The measurement of the radiation absorption as a function of the frequency of vibration produces a spectrum that can be used to identify functional groups and compounds in a sample [174].

The wavelength (Figure 7-23) of electromagnetic radiation, such as light, is a spatial period of the wave. It is defined as the distance the light travels for one complete cycle of its vibrations.

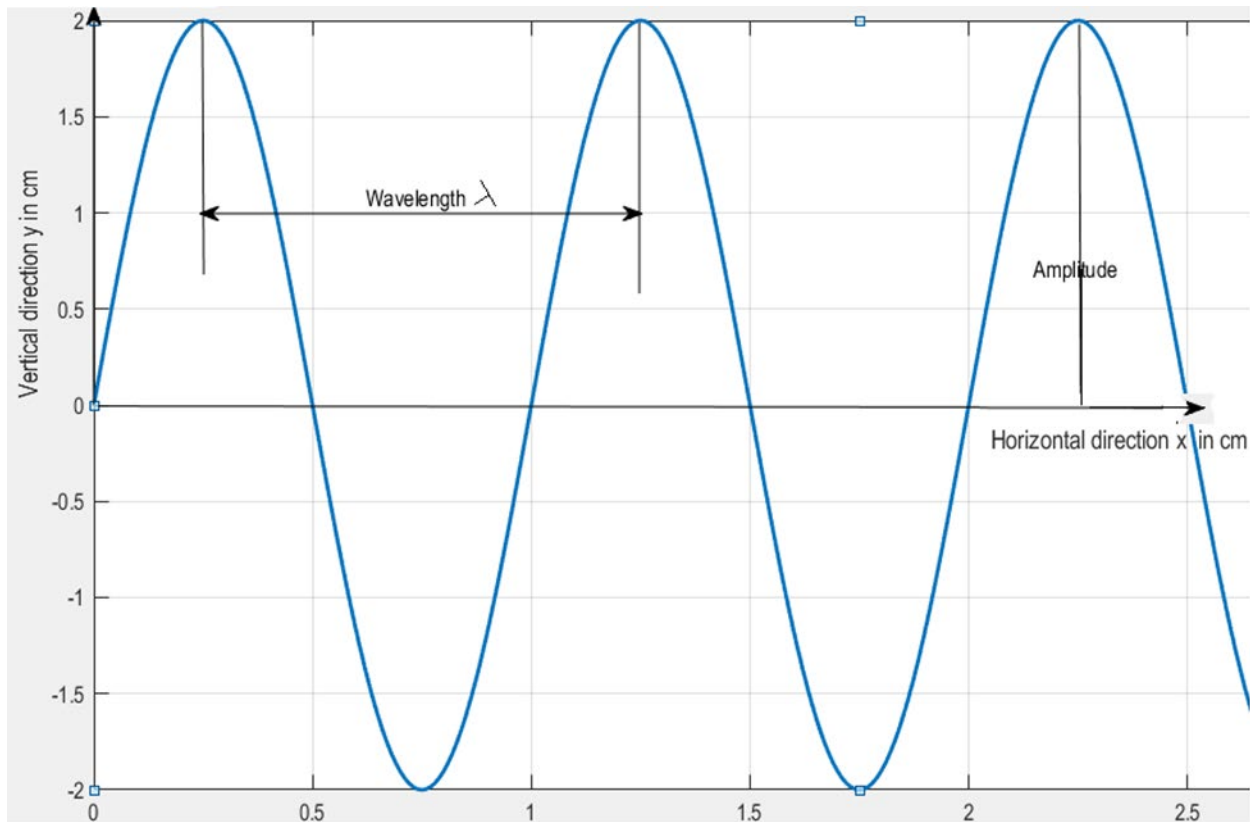


Figure 7-23: Propagation of a sinusoidal wave of electromagnetic radiation

The reciprocal of the wavelength is known as the wavenumber and is defined as the number of cycles required for the light to travel a unit length distance,

$$W = \frac{1}{\lambda} \quad (\text{Eq. 5})$$

W-is the wavenumber, and λ -is the wavelength.

The energy E of the light is proportional to the wavenumber through the following relationship:

$$E = hcW \quad (\text{Eq. 6})$$

$h = 6.63 \times 10^{-34}$ Joules-second- is the Planck's constant, and $c = 3 \times 10^{10}$ cm/second- is the velocity of the light.

Since the energy of the light is directly proportional to the corresponding wavenumber, the spectrum of the variation of absorbance versus energy of the emitted light is plotted using the wavenumber as the variable

on the horizontal axis. Most molecular vibrations fall in the mid-infrared zone, and spectra are plotted for wavenumbers varying from 4000 to 400 cm^{-1} , with high energy to the left and low energy to the right [175].

FTIR analyses were performed on nine samples in pellet and powder forms at the UFS. All infrared spectra were measured on a Thermo Scientific Nicolet iS50 ATR Infrared Spectrometer with OMNIC v9.2.86 software within a wavenumber range of 500–4000 cm^{-1} .

The FTIR spectra for HNR100, HTV145, and the combined (HNR100 + HTV145) grades in pellet and powder forms are shown in Figure 7-24 and Figure 7-25, respectively. Finally, the FTIR spectra for HNR100 + HTV145 + talc, HNR100 + HTV145 + talc + carbon black and commercial PP CP75 grades in powder forms are shown in Figure 7-26. Table 7-8 summarizes the wavenumber and the corresponding vibration modes and chemical functional groups.

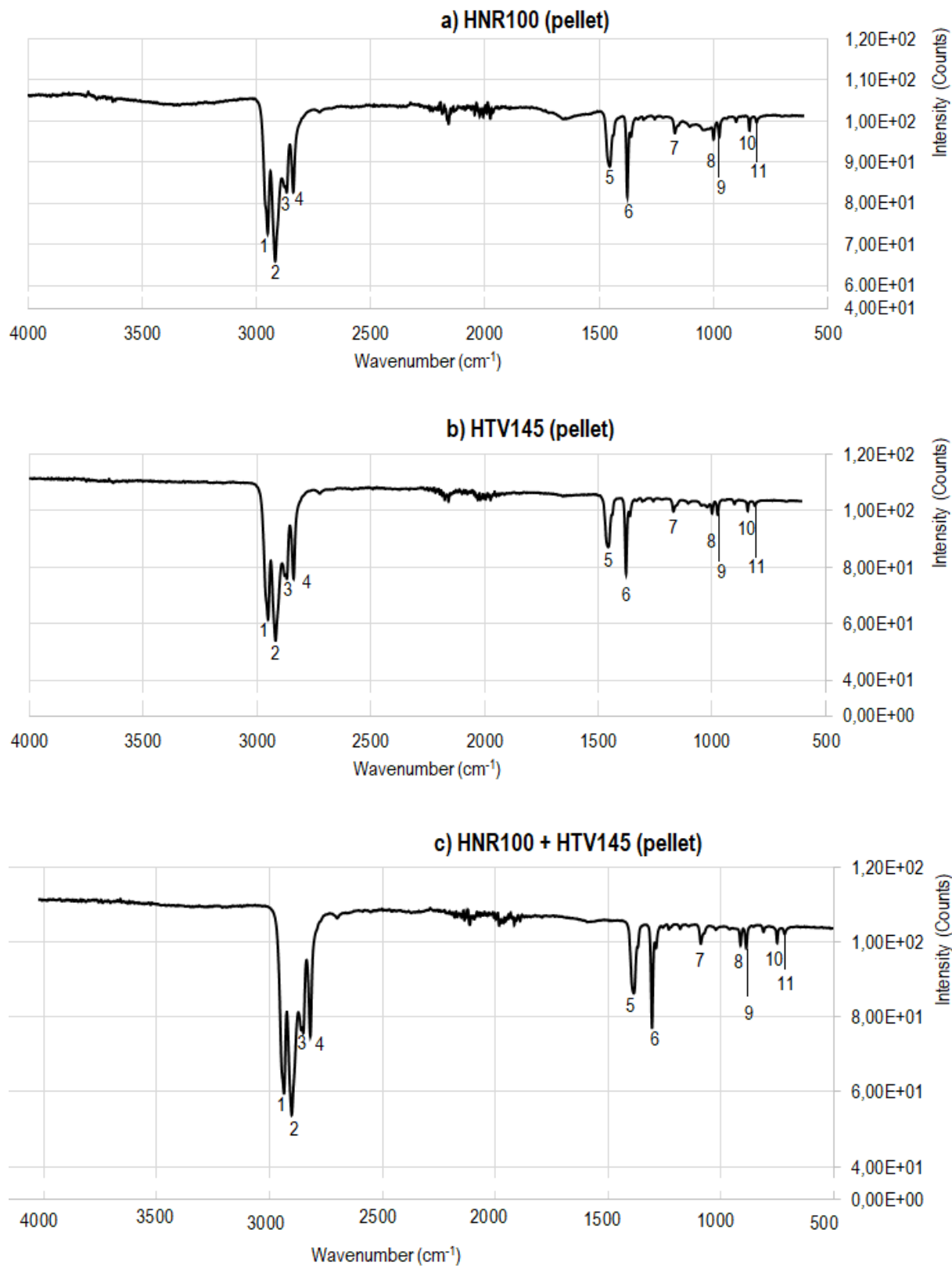


Figure 7-24: FTIR spectra for HNR100, HTV145 and (HNR100 + HTV145) in pellet form

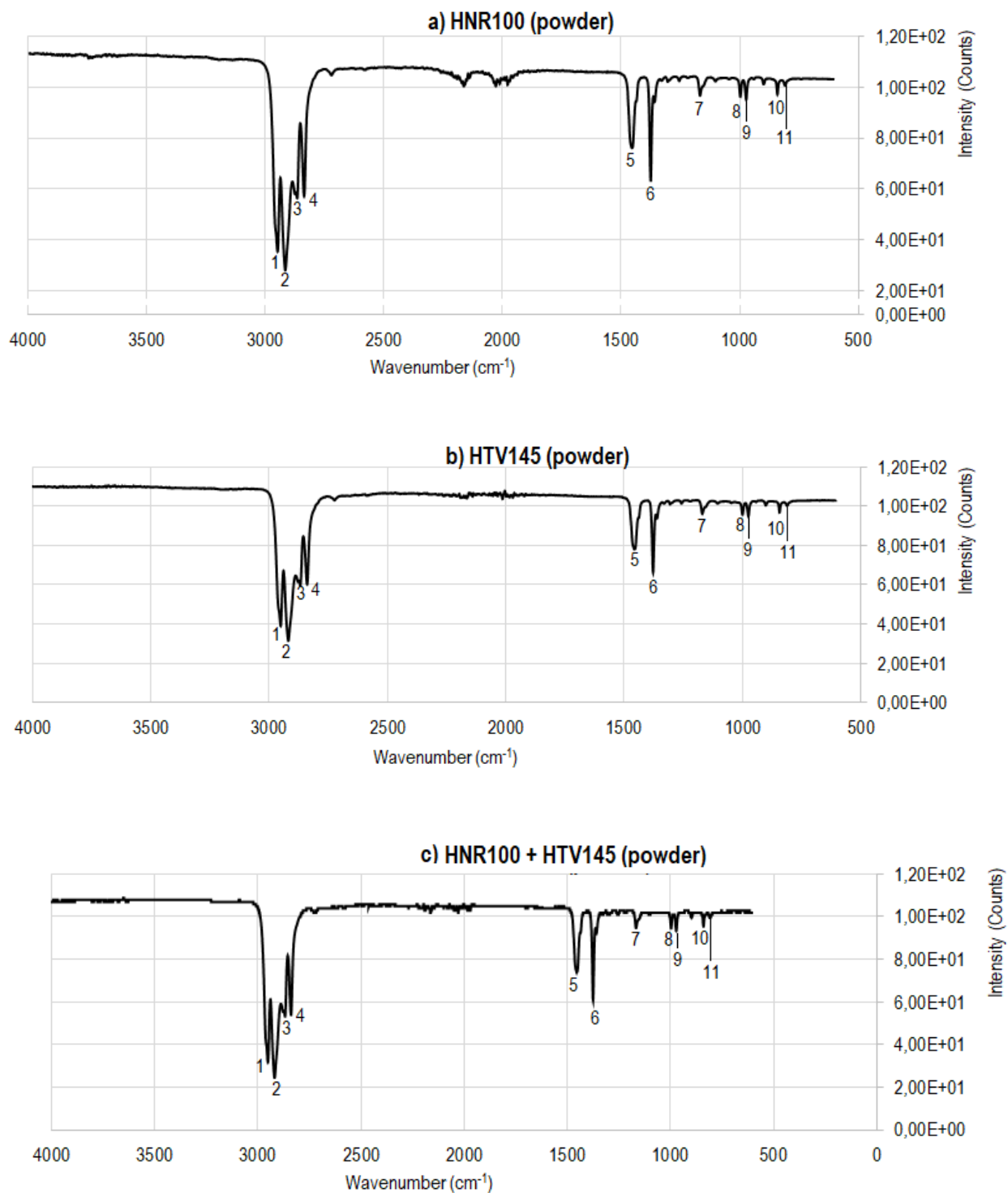


Figure 7-25: FTIR spectra for HNR100, HTV145 and (HNR100 + HTV145) in powder form

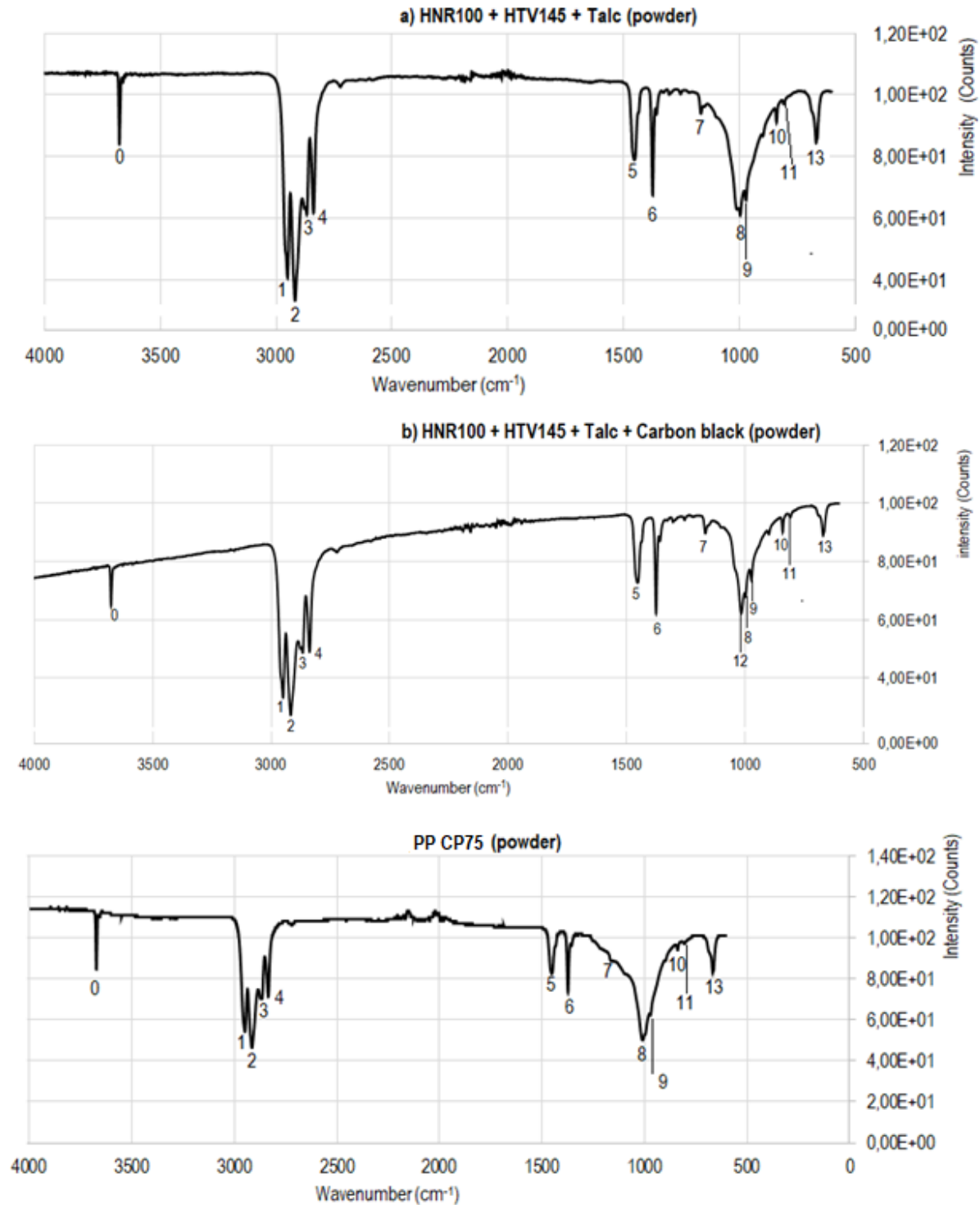


Figure 7-26: FTIR spectra of HNR100 + HTV145 + talc, HNR100 + HTV145 + talc + carbon black and PP CP75 in powder forms

Table 7-8: Summary of wavenumbers and corresponding vibration modes of functional groups of PP in pellet and powder forms

Points	Pellets			Powder						Typical wavenumber (cm ⁻¹)	Vibration mode and corresponding chemical functional groups (bonds)
	HNR100	HTV145	HNR100 + HTV145	HNR100	HTV145	HNR100 + HTV145	HNR100 + HTV145 + Talc	HNR100 + HTV145 + Talc + Carbon black	CP75 PP		
	Wavenumbers (cm ⁻¹)										
0							3675	3676	3675	3675	Stretching of hydroxyl group OH in Mg-OH bond in talc
1	2949	2949	2949	2949	2950	2950	2949	2950	2950	2950	Asymmetrical stretching of CH ₃
2	2916	2916	2916	2916	2917	2917	2917	2917	2916	2920	Asymmetrical stretching of CH ₂
3	2865	2866	2867	2867	2867	2867	2867	2866	2867	2870	Stretching of CH ₃
4	2837	2837	2837	2837	2837	2837	2838	2837	2836	2836	Symmetrical and asymmetrical stretching of CH ₃ and CH ₂
5	1451	1452	1452	1453	1451	1452	1452	1451	1454	1456	Symmetrical bending of covalent chain C-H in methyl group CH ₃
6	1375	1375	1375	1375	1375	1375	1375	1375	1376	1376	Symmetrical bending of CH ₃
7	1166	1165	1167	1166	1166	1168	1167	1167	1147	1166	Wagging of C-H and rocking of CH ₃
8	997	997	997	997	997	997	997	998	1010	996	Rocking of CH ₃ and stretching of carbon-carbon single bond C-C
9	972	972	972	972	972	972	973	972	972	973	Rocking of CH ₃ , alkene group with carbon-carbon double bond C=C
10	840	840	840	840	840	840	841	841	841	840	Rocking of C-H
11	807	807	808	807	808	809	809	808	805	808	Stretching of carbon-carbon single bond C-C
12								1015		1020	Silica SiO ₂
13							670	670	670	670	Si-O-Mg bond in talc

The FTIR spectra, as shown in Figure 7-24, Figure 7-25, and Figure 7-26, are characteristic of the FTIR fingerprint of PP, especially for the sharp peak points 1 to 6 where the spectrum is repeated for wavenumbers 2950, 2920, 2836, 1456, and 1375 cm^{-1} . These specific wavenumbers reflect the symmetric and asymmetric stretching and bending vibration modes of CH_2 and CH_3 functional groups in PP molecules. The similarity in spectra and wavenumbers is maintained for both separate grades, HNR100, HTV145, and their mixture in pellet or powder forms (Figure 7-24 and Figure 7-25). The less pronounced peaks indicated by points 7 to 11 reflect stretching and other vibration modes such as rocking and wagging of methyl group CH_3 , carbon-carbon single bond C-C, carbon-carbon double bond C=C, and carbon-hydrogen C-H bond as indicated in Table 7-8. Similar patterns and wavenumbers are conserved for both separate HNR100, HTV145, and their respective mixture in pellet or powder forms. Macroscopic effects caused by mechanical shear forces can change the polymer chains into macro-free radicals, thus leading to the degradation of the polymer [176]. Deepa, Kuppan, and Padmanabhan [177] used FTIR analysis to investigate possible changes in functional groups and bonds in PP-based Self-Reinforced Composites (SRC) when subjected to conventional cutting with a saw and unconventional cutting methods such as Abrasive Water Jet (AWJ) and laser. It was found that the laser cutting converted C-C bonds into various bonds like C=C, C=O, C-F, and C-N. The improvement of mechanical properties of laser-cut samples comparatively to conventionally cut specimens was attributed to the appearance of double bonds C=C and C=O that are more than twice as strong as C-C single bonds. On the other hand, bonds such as N-O stretching, and C-O stretching were identified after AWJ cutting indicating the presence of a new alkene group which exhibited strong stretching and bending vibrations. The repetition of the FTIR spectra in the current study indicates the closeness of the two selected grades in terms of chemical composition and the conservation of the functional groups and chemical bonds through the transformation steps from pellet to powder suitable for L-PBF. The dissolution of the pellets into m-Xylene followed by the precipitation, drying and mechanical breaking of agglomerates have no effect on the variation of functional groups and chemical bonds of the HNR100 and HTV145 polypropylene grades.

The FTIR spectrum of the powder produced by precipitation into m-Xylene of the mixture of (HNR100 + HTV145 + talc) shows additional sharp peaks indicated by points 0 and 13 (Figure 7-26a) corresponding to wavenumbers 3675 and 670 cm^{-1} , respectively. The new peaks reflect the presence of talc with the chemical formula $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$. The wavenumber 3675 cm^{-1} is assigned to the stretching of hydroxyl group OH in the Mg-OH bond, while the wavenumber 670 cm^{-1} is characteristic of the vibration mode of

the Si-O-Mg bond in the talc molecule [178]. Further addition of carbon black (Figure 7-26b) showed no significant change in the spectrum displayed by Figure 7-26a except for the appearance of peak 12 with a wavenumber 1020 cm^{-1} assigned to silica SiO_2 as a derivative of the talc. The carbon tends to absorb a large, broad range of infrared frequencies [179]. The dark grey pigmentation of the composite PP powder (HNR100 + HTV145 + talc) by adding carbon black powder did not result in additional peaks on the FTIR spectrum, as shown in Figure 7-26b. The carbon atoms joined the existing functional groups and bonds of PP to maintain a wide range coverage of wavenumbers from 2950 to 808 cm^{-1} for (HNR100 + HTV145 + talc + carbon black) powder. In addition to grey dark pigmentation required for powder sintering on a Sintratec S1 machine, the addition of carbon black to polymer acts as a photostabilizer due to its capability to absorb ultraviolet radiations, which heavily degrade chemical, physical, and mechanical properties of plastic products [180], [181].

The FTIR spectrum of the newly produced PP composite powder (HNR100 + HTV145 + talc + carbon black) is highly comparable and similar to the FTIR patterns (Figure 7-26c) of the commercial powder PP CP75. There are no significant differences in FTIR peak characteristics of the pellets compared to those of PP in powder form, meaning that the precipitation process followed by grinding did not modify the molecular structure of the PP pellets. The precipitation process of the two PP grades with talc added and finally pigmented with carbon black to obtain a dark grey PP powder proved to be a promising production method for the PP powder suitable for L-PBF.

Conclusions

1. The newly produced PP powder (HNR100 + HTV145 + talc + carbon black) and the commercial PP powder PP CP75 were characterized through TGA, DSC, SEM, XRD, and FTIR analyses.
2. The TGA analysis showed the new produced PP powder could degrade at high temperatures ranging from 385 to 495°C , thus confirming that the relatively lower operational temperatures for L-PBF should not lead to the degradation of the newly produced PP composite powder. Therefore, the unsintered powder surrounding the laser-sintered parts shall be reused in the L-PBF process.
3. The DSC analysis showed that the degree of crystallinity and the window of sinterability for the newly produced PP powder were found to be 37.34% and 31.1°C , respectively, versus 38.74% 38°C , respectively, for the commercial powder PP CP75.

4. The results obtained from SEM analysis showed that particles with smooth spherical shapes characterized the newly produced powder as opposed to rough, irregular shapes, which were predominant in the commercial powder PP CP75 particles.
5. For the newly produced PP powder, the true density of 0.986 g/cm^3 was measured. The apparent (bulk) and tap densities were measured to be $0.398 \pm 0.004 \text{ g/cm}^3$ and $0.504 \pm 0.001 \text{ g/cm}^3$, implying $\text{HR} = 1.266 \pm 0.013$, thus obtaining transitional characteristics that are very close to good loose flowing aeratable powder.
6. The PSD of the new PP powder was assessed to be favourable for the good flowability of a powder suitable for L-PBF. Half, i.e., 50% of the volume of the sample, was constituted by particles less than $60 \text{ }\mu\text{m}$ or $D_{50} = 60 \text{ }\mu\text{m}$, while 90% of the sample volume was made up of particles with size less than $60 \text{ }\mu\text{m}$ or $D_{90}=100 \text{ }\mu\text{m}$. Only 30% of the total powder volume was composed of particles of an average size of less than $50 \text{ }\mu\text{m}$.
7. The XRD analysis indicated that α and β crystallographic structures were predominant in the newly produced PP powder while the chemical analysis showed the presence of silicon dioxide (SiO_2) and magnesium oxide (MgO), which are the main components of talc and insignificant percentages of aluminium oxide (Al_2O_3) and ferric oxide (Fe_2O_3) which could result from local contamination of the powder during the drying process.
8. The FTIR analysis showed that the functional groups of the newly produced PP powder were comparable to those of the counterpart commercial powder PP CP75 against which the newly produced powder was benchmarked for this study.
9. The performance of the newly PP produced powder will finally be assessed through the evaluation of mechanical properties, dimensional accuracy, and surface finish of the laser-sintered additively manufactured samples using a Sintratec S1 machine.

CHAPTER 8: LASER POWDER BED FUSION OF THE NEW POLYPROPYLENE COMPOSITE POWDER

8.1 Description of the machine used for the L-PBF process

The specimens for mechanical testing and assessment of dimensional accuracy and surface finish quality were laser sintered on a Sintratec S1 machine. Sintratec is a Swiss-based manufacturing company specializing in producing compact laser-based AM systems. The Sintratec S1 is a desktop-size machine for L-PBF with the main advantage of accommodating research-based work and small businesses due to the relatively small volume of powder required to fill the powder supply bin. Since only 1.5 kg of the new PP powder was produced in the laboratory setup, the Sintratec S1 was ideally suited to test the laser sinterability of the new material. The specifications of a Sintratec S1 desktop machine are summarized in Table 8-1.

Table 8-1: Specifications of Sintratec S1 machine

	Descriptions	Specifications
1	Overall dimensions (length, width, and height), mm x mm x mm	670 x 365 x 757
2	Maximum build volume, mm x mm x mm	130 x 130 x 180
3	Recommended build volume, mm x mm x mm	110 x 110 x 160
4	Recommended minimal wall thickness, mm	0.8
5	Platform levelling	Automatic powder spreading
6	Weight, kg	67
7	Powder capacity, litres	7
8	Average diameter size of the powder, μm	60
9	Layer thickness, μm	100
10	Power supply	230 volts, 19 kW at maximum power
11	Energy source	Laser diode
12	Laser spot size, μm	500
13	Laser wavelength, nm	445
14	Slicing software	Sintratec central
15	File input format	STL
16	Software compatibility	Windows
17	Connectivity	USB

8.2 L-PBF of specimens for tensile test

The specimens for the tensile test were designed using SOLIDWORKS® software to obtain the CAD geometry following the dimensions specified by ASTM D638-02a, Type I. It must be noted that the test pieces were reduced by 10 mm on each end to fit the build volume of the Sintatec S1 machine. This reduction in length was only on the tabs at the ends of the test pieces and did not affect the testing area. Sintratec sells PA12 and Thermoplastic elastomer (TPE) powders for use in their machines, but in reply to an enquiry about the sinterability of PP powder on the Sintratec S1 machine, it was confirmed that it would be possible. The machine manufacturer also suggested parameters for processing the material. Through trial and error, based on the recommended process parameters, the parameters indicated in Table 8-2 were found to deliver satisfactory results. Tensile test pieces were built in the x-direction only since the available powder also did not allow for test pieces in the y- and z-directions.

Table 8-2: Process parameter for L-PBF of tensile test specimens

Temperatures			Layer thickness h, µm	Hatch distance, µm	Hatch offset µm	Boundary offset, µm	Scanning speed s, mm/s	Laser power p, W	Scaling factor in x-, y- and z- directions, %
Chamber, °C	Powder surface preheat, °C	Powder surface printing, °C							
80	130	154	100	100	260	220	570	5	1.25

The energy density was calculated as follows:

$ED = \frac{p}{s \times h} = \frac{5}{570 \times 0.1} = 0.088 \text{ J/mm}^2$, where p is laser power, s is scanning speed, and h is hatch distance.

8.2.1 Tensile test and SEM analysis of fractured surfaces of specimens

Using an MTS Criterion TM, Model 43 tensile testing machine, tensile tests were performed on five test pieces with a testing speed of 1.5 mm/min, as recommended by the ASTM 638-02a standard. The stress-strain curves are shown in Figure 8-1, and Table 8-3 summarizes the tensile test results.

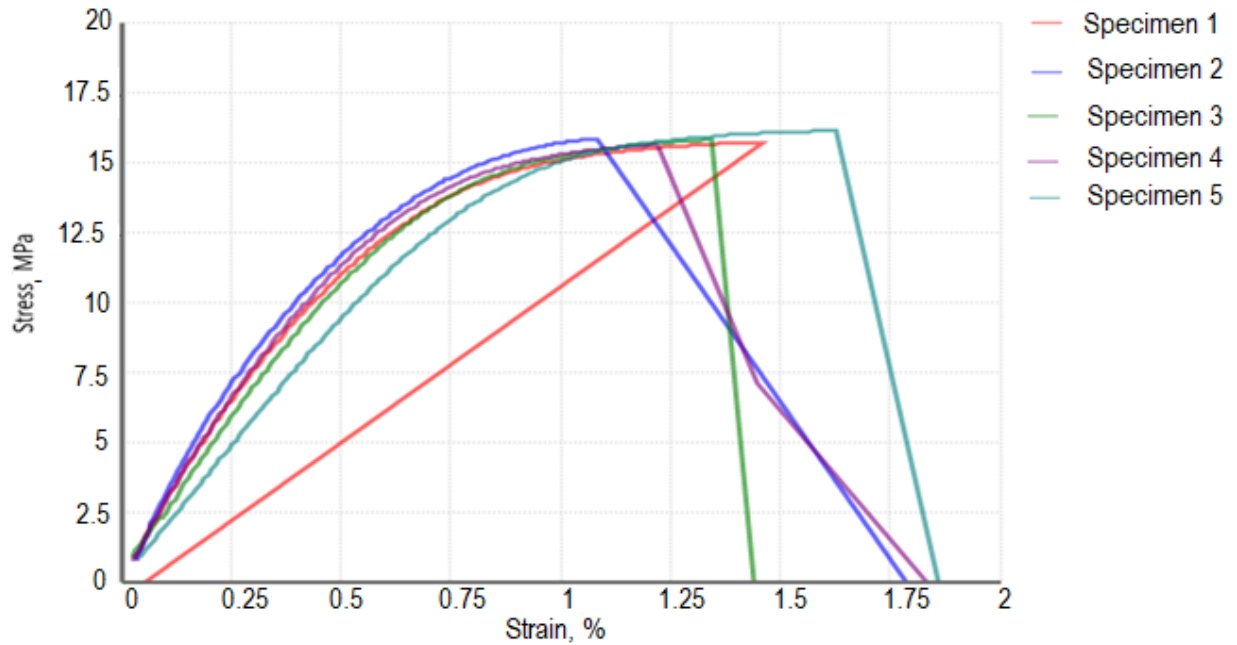


Figure 8-1: Stress-strain curve of PBF specimens

Table 8-3 summarizes the results of tensile tests of the five specimens.

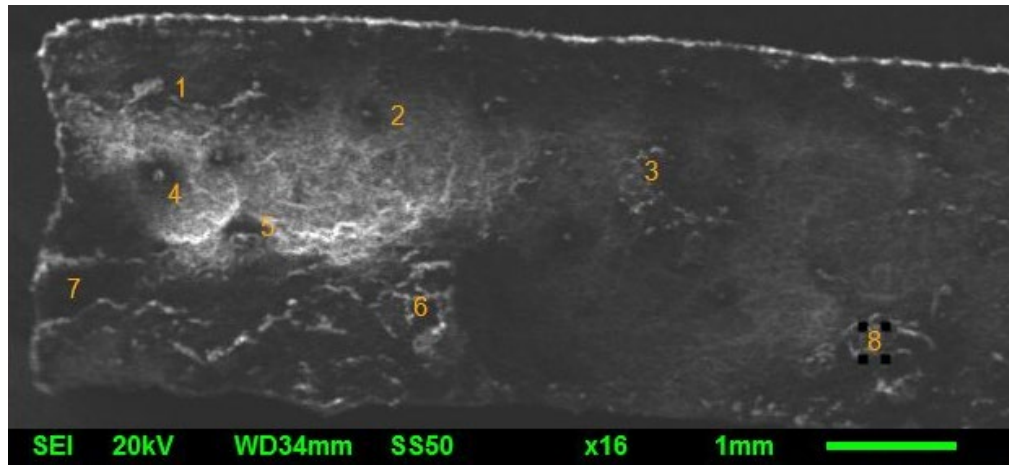
Table 8-3: Summary of tensile test results

Designation	Modulus of elasticity (E), MPa	Ultimate Tensile Strength (UTS), MPa	Elongation at Break (EAB), %
Specimen 1	2814	15.7	0.626
Specimen 2	2965	15.8	0.163
Specimen 3	2398	15.8	0.020
Specimen 4	2823	15.6	0.590
Specimen 5	1936	16.1	0.142
Average	2587	15.8	0.308
Standard deviation	421	0.79	0.2

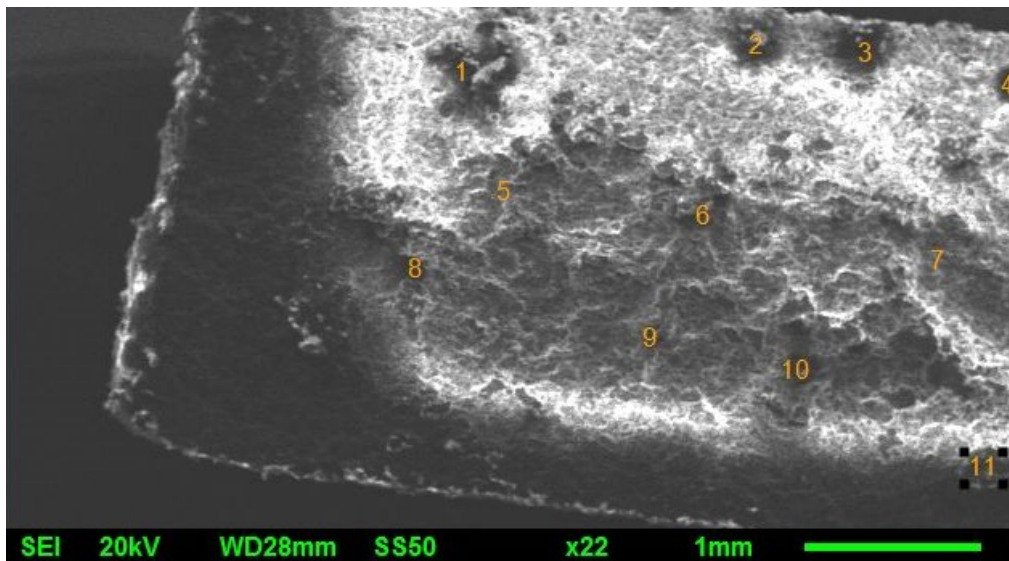
The percentages EAB reported in Figure 8-1 are influenced by the movement of the testing machine, hence overestimated and the true percentages EAB (Table 8-3) were calculated through the manual measurement of the gauge lengths, before and after, the breaking of the specimens. The breaking of sample 1 was abrupt, thus causing unexpected detachment of the recording extensometer from the specimen, thus displaying unusual shape of the plot with a trend of returning to the origin point.

Compared to the tensile elastic modulus of 2264 MPa obtained by Nsengimana *et al.* [117] for L-PBF of tensile test pieces manufactured using a commercial powder PP CP75, the new composite PP powder presented a higher average modulus of elasticity of 2587 MPa. The tensile elastic modulus was greater than the tensile moduli 1550 and 1650 MPa for HNR100 and HTV145, respectively, in pellet forms or when processed through IM. Despite a lack of practical elongation at break for both powders, the average tensile strength was slightly increased to 15.8 MPa for tensile pieces manufactured using the new composite PP powder compared to an average tensile strength of 14.6 MPa when PP CP75 powder was processed using an EOS P380 laser sintering machine.

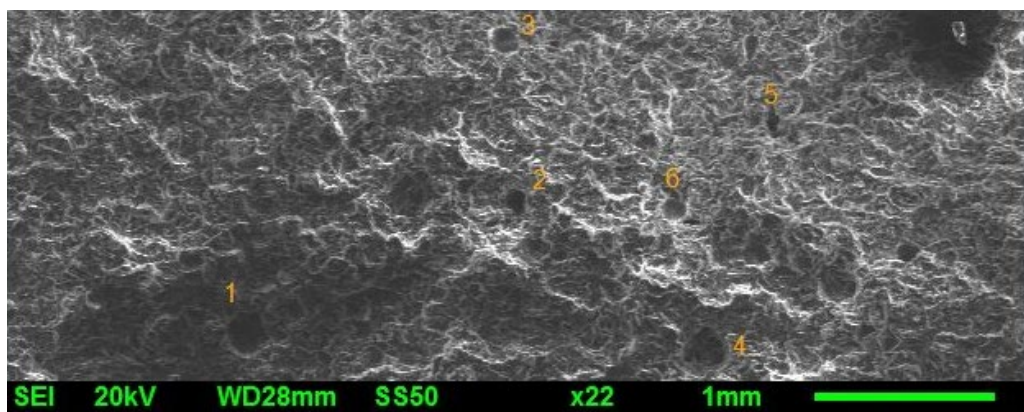
The lack of EAB was investigated by analyzing the morphologies of the fractured surfaces of the tensile test pieces using a JEOL JSM 6610 SEM machine at the UFS. The accelerating voltage was set to 20 kV. The samples were coated with carbon in a vacuum to enhance electrical conductivity before being subjected to SEM analysis. A sputter coater turbo evaporator, model Quorum Q150TE, was used to deposit a carbon film on the fractured surfaces of the tensile test specimens, which were fixed on inserts to be fitted into the SEM machine. Figure 8-2 shows the SEM images of the fractured surfaces of the tensile test specimens 1, 2, and 3, while the SEM images for fractured surfaces of specimens 4 and 5 are shown in Figure 8-3.



a. Specimen 1

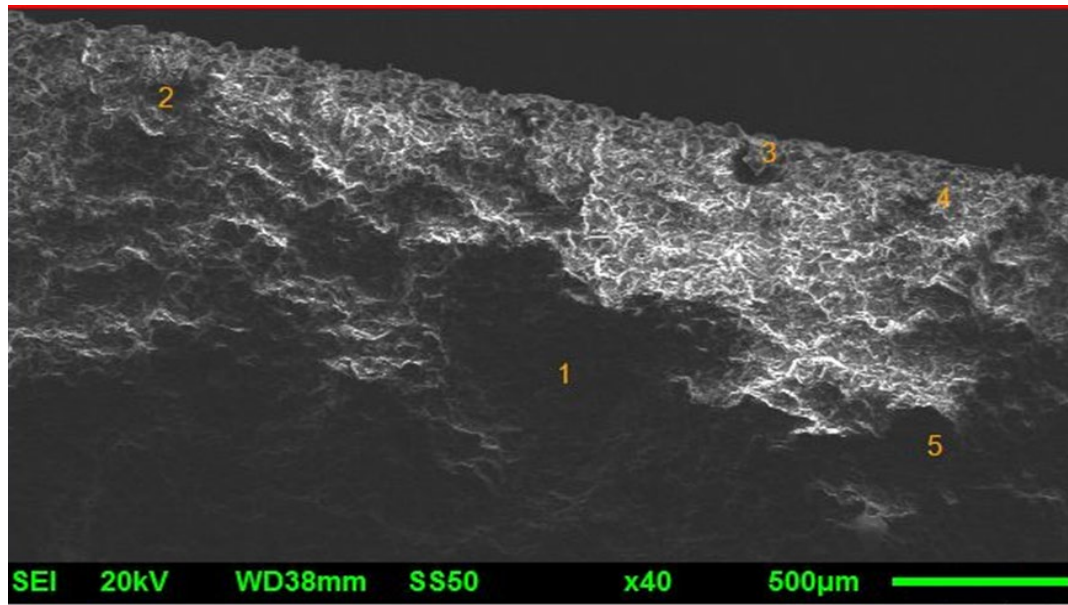


b. Specimen 2

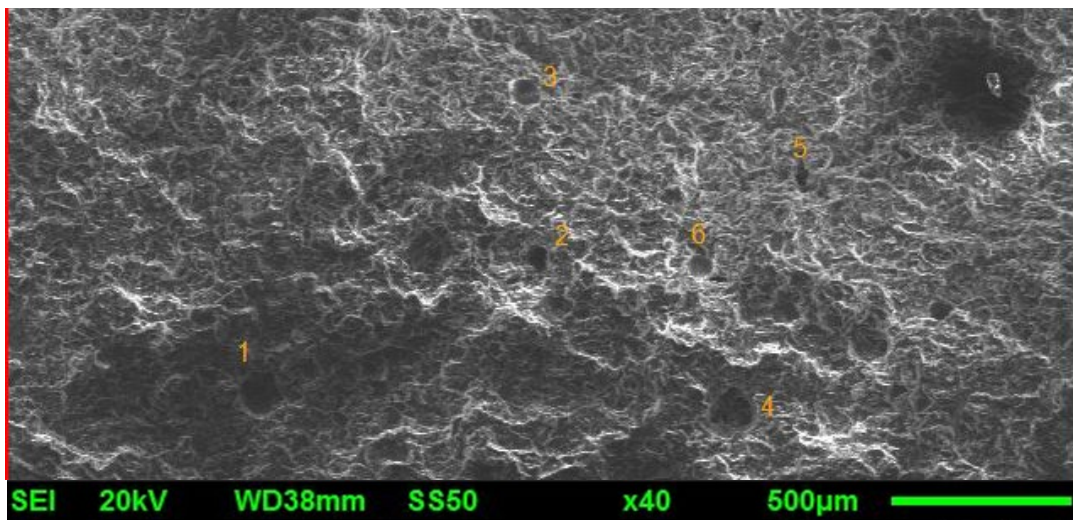


c. Specimen 3

Figure 8-2: SEM images of fractured surfaces of tensile specimens 1, 2, and 3



a. Specimen 4

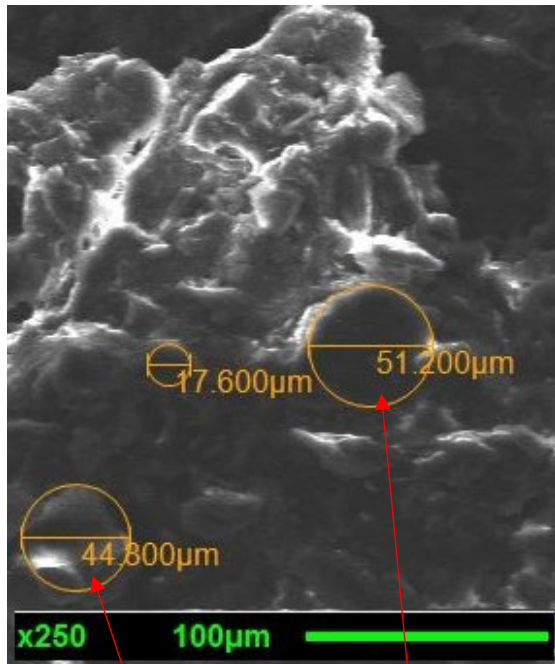


b. Specimen 5

Figure 8-3: SEM images of fractured surfaces of tensile specimens 4 and 5

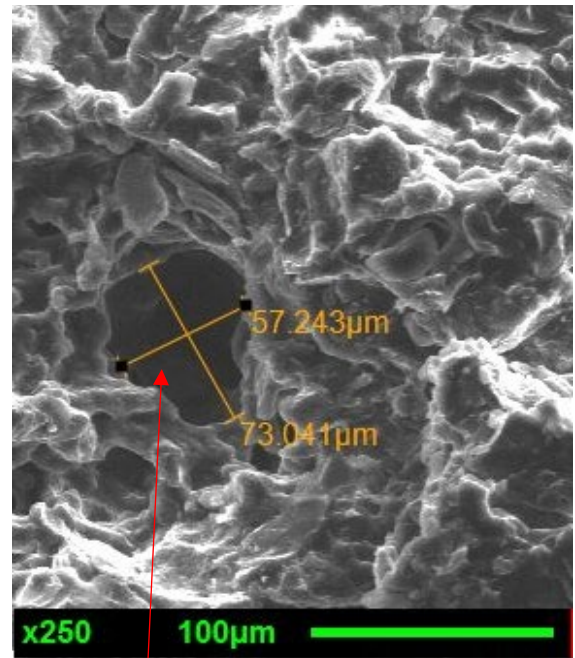
8.2.2 Observation and interpretation of results

The premature breaking of the test specimens could have been caused by the pores, insufficient melting of the powder, weak interfacial bonds between the fused PP and the talc and carbon black particles, as well as the presence of cracks perpendicular to the direction of the build orientation. These factors will be discussed next. The SEM images displayed zones with the occurrence of pores, designated with numbers 1, 2, 3, etc., on the fractured surfaces of specimens 1, 2, and 3 (Figure 8-2) and specimens 4 and 5 (Figure 8-3). The magnification of such zones could confirm the absence of big-sized pores, greater than the maximum size of the powder particles found to be around 100 μm . On the other hand, insufficient interfusion of powder particles is evident by the inclusion of unmelted spherical- and irregular-shaped particles inside the melted matrix. Pores appearing as impressions of dislodged irregular-shaped particles were identified within zone 5 of specimen 3 (Figure 8-4b).



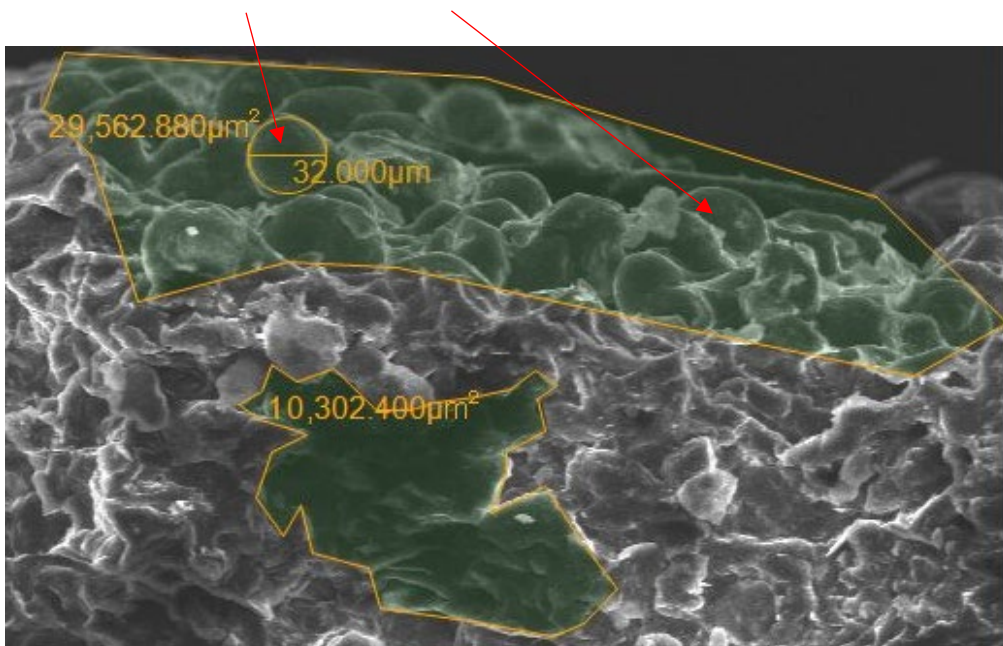
a)

Zones of inclusion of unmelted spherical particles inside the melted matrix



b)

Pore of irregular-shape as a footprint of a dislodged particle of similar irregular-shape



c)

Figure 8-4: Magnifications of zone 1 of specimen 1 (a), zone 2 of specimen 3 (b), and zone 4 of specimen 5 (c).

The SEM chemical analysis revealed the presence of zones with talc particles (Figure 8-5), which are not integrated into the polymer matrix, whereas other zones in the polymer matrix are characterized by the existence of talc with a reduced percentage of chemical content.

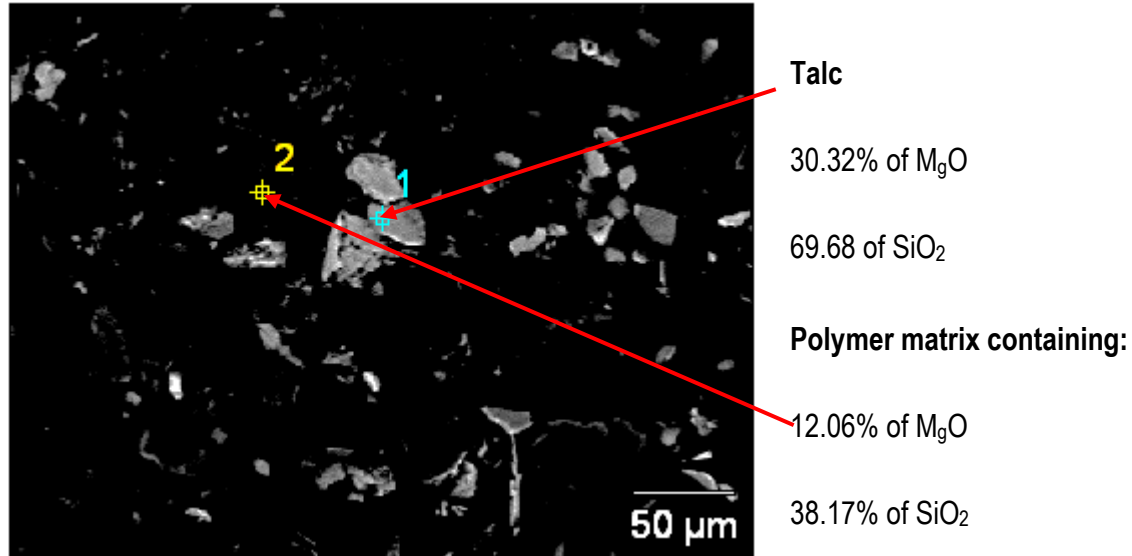


Figure 8-5: SEM chemical analysis of fractured surfaces

A non-uniform distribution of talc within the melted and consolidated PP particles will lead to a localized decrease of mechanical strength of the part in zones with 100% talc, whereas zones with embedded portions of talc will be characterized by improved mechanical properties.

The mechanical properties of the tensile test specimens produced on the Sintratec S1 machine were comparable to those of their counterparts produced using the commercial powder PP CP75 when processed on a P380 laser-sintering machine. The preheating and printing temperatures of 130 and 154 °C, respectively, were in the range of the sinterability window (from 129.22 to 160.29°C) as per DSC analysis of the new composite powder (Table 7-2). The dimensions of the tensile test specimens were close to the original CAD design, showing that minimal shrinkage occurred during L-PBF. The SEM analysis of the fractured surfaces revealed the following particularities:

1. The L-PBF of the commercial powder PP CP75 on an EOS P380 LS machine resulted in parts characterized by a generalized presence of pores [117], the diameters of which could attain as much as 0.5 mm. The absence of pores with sizes bigger than the maximum diameter size of

powder particles confirmed a good coalescence of particles of the new composite powder during its melting and the subsequent consolidation process of the built parts.

2. The filling with talc and the pigmentation with carbon black facilitated the flowability of the powder during the recoating process and increased the stiffness of the samples in localized zones. This, however, led to a lack of EAB of the tensile test specimens. Despite the presence of fillers acting as nucleating agents that could have promoted the formation of β -phase, thus leading to the increase of EAB, the L-PBF of both PP CP75 and the newly produced PP composite powders resulted in brittle specimens. This behaviour confirmed the predominance of α - over β – phase, particularly for specimens produced with the new PP composite powder where a higher Young's modulus was obtained. Additionally to the commonly present radial lamellae in both α - and β – phases, the tangential lamellae in α – phase increase the stiffness, restricting EAB and make the spherulites more rigid, thus resulting in an increase of the Young's modulus [182], [183].
3. Though the new composite PP powder was predominantly characterized by the presence of spherical-shaped particles, weak adhesion (fusion) between the polymer and the talc mineral fillers (Figure 8-4c) could have contributed to inadequate interfacial bonding with particles of spherical shape. The bonds that formed were characterized by high stiffness, thus leading to a premature breaking of the laser-sintered parts.

8.3 Dimensional and form accuracy of calibration block with small features

The dimensional accuracy of the parts obtained through the L-PBF process with the new composite powder was assessed using a printed calibration block (Figure 8-6). Seven samples of the calibration block were produced using the Sintratec S1 machine with the same process parameters as was used for the tensile test specimens and outlined in Table 8-2. A square-shaped window was designed in each of the four vertical faces of the block, and two small cubic protrusions were added to two of the faces. The four windows in the design block aimed to assess the accuracy of the downskin and upskin features on each face of the block, while the addition of the two protrusions was to evaluate the accuracy of L-PBF printing of overhanging features. Additional inscriptions in different fonts and sizes were designed to show the definition of lettering produced with L-PBF printing.

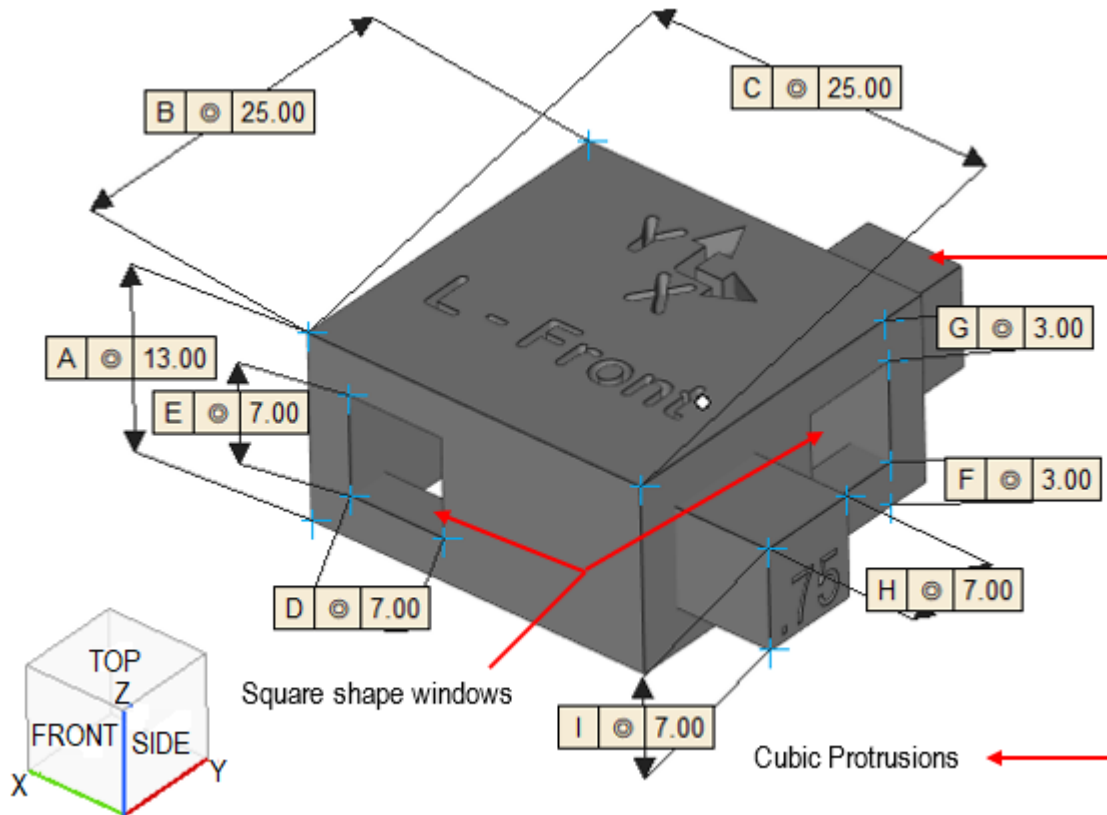


Figure 8-6: CAD of the calibration block with its features and nominal dimensions

Using an electronic Vernier calliper, model KENNEDY® KEN-331-2320K, with an accuracy of 0.01 mm, the dimensions of the following geometrical faces and features were measured:

1. The three dimensions in x-, y- and z-directions of the edges of the two cubic protrusions
2. The overall dimensions 25 mm x 25 mm x 13 mm in respective x-, y- and z-directions of the edges of the block
3. The height of 3 mm between a downskin surface and the top face of the block
4. The height of 3 mm between an upskin surface and the bottom face of the block
5. The depth and width of 7 mm x 7 mm for the four windows
6. The quality of the inscribed texts on the calibration block

The arithmetic averaged value of four randomly taken measurements for each dimension was considered as the actual measured dimension in the x-, y- or z-direction of a particular edge of a face or feature of

the sample. The deviations Δx , Δy , and Δz were calculated as the difference between the arithmetic averaged value from the measurements and the CAD dimension, as indicated in Figure 8-6.

8.3.1 Dimensional accuracy of the protrusions

The deviations from the nominal dimensions 7 mm x 7 mm x 7 mm along the x-, y- and z axes for protrusion 1 are shown in Figure 8-7.

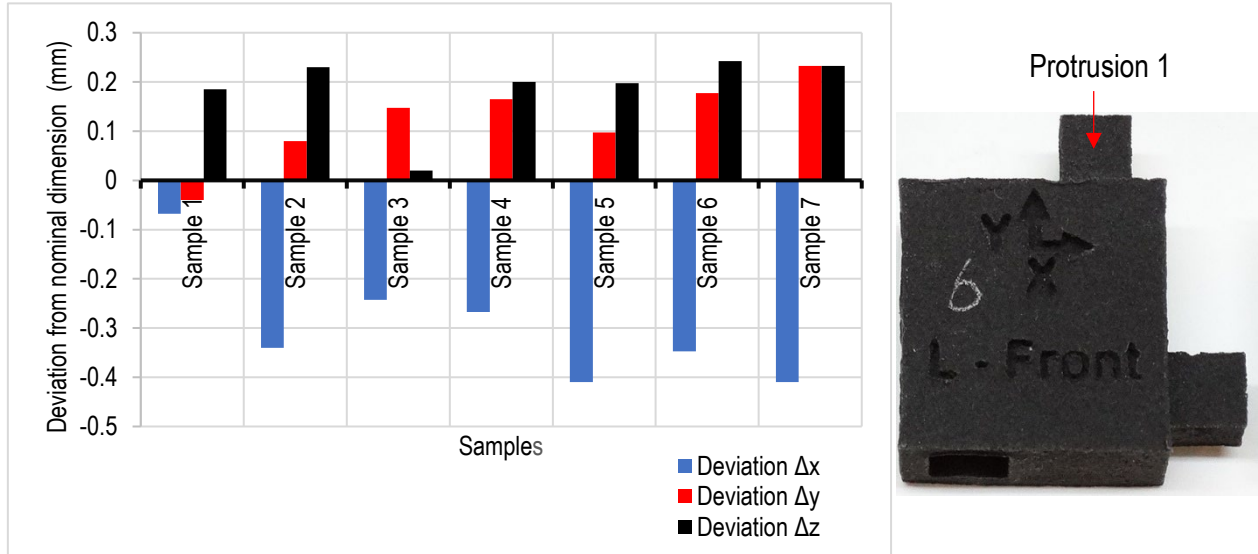


Figure 8-7: Deviations from the nominal dimensions of edges of protrusion 1

The deviations from the nominal dimensions 7 mm x 7 mm x 7 mm along the x-, y- and z axes for edges of protrusion 2 are shown in Figure 8-8.

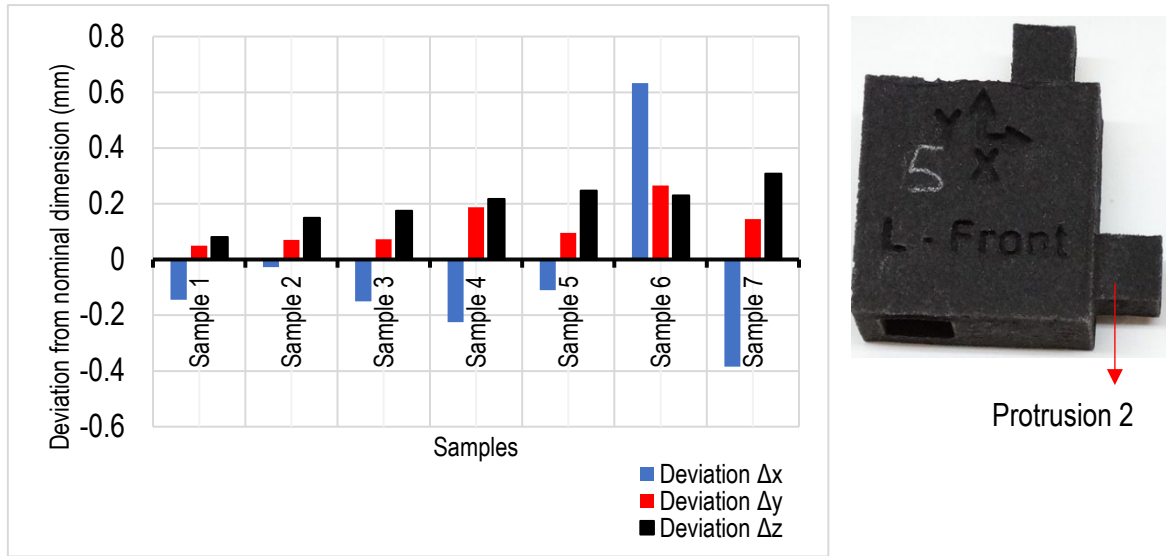


Figure 8-8: Deviations from the nominal dimensions of edges of the protrusion 2

From Figure 8-7 and Figure 8-8, except for one measurement with a positive deviation, negative deviations Δx ranging from -0.41 to -0.0675 mm were recorded, meaning the printed protrusions experienced a shrinkage in the x-direction. On the other hand, positive deviations Δy ranging from 0.05 to 0.265 mm and Δz ranging from 0.02 to 0.308 mm were obtained except for one negative deviation $\Delta y = -0.05$ mm recorded on protrusion 1 of sample 1. A combination of a decrease of dimensions in the x-direction and an increase in the y- and z-directions suggests a shrinkage in the x-direction. At the same time, the scaling factor of 1.25 could lead to enlargement in the y- and z-directions in such a way that the overall volume of the laser-sintered protrusions is conserved in the proximity of the volume of protrusion of the CAD model.

8.3.2 Dimensional accuracy of the top, front, and side faces

In a 3D square system of coordinates, the top, front, and side faces are defined as x-y, x-z, and y-z planes (Figure 8-6). The deviations from the overall nominal dimensions 25 mm x 25 mm x 13 mm of the edges of the calibration block along the x-, y-, and z-axes are shown in Figure 8-9.

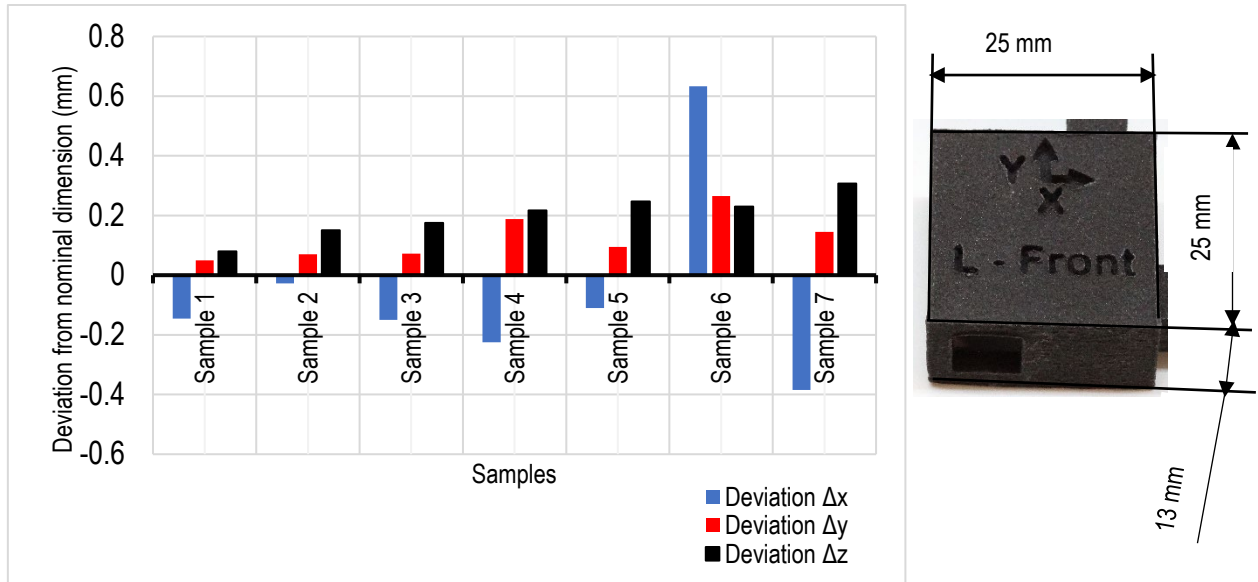


Figure 8-9: Deviations from overall nominal dimensions of edges of the top, front, and side faces of the block

With the exception of one measurement taken on sample 6, where a positive deviation $\Delta x = 0.633$ mm was recorded, negative deviations ranging from -0.385 to -0.02 mm were produced in the x-direction. Similar to deviations recorded for protrusions in the y- and z-directions, positive deviations Δy and Δz ranging from 0.08 to 0.308 mm were recorded, influencing the production of positive deviations in the y- and z-directions, implying that the scaling factor of 1.25 applied in all directions failed to avoid the shrinkage in the x-direction. The competition between negative and positive deviations testifies to the probable production of a solid part with a volume close to the CAD model. The deviations from nominal sizes of the small features, such as protrusions, also resulted from the curling of edges and corners, especially experienced by samples 1, 2, 3, 4, and 7 (Figure 8-14c).

8.3.3 Dimensional accuracy of the height associated with upskin faces

The dimensional deviations from the nominal height $h = 3$ mm of the wall between the bottom and upskin faces are shown in Figure 8-10. The deviations are designated by Δh_{u1} , Δh_{u2} , Δh_{u3} , and Δh_{u4} , respectively, and associated with the measurements taken on upskin faces related to windows 1, 2, 3, and 4.

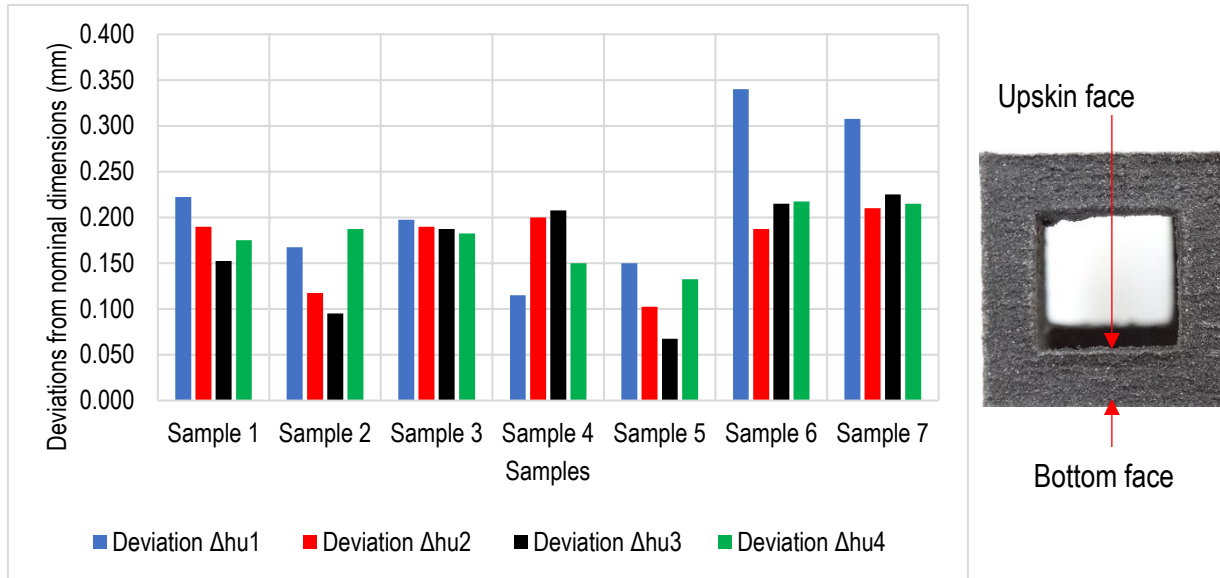


Figure 8-10: Deviations from nominal height associated with the upskin faces

The dimensional deviations from the nominal height $h = 3$ mm of the wall between the top and downskin faces are shown in Figure 8-11. The deviations are designated by Δh_{d1} , Δh_{d2} , Δh_{d3} , and Δh_{d4} , respectively, and associated with the measurements taken on downskin faces related to windows 1, 2, 3, and 4.

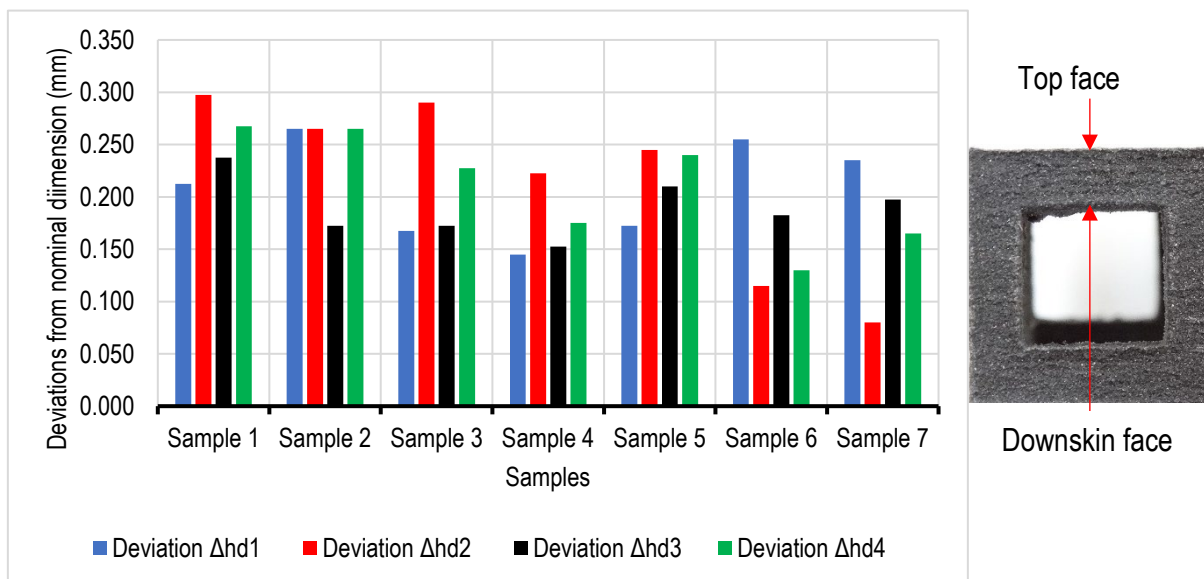


Figure 8-11: Deviations from nominal height associated with the downskin faces

From Figure 8-10 and Figure 8-11, it can be observed that dimensional deviations associated with the upskin and downskin faces are positive, implying the increase of the upper and bottom heights of the

vertical walls enclosing the windows. The lowest and highest deviations associated with the upskin face are recorded to be 0.067 and 0.340 mm, measured on windows 3 and 1 of samples 5 and 6, respectively. On the other hand, the lowest and highest deviations associated with the downskin face are found to be 0.08 and 0.298 mm, recorded on windows 2 of samples 7 and 1, respectively.

8.3.4 Dimensional accuracy of depth and width of the square-shaped window

The deviations from the nominal dimensions of the depth and width of the square-shaped windows 1, 2, 3, and 4 are shown in Figure 8-12.

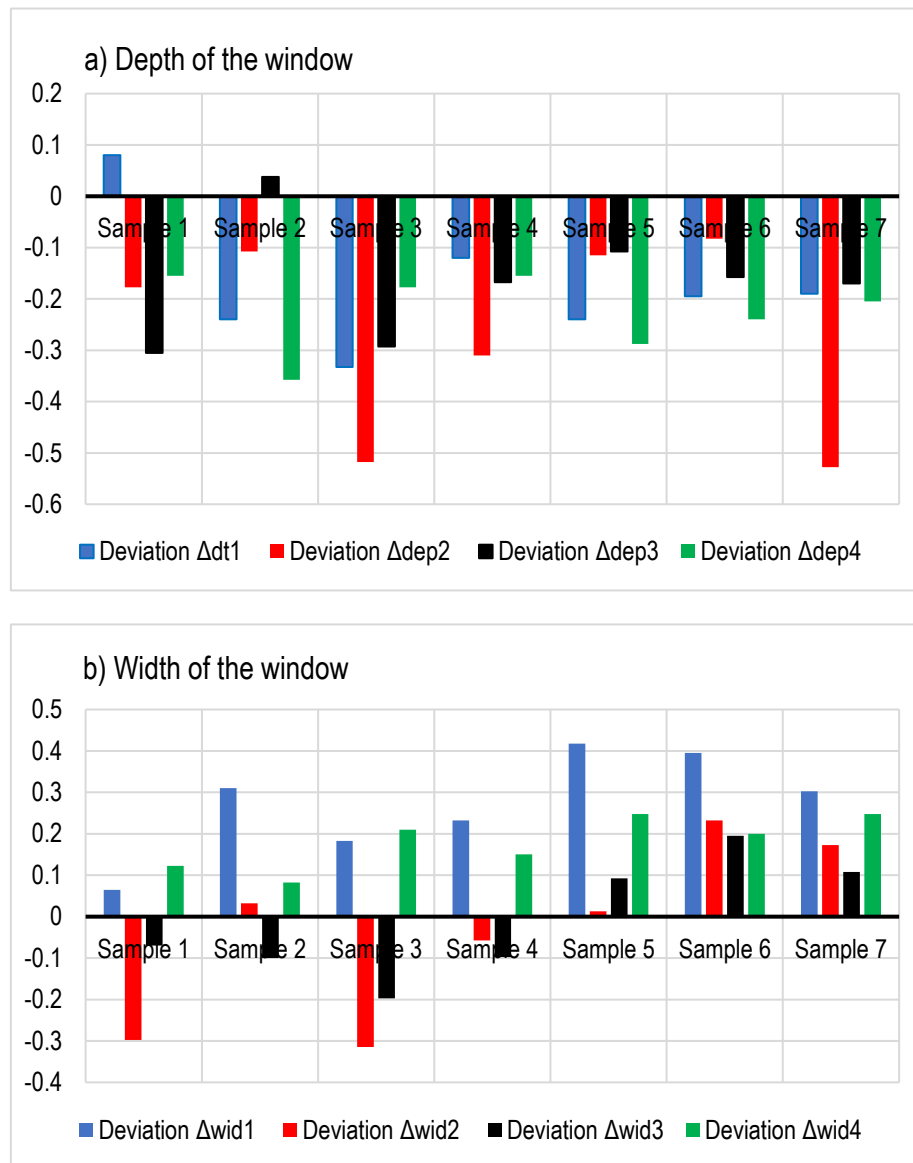


Figure 8-12: Deviations from nominal dimensions of the depth and width of the windows

The deviations associated with the depth are designated by Δdep_1 , Δdep_2 , Δdep_3 , and Δdep_4 , while the deviations associated with the width are denoted by Δwid_1 , Δwid_2 , and Δwid_3 .

Figure 8-12a shows that with the exception of two positive deviations 0.08 and 0.038 mm occurring on the depth of window 1 of sample 1 and window 3 of sample 2, respectively, negative deviations ranging from -0.528 to -0.09 mm characterize the dimensional accuracy of the depth $dep = 7$ mm. On the other hand, the predominance of positive deviations ranging from 0.01 to 0.418 mm with a share of 75% characterizes the dimensional accuracy of the width $wid = 7$ mm of the windows. A portion of 25% of the negative deviations ranging from -0.315 to -0.08 mm occurred on samples 1, 2, 3, and 4 within windows 2 and 3 (Figure 8-12b). The increase in the height of the walls associated with the upskin and downskin faces resulted in a decrease in the depth of the windows. The scaling factor was applied to counterbalance the shrinkage, which is the main drawback in L-PBF using PP powder as a feedstock material. The positive scaling factor allowed to overcome the shrinkage of the solid walls in the z-vertical direction, causing the decrease in the depth of the associated window. Depending on the functional dimension of the part, the manufacturer can optimally select the applicable tolerances to ensure that the accumulation of tolerance occurs on non-functional dimensions in a chain of dimensions. The heights h_u and h_d of both upskin and downskin walls, the depth dep of the window, and the overall height h of the calibration block form a chain of dimensions (Figure 8-13) where the depth of the window can be a closing dimension.

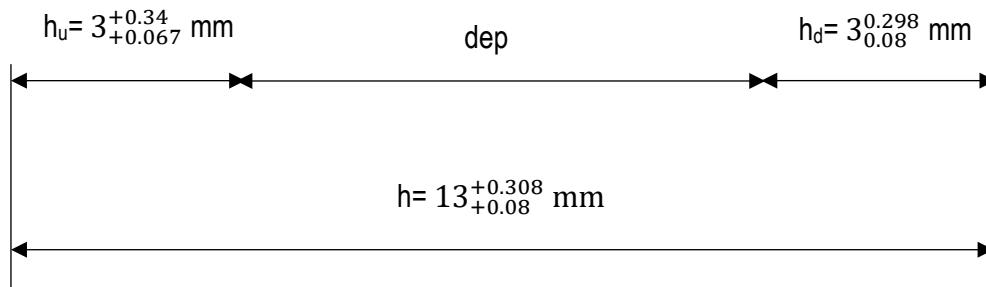


Figure 8-13: Chain of dimensions in the vertical direction of the calibration block

With such a consideration, the expected deviations or tolerances on the depth of the enclosed window can be calculated as follows:

$$dep_{\max} = h_{\max} - h_{u(\min)} - h_{d(\min)} = 13.308 - 3.067 - 3.08 = 7.161 \text{ mm}$$

$$\text{dep}_{\min} = h_{\min} - h_{u(\max)} - h_{d(\max)} = 13.08 - 3.34 - 3.298 = 6.442 \text{ mm}$$

$$\text{Lower limit} = \text{dep}_{\min} - \text{dep}_{\text{nom}} = 6.442 - 7 = -0.558 \text{ mm}$$

$$\text{Upper limit} = \text{dep}_{\max} - \text{dep}_{\text{nom}} = 7.161 - 7 = +0.161 \text{ mm}$$

The final dimension of the depth with its associated tolerances can be written as follows:

$$\text{dep} = 7^{+0.161}_{-0.558} \text{ mm}$$

The deviations obtained range from -0.558 to +0.161 mm on the closing dimension, which agrees with the trend of deviations recorded through independent measurements of the depth of the window (Figure 8-12). The predominance of negative deviations is validated by the calculation of tolerances of the closing link in a chain of dimensions. It can be concluded that the applied positive scaling affected the solid (shaft) features, such as walls, while negative tolerances can be planned on the hole features, such as the enclosing windows. Table 8-4 summarizes the dimensional deviations achieved and the corresponding tolerance grades (TG) as referenced to BS ISO 20457: 2018 standard [184] on tolerances and accepted conditions for plastic moulded parts.

Table 8-4: Summary of tolerance grades obtained

Features	Nominal dimensions	Deviation Δx		Deviation Δy		Deviation Δz	
		Lowest limit	Highest limit	Lowest limit	Highest limit	Lowest limit	Highest limit
Size of the protrusions in the x-, y- and z- directions	7 mm x 7 mm x 7 mm	-0,41	0,0675	0,05	0,265	0,02	0,308
		TG8	TG4	TG3	TG5	TG1	TG8
Overall size of the block in the x-, y- and z- directions	25 mm x 25 mm x 13 mm	-0,385	-0,02	0,05	0,265	0,08	0,308
		TG7	TG1	TG2	TG6	TG4	TG7
Upskin height	3 mm					0,067	0,34
						TG6	TG9
Downskin height	3 mm					0,08	0,298
						TG6	TG9
Depth of the window	7 mm					-0,528	-0,09
						TG8	TG4
Width of the window	7 mm	-0,315	0,418				
		TG8	TG8				

The deviations obtained are comparable to the dimensional tolerances recommended for plastic IM. However, a wide range coverage of tolerance grades from TG1 to TG8 indicates a high anisotropy generated by the effect of the positive scaling factor during the LS process and later caused by localized shrinkage mainly due to non-uniform distribution of the temperature and cooling rate during solidification of the parts.

8.3.5 Quality of inscribed texts, edges, and corners

FFF is one of the strong points of L-PBF, where small complex geometrical shapes such as texts can be designed with the CAD model and simultaneously inscribed on the component surfaces during building. The following texts (Figure 8-14) were used to assess the quality of embedded inscriptions visually:

1. On the side face (y-z plane) (Figure 8-14a), the text “**1 mm**” was designed with a regular font in a Century Gothic style with a height (size) of 3.5 mm and penetrating to a depth of 1.5 mm,
2. On the side face (y-z plane) of protrusion 2 (Figure 8-14b), the text “. **75**” was designed with a narrow font in an Arial rounded MT style with a height of 3.5 mm and penetrating to a depth of 1.5 mm and,
3. On the top face of the block (Figure 8-14c), texts “**L-Front**”, “**X**”, “**Y**” and **arrows** in x- and y- directions were inscribed with a narrow font in an Arial rounded MT style with a height of 10 mm and penetrating to a depth of 1.5 mm.

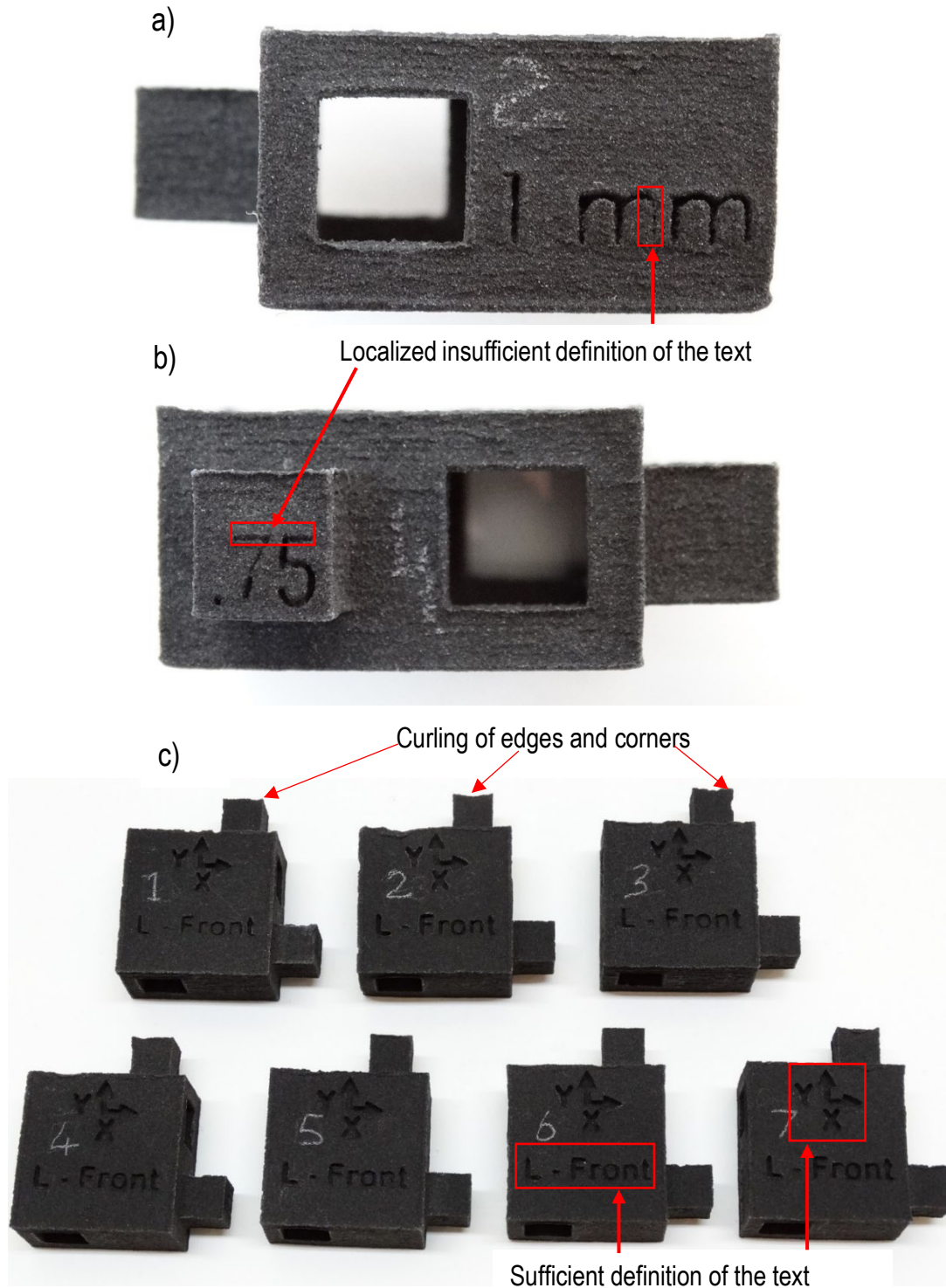


Figure 8-14: Quality of inscribed texts, edges, and corners

L-PBF with the new composite PP powder produced legible texts with sufficient definition comparable to the quality of inscribed texts when a commercial powder PP CP75 was used by Nsengimana *et al.* [117].

Insignificant localized definition was observed on the texts “1 mm” and “. 75” (Figure 8-14a & b), which was propagated to all seven laser-sintered samples. The far-right vertical groove of the first letter “m” appeared to lose resolution as if it were a result of the CAD model design. Considering the close proximity to the adjacent far-left vertical line of the second letter “m”, the shrinkage effect on hole features within a chain of dimensions may be the cause of such a localized decrease in the width of the narrow groove. On the other hand, the reduced resolution on the upper portions of “7” and “5” in contrast to the lower part may be caused by the nature of lettering in the computer system where all parts of one letter, figure number, or a symbol may not have precisely equal thickness. The horizontal lines of the upper portions of “7” and “5” were also affected by the interdependence formation of upskin-downskin faces, where the upskin face is covered by the powder, which supports the building of the downskin face. The presence of the powder in such a narrow slot could have negatively affected the resolution of horizontal lines associated with such faces. The increase in size from 3.5 to 10 mm of the inscribed texts and symbols improved the well-defined resolution on the top surface of all seven laser-sintered blocks (Figure 8-14c).

The thermal inhomogeneity, where high and low temperatures can be respectively recorded at the centre, and at the proximity of the outer walls of the build chamber, is the cause of curling and warpage of small features in L-PBF [185], [186], [187], [188]. Prominent curling of edges and corners of the protrusions was observed on calibration block samples 1, 2, 3, and 4 (Figure 8-14c). The use of an LS machine with advanced temperature control systems would minimize the thermal gradient across the build chamber and each part.

8.4 Surface roughness of tensile test specimens and features of the calibration blocks

The failure of a component can be initiated by a crack caused by a poor surface finish, which can result in the reduced fatigue lifetime of a functional part. High surface roughness increases the friction between moving parts and can promote the build-up of contaminants and other unwanted organisms on the surfaces of devices specially fabricated for food and medical applications. A component with a smooth surface finish is aesthetically pleasing, and cost can be reduced as little extra post-processing is required where specific functional requirements must be met. The surface roughness of the five laser-sintered tensile specimens and seven calibration blocks were measured using a Mitutoyo SURFTEST SJ-210 surface roughness measuring tester. The SURFTEST SJ-210 is a portable surface roughness measuring instrument that traces the surfaces of a part, calculates the parameter value of their surface roughness

based on roughness standards, and displays the results on a Liquid Crystal Display (LCD) screen [189]. The apparatus was connected to a computer through a USB cable, which displays the results in a graph representing the profile of the surface finish irregularities (Figure 8-15).

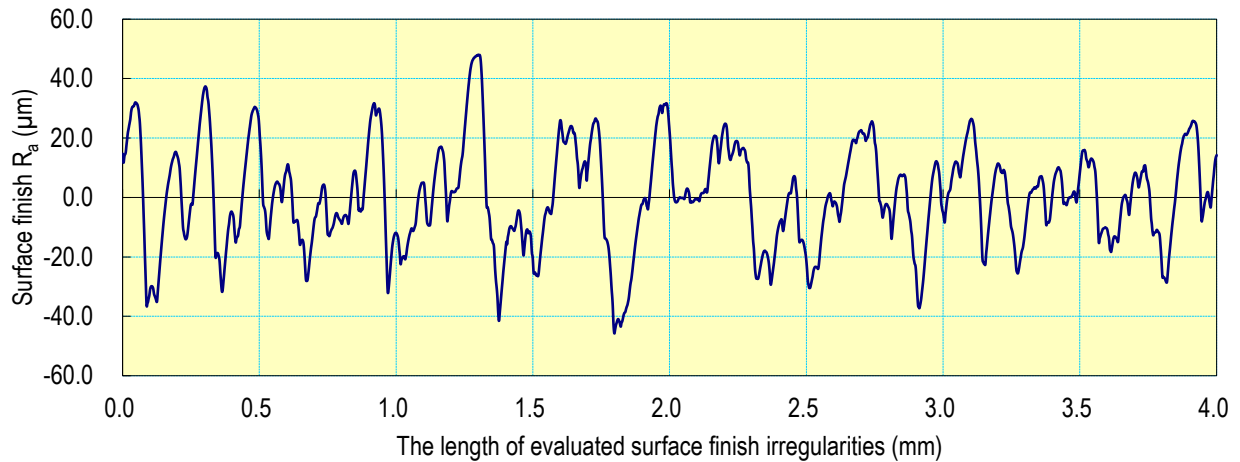


Figure 8-15: Typical surface finish profile generated by SURFTEST SJ-210

Figure 8-15 shows the trace (profile) irregularities recorded on the top horizontal surface (x-y plane) of tensile test specimen 1. The surface roughness detector stylus travelled 4 mm, and the final evaluated surface roughness was measured to be $R_a = 13.770 \mu\text{m}$.

8.4.1 Surface roughness of tensile test specimens

The surface roughness measurements were taken in three positions (Figure 8-16) on the top surface (x-y plane) of each tensile test specimen, and the calculated arithmetic average was considered as the surface roughness of the specimen.

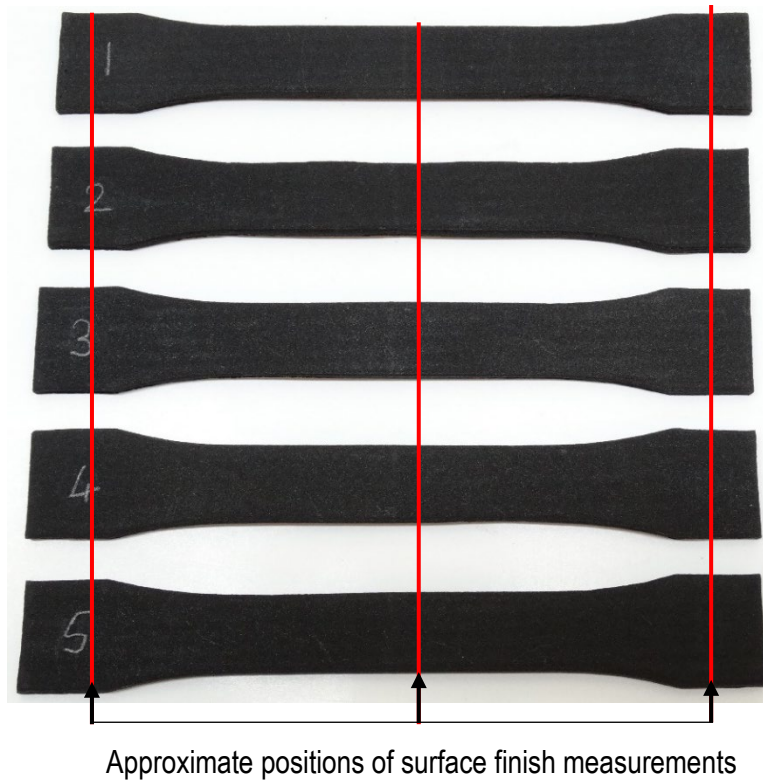


Figure 8-16: Surface roughness measurement of the tensile test specimens

The histogram of the surface roughness for the tensile test specimens is shown in Figure 8-17.

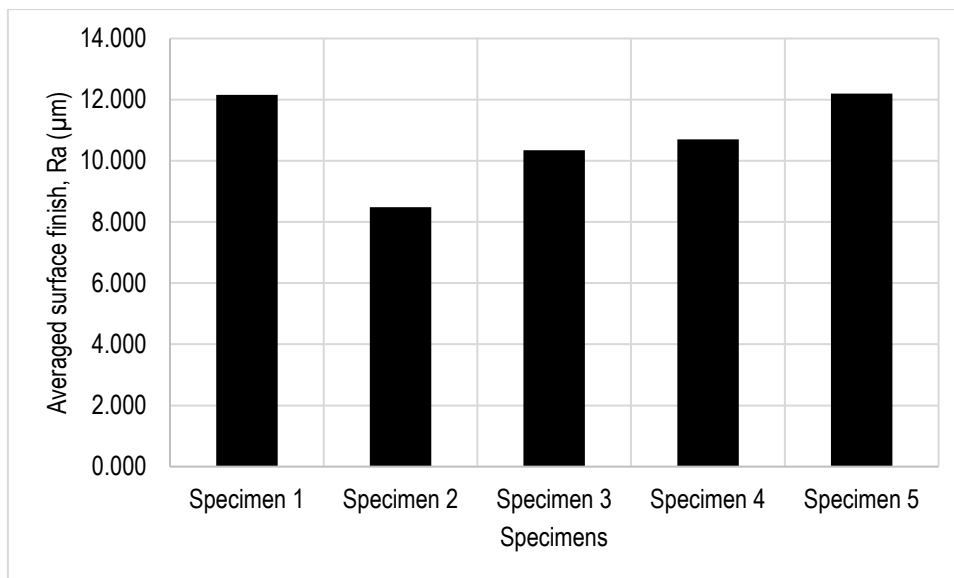


Figure 8-17: Surface roughness of top horizontal face (x-y plane) of the tensile test specimens

The overall average surface roughness of the horizontal faces of the tensile test specimens was $R_a = 10.78 \mu\text{m}$ with a standard deviation of $1.66 \mu\text{m}$. Using the new composite PP powder, the surface roughness of the laser-sintered tensile test specimens was lower than the surface finish $R_a = 12 \mu\text{m}$ of the commercial powder PP CP75 sintered on an EOS P380 LS machine with an optimized scanning speed of 1481 mm/s [117].

8.4.2 Surface roughness of the features of the calibration blocks

The surface roughness was measured for the seven samples on the following features:

1. Horizontal face of the protrusions
2. Top and side faces of the calibration blocks
3. Upskin and downskin faces of the four windows.

For each sample, three surface roughness measurements were taken on the horizontal faces of the protrusions and the top face of the calibration blocks, and the arithmetic average was considered as the surface roughness of the feature. For the upskin and downskin faces, three measurements were recorded on each of the four windows of the calibration block, and finally, the arithmetic average was used to assess the surface roughness of the upskin or downskin surfaces.

Figure 8-18 shows a comparative evaluation of the surface roughness on the assessed features.

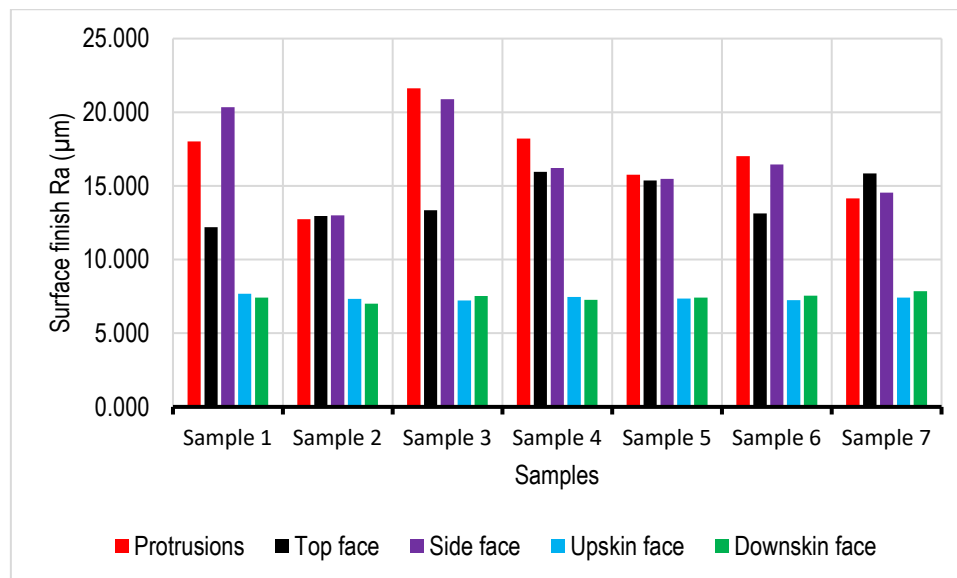


Figure 8-18: Surface roughness of features of the calibration blocks

The average surface roughness R_a for the protrusions, top face, side face, upskin, and downskin surfaces were 16.788, 14.114, 16.7, 7.386, and 7.438 μm , respectively. On the other hand, the surface roughness on the side face was high, ranging from 13 to 20.88 μm . Side faces exhibit the borders of the layer and are prone to generate high surface roughness due to the stair step effect, especially on inclined surfaces. A relatively high level of surface roughness ranging from 12.730 to 21.621 μm was measured on the horizontal protrusion surfaces. Overhang structures such as protrusions are sensitive to thermal defects caused by over-melting and residual heat build-up in powder-dense areas. This leads to the formation of dross, which negatively affects the smoothness of the associated surface [190], thus explaining the predominance of roughness on faces associated with the protrusions. As both upskin and downskin faces were horizontally oriented, there was no significant difference between the surface roughness average of 7.386 and 7.438 μm for upskin and downskin faces, respectively. In cases where the face of the part is inclined from the horizontal direction, high surface roughness occurs on downfacing surfaces as large melt pools are formed with more attached half-melted powder particles, thus leading to the slowing of local heat transfer to the surrounding powder bed [191].

Conclusion

The dimensional accuracy and surface roughness obtained through L-PBF of the new composite PP powder were assessed and found to be satisfactory as they are comparable to those obtained using traditional commercial counterpart polymeric powders such as Nylon 12, Alumide®, and PP CP75. Detailed findings are summarized as follows:

1. The dimensional accuracy of protrusions was characterized by negative deviations in the x-direction, while positive deviations were recorded in y- and z-directions. Similar trends were also observed on the overall dimensions of the calibration block.
2. Positive deviations were characteristic for both heights of walls associated with upskin and downskin surfaces at the expense of negative deviations associated with the depth of the enclosed window. A chain of dimensions is formed where the depth of the enclosed window takes the role of the closing link with an accumulation of dimensional tolerances.
3. The dimensional deviations were comparable to the recommended ISO tolerance grades for IM plastics. However, the dimensional deviations for features of the calibration blocks covered a wide range of tolerance grades (from TG2 to TG8), indicating the underlying difficulties in harmonizing the tolerance system across all features of complex components.

4. Inscribed texts with the smallest size of 3.5 mm were produced with good legible definition, thus indicating that the newly produced composite PP powder has the capability to be laser sintered to build miniature features with satisfactory definition.
5. Noticeable curling of edges and corners of protrusions was found in most of the laser-sintered calibration blocks, thus requiring advanced temperature control systems to minimize such dimensional and form deviations.
6. The averaged surface roughness for the top faces of both the tensile test specimens and calibration blocks were $R_a = 10.78$ and $14.114 \mu\text{m}$, respectively. These values were comparable to the surface roughness of 12 and $15 \mu\text{m}$ recorded on horizontal surfaces produced using commercial powders Nylon 12 and Alumide®, respectively, and close to $R_a = 12.9 \mu\text{m}$ obtained for L-PBF of PP CP75 powder.
7. The average highest surface roughness of $16.8 \mu\text{m}$ was measured on side and protrusion faces, while the lowest surface roughness of $7.4 \mu\text{m}$ was recorded on upskin and downskin faces.
8. Compared to the tensile elastic modulus of 2264 MPa obtained for L-PBF of tensile test pieces manufactured using a commercial powder PP CP75, the new composite PP powder presented a higher average modulus of elasticity of 2587 MPa. The tensile elastic modulus was greater than the tensile moduli 1550 and 1650 MPa for HNR100 and HTV145, respectively, in pellet forms or when processed through IM.
9. Despite a lack of practical elongation at break for both powders, the average tensile strength was slightly increased to 15.8 MPa for tensile pieces manufactured using the new composite PP powder compared to an average tensile strength of 14.6 MPa when PP CP75 powder was processed using an EOS P380 laser sintering machine.

CHAPTER 9: GENERAL CONCLUSIONS AND FUTURE WORK

9.1 General conclusions

The aim of the study was to produce powder suitable for L-PBF from locally produced PP, from which parts can be produced comparable to commercial PP powder in terms of mechanical properties and dimensional accuracy but at a reduced cost.

To achieve this aim, four objectives were set. The first objective was to acquire commercially available PP powder for L-PBF and to print parts to be used as the benchmark against which the newly developed PP powder and process could be compared. Secondly, a process had to be developed to reduce the PP pellets supplied by Sasol Limited to powder and determine the cost of producing the powder. As a third objective, the newly produced composite powder had to be characterized in terms of intrinsic and extrinsic properties. Finally, as a fourth objective, process parameters had to be developed for printing the powder on an L-PBF machine. Mechanical testing, as well as dimensional accuracy, and the surface finish assessment of parts produced using the newly produced powder had to be performed and compared to what was achievable using commercially available PP powder.

To meet objective 1, a batch of PP CP75 powder was acquired from Diamond Plastics GmbH and sent to Sasol Limited for FTIR, HPLC, and DSC analyses. Process parameters for processing the powder on an EOS P380 L-PBF machine were also determined, and test specimens were produced to determine mechanical properties, dimensional accuracy, and surface finish of the specimens.

Objective 2 was addressed by acquiring the necessary equipment for producing PP powder using the LLPS technique. A combination of two grades, namely HNR100 and HTV145 isotactic PP from Sasol Limited dissolved in m-Xylene at elevated temperature and with talc and carbon black added, was found to produce powder particles with the correct size and morphology suitable for L-PBF. A cost analysis was performed to determine the cost to produce the new composite powder compared to the commercially available powder. The analysis showed that the new composite powder can be produced at a cost 6.86 times cheaper than the cost of the PP CP75 imported commercial powder.

For Objective 3, the newly produced PP powder and the commercial PP CP75 powder were characterized through DSC, SEM, XRD, and FTIR analyses at UFS. The DSC analysis showed that the

newly produced powder was characterized by a degree of crystallinity of 37.3% with a wide window of sinterability of 31.1°C.

The SEM analysis showed that the newly produced powder was characterized by particles with smooth spherical shapes as opposed to rough, irregular shapes, which were predominant for particles of the commercial powder PP CP75.

The XRD analysis applied on the newly produced PP composite powder displayed a spectrum of sharp peaks with a full width half maximum angle $2\theta = 2.5^\circ$, thus revealing a crystallographic structure characterized by the predominance of α -phase.

The FTIR analysis revealed the conservation of chemical compositions and functional groups through the transformation steps from pellet to powder, which is suitable for the L-PBF process. The dissolution of the pellets into m-Xylene, followed by the precipitation, drying, and mechanical breaking of agglomerates, had no effect in modifying functional groups and chemical bonds of the raw used HNR100 and HTV145 PP grades in pellet form.

The newly produced PP composite powder was characterized through flowability tests at the CSIR in both static and dynamic regimes. The static test indicated a transitional flowability close to the free-flowing powder required for L-PBF. The stability index indicated that the particle size distribution of the powder would not be affected by multiple reuses during the L-PBF process. Results from these tests performed under Objective 3 showed that the newly developed composite powder is well suited to the L-PBF process.

To meet Objective 4, process parameters were developed for successfully printing the newly developed composite powder on a Sintratec S1 L-PBF machine. The mechanical properties of the tensile test pieces produced showed results comparable to what could be achieved with PP CP75 powder. Similarly, dimensional accuracy and surface roughness measurements showed comparable results.

Considering the above, it can be concluded that it is worthwhile and profitable to promote the production of PP powder using locally produced PP pellets. Not only could powder suitable for L-PBF be produced that delivers parts similar to commercially available powder but at a much-reduced cost. The aim of the study was therefore achieved.

9.2 Future work

The current study made a contribution to technological-scientific knowledge in the field of Polymer AM, specifically for L-PBF process through innovation of a technological process to produce new PP powder using locally sourced PP pellets. The powder was characterized and found suitable for L-PBF process. Tensile test specimens together with calibration blocks were laser sintered on Sintratec machine. The tensile test subjected to produced test specimens could give satisfactory results. The produced parts were characterized by satisfactory surface finish and dimensional accuracy measurements as compared to ones for counterparts produced using a benchmarking commercial powder PP CP75. A simplified calculation of the production cost for the new PP powder was found to be 6.86 times cheaper than the cost for imported PP CP75 powder for L-PBF process. For future development of this innovation, the following directions are recommended for future work:

1. Crystallization and nucleation leading to the formation of spherulites in semi-crystalline iPP is a complex phenomenon influenced by multiple variables such as heating and cooling rates, applied pressure, stirring speed, number, weight ratio, and respective MFR of phases. Future work should investigate the effect and interrelationship among the most influencing variables on the formation of powder particles suitable for L-PBF when PP grades HNR100 and HTV145 are processed separately or combined as a homogeneous mixture. The future work should be extended to other PP grades for homopolymer and copolymer categories produced by Sasol Limited.
2. Future work should consider the addition of compatibilizers to the blend HNR100 + HTV145 + talc for possible improvement of interfacial adhesion between talc and polymer phases.
3. Optimization of process parameters in the x-, y- and z-build directions for L-PBF of the newly produced PP composite powder should be considered in future research work for possible improvement of mechanical properties, form and dimensional accuracy, and surface finish of the laser-sintered parts.
4. The effect of carbon black on the thermal conductivity of the newly produced PP composite powder during L-PBF should be investigated to determine the extent to which such an effect could influence the modification of chamber settings, preheating, and printing temperatures.
5. The recyclability of the newly produced PP composite powder should be investigated to establish the level of degradation when the powder is re-used for multiple cycles.

6. The current study was limited to producing a small quantity of PP powder for laboratory experimental purposes. The feasibility of mass production, followed by the commercialization of the powder for industrial purposes, should be the focus of future work. The simplified cost calculation to produce 1 kg of the new PP composite powder indicated that expenditure on m-Xylene was 83% of the total cost. Future work should consider the collection and condensation of evaporated m-Xylene to be re-used for new production batches.

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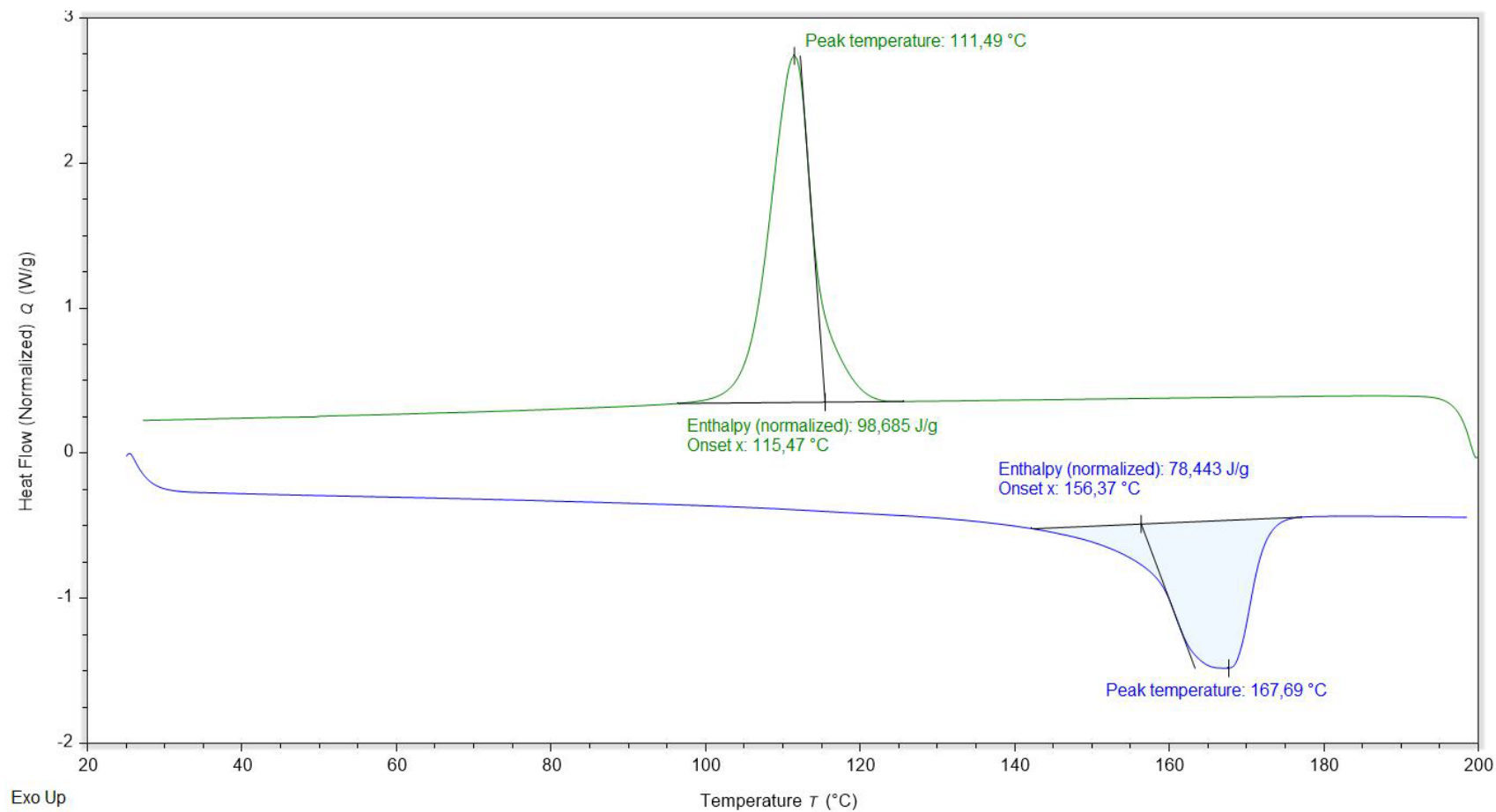
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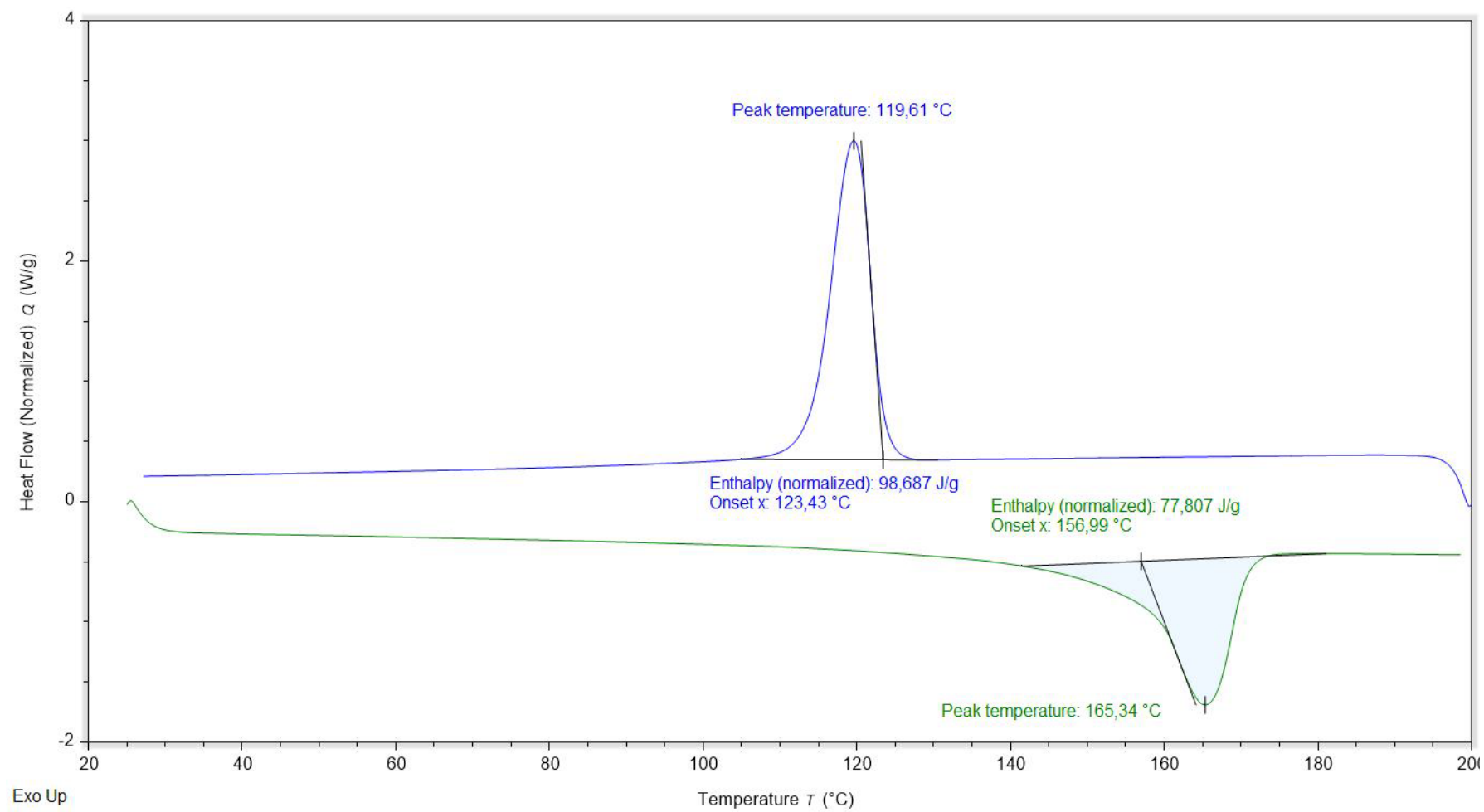
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APPENDIX: DSC OF PP GRADES AND COMBINATIONS IN PELLET AND POWDER FORMS

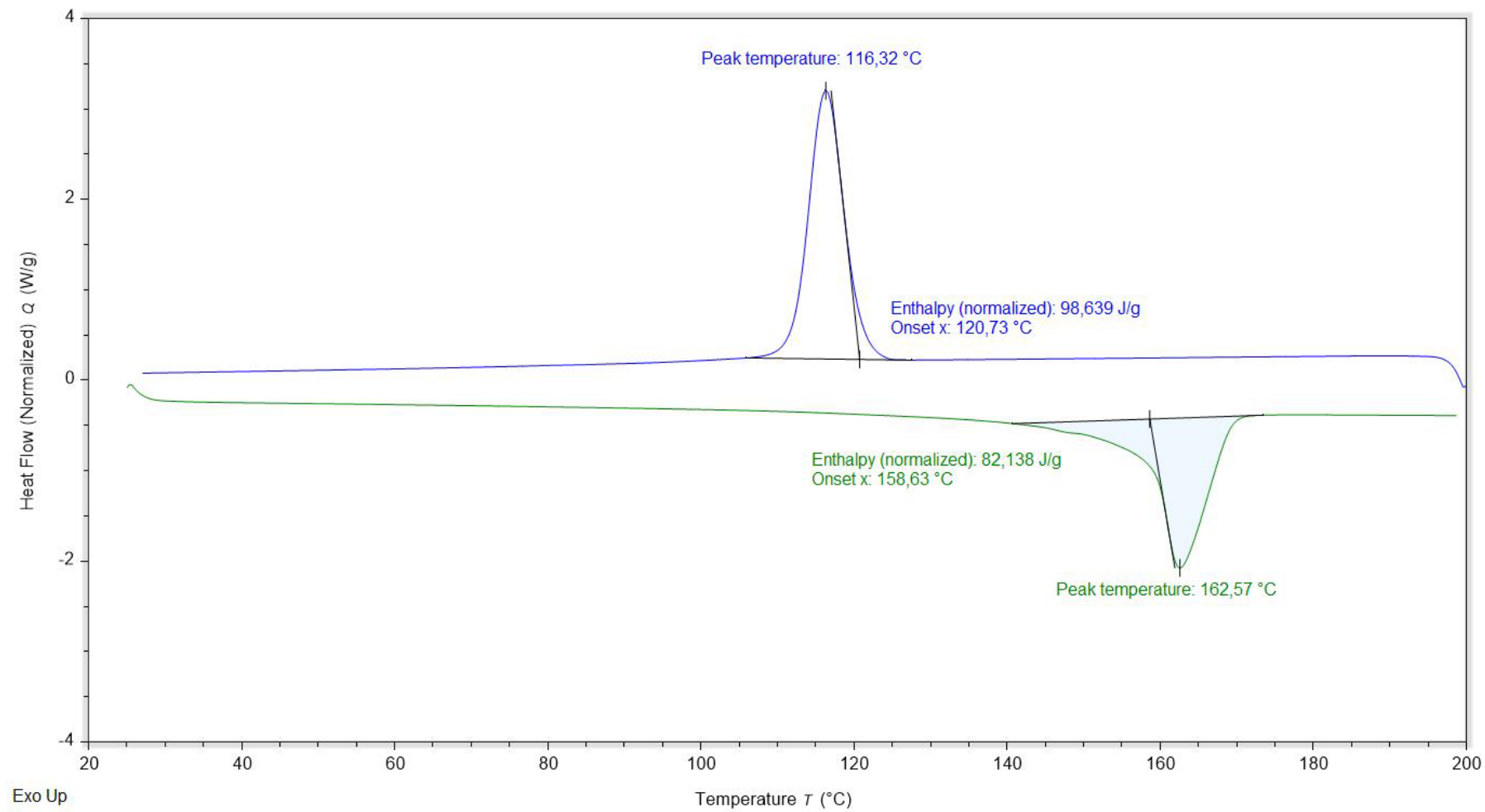
HNR100 in pellet form



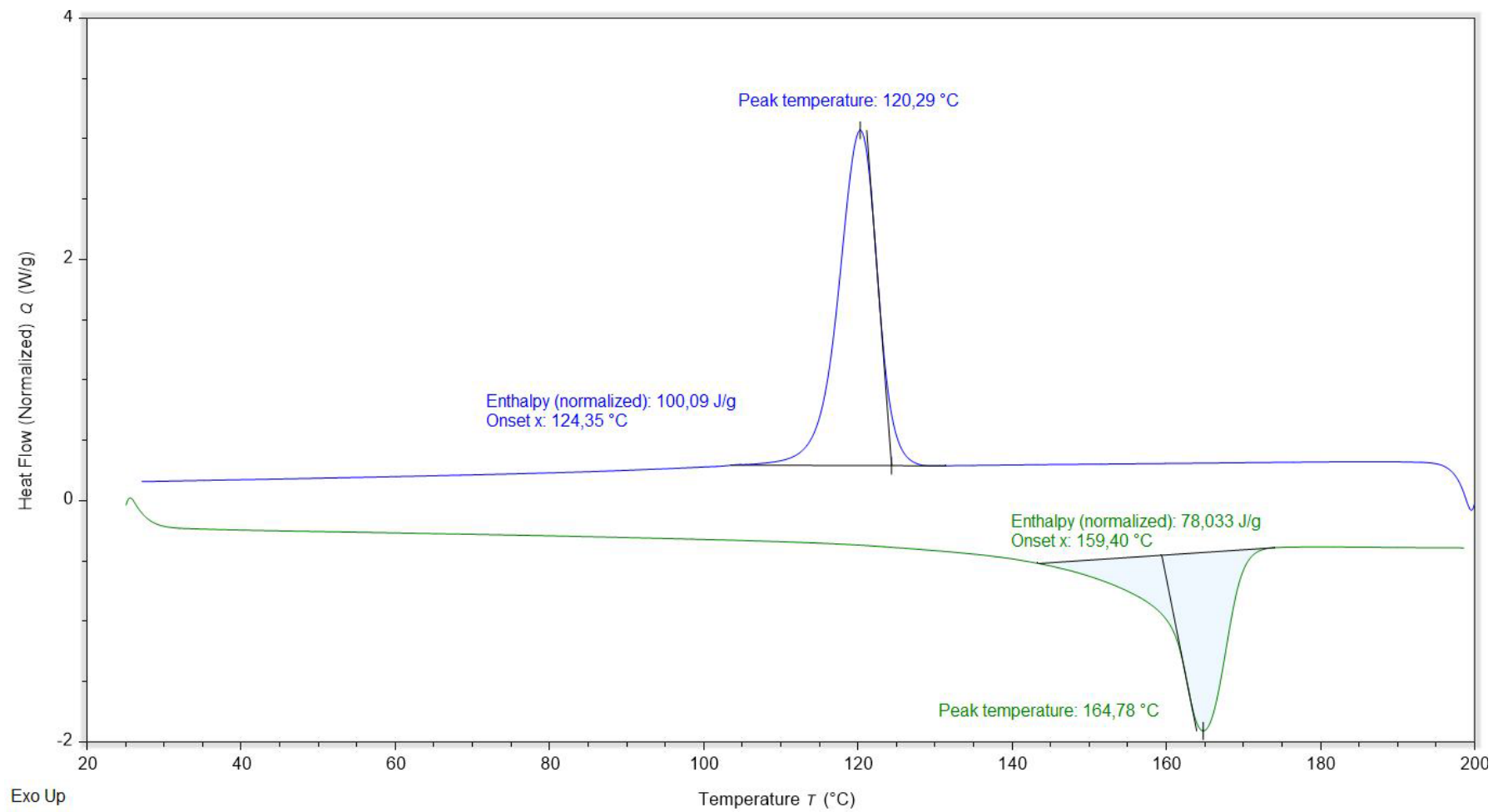
HTV145 in pellet form



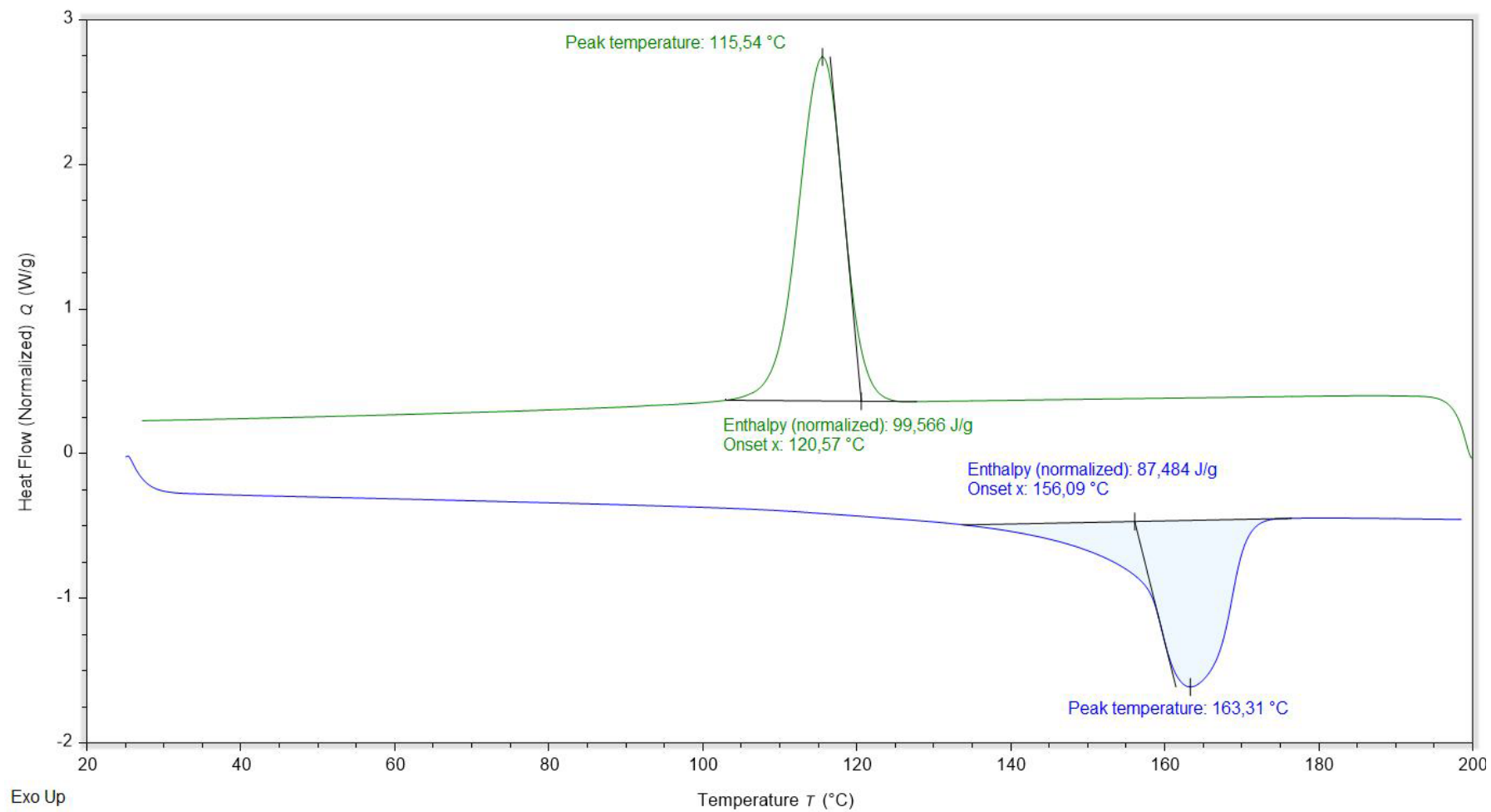
HNR100 in powder form



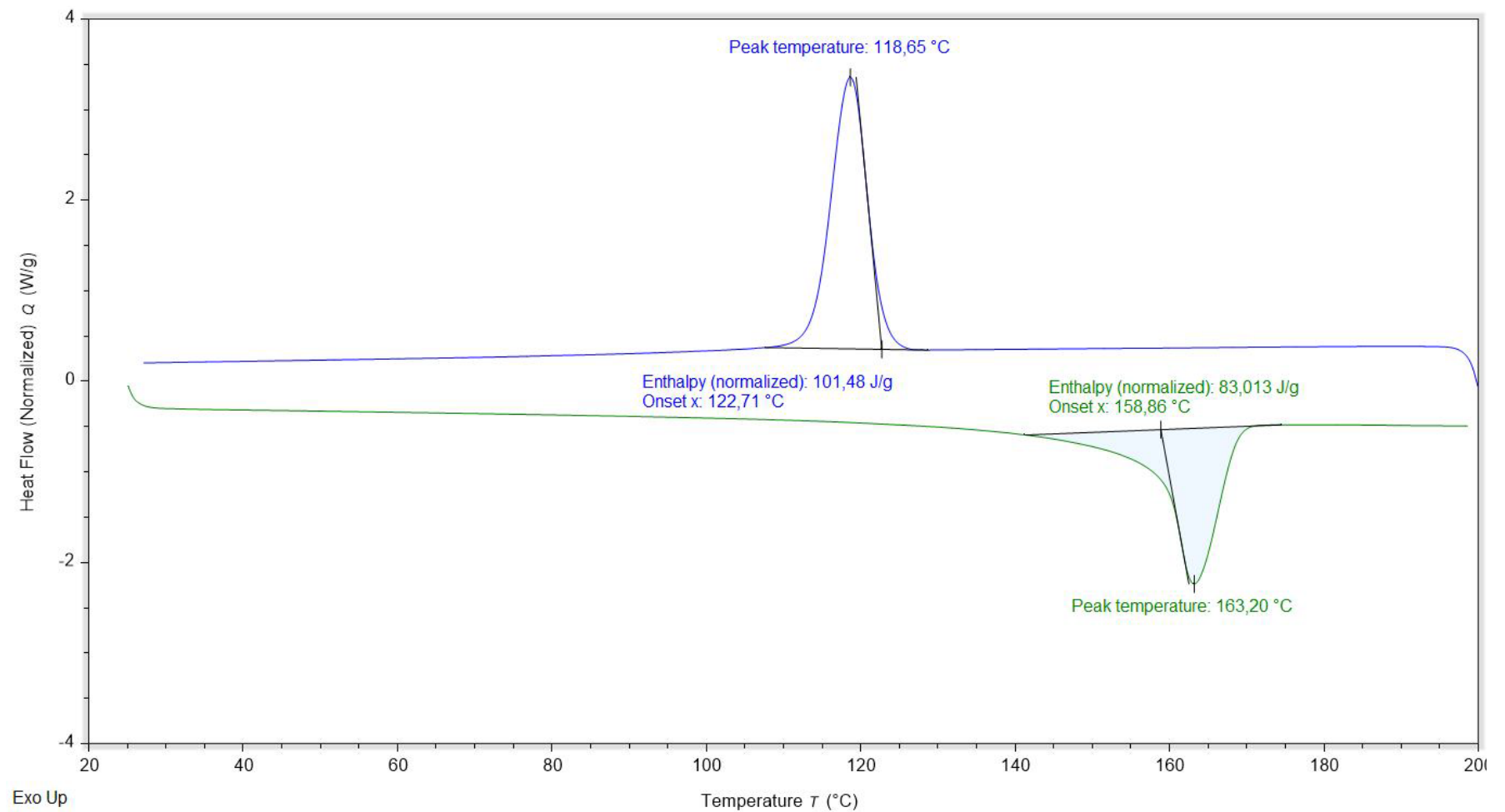
HTV145 in powder form



HNR100 + HTV145 in pellet form



HNR100 + HTV145 in powder form



HNR100 + HTV145 in powder form + Talc

