Development and optimization of polypropylene-based powders for selective laser sintering

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**NANYANG
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SINGAPORE

**DEVELOPMENT AND OPTIMIZATION OF
POLYPROPYLENE-BASED POWDERS FOR
SELECTIVE LASER SINTERING**

TAN JIAYING LISA

**SCHOOL OF MECHANICAL AND AEROSPACE
ENGINEERING**

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SCHOOL OF MECHANICAL AND AEROSPACE ENGINEERING

A thesis submitted to the Nanyang Technological University in partial
fulfilment of the requirement for the degree of
Doctor of Philosophy

2020

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarized materials, and has not been submitted for a higher degree to any other University or Institution.

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Tan Jiaying Lisa

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

23 October 2020

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Date

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Assoc Prof Zhou Kun

Authorship Attribution Statement

This thesis contains material from 3 papers published in the following peer-reviewed journals in which I am listed as an author.

Chapter 2 is published as a section of **L.J. Tan**, W. Zhu, and K. Zhou. Recent progress on polymer materials for additive manufacturing, *Advanced Functional Materials*, 2020. p. 2003062.

The contributions of the co-authors are as follows:

- I reviewed the literature and drafted the manuscript.
- Prof. Zhou proposed the review idea, provided the insights, and revised the manuscript.
- Dr. Zhu provided insights and revised the manuscript.

Chapter 3 is published as **L.J. Tan**, W. Zhu, K. Sagar, and K. Zhou. Comparative study on the selective laser sintering of polypropylene homopolymer and copolymer: processability, crystallization kinetics, crystal phases and mechanical properties, *Additive Manufacturing*, 2020. <https://doi.org/10.1016/j.addma.2020.101610>.

The contributions of the co-authors are as follows:

- I developed the experimental methods, obtained and analyzed the experimental results, and drafted the manuscript.
- Prof. Zhou proposed the research idea, supervised the research, and revised the manuscript.
- Dr. Sagar provided technical support for the research.
- Dr. Zhu provided technical support for the research and revised the manuscript.

Chapter 4 is published as **L.J. Tan**, W. Zhu, and K. Zhou. Development of organically modified montmorillonite/polypropylene composite powders for selective laser sintering, *Powder Technology*, 2020. 369: p.25-37.

The contributions of the co-authors are as follows:

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- Dr. Zhu provided technical support for the research and revised the manuscript.

23 October 2020

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Tan Jiaying Lisa

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Abstract

Polymers and their composites are widely used in modern industries. They are of great interest in additive manufacturing (AM) due to their vast potential for various applications, especially in the medical, aerospace, and automotive industries. Currently, the most widely used materials for selective laser sintering (SLS) are engineering polymers based on polyamides, with polyamide 12 making up ~90% of the SLS material market. This Ph.D. research aims to investigate the use of polypropylene (PP) and its nanocomposite powders as a more practical alternative for applications where conventional polyamide materials for SLS are not optimal in terms of the trade-off between cost and desired properties.

An in-depth investigation of SLS of PP powders is fundamental to developing PP nanocomposite powders for SLS. Isotactic PP homopolymer and copolymer powders were comparatively investigated for SLS, and the processability of the polymer powders was evaluated in terms of powder morphology, powder flowability, melting behavior, and crystallization kinetics. An isothermal differential scanning calorimetry testing protocol was employed as an effective and efficient method to determine a suitable powder bed temperature. It was established that for PP with high regio- and stereo-irregularities, SLS serves as a viable alternative manufacturing technique for producing PP parts comprising γ -phase crystals that are difficult to be manufactured by conventional molding processes.

PP composites are widely used in the traditional plastics industry; in particular, organically modified montmorillonite (OMMT) is a nanofiller known for significantly enhancing the thermal and barrier properties of PP at low loadings. OMMT/PP nanocomposite powders for SLS were first developed on a small scale using four powder preparation methods, including melt extrusion combined with cryogenic

grinding, thermally induced phase separation (TIPS), surface coating, and mechanical mixing. Evaluations were conducted on the shape and size, powder-bed surface roughness, and thermal behavior of the developed nanocomposite powders, as well as the mechanical properties of their injection molded tensile specimens. TIPS could produce powders with reduced crystallization temperatures and increased melt enthalpies that were beneficial for SLS and powder morphology ideal for SLS without post-processing. At low loadings, nanofillers with sheet-like structures such as OMMT could limit the increase in crystallization temperatures of the nanocomposite powder, thus ensuring their wide sintering windows for SLS. Nevertheless, melt extrusion proved to be the most favorable as the powders exhibited the highest thermo-oxidative stability.

OMMT/PP nanocomposite powders were thus produced at a large scale via melt extrusion and cryogenic grinding, and the properties of the powders that were critical to SLS were evaluated. The nanocomposite powders demonstrated significant widening of their sintering windows that greatly enhanced their SLS processability, and their laser-sintered specimens exhibited promising improvements in thermal stability. The developed nanocomposite powders demonstrated the potential of using OMMT to improve the SLS processability of PP and possibly other polymers by widening their sintering windows and reducing their melting range values without significantly lowering their mechanical properties. A wider range of powder bed temperature values could then be used for the nanocomposites, allowing for greater freedom in the designing and optimizing of SLS process parameters.

This Ph.D. thesis comparatively investigated PP homopolymer and copolymer powders for SLS, developed a systematic approach to the formulation of PP nanocomposite powders that could satisfy the stringent SLS material requirements,

including the thermal and rheological properties, and established a method to effectively and efficiently determine a suitable powder bed temperature. This thesis would provide an effective guide for formulating PP materials for SLS and could serve as a foundation for future studies on PP and its composites for SLS.

List of Publications

- [1] **Tan, L.J.**, W. Zhu, and K. Zhou. Recent progress on polymer materials for additive manufacturing, *Advanced Functional Materials*, 2020. p. 2003062.
- [2] **Tan, L.J.**, W. Zhu, K. Sagar and K. Zhou. Comparative study on the selective laser sintering of polypropylene homopolymer and copolymer: processability, crystallization kinetics, crystal phases and mechanical properties, *Additive Manufacturing*, 2020. <https://doi.org/10.1016/j.addma.2020.101610>.
- [3] **Tan, L.J.**, W. Zhu, and K. Zhou. Development of organically modified montmorillonite/polypropylene composite powders for selective laser sintering, *Powder Technology*, 2020. 369: p. 25-37.

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List of Abbreviations

Abbreviation	Meaning
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
ABS	Acrylonitrile butadiene styrene
AM	Additive manufacturing
CF	Carbon fiber
CNF	Carbon nanofiber
CNT	Carbon nanotube
CEC	Cation exchange capacity
CAD	Computer-aided design
DTG	Derivative thermogravimetric curve
DSC	Differential scanning calorimetry
EDX	Energy dispersive X-ray
CP 60-Extruded	Extruded CP60 powders
FESEM	Field emission scanning electron microscopy
FT-IR	Fourier transform infrared
GF	Glass fiber
GO	Graphene oxide
HR	Hausner ratio
HDT	Heat deflection temperature
HDPE	High-density polyethylene
IM	Injection molding
<i>i</i> PP	Isotactic polypropylene
LDPE	Low-density polyethylene
PPgMA	Maleic acid-grafted polypropylene

MM-OMMT/PP	OMMT/PP powder prepared by mechanical mixing
ME-OMMT/PP	OMMT/PP powder prepared by melt extrusion and cryogenic grinding
SC-OMMT/PP	OMMT/PP powder prepared by surface coating
SC-OMMT/SDS/PP	OMMT/PP powder prepared by surface coating, facilitated with sodium dodecyl sulfate
TIPS-OMMT/PP	OMMT/PP powder prepared by thermally-induced phase separation
OMMT-1/PPgMA/PP	OMMT/PP powder with 1 wt.% Cloisite 20 and compatibilized with PPgMA, prepared using CP60 powder by melt extrusion and cryogenic grinding
P-OMMT-1/PP	OMMT/PP powder with 1 wt.% Cloisite 20 prepared at a large scale using CP60 pellets by melt extrusion and cryogenic grinding
OMMT-1/PP	OMMT/PP powder with 1 wt.% Cloisite 20 prepared using CP60 powder by melt extrusion and cryogenic grinding
OMMT-3/PPgMA/PP	OMMT/PP powder with 3 wt.% Cloisite 20 and compatibilized with PPgMA, prepared using CP60 powder by melt extrusion and cryogenic grinding
P-OMMT-3/PP	OMMT/PP powder with 3 wt.% Cloisite 20 prepared at a large scale using CP60 pellets by melt extrusion and cryogenic grinding
OMMT-3/PP	OMMT/PP powder with 3 wt.% Cloisite 20 prepared using CP60 powder by melt extrusion and cryogenic grinding
OMMT-5/PPgMA/PP	OMMT/PP powder with 5 wt.% Cloisite 20 and compatibilized with PPgMA, prepared using CP60 powder by melt extrusion and cryogenic grinding
OMMT-5/PP	OMMT/PP powder with 5 wt.% Cloisite 20 prepared using CP60 powder by melt extrusion and cryogenic grinding
OMMT	Organically modified montmorillonite
PSD	Particle size distribution
PBT	Poly(butylene terephthalate)
PET	Poly(ethylene terephthalate)
PMMA	Poly(methyl methacrylate)
PPSU	Poly(phenyl sulfone)
PPS	Poly(phenylene sulfide)
PVA	Poly(vinyl alcohol)

PVC	Poly(vinyl chloride)
PA	Polyamide
PAEK	Polyaryletherketone
PB-1	Polybutylene
PC	Polycarbonate
PEEK	Polyether ether ketone
PEK	Polyetherketone
PES	Polyethersulfone
PE	Polyethylene
PI	Polyimide
PAI	Polyimideamide
POM	Polyoxymethylene
PP	Polypropylene
CoPP	Polypropylene copolymer
PS	Polystyrene
PSU	Polysulfone
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
TIPS-PP	PP powder prepared by thermally-induced phase separation
SEM	Scanning electron microscopy
SLS	Selective laser sintering
SDS	Sodium dodecyl sulfate
SSR	Stable sintering region
SAN	Styrene-acrylonitrile
sPS	Syndiotactic polystyrene
TIPS	Thermally induced phase separation
TGA	Thermogravimetric analysis
TPE	Thermoplastic elastomers

TPU	Thermoplastic polyurethane
TEM	Transmission electron microscopy
UTS	Ultimate tensile strength
UHMWPE	Ultra-high-molecular-weight polyethylene
XRD	X-ray diffraction

Chapter 1. Introduction

In this chapter, additive manufacturing (AM) and selective laser sintering (SLS) are first introduced in Chapter 1.1. The objectives and scope of this research are then highlighted in Chapter 1.2, and finally, the thesis outline is provided in Chapter 1.3.

1.1. Background

AM, commonly known as three-dimensional (3D) printing, has emerged as a disruptive technology that fabricates products of complex geometries through accumulating materials in a layer-by-layer manner according to computer-aided design (CAD) model data. AM enables low-volume, customized manufacturing and great design freedom, and products that comprise multiple components can now be redesigned and fabricated without assembly, thereby resulting in enhanced product performance and efficiency [1, 2]. AM is also viewed as an environmentally sustainable manufacturing technology and can potentially reduce up to 525.5 Mt of total carbon dioxide emissions by 2025 [3, 4]. In product development, AM can reduce development costs by up to 70% and time to market by up to 90% [2]. With such remarkable benefits, the global market for AM is projected to reach nearly \$23 billion by 2023, with a rapid compound annual growth rate of 22% [5].

Polymers are macromolecules composed of covalently bonded repeating units and can be classified into thermoplastics and thermosets according to their thermomechanical behaviors. Polymers and their composites are widely used in AM due to their intrinsic lightweight and corrosion-resistant properties and the achievable mechanical, thermal, electrical, fire-resistance, and biocompatible properties of their printed parts. Some polymer materials are responsive to external stimuli such as temperature, light, electric or magnetic fields, moisture, or pH, and can be used to print

structures that can undergo shape or property changes over time under an environmental stimulus.

Photosensitive resins, thermoplastic powders and filaments, and viscous polymer inks are the most extensively used polymer materials for various AM techniques, which have a multitude of applications in different domains, including biomedical engineering, aerospace, automotive, electronics, soft robotics, energy, environment, and social-culture (Figure 1.1).

Figure 1.1. Overview of polymer materials that are widely used for typical polymer AM techniques and applications.

As AM was originally developed as a rapid prototyping technique, the used materials only had to have sufficient mechanical and surface properties for demonstration purposes. The reproducibility and consistency of the mechanical and functional properties and the reliability of printed parts were not considered. Naturally, the need for different materials was not evident then. Now that AM is increasingly used

to manufacture end-use parts, it is apparent that one of the major constraints is the limited range of materials that AM can process. Many commercial AM materials are often insufficient for real part replacement as they lack high mechanical strength, good temperature resistance, and functionalities such as thermal and electrical conductivity, biocompatibility, and shape memory behavior required [6]. Therefore, extensive research has been done over the past decade on developing new materials for the AM of polymers. On the other end of the spectrum, improvements are constantly being made to AM systems to print parts with a wider selection of materials at a better resolution, higher accuracy, and much faster rates.

Of the various AM processes for polymers, SLS is one of the most established and widely used since many successful attempts to fabricate functional components use powders as the starting material [7, 8], and SLS of polymer powders has one of the highest potentials for achieving reproducibility [9-11]. As SLS was originally developed as a rapid prototyping technique, the materials only had to have sufficient mechanical and surface properties for demonstration purposes. The reproducibility and consistency of mechanical and functional properties, long-term stability, and in-depth understanding of material properties critical for product manufacturing were not considered. Naturally, the needs for different materials were also not evident then. Now that SLS is increasingly used to manufacture end-use parts, it is apparent that one of the major constraints restricting its wide application for manufacturing is the limited range of materials that SLS can process due to the stringent requirements that polymer powders must fulfill, as well as the complexity and the lack of understanding of processing other polymers. This problem is exacerbated by the high cost of SLS powders that can easily go beyond five times that of injection molding grade pellets. Currently, polyamides (PAs) make up a substantial 95% of the SLS material market, although its global polymer market share

is only about 8%; most published works also focused on PA [12, 13]. In contrast, commodity polymers take up a significant portion of the global polymer market share (~ 90%), yet their SLS material market share is less than 5% [14]. This stark imbalance calls for a greater focus of SLS material development on commodity polymers.

Polypropylene (PP), in particular, isotactic PP, is a popular commodity semi-crystalline thermoplastic that is widely used in automotive, biomedical, and consumer product applications. Coupled with low cost and balanced mechanical properties, PP can serve as a more practical alternative for applications where conventional PA materials for SLS are not optimal in terms of the trade-off between cost and desired properties. In particular, PP would be preferred over PA materials in applications where moisture resistance, chemical resistance, and non-toxicity are desired. For a PP material to be successfully used for SLS, it must be formed into a suitable feedstock, satisfy the stringent SLS material requirements, and exhibit appropriate service properties.

Isotactic PP is commonly available in the form of a homopolymer, and to date, most studies investigating SLS of PP have focused on the homopolymer [15-23] or its composites [24-26]. The majority of those studies focused on optimizing the SLS process parameters and the mechanical performance of the printed PP parts. Due to the low toughness of isotactic PP homopolymers, copolymers have been feasible alternatives for functional part applications and have gained some attention for SLS in the past few years [27-29]. Fiedler et al. [30] had conducted a preliminary evaluation of the potential of commercial PP homopolymers and copolymers for SLS, and compared their properties in terms of the sintering window, the degree of crystallinity, the melt viscosity, etc. Although there have been several independent investigations on SLS of isotactic PP, the studies comparing the processability of PP homopolymers and copolymers and the properties of their SLS parts are still quite limited in literature.

A major disadvantage of PP is its relatively poor thermal stability that has thus far not been addressed for SLS. The poor thermal stability of PP makes it prone to thermal degradation, thus negatively affecting the product lifetime, and at the same time puts it at a significant disadvantage, especially for use in SLS due to the prolonged heating during part fabrication. In traditional manufacturing processes, clay minerals are among the most widely investigated nanofillers due to their natural abundance, eco-friendliness, and well-studied intercalation chemistry [31]. It is widely recognized that the thermo-oxidative stability of PP can be improved by the addition of clay. Therefore, the incorporation of clay can most likely enhance the thermo-oxidative stability of PP. Furthermore, they are known to improve mechanical and physical properties, including tensile strength, Young's modulus, and heat distortion temperature, by adding a small amount to the polymer matrix [31, 32].

1.2. Motivation and objectives

Due to the nascent stage of using PP powders for SLS, there is a lack of research on the SLS of PP materials. Therefore, the use of commercially available PP powders for SLS was thoroughly investigated. This thesis also looked into the formulation and development of PP nanocomposite powders that satisfy the stringent SLS material requirements, the SLS process optimization for the developed powders, and the evaluation of the properties of printed specimens. The main objectives of this thesis are as follows.

(i) A comparative study on the SLS of PP homopolymer and copolymers

While there have been a few studies investigating the SLS of PP, there has yet been any that examined the effects of SLS on PP homopolymers and copolymers. This thesis bridges this existing gap by firstly evaluating and comparing the material properties of

PP homopolymer and copolymers, which includes the characterization of the powder properties critical to SLS, such as powder morphology, flowability, thermal behavior, and rheology. Secondly, SLS process optimization and part fabrication were carried out, and the mechanical properties of the printed specimens were evaluated. Finally, the effects of SLS on the crystal phases of the fabricated PP specimens were examined. Herein, the utilization of isothermal differential scanning calorimetry (DSC) as an effective and efficient method to determine the minimum powder bed temperature required for SLS was demonstrated. For benchmarking and comparison purposes, PA12, the most widely used SLS material currently, was also evaluated.

(ii) Evaluation of OMMT/PP powder preparation methods

A major disadvantage of PP is its relatively poor thermo-oxidative stability, making it prone to degradation that negatively affects the product lifetime. Fortunately, this disadvantage can be reduced with the addition of organically modified montmorillonite (OMMT) which exhibits good barrier properties. Coupled with its low cost due to its high abundance, OMMT serves as a feasible filler for PP. With the development of OMMT/PP nanocomposites as the focus, different powder preparation methods were attempted and evaluated. These methods include mechanical mixing, melt extrusion followed by cryogenic milling, surface coating, and thermally induced phase separation (TIPS). The powders prepared by the different methods were then characterized, and the advantages of each preparation method were assessed. Points of consideration include the extent of filler dispersion, achievable powders and part properties, and feasibility for industrial-scale production.

(iii) SLS of OMMT/PP powders

As melt extrusion followed by cryogenic milling was determined to be the most viable composite powder preparation method, the large-scale production of OMMT/PP

powders for the SLS process was achieved via this method. The OMMT/PP powders containing different OMMT loadings were characterized in terms of powder morphology, powder bed surface roughness, melt and crystallization behavior, thermal stability, and rheological behavior. The SLS process parameters were then optimized for each nanocomposite, and the thermal and mechanical properties of the printed SLS specimens were evaluated and compared.

The purpose of this Ph.D. study lies in the investigation of both PP homopolymer and copolymers for SLS and the development and production of PP nanocomposite powders suitable for SLS. The excellent prospects of using PP for SLS demonstrated in this study can serve as a strong impetus to shift the heavy focus of SLS materials away from PA.

1.3. Thesis outline

This thesis consists of seven chapters; following the introduction provided in this chapter, Chapter 2 reviews the material requirements for SLS and the state-of-art SLS materials. The advantages and limitations of different composite powder preparation methods are discussed. Finally, the scientific background of OMMT and its relevance to developing PP nanocomposites with enhanced thermo-oxidative stability are studied. Chapter 7 details the experimental methods and analytical procedures that were used.

Chapter 4 evaluates the use of PP homopolymer and copolymers for SLS. The PP powders are first characterized, and the minimum SLS powder bed temperature required for each material is then determined by the isothermal DSC protocol. The SLS process parameters are subsequently optimized, and the properties of the printed PP specimens are then evaluated. The use of the isothermal DSC protocol as a more efficient and effective way of determining the minimum powder bed temperature required for a

material is demonstrated, and the effects of the SLS process on the crystal phases of the printed PP specimens are assessed.

Chapter 5 focuses on the development of OMMT/PP nanocomposite powders for SLS. The nanocomposite powder preparation methods most used for SLS, i.e., mechanical mixing, melt extrusion followed by cryogenic milling, surface coating, and TIPS, are explored. The merits and disadvantages of each preparation method are assessed, and the melt extrusion followed by a cryogenic grinding method that was determined to be the most viable method is used to produce OMMT/PP powders at a large scale for the SLS process.

Chapter 6 looks into the production and SLS of OMMT/PP powders at various OMMT and compatibilizer loadings. The OMMT/PP powders produced are characterized, and the nanocomposite specimens are then fabricated. The mechanical and thermal properties of the laser-sintered nanocomposite specimens are evaluated, and the optimal process parameters are finally determined.

Chapter 7 summarizes the key achievements and contributions of this thesis to the research fraternity. Future works to complement this area of research are also proposed.

Chapter 2. Literature Review

This chapter describes the SLS process and details the intrinsic and extrinsic material requirements that polymer powders must fulfill to suit SLS. The state-of-art SLS materials and recent progress on polymeric material development for SLS are reviewed, and different composite powder preparation methods for SLS are evaluated. Finally, the scientific background of OMMT and its relevance to developing PP composites with enhanced thermo-oxidative stability are discussed.

2.1. SLS process

SLS is a powder bed fusion process where a heat source, typically a CO₂ laser, is used to selectively sinter thermoplastic polymer powder particles in a powder bed in successive layers to build 3D objects. The SLS process starts by preheating the powder bed up to a temperature typically just below the melting or softening temperature of the polymer powder. A thin layer of powder is then spread over the powder bed by a recoater, and the laser scans across the print bed according to the 3D CAD model. The laser provides the extra thermal energy needed to melt the powder so that the powder coalesces to form a partial 3D structure, with the un-sintered powder serving as the structural support. After sintering the first layer, the print bed is lowered by a predetermined height, i.e., layer thickness, and a layer of powder is subsequently spread over the previously sintered layer. The sintering process is repeated until the whole build is finished, after which the print bed is left to cool slowly. The printed part can be easily separated from the supporting powder and cleaned with compressed air. Sand or plastic bead blasting is typically used to further remove un-sintered powder that sticks to the surface.

SLS is one of the most established and widely used AM processes due to its high potential for the manufacturing of functional parts and is versatile as it can theoretically

process any polymer available in the powder form, as long as the powder particles are sinterable [6, 7, 12, 33, 34]. Furthermore, no support structures are required as printed parts are embedded within the powder bed. This eliminates the post-processing steps typically needed in other AM processes, enabling cost and time savings. In an analysis of the potential use of several AM processes to produce a traditionally injection molded component, the lowest costs of production were attributed to SLS, where material costs accounted for approximately 75% of the overall cost, and this is assuming that no supporting powder is recycled [6, 35, 36]. However, the SLS process is relatively slow because of the point-wise laser scanning track; endeavors by equipment manufacturers to address these challenges have brought about the development of the High-Speed Sintering (Voxeljet), LaserProFusion (EOS), Fine Detail Resolution (EOS), and Flight (Farsoon) processes that boast a higher fabrication speed and resolution by using laser arrays and different laser types.

2.2. Thermoplastic powders for SLS

Thermoplastics soften or melt upon heating and solidify upon cooling. This characteristic allows thermoplastics to be remolded and recycled. Thermoplastics are further classified into amorphous and semi-crystalline thermoplastics. Amorphous thermoplastics such as polystyrene (PS) and polycarbonate (PC) have randomly ordered molecular structures that impart flexibility to the material. They have glass transition temperatures T_g above which they slowly soften and transform into a glassy state. Amorphous polymers do not have a defined melting temperature T_m .

In contrast, semi-crystalline thermoplastics such as polyamides (PAs) have both T_m and T_g that correspond to the crystalline and amorphous regions, respectively. The viscosity of a semi-crystalline thermoplastic rapidly decreases as it changes from the

solid to the viscous liquid phase when heated above its T_m value. Thermoplastics and their composites in powder form can be processed by the PBF technique, of which SLS and MJF are two major processes. As both processes are largely similar in terms of their sintering mechanisms and material requirements, discussions in the following sections only use SLS as an example for clarity purposes.

In SLS, the consolidation of amorphous and semi-crystalline thermoplastic powders occurs by heating them above their T_g and T_m values, respectively [6, 12]. Upon the initial softening of the material, two adjacent polymer particles form a neck at the contact surface. Subsequently, the neck grows while the intermediate liquid-air interface disappears under the action of surface tension. The particle doublet then gradually transforms into a single sphere (Figure 2.1a) [37]. The particle coalescence process can be described by the modified Frenkel-Eshelby model, which assumes the isothermal condition and that two ideal spherical particles can flow and coalesce as a function of time [38]

$$\frac{x(t)}{a(t)} = \sqrt{\frac{\gamma t}{a_0 \eta}} \quad . \quad (2.1)$$

In equation 2.1, $x(t)$ and $a(t)$ are the radii (m) of the neck and the powder particle as a function of sintering time t (s), respectively; a_0 the initial radius (m) of the particle; γ and η the surface tension (N/m) and viscosity (Pa·s) of the polymer, respectively. This model applies only to the initial sintering stages when the particle radius remains relatively constant (Figure 2.1b, c). In this analytical model, the sintering process is driven by surface tension and counteracted by viscous dissipation [37]. The sintering kinetics of a polymer material is also likely affected by its viscoelastic effects, whereby a decreased relaxation time can slow down the sintering process [37]. Investigations on the sintering mechanism and kinetics of polymer powder particles are still ongoing.

Figure 2.1. Consolidation process of near-spherical particles of similar sizes during sintering. (a) A schematic of the consolidation process. (b, c) Evolution of the neck radius of PS particles ($a_0 = 60 \mu\text{m}$), observed from the top (b) and side (c) view. Reproduced with permission [37]. Copyright 2019, RSC.

There are two main consolidation mechanisms for the SLS of polymers, full melting and partial melting [34]. Full melting consolidation, as the term implies, involves complete melting of the polymer powder and can produce parts with reasonably high relative density. Nevertheless, even with full melting, the inherent porosity of the powder bed (40–60%) and the lack of external mechanical pressure in SLS prevents the fabrication of fully dense structures that are otherwise commonly obtained via conventional molding processes [39]. Post-processing is usually required to increase the density for functional applications. Full melting is mostly observed with semi-crystalline polymers. At a given temperature above T_m , semi-crystalline thermoplastics

typically have lower viscosity and better flow than amorphous thermoplastics. This results in a faster rate and a higher degree of consolidation of polymers, favoring the printing of parts with a high relative density [34].

Partial melting, on the other hand, usually occurs with amorphous polymers. When heated to or above its T_g , amorphous thermoplastics gradually soften into a viscous liquid. Although the viscosity of these materials decreases upon heating, they seldom are as easy flowing as semi-crystalline polymers under typical processing conditions. This contributes to slower sintering kinetics and a lower degree of consolidation during the timescale of the sintering process, resulting in higher porosity and lower strength, but also reduced shrinkage that is favorable for fabricating patterns for investment casting.

In its early days, SLS was used for amorphous polymers, specifically acrylonitrile butadiene styrene. The term “selective laser sintering” was coined as it was the most technically accurate description of the sintering process that amorphous polymers underwent, during which the powders melt only partially. By the time semi-crystalline materials such as PA started to be used for SLS and although they do undergo complete melting during the process, the term "SLS" was already well-established and stuck despite having become a misnomer. For accuracy, “selective laser sintering” should be used for polymers that undergo partial melting consolidation mechanism, and “selective laser melting” used for those that undergo full melting consolidation mechanism. Today, "SLS" refers to the use of a directed energy beam to selectively sinter or melt certain areas of a powder bed, especially polymers, for the layer-wise fabrication of an object, regardless of their consolidation mechanisms.

2.2.1. Polymer material requirements

2.2.1.1. Intrinsic properties

Polymer powders used for the SLS process must be able to absorb energy at the laser wavelength efficiently. During the laser scanning process, only a fraction of the laser energy is absorbed by powder particles on the powder bed surface because of laser reflection and refraction at the particle interfaces and laser transmission through the particles. CO₂ lasers are the most used in commercial SLS systems because most polymers contain C-H bonds that absorb well at the laser wavelength of 10.6 μm . When lasers of other wavelengths or different irradiation sources are used, appropriate light absorbers may be required to ensure sufficient absorbance.

The thermal properties of a polymer are crucial for its successful application in SLS. During the SLS process, polymer powders are preheated to a powder bed temperature T_b as close to the melting temperature T_m of semi-crystalline polymers or the glass transition temperature T_g of amorphous polymers as possible to lower the laser energy required to melt or sinter them. Nevertheless, for a semi-crystalline polymer, its T_b value should not be larger than its onset melting temperature $T_{m,\text{onset}}$ to avoid the premature melting of its powder particles that would lead to powder caking (Figure 2.2). The preheating of the powder bed also reduces the temperature gradient between its sintered and unsintered regions, thus mitigating the non-uniform shrinkage of sintered parts, especially at the part contours.

For a semi-crystalline polymer, the control of its powder bed temperature T_b between its onset crystallization temperature $T_{c,\text{onset}}$ and onset melting temperature $T_{m,\text{onset}}$ is especially important for suppressing the crystallization of its melt for as long as possible during the part fabrication process, as the premature crystallization of sintered layers would lead to part warpage and curling. This metastable thermodynamic

region of a polymer melt, $T_{m,onset} - T_{c,onset}$, is termed the ‘sintering window’ [40], and is a critical thermal parameter to be considered when the sinterability of semi-crystalline polymers is evaluated (Figure 2.2).

Figure 2.2. Dynamic DSC curve of a polymer and the parameters for evaluating its sinterability.

The sintering window is normally characterized by DSC at heating and cooling rates of 10 °C/min. However, the real rate of temperature change during SLS is determined by complex factors and is hardly controllable. As crystallization is a kinetic process, the measured $T_{c,onset}$ value depends on the cooling rate used, where a slower cooling rate induces a higher $T_{c,onset}$ value, which implies that during the timescale of the SLS process, crystallization may occur even if the T_b value is slightly above the $T_{c,onset}$ value obtained through the standard DSC procedure. Thus, a large difference between the T_b and $T_{c,onset}$ values is desirable to minimize such crystallization. The large difference also allows great temperature fluctuations that inevitably occur in the printing chamber, without any local temperature going below its $T_{c,onset}$ value. Isothermal DSC

can be applied to mimic the quasi-isothermal crystallization conditions at a given temperature near the T_b value and provide additional information on the actual $T_{c,onset}$ value in the SLS process.

Polymers that have wider sintering windows are favored over those that have narrower sintering windows. As a reference for developing new materials, the most popular commercial SLS material, polyamide 12 (PA12), has a sintering window in the range of 20–30 °C.

The crystallization kinetics of a polymer, which characterizes its time- and temperature-dependent crystallization behavior, greatly influence the part warpage and curling during SLS processing. Drummer et al. introduced the use of crystallization activation energy as an indicator to evaluate the sensitivity of the crystallization behavior of a polymer toward temperature changes [17]. Polymers with higher crystallization activation energy, such as polyoxymethylene (POM), are more sensitive to small temperature change, i.e., more prone to fast crystallization even at a temperature slightly below their crystallization temperature, and thus are extremely susceptible to warping and more challenging to process [17].

The melting range from the onset melting temperature $T_{m,onset}$ to the offset melting temperature $T_{m,offset}$ is also crucial for the sintering process. A polymer with a narrow melting range and a sharp melting peak is preferable because an ideal powder bed temperature T_b should be close to T_m but lower than $T_{m,onset}$, as previously discussed. Furthermore, a polymer with a wide melting range contains crystals with lamellae that vary significantly in thicknesses, and some lamellae are so thin that their melting temperatures are lower than the T_b value used. Such lamellae would soften or even melt prematurely to cause powder caking.

Specific heat capacity, defined as the energy required to induce a unit change in temperature for a unit mass of material, is a fundamental property to be considered for an SLS material as it is related to the amount of energy needed for sintering. The melting enthalpy ΔH_m of a semi-crystalline polymer is related to the specific heat capacity and can be calculated from the area under the endothermic peak in the DSC curve (Figure 2.2), is a parameter that is more commonly used for powder evaluation. A high ΔH_m value is desired during the sintering process mainly because of the increased thermal threshold of powder particles adjacent to the sintered region against undesirable melting since more energy would be required. As a result, the unintended melting of nearby powder particles can be minimized, and the dimensional accuracy of the printed parts can be increased.

The shrinkage of a polymer upon cooling from its softened or melt state is another factor that determines the warping tendency of printed layers during SLS. For amorphous polymers, shrinkage is mainly due to thermal contraction, which is influenced by their temperature-dependent coefficients of thermal expansion. In contrast, the shrinkage of semi-crystalline polymers is due to thermal contraction and crystallization shrinkage. Semi-crystalline polymers usually undergo large shrinkage upon crystallization, which aggravates the warpage issues during sintering. In contrast, amorphous polymers with much lower shrinkage tend to curl less during sintering [41]. Polymer shrinkage can be measured by volumetric dilatometry and is related to the degree of crystallinity of the polymer and its coefficient of thermal expansion; the higher the degree of crystallinity, the larger the shrinkage expected (Figure 2.3). For instance, PAs have relatively low shrinkage (3–5%) compared to highly crystalline polymers such as high-density polyethylene (HDPE), in which shrinkage can go up to 13% [39, 41].

Figure 2.3. Dilatometric measurements of PA12 (PA2200), Thermoplastic polyurethane (TPU) (Luvosint), Polybutene-1, PA11 (Rilsan), PA6 (Sinterline), and poly(methyl methacrylate). Data obtained from [41].

The rheological behavior of polymers is another essential consideration for SLS. Since the particle coalescence and flow of polymer melts in the SLS process proceed without external forces, according to the Frenkel-Eshelby model, the surface tension γ and zero-shear viscosity η_0 of a polymer are the most important parameters. Because the γ values of various commercial SLS polymer powders at operating temperatures vary only within an order of magnitude, it is currently assumed that differences in their particle coalescence behavior are dominated by η_0 [14].

Polymers with lower zero-shear viscosity η_0 have higher coalescence rates and can thus be printed into parts of higher density and strength within a given time frame [38]. In contrast, if η_0 is high, voids and air traps can remain in the printed part, reducing the achievable ultimate tensile strength (UTS) [34]. Therefore, polymers with low η_0 at the processing temperatures are desired. The η_0 value of a polymer is usually measured with cone-plate or parallel-plate rheometers, although the melt flow index is occasionally used as a rough reference. The viscosity of polymers generally follows the Arrhenius relationship and changes rapidly with temperature [14, 39]. As the temperature

increases, the viscosity of amorphous polymers such as acrylonitrile butadiene styrene (ABS) gradually decreases when $T > T_g$; in contrast, semi-crystalline polymers such as PA12 exhibit a rapid decrease in viscosity when $T > T_m$ (Figure 2.4). For reference, the η_0 value of PA12 estimated by extrapolation is 400 Pa·s at 210 °C. The coalescence of polymer powder particles is frequently studied by hot stage microscopy, where a visual representation of the sintering process can be obtained [38].

Figure 2.4. (a) Complex viscosity values of semi-crystalline PA12 and amorphous acrylonitrile butadiene styrene as a function of temperature. Reproduced with permission [17]. Copyright 2010, Elsevier. (b) Zero-shear viscosity values of PA12 (PA2200), PA12 (Orgasol), PA11 (Rilsan), PA6 (Sinterline), PP (CP60), polybutene-1, and TPU (Luvosint) as a function of temperature difference from their respective melting points. Reproduced with permission [41]. Copyright 2016, KU Leuven. (c, d) Cross-section of PA12 parts made from PA12 polymers with low (left) and high (right) viscosity. Reproduced with permission [42]. Copyright 2015, AIP Publishing.

2.2.1.2. Extrinsic properties

Unlike the above-mentioned intrinsic properties that are governed by the molecular structures of the polymer and which cannot be significantly altered by external factors, the extrinsic properties are typically determined by powder manufacturing processes. The extrinsic properties of the SLS materials include the characteristics of the polymer particles (shape, size, size distribution, etc.) and the powder behavior (packing density, flowability, etc.) resulting from there. The physical states of polymer particles at the microscopic level, i.e., particle shape, size, and size distribution, have a decisive effect on the powder flow behavior and powder packing density at the macroscopic level, which influences the deposition of a thin, dense, and smooth layer of powder that is required for SLS.

For a good powder flow and high powder packing density, spherical or potato-shaped powder particles with a narrow Gaussian distribution are desired. The ideal particle size range is 20–80 μm [6, 13, 43]. Powder flow is enhanced with low inter-particle adhesion and friction, which is facilitated by spherical or near-spherical particles as they ensure minimal contact between particles [44]. With a Gaussian powder particle size distribution, voids between larger particles can be filled by those that are smaller, which allows a high powder packing density to be achieved. Smaller particles have a faster particle coalescence rate according to equation 2.1, and thus have a faster sintering rate despite having the same melting temperature as larger particles, which favors a higher part density achievable. Smaller particles also allow a lower layer thickness to be used, thus reducing the stair-stepping effect, particularly in the printing of inclined or curved surfaces, and improving the surface quality achieved [6, 7]. However, there lies a lower limit for the particle size as particles that are too small are difficult to spread due to static forces and particle coagulation [13]. Furthermore, too small particles are

more likely to soften or even melt prematurely to induce powder caking when a high powder bed temperature is used, especially for a polymer with a wide melting range, because they have a faster sintering rate [6].

Good powder flow is necessary for the successful deposition of a thin and homogenous powder layer, which is critical to begin the SLS process. Powder flow is influenced by various factors, including but not limited to electrostatic charging, temperature, moisture content, particle shape, and attractive Van Der Waals forces between particles. Good flow is achieved with low inter-particle adhesion and friction, which is facilitated by spherical or near-spherical particles as they ensure minimal contact between particles [44]. Powder flow can be evaluated under static and dynamic conditions, but any method used to measure powder flow generates parameters that are valid only for that particular flow field applied during the measurement [41].

A standardized method for characterizing powder flow behavior during the SLS process has not yet been developed [45]. Powder flowability can be evaluated under static and dynamic conditions, but the parameters used are valid only for the particular flow field applied during the measurement [41]. The Hausner ratio (HR), the angle of repose, and the flow rate through an orifice are common indices used to assess powder flowability. Owing to the ease of measurement, many studies have used HR, defined as the ratio between the tapped and bulk density values, to gauge powder flowability; powders with $HR \leq 1.25$ are considered free-flowing. Powders with good flowability would also exhibit low angles of repose and a high flow rate through the orifice. The revolution powder analyzer, which analyzes the avalanche behavior of powders as they rotate in a sample drum, is considered a more suitable powder flowability measurement method since the temperature, dynamic, and stress conditions similar to those in SLS can be imposed [41]. Since the mechanical movement of film applicators is similar to

that of recoaters, they can be used to simulate powder deposition. Using a film applicator modified with a weighing balance and a measurement plate, the mass of the powder spread over a known layer volume can be measured [41]. The layer density, which provides a quantitative measure for powder flowability, can then be calculated.

The key material requirements for SLS are summarized in Figure 2.5. They can be classified into intrinsic and extrinsic properties. The intrinsic properties include the optical, thermal, and rheological properties, while the extrinsic properties include the size, shape, and size distribution of the powder particles. The intrinsic properties are determined by the chemistry and molecular structure of the polymer and are not easily influenced by external factors, whereas the extrinsic properties are largely controlled by powder production processes.

Figure 2.5. Key properties of a powder material and their influences on SLS processability and part properties.

2.2.2. Pure polymer powders

As a result of the stringent requirements that polymer powders must fulfill to be suitable for SLS, the variety of SLS materials available currently is incomparable to those for conventional manufacturing methods. The SLS polymer market (1,500 tons per year) is only 1/200,000th that of the entire polymer market today, with the cost of SLS polymer powders being as high as 30 times that of their conventional counterparts [14].

Amorphous and semi-crystalline polymers have been studied for SLS, with the latter being more popular. Semi-crystalline polymers that have been investigated vary from commodity polymers to engineering polymers and high-performance polymers (Figure 2.6). Although several polymer powders have been commercialized, most of them are limited to laboratory investigation and reported in scientific literature. The most widely used SLS materials are engineering polymers based on PAs, with PA12 making up ~90% of the SLS material market despite taking up only 8% of the global polymer market share [6, 12, 13]. Other engineering polymers include polyesters (e.g., poly(butylene terephthalate) (PBT) and poly(ethylene terephthalate) (PET)), polyethers (e.g., POM) and thermoplastic elastomers (TPEs). Commodity polymers, such as polypropylene (PP), polyethylene (PE) (e.g., low-density PE (LDPE), HDPE and ultra-high-molecular-weight PE (UHMWPE)), and high-performance polymers, such as polyether ether ketone (PEEK), polyether ketone (PEK), polyether ketone ketone (PEKK) and poly(phenylene sulfide) (PPS), are gaining increasing attention for SLS.

The powder preparation process is of great importance for a polymer to be used for SLS. Polymer powders are often produced in the form of pellets, and they are also occasionally obtained from monomers through direct polymerization. The methods for

producing polymer powders can be broadly classified into three categories: mechanical, solution-based, and melt-based methods (Table 2.1).

Figure 2.6. An overview of polymer powders for SLS that are commercially available or have been reported in scientific literature. The abbreviations listed in this figure that are not used in the main text are as follows: polyamideimide (PAI), polybutylene (PB-1), polyethersulfone (PES), polyimide (PI), poly(phenyl sulfone) (PPSU), polysulfone (PSU), polytetrafluoroethylene (PTFE), poly(vinyl alcohol) (PVA), poly(vinyl chloride) (PVC), polyvinylidene fluoride (PVDF), styrene-acrylonitrile (SAN) and syndiotactic polystyrene (sPS).

The mechanical method mainly refers to the mechanical grinding process, where a mill is used to break millimeter-sized polymer pellets into micro-sized powders. To embrittle viscoelastic polymers and reduce heat generated during the mechanical grinding process, a cryogenic refrigerant (e.g., liquid nitrogen) should be used to cool them below their embrittlement temperatures. Thus, this process is often termed

cryogenic grinding. Due to the high energy consumption brought about by using a continuous stream of liquid nitrogen, an alternative grinding process, wet grinding, that uses organic solvents (e.g., ethanol and hexane) as coolant was developed [46]. The mechanical grinding processes are versatile and suitable for most polymers; however, their biggest disadvantage is the irregular shape of powder particles that are produced.

To address the problem of irregular particle shape, a post-processing method involving particle rounding can be employed to produce spherical polymer powders with good flow. [47-49] The ground powder particles are fed into a downer reactor where the dispersed particles are melted and rounded due to the effect of surface tension and subsequently solidify to produce spherical powder particles [50]. This post-processing method is versatile and scalable; more importantly, it can be applied to any polymer that may be ground and melted without degradation, i.e., most thermoplastics and thermoplastic blends such as PS and PBT/PC [51, 52].

A widely used solution-based method for producing polymer powders is the dissolution-precipitation process, also known as thermally induced phase separation. In this process, a polymer is first dissolved in a solvent at high temperatures and often under high pressure. Subsequently, the solution is cooled at a controlled rate to allow polymer powder particles to precipitate. The dissolution-precipitation process is known for producing spherical micro-sized powder particles with good control over the particle size and size distribution. The dissolution-precipitation process is used to produce commercial PA12 powders; it can also be used for other polymers such as PP, PC, and POM [18, 53, 54].

Table 2.1. The advantages and disadvantages of different powder preparation methods and their applications.

Powder preparation method		Material	Advantage and disadvantage
Mechanical	Cryogenic grinding	PA11 [55]	• Simple process, widely used
		TPU [56-58]	• Suitable for most polymers
		PP [24]	▪ Irregular particle shape
		PE [27]	▪ Poor powder flowability
		PS [59-61]	▪ Particle rounding or other post-processing treatment required
		PBT/PC [52]	
	Wet grinding	PBT [51]	• Lower energy consumption than cryogenic grinding
		POM [51]	▪ Irregular particle shape
		PS [51]	▪ Poor powder flowability
		PEEK [46]	▪ Particle rounding or other post-processing treatment required
Solution-based	Dissolution-precipitation/ Thermally induced phase separation	PA12 [14, 40, 62]	• Potato-shaped particles
		PA11 [55]	• Good powder flowability
		PA6 [63]	▪ Complex and time-consuming procedure
		PP [18]	▪ Specific process know-how required
		POM [53]	
		PC [54]	▪ Solvent intensive
	Direct polymerization	PA12 [14, 64]	• Spherical particle shape
			• Good powder flowability
Melt-based	Melt emulsification/ Coextrusion		• Narrow unimodal particle size distribution
			▪ Complex and time-consuming procedure
			▪ Specific process know-how required
		PP [14]	• Spherical particle shape
		PE [15]	• Good powder flowability
		PBT [15]	• Extrusion equipment readily available
		PA12 [65]	• Continuous production possible
			▪ Complex and time-consuming procedure
			▪ Post-processing required

Another solution-based method to produce polymer powders is the direct polymerization of monomers into polymer powder particles, which is termed the direct polymerization method in this paper. In the direct polymerization process, the monomers are initially dispersed or dissolved in a solvent and subsequently stabilized into spherical droplets or micelles upon the addition of suitable surfactants [14]. The polymerization reaction then starts upon the addition of an initiator, ultimately forming polymer powder particles. This method allows good control of the average molecular weight of the polymer chains and the size of the powder particles.

The melt-based powder preparation method involves melt emulsification, also known as coextrusion (Figure 2.7). The polymer of interest is first melt-blended with an incompatible or immiscible polymer (matrix phase) at a temperature above both their T_m values. Spherical droplets of the polymer of interest are then created within the matrix phase upon shear and elongational stress, which can be achieved with, for example, extrusion, forming a melt emulsion. The melt emulsion is then cooled and the matrix phase is subsequently dissolved in a suitable solvent such as water, leaving behind insoluble spherical powder particles that can be retrieved by filtration and sieving [66]. Polyolefins such as PP that are highly hydrophobic and resistant to chemical degradation are well suited for this process using a water-soluble matrix phase. Other polymers, for example, PBT and PA12 powders, have also been produced through this melt-based method by employing different matrix phases and solvents [15, 65].

Figure 2.7. Schematic illustration of the production of spherical polymer powders by melt emulsification. Reproduced with permission [15]. Copyright 2016, Elsevier.

2.2.2.1. Amorphous polymers

Amorphous polymers were the first type of polymers to be used for SLS. Since the mobility of molecular chains increases significantly as the temperature approaches the T_g value of amorphous polymers, the T_b value should be lower than the T_g value. Although amorphous polymers gradually soften and ultimately become a viscous liquid with increasing temperature, their viscosity values remain very high in general, even when the temperature is above their T_g values. Consequently, for these amorphous polymers, proper powder particle coalescence does not typically occur within the short sintering timescale. In theory, the consolidation of amorphous polymer powders can be improved with higher energy input, which, however, tends to cause over-sintering, part curling, and even polymer degradation [67]. Therefore, in actual practice, most laser-sintered amorphous polymer parts are only partially consolidated with a high concentration of voids, and they exhibit lower strength than their conventionally manufactured counterparts.

Despite their high viscosity, amorphous polymers, especially PS and PC, are valued for their high dimensional accuracy and a low residual ash content of printed parts, which render these polymers very ideal for investment casting applications (Figure 2.8).

In addition, the common problem of shell expansion and cracking due to the formation of decomposition gases during the pattern removal process of investment casting can be mitigated since the high porosity of printed parts allows the gases to escape. The high accuracy of laser-sintered parts of amorphous polymers is a result of their low process shrinkage (0.5–1.5%) [39]; as there is no volume change associated with their glass transition, their process shrinkage is mainly attributed to thermal contraction, with sintering densification also contributing to this phenomenon. Because of its low coefficient of thermal expansion and hence higher dimensional accuracy, PS is preferred over PC and remains available in the SLS material market today [59]. A solution for producing tougher patterns is to use high-impact PS with comparable sinterability to PS but with better mechanical properties. In other cases, the mechanical properties of printed parts can be improved via post-infiltration with thermosets such as acrylic or epoxy to reduce porosity [59-61].

Figure 2.8. Process chain for investment casting using traditional and AM methods. Reprinted with permission [68]. Copyright 2018, East West Manufacturing.

2.2.2.2. Semi-crystalline polymers

As semi-crystalline thermoplastics can undergo a higher degree of consolidation than amorphous thermoplastics, the mechanical properties of their printed parts can approach and possibly exceed those of their injection-molded counterparts. However, the printed parts may still depict some porosity. As a result, semi-crystalline thermoplastics are preferred over amorphous thermoplastics for applying SLS to print functional parts and are more widely studied.

Engineering polymers

Engineering polymers promise better mechanical and/or thermal properties than amorphous polymers and have been used to replace traditional materials in the automotive, textile, food, and electronics industries. Engineering polymers that have been used for SLS include PAs, polyesters, and polyethers.

Polyamide (PA) is a generic designation for the family of polymers that contain amide linkages along the polymer backbones. A unique characteristic of PAs is their ability to form hydrogen bonds between amide groups, which gives them intrinsically high melting points and good mechanical properties. PA12, the most popular SLS material, is usually synthesized by the ring-opening polyaddition of laurolactam. The good processability of PA12 powders results from the high congruence of their material properties with the intrinsic and extrinsic properties required for SLS. The weight-average molecular mass of virgin PA12 powder is 20–50 kDa [69]. PA12 powders have wide sintering windows with values of 20–30 °C that make them more tolerant to temperature deviations and thus easier to process. Their relatively high melting points of ~180 °C also render them suitable for applications requiring thermal resistance.

Commercial PA12 powders are most commonly supplied by Evonik and distributed through EOS and 3D-Systems as PA 2200 and Duraform[®] PA, respectively (Figure 2.9a). The PA12 powder from Evonik is prepared by the dissolution-precipitation method, which exhibits higher crystallinity than the pellet feedstock due to the high mobility of the polymer chains during the process. High polymer chain mobility provides more possibilities to improve the crystalline structure and the high pressure involved that promotes the growth of larger lamellae with higher melting points [40]. Owing to the above reasons, the PA12 powder from Evonik has a much wider sintering window than the conventional polymer feedstock, making them more suitable for SLS (Figure 2.9d). The high chain mobility involved during the dissolution-precipitation process can additionally be used to convert an amorphous feed material, for example, PC, into a semi-crystalline material, which would otherwise be impossible with conventional grinding processes [54]. This is especially advantageous for widening the type of semi-crystalline powders that can be used for SLS.

PA12 powders for SLS can alternatively be produced by direct polymerization, and this method has been employed by Arkema to produce spherical PA12 powders that are commercialized as Orgasol[®] Invent Smooth. PA12 powder prepared via this method exhibits a sintering window similar to that of the polymer feedstock (10–15 °C), but has better sphericity and a narrower particle size distribution. (Figure 2.9b, d). The polymer chains of Arkema's PA12 powder are also end-capped so that post-condensation does not occur, whereas those of Evonik's PA12 powder are not (Figure 2.9e, f). Consequently, the melt viscosity of Arkema's PA12 powder is fixed, while that of Evonik's PA12 powder increases with successive process loops [40].

Figure 2.9. SEM images of the powders produced by different methods: (a) dissolution-precipitation (PA12), (b) direct polymerization (PA12), and (c) milling (PA11); (d) DSC curves of the PA12 powders from Arkema and Evonik, showing the difference between their sintering windows. Reproduced with permission [14]. Copyright 2018, Hanser. (e, f) Schematic of polymer chain end-capping and its effects on the molecular weight change. Reproduced with permission [33]. Copyright 2014, Springer Nature.

Another commercial PA12 powder, HP 3D HR PA12, is used by HP for the MJF process that it has developed. Sillani et al. revealed that the HP PA12 powder was different from the Duraform® PA powder used for SLS [70]. In particular, the HP PA12 powder was less prone to aging, i.e., post-condensation, as evidenced by the 18% increase in the weight-average molecular mass of the HP PA12 powder after MJF, compared to the 170% increase observed with the Duraform® PA powder after SLS. It was speculated that the polymer chains in the HP PA12 were end-capped, and for this reason, its powder recyclability was visibly higher than the Duraform® PA. The commonly used powder refresh ratios (the ratio of new powder to recycled powder) for HP PA12 and Duraform® PA powders are 20:80 and 50:50, respectively. It is worth highlighting that the mechanical properties of PA12 specimens printed by MJF vary minimally with different print orientations [71]. Surprisingly, several studies reported that the specimens that are built in the *z*-direction exhibited higher Young's modulus

and strength than those built in the x - or y -directions, contrary to what is typically observed with SLS [70, 72, 73]. It is conjectured here that this phenomenon is attributed to the diffusion of the fusing agent along the z -direction due to gravitational force, which creates a continuous transmission of thermal energy into the previous layer, thus promoting better melting and adhesion across the interlayers (z -direction) than within the layer planes (x - and y -directions). Nevertheless, investigations on the MJF process are limited, and further studies on its underlying process mechanisms are required.

PA11 is another type of PA produced by the polymerization of 11-aminoundecanoic acid. It has a melting peak at ~ 190 °C, and its main advantage over PA12 is the higher toughness and impact strength achievable. PA11 powders are normally prepared by mechanical grinding. As a result, the PA11 powders tend to exhibit poorer flow than spherical or potato-shaped powders (Figure 2.9c). Coupled with their inherently narrower sintering window (~ 15 °C), PA11 powders are more difficult to process than PA12 powders [74].

PA6, also a member of the PA family, has good thermal resistance and is widely used for applications requiring creep and fatigue resistance, especially in the automotive industry. PA6 has a higher Young's modulus and strength than PA12, and the price of PA6 pellets is only 20–30% that of PA12 due to the more extensive application and higher popularity of PA6 [63]. In recent years, chemical companies such as BASF and Solvay have commercialized PA6 powders as Ultrasint[®] and Sinterline[®] Technyl[®], respectively, for SLS. Nonetheless, the use of SLS for PA6 is still confronted with many challenges, the greatest being its high melting temperature (~ 220 °C) that most commercial SLS machines are unable to handle. Furthermore, it is necessary to pre-condition the highly hygroscopic PA6 powders before using them for SLS to ensure that the printed parts are not embrittled.

While PAs are the mainstay of SLS materials today, there has been an increase in studies on the use or development of new materials for SLS, with polyesters being one of them. Polyesters are another class of engineering polymers, and they contain ester linkages along the polymer backbone. They are formed from the esterification reaction between alcohols and carboxylic acids or acid chlorides, or the transesterification reaction between alcohols and esters. PET and PBT are polyesters that are commonly used in the food, textile, and electronics industries, and they are produced from the polycondensation reaction between terephthalic acid and ethylene glycol or 1,4-butanediol, respectively. SABIC and DSM have recently commercialized PET and PBT powders, respectively, for SLS.

PET exhibits high strength and stiffness, good barrier properties, and good electrical insulating properties. Highly crystalline PET has a melting peak at ~ 250 °C and a sintering window of ~ 50 °C that is much wider than that of PA12 [75]. The intermediate melting point of PET helps to bridge the gap in SLS materials that mostly either have T_m below 200 °C (e.g., PA12) or above 300 °C (e.g., PEEK) [76]. Due to the slow crystallization rate of PET, most injection molded PET parts are amorphous or have a low crystallinity. Still, with the slow cooling conditions in SLS, it has been possible to fabricate semi-crystalline PET parts [77]. Unlike PA12, of which the powder reuse is only possible by blending with virgin PA12 powder, used PET powders exhibit only a small increase in molecular weight and can be reused as they are [75]. Even with irregularly shaped PET powders formed from mechanical grinding, laser-sintered PET specimens can achieve superior dimensional accuracy, surface finish, and flexural modulus and strength over PA12 specimens [76].

PBT is another type of polyester that exhibits good impact, chemical, and thermal resistance. Similar to PET, PBT powders for SLS are produced by mechanical grinding

[78]. Most of the PBT materials used for conventional manufacturing, such as injection molding, are homopolymers with a melting temperature of ~ 230 °C. PBT homopolymer has been processed by SLS using a T_b value of 210 °C, but because of its fast crystallization rate, there was a high likelihood of warping during SLS processing [47]. To reduce the warping tendency of PBT, a PBT copolymer containing 10 mol% isophthalic acid that demonstrated a reduced melting temperature and crystallization rate was successfully processed by SLS using a T_b value of 190 °C [78]. The laser-sintered PBT specimens exhibited UTS and elongation at break values of 54.9 MPa and 3.41%, respectively.

TPEs are another type of engineering polymer; unlike most elastomers that are thermosetting, TPEs are not chemically cross-linked and can undergo repeated melting and crystallization cycles, allowing them to be processed by SLS. TPEs are categorized into blends and block copolymers. A TPE blend is produced by a mechanical mixture of semi-crystalline and amorphous polymers. In contrast, a TPE block copolymer is produced by copolymerizing two or more monomers to form discrete blocks of crystalline and amorphous domains within the same molecular chain. Regardless of the type of TPE, the rigid, crystalline polymer domains function as the thermally stable component, while the soft, amorphous domains impart elastomeric character to the material.

TPU is the most common type of TPE block copolymer used for SLS, and different grades can be produced depending on the structure and ratio of the monomers used. TPUs are produced by reacting diisocyanates with long-chain diols and short-chain diols to form flexible and rigid segments, respectively [79]. The elongation at break of laser-sintered TPU specimens generally exceeds 200%, making them extremely suitable for applications involving large strains [56, 58, 80]. One of the greatest values of TPU is

that its powders can be reused through several SLS processing cycles (~14 cycles), which generates significant material and cost savings. Even when recycled powders are used, the UTS and Young's modulus of the specimens remains largely unchanged, even though the elongation at break decreases [56].

By coupling the elastic and flexible nature of TPU with an appropriate structural design, TPU can be suitable for the fabrication of soft 3D mechanical metamaterials that can be used for wearable devices and energy absorption applications [57, 81]. Yuan et al. exemplified this with laser-sintered TPU 3D auxetic lattice structures designed using Bucklicrystal unit cells as building blocks [58]. The laser-sintered TPU 3D auxetic lattice structures exhibited the ability to sustain a wide range of compressive strains; they could also withstand repeated compression cycles over large deformations, showing a strong shape recovery capability (Figure 2.10).

Figure 2.10. Laser-sintered TPU 3D auxetic lattice structures that were designed by assembling Bulklicrystal unit cells with 6 holes (6H) or 12 holes (12H) periodically, to

form body center cubic (*bcc*) and simple cubic (*sc*) configurations: (a) *bcc*-6H, (b) *sc*-12H and (c) *bcc*-12H (scale bars represent 1 cm). (d) Stress-strain curves for the *sc*-12H lattice structure upon cyclic compressive loading at a strain rate of 1 mm/s. Reproduced with permission [58]. Copyright 2017, Elsevier.

Apart from the abovementioned engineering polymers that are already available or on the verge of entering the SLS material market, some researchers also focus on the processability of other engineering-grade polymers, for example, semi-crystalline syndiotactic PS and POM [27, 82].

High-performance polymers

High-performance polymers are characterized by their high mechanical performance and excellent thermal and chemical resistance. They can retain their desirable properties even when subjected to harsh conditions and can serve as a lightweight alternative for applications that involve high operating temperatures. Polyaryletherketones (PAEKs), PPS, polyimides [83, 84], and fluoropolymers [85] belong to this class of polymers and have been studied for SLS. Due to their high melting temperatures, high-temperature SLS systems (e.g., EOSINT P800) are needed to process these polymers.

PAEK is a family of high-performance aromatic polymers that exhibit exceptional chemical resistance and thermal stability due to their aromatic backbones. These polymers can maintain their excellent mechanical properties even at high temperatures. The polymer backbone chains of PAEK contain alternating ketone and ether groups, and the ratio and sequence of the groups affect the T_g and T_m values. In general, the higher the ratio of the ketone groups, the higher the values of T_g and T_m . In the PAEK family, PEEK, PEK, and PEKK are promising and have been studied for SLS. PEEK has a high value of T_m of ~ 340 °C, thereby requiring a high value of T_b (> 300 °C) [86]. Laser-

sintered PEEK specimens can achieve a tensile modulus and strength of 3500–4500 MPa and 80–90 MPa, respectively, which are significantly higher than those of commonly used PA12 [17, 86–88]. The high service temperature, excellent chemical resistance, and biocompatibility of PEEK parts make them very suitable for applications not only in the aerospace and automotive industries but also in the medical field. However, most attempts to sinter PEEK have been focused on the production of medical devices (Figure 2.11) [89].

PEK has a higher melting point than PEEK at $\sim 370^\circ\text{C}$, and sintered PEK specimens exhibit a higher service temperature, tensile modulus, and strength than PEEK specimens [90]. PEK demonstrates a high load-bearing capacity and excellent chemical resistance and thermal stability, making it very suitable for automotive, aerospace, and aeronautical applications. The mechanical properties of sintered PEK specimens could approach those of injection-molded specimens, and near-fully dense specimens with excellent thermal and mechanical properties that vary minimally with their build positions could be fabricated [87, 91].

Figure 2.11. SLS of a cranial implant using PEEK powder: (a) location of the implant, and (b, c) the sintered implant. Reproduced with permission [89]. Copyright 2018, Elsevier.

PEKK has a significantly higher melting point (~ 390 °C) than PEEK and PEK. PEKK not only exhibits high tensile modulus, strength, and elongation at break; it is also flame retardant and has a low hygroscopicity. Owing to its excellent properties, PEKK is extremely popular for aerospace applications. Although it is challenging to process PEKK due to its high melting point, its low shrinkage (30% lower than PA12) [84] and potentially high powder reusability rate [90] make it a promising high-performance material for SLS.

PPS is a type of polyarylene but with sulfide linkages. It has a melting temperature of ~ 285 °C. Like PAEKs, the aromatic backbone of PPS is responsible for its high chemical resistance and thermal stability. Although the achievable elongation at break and UTS of PPS specimens are lower than those of PEEK and PEK specimens, a unique characteristic of PPS is its electrical conductivity, which makes it suitable for electronic applications [90]. The use of SLS for PPS powders is thus of interest, and related investigations are in the initial stages [92, 93]. Unfortunately, the limited availability of high-temperature SLS systems has greatly restricted the research opportunities involving high-performance polymers; therefore, researchers have been devising low-temperature methods to process such polymers [85, 88, 94]. Recently, Chatham *et al.* reported the processing of PPS using a low value of T_b of 230 °C by carefully choosing the process parameters to reduce part warping and curling [92]. It is conjectured here that the successful printing might be due to the slow crystallization rate of PPS, which resulted in a low degree of crystallization and hence minimized shrinkage and warpage during the sintering process, even when a low value of T_b was used. The laser-sintered PPS specimens exhibited average UTS and elongation at break values of 61.8 MPa and 3.3%, respectively.

Commodity polymers

Commodity polymers are polymers that are used in high volumes for a diversity of applications. Polyolefins, including PP, PE, and polybutylene, are such polymers that have been reported for SLS [95]. PP and PE take up the largest market share due to their well-balanced mechanical properties and excellent chemical resistance.

PP has been gaining attention as a new SLS material due to its low cost, good chemical resistance, hydrophobicity, and widespread application in today's industries. PP homopolymer (homo-PP) is subdivided into atactic, syndiotactic, and isotactic PP (*i*PP), where the methyl side groups are oriented randomly, alternatingly, and similarly along the polymer chain, respectively. Commercial homo-PP is mostly isotactic due to the higher crystallinity, melting temperature (~ 160 °C), and modulus achievable; many studies investigating the use of SLS for PP have also focused on *i*PP [15, 17, 18, 21-23, 96, 97]. To address the brittle nature of *i*PP (elongation at break of 1–7% for SLS specimens), ethylene has been incorporated into the polymer backbone to form PP copolymers that exhibit much higher toughness (elongation at break of 75–400%) [27-29]. The melting temperature of PP varies with the tacticity and ethylene content in the polymer chain, where lower tacticity and higher ethylene content generally lead to lower melting temperatures.

Most polyolefin powders available on the market are cryogenically ground and have irregular shapes, but studies have presented alternative powder production methods. For instance, PP microspheres can be prepared via the dissolution-precipitation process using xylene [18], during which the PP concentration and quenching temperature can be adjusted to optimize the size and morphology of the spherical powder particles that are produced. When the dissolution-precipitation process is coupled with dry-coating, the powder flow can be further improved and be

comparable to that of a commercially available PA12 powder [49]. Polyolefin powders can alternatively be produced by melt emulsification [66]. Melt emulsification is currently being used by ASPECT, an SLS material supplier, to produce spherical PP powders which are commercialized as Asphia PP [14].

PE is a commodity polymer with lower melting temperatures than PP and is typically classified by its density and chain branching. UHMWPE, HDPE, and LDPE are the most popular PE materials. The use of PE in SLS has been largely restricted to research studies. Thus far, HDPE [98, 99] and UHMWPE with molecular weights ranging between 3500 kDa and 6000 kDa have been investigated because of their high potential for functional applications [100-103]. UHMWPE, in particular, has excellent corrosion and wear resistance, a low coefficient of friction, and exceptionally high elongation, toughness, and impact strength. However, the high melt viscosity resulting from the ultrahigh molecular weight of UHMWPE leads to a slow sintering rate [102]. The SLS process is complicated by the narrow sintering window ($< 5\text{ }^{\circ}\text{C}$) and low powder bed density of UHMWPE that contributes to a high degree of shrinkage [100, 102]. Therefore, despite the potentially excellent properties of UHMWPE, their printed specimens thus far unfortunately exhibit poor mechanical properties and require post-processing methods such as hot isotactic pressing to render them useful for functional applications.

2.2.2.3. Polymer blends

Polymer blending is attractive as an easy, cost-effective alternative to obtain parts with specific multiphase structures and properties [104-106]. It is versatile and has a high potential for commercial applications since the properties of polymer blends can be controlled by a wise choice of polymers that form the blends. It has been

demonstrated that a higher part accuracy and density can be achieved for SLS parts by blending amorphous polymers into a semi-crystalline matrix, e.g., the blending of PC into a PBT matrix to form a PBT/PC blend [107]. Nevertheless, polymer blends are much less studied than neat polymers and their composites due to the need for chemical compatibility between the blend materials and the thermal constraints that render the sintering of the blends more difficult [8, 108]. Furthermore, the temperature range between which the sintering process should occur tends to be narrower in polymer blends than their neat constituent polymers, implying that the polymer blend is more sensitive to changes in the powder bed temperature, and thus fine temperature control is imperative. The use of SLS for polymer blends can only be achieved by a wise selection of the blend constituents. Nevertheless, several blends for SLS, including PA12/HDPE [106], PA12/PA6 [104, 105], and PA12/PP [8], have been reported.

Driven by the need for a wider range of materials for SLS to have more potential applications, researchers have been looking into the laser sintering of various polymers apart from PA12, whether on optimizing processing parameters to sinter the polymer powders successfully or on developing new polymer powders suitable for the process (Table 2.2). TPEs such as TPU and high-performance and biocompatible polymers such as PEEK have been gaining increasing interest recently because these polymers exhibit unique properties that can enable entirely new applications, especially in the aerospace and medical fields.

2.2.3. Polymer composite powders

Polymers and their blends tend to be insufficient for producing fully functional and load-bearing parts due to a lack of mechanical strength, thermal stability, and/or functional properties. This restricts the application of SLS for the manufacture of end-

use products, and thus composite powders for SLS have been developed to overcome this limitation. The addition of inorganic fillers usually serves to improve properties such as mechanical strength, thermal stability, electrical conductivity, and bioactivity of composite parts. Achieving properties that are unattainable by any of the constituents alone is a major reason that polymer composites are the most widely studied for SLS material development.

Polymer composite powders are prepared by two major routes, one of which uses pure polymer powder as the starting material, and the other uses pure polymer pellets, although pure polymer powders can also be used for the latter. Several composite powder preparation methods can be used for SLS, including dry mixing, wet mixing, melt blending and mechanical grinding, and solution mixing. The dry mixing and wet mixing methods use pure polymer powders, while the melt blending and mechanical grinding, and solution mixing methods use pure polymer pellets. A less popular route for composite powder preparation is in situ polymerization, which uses monomers as starting materials (Figure 2.12).

Dry mixing is the process of directly mixing polymer powders and fillers under dry conditions via mechanical agitation. At present, dry mixing is well established for the large-scale production of composite powders due to its simplicity and low cost. Unfortunately, due to the lack of chemical interaction between the fillers and the polymer powders, the filler dispersion is often poor; this is especially notable with nanofillers due to their high specific surface area and high surface energy, and hence a high tendency to aggregate. Therefore, dry mixing is more suitable for microfillers.

Wet mixing, often in the form of surface coating, is the process of mixing fillers and polymer powders in the presence of a solvent in which the polymer powders are insoluble [109]. Fillers are coated onto the surfaces of polymer powder particles through

Table 2.2. Polymer powders used for SLS and the mechanical and thermal properties of their printed parts.

Polymer			T_m (°C)	Modulus (MPa)	Ultimate strength (MPa)	Elongation at break (%)	HDT ^{a)} (°C)	Part density (kg/m ³)	Manufacturer/Reference
Semi-crystalline	Engineering	PA12	176	1700	50	20	-	930	EOS
			182	1800	50	10	91	990	BASF
			183	1800	45	20	40	-	Arkema
			-	1586	43	14	95	1000	3D Systems
		PA11	201	1600	48	45	46	990	EOS
			203	1750	52	28	76	1020	BASF
			201	1500	45	45	44	-	Arkema
			-	1590	51	64	56	1020	3D Systems
		PA6	220	3700	66	2	103	1150	BASF
		PET	251	2486 ^F	67.9 ^F	-	-	1339	[76]
			242	3000	66	4.9	-	-	[21, 22]
		POM	165	2900	42	3.5	-	-	[17]
		TPU	160	69	13	350	-	1170	BASF
			-	5.3	2	220	-	780	3D Systems
	High-performance	PEEK	-	3500	82	2	-	-	[17]
			340	3700	79	-	-	-	[88]
		PEK	372	4250	90	2.8	165	1310	EOS
		PPS	285	2440	62	3	-	1190	[92]
	Commodity	PP	140	1200	27	12	-	895	EOS
			140	1400	28	30	62	890	BASF
		HDPE	128	1200	23	8.5	-	-	[17]
		UHMWPE	140	1500	0.2	-	-	-	[100, 102]
		PS	105 (T_g)	1600	5.5	0.4	-	770	EOS
			-	1604	2.84	-	-	860	3D Systems
Amorphous		PC	-	40	1	5	-	-	[59]

^{a)} Heat deflection temperature under a 1.80 MPa load.

All modulus, ultimate strength and elongation at break values were obtained under tensile conditions, except that those denoted by the superscript F were obtained under flexural conditions.

van der Waals interaction, electrostatic attraction, etc. The nature of the surface coating process allows the preservation of the initial powder particle morphology.

Surface coating is well suited for nanofillers since the use of solvent allows the dispersion of nanofillers to be improved using ultrasonication. The surface coating approach was first reported for preparing an MWCNT-coated PA12 powder, where PA12 powder and MWCNTs were dispersed in water to form a suspension, which was subsequently heated to soften the surface of the powder particles without melting them, to allow better adhesion of the MWCNTs on the powder particle surfaces [110-112]. This approach has been extended to other polymers such as TPU and PEEK [113, 114], and was further developed by adding appropriate surfactants that served to improve the dispersion of fillers [115]. The surface coating can also be used with other nanofillers, including graphene and montmorillonite [24, 114, 116].

Figure 2.12. Summary of the composite powder preparation methods.

Melt blending is a common method to produce polymer composites by incorporating fillers into a molten polymer matrix under high temperature and shear force using an extruder. The combination of melt blending and subsequent mechanical grinding is a viable way to achieve composite powders with good filler dispersion [24, 117, 118]. Goodridge et al. melt-blended 3 wt% carbon nanofiber (CNF) with PA12 and produced a CNF/PA12 composite powder by cryogenic grinding; the laser-sintered composite specimens exhibited a 22% increase in storage modulus [119]. However, the irregular powder morphology limited the enhancement in the mechanical performance of the laser-sintered specimens. To further improve filler dispersion and filler-polymer interfacial interactions in composite powders, a pre-treatment process utilizing solid-state shear milling can be employed before the melt blending and mechanical grinding steps. This method was used to produce barium titanate/PA11 and boron nitride/PA12 composite powders [74, 120].

Solution mixing is a method that utilizes a solvent in which a polymer is soluble and fillers can be dispersed. In this process, a polymer is first dissolved in a suitable solvent, followed by the dispersion of fillers, which is typically aided by ultrasonication or stirring to better mix the filler suspension with the polymer solution. Composite powder particles are subsequently produced from the solution either by precipitation or solvent removal. The dissolution-precipitation process that has been widely used to produce pure polymer powders can also be utilized to prepare composite powders for SLS. During the precipitation process, the polymer crystallizes from the solution by taking the fillers as heterogeneous nuclei, and thus the fillers are encapsulated within the powder particles formed. Nevertheless, because the addition of fillers complicates the crystallization and precipitation behavior of the polymer, careful process control is needed. Dissolution-precipitation has been used for preparing carbon fiber/PA12

(CF/PA12) [121], nanosilica/PA12 [122], and organically modified montmorillonite/PP (OMMT/PP), [24] composite powders. Another common solution mixing method is solvent evaporation, of which the spray drying process is popular. In spray drying, powder particles are produced by atomizing the composite solution through a nozzle to form a spray of fine droplets, which are subsequently subjected to contact with hot air or inert gases to vaporize the solvent rapidly. The solvent evaporation method has been used to produce, for example, HA/PLA and hectorite/PA6 composite powders for SLS [35, 123].

In situ polymerization involves the polymerization of monomers in the presence of fillers, typically nanofillers. It permits the grafting of polymer chains on filler surfaces and thus promotes the dispersion of fillers in a polymer matrix. However, the use of the in situ polymerization method for directly producing composite powders has been limited because of the involvement of numerous reactants and the fine process control required. This method has been used to prepare nano-alumina/PS core-shell and silica/PA12 powders for SLS [64, 124].

The advantages and limitations of each preparation method, and some examples of the composite powders produced are summarized in Table 2.3.

2.2.3.1. Microfillers

Composite powders with micro-sized fillers are the most popular commercially, owing to a good balance between their ease of preparation, achievable part properties, and material cost. Such composite powders are usually prepared by mechanical blending, and modification to the fillers is occasionally carried out to improve their interfacial interactions with the polymer matrix.

Table 2.3. The advantages and disadvantages of different composite powder preparation methods and their applications.

Composite powder preparation method	Material	Advantage and disadvantages
Dry mixing	Glass bead/PA12 [72] Cu/PA12 [125, 126] CF/PA12 [127] GF/PA12 [128] Carbon black/PA12 [129] OMMT/PP [24] GNP ^{a)} /PEEK [114]	<ul style="list-style-type: none"> • Simple process • Low cost ■ Poor filler dispersion ■ Poor interfacial interaction
Wet mixing Surface coating	MWCNT/PA12 [110-112, 115, 130, 131] MWCNT/TPU [113, 130] SWCNT ^{b)} /TPU [132] Carbon black/PA12 [133] Graphene/TPU [116] OMMT/PP [24] GNP/PEEK [114] GNP/PA12 [134]	<ul style="list-style-type: none"> • Low cost • Moderate filler dispersion on powder particle surfaces • Good interfacial interaction possible ■ Solvent intensive
Melt blending and mechanical grinding	CNF/PA12 [119] OMMT/PP [24] BaTiO ₃ /PA11 [74]	<ul style="list-style-type: none"> • Good filler dispersion in powder particles • Good interfacial interaction possible ■ Irregular particle shape ■ Poor powder flowability ■ Particle rounding or other post-processing treatment required
Solution mixing Dissolution-precipitation	CF/PA12 [121, 135] Nano-SiO ₂ /PA12 [122] OMMT/PA12 [122] OMMT/PP [24]	<ul style="list-style-type: none"> • Good filler dispersion in powder particles • Good interfacial interaction possible ■ Complex and time-consuming procedure ■ Difficult process control ■ Solvent intensive
Solution mixing Solvent evaporation	HA/PLA [123] Hectorite/PA6 [35] Ca-P/PHBV ^{c)} [123, 136] CHAp ^{d)} /PLA [123, 136]	<ul style="list-style-type: none"> • Good filler dispersion in powder particles • Good interfacial interaction possible ■ Solvent intensive
In situ polymerization	Nano-SiO ₂ /PA12 [64] Nano-Al ₂ O ₃ /PS [124]	<ul style="list-style-type: none"> • Good filler dispersion in powder particles • Good interfacial interaction possible ■ Complex and time-consuming procedure ■ Difficult process control

^{a)} Graphene nanoplatelet; ^{b)} single-walled CNT; ^{c)} calcium phosphate/poly(3-hydroxybutyrate-co-3-hydroxyvalerate); ^{d)} carbonated hydroxyapatite nanoparticle.

Glass beads are widely used in commercial SLS materials; in fact, many SLS material suppliers have glass bead/PA12 composite powders in their material database. Glass beads, being spherical, can produce parts with isotropic enhancements. They are also able to provide high stiffness and dimensional accuracy, which are advantageous for SLS. Most importantly, glass beads can be obtained at a low cost, making them well suited for commercialization. Metal fillers such as copper and aluminum are also used as reinforcements to improve the modulus of printed parts as well as their thermal and electrical conductivity [125, 126]. For instance, Alumide® from EOS is a commercial aluminum/PA12 composite powder used to manufacture stiff parts with metallic luster for automotive applications.

Fibers, especially glass fibers (GFs) and carbon fibers (CFs) are used for mechanical reinforcements due to their high strength and lightweight nature. Depending on the fiber material, length, and diameter, a range of property enhancements can be achieved. Generally, fibers with higher aspect ratios generate greater improvements to the Young's modulus of sintered parts. For instance, the PP copolymer composite specimens reinforced by GFs of 150 μm length exhibited higher tensile modulus than those with 50 μm long GFs of the same diameter [28]. The mechanical properties can be further enhanced by increasing the fiber loading, as seen from the increase in tensile modulus (59%) when the loading of 50 μm GFs increased from 10 wt% to 30 wt% [137]. The addition of fibers reduces the flowability of the polymer powder, which can lower the powder processability and limit the achievable part properties. Therefore, the addition of flow agents such as silica may be required to ensure good powder flow. However, in extreme cases, the poor powder flow from excessive quantities of fibers may be difficult to compensate for.

CFs normally have inert surfaces that often result in poor interfacial interactions with the polymer matrix, causing fiber pull-out of printed parts and reducing their UTS [137]. Surface modification of CFs is necessary to introduce polar functional groups such as oxygen or hydroxyl groups onto them, which would improve the interfacial interactions between the CFs and polar polymers such as PA12. Yan et al. treated CFs with nitric acid and prepared CF/PA12 composite powders via the dissolution-precipitation powder preparation method [135]. The CFs showed good interfacial adhesion and dispersion in the composite powder, and the laser-sintered composite specimens exhibited enhanced thermal stability, flexural modulus, and flexural strength compared to the PA12 specimens. Using acid-treated CFs, Wu et al. prepared CF/PA12 composite powders by dry mixing and revealed that the functional groups on the CFs were thermally decomposed and released as a gas during the sintering process, which resulted in high porosity and poor mechanical properties of the printed specimens [127]. By subjecting the acid-treated CFs to further heat treatment at 400 °C under an inert atmosphere, the acid-modification effect was partly preserved, and the porosity of the sintered composite specimens could be reduced.

The increasing popularity of sustainability and green chemistry has prompted the development of composite powders using sustainable fillers. Environmentally friendly, biodegradable, and recyclable wood/plastic composites, including eucalyptus/PA12 and eucalyptus/polyethersulfone, have been developed for SLS. The printed parts show high dimensional accuracy because of the low thermal conductivity and sintering rate of the composite powder particles [138-140]. The low mechanical properties of printed parts can be further improved via the post-densification of their green parts by infiltration [141-143].

2.2.3.2. Nanofillers

Known for delivering significant property enhancements at low loadings, nanofillers have huge advantages for load-bearing and functional applications. Unlike most microfiller-reinforced polymer composites where the increase in mechanical strength is typically accompanied by a notable reduction in elongation at break, nanofiller-reinforced polymer composites can achieve a simultaneous increase in both strength and toughness when nanofillers are well dispersed.

Carbon nanofillers, including CNTs, CNFs, graphene, graphene oxide (GO), and carbon black, have been extensively studied as nanofillers for SLS composite powders. A critical condition to fulfill the maximization of the functionalities of these nanofillers is to ensure their good dispersion in/on polymer powder particles. Yuan et al. demonstrated the importance of filler dispersion using the s-CNT/PA12 powders that were prepared by surface-coating the PA12 powder particles with the surfactant-treated CNTs [115]. The surfactant served to enhance the dispersion of CNTs onto the PA12 powder particles and improved the interfacial interaction between treated CNTs and PA12 through covalent bonds (Figure 2.13). At the loading of only 0.5 wt% s-CNTs, the laser-sintered s-CNT/PA12 specimens were shown to have 31.8%, 84.9%, and 37.5% enhancement in their UTS, toughness, and elongation at break values, respectively, compared to those of the laser-sintered PA12 specimens [144]. In addition to s-CNT/PA12, this surfactant-facilitated surface coating method has been used for preparing s-CNT/TPU [130] and s-CNT/PA11 [145] composite powders for SLS.

While the enhancement of mechanical properties may be one aspect, carbon nanofillers are more often used to impart electrical and thermal conductivity to printed parts. The near zero-shear-rate manufacturing nature of SLS, coupled with conductive composite powders prepared by surface coating, makes SLS an extremely suitable

method for fabricating segregated conductive networks. Yuan et al. proposed that segregated fillers located on the boundaries of surface-coated powder particles offered an efficient conduction path, thus allowing laser-sintered composites to exhibit enhanced conductivity and ultralow percolation behaviors (Figure 2.14a, c) [131]. The improvement in electrical conductivity of such laser-sintered composite specimens was exemplified with s-CNT/PA12 and s-CNT/TPU composite specimens, of which the electrical conductivity values increased by seven and eight orders of magnitude compared to their pure polymer specimens, respectively, at a loading of 1 wt% s-CNTs (Figure 2.14b). With carbon black/PA12 composite powders prepared by surface coating, the conductive percolation threshold of the laser-sintered specimens was at 0.87%, which was significantly lower than the reported 4.3% of compression-molded specimens [133]. Using soft polymer matrices such as TPU, the surface coating of conductive fillers is useful for flexible conductive devices such as piezoresistors [132].

Figure 2.13. (a) Illustration of the surfactant, sodium cholate, attached onto a CNT. (b) Covalent bond formed between sodium cholate and PA12 at elevated temperature. SEM images of different powder particles: (c) PA12, (d) CNT/PA12 and (e) s-CNT/PA12. Reproduced with permission [115]. Copyright 2016, Elsevier.

SLS allows the fabrication of structures with controllable microstructure and properties critical for determining the cell adhesion, cell growth, nutrient transport, and structural strength of scaffolds. This motivates the development of biocompatible composite powders that can be used to fabricate scaffolds that match complex anatomical structures.

Figure 2.14. (a) Schematic of the fabrication of a segregated conductive network by laser sintering composite powders that were prepared by surface coating, and (b) direct-current conductivity values of the laser-sintered and hot-compressed specimens using s-CNT/PA12 and s-CNT/TPU powders that were prepared by surface coating. Reproduced with permission [130]. Copyright 2018, Elsevier. (c) The microstructure of a laser-sintered specimen with segregated conductive CNT networks. Reproduced with permission [131]. Copyright 2019, Wiley.

Calcium phosphates are popular for developing biomaterials due to their osteoconductivity and biomimetic resemblance to the natural bone structure when mixed with other biopolymers [146]. HA is one of the most widely used nanofillers for SLS for biocompatible scaffolds or implants. It is a stable, crystalline calcium phosphate that,

when added, can enhance the bioactivity of scaffolds to stimulate bone growth. It can also improve the mechanical strength and cyclic fatigue resistance of scaffolds [147]. HA has been incorporated into PCL, poly(lactide-*co*-glycolide), or aliphatic PC for fabricating scaffolds with well-ordered macropores and interconnected micropores, which favor the seeding and distribution of transplanted cells [148-150]. Unlike HA that has slow resorption dynamics and mostly integrates itself into newly formed tissue after implantation, TCP is biodegradable and rapidly resorbable [151]. Therefore, TCP is popular for bone reconstruction and repair applications. The development of TCP composite powder for SLS has been exemplified with poly(methyl methacrylate) (PMMA) [152, 153] and PEEK [154], and can be extended to other polymer matrices.

BAG is another type of bioactive ceramic and can react with physiological fluids to form strong bonds with bones via the formation of bone-like HA layers. Reactions on the surfaces of BAG also lead to the release of ions that can induce favorable cellular responses and promote bone formation [155]. Furthermore, BAG can be added to reduce acidic byproducts generated by the *in vivo* degradation of polymers such as PLA [156]. However, at increasing BAG loadings, the mechanical properties of SLS-fabricated scaffold specimens deteriorate because of the poor interfacial interactions between BAG particles and the PLA matrix. Xu et al. proposed that BAG particles could be modified with cross-linkers that served as bridges between PLA and BAG to improve the interfacial interactions [157]. Using polydopamine as a cross-linker, the mesoporous structure of polydopamine-BAG (p-BAG) was preserved, and the particle dispersion and stress transfer efficiency of the composite was improved (Figure 2.15). The laser-sintered p-BAG/PLA porous scaffolds exhibited ~30% higher compressive modulus and strength than those of the unmodified BAG/PLA scaffold. Importantly, the cells preferentially adhered to, proliferated, and differentiated on the p-BAG/PLA scaffolds,

indicating the good biocompatibility and potential application of p-BAG in tissue engineering applications.

The inherent porosity of the powder bed (40–60%) and lack of external pressure in SLS allow the fabrication of porous and highly accessible structures, and the relative density of printed parts can be readily controlled by adjusting the process parameters [39]. This nature of SLS can be exploited to manufacture parts with high accessibility for various flow-related applications, such as analytical chemistry and catalysis [25, 158-161]. Since active materials for catalysis, adsorbent applications, etc. that are usually in powder form can now be incorporated into a highly accessible solid 3D structure, unfavorable adsorbent packing, uneven eluent flow, and excessive channeling are associated with the use of powder active materials can be circumvented. Importantly, the reusability of active materials can also be improved.

Figure 2.15. p-BAG/PLA composite scaffolds: (a) the schematic of the interactions between the modified BAG particles and the PLA matrix, and (b) the laser-sintered composite scaffolds measuring $12 \times 9 \times 8 \text{ mm}^3$. Reproduced with permission [157]. Copyright 2018, Elsevier.

The high accessibility of laser-sintered parts was confirmed with the metal-organic framework-PA12 (MOF-PA12) composites prepared by Li et al., in which the Brunauer-Emmett-Teller (BET) surface area of the MOF was mostly retained in the printed film after the SLS process (Figure 2.16a) [160]. The high recyclability of printed MOF-PA12 mixed matrix films was demonstrated with an $\text{NH}_2\text{-MIL-101(Al)}$ -PA12 matrix film. The

Figure 2.16. (a) Schematic of the printing of MOF-PA12 mixed matrix films using NH₂-MIL-101(Al)/PA12, HKUST-1/PA12, and ZIF-67/PA12 composite powders. (b) Recycling test of the NH₂-MIL-101(Al)-PA12 mixed matrix film. Reproduced with permission [160]. Copyright 2019, ACS.

pollutant removal efficiency was only slightly reduced from ~95% at the first absorption-desorption cycle to ~80% at the fifth cycle (Figure 2.16b). A similar adsorbent application was demonstrated with printed PA12 columns and meshes that exhibited high selectivity for [AuCl₄]⁻ in the presence of other dissolved metal ions that were at much higher concentrations, and the PA12 parts remained fully reusable after the removal of the adsorbed ions [162]. The use of SLS for catalysis was demonstrated with a laser-sintered heterogeneous Pd/silica/PP catalyst, which proved to be highly active and reusable for hydrogenation reactions [158].

Thermoplastic composite powders have been widely investigated for SLS (summarized in Table 2.4) because the parts fabricated from composite powders can achieve properties that cannot be attained by any of the constituents alone, thus enabling a myriad of applications. Fibers, for example, are the most popular for producing fully functional and load-bearing parts, while other fillers such as glass beads are used as a cost-effective solution for mechanical property enhancement. Nanofillers can significantly enhance the performance of printed parts at low loadings and are popular for imparting functional properties (e.g., thermal/electrical conductivity, piezoelectricity, bioactivity) to the polymer parts.

2.3.Nanoclays as reinforcements

Nanoclay minerals are among the most widely investigated nanofillers due to their natural abundance, environmental friendliness, and well-studied intercalation chemistry [31]. Such minerals consist of layers that are typically nanometres thick, with other dimensions in the sub-micron range. Exfoliated clay layers are known to reduce gas permeation and improve fire resistance due to the formation of tortuous paths, which impedes the diffusion of small molecules, such as oxygen and water, within the polymer. Therefore, the incorporation of clay is likely to enhance the thermo-oxidative stability of PP. Furthermore, the addition of even small amounts of clay into a polymer matrix is capable of improving part properties such as UTS, tensile modulus, and heat distortion temperature [31, 32]. Coupled with the good barrier properties and low cost of clay, it serves as a feasible nanofiller for PP. Potential applications for such a polymer nanocomposite material ranges from high-barrier packaging and water treatment to strong, heat-resistant automotive components [163, 164].

Table 2.4. Polymer composite powders used for SLS and the mechanical properties and the thermal and electrical conductivities of the printed parts.

Filler	Polymer	Modulus (MPa)	Ultimate strength (MPa)	Elongation at break (%)	Thermal/ electrical conductivity	Reference
Ceramic						
HA	PCL	2.33 ^C	0.6 ^C	-	-	[165]
	HDPE	36–161 ^F	4.5–33 ^F	3.8–8.6 ^F	-	[147]
Nano-HA	PCL	3.17 ^C	-	-	-	[148]
	PLGA ^{a)}	3.28 ^C	32.81 ^C	50	-	[149]
	PC	25.6 ^C	8.14 ^C	-	-	[150]
	PEEK	-	23.3	2.7	-	[166]
BAG	PLA	79 ^F	2.4	6.9	-	[156]
	PLA	3600 ^C	62.9 ^C	-	-	[157]
Nano-SiO ₂	PA12	1980	46.3	20.07	-	[122]
	PA11	720	-	73	-	[167]
BaTiO ₃	PA11	2500	47	11	-	[74]
BN	PA12	755	6.0	-	0.55 W/mK	[120]
TiO ₂	PEEK	-	15.3	5.0	-	[166]
Al ₂ O ₃	PEEK	-	25.3	8.0	-	[166]
ZrO ₂	PEEK	-	18.1	5.9	-	[166]
Y ₂ O ₃ -stabilized ZrO ₂	PA12	-	23	-	-	[35]
Montmorillonite	PA12	1870	47.2	17.7	-	[168]
	PLA	680 ^F	-	-	-	[118]
Hectorite	PA12	-	26	-	-	[35]
GF	PP	1117	19	-	-	[28]
	PBT	-	60	3	-	[137]
Wollastonite fiber	PP	709	19	-	-	[28]
Carbon						
CF	PA12	4700 ^F	112 ^F	-	-	[135]
	PA12	5800	80	-	-	[127]
Carbon black	PA12	1450 ^F	-	-	1×10 ⁻⁴ S/cm	[169]
GNP ^{b)}	PA12	6200	58	17	-	[170]
	PEEK	-	104	6.5	0.45 S/m	[114]
MWCNT	PA12	4000	54	21	0.13 W/mK	[110]
	PA12	1301	58	33	0.25 W/mK	[144]
	TPU	-	17.5	465	3.6 mS/m	[113]
Metal						
Potassium titanium whisker	PA12	-	68.3	-	-	[171]
Ti	PA	-	0.04	-	0.588 W/mK	[172]
Wood						
Eucalyptus	PA12	180	3.7	-	0.13 W/mK	[139]
	PES	-	0.014	-	-	[138]
Birch powder, wax	Copolyester	-	1.2	-	-	[143]

^{a)} Poly(lactic-co-glycolic acid); ^{b)} graphene nanoplatelet.

All modulus, ultimate strength and elongation at break values were obtained under tensile conditions, except that those denoted by the superscripts F and C were obtained under flexural and compressive conditions, respectively.

2.3.1. Phyllosilicates

Most clay minerals are phyllosilicates that exist naturally as stacked layers, and the gap between the layers is termed interlayer or intra-gallery. Phyllosilicates are commonly classified according to their crystalline structure into the 1:1 (tetrahedral-octahedral) and 2:1 (tetrahedral-octahedral-tetrahedral) families, with the 2:1 family of phyllosilicates being the most commonly used for the preparation of nanocomposites [164, 173].

The 1:1 phyllosilicates consist of thin layers of a tetrahedral and an octahedral sheet interconnected by oxygen atoms, and they typically have little to no layer charge (Figure 2.17a). This is because any substitution of cations within a sheet is usually accompanied by a compensating substitution in the other sheet to maintain neutrality within the layer [164].

In contrast, the 2:1 phyllosilicates consist of thin layers, within which an octahedral sheet is sandwiched between two tetrahedral sheets, and the sheets are interconnected by oxygen atoms (Figure 2.17b). The aspect ratios of such phyllosilicates are particularly high, often exceeding 1000 as their lateral dimensions can go up to several microns [31]. The 2:1 phyllosilicates usually have negatively charged layers due to isomorphic substitution of cations within the tetrahedral or octahedral sheets (i.e., the substitution of $M^{(x+1)+}$ by M^{x+} , where M is a metal cation), and the negative charge is balanced by alkaline or alkaline earth cations that are located in the interlayer. Depending on the type of counterion, the interlayer distance, the force of attraction between layers, and the exchangeability of the counterion varies. In minerals such as mica, the interlayer distance is small as the counterions fit well between layers. The layers and counterions are strongly bonded by electrostatic forces of attraction, and the counterions are non-exchangeable. In other minerals, with the most popular being

smectites, the counterions do not fit as well (in the case of smectites, it is because the cations are hydrated, Figure 2.17b) and are only loosely bonded to the negatively charged layers; hence, the counterions are often exchangeable. The layers of such clay minerals are typically held together by weak van der Waals forces. Due to the weak forces of attraction between layers, the interlayer of these clay minerals can expand, a process termed as swelling [163, 164].

Figure 2.17. Schematic representation of the crystal structure of (a) kaolinite, a type of 1:1 phyllosilicate, and (b) montmorillonite, a type of smectite clay with exchangeable cations. Reproduced with permission [164]. Copyright 2016, Taylor & Francis Group.

2.3.2. Surface modification of the phyllosilicates

The dispersion of silicate layers is generally classified into three categories: stacked, intercalated, and exfoliated. Stacked silicates consist of agglomerated silicate layers with narrow interlayer spacing. Intercalated silicate layers have slightly larger interlayer spacing than when stacked, usually due to the intercalation of polymer chains between the silicate layers; nevertheless, an ordered silicate structure remains observable. Exfoliation is achieved when the silicate layers are far apart so that no regular structure is observed. Exfoliation is desired for significant property enhancements and for the reduced tendency to agglomerate and embrittle the nanocomposite.

Nevertheless, it is rare to see fully exfoliated silicates as they often appear with some degree of intercalation [174, 175]. Stacked silicates provide poor mechanical reinforcement as it is the bulk clay mineral that provides mechanical reinforcement, whereas, in intercalated composites, the intercalated clay tactoids provide the reinforcement [176]. In an ideal exfoliated composite, the clay platelets provide the reinforcement, and such composites can exhibit tremendous improvements in mechanical properties due to the high modulus of the clay platelets of 178–265 GPa.

Due to the charged nature of pristine 2:1 phyllosilicates, they are hydrophilic and incompatible with most polymers. The addition of such phyllosilicates into a polymer matrix often results in weak interfacial interactions and poor dispersion of clay layers that limit the enhancement of physical properties and formation of tortuous paths. To improve the compatibility with polymer matrices and achieve nanoscale dispersion of the clay layers, 2:1 phyllosilicates with exchangeable cations are commonly modified with positively charged surfactants such as alkylammonium salts via cation-exchange reactions. These modified clays are commonly termed as organoclays.

The number of surfactants that a clay mineral can adsorb into its interlayer at a specific pH depends on the type of clay and surfactant used, but it is mainly determined by the cation exchange capacity (CEC) of the clay. Generally, the higher the CEC, the more the surfactants that can be adsorbed, and the more compatible the organoclay becomes with organic polymers. Among the different types of 2:1 phyllosilicates with exchangeable cations, montmorillonites are most commonly used for the preparation of polymer nanocomposites due to their high layer charge, fine particle size, high surface area, and high CEC [164, 173, 177]. Furthermore, their reinforcing potential has been well documented. An ‘ideal’ montmorillonite has a CEC value of 0.915 meq/g, equivalent to one ion per 1.36 nm² [173].

Surfactants reduce the surface energy and improve the hydrophobicity of the clay layers while increasing the interlayer spacing concurrently [173]. There exist various factors determining how well a surfactant improves the compatibility and dispersion of clay layers within a polymer matrix, but the number and length of alkyl tails on the surfactants are fundamentally critical. Generally, surfactants with longer and more alkyl tails enhance polymer-clay interactions and the exfoliation of clay layers to a larger extent. An increase in the number of alkyl tails provides greater surface area for van der Waals interaction with polymer chains, facilitating the intercalation of polymer chains into the interlayers. At the same time, it provides more steric hindrance so that the amount of weak interfacial interactions formed between polymer chains and charged layer surfaces is reduced [173].

Meanwhile, surfactants with longer alkyl tails can increase the interlayer spacing more than those with shorter tails. By increasing interlayer spacing, the tendency of the clay layers agglomerating is reduced since the forces of attraction between layers are further weakened. In addition, there is more space in the interlayer for the intercalation of polymer chains. Generally, surfactants with longer and more alkyl tails enhance the interfacial interaction between organoclay and polymer matrix to a larger extent and better facilitate the exfoliation of clay layers. Therefore, they are preferred over those with shorter or fewer alkyl tails.

2.3.3. Organically modified montmorillonite

Research on the modification of montmorillonites using various types of surfactants has been ongoing for a long time. Commercially, there are several OMMTs available that are catered for different types of polymers, such as hydrogen bond-forming PAs and non-polar polyolefins.

A commercially available OMMT that has been widely used in polyolefins, including PP, is Cloisite 20 from BYK Additives (previously known as Cloisite 20A from Southern Clay Products), with the surfactant being dimethyl-di(hydrogenated tallow) ammonium ion (Figure 2.18). The hydrogenated tallow alkyl groups can improve the interfacial interaction between OMMT and PP by increasing the hydrophobicity of the clay layers and increasing the interlayer distance to facilitate exfoliation of the clay layers. In addition to its compatibility with PP matrices, Cloisite 20 can improve the mechanical properties and thermal stability of PP [32, 177, 178]. Coupled with its commercial availability, Cloisite 20 was determined as an appropriate filler for the development of OMMT/PP nanocomposite powders for SLS.

Figure 2.18. Structure of dimethyl-di(hydrogenated tallow) ammonium cation, where HT is hydrogenated tallow, a long chain alkyl group with 16 to 18 carbon atoms.

Chapter 3. Experimental Methods

This chapter provides details on the materials and experimental methodologies that have been adopted. This includes the type of materials used, the powder preparation methodologies, part fabrication techniques, and powder and specimen characterization methods.

3.1. Materials used

Isotactic PP homopolymer (Laser PP CP20) and copolymer powders (Laser PP CP60), henceforth referred to as CP20 and CP60, respectively, were purchased from Diamond Plastics GmbH. Both powders were produced by cryogenic grinding. PP copolymer (PP1101) and PA12 (PA2200) powders were purchased from EOS GmbH. The powders were produced by solution processes.

OMMT (Cloisite 20) and maleic anhydride-grafted PP (Scona TPPP 2112 FA) were purchased from BYK Additives & Instruments. Cloisite 20 is a bentonite salt with bis(hydrogenated tallow alkyl)dimethyl ammonium ions, with particle sizes ranging between 2–30 μm . Maleic anhydride-grafted PP, PPgMA, is a compatibilizer commonly used to improve the interfacial interaction between the PP matrix and OMMT.

Chemicals including sodium dodecyl sulfate (SDS), *p*-xylene, 1-hexanol, propan-2-ol, ethanol, and acetone were purchased from Sigma-Aldrich. The chemicals were used as received.

For OMMT/PP nanocomposite powder development, 1 wt% OMMT was used with CP20 for lab-scale production. Meanwhile, 1, 3, and 5 wt% OMMT were used with CP60 for large-scale powder production using melt extrusion and cryogenic grinding.

3.1.1. Mechanical mixing

To prepare OMMT/PP composite powders by mechanical mixing, weighed amounts of CP20 powder (99 g) and Cloisite 20 (1 g, 1 wt%) were added into a tumbler mixer (Inversina 2L) and dry-mixed for 4 h. Agate balls were added to enhance the mixing. The mechanically mixed composite powder is referred to as MM-OMMT/PP.

3.1.2. Surface coating

The surface coating of OMMT onto PP powder is largely based on a patented process (WO 2009/034361 A2). Cloisite 20 (0.3 g, 1 wt%) was first mixed in deionized water (80 mL), and the suspension was sonicated for 1 h at 500 W and 20 kHz. Next, CP20 (29.7 g) and deionized water (60 mL) were added, and the mixture was stirred at 95 °C for 30 min. The suspension was then cooled to room temperature, and the precipitate was separated from the solvent by centrifuge. It was subsequently washed with propan-2-ol followed by acetone and dried under vacuum at room temperature to yield SC-OMMT/PP powder.

For better dispersion, the surface coating was facilitated with SDS. SDS (0.9 g) was first dissolved in deionized water (60 mL) before Cloisite 20 (0.3 g, 1 wt%) was added. The suspension was sonicated for 1 h at 500 W and 20 kHz. Subsequently, CP20 (29.7 g) and deionized water (80 mL) were added, and the mixture was stirred at 95 °C for 30 min. The resulting suspension was then cooled to room temperature, and the precipitate was separated from the solvent by centrifuge. It was subsequently washed with propan-2-ol followed by acetone and dried under vacuum at room temperature to yield SC-OMMT/SDS/PP powder.

3.1.3. Thermally induced phase separation

To prepare the composite powders by TIPS, the process reported by Wang et al. [18] for the production of PP powder was modified with the addition of 1-hexanol as an anti-solvent to reduce particle fusion. OMMT was first sonicated in p-xylene. Next, PP powder and 1-hexanol were added, and the suspension was stirred at 140 °C under reflux to form a homogeneous solution. The solution was then cooled with a controlled temperature profile to precipitate the composite powder out of the solvent mixture. The composite powder was subsequently separated from the solvent mixture by Buchner filtration and washed with acetone. Finally, it was dried under vacuum at room temperature to yield TIPS-OMMT/PP.

3.1.4. Melt extrusion with cryogenic milling

To prepare the composite powders on a small scale by melt extrusion and cryogenic grinding, CP60 powder and Cloisite 20 were fed into two separate hoppers and melt-blended in a co-rotating twin-screw extruder (Leistritz Micro 18 twin-screw extruder) at 165–185 °C and 275 rpm, with the hopper feed rate pre-adjusted to ensure correct filler loading (1 wt% and 3 wt%). The extruded nanocomposite filament was directly fed into a pelletizer to produce nanocomposite pellets (Figure 3.), which were then cryogenically grinded into powder form to yield OMMT-1/PP, OMMT-3/PP, and OMMT-5/PP with 1 wt%, 3 wt%, and 5 wt% of OMMT, respectively.

To produce nanocomposite pellets compatibilized with PPgMA, a masterbatch was first produced by extruding PPgMA (300 g) and Cloisite 20 (100 g). The pellets were subsequently extruded with CP60 to produce compatibilized nanocomposite pellets with 1 wt%, 3 wt%, and 5 wt% OMMT. The compatibilized nanocomposite pellets are referred to as OMMT-1/PPgMA/PP, OMMT-3/PPgMA/PP, and OMMT-5/PPgMA/PP.

For large-scale nanocomposite production, CP60 pellets were purchased from Diamond Plastics and used in place of the powder form to minimize mechanical degradation due to the cryogenic grinding process. The pellets and Cloisite 20 were dried overnight at 70°C. They were then fed into the extruder via two separate hoppers and co-extruded at 165–185 °C and 275 rpm, with the hopper feed rate pre-adjusted to ensure correct filler loading (1 wt% and 3 wt%). The extruded nanocomposite filament was directly fed into a pelletizer to produce nanocomposite pellets. By engaging the service of Diamond Plastics, the nanocomposite pellets were cryogenically ground into nanocomposite powders under similar conditions as CP60. The produced nanocomposite powders with 1 wt% and 3 wt% OMMT are referred to as P-OMMT-1/PP and P-OMMT-3/PP, respectively.

Figure 3.1. A photo of the setup for melt extrusion.

3.2. Part fabrication

SLS part fabrication was carried out using the EOS P395 from EOS GmbH equipped with a 50 W CO₂ laser (Figure 3.). Tensile and bending specimens were sintered with geometries per ISO 527-1 Type 1BA and ASTM D790 standards, respectively, except for the tensile specimens of CP20, which were sintered per the ASTM D638 Type IV standard [179-181]. Notched impact specimens were sintered according to the ASTM D256 standard.

Figure 3.2. A photo of the EOS P395 from EOS GmbH.

Tensile specimens (ISO 527-1 Type 1BA) were also fabricated by injection moulding for comparison. They were prepared using the HAAKE™ MiniJet Pro Piston Injection Moulding System. This equipment utilizes a pneumatic piston to push the material from the heated cylinder into a mold to fabricate the specimens. The temperature of the cylinder for CP20, and CP60 and PP1101 was set to 185 °C and 175 °C, respectively, while the temperature of the mold was kept at 60 °C. The injection

pressure and time, and holding pressure and time were set as 350 bar and 15 s, and 150 bar and 10 s, respectively.

3.3. Characterization

The tools employed for powder and part characterization include physical, optical, thermal, and mechanical techniques. The optical methods comprise scanning and transmission electron microscopy, laser confocal microscopy, hot stage microscopy, and X-ray diffraction. The thermal methods include differential scanning calorimetry and thermogravimetry. The mechanical methods involve tensile, flexural, and impact testing.

3.3.1. Physical measurements

The HR of the powders was evaluated as per ASTM D7481 standard, using a tap density tester purchased from Funke Gerber [182]. PA2200 powder (100 g) was poured into a measuring cylinder (250 mL) mounted on the tap density tester, and it was subjected to 5 taps to measure its bulk volume V_{bulk} . The powder was tapped for an additional 495 times and subsequently another 750 times, and its volumes were recorded as V_{500} and V_{1250} , respectively. The testing procedure was repeated using the CP20, CP60, and PP1101 powders. A lower quantity of the PP powders (80 g each) had to be used because of their lower bulk powder densities. As the difference between the V_{500} and V_{1250} values of the PA12, CP20, CP60, and PP1101 powders was negligible ($\leq 2\%$), it was assumed that the powders were fully packed by 1250 taps. Therefore, the values for V_{1250} were considered as those for the tapped volume V_{tap} . The HR of the powders was then obtained by dividing the V_{bulk} values by the V_{tap} values.

For powder bed surface roughness measurements, a thin layer of powder was first spread across a customized 100 mm $\times$ 100 mm $\times$ 5 mm base plate containing a shallow trough measuring 0.3 mm deep and 10 mm wide. An area of the powder layer measuring 4 mm $\times$ 3 mm was then observed under a 3D laser scanning confocal microscope (Keyence VK-X200 Series). The surface profiles of the powder layers were evaluated using the MultiFileAnalyzer from Keyence.

3.3.2. Optical measurements

The morphology of the powder particles was observed by scanning electron microscopy (SEM) and field-emission SEM (FESEM), which were carried out at an accelerating voltage of 5 kV using JSM-5600 and JSM-7600F, respectively, from JEOL. Energy dispersive x-ray (EDX) was carried out with JSM-7600F at an accelerating voltage of 15 kV. The samples were deposited or mounted on a carbon tape, and subsequently coated with platinum since they are non-conductive. SEM was also used to observe the cross-sections of the SLS specimens, which were prepared by cryogenic fracture. The particle size distribution (PSD) of TIPS-OMMT/PP was evaluated from the SEM images of the powders using the ImageJ software. The PSD was obtained from measuring 2000 particles.

Isothermal hot-stage microscopy was conducted with a self-developed setup that had a Peltier heater placed under a microscope (Zeiss Axio Scope.A1 equipped with Axiocam ERc 5s from Carl Zeiss). The temperature control was calibrated using an empty glass slide placed on the heater and attached with a thermocouple. The temperature setting that gave an average surface temperature of 135 °C was used. The powder samples were deposited on a glass slide using a film applicator equipped with a doctor blade (ZAA 2300 from Zehntner Testing Instruments) to achieve single-layer

particle deposition. They were then heated to 160 °C for 3 min to ensure complete melting and finally maintained at 135 °C for up to 2 h.

For the MM-OMMT/PP, SC-OMMT/PP, and ME-OMMT/PP powders, the ultra-thin foil specimens for transmission electron microscopy (TEM) were obtained by microtoming their hot-pressed nanocomposite specimens. For TIPS-OMMT/PP, the nanocomposite powder was first added to epoxy and cured, and the ultra-thin foil TIPS-OMMT/PP specimen was then obtained by microtoming the cured mixture. Hot pressing was done at 185 °C and 1 MPa using the automatic hot press QM900A from Qmesys. Microtoming was carried out under ambient temperature using Leica microtome ULTRACUT UCT. TEM images were acquired using JEOL JEM 2100 and Tecnai X-TWIN Transmission Electron Microscope, both at 200 keV. With the TEM images obtained, the average lateral sizes of the nanofiller particles in the ME-OMMT/PP and TIPS-OMMT/PP powders were evaluated using the ImageJ software.

X-ray diffraction (XRD) was used to evaluate the crystal phases present in the PP powders. XRD was carried out with the PANalytical X'Pert PRO from Malvern Panalytical. The Cu-K α radiation was operated at 40 kV and 30 mA.

3.3.3. Thermal measurements

Dynamic differential scanning calorimetry (DSC) was carried out using the DSC Q200 from TA Instruments under a nitrogen atmosphere, with heating and cooling rates of 10 °C/min. The onset melting temperature $T_{m,onset}$, peak melting temperature T_m , onset crystallization temperature $T_{c,onset}$ and peak crystallization temperature T_c were determined using the TA Universal Analysis software. The heat capacity of the powders was obtained using the conventional 3-run method, according to ASTM E1269 standard [183], using a synthetic sapphire disk for heat flow calibration. For isothermal DSC

measurements, a powder sample was heated at 10 °C/min from 20 °C to 200 °C, and then cooled at 10 °C/min to temperature T_{iso} . The sample was subsequently maintained at T_{iso} for 150 min, before being cooled to 20 °C at 30 °C/min. Finally, the sample was heated again at 10 °C/min from 20 °C to 200 °C to evaluate the crystallization that occurred during the isothermal and cooling stages.

The relative degree of crystallinity x_c of the composite powders was calculated using the following formula [184, 185]

$$x_c = \frac{\Delta H_m}{(1-\alpha)\Delta H_m^0} \times 100\% \quad , \quad (3.1)$$

where ΔH_m is the melt enthalpy of the sample, α the weight percentage of OMMT (1 wt% in this study) and ΔH_m^0 the melt enthalpy of a perfect isotactic PP crystal (i.e., 207 J/g).

Thermogravimetric experiments were carried out using thermogravimetric analysis (TGA) Q500 from TA Instruments under an air or nitrogen atmosphere with an airflow rate of 60 mL/min and a nitrogen purge gas flow rate of 40 mL/min. The samples were heated at 10 °C/min from 40 °C to 600 °C. According to the ASTM E2550-17 standard, the onset temperature of thermal degradation $T_{\text{d,onset}}$ is the temperature at which a deflection from the baseline of the first derivative of the thermogravimetric curve (DTG) is first observed. The maximum degradation rate $r_{\text{d,max}}$ and temperature $T_{\text{d,max}}$ at which $r_{\text{d,max}}$ occurs were determined from the maxima of the DTG curve. The difference between $T_{\text{d,max}}$ and $T_{\text{d,onset}}$ is defined as ΔT .

The activation energy $E_{\text{A,D}}$ for the thermal degradation reactions are obtained using the Kissinger equation which assumes a first-order reaction [186]

$$\ln\left(\frac{\beta}{T_{\text{d,max}}^2}\right) = \ln\left(\frac{AR}{E_{\text{A,D}}}\right) - \frac{E_{\text{A,D}}}{RT_{\text{d,max}}} \quad , \quad (3.2)$$

where β (K min^{-1}) is the heating rate, A the Arrhenius pre-exponential factor and R the molar gas constant (8.314 J/mol K). The heating rates of 5, 10, 15, 20 and 25 K min^{-1} were used to evaluate the activation energy for thermal degradation of the PP, ME-OMMT/PP, P-OMMT-1/PP and P-OMMT-3/PP powders under air atmosphere.

The melt viscosity values of the CP20, CP60, and PP1101 powders were evaluated using the Discovery Hybrid Rheometer-3 from TA Instruments. The powder samples were separately loaded onto a 25 mm parallel plate, and the steady-state shear measurements were carried out at a shear rate of 0.05 s^{-1} from $200 \text{ }^{\circ}\text{C}$ to $110 \text{ }^{\circ}\text{C}$ at a cooling rate of $2 \text{ }^{\circ}\text{C/min}$.

3.3.4. Mechanical measurements

All the specimens were tested as fabricated without post-processing. Tensile measurements were carried out at room temperature using the AG-X Plus universal testing machine from Shimadzu. It was coupled with a non-contact digital video extensometer, TRViewX55S, for the accurate initial strain measurement. A constant crosshead speed of 1 mm/min was used for CP20, while for CP60 and PP1101, a crosshead speed of 1 mm/min was used for initial strain up to 0.5%, followed by a crosshead speed of 50 mm/min . The elongation at break and UTS values of the specimens were obtained using the Trapezium X software. SEM was used to observe the cross-sections of the SLS specimens, which were prepared by cryogenic fracture.

Three-point bending tests were carried out at room temperature using the AG-X Plus universal testing machine from Shimadzu. The support width was set to 32 mm. A crosshead speed of 1 mm/min was used for initial strain up to 0.5%, and subsequently, a speed of 5 mm/min was used. The flexural modulus was determined in the range of

0.15–0.40% strain. The flexural modulus and flexural strength values were obtained using the Trapezium X software.

Izod impact test measurements were carried out at room temperature using the HIT25P pendulum impact tester from ZwickRoell. For notched and un-notched specimens, 5.5 J and 11 J impact pendulums were used, respectively.

3.3.5. Chemical measurements

The amount of ethylene present in CP20 and CP60 was measured using FTIR [187]. The CP20 and CP60 powders (300 mg) were separately dissolved in *p*-xylene (4 mL) at 130 °C. *p*-Xylene was purchased from Sigma Aldrich and was used as received. The polymer solutions were then drop-cast onto separate Petri dishes while hot and subsequently dried under vacuum at 35 °C for 48 h to ensure complete removal of the solvent. The cast polymer films were then used for Fourier transform infrared (FT-IR) spectroscopy measurements using the Spectrum Two FT-IR spectrometer from PerkinElmer.

Chapter 4. Selective Laser Sintering of PP Powders

There have been several studies investigating the development and laser sintering of PP powders, but most studies have focused on the homopolymer, including high- [15-18, 23, 96, 97] and low-isotactic PP [21, 22], or its composites [25, 26]. The majority of those studies explored the optimization of the process parameters and mechanical performance of the sintered PP parts. Due to the low toughness of isotactic PP homopolymers, copolymers have been feasible alternatives for functional part applications and have gained some attention for SLS in the past few years [27-29]. Although there have been a number of independent investigations on the SLS of isotactic PP, the studies comparing the processability of PP homopolymers and copolymers and the properties of their SLS parts are still quite limited in literature.

In this chapter, the SLS of both isotactic PP homopolymer (Laser PP CP20 from Diamond Plastics) and copolymer (Laser PP CP60 and PP1101 from Diamond Plastics and EOS GmbH, respectively) powders were investigated and comprehensively compared. PA12 (PA 2200 from EOS GmbH) powder was used as a benchmark material. The PP powders were first characterized in terms of powder morphology, thermal behavior, and crystallization kinetics. Herein, the use of isothermal DSC as an effective and efficient method to determine the minimum powder bed temperature required was also demonstrated. Suitable SLS process parameters were then determined, and tensile specimens were fabricated and subsequently tested to establish the optimal process parameters. Finally, the crystal phases of the printed specimens were evaluated and compared to those of the injection molded counterparts.

4.1. Powder evaluation

CP20 is an isotactic PP homopolymer, while CP60 is a propylene-ethylene random copolymer. The FT-IR spectrums of the CP20 and CP60 films are shown in Figure 4.1. The ethylene content in CP60 was estimated to be 11% by taking the ratio of absorbance of the CP60 film at 1379 cm^{-1} to 1459 cm^{-1} and substituting the value into a calibration curve [188]. The amount of ethylene content in CP20 was negligible, as supported by the absence of a peak within $750\text{--}720\text{ cm}^{-1}$ [187].

Figure 4.1. FT-IR spectrums of CP20 and CP60 used for evaluating the ethylene content present in the polymers.

4.1.1. Powder morphology

The CP20 and CP60 powders were produced by cryogenic grinding, whereas the PP1101 powder was produced by a solution process. The SEM images of the CP20 and CP60 powders showed that the powder particles were irregularly shaped, although their edges were rounded to enhance their flow for SLS (Figure 4.2a, b). Meanwhile, the PP1101 powder contained a significant number of single, spherical particles that were

mostly between 10–30 μm . Agglomerates of those single particles and larger, irregular particles that appeared to result from the solution process were also observed (Figure 4.2c). In the CP20 powder, there were powder particles of much smaller sizes adhering to the larger ones, resulting in the rough surfaces of the powder particles.

In contrast, the CP60 powder was free of very fine particles, and its powder particles had blunt edges, although they were less round than those of the CP20 powder. Meanwhile, due to numerous small particles in PP1101, its powder flow appeared comparable, if not better, than CP60. The CP20, CP60, and PP1101 powders exhibited poorer flow than the PA2200 powder that had powder particles with a near-spherical shape and smooth surface (Figure 4.2d). The flowability of the powders was quantitatively measured using HR. The HR values of CP20, CP60, PP1101, and PA2200 were found to be 1.28, 1.22, 1.23, and 1.13, respectively (**Error! Reference source not found.**); powders with $\text{HR} < 1.25$ are generally considered free-flowing [66]. The values supported the observation that PA2200 and CP20 had the best and poorest powder flowability, respectively. The poor powder flowability of CP20 is attributed to the rough powder particle surfaces and the presence of extremely fine particles ($< 15 \mu\text{m}$).

The 3D laser confocal microscope served as an effective tool to provide accurate visual descriptions of the powder bed surfaces. Mazhar et al. reported a similar surface roughness measurement method using a laser scanner, and they used the skewness and kurtosis of the surface height to evaluate the surface roughness [189]. In this study, the overall powder bed surface roughness was described by the average surface roughness S_a (Figure 4.3, left). However, although a powder bed with a low S_a value is smooth in general, it may contain localized surface imperfections in the form of holes or bumps. The average vertical and lateral sizes of the localized imperfections were determined using the mean height R_c and the mean width R_{sm} of the profile elements, respectively.

The R_c and R_{sm} values of the powder surfaces were obtained from the average of five equally spaced horizontal profiles (Figure 4.3, right).

Figure 4.2. SEM images of polymer powders: (a) CP20, (b) CP60, (c) PP1101 and (d) PA2200.

The S_a , R_c , and R_{sm} values of the CP20, CP60, PP1101, and PA2200 powders are summarized in Table 4.1. Since these values of the PP powders were significantly higher than those of the PA2200 powder, it is concluded that the PP powder bed surfaces were coarser. Meanwhile, the CP60 powder had higher values of S_a , R_c , and R_{sm} than the CP20 powder. This implies that the powder bed surface roughness of the CP60 powder was likely to be higher than that of the CP20 powder, and the localized imperfections on the CP60 powder bed would be deeper and wider. The S_a , R_c , and R_{sm} values of PP1101 were lower than those of CP60, suggesting that the powder bed surface of PP1101 would be smoother than that of CP60. PP1101 had a slightly lower value of S_a and higher values

of R_c and R_{sm} than CP20, which means that although PP1101 has a larger region of smooth surfaces, its localized imperfections were larger in size than those in CP20. The effect of high values of R_c and R_{sm} despite a moderate value of S_a was evident from the powder spreading of PP1101 during SLS; the powder bed surface was visibly uneven with gaps, especially at the corners, although the middle region appeared to be smooth. As a result, the print bed region that could be used for part fabrication was reduced.

Figure 4.3. 3D height images and surface profiles of the polymer powders: (a) CP20, (b) CP60, (c) PP1101, and (d) PA2200.

While both the depth and width of localized imperfections affect the SLS process and part properties, the depth is postulated to be more crucial for SLS than their width. A deep hole will be difficult to be filled by a subsequent layer of powder, and if left unfilled, it will contribute to part porosity. Even if the hole is filled upon subsequent recoating, the laser may not provide enough energy to completely melt the fresh layer of powder, leading to poor interlayer adhesion. The porosity and poor interlayer adhesion eventually lead to undesirable mechanical properties. For high bumps, the protruding powder particles may be dragged by the recoater leading to the formation of scratches within the powder bed and may even cause build failure. Therefore, powders with higher values of R_c may require larger layer thickness for successful build; this was exemplified by the fact that a layer height of 0.15 mm was necessary to successfully sinter CP60, whereas a layer height of 0.10 mm was sufficient for CP20.

Table 4.1. Summary of the bulk density, HR, and surface roughness values of CP20, CP60, PP1101, and PA2200.

	CP20	CP60	PP1101	PA2200
d_{50} (μm)	60	60	46	58
Bulk density (g/cm^3)	0.38	0.36	0.39	0.48
Tap density (g/cm^3)	0.49	0.44	0.48	0.54
HR	1.28	1.22	1.23	1.13
S_a (μm)	48 $\pm$ 1.9	52 $\pm$ 1.6	45 $\pm$ 1.1	30 $\pm$ 0.3
R_c (μm)	186 $\pm$ 3.9	210 $\pm$ 2.0	206 $\pm$ 1.1	124 $\pm$ 1.7
R_{sm} (μm)	452 $\pm$ 14.3	508 $\pm$ 9.9	487 $\pm$ 34.3	380 $\pm$ 7.7

4.1.2. Thermal properties

The thermal behavior of a polymer powder is a key determinant of its sinterability and the SLS process parameters to be used. The thermal properties of the CP20, CP60,

PP1101, and PA2200 powders are summarized in Table 4.2. Polymers with wide sintering windows are favored for being less sensitive to subtle changes in temperature and thus less prone to negative mid-build cooling effects [190]. The sintering windows of CP20, CP60, and PP1101 were determined to be 26.3 °C, 2.2 °C, and 7.2 °C, respectively, based on their DSC curves (Figure 4.4a). As CP60 and PP1101 had much narrower sintering windows than CP20 and PA2200 (25.8 °C), they were postulated to be much more susceptible to warping. Therefore, careful control of T_b is especially important for CP60 and PP1101 in ensuring successful part fabrication.

Table 4.2. Key thermal properties of CP20, CP60, PP1101, and PA2200.

	CP20	CP60	PP1101	PA2200
Onset melting temperature $T_{m,onset}$ (°C)	150	100	120	181
Melting peak T_m (°C)	164	133	137	186
Onset crystallization temperature $T_{c,onset}$ (°C)	124	98	113	155
Crystallization peak T_c (°C)	122	94	110	151
Melting range (°C)	21.5	51.3	17.0	13.8
Sintering window (°C)	26.3	2.2	7.2	25.8
Stable sintering region (°C)	172–271	150–298	144–286	198–360 [144]
Onset degradation temperature $T_{d,onset}$ (°C)	231	249	223	-
Melt enthalpy (J/g)	99.7	58.7	62.7	90.8 [191]
Degree of crystallinity x_c (%)	47.7	28.1	30.0	43.4

The melting range from the $T_{m,onset}$ to the offset melting temperature $T_{m,offset}$ is also important for the sintering process. A wide melting range is undesirable because the polymer powders would melt less homogeneously upon laser irradiation. Furthermore, since the polymer would contain crystal lamellae that vary significantly in thickness, some lamellae would be so thin that their melting temperatures are lower than the T_b

value used. Such lamellae would soften or even melt prematurely, leading to powder caking or over-sintering phenomenon. CP60 was observed to have the highest tendency towards poor part resolution and powder caking because of its wide melting range, and its powder could hardly be reused. Furthermore, over-sintering and thermal bleeding were substantial, making it difficult to remove excess powder from the printed CP60 parts. In contrast, the CP20 and PP1101 powders could be reused, and excess powder could be removed more easily.

Figure 4.4. (a) DSC and (b) TGA curves of the CP20, CP60, PP1101, and PA2200 powders.

The stable sintering region (SSR) of a polymer powder, which lies in between its $T_{m,offset}$ and onset thermal degradation temperature $T_{d,onset}$ values, is used to determine the temperature range within which the sintering of the polymer powder can occur without causing significant material degradation. The wider the SSR, the higher the allowable local temperature of the sintered regions, and the less likely the polymer will degrade during sintering. The $T_{d,onset}$ values of the PP powders were considered to be the temperature at which 1% mass loss occurs during their thermogravimetry testing (Figure 4.4b). The SSRs of the CP20, CP60, and PP1101 powders, evaluated under nitrogen atmosphere, were 172–271 °C, 150–298 °C and 144–286 °C, respectively. In

comparison, the SSR of PA2200 was 198–360 °C. Under ambient atmosphere, the $T_{d,onset}$ values of CP20, CP60, and PP1101 were 231 °C, 249 °C, and 223 °C, respectively. Between the two copolymers, CP60 showed higher thermo-oxidative stability than PP1101.

4.1.3. Rheological properties

The rheological properties of a polymer powder, in particular its melt viscosity η , are critical for SLS. The coalescence process of the powder particles during SLS can be described by the modified Frenkel-Eshelby model [38], and the coalescence rate is assumed to be dominated by the η value of the polymer [14]; polymers with lower values of η are expected to have higher coalescence rates [38]. The η values of CP20, CP60, PP1101, and PA12 at 25 °C above their T_m values were 237 Pa·s, 14813 Pa·s, 1045 Pa·s, and ~400 Pa·s, respectively, suggesting that CP20 and PP1101 would have similar coalescence rates to that of PA12, whereas CP60 would have a slower coalescence rate (Figure 4.5). Therefore, it was expected that CP60 would require relatively longer sintering times than CP20, PP1101, and PA12, or higher local temperatures, to ensure its full coalescence.

Figure 4.5. Plots of viscosity against temperature for CP20, CP60, PP1101, and PA12. The data for PA12 was obtained from [192].

4.1.4. Crystallization kinetics

The cooling process and the crystallization behavior of the polymer melt are crucial during SLS, as they have a significant influence on the curling or warpage phenomenon [17, 193]. The tendency of a polymer toward premature crystallization, and thus warpage, depends not only on the sintering window and T_b value used but also on its crystallization activation energy $E_{A,C}$, a property that determines the sensitivity of its crystallization rate to temperature variations. In SLS, temperature variations of ~ 5 °C can be found even within the optimal build area [194, 195], and the instantaneous temperature of the lower layers decreases as each fresh powder layer is added [191, 195]. Polymers with higher values of $E_{A,C}$ are more sensitive to small temperature changes and thus more prone to fast crystallization even at a temperature slightly below their T_c value, resulting in them being more susceptible to warping and more difficult to process.

For the determination of the $E_{A,C}$ value of a polymer, graphs of its degree of crystallization $\alpha(t)$, defined as the ratio of its crystallized volume at time t to its total crystallizable volume, against time t at various values of T_{iso} were plotted by integrating the DSC curve of heat flow against time (Figure 4.6) [196]

$$\alpha(t) = \frac{\int_0^t \frac{dH}{dt} dt}{\int_0^\infty \frac{dH}{dt} dt} . \quad (4.1)$$

The graphs were then used to construct Avrami plots according to the Avrami equation, which describes the primary nucleation processes of polymers under quiescent isothermal conditions [197]

$$\alpha(t) = 1 - e^{-kt^n} , \quad (4.2)$$

$$\log \left[-\ln(1 - \alpha(t)) \right] = n \log t + \log k \quad , \quad (4.3)$$

where n is the Avrami index and k is the isothermal crystallization rate constant.

Figure 4.6. Plots of $\alpha(t)$ against t at different T_{iso} : (a) CP20, (b) CP60, (c) PP1101, and (d) PA2200.

The n and k values were obtained from the linear fit of the Avrami plots; the conversion range was chosen so that a good linear fit with an R^2 value greater than or equal to 0.995 was obtained. The crystallization half-time $t_{1/2}$, defined as the time at which $\alpha(t) = 0.5$, can then be calculated from [196]

$$k = \frac{\ln 2}{t_{1/2}^n} \quad . \quad (4.4)$$

The isothermal crystallization parameters for CP20, CP60, PP1101 and PA2200 are summarized in Table 4.3.

Table 4.3. Isothermal crystallization parameters for CP20, CP60, PP1101, and PA2200. The times at which crystallization heat flow is maximum t_{pc} were obtained from the isothermal DSC curves directly.

	T_{iso} (°C)	n	k (min ⁻¹)	R^2	$t_{1/2}$ (min)	t_{pc} (min)
CP20	135	3.20	6.24×10^{-4}	0.9991	8.93	8.96
	140	3.17	2.55×10^{-5}	0.9997	24.94	26.04
	142	3.42	2.42×10^{-6}	0.9999	39.38	37.86
	144	3.69	1.72×10^{-7}	0.9999	61.99	59.54
	145	4.05	1.81×10^{-8}	0.9998	74.79	78.86
CP60	110	3.46	8.95×10^{-4}	0.9999	6.86	6.78
	111	3.19	7.82×10^{-4}	0.9999	8.37	8.23
	112	3.15	3.85×10^{-4}	0.9999	10.81	10.31
	113	3.20	1.58×10^{-4}	0.9999	13.75	13.46
	115	3.28	2.36×10^{-5}	0.9999	23.06	24.04
	117	3.68	1.08×10^{-6}	0.9999	37.95	36.86
PP1101	120	2.45	8.13×10^{-3}	0.9989	6.12	4.55
	122	2.58	1.97×10^{-3}	0.9998	9.70	7.43
	123	2.64	6.31×10^{-4}	0.9997	14.16	10.56
	124	2.54	4.07×10^{-4}	0.9987	18.67	14.13
	126	2.23	3.35×10^{-4}	0.9999	30.59	23.47
PA2200	162	2.72	3.01×10^{-2}	0.9998	3.16	2.95
	164	2.55	6.36×10^{-3}	0.9995	6.30	5.69
	166	2.92	8.07×10^{-4}	0.9997	10.13	9.28
	168	3.31	2.91×10^{-5}	0.9990	21.07	19.39
	170	3.63	9.30×10^{-7}	0.9994	41.39	37.14

For all four polymers, the general trend was that as the T_{iso} value increased, k decreased, whereas t_{pc} and $t_{1/2}$ increased. This is in agreement with the fact that the

crystallization rate decreases at smaller supercooling. The Avrami index n is composed of two terms

$$n = n_d + n_n \quad , \quad (4.5)$$

where n_d and n_n represent the dimensionality of the crystals and the time-dependence of nucleation, respectively. The n_d can have integer values 1, 2 or 3, corresponding to one- (1D), two- (2D) or three-dimensional (3D) crystals formed; when complex bundles or coils are formed, n_d can increase to 5 [198]. Meanwhile, n_n can have values between 0 and 1; completely instantaneous nucleation would contribute to an n_n value of 0, while entirely sporadic nucleation will contribute to an n_n value of 1. The n_n value is usually a non-integer as nucleation mechanisms are often in between being fully instantaneous and fully sporadic [199].

The $E_{A,C}$ value is also related to the Arrhenius relation (equation 4.6) or the time t_{pc} at which heat flow is maximum (equation 4.7) [17, 196]

$$k^n = A e^{\frac{E_{A,C}}{RT_{iso}}} \quad , \quad (4.6)$$

$$\ln t_{pc} = -\frac{E_{A,C}}{RT_{iso}} + C \quad , \quad (4.7)$$

where A is a temperature-dependent pre-exponential factor and R is the molar gas constant (8.31 J/(mol·K)). The $E_{A,C}$ values of the polymers were determined from the gradients of their logarithmic plots of $(\ln k)/n$ against $1/T_{iso}$ ($E_{A,C1}$, Figure 4.7a), and from the gradients of their plots of $\ln(t_{pc})$ against $1/T_{iso}$ ($E_{A,C2}$, Figure 4.7b).

Figure 4.7. Avrami and Arrhenius plots for evaluating $E_{A,C1}$ and $E_{A,C2}$: (a) $(\ln k)/n$ against $1/T_{iso}$ and (b) $\ln(t_{pc})$ against $1/T_{iso}$.

The scatter plots were fitted linearly, and the $E_{A,C1}$, $E_{A,C2}$, values and their corresponding R^2 values are summarized in Table 4.4; the $E_{A,C1}$ values are used for future discussions. The $E_{A,C1}$ of PA2200 was evaluated to be 501.0 kJ/mol, and is within the range reported by Drummer *et al.* (395.0 ± 216.2 kJ/mol) [17]. Comparatively, the $E_{A,C1}$ values of CP20, CP60, and PP1101 were found to be much lower at 300.7 kJ/mol, 306.1 kJ/mol, and 361.0 kJ/mol, respectively. This means that the adverse effects of temperature deviations on the crystallization of the polymer melts at temperatures close to their T_c values would not be as severe for CP20, CP60, and PP1101 compared to PA2200. Since CP20 has a similar sintering window to PA2200 and its $E_{A,C1}$ value was only 60% that of PA2200, its thermal processability should be comparable, if not better, than PA2200. The SLS of CP20 could be carried out at a relatively wide range of T_b values (152–157 °C). Meanwhile, although the $E_{A,C1}$ value of CP60 and PP1101 were 61% and 72% that of PA2200, their sintering windows were significantly narrower at 2.2 °C and 7.2 °C, respectively. Due to the limitations of their narrow sintering windows, the PP copolymer powders were expected to be much more difficult to process than PA2200; the SLS of CP60 and PP1101 could only be carried out within a narrow range of T_b values.

Table 4.4. Isothermal crystallization activation energy values of CP20, CP60, PP1101, and PA2200.

	$E_{A,C1}$ (kJ/mol)	R^2	$E_{A,C2}$ (kJ/mol)	R^2
CP20	300.7±4.34	0.9992	303.4±7.96	0.9973
CP60	306.1±3.92	0.9992	310.6±9.44	0.9954
PP1101	361.0±16.14	0.9921	360.1±6.11	0.9989
PA2200	501.0±19.10	0.9942	504.5±17.40	0.9953

4.2. Determination of powder bed temperature

During the sintering of semi-crystalline polymer powders, crystallization should be suppressed for as long as possible, at least for several sintered layers during the build [33]. To achieve this, an accurate determination of a suitable T_b is required. A T_b value that is too high results in powder caking and over-sintering phenomenon; If the T_b value is too low, undesired premature cooling of the sintered regions can occur, which induces curling and distortion due to accumulated stresses at the part. The T_b value should theoretically be within the sintering window, which is generally characterized by dynamic DSC at heating and cooling rates of 10 °C/min. However, as crystallization is a kinetic process, the measured value of $T_{c,onset}$ depends on the cooling rate used. This implies that during the timescale of the SLS process, crystallization may occur even if the T_b value is slightly above the $T_{c,onset}$ value obtained through the standard DSC procedure. The determination of T_b is typically empirical and requires repeated trial-and-error that is inefficient in terms of time and cost, especially for materials with very narrow sintering windows.

Herein, isothermal DSC was employed as an effective and practical method to systematically determine the minimum value of T_b that should be used for the CP20, CP60, and PP1101 powders. To verify the viability of this method, it was tested on the PA2200 powder that has known operating process parameters. In this method, a polymer

powder sample is initially completely melted by heating to 200 °C at 10 °C/min. The sample is then cooled to T_{iso} and maintained at that temperature for 150 min to mimic the quasi-isothermal conditions in SLS (Figure 4.8, stage 1). The sample crystallizes to different extents, depending on the T_{iso} value, and is subsequently rapidly cooled to 20 °C at 30 °C/min (stage 2). Finally, the sample is heated to 200 °C at 10 °C/min to evaluate the extent of crystallization in stage 1 (stage 3).

Figure 4.8. Schematic illustration of the isothermal DSC method for determining minimum T_b .

For PA2200, four values of T_{iso} , i.e., 168 °C, 170 °C, 172 °C, and 174 °C, were evaluated using the isothermal DSC method. When $T_{\text{iso}} = 168$ °C and 170 °C, crystallization of the samples occurred during stage 1 and was completed within 60 min and 120 min, respectively. The occurrence of crystallization in stage 1 was accompanied by the appearance of exothermic peaks in the plot of heat flow against time from 0–150 min (Figure 4.9a). When the T_{iso} value was increased to 172 °C, crystallization occurred slower and was incomplete during stage 1; the sample subsequently underwent further crystallization upon rapid cooling in stage 2. This was represented by the appearance of

an exothermic peak in the plot of heat flow against time between 150–160 min (Figure 4.9b) and in the plot of heat flow against temperature (Figure 4.9c).

Figure 4.9. DSC curves of PA2200 at different values of T_{iso} : (a, b) heat flow against time during stages 1 and 2, and (c, d) heat flow against temperature during stages 2 and 3.

The sample then underwent a second melting in stage 3, and two overlapping endothermic peaks were observed. The peak at a higher temperature was attributed to the crystals formed during stage 1, while the lower temperature peak was due to the crystals formed during stage 2 (Figure 4.9d). To verify the assignment of the endothermic peaks that were observed in stage 3, an additional DSC test was carried out for the T_{iso} values that were investigated. In this test, the PA2200 powder was initially completely melted by heating it to 200 °C at 10°C/min. It was subsequently maintained at the T_{iso} value for 150 min before it was immediately heated (re-melted) to 200 °C at

10°C/min. The endothermic peaks observed during the re-melting stage would thus be solely due to the crystals formed during the isothermal stage, i.e., stage 1, thus providing direct evidence for the assignment of the endothermic peaks (Figure 4.10a).

Figure 4.10. The melting endotherms of the polymer powders obtained when they were maintained at various values of T_{iso} for 150 min and quenched before being heated (—), and when they were heated immediately after being maintained at the T_{iso} values for 150 min (---): (a) PA2200, (b) CP20, (c) CP60 and (d) PP1101.

The annealing-like isothermal condition in stage 1 allowed the formation of crystals with fewer defects and hence higher melting temperature [200]. As the T_{iso} value further increased to 174 °C, crystallization of the sample was almost absent in stage 1 and mainly occurred during stage 2. The appearance of a single endothermic peak with a lower melting temperature that was observed during stage 3 supports this conclusion. Based on the above observations, it was established that a T_b value greater than 170 °C would be required for the SLS of PA12 since crystallization was complete by stage 1

when $T_{\text{iso}} = 170$ °C. This temperature lies close to the lower limit of the range of T_b values that is typically 169–175 °C [201, 202].

The T_{iso} values evaluated for CP20 to determine its minimum value of T_b were 144 °C, 146 °C, 148 °C, and 150 °C. It was found that significant crystallization occurred in stage 1 within 150 min when T_{iso} was 144 °C and 146 °C. As the T_{iso} value increased to 148 °C, crystallization during stage 1 was slowed, and a greater extent of crystallization during stage 2 was observed (Figure 4.11a–c). The crystals formed during stage 1 contributed to a broad endothermic peak (~ 170 °C) observed in stage 3. In comparison, those formed during stage 2 resulted in a slightly narrower endothermic peak at a lower temperature (~ 160 °C) (Figure 4.11d, Figure 4.10b). As the T_{iso} value further increased to 150 °C, crystallization took place mainly during stage 2. Therefore, it is concluded that a T_b value greater than 146 °C is required for CP20.

Figure 4.11. DSC curves of CP20 at different values of T_{iso} : (a, b) heat flow against time during stages 1 and 2, and (c, d) heat flow against temperature during stages 2 and 3.

Similarly, for CP60, four T_{iso} values, 121 °C, 123 °C, 125 °C, and 127 °C, were evaluated. At $T_{\text{iso}} = 121$ °C, crystallization occurred during stage 1 and was almost complete within 150 min, while crystallization in stage 2 was negligible (Figure 4.12a–c). The crystals formed during stage 1 contributed to two slightly overlapping endothermic peaks in stage 3 at 130–150 °C (Figure 4.12d, Figure 4.10c). The melting of the crystals formed upon rapid cooling during stage 2 corresponded to the broad endothermic peak at a lower temperature of ~115 °C. As the T_{iso} value increased to 123 °C, crystallization during stage 1 slowed, whereas crystallization during stage 2 increased. Upon further increase of the T_{iso} value to 125 °C and 127 °C, crystallization in stage 1 further slowed, as represented by a reduction in the peak area of the slightly overlapping endothermic peaks at 130–150 °C in Figure 4.12d. In contrast, crystallization during stage 2 became more significant, as shown by an increase in peak area in Figure 4.12c and the appearance of a broad endothermic peak (T_m at ~130 °C) in Figure 4.12d. Based on the DSC curves, the T_b value for CP60 should be greater than 123 °C.

PP1101 stood out from the other PP powders investigated because there appeared to be a maximum degree of crystallinity achievable for each T_{iso} . Additional crystallization was only possible with further cooling; this means that the appearance of a full crystallization peak in stage 1 did not necessarily correspond to complete crystallization. For all the temperatures evaluated (118 °C, 122 °C, 124 °C, and 126 °C), crystallization appeared to be complete in stage 1 as the heat flow reached a peak and subsequently approached zero within 80 min (Figure 4.13a); yet, crystallization during stage 2 was still observed especially when $T_{\text{iso}} = 122, 124$ and 126 °C (Figure 4.13b, c). The crystals formed during stage 1 contributed to two endothermic peaks in stage 3, whereas those

formed during stage two gave rise to a broad endothermic peak at 120–125 °C (Figure 4.13d, Figure 4.10d).

Figure 4.12. DSC curves of CP60 at different values of T_{iso} : (a, b) heat flow against time during stages 1 and 2, and (c, d) heat flow against temperature during stages 2 and 3.

This crystallization behavior of PP1101 has been observed with ethylene-octene copolymers, where the ethylene and octene segments of the copolymer crystallized independently [203]. Such copolymers exhibited two crystallization exotherms where the higher-temperature exotherm was attributed to the crystallization of the long ethylene sequences with a low degree of branching, while the lower-temperature exotherm was due to the crystallization of the shorter, octene-rich ethylene segments that had a higher degree of branching [204]. Unlike the long sequences that formed lamellar crystals, the short sequences with a higher degree of chain branching had to

crystallize as extended sequences to form thinner, fringed micelles with lower melting temperatures. The lower undercooling of the short sequences and the restrictions on their chain diffusion were responsible for their slow crystallization kinetics. Such bimodal crystallization kinetics has also been observed with random ethylene-butene copolymers [205]. In one of the studies, the copolymer exhibited asymmetric exotherm during isothermal crystallization, similar to what was observed for PP1101 [206]. The asymmetry was attributed to the two-stage crystallization kinetics, which resulted from a distribution in the polymer sequence lengths; therefore, it is likely that PP1101 contained PP polymer chains of varying sequence lengths and degree of branching.

Figure 4.13. DSC curves of PP1101 at different values of T_{iso} : (a, b) heat flow against time during stages 1 and 2, and (c, d) heat flow against temperature during stages 2 and 3.

According to Flory's theory of crystallization in copolymers, only molten polymer segments with sequence lengths exceeding the minimum crystallite length ζ^* can participate in the crystallization process at a given temperature, and the ζ^* decreases as the crystallization temperature decreases [207]. At T_{iso} , the polymer sequences with lengths greater than ζ^* could recrystallize, but those with lengths shorter than ζ^* could only crystallize when ζ^* was reduced upon further supercooling. Therefore, not all the crystallizable sequences could participate in crystallization during isothermal crystallization at T_{iso} . The two-stage crystallization kinetics observed with PP1101 is hypothesized to be due to the presence of a significant number of short polymer sequences, which would explain the crystallization observed during stage 2, despite the sample appearing to have completely crystallized in stage 1. Accordingly, as ζ^* increased with T_{iso} , the degree of crystallization achieved during stage 1 reduced as the T_{iso} increased. Although CP60 is also a PP copolymer, its two-stage crystallization kinetics was less obvious than that of PP1101. This is likely because the polymer sequence length distribution is much narrower in CP60 than that of PP1101; as a result, most of the polymer sequences either crystallized (sequence length $> \zeta^*$) or did not crystallize (sequence length $< \zeta^*$).

As each SLS process deals with different build time, part thickness, and polymer powder, the minimum value of T_b obtained from the isothermal DSC method is meant to serve as a more accurate guide that complements the sintering window. In real applications, T_b values slightly below the minimum value obtained from the isothermal DSC measurements may be used, such as in the case of PP1101 and PA2200. Nevertheless, as will be discussed in subsequent sections, the optimal values of T_b for both the CP20 and CP60 powders were above the minimum T_b values evaluated, demonstrating the applicability of the isothermal DSC method.

4.3. SLS parameter optimization and part fabrication

Using the minimum values of T_b determined from the isothermal DSC protocol as a guideline, the SLS process optimizations for CP20, CP60, and PP1101 were performed by varying the laser scan speed, laser power, and/or hatching distance. Tensile, flexural and impact specimens, and prototype parts were fabricated. The volumetric energy density E_{vol} for a given set of SLS parameters was calculated using the following formula [144]

$$E_{vol} = \frac{p}{shL} , \quad (4.8)$$

where p is the laser power, s the laser scan speed, h the hatching distance, and L the layer thickness. The minimum energy density E_{min} required to melt a unit volume of powder materials was calculated by

$$E_{min} = \phi \int_{T_b}^{T_{m, offset}} C_p(T) dT , \quad (4.9)$$

where ϕ is the packing density of the powders. The integral was obtained by integrating the area under the curve of specific heat against temperature from T_b to $T_{m, offset}$. The ϕ values of the CP20, CP60, and PP1101 powders were taken to be their bulk density values at 0.38 g/cm³, 0.36 g/cm³, and 0.39 g/cm³, respectively.

Considering the laser-powder interactions, only a fraction of the irradiation energy from the laser is absorbed by the thin polymer powder layer at an elevated temperature; for example, the absorptance of a 150 μ m-thick PA2200 powder layer towards CO₂ irradiation is ~80% between 70–175 °C [208]. Therefore, the E_{vol} value necessary for sintering should be higher than the calculated E_{min} . The typical T_b value, laser power, laser scan speed, hatching distance, and layer thickness used for PA2200 is 169–175 °C, 7–25 W, 3000 mm/s, 0.25 mm, and 0.1 mm, respectively [201]. The intrinsic optical absorption coefficients of CP20, CP60, and PP1101 were assumed to be the same.

Based on the isothermal DSC results and the actual processing conditions, the optimal value of T_b for CP20 was determined to be 154 °C and was used for subsequent sintering experiments. For CP60, a T_b value of 124 °C was determined to be the best possible. The temperature was limited to 124 °C; a further increase in temperature led to significant powder caking and poor powder flow, whereas at temperatures below 123 °C that is the minimum T_b value determined from isothermal DSC, warpage was significant, and the prints failed. Meanwhile, the T_b value used for PP1101 was 123 °C.

Based on the T_b and ϕ values, the $E_{\min}$ values for CP20, CP60, and PP1101 were determined to be 0.061 J/mm³, 0.034 J/mm³, and 0.044 J/mm³ respectively. The process parameters used to sinter the CP20, CP60, and PP1101 powders were varied so that their E_{vol} values were 0.100–0.400 J/mm³, 0.079–0.158 J/mm³, and 0.038–0.203 J/mm³, respectively. Process optimizations for the powders were carried out by varying the laser power and/or scan speed while keeping the other parameters unchanged (Table 4.5). The effects of the hatching distance and layer thickness on the mechanical properties of printed specimens were also investigated using CP20.

Table 4.5. SLS process parameters used for CP20, CP60, and PP1101.

Process parameter	CP20	CP60	PP1101
Laser power p (W)	6–18	5.6–37.3	6–32
Laser scan speed s (mm/s)	3000–6000	900–6000	3500
Laser beam diameter (mm)	0.42	0.42	0.42
Hatching distance h (mm)	0.1–0.3	0.3	0.3
Layer thickness L (mm)	0.10	0.15	0.15
Powder bed temperature T_b (°C)	154	124	123
Removal chamber temperature (°C)	110	100	100

4.3.1. CP20 powder

To evaluate the optimal value of E_{vol} for CP20, tensile specimens were first printed at different energy densities (Table 4.6, specimens 1–7). The laser power was varied between 6–18 W, while the laser scan speed and hatching distance were kept constant at 3000 mm/s and 0.2 mm, respectively. This corresponded to E_{vol} values between 0.100 J/mm³ and 0.400 J/mm³.

Table 4.6. Parameters used for the SLS process optimization for CP20.

Specimen	Laser power p (W)	Laser scan speed s (mm/s)	Hatching distance h (mm)	E_{vol} (J/mm ³)
1	6	3000	0.2	0.100
2	8	3000	0.2	0.133
3	10	3000	0.2	0.167
4	12	3000	0.2	0.200
5	14	3000	0.2	0.233
6	16	3000	0.2	0.267
7	18	3000	0.2	0.300
8	12	4000	0.2	0.150
9	12	5000	0.2	0.120
10	12	6000	0.2	0.100
11	12	3000	0.1	0.400
12	12	3000	0.3	0.133

The mechanical properties of the printed specimens are shown in Figure 4.14a. When the laser power used was 6 W ($E_{vol} = 0.100$ J/mm³), the powder remained loose after sintering, and tensile specimens could not be obtained; the powder coalescence process either could not start at all or at best started but stopped short due to insufficient energy (Figure 4.14b). As the laser power increased to 10 W ($E_{vol} = 0.167$ J/mm³), the mechanical performance of the tensile specimens improved, as demonstrated by the increase in the UTS and elongation at break values. The higher values of E_{vol} allowed higher local temperatures to be achieved, which led to a larger degree of coalescence (Figure 4.14c). Consequently, specimens with lower porosity and higher density and

strength could be obtained. As the laser power further increased to 18 W ($E_{vol} = 0.300$ J/mm³), the mechanical performance of the specimens deteriorated despite better interlayer adhesion (Figure 4.14d). This phenomenon is commonly reported and was attributed to polymer degradation at excessive energy densities [22]. The increase in the UTS values of sintered specimens with increasing E_{vol} and the subsequent reduction in the UTS past an optimal value of E_{vol} has been observed with PA2200 [201, 209]. Based on the mechanical performance, the optimal value of E_{vol} for sintering CP20 was determined to be 0.167 J/mm³.

Figure 4.14. SLS CP20 specimens printed at different values of E_{vol} : (a) tensile properties and (b–d) SEM images of the cross-sections.

Tensile specimens were then fabricated at varying scan speeds and hatching distances (Figure 4.15a, b). As the laser scan speed increased from 3000 to 6000 mm/s (Table 4.6, specimens 4, 8–10), the corresponding E_{vol} values decreased from 0.200

J/mm^3 to 0.100 J/mm^3 , and the mechanical performance of the specimens generally worsened, as expected. Although specimens 1 and 10 had the same E_{vol} values of 0.100 J/mm^3 , sintering was only successful for specimen 10, where a higher laser power was applied. Unlike specimen 1 that was sintered at 6 W and 3000 mm/s, the higher laser power and a scan speed of 12 W and 6000 mm/s used for sintering specimen 10 allowed higher achievable maximum local temperatures, which promoted the coalescence between the powder particles. Modeling studies have shown that this can occur even when the overall E_{vol} value is lower (Figure 4.15c, d) [210].

Figure 4.15. (a, b) Tensile properties of SLS CP20 specimens fabricated with different scan speeds and different hatching distances. (c, d) Evolution of melt pools under two sets of process parameters. Reproduced with permission [210]. Copyright 2018, Elsevier. (e) Schematic illustration of the effect of hatching distance on inter-track adhesion; the d_e is typically greater than the laser beam diameter d due to effects of thermal conduction.

Hatching distance, defined as the distance between two printing tracks, and effective sintering diameter d_e affects the degree of inter-track adhesion and mechanical performance (Figure 4.15e). For a given powder material, the optimal hatching distance changes with the laser power and laser scan speed since d_e varies with these parameters. Based on the mechanical performance of specimens 4, 11, and 12, the optimal hatching distance was 0.2 mm when the laser power and scan speed were at 12 W and 3000 mm/s, respectively.

At a lower hatching distance of 0.1 mm, there was a significant overlap of the effective sintering regions, increasing the E_{vol} value to 0.400 J/mm³. The excessive E_{vol} resulted in powder degradation and worsened the mechanical properties. In contrast, when the hatching distance increased to 0.3 mm (Table 4.6, specimen 12), the extent of overlap between effective sintering regions was reduced; the E_{vol} and maximum local temperature values were decreased, which resulted in a lower degree of coalescence between the powder particles and poorer mechanical performance of the printed specimens.

Based on the mechanical performance of the SLS CP20 specimens, the optimal values of E_{vol} , laser power, laser scan speed, and hatching distance for sintering CP20 were 0.167 J/mm³, 10 W, 3000 mm/s, and 0.2 mm, respectively. With the optimal SLS process parameters, the achievable values of UTS and elongation at break were 14.9 MPa and 1%, respectively.

4.3.2. CP60 powder

For the SLS process optimization for CP60, only the laser power and scan speed were varied; all the other parameters were kept constant. The parameters used for the process optimization for CP60 are summarized in Table 4.7. To evaluate the optimal

value of E_{vol} for CP60, tensile specimens were first fabricated with nine sets of parameters (Table 4.7, specimens 1–9). The laser power was varied between 16–32 W, while the laser scan speed was kept constant at 4500 mm/s. This corresponded to E_{vol} values between 0.079 J/mm³ and 0.158 J/mm³.

Due to the tough nature of CP60, it would be suitable for applications that involve bending; therefore, bending specimens were also printed. The mechanical properties of the fabricated specimens were evaluated, and the results are shown in Figure 4.16a.

Table 4.7. Parameters used for the SLS process optimization for CP60.

Specimen	Laser power p (W)	Laser scan speed s (mm/s)	E_{vol} (J/mm ³)
1	16.0	4500	0.079
2	18.0	4500	0.089
3	20.0	4500	0.099
4	22.0	4500	0.109
5	24.0	4500	0.119
6	26.0	4500	0.128
7	28.0	4500	0.138
8	30.0	4500	0.148
9	32.0	4500	0.158
10	5.6	900	0.138
11	11.2	1800	0.138
12	16.8	2700	0.138
13	22.4	3600	0.138
14	28.0	4500	0.138
15	33.6	5400	0.138
16	37.3	6000	0.138

As the E_{vol} value increased from 0.079 J/mm³ to 0.138 J/mm³, the UTS, Young's modulus, and elongation at break values displayed an increasing trend. This was attributed to the fact that the polymer powders coalesced better at higher energy densities, which contributed to lower porosity and higher part density, resulting in better mechanical performance (Figure 4.17). Upon further increase of the E_{vol} value to 0.138

J/mm^3 , the Young's modulus values decreased, although the UTS and elongation at break values remained relatively constant. The deterioration of tensile properties was attributed to the degradation of polymer powders when the E_{vol} value was too high. Furthermore, the trapped volatile degradation products could contribute to pore formation, which would reduce the part density and further lower the mechanical properties [67]. The flexural strength values of the specimens showed an upward trend initially and subsequently remained relatively constant as the E_{vol} values increased (Figure 4.16b). In contrast, the flexural modulus values reduced as the E_{vol} values increased to 0.138 J/mm^3 , and increased when the E_{vol} values increased beyond 0.138 J/mm^3 . Nevertheless, since the variation in the flexural modulus values ($<15\%$) was less significant than that of the Young's modulus ($<46\%$), the optimal value of E_{vol} for sintering CP60 was determined to be 0.138 J/mm^3 .

Figure 4.16. Mechanical properties of SLS CP60 specimens: (a) tensile and (b) flexural properties of specimens fabricated with different E_{vol} values, and (c) tensile and (d) flexural properties of specimens fabricated with different laser power ($E_{\text{vol}} = 0.138 \text{ J/mm}^3$).

Tensile and bending specimens were then fabricated at the optimal E_{vol} value of 0.138 J/mm^3 using different process parameters (Table 4.7, specimens 10–16). The laser power and laser scan speed varied between 5.6–37.3 W and 900–6000 mm/s, respectively. The mechanical properties of the fabricated specimens are shown in Figure 4.16c, d. The UTS values of the specimens remained relatively constant except when laser power was 5.6 W. The flexural strength and flexural modulus values of the specimens also varied minimally. Based on the Young's modulus and elongation at break values of the specimens, the optimal value of E_{vol} for CP60 was 0.138 J/mm^3 , and the ideal laser power and scan speed were 33.6 W and 5400 mm/s, respectively. With the optimized process parameters, UTS, Young's modulus, and elongation at break values of 20.4 MPa, 1113 MPa, and 238%, respectively, could be achieved. The flexural modulus and strength values were 381 MPa and 26.3 MPa, respectively.

Figure 4.17. SEM images of the cross-sections of the SLS CP60 specimens fabricated at different values of E_{vol} : (c) 0.079 J/mm^3 and (d) 0.138 J/mm^3 .

To evaluate the impact strength of the SLS CP60 specimens, the optimized process parameters were used to fabricate impact specimens (Figure 4.18a, b). The notched and un-notched Izod impact strengths were $53 \pm 4.0 \text{ J/m}$ and $484 \pm 20.5 \text{ J/m}$, respectively. Cubes measuring $30 \text{ mm} \times 30 \text{ mm} \times 30 \text{ mm}$ were printed for shrinkage measurements

(Figure 4.18c), and the shrinkage values were obtained by comparing the dimensions of the printed part to that of the 3D CAD model. The x -, y -, and z - shrinkage values are 0.3%, 0.7%, and 1.8%, respectively. Finally, gears of different sizes were printed for demonstration (Figure 4.18d).

Figure 4.18. Photographs of SLS CP60 parts: (a) tensile specimens fabricated with increasing energy densities (specimens 1–9), (b) notched and un-notched impact specimens, (c) cubes, and (d) gears. The impact specimens, gears, and cubes were fabricated with the optimal process parameters.

4.3.3. PP1101 powder

Tensile specimens were fabricated at different energy densities to evaluate the optimal value of E_{vol} for PP1101 (Table 4.8). The laser power was varied from 6–32 W, and the laser scan speed and hatching distance were constant at 3500 mm/s and 0.3 mm, respectively. The E_{vol} values ranged between 0.038 J/mm³ and 0.203 J/mm³.

Table 4.8. Parameters used for the SLS process optimization for PP1101.

Specimen	Laser power P (W)	Laser scan speed s (mm/s)	Hatching distance h (mm)	E_{vol} (J/mm ³)
1	6	3500	0.3	0.038
2	8	3500	0.3	0.051
3	10	3500	0.3	0.063
4	12	3500	0.3	0.076
5	14	3500	0.3	0.089
6	16	3500	0.3	0.102
7	18	3500	0.3	0.114
8	20	3500	0.3	0.127
9	22	3500	0.3	0.140
10	24	3500	0.3	0.152
11	26	3500	0.3	0.165
12	28	3500	0.3	0.178
13	30	3500	0.3	0.190
14	32	3500	0.3	0.203

The mechanical properties of the printed specimens are shown in Figure 4.19a. At an extremely low laser power of 6 W ($E_{vol} = 0.038$ J/mm³), sintering was incomplete and the fusion between the powder particles was poor, leading to the poor mechanical performance of the specimens (Figure 4.19b). This was expected since the E_{vol} value was less than the calculated E_{min} value. As the laser power increased, the melting and sintering of the powder particles were facilitated, resulting in denser specimens that exhibited better mechanical properties (Figure 4.19c). Past an optimal E_{vol} value of 0.102 J/mm³, the UTS and Young's modulus values decreased, while the elongation at break value remained almost unchanged. The reduction in the UTS and Young's modulus values was due to polymer degradation at excessive energy densities and the formation of large pores by the trapped volatile degradation products (Figure 4.19d).

Figure 4.19. SLS PP1101 specimens printed at various values of E_{vol} : (a) tensile properties and (b–d) SEM images of the cross-sections.

As the E_{vol} value further increased, the over-sintering phenomenon became evident as the contour of the specimen markings was blurred, and the removal of excess powder became increasingly difficult (Figure 4.20). Based on the mechanical performance of the specimens, the optimal value of E_{vol} for sintering PP1101 was determined to be 0.102 J/mm^3 . With the optimal SLS process parameters, the highest UTS, Young's modulus, and elongation at break values were 26.0 MPa, 1038 MPa, and 9%, respectively.

Figure 4.20. Photo of the tensile specimens sintered with increasing E_{vol} values.

4.4. Evaluation of mechanical properties of PP specimens

The mechanical properties of the PP specimens printed by SLS are summarized in Table 4.9. The CP20 specimens exhibited the lowest UTS and elongation at break values. Meanwhile, the elongation at break value of CP60 was considerably larger than PP1101, whereas its UTS was lower. The Young's modulus, flexural modulus, and flexural strength of both copolymers were similar. While CP60 offers high toughness and moderate strength, PP1101 had relatively high strength and low toughness.

Table 4.9. Properties of SLS parts sintered using the optimal process parameters.

Property	CP20	CP60	PP1101
Young's modulus (MPa)	-	1113±45.2	1038 ±101.3
Ultimate tensile strength (MPa)	14.9±1.12	20.4±0.59	26.1±0.46
Tensile elongation at break (%)	1±0.13	238±55.0	9±1.1
Flexural modulus (MPa)	-	381±47.0	305±25.3
Flexural strength (MPa)	-	26.3±0.31	24.1±.93
x-Shrinkage (%)	-	0.3	2.6
y-Shrinkage (%)	-	0.7	3.0
z-Shrinkage (%)	-	1.8	2.9

The UTS and elongation at break values of the laser-sintered and injection molded PP specimens are summarized in Table 4.10. The mechanical properties of the SLS

specimens were poorer than those of the injection molded counterparts because there was a lack of external pressure during SLS that would otherwise densify the fabricated specimen while removing trapped gases. It was most likely the presence of voids within the SLS specimens that reduced their UTS and elongation at break values. The reduction in the elongation at break values of the SLS specimens might have been exacerbated by the larger crystals formed due to the slow cooling in SLS, which led to the more brittle behavior of the specimens [21].

Table 4.10. Mechanical properties of the laser-sintered and injection molded tensile specimens.

	UTS (MPa)			Elongation at break (%)		
	SLS	Injection molded	Ratio ^{a)}	SLS	Injection molded	Ratio ^{a)}
CP20	14.9±1.12	37.5±1.29	0.40	1.0±0.13	11.3±0.54	0.09
CP60	20.4±0.59	30.9±0.86	0.66	237.7±54.96	951.4±106.04 ^{b)}	0.25
PP1101	26.1±0.46	30.5±0.75	0.86	9±1.1	1027±122.1	0.009

^{a)} The ratio of the UTS or elongation at break of the SLS specimens to that of the injection molded counterparts.

^{b)} The elongation at break value for the injection molded CP60 and PP1101 specimens was determined using stroke strain.

The UTS values of the injection molded CP20 specimens were higher than those of the CP60 and PP1101 specimens, whereas the elongation at break values of the CP20 specimens was lower. This was as expected since the ethylene component present in CP60 and PP1101 is known to toughen the polymer at the cost of reduced strength. However, it was found that the UTS value of the laser-sintered CP20 specimens was lower than that of the laser-sintered CP60 and PP1101 specimens. Furthermore, the ratios of the UTS values of the SLS specimens to those of the injection molded counterparts were lower for CP20 than CP60 and PP1101. A reason for the significantly reduced value of UTS of the SLS CP20 specimens was its intrinsically low elongation

at break that was exacerbated by the large number of voids formed during the SLS process, which resulted in the SLS specimens breaking before yielding.

As seen from the SEM images of the cross-section of the SLS CP20 specimen (Figure 4.14c), voids were formed in the interlayers, although the powder particles were sufficiently sintered within each layer. Since the η values of CP20 were substantially lower than those of CP60 and PP1101 at the temperature range investigated (Figure 4.5), the poorer coalescence observed with the SLS CP20 specimens was likely a result of the powder flowability rather than the viscosity effect. During the printing process, the flowability of the CP20 powder was significantly poorer than that of the CP60 powder, so that the CP20 powder could not flow from the hopper easily, and the surface of the SLS powder bed was visibly rougher. The localized imperfections, especially holes, present on the powder bed surface contributed to the part porosity, as discussed in Chapter 4.1.1. Even with a higher value of E_{vol} of 0.300 J/mm^3 , the degree of coalescence could not be improved sufficiently, and the mechanical properties deteriorated instead (Figure 4.14d). As a result of the poor interlayer adhesion and high part porosity, the CP20 specimens exhibited poor mechanical performance.

4.5. Crystal phases of PP specimens

Due to the dependence of crystal formation on the thermal processing conditions, the effects of different processing methods, i.e., SLS and injection molding, on the crystal phases of the printed specimens were investigated using XRD and DSC. It is known that the SLS and injection molding specimens of PA12 contain crystals that are predominantly of the γ -phase [104, 211]. PA12 has three main crystal phases, γ -, α' -, and α -phase, with the γ -phase being the most stable and prevalent. The γ -phase can be obtained by slow cooling, annealing, or rapid quenching [212]. In contrast, the α -phase

is only obtained under specific conditions, including high pressure and casting from solution [213]. While the α -phase can transform into the γ -phase at temperatures higher than 150 °C, the reverse does not occur even under high pressures. Meanwhile, the α' -phase is formed from the thermal expansion of the γ -phase and is the major phase found during isothermal crystallization at temperatures greater than 140 °C [214]. Although the SLS of PA12 occurs under a similar isothermal condition ($T_b > 165$ °C), the α' -phase is typically not observed in the SLS specimens because they transform into the γ -phase upon cooling to room temperature [212, 214].

There are three known crystal phases for PP, α -, β -, and γ -, of which the α -phase is kinetically favored and the most commonly observed (Figure 4.21). The β -phase is a metastable phase relative to the α -phase and can only be formed under certain crystallization conditions (e.g., large shear, high cooling rates, or use of β -nucleating agents) [215]. The γ -phase is more thermodynamically stable than the α -phase [216] but is typically present in small quantities with respect to the α -phase. Formation of the γ -phase is only favored in cases where the chain folding required for α -phase formation is suppressed [217-219].

The melt enthalpies and equilibrium melting points of the α - and γ -phase were reported to be 209 J/g and 186.1 °C, and 150 J/g and 187.2 °C, respectively [221]. If the γ -phase is negligible, the degree of crystallinity x_c of a specimen was calculated by

$$x_c = \frac{\Delta H_m}{209} \times 100\% \quad , \quad (4.10)$$

where ΔH_m is the melt enthalpy obtained from the DSC curve. When both the α - and γ -phase were present, the fraction of the γ -phase (X_γ) was first calculated using the XRD data [219]

$$X_\gamma = \frac{h_\gamma}{h_\gamma + h_\alpha} \quad , \quad (4.11)$$

Figure 4.21. Schematic lattice structures: (a) helical structure of polypropylene with ‘down’ positions of the methyl groups (black spheres) and the representation of the helix in a triangular bar. (b–d) The arrangement of PP-helices in the α -, β - and γ -phases, respectively. Reproduced with permission [220].

where h_γ and h_α are the heights of the (117)- and (130)-reflections, respectively. The x_c was then obtained by

$$\Delta H_{m,100\%} = 150X_\gamma + 209(1 - X_\gamma) \quad , \quad (4.12)$$

$$x_c = \frac{\Delta H_m}{\Delta H_{m,100\%}} \times 100\% \quad , \quad (4.13)$$

where $\Delta H_{m,100\%}$ is the melt enthalpy of a 100% crystalline specimen.

The XRD patterns of the CP20 powder and the injection molded and SLS specimens showed that the crystals present were mostly of the α -phase, which was expected (Figure 4.22a, b) [218, 222, 223]. The reflections of the SLS specimen were much more resolved than the powder and the injection molded specimen, with the (111)- and (131)-reflections having a smaller overlap, indicating a higher relative degree of crystallinity. The DSC results supported this observation, as a rightward shift of the melting peak and

a higher melt enthalpy were observed for the SLS specimen (Figure 4.22c). The high value of x_c calculated for the SLS specimen (53.1%) was a result of the prolonged heating and slow cooling conditions during SLS, which promoted chain rearrangement and the formation of crystals with thicker lamellae and fewer defects. In contrast, the x_c value of the injection molded specimen was the lowest at 47.7%; unlike SLS, the rapid cooling involved during the injection molding process gave the polymer chains less time for crystal formation.

The XRD patterns of the CP60 and PP1101 powders and their injection molded specimens showed that the crystals present were mostly of the α -phase (Figure 4.23a–d). In contrast, the XRD pattern of the SLS specimens showed that the γ -phase was predominant; the (117)-reflections of the γ -phase at $2\theta = 20.21^\circ$ and 19.94° were observed for CP60 and PP1101, respectively, while the (130)-reflections of the α -phase at $2\theta = 18.82^\circ$ and 18.52° for CP60 and PP1101, respectively, were barely visible. The formation of γ -phase was also presented in the DSC curve by the appearance of a second melting peak at a lower temperature (Figure 4.23e, f) [224]. The x_c values of the SLS CP60 and PP1101 specimens were 33.3% and 52.3%, respectively, according to equations 4.10–4.13, with the γ -phase contributing ~72% of the overall crystallinity for both PP copolymers. The increase in the x_c values of the SLS specimens with respect to their powders was attributed to the thermal conditions of the SLS process. The injection molded specimens of CP60 (23.2%) and PP1101 (28.5%) had low x_c values due to the rapid cooling of the polymer melt, similar to what was observed for CP20.

Some polyethylene crystals might be present in CP60 and PP1101 due to the ethylene content in the copolymers, but the formation of polyethylene crystals was unlikely due to the random nature of the copolymer used in this study; the characteristic (200)-reflection of polyethylene at $\sim 24^\circ$ was not visible in the XRD patterns, either

[225]. Therefore, it is concluded that the quantities of ethylene crystals present in both the polymer powder the specimens were few to none.

Figure 4.22. (a, b) XRD patterns and the corresponding miller indices of the crystal phases of the CP20 powders and its injection molded and SLS specimens. (c) DSC curves showing the melting endotherms of the CP20 powders and its specimens.

It has been suggested that the presence of γ -phase crystals in PP enhances compressive modulus and strength, and tensile modulus, strength, and elongation at break [226–228]. The γ -phase crystals are known to grow epitaxially on parent α -phase lamellae during crystallization [229] and is a result of accommodating chain defects outside the α -phase crystals and reducing the number of chains emerging from the crystal planes (5.73 and 4.39 chains/nm² for α - and γ -phase crystals, respectively) [217, 230]. Therefore, a larger quantity of γ -phase crystals will be formed in PP with higher chain defects (which hinders sharp chain backfolding and impedes the formation of the

α -phase to a larger extent), such as those with a larger number of stereo-irregularities [217, 219], or regio-irregular copolymers with 2.5–20 wt% comonomer units [217, 219, 231], i.e., CP60. The formation of the γ -phase is also known to be promoted by low molecular weight polymers [216, 219], crystallization under slow cooling [218, 231], low supercooling [224, 231], or elevated pressures [216, 219].\

Figure 4.23. XRD patterns and the corresponding miller indices of the crystal phases of the PP powders and the injection molded and SLS specimens: (a, b) CP60 and (c, d) PP1101. DSC curves showing the melting endotherms of the PP powders and their specimens: (e) CP60 and (f) PP1101.

Since γ -phase crystals were neither observed in the SLS CP20 specimens nor the injection molded copolymer specimens, it is concluded that the formation of the γ -phase crystals in the SLS copolymer specimens was a combined result of the regio-irregularity due to the comonomer, and the crystallization conditions of slow cooling and low supercooling during SLS. The unique thermal condition of SLS, i.e., prolonged processing times at high temperatures, allows printed parts to cool slowly; this makes SLS a viable manufacturing technique that is capable of altering the crystal phases or crystallinity of some polymers, which is difficult to achieve under typical injection molding conditions. This advantage of SLS has been demonstrated with PET, where crystalline parts that could not be produced directly via injection molding because of the slow crystallization kinetics of PET were printed by SLS instead [77].

4.6.Summary

The laser sintering of isotactic PP homopolymer and copolymers was investigated. The CP20, CP60, and PP1101 powders were characterized in terms of powder morphology, powder flowability, melting behavior, and crystallization kinetics. The HR values suggested that the flowability of the CP20 powder was inferior to that of the CP60 and PP1101 powders, which is attributed to the rough surface of the CP20 powder particles. Meanwhile, the powder bed surface analysis implied that the overall powder bed surface of CP60 was rougher than that of CP20 and PP1101, and the localized imperfections on the CP60 powder bed were deeper and wider. Although the $E_{A,C}$ values of CP20 (300.7 kJ/mol), CP60 (306.1 kJ/mol), and PP1101 (361.0 kJ/mol) were ~60% that of PA2200, the sintering windows of CP60 (2.2 °C) and PP1101 (7.2 °C) were significantly narrower than that of CP20 (26.3 °C). Therefore, CP60 and PP1101 were

less tolerant to temperature deviations during printing and were thus more difficult to process than CP20.

This chapter also demonstrated that the isothermal DSC method could be employed to determine the minimum value of T_b , and the temperature range within which the optimal value of T_b existed could be narrowed and evaluated more efficiently and effectively. With optimal sintering parameters, the UTS and elongation at break values of the printed CP20, CP60, and PP1101 specimens were 14.9 MPa and 1%, 20.4 MPa and 238%, and 26.1 MPa and 9%, respectively.

For CP20, both SLS and injection molding produced specimens that mainly consisted of α -phase crystals. In contrast, for CP60 and PP1101, specimens with different major crystal phases were produced, depending on the process used; with injection molding, the α -phase was the major crystal phase, while with SLS, the γ -phase was mainly observed. SLS serves as an alternative manufacturing technique capable of producing PP parts that are mainly composed of γ -phase crystals, which is difficult to achieve under typical molding conditions, especially when PP powders with high regio- and stereo-irregularities are used.

Chapter 5. Development of OMMT/PP Powders

Despite the many advantages of PP, one of its major disadvantages is its relatively poor thermo-oxidative stability that can be improved with clay minerals that consist of silicate layers that are typically nanometres thick, with other dimensions in the sub-micron range [31]. The thin, sheet-like nature of the layers can create tortuous paths within a polymer that impede the diffusion of small molecules such as oxygen, water, and volatile decomposition products [232, 233]. Furthermore, their reinforcing potential for physical and thermal properties are well documented [31, 32].

Montmorillonites are one of the most commonly used types of clay to prepare nanocomposites due to their fine particle size, high surface area, and high cation exchange capacity [173, 177]. To improve the compatibility of hydrophilic montmorillonites with non-polar polymers, they are usually modified with surfactants, for instance, alkylammonium salts to form OMMTs. OMMT/PP nanocomposites have an established history in conventional manufacturing processes, and their applications range from high-barrier packaging and water treatment to strong, heat-resistant automotive components [163, 164, 234]. Despite their popularity in the plastics industry, the development of OMMT/PP nanocomposite powders for SLS has not been reported to date.

This chapter aims to develop OMMT/PP nanocomposite powders with enhanced thermo-oxidative stability and mechanical properties for use in SLS. Four different composite powder preparation methods, i.e., mechanical mixing, surface coating, melt extrusion and grinding, and TIPS were investigated. The advantages and limitations of each preparation method were assessed in terms of nanocomposite powder morphology, OMMT dispersion, melt and crystallization behavior, thermal stability, and mechanical properties. The preparation method evaluated to be the most viable for SLS was then

used to prepare the nanocomposite powders at a large scale that was subsequently used for the SLS process.

5.1. OMMT/PP powder preparation

There exist several methods to produce composite powders for SLS [235], with the most common and straightforward being mechanical mixing, where polymer powders are physically mixed with nano-/ micro-sized fillers at a high rotation speed. Another method that utilizes polymer powders as feedstock is surface coating, which has been used for the coating of multi-walled CNTs onto the surface of PA12 and TPU powders [113, 115]. Melt extrusion boasts better filler dispersion and has traditionally been used to produce polymer composite filaments or pellets. Composite powders can then be obtained by cryogenic milling. Lastly, the thermally TIPS process, also known as dissolution-precipitation, is a solution-based process that involves polymer dissolution and precipitation in a compatible solvent [235]. It is currently being used to produce commercial PA12 powders due to the good particle shape and size distribution achievable [40]. While polymer powders have to be used as the feed material in mechanical mixing and surface coating, such restriction is not imposed on melt extrusion and TIPS.

5.1.1. Mechanical mixing

Even though composite powders can be produced with ease by mechanical mixing, this method was expected to produce poor enhancements in the properties of the resulting OMMT/PP nanocomposites. This is because the clay layers in OMMT will remain largely agglomerated, especially with their high surface area to volume ratio. As a result, the interfacial interaction between the PP polymer chains and the OMMT layers

would be minimal. Furthermore, because the clay layers remain agglomerated and there is no nano-scale dispersion, the clay particles can act as stress concentrators and embrittle the composite. The mechanically mixed composite powder is referred to as MM-OMMT/PP.

5.1.2. Surface coating

The surface coating of fillers onto polymer powders has been reported for PA12 and TPU using CNTs but has not yet been reported for PP composites and OMMT [113, 115]. While the fillers cannot be fully intercalated into the PP polymer matrix using this method, the coating of fillers onto the surface of polymer powders may serve as a viable up-scalable method for mass production of OMMT/PP nanocomposite powders. A unique characteristic of this method is that the morphology of the powders is largely retained, which can be advantageous or disadvantageous depending on the size and shape of the polymer powders used. Due to the presence of fillers on the surface of the polymer powders, the laser absorption and degree of coalescence of the nanocomposite powder may be impeded; therefore, there is a limit to the amount of filler that should be added to ensure the processability of the nanocomposite powders. The surface-coated composite powders, with and without SDS, are referred to as SC-OMMT/PP and SC-OMMT/SDS/PP, respectively.

5.1.3. Thermally induced phase separation

To enhance the interfacial interactions between the polymer and the filler, composites should be produced as a chemical mixture. Of the various methods, the in-situ polymerization of propylene is well-known to produce OMMT/PP nanocomposite with a high degree of clay exfoliation [234, 236-238]. Nonetheless, due to the fine

control of polymerization reaction required, elaborate experimental setup, and challenging polymerization conditions, this method was determined to be unsuitable in fulfilling the objective of this research. The solution intercalation method is an alternative option for the fabrication of OMMT/PP nanocomposite, but. However, although good dispersion of clay layers can be achieved, it was difficult to obtain the nanocomposite in powder form. This was because PP tended to form a film upon solvent removal or cooling [239]. Therefore, the solution intercalation method had to be modified so that OMMT/PP nanocomposite powder can be obtained; in this regard, the production of PP powder was used as a relevant reference.

Among the various PP powder fabrication methods, the production of PP powder from solution was of interest because OMMT can then be introduced directly into the PP matrix via solution intercalation. One of the methods is TIPS, which can be applied on a small scale. In this process, PP is initially dissolved in a suitable solvent such as xylene, and the solution is subsequently cooled to precipitate PP powder that can then be obtained by filtration [18, 240]. The size and morphology of the particles can be optimized for SLS by adjusting the PP concentration and quenching temperature. As the equipment and reagents used in this process are readily available, the experimental setup can be applied to develop PP and PP composite powders without much difficulty. Thus, this method was determined to be the most relevant for producing OMMT/PP powder. The OMMT/PP nanocomposite powders prepared by the TIPS process are referred to as TIPS-OMMT/PP.

5.1.4. Melt extrusion and cryogenic grinding

Melt extrusion is a good alternative and has been used to produce OMMT/PP nanocomposite filaments with exfoliated clay layers under appropriate extrusion

conditions [177, 241-243]. However, processing the nanocomposite filaments into a powder form that is suitable for SLS is a challenge. The most common method to produce PP powders from filaments is cryogenic grinding, which results in irregular powder particle shapes that are not ideal for SLS. The OMMT/PP nanocomposite powders prepared by melt extrusion followed by cryogenic grinding are referred to as ME-OMMT/PP.

5.2.OMMT/PP powder and specimen characterization

The SLS process demands stringent requirements on the extrinsic and intrinsic properties of polymer powders used. This section provides a comprehensive discussion of the critical properties and behavior of the OMMT/PP nanocomposite powders prepared.

5.2.1. Powder shape and size

The shape and size of powder particles are known to affect the powder packing and flow, which influences the sintering kinetics among powder particles as well as the surface roughness and the density of manufactured parts. The size and shape of the powder particles prepared by mechanical mixing, melt extrusion, and surface coating (MM-OMMT/PP, ME-OMMT/PP, SC-OMMT/PP, and SC-OMMT/SDS/PP) were similar to those of the PP powder particles (Figure 5.1b–f). The irregular shape of the ME-OMMT/PP particles was expected due to the cryogenic grinding process. Nonetheless, their shape and size appeared more irregular and larger than those of the PP particles since no post-processing was done for optimization. In the case of surface coating, the shape and size of the powder particles were retained because the majority of the powder neither melted nor dissolved during the experimental procedures. Similar

observations were reported when the same method was used to prepare CNT/PA12 and CNT/thermoplastic polyurethane powders [113, 115]. The retention of powder morphology can be advantageous if PP powders have particle sizes and shapes that are more appropriate for SLS.

Figure 5.1. SEM images of the OMMT particles, and the PP powder and the prepared nanocomposite powders: (a) OMMT, (b) PP, (c) MM-OMMT/PP, (d) SC-OMMT/PP, (e) SC-OMMT/SDS/PP, (f) ME-OMMT/PP, (g) TIPS-OMMT/PP obtained without 1-hexanol, and (h) TIPS-OMMT/PP obtained with 1-hexanol. (i) Particle size distribution curves of the TIPS-OMMT/PP powder prepared with 1-hexanol.

TIPS has been used to produce PP powders from solution but not yet for producing OMMT/PP nanocomposite powders suitable for SLS [18]. As the nanofiller particles contributed to inhomogeneities in the solution, the addition of OMMT complicated the precipitation process. Simple replication of the solution processes meant for neat PP powders could not yield OMMT/PP nanocomposite powders with the same physical

characteristics. Although OMMT could serve as nucleation sites to favor PP particle growth, it was insufficient to reduce the particle agglomeration and fusion since PP materials tended to form a film upon solvent removal or cooling (Figure 5.1g) [239]. The addition of an anti-solvent was needed to reduce the particle fusion, and 1-hexanol was chosen in this study for its high boiling point, miscibility with p-xylene, and incapability in dissolving PP. With the addition of 1-hexanol and optimized process parameters, a TIPS-OMMT/PP powder with appropriate particle size and shape was obtained (Figure 5.1h, i). The powder particles produced had a Gaussian-like size distribution curve and d_{10} , d_{50} , and d_{90} values of 39 μm , 62 μm , and 87 μm , respectively, well within the ideal range for SLS.

The surface roughness of the powder bed containing the powder particles is a good reflection of the powder flowability and is an important consideration for the SLS process, which requires a smooth and even powder bed surface. The rough and elevated regions of the powder bed can lead to the formation of surface scratches upon powder recoating, leading to defects during printing and may even cause build failure. The surface profiles of the PP, MM-OMMT/PP, SC-OMMT/PP, SC-OMMT/SDS/PP, ME-OMMT/PP, and TIPS-OMMT/PP powder beds were separately evaluated (Figure 5.2), and their corresponding average powder-bed surface roughness values were 41, 43, 37, 41, 78, and 46 μm , respectively.

The values of the surface roughness of the MM-OMMT/PP, SC-OMMT/PP, and SC-OMMT/SDS/PP powder beds were similar to that of the PP powder bed as expected, due to the nature of the nanocomposite powder production processes which retained the PP powder morphology. The TIPS-OMMT/PP powder bed had a slightly higher surface roughness, probably due to the presence of few large particles. Meanwhile, the surface roughness of the ME-OMMT/PP powder bed was significantly higher than those of the

other powder beds; this is because the grinding process in this study was not followed by particle rounding and the addition of flow agents, which are typical post-processing steps that commercial manufacturers adopt to improve powder flowability. Therefore, the achievable surface roughness of the ME-OMMT/PP powder bed can potentially be lower.

Figure 5.2. Surface profiles of the powder beds formed by the powder particles: (a) PP, (b) MM-OMMT/PP, (c) SC-OMMT/PP, (d) SC-OMMT/SDS/PP, (e) ME-OMMT/PP, and (f) TIPS-OMMT/PP.

5.2.2. OMMT dispersion

The dispersion of OMMT in the nanocomposite powders was examined using TEM. Large agglomerates ($>2\ \mu\text{m}$) were randomly distributed in the MM-OMMT/PP powder (Figure 5.3a), which was expected as mechanical mixing did not provide enough energy to break down the OMMT particles further. In the SC-OMMT/PP powder, the agglomerated OMMT particles with some degree of exfoliation were observed due to the ultra-sonication process. The dispersion of OMMT was improved with SDS as a surfactant; the agglomerates were significantly reduced in size and the face-face agglomeration was lessened, resulting in the SC-OMMT/SDS/PP powder having visibly thinner OMMT agglomerates (Figure 5.3b). The ME-OMMT/PP powder exhibited a

much more homogenous nanofiller dispersion and the OMMT particles were broken down into smaller sizes of 340 nm on average, with individual silicate layers visible (Figure 5.3c, e). In the TIPS-OMMT/PP powder, the dispersion of OMMT was less homogeneous and the average lateral size of those particles was further reduced to 45 nm (Figure 5.3d, f).

Figure 5.3. TEM images of the OMMT/PP nanocomposites at low and high (inset) magnifications: (a) MM-OMMT/PP, (b) SC-OMMT/SDS/PP, (c) ME-OMMT/PP, and

(d) TIPS-OMMT/PP. Lateral size distribution of OMMT particles in the nanocomposites: (e) ME-OMMT/PP and (f) TIPS-OMMT/PP.

In melt extrusion, OMMT was fed constantly into the extruder and mixed with the polymer matrix, and thus consistent nanofiller distribution across the extruded nanocomposite filaments was expected. The shear stress from melt extrusion improved OMMT exfoliation by breaking down the tactoid agglomerates and peeling some silicate layers from those tactoids; meanwhile, it aligned the silicate layers to a moderate extent, as represented by the red arrows in Figure 5.3c.

The precipitation of nanocomposite powder particles from solution via TIPS was instead more random than controlled. As a result, some TIPS-OMMT/PP powder regions had a higher concentration of OMMT particles while others had fewer to no nanofiller particles. The reduced nanofiller size in the nanocomposite powder was a result of the long ultra-sonication pre-treatment involved during the powder preparation process, which promoted the delamination and reduction of the OMMT particle size due to cavitation [244-246]. The fragmented OMMT particles had remarkably reduced aspect ratios, as observed in Figure 5.3d.

The dispersions of OMMT on the surface-coated nanocomposite powders were also observed through SEM. The OMMT layers appeared as rough regions on the particle surface, and their identity was confirmed by EDX (Figure 5.4). The OMMT layers were barely present on the surface of the SC-OMMT/PP powder particles, and evidently, OMMT was not well-coated. Meanwhile, for the SC-OMMT/SDS/PP powder, the addition of SDS as an anionic surfactant significantly improved the dispersion and promoted the coating of OMMT layers onto the powder surface.

While montmorillonites are commonly modified with cationic surfactants, it has been suggested that the use of both anionic and cationic surfactants produces a

synergistic effect in improving the aqueous solubility, interaction with polymers, and adsorption and absorption capacities [247]. Instead of the conventional ion exchange reactions observed with cationic surfactants, anionic surfactants are adsorbed by electrostatic interaction with cations at positive edge sites and ‘ligand exchange’ with structural -OH groups [248, 249]. Anions can be adsorbed in larger quantities by ligand exchange than by counterion binding as ligand exchange occurs even when the surface is neutral or negatively charged [249].

Figure 5.4. SEM images of the PP and the surface-coated nanocomposite powders: (a) PP, (b) SC-OMMT/PP and (c) SC-OMMT/SDS/PP. (d) EDX profiles of sites 1 and 2. Regions with OMMT are encircled with solid lines.

In the SC-OMMT/SDS/PP powder, the addition of SDS could influence the arrangement of pre-intercalated alkyl ammonium ions in OMMT and contribute to interlayer expansion [247]. The adsorbed SDS molecules also acted as nuclei around

which additional SDS molecules could cluster, increasing the negative edge charge density and stability of the OMMT dispersion [249]. The adsorption of SDS was expected to be accompanied by an increase in the pH of the solution, as it was likely that hydroxides and possibly oxides were released when SDS underwent ligand exchange [250]. The interaction between SDS and OMMT was confirmed experimentally by measuring an increase in the pH from 7.5 (OMMT dispersed in water) to 9.6 upon the addition of SDS.

5.2.3. Melt and crystallization behavior

Since SLS involves the melting and crystallization of polymer powders, it is imperative to consider the material's thermal processing window, i.e., the sintering window. The MM-OMMT/PP, SC-OMMT/PP, and SC-OMMT/SDS/PP powders had T_m and T_c values similar to those of the PP powder (Figure 5.5a, b and Table 5.1) because of limited interactions between the OMMT particles and the polymer matrix. Although the T_m value of the ME-OMMT/PP powder was also almost unchanged from PP, it had a slightly higher $T_{c,onset}$ value than that of PP (+1.4 °C). Nevertheless, despite the increase in $T_{c,onset}$, its sintering window remained sufficient for SLS at 24.4 °C. The TIPS-OMMT/PP powder, on the other hand, showed a more significant increase in the $T_{m,onset}$ and T_m values with a concurrent reduction in the $T_{c,onset}$ and T_c values, giving it the largest sintering window of 32.2 °C.

In SLS, the sintered parts are maintained at an elevated temperature to delay crystallization as much as possible until the build is completed. This is to minimize non-uniform process shrinkage and the accumulation of residual stresses that can cause part distortion and warpage. To further investigate the melt crystallization behaviors of PP and the nanocomposite powders, isothermal DSC was used to mimic the quasi-

isothermal conditions in SLS and compare the relative rates of crystallization at a given temperature. At 135 °C, the crystallization peak of the ME-OMMT/PP powder was shifted left from that of PP, while that of the TIPS-OMMT/PP powder was broadened and shifted to the right (Figure 5.5c). The mechanically mixed and surface-coated nanocomposite powders showed little deviation from PP. It could be concluded that at 135 °C, the ME-OMMT/PP powder crystallized slightly faster than PP, while the TIPS-OMMT/PP powder crystallized much slower.

Figure 5.5. DSC curves of the PP and the nanocomposite powders under different conditions: (a) heating rate of 10 °C /min, (b) cooling rate of 10 °C /min, and (c) isothermal cooling at 135 °C.

The crystallization processes visualized with hot-stage microscopy supported the above conclusion (Figure 5.6). The crystallization of the molten ME-OMMT/PP powder particles started with a visibly higher density of growing crystal sites than that of the molten PP powder particles. It took 30 min and 40 min for the ME-OPMT/PP and PP

powders, respectively, to crystallize completely. On the contrary, the molten TIPS-OMMT/PP powder particles remained almost crystal-free even until 90 min. In fact, till the end of the experiment at 120 min, only a few crystals were observed, and significant crystallization was only observed upon further cooling.

Figure 5.6. Optical microscope images of the powder melt of PP, ME-OMMT/PP, and TIPS-OMMT/PP.

To examine the causes of the melting and crystallization behavior observed, especially with the TIPS-OMMT/PP powder, a PP powder named TIPS-PP was produced via a similar solution process, and its thermal behavior was studied for comparison. Both the powders prepared via TIPS had slower crystallization rates, lower T_c , and higher melt enthalpies ΔH_{melt1} (115.2 J/g for TIPS-PP and 114.5 J/g for TIPS-OMMT/PP) than the PP powder (99.6 J/g) (Figure 5.7 and Table 5.1). The higher melt enthalpy attained is beneficial for increasing the threshold against the unwanted sintering of neighboring powder particles [40].

The annealing-like cooling conditions involved in TIPS and the use of solvents allowed high chain mobility while ensuring sufficient time for chain diffusion [251]. While this led to an increased polymer chain entanglement density due to the conformational entropy effect [252], the annealing-like conditions also facilitated

crystallization and promoted the reduction or elimination of crystal defects in crystalline regions [200]. As a result of the formation of crystals with a higher degree of perfection and possibly thicker lamellas, the ΔH_{melt} for the powders prepared by TIPS were higher than those of the raw PP material and the other developed nanocomposite powders.

Figure 5.7. DSC curves of the PP, TIPS-PP, and TIPS-OMMT/PP powders under different conditions: (a) heating rate of 10 °C /min, (b) cooling rate of 10 °C /min, and (c) isothermal cooling at 135 °C.

The entanglements formed during the solution process are expected to be preserved throughout the melt crystallization process [253]. Polymer chain motion became more constrained once entanglement occurred; since crystal growth necessitated the disentanglement and large-scale conformational rearrangement of polymer chains, slower crystal growth resulted from entanglements [254-256]. Furthermore, when the molecular chains crystallized from the polymer melt, the high chain mobility initially offered by the solvents used in TIPS was absent. As a result, the TIPS-PP and TIPS-

OMMT/PP powders crystallized slower and had lower T_c values than PP and the other nanocomposite powders. In addition, their melt enthalpies were reduced from the first (ΔH_{melt1}) to the second DSC cycle (ΔH_{melt2}) (Table 5.1). The melt and crystallization behavior of the powders prepared by TIPS demonstrated the potential of using TIPS to produce PP and its nanocomposite powders with reduced T_c and melt crystallization rates, both of which are desired for SLS.

The nanocomposite powder prepared by TIPS showed a more significant delay in melt crystallization than the PP powder prepared by the same method, suggesting that OMMT had some effects in impeding crystallization. Although the delay is counterintuitive and contrary to most OMMT nanocomposites, it has been observed with PP and other polymer matrices (e.g., poly(ϵ -caprolactone), PA6 and PA6,6) [257-262]. The crystallization of a polymer melt is affected by nucleation and diffusion. Even though OMMT particles served as additional nucleation sites, they hindered the diffusion of polymer segments to a growing crystallite. The barrier effect of the nanofillers with platelet-like structures on polymer chain movement was also reported with graphene [263]. When the nucleation effect was dominant in the ME-OMMT/PP powder, crystallization was promoted. When the barrier effect was dominant in the TIPS-OMMT/PP powder, crystallization was impeded.

The differences in the nanofiller sizes (340 nm and 45 nm on average in ME-OMMT/PP and TIPS-OMMT/PP powders, respectively) led to different effects on the crystallization behavior. While the ME-OMMT/PP powder contained larger OMMT particles, which predominantly resulted in a nucleation effect, the OMMT fragments with sheet-like structures in the TIPS-OMMT/PP powder were too small to act as effective nucleation sites. Instead, the barrier effect became dominant as their surface-area-to-volume-ratio increases. Hence, the OMMT fragments in the TIPS-OMMT/PP

Table 5.1. The key melting and crystallization properties of the PP powder and the prepared nanocomposite powders.

Sample	$T_{m,onset}$ (°C)	T_m (°C)	$T_{c,onset}$ (°C)	T_c (°C)	Sintering window (°C)	ΔH_{melt1} (J/g)	x_{c1} (%)	ΔH_{melt2} (J/g)	x_{c2} (%)
PP	150.1 (± 0.11)	163.8 (± 0.03)	123.8 (± 0.01)	121.6 (± 0.06)	26.3 (± 0.12)	99.6 (± 1.36)	48.6	107.0 (± 0.50)	52.2
MM-OMMT/PP	151.2 (± 1.19)	164.1 (± 0.12)	123.8 (± 0.01)	121.8 (± 0.03)	27.4 (± 1.18)	94.1 (± 2.73)	45.9	105.9 (± 2.76)	51.7
SC-OMMT/PP	151.8 (± 0.81)	164.1 (± 0.13)	123.9 (± 0.02)	121.9 (± 0.08)	27.9 (± 0.82)	99.2 (± 1.19)	48.4	105.6 (± 1.89)	51.5
SC-OMMT/SDS/PP	151.9 (± 1.31)	164.3 (± 0.26)	123.5 (± 0.05)	121.5 (± 0.19)	28.5 (± 1.29)	97.4 (± 0.25)	47.4	105.8 (± 0.78)	51.9
TIPS-OMMT/PP	154.0 (± 1.95)	165.4 (± 0.08)	121.9 (± 0.01)	120.0 (± 0.18)	32.2 (± 1.95)	114.5 (± 0.10)	55.9	105.7 (± 0.70)	51.6
TIPS-PP	149.8 (± 0.82)	162.6 (± 0.42)	121.8 (± 0.01)	119.5 (± 0.17)	27.9 (± 0.82)	115.2 (± 2.09)	56.2	105.5 (± 2.87)	51.5
ME-OMMT/PP	149.6 (± 0.76)	164.4 (± 0.18)	125.2 (± 0.01)	122.3 (± 0.04)	24.4 (± 0.75)	95.4 (± 0.55)	46.6	107.3 (± 1.68)	52.4

* x_{c1} and x_{c2} represent the degree of crystallinity calculated from the melt enthalpies of the first and second DSC heating cycles, respectively.

powder reduced the mobility of the polymer chains and impeded crystallization. Such particle-size-dependent crystallization behavior was also observed with layered double hydroxide/PP composites, where micro-sized fillers exhibited much higher nucleation activity than their nano-sized counterparts [264].

The T_m values of the TIPS-OMMT/PP powder in both the first and second DSC heating cycles (165.4 °C and 162.6 °C, respectively) were higher than those of the TIPS-PP powder (161.9 °C and 160.3 °C, respectively). In fact, the TIPS-OMMT/PP powder had the highest T_m amongst all prepared nanocomposite powders. Since the TIPS-PP powder had a lower T_m than PP, the observed increase in T_m of the TIPS-OMMT/PP powder was not attributed to the process history but rather the presence of nano-sized OMMT fragments. It was postulated that the barrier effect of those OMMT fragments in both the solution and polymer melt slowed down the formation of crystallite nucleation sites that had sizes exceeding the minimum value necessary for crystal growth. As a result of the fewer crystal growth centers, the average lamellar thickness increased, accounting for the higher T_m . Another contributing factor was the lateral size of OMMT fragments that was of the same order of magnitude as the average thickness of PP lamellae (17–20 nm) [265]. OMMT has been known to disrupt or hinder the formation of homogeneous, ordered lamellar structures [266, 267], but in the case of nano-sized OMMT fragments, their small lateral size might have contributed less to the disruption.

All the nanocomposite powders prepared had sintering windows ranging from 24.4 °C to 32.2 °C that were sufficient for the SLS process, with the TIPS-OMMT/PP powder exhibiting the widest window. While it is common for T_m and T_c to increase simultaneously upon the addition of nanofillers as they mostly act as nucleation sites [33], the observations with the TIPS-OMMT/PP powder suggested the possibility of

incorporating small amounts of nano-sized fillers with layered structures to widen sintering windows by limiting the increase in T_{ic} and T_c . In addition, TIPS was able to yield powders with lower T_{ic} and T_c than the raw PP material used, which is desirable for SLS.

5.2.4. Thermal stability

Functional parts with enhanced thermal stability, especially under air atmosphere, are desired for high-temperature and long-term usage typical of engineering applications. Thermal stability is important for SLS materials due to the prolonged heating involved during part fabrication. The thermal degradation parameters $T_{d,onset}$, $T_{d,max}$, and $r_{d,max}$ of a material affect its tolerance to the processing conditions and thus are important considerations.

All the prepared nanocomposite powders had reduced $r_{d,max}$ and slightly lower $T_{d,onset}$ under air atmosphere (Figure 5.8 and Table 5.2) because of the two contradicting effects of the OMMT particles on PP. On the one hand, the barrier properties of the OMMT layers impeded the degradation and the escape of volatile decomposition products, leading to a lower $r_{d,max}$. On the other hand, the Bronsted acid sites formed from the thermal decomposition of the bis(hydrogenated tallow alkyl)dimethyl ammonium cations catalyzed the degradation of the PP molecular chains via Hoffman's reaction, leading to slight reductions in $T_{d,onset}$ [233, 268-270].

Due to the poor interactions between the OMMT and the polymer matrix in the MM-OMMT/PP and SC-OMMT/PP powders, the values of their ΔT , defined as the difference between $T_{d,max}$ and $T_{d,onset}$, were similar to that of PP (98 °C). Meanwhile, the observed reduction in their $r_{d,max}$ was likely due to the adsorption of volatile decomposition products by the OMMT layers [271]. The barrier effect of OMMT was

more prominent in the SC-OMMT/SDS/PP powder and the ΔT increased to 116 °C. Its enhanced thermo-oxidative stability was attributed to the high surface concentration and better dispersion of the OMMT layers that translated to higher efficiency and effectiveness in degradation impediment, as well as enhanced adsorption of volatile decomposition products.

Figure 5.8. Thermal stability of the PP and the nanocomposite powders under air atmosphere: (a) TGA and (b) DTG curves.

The thermo-oxidative stability of the TIPS-OMMT/PP powder was higher than those of the mechanically mixed and surface-coated nanocomposite powders; its $r_{d,max}$ was 1.0 %/°C, only 60% that of PP, and its ΔT increased to 117 °C. Since the OMMT layers were embedded within the polymer matrix in this nanocomposite powder, the barrier effect was more apparent and so was the resistance to oxidative thermal degradation. Nevertheless, due to the lower aspect ratio and shorter lateral dimension of the OMMT fragments, the tortuous paths that served to impede the diffusion of small molecules were also shorter, therefore limiting their barrier properties.

The ME-OMMT/PP powder exhibited the highest thermo-oxidative stability amongst all the prepared nanocomposites, as shown from the substantial increase of ΔT to 168 °C and a relatively low $r_{d,max}$ of 1.2 %/°C. Its $T_{d,max}$ occurred at a much higher temperature; at temperatures up to 335 °C, this nanocomposite powder had the lowest

degradation rate. Its enhanced stability was supported by the fact that its activation energy for thermal degradation $E_{A,D}$ under air atmosphere was 84 kJ/mol, higher than that of PP at 71 kJ/mol (Figure 5.9). The significant improvement in thermo-oxidative stability was a consequence of the homogeneous dispersion of OMMT particles in the polymer matrix that was achieved by the shear forces exerted during the melt extrusion process.

Figure 5.9. Plots of $\ln(\beta/T_{d,max}^2)$ against $1/T_{d,max}$: (a) CP20 and (b) ME-OMMT/PP.

The above results confirmed that the thermo-oxidative stability of PP could indeed be improved by incorporating OMMT. The improvement was most significant in the ME-OMMT/PP powder when the OMMT layers retained their high aspect ratios and lateral dimensions while being homogeneously dispersed within the polymer matrix. The substantial enhancement in thermo-oxidative stability would be useful for alleviating the tendency of PP to degrade upon exposure to the long hours of high-temperature operating conditions during SLS.

The residual masses of the nanocomposite powders at 600 °C during the TGA tests indicated that most of the OMMT particles were incorporated into the nanocomposite powders, except the surface-coated samples where the residual masses were slightly lower (Table 5.2). The loss of OMMT during the surface coating process was confirmed

by the appearance of grey residue upon centrifugation. Thus, the actual amounts of OMMT in both the SC-OMMT/PP and SC-OMMT/SDS/PP powders were slightly lower than intended.

Table 5.2. The thermal stability of the PP powder and the prepared nanocomposite powders.

Sample	$T_{d,onset}$ (°C)	$T_{d,max}$ (°C)	ΔT (°C)	r_{max} (%/°C)	Residual mass at 600°C (%)
PP	217 (± 0.2)	314 (± 1.2)	98 (± 1.4)	1.7 (± 0.03)	0.1 (± 0.03)
MM-OMMT/PP	215 (± 0.9)	312 (± 1.6)	97 (± 0.8)	1.4 (± 0.03)	0.8 (± 0.03)
SC-OMMT/PP	214 (± 0.9)	312 (± 0.3)	98 (± 0.8)	1.3 (± 0.05)	0.5 (± 0.06)
SC-OMMT/SDS/PP	210 (± 1.8)	326 (± 0.9)	116 (± 1.8)	1.3 (± 0.08)	0.6 (± 0.13)
TIPS-OMMT/PP	204 (± 1.7)	321 (± 5.8)	117 (± 4.2)	1.0 (± 0.01)	0.8 (± 0.07)
ME-OMMT/PP	210 (± 2.7)	378 (± 2.8)	168 (± 5.5)	1.2 (± 0.09)	0.7 (± 0.01)

* Residual mass of OMMT at 600 °C is 66%.

5.2.5. Mechanical properties

The tensile properties of the injection-molded specimens are illustrated in Figure 5.10. It is widely known that well-dispersed OMMT can serve as mechanical reinforcements [31]. However, when poorly dispersed, agglomerated silicate layers can act as stress concentrators and embrittle the nanocomposite, which worsens the mechanical properties, especially the UTS and elongation at break.

Since the silicate layers in the SC-OMMT/PP and SC-OMMT/SDS/PP tensile specimens were not distributed within the polymer matrix, the improvement of the mechanical properties was difficult to achieve. The UTS and elongation at break of the SC-OMMT/PP specimens were lower than those of PP. Especially, the elongation at break was half that of PP, which was likely caused by the poor dispersion of the OMMT layers that embrittled the specimens. With a better dispersion of the OMMT layers, for

example, in the SC-OMMT/SDS/PP specimens, the UTS, Young's modulus, and elongation at break were comparable to those of PP.

Figure 5.10. Tensile properties of the PP and the nanocomposite specimens prepared by injection molding.

The mechanical properties of the MM-OMMT/PP tensile specimens were much better than expected because the injection molding process provided shear stresses that slightly enhanced the nanofiller dispersion. The effect of the injection molding process on the nanofiller dispersion was expected to be the most prominent in the mechanically

mixed samples where the movement of nanofiller particles was not bound by pre-existing interactions with the polymers.

The ME-OMMT/PP tensile specimens exhibited the highest UTS and elongation at break values of 36.3 MPa and 11.9%, respectively, due to the well-dispersed OMMT particles and the good interfacial interaction between the OMMT particles and the polymer matrix. The enhanced elongation at break is possibly due to the delamination of the clay platelets as well as the structural and morphological changes induced by the clay particles, including the transition of spherulites to thin, fiber-like crystallites that are re-oriented in the strain field [272]. Coupled with its exceptional thermo-oxidative stability, the ME-OMMT/PP powder proved to be the most suitable for functional SLS applications among all the nanocomposite powders prepared by the four methods.

5.3. Summary

Four types of OMMT/PP powders were prepared by four different powder preparation methods, i.e., mechanical mixing, surface coating, melt extrusion followed by cryogenic grinding, and TIPS. The powders were comprehensively investigated and compared in terms of SLS processability, thermal stability, and mechanical properties. Their key properties are summarized in Table 5.3.

Mechanical mixing was the most cost-effective and straightforward but had limited enhancement in thermal stability due to the poor dispersion of OMMT. For the surface coating method, even though a good dispersion and adhesion of OMMT onto PP powder particles could be achieved with the addition of SDS, the thermo-oxidative stability was only slightly enhanced. Since the mechanical mixing and surface coating methods used powdered materials as feedstock, the prepared nanocomposite powder particles largely inherited the morphology and shape of the PP powder particles used. Their melt and

crystallization behaviors remained almost unchanged because of limited interactions between the nanofiller particles and the matrix.

The TIPS-OMMT/PP powder had the widest sintering window of 32.2 °C due to the combined effects of an increased T_{im} and a reduced T_{ic} . TIPS could be used to produce nanocomposite powders with a significantly lower rate of crystallization than PP powder due to the process history and the presence of nano-sized OMMT fragments that hindered the diffusion of polymer chains during the crystallization of the polymer melt. It was postulated that the annealing-like condition involved in TIPS contributed to a higher chain entanglement density and hence reduced crystallization rate and temperature. An additional advantage of TIPS was that it could directly produce near-spherical nanocomposite powder particles with powder particle size distribution desired for SLS without post-processing.

Of all the nanocomposite powder preparation methods attempted, melt extrusion was the most balanced option. The OMMT particles were homogeneously dispersed within the polymer matrix and retained their high aspect ratio and lateral size, contributing to a substantial enhancement in the thermo-oxidative stability of the ME-OMMT/PP powder. Furthermore, the UTS, Young's modulus, and elongation at break of the tensile specimens were simultaneously enhanced from that of PP.

Table 5.3. The key properties of the PP powder and the nanocomposite powders developed.

Properties		PP	MM-OMMT/PP	SC-OMMT/PP	SC-OMMT/SDS/PP	TIPS-OMMT/PP	ME-OMMT/PP
Shape		Irregular	Irregular	Irregular	Irregular	Near spherical	Irregular
Thermal	T_m (°C)	163.8 (±0.4)	164.1 (±0.2)	164.2 (±0.3)	164.2 (±0.3)	165.2 (±0.2)	164.3 (±0.1)
	T_c (°C)	121.7 (±0.1)	121.7 (±0.03)	121.8 (±0.1)	121.4 (±0.2)	119.8 (±0.3)	122.1 (±0.3)
	Sintering window (°C)	26.9 (±1.1)	30.1 (±2.2)	28.9 (±1.3)	28.0 (±1.4)	33.2 (±2.2)	24.6 (±1.0)
	ΔH_{melt1} (J/g)	99.6 (±1.4)	95.7 (±2.0)	99.2 (±1.2)	97.2 (±0.1)	114.5 (±0.1)	95.4 (±0.6)
	ΔH_{melt2} (J/g)	107.0 (±0.5)	107.7 (±1.3)	105.6 (±1.9)	106.3 (±0.5)	105.7 (±0.7)	107.3 (±1.7)
	$T_{d,\text{onset}}$ (air) (°C)	216.8 (±0.2)	215.1 (±0.9)	214.0 (±0.9)	210.0 (±1.8)	204.3 (±1.7)	209.8 (±2.7)
	$T_{d,\text{max}}$ (air) (°C)	314.4 (±1.2)	312.4 (±1.6)	312.0 (±0.3)	325.9 (±0.9)	321.2 (±5.8)	377.6 (±2.8)
	ΔT (air) (°C)	97.7 (±1.4)	97.2 (±0.8)	98.0 (±0.8)	115.9 (±1.8)	116.9 (±4.2)	167.8 (±5.5)
	r_{max} (air) (%/°C)	1.65 (±0.03)	1.36 (±0.03)	1.29 (±0.05)	1.27 (±0.08)	0.96 (±0.002)	1.15 (±0.09)
Mechanical	Young's modulus (MPa)	892 (±23)	1018 (±107)	996 (±85)	838 (±11)	-	905 (±69)
	Ultimate tensile strength (MPa)	33.4 (±0.4)	34.4 (±0.3)	31.1 (±0.4)	34.1 (±0.6)	-	36.3 (±0.3)
	Elongation at break (%)	9.1 (±1.3)	11.3 (±2.0)	4.4 (±0.8)	9.5 (±2.4)	-	11.9 (±0.4)

Chapter 6. Selective Laser Sintering of OMMT/PP Powders

This chapter describes the large-scale production of OMMT/PP nanocomposite powders via melt extrusion and cryogenic grinding, and the laser-sintering of these powders. Nanocomposites with different OMMT loadings, with and without compatibilizers, were first investigated by producing the nanocomposite pellets at a small scale using CP60 powders. The suitability of the nanocomposites for SLS was then determined based on the melt, crystallization, and rheological behavior as well as the thermal stability of their pellets and the mechanical performance of their injection molded specimens. The nanocomposites that were deemed to be suitable for SLS were then produced at a large scale in the pellet form, after which the pellets were cryogenically ground into powders. The nanocomposite powders produced were finally used for SLS, where the optimal process parameters were determined, and the mechanical and thermal properties of the SLS specimens were evaluated.

6.1. Effects of OMMT on the sinterability of the nanocomposite powders

For the development of the OMMT/PP nanocomposite pellets, filler loadings of 1 wt% (OMMT-1/PP), 3 wt% (OMMT-3/PP), and 5 wt% (OMMT-5/PP) were evaluated. It is widely recognized that a compatibilizer, commonly maleic acid-grafted PP (PPgMA), can be added as a third component to further enhance the interfacial interaction between OMMT and PP as well as the dispersion of the OMMT particles [174, 273]. Therefore, the effects of PPgMA on the thermal behavior and sinterability of the OMMT/PP nanocomposites were investigated. The ratio of OMMT to PPgMA in the ternary nanocomposites was 3, and these nanocomposites with 1 wt%, 3 wt%, and 5 wt% OMMT are referred to as OMMT-1/PPgMA/PP, OMMT-3/PPgMA/PP, and OMMT-5/PPgMA/PP, respectively.

The TGA and DSC were used to evaluate the thermo-oxidative stability and sinterability of the nanocomposites, respectively (Figure 6.11). All the nanocomposites demonstrated significantly enhanced thermo-oxidative stability compared to that of CP60, as represented by the rightward shift of their TGA curves from that of CP60 and the increase in their $T_{d,max}$ values, with the ternary nanocomposites exhibiting higher thermo-oxidative stability than the binary nanocomposites. This was attributed to the higher degree of filler dispersion in the ternary nanocomposites enabled by PPgMA. The optimal loading of OMMT for thermo-oxidative stability enhancement was determined to be 3 wt% since the nanocomposites with 5 wt% OMMT had similar thermo-oxidative stability to those with 3 wt%.

Figure 6.11. (a) TGA and (b) DSC curves of the CP60 powder and the OMMT/PPgMA/PP and OMMT/PP nanocomposite pellets.

The melt and crystallization properties of the ternary nanocomposites were determined from their DSC curves and are listed in

Table 6.1. Since the $T_{c,onset}$ and T_c values of PPgMA were higher than those of CP60, the addition of PPgMA would result in a shift of the $T_{c,onset}$ and T_c values of the ternary nanocomposites toward higher temperatures. Meanwhile, because the T_m value of PPgMA was higher than that of CP60, the $T_{m,onset}$ values of the nanocomposites were unaffected. As a result, the sintering windows of the ternary nanocomposites were much narrower than those of the binary nanocomposites. The melting of the PPgMA component in the ternary nanocomposites was observed as an endothermic peak from 150 – 160 °C (Figure 6.11 b) , which significantly increased the melting range values of the nanocomposites. Owing to the negative sintering windows and the large melting range values (58–60 °C) of the ternary nanocomposites, it is concluded that they are unsuitable for SLS and are not further discussed.

Table 6.1. Key thermal properties of the CP60 powder, and the OMMT/PP and OMMT/PPgMA/PP nanocomposite pellets.

OMMT content (wt%)	CP60	OMMT/PPgMA/PP		
	0	1	3	5
Onset melting temperature $T_{m,onset}$ (°C)	100	103	104	104
Melting peak T_m (°C)	133	134	135	136
Onset crystallization temperature $T_{c,onset}$ (°C)	98	112	113	115
Crystallization peak T_c (°C)	94	107	108	110
Melting range (°C)	51	58	58	60
Sintering window (°C)	2	−9	−9	−11
$T_{d,max}$ (°C)	322	407	428	427

For the binary OMMT/PP nanocomposites, the loading of OMMT should be limited to 3 wt%. This is because the thermo-oxidative stability of OMMT-3/PP was similar to

that of OMMT-5/PP, and thus, there was no imperative to further increase the OMMT loading beyond 3 wt%.

Depending on the filler dispersion and the strength of the interfacial interactions, OMMT can enhance or reduce the mechanical properties of PP. To assess the effects of OMMT on the mechanical performance of the binary nanocomposites, the properties of the injection molded nanocomposite tensile specimens were evaluated (Figure 6.12). As the thermal cycle that the nanocomposites were exposed to during melt extrusion could influence the mechanical properties of the specimens, the CP60 powder was extruded once (CP60-Extruded), and the properties of its injection molded specimens were compared against those of the injection molded nanocomposite specimens.

The CP60-Extruded specimens exhibited slightly lower Young's modulus and elongation at break values than the CP60 specimens, likely due to some polymer degradation during the extrusion process. The UTS values of the nanocomposite specimens only slightly reduced with increasing OMMT loading, and their Young's modulus values were significantly higher than that of the CP60-Extruded specimen. Meanwhile, the elongation at break values of the OMMT-1/PP and OMMT-3/PP specimens were similar to that of the CP60-Extruded specimen. In contrast, the elongation at break value of the OMMT-5/PP specimen was less than half that of the CP60-Extruded specimen. Due to the poor elongation at break of the OMMT-5/PP specimens, OMMT-5/PP was undesirable for SLS, and this conclusion is complementary to that derived from the DSC and TGA results. Therefore, OMMT-5/PP was not studied further.

Figure 6.12. Tensile properties of the injection molded CP60 and OMMT/PP nanocomposites and the laser-sintered CP60 specimens. CP60-Extruded is the sample produced by subjecting CP60 powder to a single extrusion cycle. The elongation at break values were determined from stroke strain.

The rheological behaviors of OMMT-1/PP and OMMT-3/PP were investigated since OMMT influences the η value of a polymer, which is critical to the sintering kinetics (Figure 6.13). The η values of CP60, OMMT-1/PP, and OMMT-3/PP at 160 °C were 14.1 kPa·s, 15.3 kPa·s, and 17.3 kPa·s, respectively. Since the silicate layers of OMMT hindered the movement and diffusion of polymer chains, it was expected that the η values would increase with increasing amounts of OMMT, which indicates that the sintering kinetics of the nanocomposites would be reduced. Nevertheless, because

the η values of the nanocomposites were well within an order of magnitude of that of CP60, they were expected to remain processable by SLS.

Figure 6.13. Viscosity curves of CP60, OMMT-1/PP, and OMMT-3/PP powders: (a) temperature and (b) frequency sweep.

The storage modulus G' , a measure of the elastic character of a viscoelastic material, was expected to increase with higher OMMT loadings since OMMT promotes elastic behavior. The G' value of OMMT-1/PP was the same as that of CP60 at 11.2 Pa, while that of OMMT-3/PP increased to 16.5 Pa. The unchanged value of G' of OMMT-1/PP was likely because of the low concentration of OMMT that did not contribute significantly to the elastic behavior of the nanocomposite. Meanwhile, the crossover frequency, which is inversely related to the relaxation time, decreased as the amount of OMMT increased; the crossover frequency values of CP60, OMMT-1/PP, and OMMT-

3/PP were 47.2, 43.5, and 42.7 rad/s, respectively. This corresponded to an increase in relaxation time with higher loadings of OMMT and could be explained by the confinement effects of the silicate layers on the movement of the polymer chains.

Based on the melt and crystallization behaviors of the prepared nanocomposites, PPgMA was determined to be detrimental to the sinterability of the nanocomposites. Thus, the ternary nanocomposites were not further studied. Meanwhile, OMMT-5/PP had inferior mechanical properties compared to OMMT-3/PP, yet its thermo-oxidative stability was similar to OMMT-3/PP. Since there was no impetus in using 5 wt% of OMMT, the loading of OMMT in the binary nanocomposites was limited to 3 wt% for future studies.

6.2. Characterization of OMMT/PP powders

The OMMT-1/PP and OMMT-3/PP nanocomposite pellets were produced at a large scale using CP60 pellets and Cloisite 20. They were subsequently cryogenically ground to produce P-OMMT-1/PP and P-OMMT-3/PP nanocomposite powders, respectively. The particle morphology, melt and crystallization behavior, thermal degradation properties, and filler dispersion of the powders were then characterized. The characterization procedure of the nanocomposite powders is similar to those as discussed in Chapters 3 and 4.

6.2.1. Powder morphology

The CP60, P-OMMT-1/PP, and P-OMMT-3/PP powder particles were irregularly shaped but had rounded edges that served to improve the packing and flow of the powders. Both the nanocomposite powders contained large quantities of small particles (<30 μm), and the surfaces of their powder particles were visibly rougher than those of

the CP60 powder particles (Figure 6.14). The HR values of CP60, P-OMMT-1/PP, and P-OMMT-3/PP were 1.22, 1.22, and 1.25, respectively, suggesting that the flowability of P-OMMT-3/PP was the poorest, whereas the flowability of P-OMMT-1/PP was similar to that of CP60.

Figure 6.14. SEM images of the CP60, P-OMMT-1/PP, and P-OMMT-3/PP powders.

The powder bed surface roughness of CP60, P-OMMT-1/PP, and P-OMMT-3/PP was studied using a 3D laser confocal microscope, and their S_a , R_c , and R_{sm} values were evaluated (Figure 6.15). As elaborated in Chapter 4.1, the S_a value is an indicator of the overall powder bed surface roughness, while the R_c and R_{sm} values are used to assess the vertical and lateral sizes of the localized imperfections, i.e., holes or bumps, present on the powder bed surfaces.

The S_a , R_c , and R_{sm} values of P-OMMT-1/PP and P-OMMT-3/PP were lower than those of CP60 (Table 6.2). This was attributed to the large quantities of small particles in the nanocomposite powders that could fill the gaps between the larger particles. As a result, the nanocomposite powders had smoother powder bed surfaces, and the sizes of the localized imperfections on their powder beds were smaller. The S_a , R_c , and R_{sm} values of P-OMMT-3/PP were higher than those of P-OMMT-1/PP due to the poorer powder flowability of P-OMMT-3/PP that negatively affected its powder spreading, thus increasing its powder bed surface roughness and size of localized imperfections.

Figure 6.15. 3D height images and typical surface profiles of the polymer powders: (a) CP60, (b) P-OMMT-1/PP and (c) P-OMMT-3/PP.

Nonetheless, since the S_a , R_c , and R_{sm} values of the nanocomposite powders were lower than those of CP60, a printing layer thickness of 0.15 mm used for the SLS of CP60 was determined to be suitable for the nanocomposite powders and was subsequently employed.

Table 6.2. Summary of the physical properties of CP60, P-OMMT-1/PP, and P-OMMT-3/PP powders.

	CP60	P-OMMT-1/PP	P-OMMT-3/PP
Bulk density (g/cm ³)	0.36	0.37	0.36
Tap density (g/cm ³)	0.44	0.46	0.45
Hausner Ratio	1.22	1.22	1.25
S_a (μm)	52	30	42
R_c (μm)	210±2.0	157±3.7	172±1.6
R_{sm} (μm)	508±9.9	399±14.8	445±10.2

6.2.2. Melt and crystallization properties

The thermal properties of the CP60 and nanocomposite powders are summarized in Table 6.3. Based on the DSC curves of CP60, P-OMMT-1/PP, and P-OMMT-3/PP (Figure 6.16a), their sintering windows were determined to be 2.2 °C, 14.7 °C, and 15.9 °C, respectively. The significant widening of the sintering windows of P-OMMT-1/PP and P-OMMT-3/PP resulted from large increases in their $T_{m,onset}$ values from that of CP60 by 14 °C and 16 °C, respectively, and slight increases in their $T_{c,onset}$ values by 1 °C and 2 °C, respectively. The melting range values of P-OMMT-1/PP (39.3 °C) and P-OMMT-3/PP (36.7 °C) were significantly narrower than that of CP60 (51.3 °C) because the nanocomposites had higher $T_{m,onset}$ values than CP60, whereas their $T_{m,offset}$ values were only slightly higher. Due to the wider sintering windows of the nanocomposites than CP60, they would be less sensitive to subtle changes in temperature and thus less prone to negative mid-build cooling effects, i.e., warping. Moreover, their narrower melting range values than that of CP60 suggested that their powder particles would melt more homogeneously upon laser irradiation. Therefore, they would be less prone to powder caking or over-sintering phenomenon.

To study the isothermal crystallization kinetics of CP60, P-OMMT-1/PP, and P-OMMT-3/PP, graphs of their degree of crystallization $\alpha(t)$ against time t at various T_{iso} values were first plotted (Figure 6.16b–d). The graphs were then used to construct Avrami plots according to the Avrami equation; the Avrami plots were subsequently linearly fitted, and the conversion range for each plot was chosen so that a good linear fit with an R^2 value greater than or equal to 0.9995 was obtained. The linear fits were then used to determine the k and $t_{1/2}$ values of the powders at different T_{iso} values. The $E_{A,c}$ values of CP60, P-OMMT-1/PP, and P-OMMT-3/PP were finally determined from the gradients of their logarithmic plots of $(\ln k)/n$ against $1/T_{iso}$.

Table 6.3. Summary of the thermal properties of CP60, P-OMMT-1/PP, and P-OMMT-3/PP powders.

	CP60	P-OMMT-1/PP	P-OMMT-3/PP
Onset melting temperature $T_{m,onset}$ (°C)	100	114	116
Melting peak T_m (°C)	133	140	141
Onset crystallization temperature $T_{c,onset}$ (°C)	98	99.06	99.78
Crystallization peak T_c (°C)	94	95	96
Melting range (°C)	51.3	39.3	36.7
Sintering window (°C)	2.2	14.7	15.9
Crystallization activation energy $E_{A,c}$ (kJ/mol)	306.1±3.92	284.7±3.14	273.6±4.13
Melt enthalpy (J/g)	58.7	52.4	53.9
Degree of crystallinity x_c (%)	28.1	25.1	25.8

The isothermal crystallization parameters obtained for the powders are summarized in Table 6.4. The $E_{A,c}$ values of CP60, P-OMMT-1/PP, and P-OMMT-3/PP were 306.1 kJ/mol, 284.7 kJ/mol, and 273.6 kJ/mol, respectively (Figure 6.16e). The $E_{A,c}$ values of the nanocomposites were lower than that of CP60 and appeared to decrease with increasing filler loading; therefore, the adverse effects of temperature deviations on the crystallization of the polymer melts at temperatures close to their T_c values were postulated to be less severe with increasing filler loading.

At a given T_{iso} value, the k values of the powders increased with filler loading, whereas the $t_{1/2}$ values decreased. For example, at 113 °C, the k values of CP60, P-OMMT-1/PP, and P-OMMT-3/PP were $1.58 \times 10^{-4} \text{ min}^{-1}$, $6.18 \times 10^{-4} \text{ min}^{-1}$, and $1.78 \times 10^{-3} \text{ min}^{-1}$, respectively, while their $t_{1/2}$ values were 13.73 min, 9.20 min, and 7.62 min, respectively. The observed increase in crystallization rates with an increase in filler loading was because the OMMT particles could act as heterogeneous nucleation

Figure 6.16. (a) DSC curves of CP60, P-OMMT-1/PP, and P-OMMT-3/PP powders. (b–d) Plots of $\alpha(t)$ against t at different T_{iso} values for CP60, P-OMMT-1/PP, and P-OMMT-3/PP, respectively. (e) Plots of $(\ln k)/n$ against $1/T_{iso}$ for evaluating the isothermal crystallization activation energies of CP60, P-OMMT-1/PP, and P-OMMT-3/PP powders.

sites that promoted crystallization; this conclusion was supported by the decrease in the n values of the powders with increasing filler loading, signifying the tendency toward instantaneous nucleation at higher filler loadings. Nevertheless, the increase in the

crystallization rate of the nanocomposites was expected to pose a minimal challenge to their SLS processing as they had wider sintering windows than CP60, allowing higher values of T_b to be used.

Table 6.4. Isothermal crystallization parameters for CP60, P-OMMT-1/PP, and P-OMMT-3/PP powders. The time t_{pc} at which crystallization heat flow was maximum was obtained directly from the isothermal DSC curve.

	T_{iso} (°C)	n	k (min ⁻¹)	$t_{1/2}$ (min)	$E_{A,C}$ (kJ/mol)	R^2
CP60	110	3.46	8.95×10^{-4}	6.86	306.1±3.92	0.9992
	112	3.15	3.85×10^{-4}	10.81		
	113	3.20	1.58×10^{-4}	13.75		
	115	3.28	2.36×10^{-5}	23.06		
	117	3.68	1.08×10^{-6}	37.95		
P-OMMT-1/PP	110	3.12	5.76×10^{-3}	4.65	284.7±3.14	0.9995
	111	3.10	2.91×10^{-3}	5.83		
	112	3.12	1.35×10^{-3}	7.40		
	113	3.16	6.18×10^{-4}	9.20		
	114	3.31	1.93×10^{-4}	11.84		
P-OMMT-3/PP	110	2.85	1.25×10^{-2}	4.11	273.6±4.13	0.9991
	111	2.81	6.88×10^{-3}	4.98		
	112	3.19	1.68×10^{-3}	6.57		
	113	2.88	1.78×10^{-3}	7.62		
	114	2.90	8.62×10^{-4}	9.63		

Owing to the complementary effects of the wider sintering windows and the narrower melting range and lower $E_{A,C}$ values, it was determined that the nanocomposites were easier to process than CP60. Importantly, unlike CP60 where its range of suitable T_b values was limited to 2 °C ($T_b = 123$ – 124 °C), a wider range of T_b values could be used for the nanocomposites, allowing for greater freedom in the

designing of their SLS process parameters. Notably, the developed nanocomposite powders demonstrated the potential of OMMT in improving the SLS processability of PP powder materials by widening their sintering windows and reducing their melting range values.

6.2.3. Thermal stability

The thermal stability of the powders was evaluated with TGA (Figure 5.7a), and their $T_{d,onset}$, $T_{d,max}$, and $r_{d,max}$ values under air and nitrogen atmosphere are summarized in Table 6.5. The $T_{d,onset}$ values of the powders were taken to be the temperature at which 1% mass loss occurs during their thermogravimetry testing. Based on the $T_{d,onset}$ values of CP60, P-OMMT-1/PP, and P-OMMT-3/PP in a nitrogen atmosphere, their SSRs were determined to be 150–298 °C, 153–295 °C, and 152–292 °C, respectively. Since the SSRs of the nanocomposites were similar to that of CP60, it is concluded that the addition of OMMT did not result in detrimental effects on the thermal processability of the nanocomposites.

Figure 6.17. Thermal behaviour of the CP60, P-OMMT-1/PP, and P-OMMT-3/PP powders: (a) TGA curves and (b) plots of $\ln(\beta/T_{d,max}^2)$ against $1/T_{d,max}$.

The nanocomposites exhibited significantly higher values of $T_{d,max}$ than CP60 under air atmosphere, and their ΔT values were substantially increased from 75.5 °C (CP60) to 146.0 °C (OMMT-1/PP) and 168.5 °C (OMMT-3/PP). Furthermore, the $E_{A,D}$ values of P-OMMT-1/PP and P-OMMT-3/PP, which were determined from their plots of $\ln(\beta/T_{d,max}^2)$ against $1/T_{d,max}$, were 120.7 kJ/mol and 137.2 kJ/mol, respectively, higher than that of CP60 at 33.4 kJ/mol (Figure 6.17b). The ΔT and $E_{A,D}$ values of the nanocomposites approximately doubled, and more than tripled than those of CP60, respectively, suggesting the viability of the nanocomposites for long-term usage and high-temperature applications.

Table 6.5. Summary of the thermal degradation properties of the CP60, P-OMMT-1/PP, and P-OMMT-3/PP powders.

	CP60	P-OMMT-1/PP	P-OMMT-3/PP
Maximum degradation temperature $T_{d,max}$ (°C)	324.7	377.3	398.6
ΔT (°C)	75.5	146.0	168.5
Thermal degradation activation energy $E_{A,D}$ (kJ/mol)	33.4	120.7	137.2
Onset degradation temperature $T_{d,onset}$ (in N ₂) (°C)	297.5	295.3	291.5
Maximum degradation temperature $T_{d,max}$ (in N ₂) (°C)	428.9	421.3	423.1
Stable sintering region (in N ₂) (°C)	150–298	153–295	152–292

6.3. Determination of powder bed temperature

Following the characterization of the P-OMMT-1/PP and P-OMMT-3/PP powders, the powders were used to print tensile, bending, and impact specimens as well as cubes and gears as prototypes using SLS. Suitable values of T_b for the nanocomposite powders were first determined, and nanocomposite specimens were printed using different laser powers. The optimal process parameters were established by assessing the mechanical

properties of the printed specimens. As it was earlier concluded that SLS had a significant influence on the crystal phases of printed PP copolymer parts (Chapter 4.5), the effect of SLS on the crystal phases of the printed nanocomposites was analyzed as well. Finally, to determine the effects of OMMT on the printed PP specimens, the dispersion of OMMT and the thermal degradation properties of the printed P-OMMT-1/PP and P-OMMT-3/PP specimens were evaluated.

The isothermal DSC method, which viability was verified in Chapter 4.2, was employed as an effective and efficient approach to determine the minimum value of T_b that should be used with P-OMMT-1/PP and P-OMMT-3/PP. The T_{iso} values evaluated for the nanocomposite powders (Figure 6.18) were the same as that for CP60 (Figure 4.12), at 121 °C, 123 °C, 125 °C, and 127 °C.

The isothermal crystallization behaviors of both the nanocomposite powders were similar. When $T_{iso} = 121$ °C, crystallization of the nanocomposites occurred during stage 1 and appeared to be complete within 130 min and 110 min, respectively (Figure 6.18a). When the T_{iso} value was increased to 123 °C, crystallization during stage 1 was slower, but nevertheless, appeared to be almost complete by 150 min. Crystallization during stage 2 was relatively negligible when $T_{iso} = 121$ °C and 123 °C (Figure 6.18b, c). The crystals formed during stage 1 when $T_{iso} = 121$ °C and 123 °C contributed to two overlapping endothermic peaks at ~135 °C and ~147 °C that were observed in stage 3 (Figure 6.18d). The third endothermic peak at ~115 °C was attributed to the crystals formed during cooling in stage 2. The endothermic peaks corresponding to the crystals formed during stage 1 occurred at a higher temperature than that of the crystals formed during stage 2 because the annealing-like isothermal condition in stage 1 allowed the formation of crystals with fewer defects, and hence, of higher melting temperature [200].

Figure 6.18. DSC curves of (i) P-OMMT-1/PP and (ii) P-OMMT-3/PP powders and at different T_{iso} values: (a, b) plots of heat flow against time during stages 1 and 2, and (c, d) plots of heat flow against temperature during stages 2 and 3.

As the T_{iso} value further increased to 125 °C and 127 °C, crystallization during stage 1 slowed, and crystallization in stage 2 became increasingly significant. This was represented by a reduction in the peak areas in Figure 6.18a and an increase in the peak areas in Figure 6.18c. In addition, a broad endothermic peak formed during stage 3 (T_m at ~135 °C) became increasingly prominent, whereas the peak areas of the slightly overlapping endothermic peaks at 135–150 °C decreased (Figure 6.18d). Since the endothermic peaks observed in stage 3 that corresponded to stage 1 crystallization were still evident when $T_{\text{iso}} = 125$ °C, a T_b value greater than 125 °C would be required for SLS of P-OMMT-1/PP and P-OMMT-3/PP.

6.4. Properties of printed OMMT/PP specimens

Using the minimum values of T_b for the nanocomposite powders obtained from the isothermal DSC protocol as a guideline, their optimal T_b value was established to be 130 °C. Based on the ϕ values of P-OMMT-1/PP (0.37 g/cm³) and P-OMMT-3/PP (0.36 g/cm³), their E_{min} values were calculated to be 0.032 J/mm³ and 0.030 J/mm³, respectively, similar to that of CP60 at 0.034 J/mm³. To determine the optimal values of E_{vol} for the nanocomposite powders, tensile and flexural specimens were first fabricated at different energy densities (0.049–0.158 J/mm³) by varying the laser power (10–32 W) while keeping the laser scan speed (4500 mm/s) and hatching distance (0.3 mm) constant. The thermal and mechanical properties of the specimens were then evaluated.

6.4.1. Mechanical properties

The tensile properties of the laser-sintered CP60, P-OMMT-1/PP, and P-OMMT-3/PP specimens are shown in Figure 6.19. As discussed in Chapter 4.3.2, the UTS and elongation at break values of the CP60 specimens reached a maximum of 19.5 MPa and

207%, respectively, when the E_{vol} value was 0.138 J/mm³ and the laser scan speed was 4500 mm/s. Upon further increase of the E_{vol} value to 0.158 J/mm³, the elongation at break and UTS values remained relatively constant. This trend was also observed for P-OMMT-1/PP and P-OMMT-3/PP; their UTS and elongation at break values approached a maximum of 20.1 MPa and 53% and 19.7 MPa and 23%, respectively, as the E_{vol} values increased from 0.049 J/mm³ to 0.109 J/mm³. The UTS and elongation at break values remained almost unchanged even as the E_{vol} values further increased to 0.158 J/mm³.

The observed improvement in the mechanical properties of the CP60 and nanocomposite specimens as the E_{vol} values increased to their optimal values was due to the powder particles coalescing to greater extents at higher energy densities (Figure 6.20). At low E_{vol} values, the energy from the laser was insufficient to ensure complete melting and coalescence of the powder particles; as a result, gaps and partially sintered powder particles were present, especially in the interlayers (Figure 6.20a, d, g). The poor interlayer adhesion and high part porosity led to the low UTS and elongation at break of the SLS specimens. As the E_{vol} values increased to the optimal values, higher local temperatures could be achieved, and the melting and coalescence of the powder particles were promoted (Figure 6.20b, e, h); consequently, the UTS and the elongation at break of the specimens improved.

When E_{vol} further increased past the optimal values to 0.158 J/mm³, the UTS and elongation at break values of all the specimens remained relatively constant instead of deteriorating. The mechanical properties of printed specimens typically worsen at excessive E_{vol} values due to polymer degradation and formation of trapped volatile degradation products that contribute to porosity, but this was not observed for the CP60, P-OMMT-1/PP, and P-OMMT-3/PP specimens. For the CP60 specimen, it was because

the E_{vol} value at 0.158 J/mm^3 was relatively close to its optimal value of E_{vol} , and thus, no significant polymer degradation had occurred yet. The observation made with the nanocomposite specimens could be explained by the two types of pores in the specimens; the first type (Type I) was formed from the poor packing of the powder particles, while the second type (Type II) was formed from the entrapment of volatile degradation products.

Figure 6.19. Tensile properties of the SLS CP60, P-OMMT-1/PP, and P-OMMT-3/PP specimens that were fabricated at different E_{vol} values: (a) UTS and (b) elongation at break.

Most of the pores in the nanocomposite specimens printed at the optimal values of E_{vol} were due to poor powder packing (Figure 6.20e, h). As the E_{vol} values increased, higher local temperatures could be achieved. As a result, powder particle coalescence was improved, and the pores that were initially present due to poor powder packing were significantly reduced. However, due to the higher temperatures, polymer degradation was promoted, and the entrapment of volatile degradation products become more prominent (Figure 6.20f, i). Therefore, as the E_{vol} increased past the optimal values, the pores in the nanocomposite specimens that were formed due to poor powder packing decreased, whereas those that were formed due to trapped gases increased. Consequently, the UTS and elongation at break values of the nanocomposite specimens did not significantly worsen at the high E_{vol} values investigated.

Figure 6.20. SEM images of the cross-sections of the SLS specimens fabricated at low, optimal, and high E_{vol} values: (a–c) CP60, (d–f) P-OMMT-1/PP, and (g–i) P-OMMT-3/PP. Type I and Type II pores were formed from poor powder packing and entrapment of volatile degradation products, respectively.

The achievable UTS values of the P-OMMT-1/PP and P-OMMT-3/PP specimens were higher than that of the CP60 specimen, as expected, but their elongation at break values evidently decreased with an increase in filler loading (Figure 6.19b). This was hypothesized to be due to the presence of agglomerated OMMT particles. The nanocomposite pellets, precursors to the nanocomposite powders, were prepared by melt extrusion that promoted the dispersion and exfoliation of the OMMT particles by shear force. However, the extrusion process alone was insufficient to prevent the agglomeration of the silicate layers entirely; small quantities of agglomerated OMMT particles that embrittled the nanocomposite specimens were present in the polymer matrix (encircled with a yellow box in Figure 6.21), which reduced the elongation at break of the nanocomposite specimens. As there were more agglomerated OMMT particles in the P-OMMT-3/PP specimen, its elongation at break value was reduced to a greater extent than that of the P-OMMT-1/PP specimen.

Figure 6.21. TEM images of the cross-sections of the SLS specimens: (a) P-OMMT-1/PP and (b) P-OMMT-3/PP.

The flexural strength values of the nanocomposite specimens increased with increasing E_{vol} values up to 0.138 J/mm^3 before decreasing slightly as the E_{vol} values

further increased to 0.158 J/mm^3 (Figure 6.22a). The maximum flexural strength values of the P-OMMT-1/PP and P-OMMT-3/PP specimens were similar at 25.4 MPa and 25.3 MPa, respectively, and their corresponding flexural modulus values were 403 MPa and 388 MPa, respectively (Figure 6.22b). Considering the tensile and flexural properties of the printed P-OMMT-1/PP and P-OMMT-3/PP specimens, their optimal values of E_{vol} were determined to be 0.109 J/mm^3 .

Figure 6.22. Flexural properties of the SLS CP60, P-OMMT-1/PP, and P-OMMT-3/PP specimens that were fabricated at different E_{vol} values: (a) flexural strength and (b) flexural modulus.

The mechanical properties of the SLS and injection molded CP60, P-OMMT-1/PP, and P-OMMT-3/PP specimens are summarized in Table 6.6. The UTS and elongation at break values of the SLS specimens were lower than those of the injection molded counterparts. This was attributed to the lack of external pressure during the SLS process that would otherwise densify the fabricated specimen while removing trapped gases [21]. The reduction in the elongation at break values of the SLS specimens might have been exacerbated by the larger crystals that were formed due to the slow cooling in SLS, which led to the more brittle behavior of the specimens [21]. Although the ratio of the UTS values of the CP60 and SLS nanocomposite specimens to those of the injection molded counterparts was 0.6–0.7, the ratio of the elongation at break values of the SLS specimens to those of the injection molded counterparts was substantially lower for the P-OMMT-1/PP (0.05) and P-OMMT-3/PP (0.02) specimens than that of the CP60 (0.22) specimens. This disparity in the elongation at break of the SLS nanocomposite specimens was attributed to the higher porosity and the presence of agglomerated OMMT particles, both of which embrittled the specimens.

Table 6.6. Mechanical properties of the SLS and injection molded CP60, P-OMMT-1/PP, and P-OMMT-3/PP specimens. The SLS specimens were printed with a laser scan speed of 4500 mm/s.

	UTS (MPa)			Elongation at break (%)		
	SLS	Injection molded	Ratio ^{a)}	SLS	Injection molded ^{b)}	Ratio ^{a)}
CP60	19.5±0.56	30.9±0.86	0.63	207±43.9	951±106.0	0.22
P-OMMT-1/PP	20.1±0.76	31.6±2.93	0.64	53±5.4	1156±73.7	0.05
P-OMMT-3/PP	19.7±0.42	28.2±2.29	0.70	23±1.3	1132±155.2	0.02

^{a)} The ratio of the UTS or elongation at break of the SLS specimens to that of the injection molded counterparts.

^{b)} The elongation at break value for the injection molded specimens was determined using stroke strain.

6.4.2. Thermal properties

In addition to the mechanical properties, the thermal properties of the SLS nanocomposite specimens were evaluated and compared against those of the SLS CP60 specimens (Figure 6.23). The $T_{d,max}$ values of the P-OMMT-1/PP and P-OMMT-3/PP specimens under air atmosphere were 391 °C and 415 °C, respectively, which were significantly higher than that of the CP60 specimen at 350 °C. The DSC curves of the nanocomposite specimens showed two overlapping melting peaks, similar to what was observed with the CP60 specimen. However, the T_m values of the nanocomposite specimens were 140 °C and 146 °C, higher than those of the CP60 specimens at 134 °C and 142 °C.

Figure 6.23. (a) TGA and (b) DSC curves of the SLS CP60, P-OMMT-1/PP, and P-OMMT-3/PP specimens.

The OMMT particles in the SLS nanocomposite specimens were mostly intercalated or exfoliated and were well-dispersed within the polymer matrix (Figure 6.24). As a result, tortuous paths that impeded the diffusion of small molecules such as oxygen were formed, which produced a barrier effect and enhanced the thermo-oxidative stability of the specimens. Since the P-OMMT-3/PP specimen had a higher filler loading, the barrier effect of the OMMT particles was more prominent, and thus, its thermo-oxidative stability was higher than that of the P-OMMT-1/PP specimen.

Figure 6.24. TEM images of the cross-sections of the SLS specimens: (a) P-OMMT-1/PP and (b) P-OMMT-3/PP.

The mechanical and thermal properties of the SLS CP60, P-OMMT-1/PP, and P-OMMT-3/PP specimens that were printed at their optimal values of E_{vol} are summarized in Table 6.7. The significantly reduced elongation at break of the nanocomposite specimens was due to the agglomeration of the OMMT particles that embrittled the specimen. Nevertheless, because the nanocomposite specimens had comparable UTS and flexural properties to the CP60 specimens and demonstrated higher melting temperatures and superior thermo-oxidative stability, they were more suitable than CP60 for high-temperature applications that require enhanced thermal resistance and thermal stability.

Table 6.7. Properties of the SLS CP60, P-OMMT-1/PP, and P-OMMT-3/PP specimens that were printed using the optimal process parameters, with a laser scan speed of 4500 mm/s.

Property	CP60	P-OMMT-1/PP	P-OMMT-3/PP
Optimal E_{vol} (J/mm ³)	0.138	0.109	0.109
Ultimate tensile strength (MPa)	19.5±0.56	20.1±0.76	19.7±0.42
Tensile elongation at break (%)	207±43.9	53±5.4	23±1.3
Flexural modulus (MPa)	379±27.6	400 ±47.9	388±50.3
Flexural strength (MPa)	26.1±1.07	24.6±1.33	24.3±1.92
Maximum degradation temperature $T_{d,max}$ (°C)	350	391	415

6.5. Crystal phases of OMMT/PP specimens

As discussed in Chapter 4.5, PP with higher chain defects such as those with a large number of stereo-irregularities [217, 219] or regio-irregular copolymers with comonomer units, and that are additionally crystallized under slow cooling and low supercooling [218, 224, 231], are more inclined to form γ -phase crystals. The γ -phase crystals were observed in the SLS CP60 specimens, and the same was expected for the SLS P-OMMT-1/PP and P-OMMT-3/PP specimens.

The XRD patterns of the CP60 and nanocomposite powders, and their injection molded and SLS specimens are shown in Figure 6.25. If the γ -phase was negligible, the degree of crystallinity x_c of a sample was calculated by

$$x_c = \frac{\Delta H_m}{209(1-W)} \times 100\% \quad , \quad (6.1)$$

where ΔH_m is the melt enthalpy obtained from the DSC curve and W is the mass fraction of OMMT. When both the α - and γ -phases were present, the fraction of γ -phase X_γ in a sample was first calculated using its XRD data

$$X_\gamma = \frac{h_\gamma}{h_\gamma + h_\alpha} \quad , \quad (6.2)$$

where h_γ and h_α are the heights of the (117)- and (130)-reflections, respectively. The overall degree of crystallinity was then obtained by

$$\Delta H_{m,100\%} = (1-W)[150X_\gamma + 209(1-X_\gamma)] \quad , \quad (6.3)$$

$$x_c = \frac{\Delta H_m}{\Delta H_{m,100\%}} \times 100\% \quad , \quad (6.4)$$

where $\Delta H_{m,100\%}$ is the melt enthalpy of a 100% crystalline specimen.

The XRD patterns showed that the CP60 and nanocomposite powders and their injection molded specimens contained mainly α -phase crystals. In contrast, their SLS

specimens contained both α - and γ -phase crystals, with the γ -phase present in higher amounts than the α -phase. The x_c values of the CP60, P-OMMT-1/PP, and P-OMMT-3/PP powders were relatively similar at 28.1%, 25.3%, and 26.6%, respectively, which were similar to those of their injection molded specimens at 23.2%, 25.9%, and 25.8%, respectively, but lower than that of their SLS specimens at 33.3%, 43.9%, and 44.7%, respectively. The high x_c values of the SLS specimens were due to the slow cooling and low undercooling during SLS.

It was noted that the difference in the x_c values between the SLS specimens and the powders was more significant for the nanocomposites (~19%) than CP60 (~5%); the larger increase in the degree of crystallinity of the SLS nanocomposite specimens was attributed to the nucleating effect of the OMMT particles, which promoted crystal formation during the SLS process. The OMMT particles also appeared to promote the formation of larger crystals, as the reflections of the SLS P-OMMT-1/PP and P-OMMT-3/PP specimens were shifted to the left by $\sim 0.4^\circ$ relative to those of the SLS CP60 specimens. Since the amount of γ -phase as a percentage of the total degree of crystallinity in the SLS specimens was similar for all three materials at $\sim 68\%$, the differences in the mechanical properties of the specimens were unlikely due to the crystal phases. However, the higher degree of crystallinity and larger crystal sizes of the SLS nanocomposite specimens would have influenced their mechanical properties, including the elongation at break.

Figure 6.25. XRD patterns and the corresponding miller indices of the crystal phases of the powders and injection molded and SLS specimens: (a) CP60, (b) P-OMMT-1/PP, and (c) P-OMMT-3/PP.

The DSC curves of the SLS nanocomposite specimens had a shoulder that was associated with the melting of shorter PP sequences, which lengths were below the minimum crystallite length ζ^* required for crystallization at the T_b value used (Figure 6.26) [207]. The SLS specimens also exhibited two overlapping melting peaks in their DSC curves, and the peak at the lower temperature ($T_m = 140$ °C) was attributed to the

γ -phase crystals. Due to the slow cooling and low undercooling during SLS, the α -phase crystals in the SLS specimens were likely to be thicker and contain fewer imperfections; therefore, the melting temperatures of the α -phase crystals were expected to be higher than those in the powder (T_m at $\sim 142^\circ\text{C}$), and thus, the melting peak at $T_m = 147^\circ\text{C}$ was assigned to the α -phase. The observation that the γ -phase crystals melted at a lower temperature than the α -phase crystals was consistent with the fact that γ -phase crystals grow epitaxially on parent α -phase lamellae [229], and has been observed in other studies [224, 231].

Figure 6.26. DSC curves of the powders and injection molded and SLS specimens: (a) CP60, (b) P-OMMT-1/PP, and (c) P-OMMT-3/PP.

6.6. Summary

OMMT/CP60 nanocomposites with (OMMT-1/PPgMA/PP, OMMT-3/PPgMA/PP, and OMMT-5/PPgMA/PP) and without (OMMT-1/PP, OMMT-3/PP, and OMMT-5/PP) PPgMA as a compatibilizer were investigated. The maximum loading of OMMT was determined to be 3 wt% for both the binary and ternary nanocomposites, beyond which further enhancement of the thermo-oxidative stability was minimal. Since significant narrowing of the sintering windows and increment of the melting range values were observed with the ternary nanocomposites, they were unsuitable for SLS. Meanwhile, because the UTS and elongation at break values of the injection molded

OMMT-1/PP and OMMT-3/PP specimens were comparable to those of the CP60 specimens, it was established that OMMT-1/PP and OMMT-3/PP were suitable for SLS.

The OMMT-1/PP and OMMT-3/PP nanocomposite pellets were produced at a large scale by melt extrusion, after which the pellets were cryogenically ground to produce P-OMMT-1/PP and P-OMMT-3/PP powders. The HR value of P-OMMT-1/PP was the same as that of CP60 at 1.22, whereas the HR value of P-OMMT-3/PP was slightly higher at 1.25, suggesting that the flowability of P-OMMT-3/PP was inferior to that of P-OMMT-1/PP and CP60. Meanwhile, the S_a , R_c , and R_{sm} values of P-OMMT-1/PP and P-OMMT-3/PP were lower than those of CP60 because the small particles in the nanocomposite powders could fill the gaps between the larger particles, leading to a smoother powder bed surface with smaller localized imperfections.

The sintering windows and melting range values of CP60, P-OMMT-1/PP and P-OMMT-3/PP were 2.2 °C and 51.3 °C, 14.7 °C and 39.3 °C, and 15.9 °C and 36.7 °C, respectively. Coupled with the low $E_{A,C}$ values of P-OMMT-1/PP (284.7 kJ/mol) and P-OMMT-3/PP (273.6 kJ/mol) compared to that of CP60 (306.1 kJ/mol), the nanocomposite powders were determined to be more suitable for SLS than CP60 as they were less prone to warping, powder caking and over-sintering. Importantly, a wider range of T_b values could be used for the nanocomposite powders, allowing for greater freedom in designing the SLS process parameters. Furthermore, the $T_{d,max}$ and $E_{A,D}$ values of P-OMMT-1/PP (377.3 °C and 120.7 kJ/mol) and P-OMMT-3/PP (398.6 °C and 137.2 kJ/mol) were significantly higher than those of CP60 (324.7 °C and 33.4 kJ/mol), suggesting the viability of the nanocomposite powders for long-term usage and high-temperature applications.

The minimum value of T_b of the nanocomposite powders, evaluated using the isothermal DSC protocol, was determined to be 125 °C. Even with optimal sintering

parameters and T_b value (130 °C), the elongation at break values of the printed P-OMMT-1/PP and P-OMMT-3/PP specimens were 53% and 23%, respectively, lower than that of the CP60 specimens at 207%. This reduction in the elongation at break values of the SLS nanocomposite specimens was attributed to the porosity as well as the presence of agglomerated OMMT particles. Nevertheless, because the UTS and $T_{d,max}$ values of the P-OMMT-1/PP (20.1 MPa and 391 °C) and P-OMMT-3/PP (19.7 MPa and 415 °C) specimens were higher than those of the CP60 specimens (19.5 MPa and 350 °C), the nanocomposite powders were more suitable than CP60 for high-temperature applications that require enhanced thermal resistance and thermal stability.

The OMMT filler served its intended purpose of enhancing the thermo-oxidative stability of PP. In addition, the developed nanocomposite powders exhibited significantly enhanced thermal processability as their sintering windows were ~7 times that of the CP60 powder and their melting range values were 75% that of the CP60 powder. Therefore, OMMT can potentially be used to improve the SLS processability of other polymer materials by widening their sintering windows and reducing their melting range values.

Chapter 7. Conclusions and Recommendations

In this chapter, the key conclusions of this research conducted are given, and corresponding future works are recommended.

7.1. Conclusions

This thesis comparatively investigated the use of isotactic PP homopolymer and copolymer powders for SLS. Notably, both the SLS and injection molding PP homopolymer specimens mainly consisted of α -phase crystals, whereas the major crystal phases of the injection molded and SLS PP copolymer specimens were α - and γ -phase, respectively. The formation of the γ -phase crystals in the SLS PP copolymer specimens was a combined result of the regio-irregularity in the copolymers and the unique thermal conditions of SLS, i.e., long processing times at high temperatures and slow cooling of the printed parts. SLS is patently capable of altering the crystal phases or crystallinity of some polymers that are difficult to achieve under typical injection molding conditions. This advantage can be extended to polymers other than PP.

The isothermal DSC protocol was established to systematically evaluate the minimum value of T_b , which by far, is determined empirically and requires repeated trial-and-error that is cost- and time-inefficient. This protocol proved to be a more effective and efficient method for narrowing the temperature range within which the optimal value of T_b existed, facilitating the determination of a suitable value of T_b for the SLS process.

Four nanocomposite powder preparation methods, including mechanical mixing, surface coating with and without a surfactant, TIPS, and melt extrusion and grinding, were adopted to produce OMMT/PP powders and were comparatively assessed. Mechanical mixing was the most cost-effective and straightforward but led to poor filler

dispersion. For the surface coating method, even though good dispersion and adhesion of OMMT onto PP powder particles could be achieved by adding SDS, the thermo-oxidative stability of the OMMT/PP powder was only slightly enhanced. The OMMT/PP powder particles prepared by mechanical mixing and surface coating inherited the morphology and shape of the PP powder particles used. TIPS could produce OMMT/PP powder with a significantly reduced rate of crystallization due to the presence of nano-sized OMMT fragments that hindered the movement and diffusion of the polymer chains, as well as the annealing-like condition that increased chain entanglement and reduced the crystallization rate and temperature. Another advantage of TIPS was that it could produce near-spherical powder particles with a desirable powder particle size distribution for SLS without any post-processing.

The OMMT particles in the OMMT/PP powder prepared by melt extrusion and grinding were homogeneously dispersed within the polymer matrix while retaining their high aspect ratio and lateral size, which resulted in a substantial enhancement in the thermo-oxidative stability of the nanocomposite. Melt extrusion combined with cryogenic grinding was determined to be the most balanced option of all the evaluated composite powder preparation methods. Thus, it was used for the large-scale production of OMMT/PP powders for the SLS process.

Ternary and binary nanocomposites with 1 wt%, 3 wt%, and 5 wt% OMMT, with and without PPgMA as compatibilizers, respectively, were investigated by producing the nanocomposite pellets via melt extrusion at a small scale. The addition of PPgMA was determined to be undesirable for SLS as it narrowed the sintering window excessively and increased the melting range values of the ternary nanocomposites. Meanwhile, the maximum loading of OMMT was 3 wt%, beyond which further

enhancement of the thermo-oxidative stability of the binary and ternary nanocomposites was minimal.

The binary nanocomposites with 1 wt% and 3 wt% OMMT were deemed suitable for SLS, and their powders were produced at a large scale by melt extrusion and grinding. It was remarkable that the nanocomposite powders exhibited significantly wider sintering windows, lower melting range values and crystallization activation energy values, and higher thermo-oxidative stability than its pure polymer; these made the nanocomposite powders more processable for SLS and more suitable for long-term usage and high-temperature applications.

7.2. Recommendations

A systematic study towards the development of PP nanocomposite powders for SLS, including an investigation on the use of PP for SLS, the evaluation of composite powder preparation methods, and the formulation, optimization, and manufacturing of PP nanocomposite powders, was conducted. Nevertheless, with PP being an emerging material that is gaining exponential popularity for SLS, there remains much to be researched on for PP and its composite materials to fulfill the stringent requirements of SLS and be widely applicable. Based on the current research findings, future works are recommended as follows.

Firstly, this thesis has demonstrated the advantages of the developed OMMT/PP powders for SLS, and it would be worthwhile to bring the development of OMMT/PP composite powders to a mass production level. The commercial availability of OMMT/PP powders for SLS would contribute as a new type of material for the SLS market. Furthermore, with the introduction of this new material, the possible applications of SLS could be further expanded.

Secondly, bottom-up approaches to the design and synthesis of molecular structures can be utilized to develop new polymers with intrinsic properties tailored specifically for the SLS process. To ensure that the polymer fusion, solidification, and reaction kinetics are aligned with the time-scale of the SLS process, the molecular structure of polymers can be rationally designed at the molecular level to adapt the polymers to the SLS process instead of using readily available polymers that are designed for conventional manufacturing processes. The optical (e.g., absorptance), thermal (e.g., melting and recrystallization behaviors), rheological (e.g., viscosity and relaxation dynamics) properties, etc., of the polymers could be tailored for SLS by tuning their molecular chain structure, molecular weight distribution, functional group, degree of functionality, etc. For example, the crystallization of polymers is critical to SLS since undesired crystallization can lead to part curling and warping, which can cause part inaccuracies and even build failure. It would then be worth looking into polymers that exhibit bimodal crystallization kinetics, such as PP copolymers, where not all of the polymer sequences can participate in crystallization at the powder bed temperature. The extent of crystallization of such polymers during SLS can be controlled, for instance, by modifying the degree of polymer branching or polymer sequence length distribution to alleviate the warping and curling phenomenon that is prevalent in SLS.

Thirdly, processes and materials are tightly related, and an in-depth understanding of the process fundamentals is important for the successful development of materials. Numerical modeling can aid the multi-scale investigations on the materials at different stages of the SLS process, such as the light-matter interactions, viscous flow behaviors, and solidification mechanisms of polymers or polymer composites during printing, and the physical and mechanical properties of the final printed parts. In SLS, where different light sources (e.g., laser and IR) are involved, energy absorption models for the

interactions between the light sources and the polymer powders can be established using numerical modeling. Computational fluid dynamics serves as a mathematical method for solving problems that involve thermal and fluid flow phenomena at the mesoscopic scale, which is particularly useful for SLS as it can be utilized to gain an in-depth understanding of the viscous flow of non-Newtonian polymer melts during the SLS process. The finite element method can be used to simulate the thermo-mechanical behavior of polymer materials, at the macroscale, during and after printing. It can conduct process simulations that can be used to predict the actual state of the materials that are being processed, such as the temperature and stress distribution of a sintered region, by taking into consideration the time- and temperature-dependent material properties. The predictions can additionally serve to guide process parameter optimization and for improving processing efficiency. The finite element method can also be applied to investigate the mechanical and functional performance of SLS-fabricated parts.

Finally, to achieve a greater understanding and better control of the AM processes, in situ measurements, offline measurements under conditions analogous to a specific AM process, and in situ process monitoring can be employed to acquire accurate material- and process-related data. The time-, temperature-, and pressure-dependent material properties and the process conditions (e.g., heating rate, cooling rate, and shear rate) can be obtained by employing in situ and offline measurement techniques. The measurements can be used as reliable inputs for establishing robust numerical models. In situ process monitoring methods can be utilized to collect real-time data during build processes, which can subsequently be used as high-quality outputs to validate theoretical models. The real-time data can also be fed into closed-loop control algorithms for assessing and managing AM machine operations, which helps to enhance the quality

assurance of AM-fabricated parts. Depending on the type of measurement method (e.g., laser flash DS and in-situ X-ray scattering/diffraction/microtomography) and monitoring system (e.g., visual camera, pyrometer, and IR camera) employed, information regarding polymer viscosity, the surface topography of printed parts, temperature and pressure of the build chamber, etc. can be acquired. These data can provide unprecedented insights and be used to better understand the process fundamentals, which can then be utilized to develop polymer materials with more suitable properties for the AM process.

AM technology that is considered essential for Industry 4.0 offers tremendous opportunities for product development, efficient production, low-volume production of bespoke products on demand, and production flexibility. The progress of AM has been phenomenal as better-performing materials are continuously introduced into the market. Given the rapid pace of technological advancements, it is only a matter of time before AM becomes a feasible technology that complements traditional manufacturing techniques.

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