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Investigation into Crystallinity and Degree of Particle Melt in Selective Laser Sintering

By

Hadi Zarringhalam

Doctoral thesis submitted in partial fulfilment of the requirements of the award of Doctor of Philosophy of Loughborough University

February 2007

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5 PRELIMINARY HYPOTHESIS AND RESEARCH OBJECTIVES

6 EXPERIMENTS TO ASSESS EFFECTS OF POST BUILD COOLING RATE ON MECHANICAL PROPERTIES AND CRYSTALLINITY

6.1 AIMS AND THEORY

6.2 METHODOLOGY

6.2.1 Part Building

6.2.2 Temperature logging

6.2.3 Part Cool down

6.2.4 Measurement of mechanical properties

6.2.5 DSC analysis

6.3 RESULTS & DISCUSSION

6.3.1 Cooling rate

6.3.2 Tensile results

6.3.3 Percentage Crystallinity

6.4 CONCLUSIONS

7 PRINCIPAL HYPOTHESIS AND RESEARCH OBJECTIVES

7.1 BACKGROUND

7.2 PROPOSED RELATIONSHIP BETWEEN DSC PEAKS AND MATERIAL MICROSTRUCTURE

7.3 PREVIOUS USE OF DSC TO DETECT MULTIPLE PHASES IN SINTERED POLYMER

7.4 'DEGREE OF SINTERING'

7.5 PRINCIPAL HYPOTHESIS AND RESEARCH OBJECTIVES

8 EXPERIMENTS TO ASSESS THE EFFECTS OF DPM ON MECHANICAL PROPERTIES & CRYSTALLINITY

8.1 METHODOLOGY

8.1.1 Introduction (aims & theory)

8.1.2 Build

8.1.2.1 Part design

8.1.2.2 Build setup

8.1.2.3 Machine parameters

8.1.2.4 Part removal

8.1.3 Data gathering

8.1.3.1 DSC

8.1.3.2 Tensile testing

8.1.3.3 Optical microscopy

8.2 RESULTS AND DISCUSSION

8.2.1 DSC

8.2.2 Mechanical properties

8.2.3 Optical microscopy

9 OVERALL ANALYSIS & DISCUSSION

9.1 EFFECTS OF BUILD PARAMETERS ON MATERIAL PROPERTIES

9.1.1 Post build cooling rate (Chapter 6)

9.1.2 Partial melting of particles (Chapter 7)

9.1.3 Energy input (Chapter 8)

9.2 QUALITATIVE DESCRIPTION OF VARIATION IN DPM

9.3 RELATIONSHIP BETWEEN DSC READINGS AND MECHANICAL PROPERTIES

9.3.1 Selection of DSC readings to quantify relationships

9.3.2 Further analysis of selected DSC readings

9.4 EFFECT OF DPM ON SELECTED DSC READINGS
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I would like to dedicate this work to those people, past and present, who have striven and strive to better themselves and those around them and who seek to bring peace to this world.

Hadi Zarringhalam

8th February 2007
Abstract

Selective Laser Sintering (SLS) is a manufacturing process which has emerged from numerous other technologies as the leading process considered viable for Rapid Manufacturing. SLS of polymers has found use in a wide range of industries ranging from aerospace to medicine. The ability to easily manufacture previously difficult or impossible to produce parts, without tooling, has proved invaluable. This industry backed manufacturing engineering PhD investigation examined material properties of Nylon-12 parts produced by the SLS process.

Crystallinity relates to and determines mechanical properties in traditionally processed polymers. The nature of crystallinity in SLS processed Nylon-12 has been examined in this study and shown to be fundamentally different to that of traditionally processed polymers. Rather than depending primarily upon crystallisation factors such as cooling rate, it was shown to depend on the degree of particle melt (DPM). DPM was shown to be quantifiable by DSC measurements (by the degree of crystallinity and Core Peak Height) and distinct relationships between the quantified DPM and mechanical properties were found. Additionally, this study showed for the first time that parts remain above the crystallisation onset temperature even after build completion.

This work has expanded the knowledge base of SLS by shedding light on critical aspects of the process. The ability to quantify the degree to which particles melt (DPM) provides a new level of understanding into the causes of changes in mechanical properties with changes in process parameters. This new understanding can lead to improved process modelling and could aid in the development of new processes and materials. DPM could be implemented into new quality control methods and the knowledge of post build crystallisation shows that post build cool down is an aspect of the build process that requires control for improved consistency of properties.
List of figures

Figure 1 Thesis structure..............................................................................................................2
Figure 2 Rapid Manufactured Hearing aid body ........................................................................7
Figure 3 Renault Formula 1 race car [Renault, 2006].................................................................7
Figure 4 RM parts used on the Renault Formula 1 race car.......................................................8
Figure 5 Boeing F/A-18 Super Hornet military aircraft [Venik's Aviation, 2006].....................8
Figure 6 Redesigned air duct for RM [Hague, 2006].................................................................9
Figure 7 Grumman Tiger single engine aircraft [Porter, 2000]..................................................9
Figure 8 Conventionally produced (left) and selective laser sintered (right) windshield defroster for Grumman Tiger aircraft.............................................................10
Figure 9 Conventionally produced (left) and selective laser sintered (right) fresh air vent for Grumman Tiger aircraft.............................................................10
Figure 10 Photograph of 3D Systems Vanguard SLS machine and schematic illustration of SLS process..................................................................................................................13
Figure 11 Slicer Fill Scan Spacing and beam overlap..............................................................15
Figure 12 SEM micrographs of selective laser sintered Polystyrene. (a) High MFI (low viscosity) (b) Low MFI (high viscosity) [Shi et al, 2004] .......................................................21
Figure 13 DSC curve for Nylon-12 SLS powder showing difference between melt and crystallisation temperatures..............................................................22
Figure 14 Relationship between energy density and powder bed temperature to maintain maximum part density for DuraForm PA [Tontowi and Childs, 2001] ......................25
Figure 15 Examples of typical parts made by PM [Kalpakjian and Schmid, 2001]..................28
Figure 16 Major stages in manufacture of parts by PM............................................................29
Figure 17 Map of traditional sintering processes [adapted from German, 1996]..................30
Figure 18 Particle neck formation [German, 1997]................................................................31
Figure 19 Two sphere sintering model [German, 1997]............................................................32
Figure 20 Development of pore structure with sintering [German, 1997]...............................33
Figure 21 Porosity and elongation for pure iron [Haynes, 1977]..............................................35
Figure 22 Principle of rotational moulding [Adapted from Crawford, 1996].........................37
Figure 23 Amorphous and Crystalline regions in a semi-crystalline polymer [Kalpakjian & Schmid, 2001].................................................................................................................44
Figure 24 Tensile strength and elongation of a semi-crystalline thermoplastic [adapted from Michaeli, 1995]..............................................................................................45
Figure 25 Principle of DTA [Plaats, 1992]..................................................................................49
Figure 26 Principle of heat-flux DSC [Plaats, 1992]................................................................50
Figure 27 Crimped DSC specimen pan....................................................................................50
Figure 28 Principle of power-compensation DSC [Plaats, 1992]...............................................51
Figure 29 Shimadzu DSC-60 Calorimeter and DSC Cell in situ..............................................51
Figure 30 Shimadzu DSC-60 DSC cell....................................................................................52
Figure 31 DSC trace for SLS Nylon-12....................................................................................53
Figure 32 Tensile testing machine............................................................................................54
Figure 33 Tensile test stress-strain curve (Kalpakjian 2001)......................................................55
Figure 34 Amide group .............................................................................................................56
Figure 35 Nylon-12 repeat unit in a Nylon-12 polymer chain..................................................57
Figure 36 Stress Strain behaviour as a function of % crystallinity for Nylon-6 [Bessell et al, 1975].........................................................................................................................61
Figure 37 Effect of cooling rate on % crystallinity for polypropylene [Michaeli, 1995]...........62
Figure 38 DSC chart for SLS Nylon-12 powder.......................................................................63
Figure 39 Specimens attached to frame, and thermocouple guides/channels.........................65
Figure 40 Thermocouple placement.....................................................................................66
Figure 41 Preparatory schematic cool down curves for T2 and T7...........................................67
Figure 42 Cool down profile for T1.....................................................................................70
Figure 43 Cool down profile for T2, Benchmark.....................................................................71
Figure 44 Cool down profile for T3.....................................................................................71
List of tables

Table 1 Current SLS machines [3D Systems, 2004, 2006a, 2006b; EOS, 2005(a-c), 2007(a-c)] .......................................................................................................................... 17
Table 2 3D Systems SLS powder properties [Wohlers, 2006] ................................................. 18
Table 3 Manufacturer supplied mechanical properties [3D Systems, 2007; EOS, 2005d; 3T RPD, 2007; Windform, 2007] ...................................................................................... 19
Table 4 Major thermal analysis techniques [Plaats, 1992] ....................................................... 47
Table 5 Cool down phases ........................................................................................................ 64
Table 6 Test descriptions .......................................................................................................... 68
Table 7 Cooling rate during crystallisation .............................................................................. 74
Table 8 Build duration ........................................................................................................... 91
Table 9 Machine parameters ................................................................................................ 92
Table 10 Importance of R² values ....................................................................................... 135
Table 11 Importance of R² values (Fill Scan Count - High excluded) ................................. 139
<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPM</td>
<td>Degree of Particle Melt</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermal Analysis</td>
</tr>
<tr>
<td>EaB</td>
<td>Elongation at break</td>
</tr>
<tr>
<td>MCM</td>
<td>Melted and Crystallised Material</td>
</tr>
<tr>
<td>MFI</td>
<td>Melt Flow Index</td>
</tr>
<tr>
<td>PM</td>
<td>Powder Metallurgy</td>
</tr>
<tr>
<td>RM</td>
<td>Rapid Manufacturing</td>
</tr>
<tr>
<td>SLS</td>
<td>Selective Laser Sintering</td>
</tr>
<tr>
<td>$M_w$</td>
<td>Weight-average molecular weight</td>
</tr>
</tbody>
</table>
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properties of SLS Nylon parts, Journal of Materials Processing Technology

Conferences presented at

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>02/2004</td>
<td>Post Processing of SLS Duraform Rapid Manufactured Parts, PowderMatrix Reloaded, Gaydon, UK</td>
</tr>
<tr>
<td>04/2004</td>
<td>Effects of Cooling Rate on Mechanical Properties for SLS DuraForm Material, 3D Systems NASUG SLSUG Joint Conference 2004, Anaheim, California, USA</td>
</tr>
<tr>
<td>10/2004</td>
<td>Group Presentations (Internal), Loughborough University, UK</td>
</tr>
<tr>
<td>01/2005</td>
<td>Research Student Conference (Internal), Loughborough University, UK</td>
</tr>
<tr>
<td>02/2005</td>
<td>Controlling Ductility in SLS Nylon Parts, PowderMatrix Revolution, UK</td>
</tr>
<tr>
<td>07/2005</td>
<td>Effects of powder history on material and mechanical properties in Selective Laser Sintering, 16th Solid Freeform Fabrication Symposium, Austin, Texas, USA</td>
</tr>
<tr>
<td>03/2006</td>
<td>Controlling Ductility of SLS Nylon Parts, PowderMatrix Evolution, UK</td>
</tr>
<tr>
<td>04/2006</td>
<td>Group Presentations (Internal), Loughborough University, UK</td>
</tr>
<tr>
<td>04/2006</td>
<td>Effects of build parameters on degree of particle melt in SLS DuraForm parts, 2006 3D Systems Users group conference, Tucson, Arizona, USA</td>
</tr>
<tr>
<td>06/2006</td>
<td>Sintering Technology Group (Internal), Loughborough University, UK</td>
</tr>
<tr>
<td>07/2006</td>
<td>Degree of particle melt in SLS (poster), Rapid Manufacturing, 1st International Conference, Loughborough University, UK</td>
</tr>
</tbody>
</table>
1 Introduction

1.1 Context

This Manufacturing Engineering PhD thesis is the culmination of a 3 year industry supported investigative project. The project was an EPSRC funded PowderMatrix Faraday industrial CASE project which involves UK Research Council funding to bolster links between academia and industry. Therefore, such investigations have a focus on applicability of research findings to scenarios in industry. PowderMatrix is a Faraday partnership focussed on the use of particulate material in manufacturing. Findings of this work have been presented at numerous international conferences.

The industrial collaborators were Solid Concepts, USA and 3D Systems, UK. Solid Concepts is a service bureau specialised in the field of Rapid Manufacturing and 3D Systems is the manufacturer of the manufacturing equipment used by Solid Concepts and also used for this investigation.

The project was initially entitled ‘Controlling Ductility in SLS Nylon Parts’. This title was chosen to reflect the initial direction of the work since one of the industrial collaborators had anecdotally observed changes to mechanical properties and particularly ductility under certain processing conditions and suggested this as an initial course of research. The initial title of the investigation does not reflect the eventual course it took. This initial work (covered in Chapter 6) and a collaborative study (overviewed in Chapter 7) lead to the principal hypothesis and the focus of the thesis.

1.2 Thesis Structure

The bulk of this thesis is presented in three distinct stages as illustrated in Figure 1. The initial stage was the literature search. The second stage was a preliminary investigation which focussed on a preliminary hypothesis. A key observation was made which led to the principal hypothesis which was put to the test in the third stage, the principal investigation. The principal investigation is the focus of this work.
Figure 1 Thesis structure
2 Rapid Manufacturing and Selective Laser Sintering

2.1 Rapid Prototyping

2.1.1 Introduction

Selective Laser Sintering (SLS) is one of numerous advanced manufacturing technologies which are traditionally collectively known as 'Rapid Prototyping'. The first Rapid Prototyping method emerged in the late 1980s [Wohlers 2002]. Some ambiguity surrounds the definition of the term 'Rapid Prototyping', however there are two definitions that are generally accepted. The first is very general and relates, as the term suggests, to almost any prototyping method that operates quicker than historically expected [Wohlers 2002]. The second is: "A special class of machine technology that quickly produces models and prototype parts from 3-D data using an additive approach to form the physical models." [Wohlers 2000]. This second definition is the 'classic' definition and is what is referred to as 'Rapid Prototyping' in this thesis.

As the technology has evolved, production of parts for end use has become possible, rather than just for prototypes. Where production of parts for end use is discussed, the term 'Rapid Manufacturing' arises (described later in Section 2.2). However, since the basic technology is essentially the same, the term 'Rapid Prototyping' is still often used to describe the processes/technology.

As mentioned above, Rapid Prototyping processes are characterised by producing parts 'additively' which means building the parts by adding material where needed. This is in contrast to conventional 'subtractive' manufacturing methods which require the removal of material from a work piece larger than the final part. To put this in its full context, the main categories of conventional manufacturing methods into which most material forming manufacturing methods fall under are as follows [Cooper 2001]:

- Casting
- Forming and shaping
- Machining
Currently all commercially available Rapid Prototyping processes build parts layer by layer. Thin, essentially 2D, cross sections of the part are built one on top of the other enabling parts to be built with geometries often impossible to achieve by machining and other methods. Such geometries include intricate internal structures, parts within parts, and very thin-wall features which are just as easy to build as a simple geometry such as a cube.

Another important characteristic of Rapid Prototyping processes is that they need no part specific tooling to produce parts. The manufacture of tooling for conventional manufacturing processes is expensive and time consuming. The lack of tooling therefore means Rapid Prototyping processes can offer advantages from both time and direct cost points of view.

Numerous Rapid Prototyping systems exist on the market today and these can generally be divided into two groups [Cooper, 2001] which are ‘Concept Modellers’ and ‘Functional Modellers’.

These can briefly be described as follows:

- Concept modellers generally offer advantages in speed and cost but the parts produced generally have inferior physical strength characteristics. For this reason they are primarily used for creating prototypes for concept/aesthetic appraisal only.

- Functional modellers can generally build parts that are larger, more accurate, and with superior mechanical properties. Therefore they are widely used for the creation of ‘functional prototypes’ where the prototype must have certain or all properties of the final end use part. Due to these characteristics it is systems within this class that are predominantly used for Rapid Manufacturing.
2.2 Rapid Manufacturing

2.2.1 Introduction

In essence, Rapid Manufacturing (RM) is the use of Rapid Prototyping processes to produce end use products, rather than prototypes. Hopkinson et al [2006] defined RM as ‘the use of a computer aided design (CAD)-based automated additive manufacturing process to construct parts that are used directly as finished products or components’. RM has already found numerous uses for production of parts in relatively small quantities and where production of certain geometries is not feasible with conventional methods. Notable examples are hearing-aid bodies, Formula 1 race car components and air ducts and related parts for aircraft. These are discussed further in section 2.2.2.

The capabilities of Rapid Prototyping and RM techniques have resulted in numerous changes to the traditional Product Design Process. One of the main problems encountered in the traditional Product Design Process is that of designers creating geometries in designs that are difficult to manufacture which have to be corrected resulting in high inefficiency during production. Concurrent engineering tools such as Design For Manufacture do exist to help overcome these problems by guiding designers and making them aware of the particular geometry manufacturing limitations right at the start [Hague et al, 2003]. However with RM such geometrical limitations are greatly reduced which means there is less chance of the designer creating problematic designs in the first place: there is far greater ‘design freedom’. Since tooling is not needed the design does not need to be finalised at such an early stage in the Product Design Process. Also, unlike with conventional methods, costs are independent of design complexity [Hopkinson & Dickens, 2001]. Another aspect is the ability to produce large numbers of customised products [Hague et al, 2003].

It has been predicted that as Rapid Prototyping and dedicated RM technology evolves RM will be able to compete with current mass production techniques such as injection moulding and metal casting and that this will revolutionise the manufacturing industry [Stocker, 2002]. Already it has been demonstrated that it is economically feasible to use existing commercial Rapid Prototyping systems to manufacture parts in quantities up to 14,000 [Hopkinson & Dickens, 2001]. Another study found that it was more economical to produce a particular part by SLS than injection moulding in quantities
up to approximately 8,000 [Ruffo et al, 2006]. The same author conducted studies for various parts and the break even points ranged from 35 to approximately 16,000 parts [Ruffo, 2006].

Much research is currently being conducted in the field of RM. In order for RM to become more widely used for end use manufacture, problems in certain areas have to be addressed. The areas of particular importance are:

- Improving mechanical properties
- Improving process speed
- Improving accuracy
- Improving surface finish
- Reducing costs

The Rapid Manufacturing Research Group at Loughborough University, UK is a notable example of a body carrying out research in the development of existing Rapid Prototyping technology for RM use. Other universities or institutes investigating RM include The University of Texas at Austin (USA), TNO Science and Industry (The Netherlands), The University of Liverpool (UK), FHS St.Gallen - University of Applied Sciences (Switzerland), Massachusetts Institute of Technology (USA), Leeds University (UK) and De Montfort University (UK).

2.2.2 Example applications
There are already numerous existing applications of RM and some of these are mentioned below.

RM technology is used to manufacture custom fitting hearing aid bodies by companies such as Siemens Hearing Instruments Inc. and Phonak Hearing Systems [Caloud et al, 2002]. '3D imprints' of an individual's ear are obtained using 3D scanning equipment. This data is then used to create a custom fitting hearing aid body (using Stereolithography or Selective Laser Sintering processes) into which the electronics are installed as shown in Figure 2.
RM technology is used by various teams in Formula 1 racing including Jordan, Toyota Motorsport, Renault and Williams [Tromans, 2006; Dean, 2006]. The Renault Formula 1 race car, shown in Figure 3, includes a number of parts built by RM. Such parts include air ducts and aerodynamic fins, shown in Figure 4. The WilliamsF1 car contained approximately 20 selective laser sintered parts in the 2006 Formula 1 season which included electrical enclosures, cooling ducts and the antenna housing, which was previously produced by hand-laying Kevlar [Dean, 2006].
RM has found various uses in the Aerospace industries. On-Demand Manufacturing (ODM) was a Boeing owned subsidiary sold to RMB Products in 2005 [RMB Products, 2006]. RMB specialises in producing polymer parts, notably by rotational moulding for aerospace use. ODM used SLS to manufacture parts such as air ducts for the F-18 Military jet [DeGrange, 2003], shown in Figure 5. The part count of these complex products was greatly reduced. Figure 6 depicts the redesign of such a part. The original part count is 16 parts including fasteners but the redesign is one part. The use of such parts resulted in a 20% weight saving over the replaced parts and a 25% system level cost reduction [Wooten, 2006].
Advatech Manufacturing, a division of Butler Tool & Design, produces certain end use products by SLS to fit on civilian aircraft such as the Grumman Tiger single engine aircraft\(^1\). This model of aircraft, shown in Figure 7, has been in production since the mid 70s and is still a popular aircraft among private aircraft users [AYA, 2006].

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Example replacement parts which were redesigned and built by SLS are shown in Figure 8 and Figure 9. Figure 8 shows a windshield defroster. The original part consisted of three components and six rivets [Wohlers 2006]. The part was redesigned as one part produced by SLS and included the addition of an integrated hose clamp. Figure 9 shows a ‘Fresh Air Vent for a Grumman Tiger single engine airplane’. This part was redesigned with improved functionality over the original with improved ability to direct the flow of air².

Figure 8 Conventionally produced (left) and selective laser sintered (right) windshield defroster for Grumman Tiger aircraft

Figure 9 Conventionally produced (left) and selective laser sintered (right) fresh air vent for Grumman Tiger aircraft

2.3 Selective Laser Sintering

Selective Laser Sintering is currently the most common process used for RM [Wohlers, 2006] and produces parts by selectively sintering individual layers of powder material. It uses a wide range of materials (polymers, metals, ceramics) and can produce parts with good mechanical properties. In addition the process does not require the supports for overhanging features found in most RP processes. For these reasons there is much research currently being conducted into the use of SLS for RM.

2.3.1 Build procedure

2.3.1.1 Powder preparation

SLS Nylon-12 powder does not need to be dried as is needed with some other processes such as drying of Nylon prior to injection moulding. Some preparation for SLS may be necessary however which is described below.

The SLS process results in a lot of 'used' powder left over from every run. This is mainly from the overflow bins and from the part cake (illustrated in Figure 10, described later), after part removal. Also, when the machine requires emptying, powder is removed from the part build and feed cylinders. The powder can be reused but a certain amount of degradation occurs, depending on the location in the machine and how many times the powder has been used. This degradation may be due to increased molecular weight which hinders the sintering process as described later. With repeated builds of used powder, part quality and indeed the ability to build reduce [Gomet et al, 2002; Gomet & Davis, 2004].

From a technical perspective it would seem ideal to only build with virgin powder but the powder is currently expensive and so this is normally only used for research and development purposes. It is standard practice in industry to mix used powder with virgin powder. This was originally performed using predefined proportions however this does not eliminate the problem of variation in properties. An alternative is to analyse powder using Melt Flow apparatus to determine specific mixing proportions for each individual batch to achieve repeatability between batches. This works by measuring the flow rate of molten plastic to indicate the molecular weight which is considered a good indicator of relative powder quality [Gornet et al, 2002]. It should
be noted that the melt flow procedure measures the effects of shear stress which would not occur to such an extent during the SLS process.

### 2.3.1.2 Build process

Prior to a build, a CAD model must be created and the data processed correctly. The steps in this procedure are as follows:

- CAD model generation
- Conversion to STL file format (generic surface model format)
- Pre-processing (STL file repair, build platform set-up etc.)
- File transfer to SLS machine

Standard procedure in SLS is to deposit a certain amount of powder during the warm up stage, which precedes the build process, and to deposit a small amount of powder afterwards during the cool down stage. The heights associated with these are typically 12mm and 2.54 mm for warm up and cool down respectively.

The build process is outlined below and illustrated in Figure 10. Figure 10 also includes a photograph of the 3D Systems Vanguard SLS machine with the approximate location of the illustrated build process area indicated.

1. Layer of powder deposited across part-build cylinder.
2. Laser ‘draws’ cross-section matching corresponding layer in STL file, bonding particles and fusing to the previous layer.
3. Platform in part-build cylinder moves part downwards a layer.
4. Roller mechanism deposits another powder layer and steps 1-4 repeated.

Regarding the function of the laser, the powder is preheated in the powder feed cylinders and the part bed is also preheated so that the powder is at an elevated temperature just below the melt temperature. This heating is started during the warm-up stage mentioned above. The function of the laser is therefore to selectively increase the temperature of powder from the part bed temperature above the melt temperature rather than to heat the powder from room temperature. This is discussed further in section 6.1.
After the build process completes, the powder and parts within the part build cylinder are collectively referred to as the ‘part cake’. Following build completion and cool down the part cake is removed from the machine. Then the part or parts are removed from the part cake and loose powder shaken or brushed off. Post-processing such as bead-blasting is performed if required.
2.3.1.3 Build parameters

The main build parameters over which the machine operator has control are the machine parameters and part placement and orientation. Machine parameters are 'dialed in' by a trial-and-error process [Gibson and Shi, 1997]. This is partly because individual machines require slightly different parameters. It has been observed by the author of this thesis that multiple SLS machines, at the same location, will have different optimum parameters. There are no universally accepted specific criteria for choice of parameters and Gornet and Davis [2006] showed that mechanical properties of SLS parts produced by different users varied considerably. Important build parameters (using 3D Systems terminology) include Part Heater Set Point, Slicer Fill Scan Spacing, Fill Laser Power, and Fill Scan Count.

Part Heater Set Point is the value registered by an infrared optical pyrometer in the SLS machine which monitors the temperature at the part bed surface (part bed temperature). The value for Part Heater Set Point and the pyrometer measured part bed temperature are notionally readings in degrees centigrade however the pyrometers need calibrating to give absolute readings and are typically otherwise 10-20°C out. The actual part bed temperature also varies across the part bed [DeGrange, 2004] though the part bed temperature is measured by the pyrometer from a small area only. The terms 'Part Heater Set Point' and the pyrometer measured part bed temperature are therefore differentiated from the actual part bed temperature. For typical use, calibration of the pyrometer is not essential since absolute values are not actually required though the newer SLS machines from 3D Systems (HiQ and Pro systems) do incorporate automatic in-process calibration of the pyrometers. For experiments conducted in Chapter 6 it was necessary to obtain absolute values for part bed temperature and so the Part Heater Set Point readings were manually calibrated, as described later.

The correct required value of Part Heater Set Point for building with DuraForm PA is determined for a particular powder batch in a particular machine by slowly raising the pyrometer measured part bed temperature until the material glistens as it starts to melt (termed the 'glaze point') and then subtracting 12°C from this value to determine the Part Heater Set Point [3D Systems, 2001]. This value to subtract from the glaze point is supplied by manufacturers for each material and/or machine and could be affected by the molecular weight distribution. The Part Heater Set Point value must be
determined frequently since different batches of powder require different part bed temperatures due to slight batch to batch variation of melt temperature.

Slicer Fill Scan Spacing is the distance in millimetres between parallel scan vectors of the laser. The laser scans backwards and forwards so that subsequent paths of the laser overlap due to the diameter of the laser and the scan spacing. For a given beam diameter the closer these vectors are (i.e. lower Slicer Fill Scan Spacing numeric value) the higher the energy input is (due to increased overlap). This is illustrated to scale in Figure 11 for scan spacing values of 0.17mm, 0.15mm and 0.13mm.

![Figure 11 Slicer Fill Scan Spacing and beam overlap](image)

Fill Laser Power refers to the applied power of the laser as it ‘fills in’ the area contained by the geometry perimeter. Increased laser power naturally results in increased energy input.

Fill Scan Count refers to the number of times the beam traverses a scan vector for one layer. This is by default once but can be increased resulting in increased net energy input.

**2.3.1.4 Post processing**

Post processing refers to additional separate operations following build completion and part removal from the part-cake. All post processing stages following removal of powder are optional and employed depending on the intended use of the parts. The
most common form of post processing is bead blasting which smoothens the part surface. Methods of post processing are discussed further in Section 2.3.3 below.

### 2.3.2 Hardware

In 1986 the first SLS machine was created, at the University of Texas at Austin, Texas. In 1987 DTM Corporation was founded and the SLS Model 125 machine was produced. The first production machine, based on the Model 125, was the Sinterstation 2000 and was launched in 1993 [Juster, 1994].

Today there are two leading manufacturers worldwide that manufacture commercially available SLS machines. These are 3D Systems of the United States (previously DTM) and EOS of Germany. Both companies market solutions to produce parts from polymers, metals and ceramics. 3D Systems currently produce two types of machine. The first is the Vanguard or the faster Vanguard HS, recently replaced by the HiQ and HiQ HS, which can use all 3 classes of material. The models designated HS for 'high speed' have a higher power laser which enables them to scan faster thus producing parts quicker than their lower power counterparts. The second type is the Sinterstation Pro series (140 and 230) which is a modular system with larger build volume, focussed towards RM. The Sinterstation Pro 230 currently has the largest build volume available, almost 1.5 times bigger than the next largest, by EOS. The large build volume in the Pro 230 is achieved by having a tall build, unlike the EOS P700 and P730 which have a wide build and use two lasers instead of one. EOS produces different machines for each material class (polymers, metals, ceramics). In this respect the 3D Systems solutions could be considered more versatile, however there are some critical advantages of the EOS systems. The method in which they produce metal parts is different. The 3D Systems machine produces a 'green part' requiring infiltration to achieve the final part. The process of producing the part is almost identical to some powder metallurgy methods the fundamental difference being the method in which the green part is created. In contrast, the EOS machines for metal (M270) can produce parts directly without the need for infiltration. Table 1. shows the most current SLS machine models available. The 3D Systems Vanguard machines are also included since a Vanguard machine was used in this investigation.
<table>
<thead>
<tr>
<th>Company</th>
<th>Country</th>
<th>Machine</th>
<th>Build Dimensions (mm)</th>
<th>Build Volume ($\times 1000$ cm$^3$)</th>
<th>Common Materials</th>
</tr>
</thead>
<tbody>
<tr>
<td>3D Systems</td>
<td>U.S.</td>
<td>Vanguard/HiQ Vanguard HS/ HiQ HS</td>
<td>381 x 330 x 457</td>
<td>57.5</td>
<td>Polyamide, glass filled polyamide, elastomer polystyrene, foundry sands, stainless steel</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sinterstation Pro 140</td>
<td>550 x 550 x 460</td>
<td>139.2</td>
<td>Polyamide, glass filled polyamide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sinterstation Pro 230</td>
<td>550 x 550 x 750</td>
<td>226.9</td>
<td>Polyamide, glass filled polyamide</td>
</tr>
<tr>
<td>EOS</td>
<td>Germany</td>
<td>FORMIGA P100</td>
<td>200 x 250 x 330</td>
<td>16.5</td>
<td>Polystyrene, polyamide, glass filled polyamide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EOSINT P390</td>
<td>340 x 340 x 620</td>
<td>71.7</td>
<td>Polystyrene, polyamide, glass filled polyamide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EOSINT P700/P730</td>
<td>700 x 380 x 580</td>
<td>154.3</td>
<td>Polystyrene, polyamide, glass filled polyamide</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EOSINT M270</td>
<td>250 x 250 x 215</td>
<td>13.4</td>
<td>bronze-based, steel-based</td>
</tr>
<tr>
<td></td>
<td></td>
<td>EOSINT S750</td>
<td>720 x 380 x 380</td>
<td>104.0</td>
<td>Resin coated sand</td>
</tr>
</tbody>
</table>

Table 1 Current SLS machines [3D Systems, 2004, 2006a, 2006b; EOS, 2005(a-c), 2007(a-c)]

2.3.3 Material properties of SLS polymer parts
Reported properties (excluding mechanical properties) of polymer materials typically used in 3D Systems machines are shown in Table 2.

Manufacturer supplied mechanical properties for commercially available SLS polymer materials are listed in Table 3. Many of the reported tensile strength and E-modulus values are comparable with traditionally processed parts but elongation values (indicating ductility) are generally far lower. This, as well as the initial directions of the industrial collaborators, led to the literature review focussing on the elongation and ductility of materials in this thesis.

DuraForm PA was used in this research project. DuraForm PA is a Nylon-12 powder available from 3D Systems[Childs and Tontowi, 2001; Shellabear, 1998] whereas PA 2200 is Nylon-12 supplied by EOS [EOS 2005d].
<table>
<thead>
<tr>
<th>Material</th>
<th>DuraForm PA</th>
<th>DuraForm GF</th>
<th>DuraForm AF</th>
<th>CastForm</th>
<th>DuraForm Flex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type of material</td>
<td>Polyamide powder</td>
<td>Glass-filled</td>
<td>Polyamide-aluminium</td>
<td>Polystyrene powder</td>
<td>Elastomeric plastic powder</td>
</tr>
<tr>
<td>Notes</td>
<td>Good thermal stability and chemical resistance</td>
<td>High-durability material; good thermal stability and chemical resistance</td>
<td>Cast aluminium look with excellent surface finish detail, and wear resistance</td>
<td>Performs almost identically to foundry wax for shell investment casting</td>
<td>Rubber-like performance to simulate gaskets, hoses, seals; can be coloured or pressure-sealed with infiltrants</td>
</tr>
<tr>
<td>Tap density (g/cm³)</td>
<td>0.59</td>
<td>0.84</td>
<td>0.89</td>
<td>0.46</td>
<td>0.44</td>
</tr>
<tr>
<td>Average particle size (μm)</td>
<td>58</td>
<td>48</td>
<td>Not available</td>
<td>62</td>
<td>85</td>
</tr>
<tr>
<td>Specific gravity at 20º C</td>
<td>0.097</td>
<td>1.4</td>
<td>Not available</td>
<td>0.86</td>
<td>Not available</td>
</tr>
<tr>
<td>Melting point (ºC)</td>
<td>184</td>
<td>185</td>
<td>Not available</td>
<td>Not available</td>
<td>192</td>
</tr>
<tr>
<td>Cost of raw material ($/kg)</td>
<td>132</td>
<td>88</td>
<td>Not available</td>
<td>132</td>
<td>Not available</td>
</tr>
</tbody>
</table>

Table 2 3D Systems SLS powder properties [Wohlers, 2006]
<table>
<thead>
<tr>
<th></th>
<th>Tensile strength (MPa)</th>
<th>E-modulus (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>3D Systems</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DuraForm PA</td>
<td>44</td>
<td>1,600</td>
<td>9</td>
</tr>
<tr>
<td>DuraForm GF</td>
<td>38</td>
<td>5910</td>
<td>2</td>
</tr>
<tr>
<td>DuraForm AF</td>
<td>35</td>
<td>3960</td>
<td>1.5</td>
</tr>
<tr>
<td>DuraForm EX</td>
<td>48</td>
<td>1517</td>
<td>47</td>
</tr>
<tr>
<td>DuraForm Flex</td>
<td>1.8</td>
<td>7.4</td>
<td>110</td>
</tr>
<tr>
<td>DuraForm Flex (infiltrated)</td>
<td>2.3</td>
<td>9.2</td>
<td>151</td>
</tr>
<tr>
<td>CastForm (infiltrated)</td>
<td>0.3</td>
<td>1604</td>
<td>Not available</td>
</tr>
<tr>
<td><strong>EOS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PA 2200</td>
<td>45</td>
<td>1700</td>
<td>20</td>
</tr>
<tr>
<td>PrimePart</td>
<td>47</td>
<td>1700</td>
<td>15</td>
</tr>
<tr>
<td>PA 3200 GF</td>
<td>48</td>
<td>3200</td>
<td>6</td>
</tr>
<tr>
<td>PrimeCast 100</td>
<td>1.2</td>
<td>1600</td>
<td>0.4</td>
</tr>
<tr>
<td>PrimeCast 100 (infiltrated)</td>
<td>5.5</td>
<td>1600</td>
<td>0.4</td>
</tr>
<tr>
<td>Alumide</td>
<td>45</td>
<td>3600</td>
<td>3</td>
</tr>
<tr>
<td><strong>CRP Technology</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>WindForm GF</td>
<td>48</td>
<td>4410</td>
<td>2.5</td>
</tr>
<tr>
<td>WindForm PRO</td>
<td>53</td>
<td>4960</td>
<td>2.9</td>
</tr>
<tr>
<td>WindForm PRO B</td>
<td>47</td>
<td>3610</td>
<td>3.8</td>
</tr>
<tr>
<td>WindForm XT</td>
<td>78</td>
<td>7320</td>
<td>2.6</td>
</tr>
<tr>
<td><strong>Solid Concepts</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NyTek 1100/1100B (max)</td>
<td>52</td>
<td>1900</td>
<td>45</td>
</tr>
<tr>
<td>NyTek 1100/1100B (min)</td>
<td>41</td>
<td>1390</td>
<td>12</td>
</tr>
<tr>
<td>NyTek 1200 CF (max)</td>
<td>66</td>
<td>2900</td>
<td>3.6</td>
</tr>
<tr>
<td>NyTek 1200 CF (min)</td>
<td>28</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 3 Manufacturer supplied mechanical properties [3D Systems, 2007; EOS, 2005d; 3T RPD, 2007; Windform, 2007]

It is possible in theory to laser sinter most thermoplastic polymers though different polymers respond more favourably than others when considering the requirement to build parts comprised of multiple layers. Those polymers that have been determined to be suitable for SLS must be treated differently depending on whether they are amorphous or (predominantly) crystalline i.e. semi crystalline. Kruth et al [2003] describe the differences between amorphous and semi crystalline polymers in relation to SLS. Amorphous powders (predominantly polycarbonate in SLS) can produce parts with very good dimensional accuracy and feature resolution. However, since the particles do not completely consolidate, the resultant parts lack strength and durability compared with parts built from crystalline material [Kruth et al, 2003; Dickens et al 2000]. SLS crystalline materials are heated to their melting temperature whereas amorphous materials do not melt and instead the critical sintering temperature for amorphous polymers is the glass transition temperature. Melting and the glass transition are discussed further in Chapter 4.
Semi-crystalline polymers (predominantly Nylon-12 and Nylon-11) can be successfully sintered and it has been reported [Tontowi and Childs, 2001] that it is possible to achieve fully dense parts with respect to porosity. However, with SLS of semi-crystalline polymers shrinkage during crystallisation hinders production of accurate parts [Shi et al, 2004]. For this reason it is essential that for materials to be processed by SLS the melt temperature must be considerably higher than the crystallisation temperature so that crystallisation can be delayed and reduced during the build process [Scholten & Christoph, 2001] to allow new layers to bond to previous layers with a more homogenous microstructure. A high enthalpy of fusion is also preferable to prevent melting of powder particles local to the particles targeted by the laser due to conduction of heat. In addition, during laser sintering, a narrow melt temperature range in combination with a low melt viscosity is required to achieve the necessary level of fluidity very quickly without inputting excess energy [Scholten & Christoph, 2001]

Shi et al [2004] investigated the effects of powder molecular weight, percentage crystallinity and particle size on part properties. Molecular weight is one of the most important characteristics in describing polymers in general [Boyd & Philips, 1993] and the weight-average molecular weight ($M_w$) affects the melt viscosity directly. The relationship is described in Equation 1. As mentioned in 2.3.1.1 the Melt flow procedure is used to characterise melt viscosity by the melt flow index (MFI). High MFI is associated with low viscosity.

$$
\eta_0 = k(M_w)^n
$$

$\eta_0$ = melt viscosity
k = constant
n = 1 (if $M_w < \text{critical molecular weight}$
$= 3.4$ (if $M_w > \text{critical molecular weight}$

Equation 1 melt viscosity and molecular weight [Shi et al, 2004]

Shi et al [2004] sintered samples of polystyrene powder of different MFI and found that lower MFI (higher viscosity) resulted in parts of lower density. SEM
micrographs showed improved particle consolidation with the higher MFI (lower viscosity) sample as shown in Figure 12.

Figure 12 SEM micrographs of selective laser sintered Polystyrene. (a) High MFI (low viscosity) (b) Low MFI (high viscosity) [Shi et al, 2004]

The pre-process percentage crystallinity of Nylon-12 powder and its effect on part accuracy was also investigated. It was found that the accuracy of samples was affected mostly by 'crystal shrinkage' (as opposed to 'sintering shrinkage' and 'temperature shrinkage'). Shrinkage was measured and it was found that the greater the percentage crystallinity, the greater the shrinkage. This shrinkage is specifically due to the sudden drop in specific volume below the melt temperature with crystalline polymers [Gibson & Shi, 1997]. Above a certain degree of crystallinity parts distorted so much that shrinkage could not be measured. Warping of parts produced from two different grades of Nylon-12 powder was also investigated and a notable difference was found between the two. This was attributed to the difference, on a DSC (Differential Scanning Calorimetry) curve, between the melting peak and the crystallisation peak. If the crystallisation peak was significantly lower than the melting peak the parts would remain liquid for a while during cooling however with the crystalline peak close to the melting peak the parts would solidify quickly resulting in accumulation of stress and distortion of parts. The difference between the melting and crystallisation peak temperature is illustrated in Figure 13. Figure 13 shows a DSC trace for DuraForm PA Nylon-12 which is designed for SLS and therefore exhibits a large difference.
Work has been conducted on the effects of particle size and size distribution on part properties. Ho et al [2003] showed that, for polycarbonate powder, part density increases with decreasing particle size and also increases with increasing quantities of fine graphite powder blended in (up to 5% total mass). The absorbance, that is the degree of radiation absorption, was also shown to increase with graphite and this is of importance since the higher the material absorbance, the lower the laser power required. Shi et al [2004] found that, for polystyrene too, part density and accuracy increases with decreasing particle size. However, they also found that very small powder particles cause difficulties with spreading of powder and so an optimum must be found. This diameter was suggested to be in the range of 75 – 100 μm.

Moeskops et al [2004] investigated tensile creep behaviour of Nylon-12. They found SLS processed Nylon-12 to be less affected than injection moulded Nylon-12 and that it may be possible to predict the creep behaviour for 11 years.
Considerable attention has been paid to process parameters and modelling. Both mechanical properties and appearance are influenced by process parameters but with SLS it is generally accepted that it is not possible to achieve the highest quality appearance with the best mechanical properties and so a balance is required. Tontowi & Childs [2001] investigated the effect of powder bed temperature on density of Nylon-12 parts. They showed that part density increased with part bed temperature with fully dense parts achievable and that part density varied with bed position, apparently due to bed temperature variation. However, high part bed temperatures can result in 'growth' as surrounding powder bonds to the part resulting in poor surface finish and accuracy [Juster, 1994]. Gibson & Shi [1997] investigated the relationships between the various parameters and general material properties. They observed that the fill laser power can play an important role in altering porosity since it controls the viscosity of the powder as it is sintered. The less viscous the material, the lower the porosity i.e. greater density. However, too high a fill power can cause shear stress between layers and possible curling or part distortion. Tensile test specimens were built using various sets of parameters. Decreasing scan speed, scan spacing and increasing laser power increased density and tensile strength. Higher scan spacing (distance between parallel laser scans) was found to reduce density and tensile strength.

Various work has looked at part placement within builds. Saleh et al [2002] and Gibson and Shi [1997] showed considerable variability of mechanical properties for different part orientation and parts built in different locations in the build volume within the same build. Part orientation affected properties so that parts built in the z-axis (i.e. tensile specimens standing vertically) were weaker than those built parallel with the x or y axis. It has been demonstrated that parts built central to the build volume yield improved properties [Saleh et al, 2002; Tontowi & Childs, 2001].

The energy applied per unit area by the laser can be indicated by the 'energy density' also known as the 'Andrew number' [Lu et al, 2001]. The energy density equation relates the laser parameters Fill Laser Power, Beam speed and Slicer Fill Scan Spacing and is shown in Equation 2.
ED = \frac{P}{BS \times SS}

ED (J/mm²): energy density
P: Fill laser power
BS: beam speed
SS: Slicer fill scan spacing

Equation 2 Energy density equation

Numerous authors have described effects of build parameters on material properties in SLS in terms of energy density. Gill and Hon [2004] investigated the production of silicon carbide (SiC) polyamide matrix parts by SLS and found that higher energy density resulted in higher tensile strength and lower porosity but that after a certain value for energy density, tensile strength reduced and porosity increased. They were therefore able to determine an optimum energy density for their experiments. Ho, Cheung and Gibson [2003] processed amorphous bisphenol A polycarbonate by SLS and reported effects of varied energy density on the morphology and mechanical properties of parts produced. They found that higher energy density resulted in better fusion of particles and improved mechanical properties but again that excessively high energy density resulted in severe degradation and inferior mechanical properties.

Tontowi and Childs [2001] researched the relationship between energy density and the physical density of SLS parts built from DuraForm PA Nylon-12. They determined a maximum possible density of parts built and then developed a model showing a linear relationship between energy density and powder bed temperature in order to maintain this maximum possible part density. This relationship is illustrated in Figure 14.
Actual quantification of the energy supplied to the material as a function of both laser parameters (energy density) and part bed temperature has not been reported to date, even as a unit-less relative quantity. This is presumably because of the complexity of the problem due to 2 energy sources (part bed heat and the laser) and hence the need to determine the relative effects of these compared with each other which is absent when considering only one energy source (the laser).

Ghanekar et al [2003] investigated the selection of optimum parameters by applying ‘D-optimality’ criterion to a series of factorial experiments. For a selected example part they specified the importance of certain criteria (such as tensile strength and dimensional accuracy) and were able to determine appropriate build parameters to achieve these.

As mentioned in Section 2.3.1.4 a certain degree of post processing is always required for SLS polymer parts in that non sintered powder must be removed. It is common practice to bead blast Nylon parts with glass beads to improve surface finish and other similar methods are sometimes used. For example, polycarbonate can be sanded and painted with a thin coat of epoxy resin and Nylon can be wet sanded and painted. Various novel approaches to post processing have also been looked at. Saleh et al [2004] investigated electroplating of Nylon-12 parts and found that copper and nickel increased E-modulus, tensile strength and impact strength as well as imparting a smooth surface finish. Fritz et al [2002] studied cryogenic treatment of Nylon-12
parts due to their high crystallinity and the fact that cryogenic treatment of metals yields improvements in properties directly related to the crystal structure. Impact strength was increased as well as tensile strength though consistent results were difficult to achieve with the latter. Zarringhalam [2003] conducted trials into infiltration and post process heating of Nylon-12 parts. Heating close to the melt temperature resulted in increased impact strength, E-modulus, tensile strength and elongation at break with visible ductile failure (necking of specimens prior to failure). However, post process heating very close to the melt temperature caused parts to distort severely.

It is common practice to blend Nylon powders with glass spheres resulting in parts with increased stiffness, accuracy and heat deflection properties [Childs & Tontowi, 2001; Saleh et al, 2002]. Das et al [2003] experimented with SLS fabrication of bio-compatible tissue engineering scaffolds from Nylon-6 (rarely used in SLS) with some positive results for that application area. Nylon coated copper powder (70% copper/30% Nylon) can be used for injection moulding tool production without removal of the Nylon phase or further post-densification/infiltration processes as with some other SLS metal processes [Kruth et al, 2003; Upcraft & Fletcher, 2003].

2.3.4 Mechanical properties of SLS metal parts

SLS metal parts, as with conventionally sintered parts, often suffer from increased brittleness (low ductility) compared with machined or other parts. By far the most work carried out related to increasing the ductility of SLS metal parts is that where the objective is related to reducing porosity. This is partly because many SLS metal processes inherently involve production of a porous ‘green’ part requiring infiltration. Uzunsoy et al [2003] investigated the effects of infiltration of ‘Rapidsteel’ parts in different processing atmospheres and found that this does have a significant effect on mechanical properties. They found that parts infiltrated in a vacuum and Argon atmosphere had significantly greater ductility and crack growth resistance compared with those infiltrated in a Hydrogen/Nitrogen atmosphere. This was mostly attributed to elimination of nitrides. Zhou et al [2004] investigated the possibilities of low temperature polymer infiltration because of limitations with conventional high temperature infiltration using metals. Such limitations relate to cracks, distortion and shrinkage as well as generally poor surface quality. Phenolic resin, Epoxy resin and Acrylic resin were tried but found to offer inferior mechanical properties compared
with metal infiltrants. Sercombe & Schaffer [2004] investigated a novel approach to infiltrating by infiltrating an aluminium alloy with a second aluminium alloy. This was achieved by using a nitrogen atmosphere after the debinding stage to enable nitriding of the remaining aluminium in effect creating a hard skeleton which could then be infiltrated with aluminium, apparently retaining intricate parts and avoiding distortion. This improved wettability enabling better 'filling' of pores and hence greater density. Storch et al [2003] found that ductility of Rapidsteel parts was significantly affected by build orientation. Parts built horizontally showed almost double the elongation of parts built vertically.

Tolochko et al [2003] compared characteristics of SLS of single and two-component powders. They describe how in single-component powders a liquid phase occurs from the melting of the surface of the powder particles which thus joins the non-melted powder cores. However this requires very precise control to avoid complete melting of the particles. With two-component powders, the powder can be heated above the melt temperature of the binder component but below that of the main component. The liquid phase is therefore generated almost entirely from the complete melting of the binder component which results in easier control. In order to achieve parts with maximum density and thus ductility, the volume of space between the solid particles and the volume of liquid phase must be equal. However, high volumes of liquid phase can cause problems such as 'balling' where the molten particles merge into droplets [Tolochko et al, 2004]. They also stated that, due to the short interaction time between the laser and powder, solid state sintering cannot occur in laser sintering processes and therefore only liquid phase sintering can join particles. Solid state and liquid phase sintering are discussed further in Section 3.1.2.
3 Traditional Powder Processing Techniques

3.1 Traditional sintering of metals (powder metallurgy)

3.1.1 Powder metallurgy

Powder metallurgy (PM) has been defined as “the study of the processing of metal powders, including the fabrication, characterization, and conversion of metal powders into useful engineering components” [German, 1997]. The ‘conversion of metal powders into engineering components’ involves sintering and so the term powder metallurgy subsequently refers to the process of sintering metal powder for consolidation. PM therefore has similarities with SLS processing of polymers and is subsequently discussed further. Sintering itself is generically defined as a processing technique which increases the strength of a powder mass by bonding adjacent particles by applying thermal energy [German, 1997; Kang, 2005].

A wide variety of parts can be made via PM including balls used in ball-point pens, gears, cams, bushings, cutting tools, filters and oil-impregnated bearings [Kalpakjian and Schmid, 2001]. Example gears and related components made by PM are shown in Figure 15.

Figure 15 Examples of typical parts made by PM [Kalpakjian and Schmid, 2001]
The fundamental similarity between PM and SLS of crystalline polymers such as Nylon-12 is that both processes involve the sintering or melting of powder material to form solid parts. A fundamental difference between the PM and polymer SLS processes is that in PM the powder is completely formed into the part's net shape and sintered as a whole whereas in SLS of polymers the part net shape is formed and sintered layer by layer.

The major stages involved in creating PM parts are preparation of the powder, compaction and sintering, and secondary and finishing operations. These stages are illustrated in Figure 16. Powder preparation involves the manufacture of the powder (for example, by atomization) and the addition of additives such as lubricants.

Parts made by PM are shaped by compaction in dies. Sintering can either take place after the parts are compacted or during the compaction process. Also, sintering can be conducted under pressure after the powder has been cold compacted. Sintering is therefore either 'pressureless' or 'pressure-assisted'.

![Figure 16 Major stages in manufacture of parts by PM](image)

Cold compaction produces parts called 'green compacts' or 'green parts'. The green compact is relatively brittle until strengthened by sintering. Considerable shrinkage can occur at this stage depending upon the porosity of the green compact and whether the part is sintered under pressure or not. An alternative method is where the metal powder is mixed with a polymer binder which is melted during compaction resulting in the powder being held in a matrix. The binder is then 'burnt out' in a secondary operation and the part sintered (called a brown part or brown compact) and then infiltrated with a metal or other material with melting temperature below that of the
main metal matrix. SLS of metals sometimes involves a similar process where a 'green compact' is produced layer by layer and then debound, sintered and infiltrated afterwards [Agarwala et al, 1995].

3.1.2 Sintering theory

Figure 17 shows different categories of traditional sintering. As discussed previously, sintering can be categorised as 'pressureless' or 'pressure-assisted'. Sintering in SLS does not occur under applied pressure and so is comparable with pressureless rather than pressure-assisted sintering.

---

![Sintering Processes Diagram](image)

**Figure 17 Map of traditional sintering processes [adapted from German, 1996]**

Figure 17 shows that pressureless sintering can be divided into two subcategories which are 'solid-state' and 'liquid phase'. The essential definitions of these are that solid state sintering occurs when the entire compact is densified in a solid state while liquid phase sintering occurs with the coexistence of both liquid and solid phases within the compact [Kang, 2005, German, 1997]. The scope of the definition of liquid phase sintering is far broader than that of solid state sintering since there are numerous potential sources for the liquid phase. The coexistence of a liquid and solid phase can be due to chemical reactions, partial melting, or eutectic liquid formation [German, 1997]. As mentioned in Section 2.3.4 sintering of Nylon-12 in SLS is considered liquid phase since solid state sintering cannot occur due to the short laser/powder interaction time and SLS elevates the particle temperature above the melt temperature.

Sintering occurs via the formation of necks between particles as shown in Figure 18. When two particles are considered, after point contact neck growth creates a new grain boundary and with sufficient time the particles will start to coalesce and,
theoretically, eventually form a new larger particle. This transition is illustrated in Figure 19.

Figure 18 Particle neck formation [German, 1997]
Figure 19 Two sphere sintering model [German, 1997]

3.1.3 General mechanical properties of PM parts

Density is a fundamental concept in PM and the sintering process itself is sometimes alternatively referred to as ‘densification’ [Greetham, 2006]. It should be noted however that densification is not a necessary aspect of sintering since interparticle neck growth, with a loss of surface area, occurs in some powder compacts without a density change [German, 1996]. Nevertheless, German [1996] has stated that density is probably the most important parameter involved in the study of sintering. It relates to the sintering kinetics and correlates with many properties of sintered materials.

When brought into contact with other particles, particulate material can be described in terms of its ‘packing’. The packed powder will contain voids due to the geometry and size distribution of the particles [Kalpakjian and Schmid, 2001]. As the particles
coalesce during sintering the geometry of the voids changes. Figure 20 illustrates that as sintering progresses and neck growth continues pore volume decreases and the pores become smoother. Figure 20 illustrates the case for solid state sintering but the same principle applies for liquid phase sintering in terms of the void geometry. A material which has zero voids or porosity is considered to have a density of 100%. The presence of porosity therefore reduces this percentage or fractional density.

The presence of voids and porosity has detrimental effects on mechanical properties. Density correlates with many properties of sintered material including part strength and ductility so that increased density results in improved mechanical properties [Haynes, 1977; Agarwala et al, 1995; German, 1996]. There are two main factors that cause decreased strength with lower densities. At densities less than 80% of maximum density, the size of inter particle bonds is the main factor and at densities of over 80% it is the pore size, shape and spacing which becomes the predominant factor [Agarwala et al, 1995]. This relates to the fact that porosity may consist either of a network of interconnected pores or of sealed holes, and that interconnected pores are generally found with densities less than 80% of maximum density [Kalpakjian and Schmid, 2001].

Compaction can be carried out or improved using various methods such as rolling, forging or isostatic pressing. This increases part density. Categories of Isostatic pressing are Cold Isostatic Pressing (CIP) and Hot Isostatic Pressing (HIP). CIP generally uses considerably higher pressures than HIP which introduces temperatures typically around 1100°C. Hot Isostatic Pressing (HIP) can produce parts with almost 100% density with good mechanical properties however the process has wider dimensional variation than other compacting processes. Both HIP and CIP involve
sealing the part and then placing the sealed part in a pressure vessel filled with fluid for hydrostatic pressurisation [German, 1997; Kalpakjian and Schmid, 2001].

3.1.4 Ductility of PM parts

A study of the effects of porosity on the ductility of sintered metals [Haynes, 1977] derived a simple equation relating ductility and porosity (Equation 3). This was based on a model of sintered material from a study on cermet by Cope [1965] where a metallic matrix of a sintered metal was considered to be a network in which particles are linked together by necks. Cermets are sintered material combining a ceramic phase bonded with a metallic phase. In this model the individual necks behave like miniature tensile specimens when stressed. Haynes showed that for the purpose of this equation it was better to regard the matrix of sintered material as a network of nodes joined by branches and this allowed the concept of ‘n branches per unit area of cross section’ to be applied which aided development of the equation.

\[
\delta_{rel} = \frac{(1 - \varepsilon)^{\frac{1}{2}}}{(1 + Ce^{2})^{\frac{1}{2}}}
\]

\[\delta_{rel} \quad = \text{relative elongation (ductility) compared to 100\% dense material} \]
\[\varepsilon \quad = \text{fractional porosity content (1 - fractional density)} \]
\[C \quad = \text{material constant} \]

Equation 3 Ductility as a function of porosity [Haynes, 1977]

The value of C is a measure of the sensitivity of ductility to porosity content. Higher values of C correspond to higher sensitivity. C generally varies between 100 and 100,000 [Bourell, 2006]. Depending on the sensitivity of the material, the presence of only a few percent porosity can reduce ductility to a small fraction of fully dense material. [Haynes, 1977] suggested that the effect of the porosity may be influenced by the ability of the matrix to work harden and the resulting increase in volume of material in a branch that underwent deformation and thus elongation.

Figure 21 illustrates the relationship between elongation and porosity (the inverse of density) for iron of various particle sizes and purity.
[Niu & Chang, 1999] modelled the effect of porosity on ductile fracture of PM titanium alloy. They state that ductile fracture of two-phase alloys occurs by initiation (at the primary particles, the titanium solvent), growth and coalescence of voids which nucleate at the second-phase particles (solute additives). This sequence starts because of the inherent presence of microstructural defects or pores and inclusions with PM titanium alloys and indeed all PM materials. A model of void growth based on Wilkinson and Vitek crack theory [Wilkinson & Vitek, 1982] was used to describe crack propagation in PM titanium alloy. For titanium alloys, the model was found to predict fairly well the fracture toughness of porous samples using data of fully dense samples.

Intrinsically the tensile ductility of metals and polymers increase when tested at elevated temperature. However in PM it has been observed with fine grain-sized
alloys that tensile ductility can actually reduce at higher testing temperatures [Porr & Gangloff, 1994; Kim and Park, 2000]. Kim and Park [2000] suggest that rapid dynamic recovery during deformation in fine grain-sized materials would be more effective at higher temperatures and therefore decrease the ductility. This would 'compete' with the intrinsic ductility rise with temperature, apparently surpassing it at higher temperatures.

Surface texture can affect a material's ductility since pores on the surface can have a notch effect, leading to stress concentrations and crack propagation, particularly under bending [Storch et al, 2003; Kalpakjian and Schmid, 2001]. The method of powder manufacturing will affect this. For example, water jetted iron particles are poly-angular and have a rough surface compared to air jetted iron powder particles which are smoother and rounder.

Alexander et al [1998] compared tensile and impact properties of iron aluminide samples made by PM with samples made by casting. Differences in tensile properties were attributed to differences in fine-scale precipitation and dislocation structures, and the different grain sizes. Grain size (crystal size) had a significant effect on the ductility of PM samples with finer grains resulting in greater ductility.

3.2 Traditional polymer powder processing

Methods to process polymer powder other than by SLS are now reviewed. Rotational moulding is discussed in most detail since it is routinely used to produce parts from Nylon-12, the material used in this PhD investigation and most widely used in the field of SLS.

3.2.1 Rotational moulding

Rotational moulding uses heat without high pressure to produce hollow, one-piece parts by rotating polymer in a mould bi-axially [Beall, 1998]. The polymers used are predominantly in powder form but are also, less commonly, in liquid form [Harkin-Jones and Crawford, 1996]. Rotational moulding described in this thesis subsequently refers only to the processing of powder polymers.
Figure 22 illustrates the basic operation of a rotational moulding machine. This shows a mould being filled with polymer powder. The mould is then closed and heated while being rotated about two perpendicular axis. The powder tumbles inside the mould, fusing together and coating the mould inner surface. The mould is then cooled while continuing to be rotated and finally the part is removed from the mould.

1. Mould Charging

2. Mould Rotation and Heating

3. Mould Rotation and Cooling

4. De-moulding

Figure 22 Principle of rotational moulding [Adapted from Crawford, 1996]

Throne [1995] states that the ‘tack temperature’ is a certain characteristic temperature of the powder above which particles start to stick to the mould surface. For crystalline polymers this is a few degrees above the peak melt temperature. Heat flows from the mould to the powder in contact with the mould surface via conduction which in turn heats the air within the mould by convection. Loose powder is then heated by conduction through the fused powder and by convection of the hot air.
Crawford [1996] describes fundamental characteristics of materials suitable for rotational moulding as:

- Flow characteristics of the powder suitable for correct distribution within the mould.
- Flow characteristics of the melt suitable to achieve uniform wall thickness and to flow into complex shapes.
- Thermal stability sufficient to withstand prolonged exposure to elevated temperature.

Major materials which fulfil these requirements and are currently used for rotational moulding are Polyethylene (Low, Medium and High Density); Polyvinylchloride (PVC); Polyester; Polycarbonate; Nylon-6; Nylon-11; Nylon-12; Polyvinylidene Fluoride and Fluoropolymers. Certain reactive materials can also be used which are normally placed in the mould as low viscosity liquids.

The use of Nylons, particularly Nylon-12, for rotational moulding is now discussed since Nylon-12 is also widely used in SLS. Petruccelli [1996] reviewed the use of Nylons in rotational moulding and stated that while numerous Nylons have been determined suitable for rotational moulding, the most commercially successful are Nylon-6, Nylon-11 and Nylon-12. Nylon-6 provides the best resistance to oxidation during heating. Nylon-12 is more common in rotational moulding than Nylon-11 which has lower falling weight impact properties. To avoid oxidation during heating, Nylon based resins must be blended with anti-oxidants and/or processed in an inert atmosphere within the mould.

Due to its resistance to oxidation, it is possible to process Nylon-6 without an inert atmosphere. Nylon-11 and Nylon-12, which are compounded with anti oxidants, can be processed without an inert atmosphere though better material properties are achievable with an inert atmosphere.

Nylons used in rotational moulding are hygroscopic and will degrade if processed with excessive moisture [Petruccelli, 1996]. The moisture content should be no more than 0.2% for Nylon-6 and 0.1% for Nylon-11 and Nylon-12 for satisfactory performance. According to Petruccelli the equilibrium moisture absorption at 50% relative humidity for Nylon-6, Nylon-11 and Nylon-12 are 2.7%, 0.8% and 0.7%
respectively. Although Nylon-11 and Nylon-12 absorb moisture considerably less than Nylon-6, it may still be necessary to dry all of these powders before processing. It should be noted that most Nylon powder is supplied dry, in air tight containers, ready for rotational moulding.

The manner in which a polymer is cooled from the molten state directly affects the properties of the solid state material [Michaeli, 1995]. The cooling rate during crystallisation of the material is the most critical factor and so is important to understand and control in polymer processing methods, including rotational moulding. Petruccelli [1996] stated that the more efficient (i.e. quicker and uniform) the cooling of Nylon in rotational moulding, the higher the impact strength. This statement conforms with fundamental polymer science related to the crystallinity of polymers discussed later in section 4.2.1. Quick cooling, even quenching, of parts may therefore be desirable in rotational moulding and is achieved by spraying water onto the hot mould but care must be taken to avoid premature release of the part which can result in inefficient cooling and warping. An optimum cooling cycle should consist of the minimum cooling time in air to avoid premature part release followed by water cooling [Petruccelli, 1996]. A slight gas pressure introduced inside the mould during the cooling cycle can reduce the minimum cooling time further.

Sometimes it is necessary to remove a part from the mould which is still relatively hot due to difficulty of part removal when cooler because of geometrical complexity [Petruccelli, 1996]. In such cases it is still possible to quench the part by immersion and/or filling with tap water. Quenching the inside of a 9.5mm thick Nylon-6 specimen in this manner resulted in a 37% increase in impact strength and a further 2 hours soak resulted in a 63% increase though the individual effects of quenching and water absorption (which causes plasticisation and thus increased impact strength) were not determined.

Godinho, Cunha and Crawford [1998] investigated material properties across the thickness of a linear medium density polyethylene (LMDPE). Crystallinity was shown to vary throughout parts with distance from the mould surface. Cooling rates at these points were calculated using readings from thermocouples. The maximum cooling rate of 12.53 K min⁻¹ (at the mould wall) resulted in the minimum crystallinity of 51.31% while the minimum cooling rate of 4.41 K min⁻¹ (furthest from
the mould wall) resulted in the maximum crystallinity of 57.83%. Increased crystallinity was related to increased tensile and flexural properties though it was concluded that mechanical properties were also affected by other microstructural parameters.

3.2.2 Powder coating

Powder coating refers to various processes which involve applying polymer powder to a substrate, using heat to fuse particles together and to the substrate resulting in a uniform coating [Utech, 2002; Richart, 1995]. The main methods used in powder coating [Richart, 1995] are Fluidized bed coating; Electrostatic spray coating; Electrostatic Fluidized bed coating; and Flame spraying.

In Fluidized bed coating, which was the first powder coating technique used, the powder is suspended in air inside a container. The air flows into the container through a porous bottom plate. Typically the part to be coated, usually a metal, is heated above the melt temperature of the polymer and then dipped into the fluidised bed causing the powder which makes contact to melt and fuse to the substrate surface [Richart, 1995].

In Electrostatic spray coating the powder is electrostatically charged and sprayed onto a metal part which is neutrally grounded [Utech, 2002]. The charged particles therefore affix to the part which is then placed in a curing oven and heated so that the particles melt and fuse resulting in a smooth coating. An important advantage of electrostatic spray coating over Fluidized bed coating is the ability to deposit thinner coatings.

Electrostatic Fluidized bed coating combines aspects of the previously described powder coating methods [Richart, 1995]. A small amount of powder is fluidised as in fluidized bed coating but is in contact with high voltage electrodes which charge the powder particles causing them to disperse in a cloud above the fluidised bed. A grounded part is brought into contact with the cloud and the particles are attracted as with electrostatic spray coating. Similarly, the part is placed in a curing oven to consolidate the powder particles.
Flame spraying involves directing polymer powder through a flame of a hand held gun [Richart, 1995]. The flame is aimed at the substrate to be coated which is thus heated. The powder is melted by the flame and transported to the substrate by gas pressure. The heated substrate enables improved adhesion. Flame spraying equipment is often portable and so can be operated in the field unlike other powder coating methods.

Both thermoplastic and thermosetting polymers are used in powder coating but the use, by volume, of thermosetting polymers is 15-20 times greater than that of thermoplastic polymers worldwide, partly because of the ability to achieve thinner coating thickness [Richart, 1995]. Thermoplastic polymers used for powder coating (which are mainly used in the fluidised bed coating method) are Nylons (Nylon-11 and Nylon-12), Polyvinylchloride (PVC), Polyethylene, Polypropylene and Polyvinylidene Fluoride.

3.2.3 ‘Powder metallurgy’ of polymers
Certain polymers which are difficult to process by conventional methods are commonly processed by techniques similar to those used in powder metallurgy [Narkis, 1995]. This involves high pressure compaction resulting in a ‘green compact’ which is subsequently sintered with heating which occurs through inter-particle coalescence.

Polymers commonly processed in this way are difficult to process or cannot be processed by conventional melt processing methods because their melt viscosity is too high. Polytetrafluoroethylene (PTFE) and Ultra-high molecular weight polyethylene (UHMWPE) are notable examples. According to Narkis [1995] it has been demonstrated as feasible to sinter various thermosetting and thermoplastic polymers but the most suitable materials in general for the first stage, compaction, are high molecular weight semicrystalline polymers such as PTFE, UHMWPE, polyimides, polyamide-imides, aromatic polyamides and aromatic polyesters. It should be noted that Nylon-12 is aliphatic rather than aromatic.

3.2.4 Other processes
Compression moulding is the oldest method used for producing polymer parts [Vlachopoulos and Strutt, 2003]. It is mainly used to process thermosetting polymers
and though it is possible to compression mould thermoplastic polymers this is less common [Crawford, 1998]. Compression moulding forms parts by compressing material inside mating moulds which can be heated or unheated. Cross linking occurs between the parts resulting in a solid part.

Ram extrusion of polymer powders involves feeding polymer powder into an elongated die. A ram pushes the powder into the die’s heated section, where sintering occurs, after which it exits the die in a continuous form [Rosenzweig, 1995]. Ram extrusion mostly involves no shear and is therefore suitable for processing highly viscous materials such as PTFE, UHMWPE and Polymethyl methacrylate (PMMA). It is also suitable for processing cross linking polymers such as PPS and some polyimides.
4 Characteristics of Polymers

'Polymer science' is an extremely broad topic and a comprehensive summary of this topic is beyond the remit of this thesis. An overview of polymer science relevant to SLS of polymers is therefore provided below.

4.1 Definition of a polymer

A polymer is defined as a substance composed of extremely large molecules, referred to as 'long-chain molecules' or 'macromolecules' [Campbell, 2000]. They are formed by polymerisation which is the linking and cross-linking of different monomers. A monomer is a small molecule which can be considered to be the basic 'building block' of a polymer. The monomer for Nylon-12 (DuraForm PA) is called laurolactam and hence the polymer, Nylon-12, is also called polylaurolactam [Rohde-Liebenau, 1995]. Polymers can be classified as thermoplastic or thermosetting. Thermoplastics can be melted and remelted and are used in SLS. Thermosets cannot be remelted due to the high degree of crosslinking during curing and are thus not used in SLS.

4.2 Microscopic features/ transitions

4.2.1 Crystallinity

Polymers in the solid state can be described as containing either crystalline or amorphous regions. Crystalline regions in a polymer, known as crystallites, are formed when macromolecules arrange themselves in an 'orderly' manner thus demonstrating long range crystalline order. Amorphous regions are where macromolecules exist without long range order. This arrangement is often described as being like a ‘bowl of spaghetti’. Semicrystalline polymers contain both crystalline and amorphous regions and amorphous polymers contain only amorphous regions. Polymers consisting of only crystalline regions are very rare [Elias, 1997]. The term 'crystalline' is therefore generally, and subsequently in this thesis, used as the adjective to relate to crystalline regions rather than an entirely crystalline material. The amorphous and crystalline regions of a semi crystalline polymer are illustrated in Figure 23. It should be noted that while in the molten state all polymers are amorphous. Polycarbonate is a common example of an amorphous polymer and Nylon-12 an example of a semi-crystalline polymer.
The degree of crystallinity, often expressed as percentage crystallinity (% crystallinity), is the fraction of the entire crystalline phase within a specimen by mass [Elias, 1997]. The % crystallinity of a material can vary according to processing conditions and it is possible, by quenching, to obtain a purely amorphous specimen of a material which is normally semi-crystalline [Michaeli, 1995].

4.2.2 Thermal transitions

When an amorphous region is in the solid state (glassy state) molecular motion is restricted to molecular vibrations and the chains cannot rotate or move in space. As the polymer is heated it eventually will reach its 'glass transition temperature' (T_G). At T_G the intermolecular secondary bonds (Van der Vaals bonds) are 'broken' allowing portions of the molecules to move relative to each other. Above T_G, in the 'liquid state', high molecular weight polymers convert to a 'rubbery' state but low molecular weight polymers behave more like fluids [Elias, 1997]. This fluid state is often described as a 'melt' even though melting has not actually occurred since only crystalline regions can melt.

Above a crystalline material’s melting temperature the long range order is destroyed and the resulting melt is an amorphous fluid, though the viscosity can be very high so that the melt does not visibly flow [Elias 1997]. This melting occurs when
intermolecular bonds are broken so that molecules can move freely with respect to each other.

The larger each crystallite is, the higher the melt temperature required to melt it. Crystalline polymers contain crystallites of varying size and hence melting occurs over a range of temperatures [Greco and Maffezzoli, 2003]. This temperature range, including the peak melt temperature, can vary depending on factors such as the temperature the material originally crystallised at. Additionally, the measured melting behaviour can vary according to the methods used to determine it, such as the heating rate during melting.

Figure 24 shows how the deformation behaviour of a semicrystalline polymer changes with increasing temperature. Below $T_G$ the amorphous regions are solid and so the material is relatively brittle. At $T_G$ the amorphous regions become rubbery or liquid (see above) but the crystalline phase remains stiff. The material therefore exhibits toughness and strength [Michaeli, 1995]. As the material enters the crystalite melting range the intermolecular forces are no longer strong enough to prevent displacement or sliding of molecules and hence these bonds break. The crystalline phase therefore begins to melt and there is a sharp decrease in strength and increase in elongation.

![Figure 24 Tensile strength and elongation of a semi-crystalline thermoplastic](adapted from Michaeli, 1995)
4.2.3 Polymorphism

Polymorphism means the presence of more than one crystalline structure [Puffr et al, 1991]. This means that within the total crystalline content of a material, different crystal structures are present. The different crystal forms may result in different material properties and can be detected and differentiated by various analytical techniques due to, for example, different melt temperature ranges. The crystal forms present can arise as a result of the processing conditions. For example, cold drawing can result in the presence of a different crystal structure for a given material than injection moulding [Xenopoulos and Clark, 1995].

For Nylons the different crystal structures are labelled with the notation ‘α’ or ‘γ’ depending upon the general crystal geometrical arrangement [Xenopoulos and Clark, 1995]. These structures, though similar, are different for various Nylons so that, for example the γ crystal form found in Nylon-12 is different to the γ crystal form found in Nylon-11. Generally in Nylons there will exist a ‘stable’ crystal form which is most prevalent in addition to other less stable and less common crystal forms. For example, in Nylon-12 the γ form is more stable than the α form and always has a melt temperature a few degrees higher [Aharoni, 1997; Baldrian & Lednický, 1991]. The crystal forms present in Nylon-12 (generally) and SLS processed Nylon-12 are discussed later in sections 4.4.3 and 4.4.4 respectively.

4.3 Polymer characterisation

The methods used to analyse specimens in this investigation were DSC (Differential Scanning Calorimetry), tensile testing and optical microscopy. These are discussed below.

4.3.1 Thermal analysis

DSC is a method of materials characterisation that falls within the broader category of thermal analysis. Thermal analysis, not restricted to polymers, was formally defined by the International Confederation for Thermal Analysis and Calorimetry (ICTAC) as follows:
"Thermal analysis (TA) refers to a group of techniques in which a property of a sample is monitored against time or temperature while the temperature of the sample, in a specified atmosphere, is programmed" [Brown, 2001]

The Thermal Methods Group of the Royal Society of Chemistry defines thermal analysis more concisely as:

"the measurement and interpretation of the relationship between the physical and/or chemical properties of a sample and its temperature" [Thermal Methods Group, 2006]

Exothermic or endothermic events that occur during heating or cooling, such as crystallisation (exothermic) or melting (endothermic) can be detected by numerous thermal analysis techniques.

Modern thermal analysis is considered to have started with experiments conducted by the French scientist Henri Le Chatelier in 1887 [Plaats, 1992]. These experiments used thermocouples to measure the temperature of materials as they were heated and cooled. The thermocouple readings were fed to a mirror galvanometer to create recordings on a photographic plate. The thermocouple effect through which thermocouples operate had been discovered in 1821 by Thomas Johann Seebeck of Estonia. The mirror galvanometer, needed to sense the electric current, had been developed in 1826 by Johann Christian Poggendorff of Germany.

The most important and commonly used thermal analysis techniques today and the properties they measure are listed in Table 4.

<table>
<thead>
<tr>
<th>Name</th>
<th>Abbreviation</th>
<th>Measured property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Differential Thermal Analysis</td>
<td>DTA</td>
<td>Temperature difference</td>
</tr>
<tr>
<td>Differential Scanning Calorimetry</td>
<td>DSC</td>
<td>Heat flow</td>
</tr>
<tr>
<td>Thermogravimetry</td>
<td>TG</td>
<td>Mass</td>
</tr>
<tr>
<td>Thermomechanical Analysis</td>
<td>TMA</td>
<td>Deformation</td>
</tr>
<tr>
<td>Dynamic Mechanical Thermal Analysis</td>
<td>DMA</td>
<td>Storage and loss moduli</td>
</tr>
</tbody>
</table>

Table 4 Major thermal analysis techniques [Plaats, 1992]
Differential Thermal analysis (DTA) and DSC are both differential techniques in that sample behaviour is determined by comparison with an inert reference [Plaats, 1992]. This allows more accurate measurement of temperature change of the sample than if only the absolute temperature of the sample was measured.

There are two fundamental categories of DSC which are heat-flux DSC and power-compensation DSC [Brown, 2001]. Heat-flux DSC is a direct derivative of DTA and was originally referred to as quantitative DTA [Plaats, 1992]. Additionally, currently some systems are described as employing aspects of both Heat-flux DSC and power-compensation DSC. To clarify, the 4 categories of system described are:

- DTA
- Heat-flux DSC (originally quantitative DTA)
- Power-compensation DSC
- DSC Systems combining heat-flux and power-compensation DSC principles

An example of a system described as combining aspects of heat-flux DSC and power-compensation DSC in its design is the Shimadzu DSC-60 differential scanning calorimeter [Trilogica, 2006]. This was the system used in this study and so in order to explain its method of operation DTA, heat-flux DSC and power-compensation DSC are subsequently described.

DTA, which is the simplest thermal analysis method, measures the temperature difference between a sample and an inert reference as the same temperature programme is applied to both [Brown, 2001]. The British scientist William C. Roberts introduced this differential aspect to thermal analysis, publishing for the first time a DTA curve in 1899 [Plaats, 1992]. The DTA principle is illustrated in Figure 25. A block which can be heated and cooled at constant rates contains a sample (S) and an inert reference material (R). The temperature of the reference (Tr) follows the temperature programme. The temperature difference (ΔT), which is measured by a thermocouple, remains constant until certain reactions such as melting or crystallisation resulting in characteristics peaks. A DTA curve therefore plots the temperature difference (ΔT) against time or the reference temperature (Tr).
As mentioned above, heat-flux DSC is similar to DTA in principle however heat-flux DSC adds the capability for reliable quantitative measurements to be made due to controlled thermal resistances within the apparatus [Plaats, 1992]. The heat-flux DSC principle is illustrated in Figure 26. The sample (S) and reference (R) are placed within pans which are placed upon a heat-flux plate. Solid specimens can be placed within pans which are crimped to ensure good contact between pan and specimen as shown in Figure 27. As the furnace is heated, the plate generates a controlled heat flow from the furnace wall through to the sample and reference. Temperature measurements are taken from the heat-flux plate directly below the pans which eliminates the influence of changes in the thermal resistance of the sample. This allows enthalpy changes in the sample to be measured.
In power-compensation DSC the sample (S) and reference (R) are isolated in separate furnaces. Each has its own thermocouples and heaters. A temperature programme is applied so that both sample and reference always have the same temperature. This means that when the sample undergoes certain changes (such as melting which is endothermic) the power supplied to the sample heater must compensate for this change to ensure the same temperature as the reference which does not undergo the change. Power and therefore heat flow and enthalpy change are measured [Plaats, 1992].
Figure 28 Principle of power-compensation DSC [Plaats, 1992]

Figure 29 shows the Shimadzu DSC-60 differential scanning calorimeter and a close-up view of the DSC cell. The DSC cell is covered by a lid with a hole to vent possible gases emitted by the sample and to avoid pressure build up within the cell.

Figure 29 Shimadzu DSC-60 Calorimeter and DSC Cell in situ

Figure 30 shows the DSC cell removed from the calorimeter. The DSC cell is ostensibly designed according to classic heat-flux DSC principles. However, rather than a continuous uniform heat-flux plate, the heat-flux plate has portions removed so that the sample and reference pans each sit on regions physically isolated except for three thermal bridges through which heat is conducted. For the DSC cell of the Shimadzu DSC-60 above temperatures of 400°C transfer of heat by radiation occurs however below this temperature conduction through the bridges is the only significant method of heat transfer to the sample and reference from the furnace wall\(^3\). These bridges provide a higher and more accurately quantifiable thermal resistance.

\(^3\) Fisher, J., 2006, Triton Technology Ltd., UK Shimadzu distributor, Private communication (telephone), 30th August 2006
Figure 31 shows a typical DSC plot (of SLS Nylon-12 powder). According to British Standards [BSi, 1997] temperature or time are plotted on the x-axis and heat flow difference is plotted on the y-axis. British Standards state that the direction corresponding to exothermic or endothermic is normally indicated on the plots though whether endothermic is up or down is not specified since there is no universally agreed consensus on this. According to the standards of the International Confederation for Thermal Analysis endothermic peaks are plotted downwards and exothermic peaks upwards [Plaats, 1992].

Figure 31 shows that as the Nylon-12 sample is heated between approximately 50 and 160°C the baseline remains steady which is due to the constant heat capacity of the sample. At approximately 160°C the sample starts to melt and a peak starts to develop. The baseline must be interpolated between the start and end of the peak and the enthalpy change associated with melting is given by the area of this peak to the interpolated baseline. In Figure 31 the melting peak is well defined and the interpolated baseline is a simple straight line however numerous methods exist for baseline construction [Brown, 2001] which may be required if, for example, the heat capacity changes significantly after the peak. The crystallisation peak during cool down is treated in the same manner.
The enthalpy change associated with melting (i.e. the heat of melting) is proportional to the % crystallinity and by dividing the heat of melting of the sample by the known heat of melting for a 100% crystalline specimen the % crystallinity value of the sample can be calculated [Campbell and White, 1989].

British Standards [BSi, 1997] state that the energy and temperature measurement devices of the calorimeter should be calibrated at least in accordance with the instrument manufacturer’s recommendations. In accordance with British Standards and the procedure described by Shimadzu for the DSC-60 Calorimeter [Shimadzu North America, 2004] the DSC hardware in this investigation was calibrated for energy and temperature measurements using Tin and Indium samples classified as 99.999% pure by the supplier (The Fine Work Co Ltd). Following calibration and also after completion of all tests the melt temperatures and heat of melting of the Tin and Indium samples were checked. These were within the specified limits of +/- 0.5°C and +/- 1 J/g for all samples.

Figure 31 DSC trace for SLS Nylon-12
4.3.2 Mechanical analysis

Tensile testing is used to determine a variety of mechanical properties such as tensile strength, elastic modulus (E-modulus) and elongation at break (EaB). Figure 32 shows typical apparatus which was used in the 'principal investigation' stage of this study. Figure 32 also pictures optional ancillary equipment which are the temperature chamber (not used in this study) and contact extensometer (used in this study). The temperature chamber allows testing at elevated and reduced temperatures. The contact extensometer measures strain directly from central portion of the surface of the test specimen rather than using the crosshead position. This can provide more accurate readings since potential erroneous results arising from stress induced by clamping forces on the specimen and deflection of structural components of the machine are avoided [Ward and Sweeney, 2004].

The typical tensile testing procedure is as follows:
1. Test specimen prepared (according to international standards).
2. Variables: original gauge length and cross-sectional area measured and recorded.
3. Specimen mounted between machine jaws.
4. Specimen pulled apart and stress/strain recorded by controller (computer).

Figure 32 Tensile testing machine
Figure 33 shows a typical stress-strain curve obtained from a tension test showing various features.

4.3.3 Transmitted light Optical Microscopy

Microscopy has been defined as "the study of the fine structure, or details, of an object using a microscope" [Johnson, 1996]. Specimens of unfilled polymer parts, such as those under investigation in this thesis, are prepared by cutting thin slices (typically 10-50μm thick) using a microtome. These are placed between glass slides and, for semicrystalline polymers, typically examined using transmitted polarised light with magnifications from 20x to 400x [Johnson, 1996]. In transmission microscopy white light is transmitted through the specimen (instead of reflected off the surface) and contrast is produced by differences in optical density and/or differences in absorption of different wavelengths [Campbell and White, 1989].
4.4 Nylon-12

4.4.1 Chemical structure

‘Nylon’ is the common term for linear aliphatic polyamides [Apgar and Koskoski, 1986]. Aliphatic molecules generally consist of a backbone of carbon atoms with other atoms bound to this carbon chain. A polyamide is a polymer containing repeated amide groups [Lanska and Stehlicek, 1991]. The amide group is illustrated in Figure 34.

\[
\begin{array}{c}
\text{H} \\
- \text{N} - \text{C} - \\
\text{||} \\
\text{O}
\end{array}
\]

Figure 34 Amide group

Laurolactam is the monomer polymerised to create Nylon-12. Hence, as mentioned previously, Nylon-12 is also referred to as Polylauro lactam. A variety of alternatives of this terminology is used such as Polyamide-12 or PA-12. The monomer Laurolactam is manufactured from butadiene feedstock [Rohde-Liebenau, 1995]. Butadiene feedstock, also known as ‘crude C4’ [BASF, 2004], is a by-product of ethylene production, separated by fractional distillation in the petrochemical industry [Chevron Phillips Chemical Company, 2004].

One repeat unit (from the Laurolactam monomer) in a Nylon-12 chain is shown in Figure 35. This contains 12 carbon atoms hence the notation Nylon-12. Other Nylons will have similar arrangements with the number of carbon atoms present reflected in the Nylon’s name. The more carbon atoms per repeat unit, the further the amides will be spaced apart along the molecule and hence the lower the amide density will be [Apgar and Koskoski, 1986]. Amide density affects moisture absorption, discussed below in Section 4.4.2.
4.4.2 Effects of Moisture

Amide groups are polar and able to hydrogen bond to various entities including water [Apgar and Koskoski, 1986]. The amide density therefore determines the extent of moisture absorption i.e. its degree of hygroscopicity. The absorption of water by Nylons can negatively effect processing [Khanna et al, 1996] and alter numerous material properties including improved toughness but lower tensile strength and flexural modulus [Petruccelli, 1996].

Lower amide density results in lower moisture absorption at a given time, temperature and humidity [Apgar and Koskoski, 1986]. Low amide densities are found in Nylon-12 and hence Nylon-12 is characterised by very low moisture absorption [Ahroni, 1997; Apgar and Koskoski, 1986]. The equilibrium moisture absorption of Nylon-12 is 0.7% - 0.8% at 50% relative humidity and 1.4% - 1.6% immersed in water at room temperature [Petruccelli, 1996; Rohde-Liebenau, 1995]. Nylon-6 by comparison is considerably more hygroscopic with equilibrium moisture absorption (at 50% relative humidity) of 2.7% and 9.5% when immersed in water [Petruccelli, 1996].

As mentioned in section Error! Reference source not found., for rotational moulding the moisture content of Nylon-12 powder prior to processing should be no more than 0.1%. Powder is supplied dry in sealed containers but if left for extended duration exposed to the atmosphere it may be necessary to dry at 80°C [Petruccelli, 1996]. For injection moulding the moisture content should also be less than 0.1% [Sibila et al, 1995]. In SLS the manufacturers and material suppliers have not put forward recommendations relating to drying powder and no literature is available.
relating to effects of moisture on processing. In SLS, powder is preheated within the machine under an inert atmosphere prior to processing. Also, during processing each layer is directly in contact with the heated inert atmosphere immediately prior to spreading over the powder bed which is considerably hotter than the recommended 80°C (discussed later in section 6.1). This may negate the need for drying the powder before processing, if drying was required, since the powder is effectively dried during processing.

4.4.3 Crystal forms of Nylon-12

As mentioned in section 4.2.3, for Nylon-12 the \( \gamma \) form is more stable than the \( \alpha \) form and always melts at a higher temperature. It has been demonstrated that under the majority of processing conditions the liquid phase will crystallise to the \( \gamma \) form, which is therefore the most commonly found crystal form in Nylon-12. However, certain conditions do result in the \( \alpha \) form. These have been reported as solution casting (at atmospheric or reduced pressure, below 90°C) [Ishikawa & Nagai, 1980a], drawing just below the melt point and high pressure crystallisation [Ramesh, 1999]. It has been demonstrated that the proportions of \( \alpha \) and \( \gamma \) form can be altered (from 0-100% for each) by controlling the thermal history [Ishikawa & Nagai, 1980a; Rohde-Liebenau, 1995]. Different variations of the \( \alpha \) and \( \gamma \) crystal forms have been created depending on processing conditions and these can be transformed from one to another by numerous methods depending from which and to which crystal form the material will be transformed [Ishikawa & Nagai, 1980b; Mathias & Johnson, 1991; Ramesh, 1999; Xenopoulos & Clark, 1995]. Studies reporting melting points for the \( \gamma \) form were reviewed by Aharoni [1997] and values ranged from 172°C to 185°C with most data points close to 179°C. The melt point of the less common \( \alpha \) form has been reported as ca. 173°C [Ishikawa & Nagai, 1980a].

4.4.4 Crystal forms of SLS Nylon-12 powder

SLS Nylon-12 powder is obtained by dissolving polyamide-12 in ethanol under pressure at elevated temperatures followed by slow crystallization thereby forming crystals with a relatively high melting point in the region of 190°C and a relatively high heat of melting [Dickens et al, 2000; Scholten & Christoph, 2001]. DSC analysis of Virgin SLS powder in this PhD investigation showed a single melting peak with a peak melt temperature of \( \sim \)185°C (Figure 38, section 6.1). The crystal structure of SLS Nylon powder or parts has not previously been reported, however the
slow cooling rate during production would likely result in the virgin powder being comprised of relatively large crystals. The production process for SLS Nylon-12 does not meet the requirements for formation of the α crystal form described previously and the high melt temperatures measured indicate the γ-form.

Ishikawa and Nagai [1980a] demonstrated that a single endotherm in a DSC test on Nylon-12 is only characteristic of a sample containing 100% γ crystal form since samples consisting of 100% α crystal form invariably develop a second melt peak during the DSC run due to recrystallisation of a portion of the specimen to the γ crystal form. Their test parameters were the same as those used in the present investigation supporting the view that the crystal structure present in virgin SLS Nylon-12 powder is of the γ crystal form.
5 Preliminary hypothesis and research objectives

SLS of Nylon-12 (DuraForm PA™) has proved to be a suitable RM approach for various niche applications including the creation of bespoke hearing aids and parts for Formula 1 racing cars. The aerospace industry in particular has adopted SLS for RM and some aircraft already have numerous SLS production parts as standard.

Although the aerospace industry has recognised the advantages of SLS for RM, the applications are still somewhat limited. This is partly due to the mechanical properties of parts produced. While tensile strength and E-modulus of Nylon-12 tensile specimens produced by SLS is comparable with injection moulded specimens, EaB is significantly lower. Further to this, relatively little work currently exists in the public domain characterising SLS processed crystalline polymers and none exists addressing the issue of low EaB.

One of the industrial collaborators on this project (Solid Concepts) observed that parts seemingly had greater EaB when removed quickly from the part cake instead of being allowed to cool for some time. Theory shows that faster cooling rate can result in increased EaB due to reduced part % crystallinity. Therefore, the preliminary hypothesis of this study was that certain variables of the SLS process (specifically the post build cooling rate) can be varied, to yield an improvement in EaB of tensile specimens. The industrial collaborators stated that the method should not add additional, time consuming steps. It was expected that faster cooling would result in lower % crystallinity and higher EaB. This is explained in Section 6.1.

The preliminary objectives of this work were twofold. Firstly to investigate methods of increasing EaB and secondly to gain a greater understanding of SLS processed crystalline polymeric material. The successful completion of the first objective would itself be a direct and specific accomplishment but the completion of the second objective could help address further issues.
6 Experiments to assess effects of post build cooling rate on mechanical properties and crystallinity

6.1 Aims and theory

The crystalline content of a material makes it strong and stiff but also brittle. A completely crystalline polymer would be extremely brittle since it is the amorphous regions which give a polymer its toughness, that is, the ability to yield without breaking [Kong and Hay, 2003]. Nylon-11 is similar to Nylon-12 but is more ductile and has a lower modulus. Its low crystallinity is cited as an important reason for this [Apgar, 1995]. Bessell et al [1975] described effects of % crystallinity on properties of non porous semi crystalline Nylon-6. Stiffness was shown to increase proportionally with increasing % crystallinity while the toughness decreased. The fracture behaviour of the material was shown to change from brittle to ductile with variations in % crystallinity (see Figure 36). At 44% crystallinity the material was relatively brittle with EaB ca. 16% but at lower crystallinities (42-37%) the material became ductile with EaB values from 50-80%. At 32% crystallinity the material became highly ductile with EaB reaching 240%.

Figure 36 Stress Strain behaviour as a function of % crystallinity for Nylon-6 [Bessell et al, 1975]
Percentage crystallinity is closely linked to processing methods and parameters since the cooling rate has a direct influence on crystallisation. Cartledge and Baillie [1999] showed that for a Nylon-6/glass fibre composite, cooling rates of 1°C/min, 3°C/min and 60°C/min resulted in % crystallinity of 37%, 33% and 28% respectively. The relationship for polypropylene, another widely used semicrystalline polymer, is shown in Figure 37. It also illustrates that faster cooling results in lower % crystallinity.

![Figure 37 Effect of cooling rate on % crystallinity for polypropylene [Michaeli, 1995]](image)

The complete SLS build process essentially involves heating the material from room temperature to above the melt temperature for sintering to occur and eventually cooling it back to room temperature. The stages of the build process can therefore be related to a generic DSC plot for the material which is heated and cooled, as shown in Figure 38. This shows a DSC chart for SLS Nylon-12 powder.
The DSC chart for Nylon-12 in Figure 38 shows that melting during heating occurs between 160-194°C and crystallisation during cool down occurs in the range of 152-132°C. The glass transition ($T_g$) is just visible at approximately 50°C. The melt peak is $\sim$41°C higher than the crystallisation peak and the crystallisation onset is 8°C lower than the melt onset. In SLS this allows the material to remain fluid after being melted by the laser resulting in bonding of subsequent layers to each other without extra energy input, and reduction of the build up of internal stresses. Powder and parts are held at a temperature close to the melt onset during building but the precise internal temperature profile and whether and for how long the parts are at a higher temperature than the crystallisation onset is currently undetermined. Moeskops [2000] performed temperature logging during the SLS process and obtained results for the un-sintered powder but not from within parts. Thermocouples were installed within an EOS machine at a fixed height (3 cm) above the part bed cylinder top plate so that as the build progressed the thermocouples moved lower down, with more powder deposited on top. The results showed that during build the material was hotter towards the centre of the part-cake than the edges and that the temperature of the un-sintered...
powder varied between approximately 145°C and 125°C during the 7 hour build stage.

In this investigation experiments were designed with the objective of increasing EaB of tensile specimens by varying the cool down rates in order to reduce % crystallinity. Temperature logging methods (including within parts) were designed to help further understand the effects of variations in cooling rate on % crystallinity and mechanical properties.

6.2 Methodology

The objective of the experiments was to vary the cooling rate during the cool down stage and the period following that i.e. to vary the cooling rate during the ‘post build’ cool down. As shown in Figure 38 crystallisation occurs in the approximate range of 152-132°C. The experiments were thus designed to attempt to vary the cooling rate within this temperature range.

The cool down consisted of 3 phases which are listed in Table 5. These are referred to as ‘machine’, ‘part-cake’ and ‘breakout’ indicating the location of the parts during that phase. Following build completion (referring to a typical build) the parts were left in the machine to cool (‘machine’). The parts were then removed from the machine, still surrounded by the un-sintered powder (‘part-cake’). After further cooling the parts were then removed from the part-cake (‘breakout’) and left to cool further at room temperature. There are currently no strict guidelines indicating specific cool down duration which is normally left to user discretion.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>‘Machine’</td>
<td>Specimens left in SLS machine following build completion</td>
</tr>
<tr>
<td>‘Part-cake’</td>
<td>Specimens removed from machine while in part-cake and left to cool in part-cake</td>
</tr>
<tr>
<td>‘Breakout’</td>
<td>Removal of specimens from part-cake</td>
</tr>
</tbody>
</table>

Table 5 Cool down phases

The experiment consisted of seven tests. These were designed to test different cooling rates following build completion. In order to vary cooling rates the three cool down phases (‘machine’, ‘part-cake’ and ‘breakout’) were varied in each test.
6.2.1 Part Building

A 3D Systems™ Vanguard™ machine was used to produce parts from 3D Systems DuraForm PA Nylon-12 powder. Virgin powder from one powder batch was used for all builds in this experiment. Specimens were built horizontally in the machine x-axis in order to conserve powder, decrease build time, and to avoid 'end of vector' issues. With builds initially ordered by approximate total cool down time to room temperature, the sequence of builds was re-arranged randomly to help avoid unknown time dependant issues that could cause misleading trends in results. An example potential issue is a theoretical gradual increase or reduction in part bed temperature if the pyrometer readings 'drift'. The build order is included in Table 6 which describes each test.

Six tensile test specimens were designed attached to a 'snap-away' frame to allow removal of all specimens at once and also to guide attachment of thermocouples. Figure 39 shows this arrangement. Specimens for DSC testing were also built. 'Dummy' specimens allowed attachment of thermocouples through channels into specimens and provided insulation for test specimens in order to prevent abnormal cooling due to air exposure during powder removal. The specimens were built in the centre of the build volume, oriented along the machine x-axis.

![Figure 39 Specimens attached to frame, and thermocouple guides/channels](image)

The holes in the dummy specimens and the thermocouple channels were included to enable the thermocouples to be quickly located in the correct position once the build was completed and the machine door opened. The cool-down height was set at 0mm
so that thermocouples could be attached at the powder bed surface. Figure 40 shows the positioning of the thermocouples through a cross section of the parts.

6.2.2 Temperature logging

Temperatures were logged using the machine’s built-in pyrometer with the machine door closed and using thermocouples with the machine door open. The pyrometer values were corrected by blackbody calibration using the method described by Allison and Alexander [2004]. The calibration procedure is described in appendix 1. K-type thermocouples were fabricated and calibrated as detailed in appendix 2. The data gathered was used to calculate cooling rates and generate cool down profiles.

6.2.3 Part Cool down

The cool down tests were planned using ‘preparatory schematic cool down curves’. The purpose of these schematics was to illustrate expected cooling periods and rates in order to plan the experiments rather than accurately represent the actual recorded cool down profiles. Figure 41 shows the curve for the benchmark procedure T2 (dotted line) compared with that for T7 where the parts are quickly removed from the machine and part-cake (solid line). Seven tests were conducted and the cool down curves for all of these are included in appendix 3.
The tests were designed to show results for practical extremes in the 'time to breakout' (part removal) following build completion. T1 involved the slowest practical cool down with the parts left inside the part cake within the machine far longer than during normal practice. T2 is the benchmark and represents typical part removal procedure. T3, T4 and T5 all involve removal of the part cake after 30 minutes. This is the approximate time it takes for the recorded part bed temperature (and powder feed bed temperatures) to drop below 100°C above which the machine cannot be unlocked and opened due to high temperatures. For tests T3, T4 and T5 the time the parts are left in the part cake following its removal from the machine is varied. For T6 and T7 the part cake is removed quickly from the machine by circumventing the previously mentioned safety function of the machine. This is achieved by lowering the powder and parts in the part build and powder feed cylinders. This effectively moves the powder out of the lines of site of the machine pyrometers so that they instead record the temperature of the part build and powder feed cylinder walls which are far cooler. T7 varies from T6 by having the parts placed in a freezer rather than being left at room temperature. All seven tests are summarised in Table 6. Durations given are those estimated prior to testing. The actual cooling rates were calculated subsequently using the data gathered by temperature logging.
### Table 6 Test descriptions

<table>
<thead>
<tr>
<th>Test</th>
<th>Build order</th>
<th>'Machine'</th>
<th>'Part-cake'</th>
<th>'Breakout'</th>
<th>Estimated time to breakout</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>5</td>
<td>66 hrs</td>
<td>n/a</td>
<td>n/a</td>
<td>66 hrs</td>
<td>Parts left to cool to room temp. inside machine</td>
</tr>
<tr>
<td>T2</td>
<td>2</td>
<td>2 hrs</td>
<td>6 hrs</td>
<td>4 min</td>
<td>8 hrs</td>
<td>Benchmark (typical cool down)</td>
</tr>
<tr>
<td>T3</td>
<td>4</td>
<td>½ hr</td>
<td>3 ½ hrs</td>
<td>4 min</td>
<td>4 hrs</td>
<td>-</td>
</tr>
<tr>
<td>T4</td>
<td>3</td>
<td>½ hr</td>
<td>½ hr</td>
<td>4 min</td>
<td>1 hr</td>
<td>-</td>
</tr>
<tr>
<td>T5</td>
<td>1</td>
<td>½ hr</td>
<td>n/a</td>
<td>4 min</td>
<td>½ hr</td>
<td>Parts removed from machine and immediately broken out</td>
</tr>
<tr>
<td>T6</td>
<td>7</td>
<td>6 min</td>
<td>n/a</td>
<td>4 min</td>
<td>6 min</td>
<td>Parts removed quickly after build completion</td>
</tr>
<tr>
<td>T7</td>
<td>6</td>
<td>6 min</td>
<td>n/a</td>
<td>4 min</td>
<td>6 min</td>
<td>Parts removed quickly after build completion &amp; placed in freezer</td>
</tr>
</tbody>
</table>

#### 6.2.4 Measurement of mechanical properties

The tensile test specimens were built to ISO 527-2:1996 1A. Prior to testing the specimens were conditioned for at least 88 hours at 23±2°C and 50±10% relative humidity. Parts were tested by Rapra Technology, a UKAS accredited testing laboratory. E-modulus was measured at 1mm/min and specimens were then tested to failure at 5mm/min. Strain was measured using a video extensometer.

#### 6.2.5 DSC analysis

DSC was used to measure thermal transitions and % crystallinity. Samples were cut from the centres of DSC specimens. Samples were placed in aluminium crimp pans and sample weight was 12±3 mg. Samples were heated at 10°C/min from room temperature, held at 220°C for 2 minutes and then cooled at 10°C/min. 5 samples were tested for each cool down test and the results averaged for % crystallinity values.

#### 6.3 Results & discussion

##### 6.3.1 Cooling rate

Figure 42 - Figure 48 show temperature logging during the first 6 hours of cool-down following build completion for each of the seven tests (T1-T7). These cool down profiles show data from the pyrometer within the machine while the machine was closed (corrected using blackbody calibration) and then data from thermocouples
(TC) attached after the machine was open. In practice each channel had to be cleared of powder using a miniature drill. No valid data was collected in the period between opening the machine and inserting the thermocouples and there is a slight discontinuity between the final surface value reading of the IR sensor and that of the thermocouple because the thermocouple tip was below the surface where the temperature was up to 20°C higher. Also, the thermocouples were closer to the centre of the bed which is hotter than the rear portion of the part bed from where the pyrometer reading is taken.

Figure 42 shows the cool down profile for T1 where the parts were left to cool in the machine for over 2 days. Since the machine was not opened during this time, temperature readings are only included from the machine’s infrared sensors. These results are superimposed in subsequent cool down profiles for comparison. Figure 42 and all the other cool down profiles show that at build completion the powder bed surface is approximately 8°C above the crystallisation onset temperature. It can therefore be inferred that in build the powder is at least 8°C above the crystallisation onset temperature also. Figure 42 - Figure 46 (T1-T5) show that once the machine heaters are turned off there is a rapid drop in powder surface temperature but Figure 43 - Figure 47 show that below the powder surface the temperature reduces at a far slower rate until the machine is opened.

Although the specimen centre temperatures could not be logged during the ‘machine’ phase of cool down, Figure 44, Figure 45 and Figure 47 show that the specimen centres were still above the crystallisation onset temperature after the build had finished and the machine is opened. Figure 44 and Figure 45 show the specimen centres reaching the crystallisation onset temperature approximately 40-45 minutes after build completion indicating that parts can be left for a certain amount of time after build completion before employing methods to increase cooling rate to affect crystallisation, if required. Figure 45-Figure 48 show cooling is significantly quicker once parts are removed from the part-cake. It should be noted that since laser processing increases the molecular weight [Zarringhalam et al, 2006] the crystallisation onset temperature could reduce implying parts remain above the crystallisation onset temperature for longer than observed in these results since the crystallisation temperature as measured by DSC is used.
The time at which the specimen centres reached the crystallisation end temperature (132°C) when left to cool in the machine was indeterminable from the data collected (Figure 42) however with the part-cake removed at 30 minutes (Figure 44 and Figure 45) the centres took approximately 1 hour to reach the crystallisation end point. Since the parts in the removed part-cake cannot cool more slowly than those in the machine it can be concluded that for parts to crystallise at the slowest possible cooling rate, with the machine heaters switched off, they must be left for at least 1 hour in the machine and likely much longer. If slower cooling rates are desired then the machine could be set to cool down gradually rather than switching the heaters off.

The build height in these experiments was relatively low so it would be important to investigate in future how the internal part temperature varies with increasing build height as Moeskops [2000] did for powder temperature. Even with such shallow builds Figure 43 - Figure 46 show considerable difference between the powder surface temperature and specimen centre. This highlights how the machine pyrometer cannot be used to reliably indicate internal temperatures. It is therefore common practice to measure the internal temperature of removed part-cake using thermocouple probes.

![Figure 42 Cool down profile for T1](image)
Figure 43 Cool down profile for T2, Benchmark

Figure 44 Cool down profile for T3
Figure 45 Cool down profile for T4

Figure 46 Cool down profile for T5
The cool down profiles were used to determine approximate average cooling rates during post build crystallisation as shown in Table 7. These were calculated by dividing 20°C (152-132) by the time it took the material to cool from 152°C to 132°C. The temperature range of 152°C to 132°C was determined by DSC with a cooling rate...
of 10°C/min which equates to roughly the median cooling rate shown in Table 7. It should be noted that cooling rate can affect crystallisation temperature and therefore it may be useful to establish the crystallisation temperature range by performing DSC analysis with a cooling rate of ~ 1°C/min in any future work. The charts used to calculate the cooling rates are shown in appendix 4.

<table>
<thead>
<tr>
<th>Test</th>
<th>Powder Surface</th>
<th>Specimen Centre</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td>5.1</td>
<td>indeterminable</td>
</tr>
<tr>
<td>T2</td>
<td>5.1</td>
<td>indeterminable</td>
</tr>
<tr>
<td>T3</td>
<td>5.1</td>
<td>1.2</td>
</tr>
<tr>
<td>T4</td>
<td>5.1</td>
<td>1.0</td>
</tr>
<tr>
<td>T5</td>
<td>5.1</td>
<td>indeterminable</td>
</tr>
<tr>
<td>T6</td>
<td>indeterminable</td>
<td>23.5</td>
</tr>
<tr>
<td>T7</td>
<td>indeterminable</td>
<td>indeterminable</td>
</tr>
</tbody>
</table>

Table 7 Cooling rate during crystallisation

Ideally all cooling rates would have been recorded but T3 – T6 provide sufficient data to compare with previous research. Values for internal cooling are not available for T1 and T2 since the minimum crystallisation temperature was reached before thermocouples could be attached. The values for T5 and T7 were indeterminable since the thermocouples were not inserted in time (i.e. before crystallisation started). The cooling rates at the powder surface for T1-T5 are the same since the crystallisation end temperature was reached in these tests during the ‘machine’ phase and so they were all calculated using the readings from the IR sensors which were the same for each of the builds.

The values for cooling rate which were obtainable give a general indication of the magnitude of cooling rate involved and the amount by which it changes between the slowest and fastest cooled specimens. It should also be noted that average cooling rates do not fully describe the crystallisation behaviour since crystallisation will differ depending how long the material is held at particular temperatures within the crystallisation range. However, based on previous research results for Polypropylene [Michaeli, 1995] and Nylon-6 [Bessell et al, 1975; Cartledge and Baillie, 1999] the range of values obtained is of the magnitude to potentially affect the % crystallinity and mechanical properties considerably.
6.3.2 Tensile results

Figure 49 shows example stress strain plots for parts built in T1, T3, T4 and T6. All original stress strain plots are shown in appendix 5. T4 and T6 are similar to each other but show similar changes to the lower % crystallinity Nylon-6 specimen in Figure 36 with both showing increased strain at break (EaB) and reduced tensile strength compared with T1 and T3. All stress strain curves had repeated fluctuations in the stress axis. The reason for this is not clear but may relate to the porosity and or anisotropic microstructure of the material resulting in continuous local failures and accommodation of these within the material.

![Stress Strain plots for T1, T3, T4, T6](image)

Figure 49 Stress Strain plots for T1, T3, T4, T6

Figure 50 shows the values for EaB for the range of cooling conditions. The faster cooling resulted in higher EaB which supports the theory of increasing EaB by increasing cooling rate and correlates with the maximum and minimum cooling rates.
associated with Figure 36 [Cartledge and Baillie, 1999]. T7, the theoretically fastest cooled specimen, resulted in a 1.36X increase from the benchmark (T2) though with a larger spread of results while T4 gave a 1.21X increase with little change in spread. A slight discrepancy can be observed for the cooling rates for T3 and T4 due to the similarity of the readings (the cooling rate for T3 is higher than T4) and this is attributed to random error.

A general trend of increasing spread of EaB with increasing cooling rate can be observed (with the exception of T3). The benchmark has a spread of approximately +/- 1% EaB but rises to +/- 3% EaB for T7. T1 and T2, the slowest cool downs, had the narrowest spread indicating slow cool down gives the most consistent and repeatable EaB but there was no advantage of T1 over T2 in this respect. The increasing spread could be attributed to the physical handling and anisotropic cooling which could have occurred with the various cool down procedures. The spread in data points for even the tightest spread may exist, for example, due to variation in mechanical properties due to slight differences in build position in the bed for the individual specimens.

![Figure 50 Elongation at break](image)
Figure 51 shows the values for tensile strength. It shows a trend of slowly decreasing tensile strength with increasing cooling rate unlike EaB. The spread is similar for all values. The reduction in strength is only a small change (0.95X benchmark) however the trend supports the theory that increased cooling rate has reduced the % crystallinity since lower % crystallinity is known to reduce tensile strength [Bessell et al, 1975]
Figure 52 indicates a slight trend of increased E-modulus with increased cooling rate (1.08X benchmark) however the spread is relatively large. In theory reduced % crystallinity would decrease E-modulus rather than increase it so, assuming the trend is valid, the cause of this is currently unknown.

Comparison of spread in Figure 50, Figure 51 and Figure 52 indicates that EaB is more sensitive to these factors than other properties. There was no discernable trend in variations of spread for tensile strength and E-modulus (Figure 51 and Figure 52).

6.3.3 Percentage Crystallinity

The results for EaB and tensile strength supported the initial hypothesis however to help explain this further, measurements of % crystallinity at the different cooling rates were conducted. Figure 53 shows the % crystallinity of samples and does not show the expected relationship between cooling rate and % crystallinity. Only the slowest cooled specimen (T1) and the theoretically fastest cooled specimen (T7) reflected the theory that % crystallinity would be reduced by increased cooling rate with a slight drop in % crystallinity for T7. There was no trend shown for the other five specimens, four of which actually had identical average % crystallinity values.
Although no distinct relationship was observed for the series of tests, the maximum reduction in % crystallinity (0.97X) between T1 and T7 and the maximum measured change in cooling rate (1.2 – 23.5°C/min) is comparable with the results presented by Cartledge and Baillie [1999] for Nylon-6/glass composite though the difference is smaller. The 0.97X difference between the maximum and minimum % crystallinity values is close to the 0.95X difference between the specimens of 44% and 42% crystallinity in the study by Bessell et al [1975]. The changes in EaB and tensile strength reported by Bessell et al [1975] are also similar to those in this present study.

Since there was no marked change in crystallinity with cooling rate (across the range of tests) to match the changes to mechanical properties an alternative explanation is required. A study by Schrauwen [Schrauwen, 2003] analysed the deformation and failure of a series of semi-crystalline polymers. Tensile specimens of High-density Polyethylene, Polypropylene and Polyethylene terephthalate (PET) were produced by moulding with relatively high cooling rates (quenched) and low cooling rates. Additionally, some quenched parts were subsequently subjected to sub-melt temperature isothermal crystallisation (annealing) resulting in the same % crystallinity as the slowly cooled specimens. For a given material, the different processing conditions resulted in either brittle or ductile failure. Schrauwen [2003] stated that
brittle failure in tension was either due to an increase in yield stress due to an increase in crystallinity (as expected in this present study) or due to a decrease in strain hardening due to lower chain entanglement density (of the amorphous phase) caused by slower crystallisation cooling rates. For example, % crystallinity of slow cooled and fast cooled/annealed PET was equal however the fast cooled/annealed specimens exhibited less brittle failure which was attributed to higher chain entanglement density. In this present study faster cooling resulted in increased ductility with no distinct change to % crystallinity. It is therefore suggested that increased chain entanglement density due to faster cooling may be the factor responsible for the observed changes to mechanical properties. The investigation of this could be the subject of future study.

6.4 Conclusions

The temperature logging showed that parts do not cool below the crystallisation onset temperature during the build showing that control of post build cooling rate can indeed directly affect the crystallisation of parts. This investigation also demonstrated that increased cooling rate in the post build stage of the SLS process is feasible and results in a marked increase in EaB. It seems unlikely however that EaB of SLS parts can be increased by an order of magnitude via changes in post build cooling rate. The results did not show the relationship between % crystallinity and mechanical properties that had originally been expected and it was suggested that chain entanglement density of the amorphous phase may relate to the mechanical properties instead.
7 Principal hypothesis and research objectives

7.1 Background
Following on from research detailed in Chapter 6, a collaboration with TNO Science and Industry of The Netherlands was initiated in order to investigate deeper issues relating to chemical level effects on mechanical properties of SLS Nylon-12 parts. The objective was to understand some parameters which are potential sources of a lack of reproducibility of properties. A journal paper detailing this work ([Zarringhalam et al, 2006]) was published in the journal, Materials Science and Engineering: A and is included in appendix 6.

During the collaborative investigation the author of this thesis made the key observation that individual peaks on a DSC plot for a specimen of an SLS produced part appear to relate to distinct regions in the specimen’s observable microstructure. This proposed relationship is described in section 7.2.

7.2 Proposed relationship between DSC peaks and material microstructure
Zarringhalam et al [2006] used DSC to analyse SLS Nylon-12 specimens, the results of which were compared against micrographs of specimen cross sections. The micrographs were obtained by optical microscopy of microtomed specimens.

Tolochko et al [2003] described how SLS of single component metal powders involves partial melting of the particles. Shi et al [2004] stated that in SLS of polymers also, the particles are only partly melted by the laser which ensures dimensional precision. The annotated micrograph in Figure 54 shows the SLS part microstructure composed of particle cores surrounded by spherulites. The microstructure of SLS polymer parts was previously analysed by Moeskops et al [2004] who proposed that these cores are the un-melted central regions of particles occurring when particles do not receive enough heat to fully melt. In injection moulding of semi-crystalline polymers the presence of un-melted particles (and non uniform microstructure) is considered to be a major cause of part failure. These un-melted particles result in high residual stress, brittleness, and reduced mechanical properties [Johnson, 1996].
The author of this thesis proposed that two distinct melting peaks observed on a DSC trace for the sintered material relate to distinct regions in the material which are the un-melted particle cores and the surrounding material which melted and crystallised. This theory is illustrated in Figure 55.

Figure 55 shows DSC traces for un-sintered virgin powder and a sintered part. The powder (green) has one peak and the part (red) has two peaks. After virgin powder particles are partially melted, the material which melted crystallises with smaller crystallite sizes due to presumably different cooling rates in the SLS process to the powder production method. This material ('melted & crystallised region') therefore results in a new peak on the DSC trace for the part (red) with a relatively low peak melt temperature of 181°C. The regions of the powder particle which do not melt ('un-melted particle core') increase in melt temperature slightly but the peak is reduced in size since there is relatively less of this material present in the specimen. It was therefore proposed, for the part trace (red), that the size of the left peak relates to the amount of melted and crystallised material and the size of the right peak relates to the amount (and thus size) of the un-melted particle cores.
For the collaborative investigation between Loughborough University and TNO, parts were built by both partners using their respective machines and Nylon-12 SLS powder. These machines (and powder) were from different suppliers (3D Systems at Loughborough and EOS at TNO) and were also configured differently. The Loughborough machine was optimised for superior accuracy using lower thermal energy input (for example, lower laser power) while the TNO machine was optimised for superior mechanical properties using higher thermal energy input. Figure 56 shows DSC traces for parts built by Loughborough (Lboro) and TNO. The right hand side peak in each trace had a peak melting temperature that closely matched that of the virgin powder. However the left hand side peaks varied considerably from each other in terms of size and peak melt temperature; this was attributed to the numerous differences in build setup (i.e. different powder, machines and parameter optimisation).
Figure 56 DSC results for SLS parts built by Loughborough and TNO [Zarringhalam et al, 2006]

Mechanical properties of parts were compared and TNO parts were found to have considerably higher EaB and tensile strength than Loughborough parts and also slightly higher E-modulus. This was attributed to the higher energy input used to create the TNO parts.

Figure 57 compares the microstructure of parts built by Loughborough and TNO. It was proposed that a higher ‘degree of melting’ resulted in smaller cores in the TNO specimen which was linked to potentially improved fusion/sintering of particles and hence superior mechanical properties.

Figure 57 Microstructure of TNO and Lboro parts, adapted from [Zarringhalam et al, 2006]

In summary, a key concept, the relationship between peaks and microstructure in SLS processed material, was proposed. Results suggested this may vary between different parts due to differences in the ‘degree of melting’ of particles and this may in turn cause variations in mechanical properties of parts.
7.3 Previous use of DSC to detect multiple phases in sintered polymer

Following the publication of the paper by Zarringhalam et al [2006] it was found that the use of DSC to detect multiple phases of sintered PTFE, due to different melt temperatures of the virgin and melt-crystallised material, had been mentioned in a paper 30 years ago by Beckett [1976]. Beckett [1976] described the use of DSC to determine whether PTFE blocks have been correctly sintered. The blocks were made by cold pressing virgin (as-polymerised) powder into compacts followed by heating (sintering). The centre of a large block not melting due to low sintering temperature or time was termed ‘undersintering’ while degradation due to high sintering temperature or time was termed ‘oversintering’. Khanna [1988] studied the melting temperature of PTFE in detail and reported that virgin PTFE exhibits a melting temperature of approximately 342 ± 2°C while the temperature for sintered PTFE (i.e. melted and crystallised) is 328 ± 2°C. It is due to this drop in melting point of PTFE after sintering that DSC can be used to detect undersintering. Beckett [1976] compared a DSC trace of virgin PTFE powder with those for blocks sintered to varying degrees as shown in Figure 58. The trace for virgin powder (a) shows a peak melt temperature of 344°C. The fully sintered sample (b), which is comprised entirely of material that has melted and crystallised, shows a single peak with a melt temperature of 328°C corresponding with the values later given by Khanna [1988]. Multiple melting peaks are observed in traces (c) and (d) and Becket [1976] stated that the presence of any ‘high-melting’ phase (shown by peaks with higher melt temperatures) show incomplete sintering i.e. incomplete melting of the virgin powder. The use of DSC to detect incorrect sintering of polymers by observation of multiple melting peaks has been used since that study. For example, in a more recent investigation into compressive properties of sintered PTFE billets, Rae and Dattelbaum [2004] rejected specimens which exhibited double DSC melting peaks describing these specimens as containing “only partially sintered molding powder at [the billet] centre”.

85
Figure 58 DSC traces for virgin and sintered PTFE [Becket 1976]

Becket [1976] also stated that using suitable control material the degree of sintering can be measured using the individual peak heights, as labelled on traces (c) and (d) in Figure 58, though the actual procedure used was not described. This method of quantifying the degree of sintering was not the focus of the paper by Becket [1976] and the author of this present thesis did not find more recent mention of the concept in the available literature. This may indicate that the ability to measure the degree of sintering was considered by Beckett and others to be a peripheral issue with little practical use.

7.4 ‘Degree of sintering’

Becket [1976] used the phrase ‘degree of sintering’ (which is taken as a qualitative description of the amount of sintering that occurred) and implicitly related this to the degree to which the virgin powder melts. Searching the available literature showed that the qualitative phrase ‘degree of sintering’ is, as would be expected, commonly
used in the various fields which involve sintering, including Rapid Prototyping and RM [Agarwala et al, 1995; Ang et al, 2000; Chua et al, 2004; Fischer et al, 2005; Hao et al, 2006]. However, the phrase ‘degree of sintering’ was not related necessarily to DSC measurements or directly quantified in any other manner. The only exception to this was in a study by Kruth et al [2004] which suggested that the degree of sintering occurring between two metal particles due to solid state sintering could be quantified using the ratio of neck diameter to powder particle diameter. Since the phrase is widely used, particularly in a qualitative manner, it was deemed appropriate to employ new terminology to describe the quantified variation of particle melt occurring in SLS processed material. The term chosen was ‘degree of particle melt’.

### 7.5 Principal hypothesis and research objectives

The investigation into post build cooling rate detailed in Chapter 6 shed light on the crystallisation behaviour of SLS processed material and showed that faster post build cooling rate could improve EaB to a certain degree. However, the practical extremes of cooling rate were investigated and an order of magnitude improvement seem unattainable by this approach. It was therefore decided to pursue other methods to vary and improve mechanical properties. Collaborative research with TNO resulted in a key observation by the author. This was that un-melted particle cores and the surrounding material which has melted and crystallised apparently relate to separate peaks on a DSC plot. This led to the principal hypothesis which is that ‘DSC can be used to quantify variability in the degree that particles melt in SLS processed material’. This ‘degree of particle melt’ (DPM) as measured by DSC should correlate with mechanical properties including EaB. It is hypothesised that increased DPM will result in higher EaB due to improved inter-particle fusion and consolidation. The ability to quantify DPM would be useful in the field of SLS as it would provide a common link between build parameters and mechanical properties by directly measuring the effect of the build parameters on the material itself.

The principal research objectives are:

1. Produce parts with various levels of DPM
2. Determine a suitable quantified measure of DPM
3. Establish the relationship between DPM and mechanical properties
8 Experiments to assess the effects of DPM on mechanical properties & crystallinity

8.1 Methodology

8.1.1 Introduction (aims & theory)

The principal research objectives, as introduced in Chapter 7, are to produce parts with various levels of DPM, determine a suitable quantified measure of DPM and establish the relationship between DPM and mechanical properties.

The comparison of parts built on different machines in Chapter 7 suggested that increased energy input resulted in an increased DPM. For the principal investigation, standard machine parameters for a single machine were varied in order to produce parts with varying DPM.

Certain machine parameters can be varied to cause an unspecified but certain increase or decrease in energy supplied to the material being melted. As described previously, in SLS heat supplied to the material originates from numerous heaters preheating certain areas within the machine and from the laser itself. Parameters directly related to these can be varied to cause an increase or decrease in energy supplied. For example, with all other parameters unchanged, an increase in laser power or the part bed temperature results in increased energy input. Other parameters could possibly affect energy input but whether they result in increased or decreased energy input is not implicit. An example of this is roller speed where it is likely the roller is on average at a different temperature than the powder bed and so the duration of the roller/powder bed interaction may have an unknown influence on the energy supplied to the material.

For these experiments parameters were selected which can be implicitly matched to an inherent increase or decrease in energy input. Therefore an increase or decrease for any of these parameters will result in an increase or decrease of unspecified value in net energy input. It is important to note that only net energy input is being considered whereas the time dependence is not considered. Sintering and melting are time dependant processes so this must be considered in analysis of results. As mentioned in Section 2.3.3 quantification of the energy input involving laser and part
bed temperature would be more complex than the quantified energy density. Energy input could be quantified however many additional factors would have to be considered such as % absorption, % transmission and % reflection of the laser. Time dependence may need to be considered in order to quantify energy input for variation of Fill Scan Count. The variation of part bed temperature across the part bed would also need to be considered. For this study quantification of the energy input was not attempted since the high number of unknowns could result in misleading results. Essentially the parameters were varied simply to vary the DPM so that the effect of DPM on other properties could be investigated.

The general experimental plan was to build sets of parts in separate builds. For each build the value for one parameter would be varied with all other parameters kept at default values. The parts would then be analysed for DPM and other properties and the relationships (if any) analysed. A Design of Experiment was not conducted since the objective was to analyse clearly the independent effects of the various parameters and it was preferred to avoid potential secondary effects of the combinations of parameters.

8.1.2 Build

8.1.2.1 Part design
6 tensile specimens were built in each build according to ISO-527-2:1996 type 1A as shown in Figure 59. As in previous builds these were built in the x-axis to avoid end of vector related issues. Parts were built flat to reduce build time.

In addition to 6 tensile specimens, 1 part was built to obtain specimens for DSC and optical microscopy. This is shown in Figure 60 which shows 5 equally spaced locations (labelled A-E) corresponding to the straight section of the tensile specimens. 1 DSC specimen was cut from the centre of the part at each of these locations. Optical microscopy was conducted through a cross section taken at the central location (C).
8.1.2.2 Build setup

For these experiments the common 12mm warm up height was selected and a further 8mm of powder deposited at the final part bed temperature to provide further insulation to the parts due to the relative shallow build volume as shown in Figure 61. The total powder deposited below the parts was therefore 20mm. The parts are 4 mm in height as specified in ISO-527-2:1996. The standard 2.54mm cool down height was selected and therefore a further 17.46mm deposited at final part bed temperature above the parts so that the total powder height above the parts matched that below at
20mm. This was intended to combat uneven cool rates above and below parts which could occur with significantly different heights.

Figure 61 Part build cross section

Table 8 lists the duration of major stages of the build process. ‘Machine warm up’ refers to the time the machine is given to heat to an initial temperature of 100°C (without powder deposition). The build time varied when some parameters were changed (e.g. fill scan count) but was approximately 3.5 hours for specimens built using default parameters. After the final layer was deposited, all part heaters were switched off and the powder and machine allowed to cool with the machine door closed. This was set at 2 hours after which the still hot part-cake was removed from the machine and left to cool for 24 hours after which the cake had completely cooled to room temperature.

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Machine warm up</td>
<td>1 hour</td>
</tr>
<tr>
<td>Part build</td>
<td>~ 3.5 hours</td>
</tr>
<tr>
<td>Post build cool down in machine</td>
<td>2 hours</td>
</tr>
<tr>
<td>Part-cake cool down to ambient</td>
<td>+ 24 hours</td>
</tr>
</tbody>
</table>

Table 8 Build duration

8.1.2.3 Machine parameters

Table 9 lists the machine parameters varied in these experiments. For all parameters except ‘Fill scan count’ a high and low value (relative to the default value) are shaded red and blue respectively. High values (red) relate to increased energy input (compared with the benchmark; Default) and Low values (blue) relate to decreased
energy input compared with Default. The pyrometer measuring the part bed temperature was not calibrated and so Part Heater Set Point values are reported as relative values of arbitrary units.

<table>
<thead>
<tr>
<th>Build</th>
<th>Part heater set point (PHSP)</th>
<th>Slicer fill scan spacing (SFSS) (mm)</th>
<th>Fill laser power (FLP) (W)</th>
<th>Fill scan count (FSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1, Default</td>
<td>148</td>
<td>0.15</td>
<td>11.5</td>
<td>1</td>
</tr>
<tr>
<td>2, PHSP-High</td>
<td>150</td>
<td>0.15</td>
<td>11.5</td>
<td>1</td>
</tr>
<tr>
<td>3, PHSP-Low</td>
<td>146</td>
<td>0.15</td>
<td>11.5</td>
<td>1</td>
</tr>
<tr>
<td>4, SFSS-High</td>
<td>148</td>
<td>0.13</td>
<td>11.5</td>
<td>1</td>
</tr>
<tr>
<td>5, SFSS-Low</td>
<td>148</td>
<td>0.17</td>
<td>11.5</td>
<td>1</td>
</tr>
<tr>
<td>6, FLP-High</td>
<td>148</td>
<td>0.15</td>
<td>13.5</td>
<td>1</td>
</tr>
<tr>
<td>7, FLP-Low</td>
<td>148</td>
<td>0.15</td>
<td>9.5</td>
<td>1</td>
</tr>
<tr>
<td>8, FSC-High (2)</td>
<td>148</td>
<td>0.15</td>
<td>11.5</td>
<td>2</td>
</tr>
<tr>
<td>9, FSC-High (3)</td>
<td>148</td>
<td>0.15</td>
<td>11.5</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 9 Machine parameters

8.1.2.4 Part removal

Parts were removed from the cooled part-cake as per normal procedure but with the additional step of numbering and labelling specimens before complete removal.

8.1.3 Data gathering

8.1.3.1 DSC

For DSC, sample mass was 5mg +/- 0.05mg. This sample mass was less than those used in Chapters 6 and 7 since the objective was to analyse individual peaks therefore requiring greater resolution. Smaller samples improve resolution due to reduced thermal gradients and thermal lag within specimens [Wunderlich, 1990; Greco and Maffezzoli, 2003]. The mass range was also much lower to prevent variation due to the same phenomena. Samples were heated from ~20°C to 220°C @10°C/min, held at 220°C for 2 minutes and then cooled at 10°C/min. At approximately 70°C, as room temperature is approached during cool down the DSC hardware used can no longer cool at the specified 10°C/min cooling rate. Data beyond this point is therefore invalid which is inconsequential for this study since only melting is considered.
Figure 62 shows a DSC trace for a typical SLS part starting to heat the specimen at 20°C, heating it to 220°C and eventually cooling it to ~20°C. For determining DPM it is only necessary to consider the melting peaks and the region immediately before and after (see dashed region). Figure 63 shows this region cropped.

![DSC Trace](image)

**Figure 62 Typical DSC chart for SLS Nylon-12 part**

Using DSC analysis software numerous readings can be taken from the DSC trace to characterise the melt peaks. These are annotated as illustrated in Figure 63. As described in section [Error! Reference source not found.](#), the % crystallinity was determined by dividing the heat of melting of the sample by the known heat of melting for a 100% crystalline specimen. The heat of melting of the specimen is the area of the peaks below the interpolated baseline (dashed green). The heat of melting for 100% crystalline Nylon-12 was taken as 209.3 J/g, as reported by Gogolewski et al [1980]. The peak heights were measured from the tip of the peaks to the parallel drawn from the intersection point of the interpolated base line and DSC trace line. The peak temperatures are the temperatures at the tip of the peaks.
8.1.3.2 Tensile testing
As in Chapter 6 E-modulus was measured @ 1 mm/min strain rate and tensile strength and EaB @ 5 mm/min. A Zwick testing machine with long travel contact extensometer was used (pictured previously in Figure 32).

8.1.3.3 Optical microscopy
Specimens were cut to 5 μm using a microtome, pictured in Figure 64. This shows the specimen held in ice being cut with a glass knife. Micrographs were recorded in transmitted light, dark-field, un-polarised mode. Polarised mode was attempted but it was found more difficult to differentiate between the cores and surrounding material. Micrographs taken in polarised and un-polarised mode are shown for comparison in appendix 6.
Figure 64 Microtome
8.2 Results and Discussion

This section presents the results of the DSC analysis and the associated mechanical properties and optical microscopy. A general description of results is given but Chapter 9, (Overall analysis & discussion), provides in depth analysis including comparison of the results.

8.2.1 DSC

Figure 65 shows 9 superimposed DSC traces. Each trace represents one combination of build parameters and is plotted from the averaged results of the 5 DSC runs performed for each part. The original 5 traces for each of the 9 parts are included in appendix 8. Figure 65 shows all 9 traces following roughly the same path except during melting where they differ to varying degrees. These differences occur within a window of 150°C and 200°C during the heating of the specimen. The differences manifest themselves in the geometry of the endothermic melt peaks.

Figure 65 DSC results superimposed

Figure 66 - Figure 69 show sets of DSC traces focussed on the melt region, between 150°C and 200°C. Once again, each trace is calculated as the average of the 5 separate DSC traces. Each chart shows the results for parts built with default parameters compared against results built with one parameter varied. For example,
Figure 66 shows results for parts built with a default Part Heater Set Point of 148 and high and low values of 150 and 146 respectively. Traces for parts built with default parameters are coloured green and those for 'high' and 'low' parameters are red and blue respectively where high/red indicates the higher energy input.

Figure 66 shows DSC traces for variations of Part Heater Set Point. In Figure 66 there is apparently a small change between the peaks for Default (148) and Low (146). The Low trace (blue) has a marginally smaller left-hand side peak and a marginally bigger right-hand side peak. The High trace (red) has a marginally larger left-hand side peak but a considerably smaller right-hand side peak.
Figure 67 shows DSC traces for variations of Slicer Fill Scan Spacing. In Figure 67 the variation from the Default trace (green) for the High (red) and Low (blue) traces is more apparent than in Figure 66. The Low trace (blue) has a marginally smaller left-hand side peak and a more noticeably bigger right-hand side peak. As with Figure 66 the High trace (red) has a larger left-hand side peak and a smaller right-hand side peak but the difference is greater.
Figure 68 shows DSC traces for variations of Fill Laser Power. It follows an emerging trend (based on observations of Figure 66 and Figure 67) where the Low trace (blue) shows a slightly smaller left-hand peak compared with the Default trace (green) but a relatively larger right-hand side peak compared with that of the Default trace. Continuing this trend, the High trace (red) shows both considerably larger and smaller peaks (relatively) for the right-hand side and left-hand side peaks respectively.

Figure 68 DSC results for Fill Laser Power
Figure 69 shows DSC traces for variations of Fill Scan Count. Since the variations both involve higher energy input than the default value of 1 they are both coloured red (different shades). Both High traces show left-hand side peaks larger than that of the Default trace. The peak for Fill Scan Count - High (3) (dark red) is slightly smaller than that of Fill Scan Count - High (2) (light red) which is an exception to the trend of increasing size of the left-hand peak for increased energy input. Both High traces show no apparent right-hand peak.

Figure 69 DSC results for Fill Scan Count

Figure 70 shows the curves presented in Figure 66 - Figure 69 superimposed upon one another. The right-hand side melt peaks are focussed on in Figure 70b to facilitate easier interpretation. The traces are coloured so that for each parameter (e.g. Fill Laser Power) the High trace will have a distinct colour and the low trace will have the same colour but with a dotted line. For example, Fill Laser Power - High is solid pink and Fill Laser Power - Low is dotted pink. As before, Fill Scan Count differs slightly (because there are two High traces and no Low trace) with its High (2) trace solid red with a marker and its High (3) trace solid red. The observations made from Figure 66 - Figure 69 relating to the left-hand side peaks are not discernable in Figure 70a. However, Figure 70a and Figure 70b clearly show the decrease and increase in the
size of the right-hand side peak for High and Low traces (respectively) and that the magnitude of this varies for different parameters. There is a symmetry apparent in Figure 70b with High and Low traces somewhat reflected about the Default trace (green): Both blue traces are present either side of the green trace; both grey traces are present either side of the green trace; and both pink traces are present either side of the green trace. Figure 70b suggests that, for the parameter values chosen, the right-hand side peak size is affected most by Fill Scan Count (red), then by Fill Laser Power (pink), then by Slicer Fill Scan Spacing (grey), and the least by Part Heater Set Point (blue).
Figure 70 All DSC melt peaks superimposed (a) and right-hand side melt peaks only (b)
Appendix 9 lists the quantified data gathered from the DSC traces. It lists the average values and standard deviations from each set of 5 traces. These values are analysed in Chapter 9. Figure 71, Figure 72 and Figure 73 show average values and range values for Crystallinity and the peak heights for the right-hand side and left-hand side peaks. Values for specimens built with default parameters are shaded green; those for High values red and those for Low values blue.

Figure 71 shows Crystallinity values. All High values are less than Default and all Low values are greater than Default. Spread for all values is broadly constant. Figure 72 shows right-hand side peak height values. As with Crystallinity all High values are less than Default and all Low values are greater than Default. Spread is again broadly constant for all values. Figure 73 shows left-hand side peak height values. The trend present is opposite to that in Figure 72 with all High values greater than Default and all Low values lower than Default. Additionally, the spread is markedly greater in Figure 73 than in Figure 72. Comparing Figure 72 and Figure 73, a higher right-hand side peak height corresponds with a lower left-hand side peak and a lower left-hand side peak corresponds with a higher right-hand side peak. This matches the observations of the DSC traces presented previously.
Figure 72 Right-hand side peak height

Figure 73 Left-hand side peak height
8.2.2 Mechanical properties

Figure 74 - Figure 82 show stress-strain plots for the tensile specimens produced using the different build parameters. They illustrate engineering stress and strain. The horizontal blue lines indicate the points at which tensile strength was measured (the maximum tensile stress); the vertical blue lines indicate the points at which EaB was measured (the maximum tensile strain) and the diagonal blue lines indicate the gradient at the initial part of the curve from where E-modulus was measured. Numerical values obtained from these charts are presented later in Figure 83, Figure 84 and Figure 85.

Figure 74 shows the stress-strain plot for the tensile test specimens built with Default parameters. The specimens exhibit brittle behaviour since according to Ward & Sweeney [2004] brittle behaviour is designated when specimens fail at their maximum loads at comparatively low strains (less than 10%).

Figure 75 and Figure 76 show the stress-strain plots for tensile test specimens built with Part Heater Set Point set high (150) and Low (146) respectively. Figure 75 (High) shows greater EaB values though they are still generally less than 10% and
failure occurs at the maximum loads indicating brittle behaviour. Figure 76 (Low) shows significantly lower strains and is also classified as brittle. Stress at break values in Figure 75 (High) are on average higher than the default values (Figure 74) and are lower than the default values in Figure 76 (Low).

Figure 77 and Figure 78 show the stress-strain plots for tensile test specimens built with Slicer Fill Scan Spacing set High (0.13mm) and Low (0.17mm) respectively. Figure 77 (High) shows EaB values above and below 10% and failure in some specimens occurs just below maximum load indicating a transition from brittle to ductile behaviour. Figure 78 (Low) shows significantly lower strains and is classified as brittle. As before, the High and Low charts show higher and lower maximum stress than the Default chart.

Figure 79 and Figure 80 show the stress-strain plots for tensile test specimens built with Fill Laser Power set High (13.5W) and Low (9.5W) respectively. As with Figure 77, Figure 79 (High) shows EaB values above and below 10% and failure in some specimens occurs just below maximum load indicating a transition from brittle to ductile behaviour. Figure 80 (Low) shows significantly lower strains and is classified as brittle. Once again the High and Low charts show higher and lower maximum stress than the Default chart.

Figure 81 and Figure 82 show the stress-strain plots for tensile test specimens built with Fill Scan Count set High at 2 and 3 counts respectively. Figure 81 and Figure 82 both show EaB values above 10% and failure in all specimens occurs below maximum load indicating fully ductile behaviour. Stress at break is greater than default in both cases and yielding is also apparent.
Figure 75 Tensile test curves for Part Heater Set Point - High (150)

Figure 76 Tensile test curves for Part Heater Set Point - Low (146)
Figure 77: Tensile test curves for Slicer Fill Scan Spacing - High (0.13mm)

Figure 78: Tensile test curves for Slicer Fill Scan Spacing - Low (0.17mm)
Figure 79 Tensile test curves for Fill Laser Power - High (13.5W)

Figure 80 Tensile test curves for Fill Laser Power - Low (9.5W)
Figure 81 Tensile test curves for Fill Scan Count - High (2)

Figure 82 Tensile test curves for Fill Scan Count - High (3)
Figure 83, Figure 84 and Figure 85 show average values and range values for EaB, tensile strength and E-modulus respectively. As before, values for specimens built with default parameters are shaded green; those for High values red and those for Low values blue.

Figure 83 shows EaB values. As expected, all High values are greater than Default and all Low values are less than Default. The highest EaB value is more than double that of the Default value and the lowest is just over half the Default value. Spread for all High values and Default is broadly constant but is considerably tighter for all Low values.

![Figure 83 Elongation at break](image-url)
Figure 84 shows tensile strength values. As with EaB all High values are greater than Default and all Low values are less than Default however the difference is not as great. Fill Scan Count - High (2) and Fill Scan Count - High (3) showed the highest EaB values however they show the lowest of the High values for tensile strength. Spread for all values is broadly constant.
Figure 85 shows E-modulus values. As with EaB and tensile strength all High values are greater than Default except Fill Scan Count – High (3). However, while all Low values are less than their associated High values, they are all higher than the Default values. Spread is broadly constant except for Slicer Fill Scan Spacing – Low which shows considerably wider spread and Fill Scan Count – High (3) which shows much tighter spread. As with the results from Chapter 6 the results for E-modulus do not follow the same clear trends as EaB and tensile strength.

![Figure 85 E-modulus](image)

**Figure 85 E-modulus**

### 8.2.3 Optical microscopy

Figure 86 - Figure 103 show micrographs taken in dark-field, un-polarised, transmitted light mode. For each specimen micrographs are presented at 10x and 40x objective magnification. All micrographs show sections through parts in the same orientation and this orientation in relation to the build setup is annotated in Figure 86.

Figure 86 and Figure 87 show micrographs for specimens built with Default parameters. Figure 86 shows well defined un-melted particle cores apparently
distributed in lines dispersed approximately every 100μm which may relate to the layer thickness which is 100μm. The black circle in the bottom right hand corner of Figure 86 shows a bubble trapped between the specimen and glass slide in the resin which is difficult to completely avoid. Such perfectly spherical black circles are found in subsequent micrographs and are all trapped air bubbles. Voids in the specimen are also visible as indicated in Figure 86. These voids are shown clearly contrasted against the bulk material in micrographs taken in polarised light (see appendix 7).

Figure 87 shows the particle cores surrounded by spherulitic structure (spherulites) which, by observing the orientation of the lamellar fibrils, appears to have crystallised outwards from the surface of the cores. Spherulitic structure within the cores is not discernable in Figure 87.
Figure 86 Default, x10

Figure 87 Default, x40
Figure 88 and Figure 89 show micrographs for specimens built with Part Heater Set Point set to High (150) while Figure 90 and Figure 91 show micrographs for specimens built with Part Heater Set Point set to Low (146). In Figure 88 particle cores are apparent however they are not clearly dispersed in 100μm spaced lines as observed in Figure 86 (Default). Figure 89 (Part Heater Set Point - High) shows some particle cores are present though to a lesser extent than in Figure 86 (Default) and they are not clearly contrasted. Instead they are located by observing the less well defined spherulitic structure within the clearly observable spherulites.

Figure 90 (Part Heater Set Point - Low) shows particle cores dispersed in 100μm spaced lines as in Figure 86 (Default). However in Figure 90 the cores appear more highly contrasted against the surrounding material. As with Figure 87 (Default), Figure 91 (Part Heater Set Point - Low) shows the particle cores contained within spherulites which appear to have crystallised outwards from the surface of the cores.

Figure 92 and Figure 93 show micrographs for specimens built with Slicer Fill Scan Spacing set to High (0.13mm) while Figure 94 and Figure 95 show micrographs for specimens built with Slicer Fill Scan Spacing set to Low (0.17mm). As with previous figures for Part Heater Set Point High and Low, the micrographs for specimens built with Low parameters show particle cores dispersed in 100μm spaced lines and the micrographs for specimens with High parameters do not clearly show this. As before, the particle cores for specimens built with Low parameters are highly contrasted to the surrounding material.

Figure 96 and Figure 97 show micrographs for specimens built with Fill Laser Power set to High (13.5W) while Figure 98 and Figure 99 show micrographs for specimens built with Fill Laser Power set to Low (9.5W). Dust particles were present within the microscope assembly during the capture of the micrographs presented in Figure 96 - Figure 99 and these show up as blurred dots. As with Part Heater Set Point and Slicer Fill Scan Spacing, the micrographs for specimens built with Low parameters show particle cores dispersed in 100μm spaced lines and the micrographs for specimens with High parameters do not show this.
Figure 88 Part Heater Set Point-High, x10

Figure 89 Part Heater Set Point-High, x40
Figure 92 Slicer Fill Scan Spacing - High x10

Figure 93 Slicer Fill Scan Spacing - High x40
Figure 94 Slicer Fill Scan Spacing - Low x10

Figure 95 Slicer Fill Scan Spacing - Low x40
Figure 98 Fill Laser Power - Low x10

Figure 99 Fill Laser Power - Low x40
Figure 100 and Figure 101 show micrographs for specimens built with Fill Scan Count set to High (2 scan counts) and Figure 102 and Figure 103 show micrographs for specimens built with Fill Scan Count set to High (3 scan counts). Both sets of micrographs show no particle cores present at any magnification. At 40x magnification both Fill Scan Count - High (2) and Fill Scan Count - High (3) show the microstructure consisting of spherulites with crystallisation apparently initiated from point nucleation sites (as opposed to the surface of particle cores). Figure 102 (Fill Scan Count - High, 3 counts) shows a particularly fine, evenly distributed microstructure.
Figure 102 Fill Scan Count - High (3) x10

Figure 103 Fill Scan Count - High (3) x40
9 Overall Analysis & Discussion

9.1 Effects of build parameters on material properties

Numerous parameters and variables were altered and their effects on material properties observed. These effects, reported previously in Chapter 6, Chapter 7, and Chapter 8, are now summarised. No new results or analysis are presented in sections 9.1.1 - 9.1.3.

9.1.1 Post build cooling rate (Chapter 6)

Most conventional plastics processing techniques involve cooling of the entire molten volume at once. The nominal cooling rate during the material shaping process (for example, cooling of the melt in a moulding tool) can therefore be controlled to obtain a certain % crystallinity and associated mechanical and other properties. Due to the layer by layer nature of SLS, melting and crystallisation have the potential to occur throughout the process. At the end of the process the parts still require cooling down. Therefore the investigation into post build cooling rate intended to verify that % crystallinity of parts could be altered by varying post build cooling rate and to assess the effects on mechanical properties.

Cooling rates were altered by varying the procedure of part-cake removal from the machine. Temperature cool down profiles were generated using the machine's internal pyrometer and thermocouples which were attached after the machine was opened. These measurements showed that the material which was melted by the laser remained above the crystallisation onset temperature (152°C) after the entire build had completed. This means that this material remained in the molten state after build completion. This was so even after the part-cake was left to cool inside the machine for 30 minutes and the part-cake surface had cooled to ~90°C, considerably below the crystallisation temperature range. The implication of this finding is that post build cooling rate of the part-cake can theoretically affect the crystallisation of parts.

Using the temperature cool down profiles, the approximate average cooling rate during crystallisation was calculated. This was problematic due to the nature of the process but generated some data for comparison with previous research into effects of
cooling rate for other polymers including Nylon-6. The values ranged from 1.0°C/min for slowly cooled parts to 23.5°C/min for faster cooled parts even though cooling rates at the centres of the parts expected to cool slowest and fastest were indeterminable. These changes in cooling rate were associated with changes in mechanical properties, particularly EaB. The slowest cooled parts had average EaB value of 13.5%, Strength at break of 42.5MPa and E-modulus of 1.69 GPa. The fastest cooled parts had markedly higher EaB (19.1%), marginally lower strength at break (40.6MPa), and slightly higher E-modulus (1.80 GPa). Percentage crystallinity of specimens was measured and varied from 27.9% for the slowest cooled parts to 27.2% for the fastest cooled parts. However apart from these two extremes all other values were virtually the same. It was concluded that % crystallinity was not responsible and that a different explanation would be required which could be addressed in future study.

9.1.2 Partial melting of particles (Chapter 7)

In the collaborative study with TNO, parts were built on SLS machines from different machine manufacturers, using powder supplied from the respective manufacturers, with parameters set diametrically opposite to each other. The machine at Loughborough (from 3D Systems) was set up for improved accuracy while the machine at TNO (from EOS) was set up for improved mechanical properties.

Comparison of DSC traces for TNO parts and Loughborough parts showed that both have double melt peaks whereas their respective powders had only one peak each. It has been shown in previous studies that SLS processed material contains apparently un-melted particle cores [Moeskops, 2004]. It was therefore hypothesised that the right hand side peak relates to the melting of these cores (which were not melted in the SLS process) which maintain the crystal form similar to the original powder. The left-hand side peak was hypothesised to relate to the melting of the material which during the SLS process had been melted by the laser and then crystallised. The properties of this peak are considered to be dependent on processing conditions which resulted in significant differences between the left-hand side peak for the TNO and Loughborough parts in the collaborative study. This concept has been mentioned in literature relating to sintering of other crystalline polymers.
9.1.3 Energy input (Chapter 8)

In order to investigate the double melt peak phenomenon and its relationship with un-melted particle cores, parts were built with parameters varied to increase or decrease the applied energy input to the material during melting. Default parameters were selected based on the existing user optimised machine setup and individual parameters chosen and varied separately for each build. For each parameter a high and low value was chosen indicating higher and lower energy input (respectively) compared with the default parameters. The parameters chosen to investigate were Fill Laser Power, Slicer Fill Scan Spacing and Fill Scan Count (laser parameters) and the Part Heater Set Point.

All 'high' values resulted in a marked reduction in size of the right-hand side peak and a small increase in size of the left-hand side peak. Fill Scan Count parts showed no right-hand side peak. All 'low' values resulted in an increase in the size of the right-hand side peak and decrease in size of the left-hand side peak. These findings correlated with optical microscopy results where 'low' values resulted in highly contrasted large particle cores and 'high' values resulted in smaller cores, less clearly defined. Fill Scan Count parts showed no cores and Fill Scan Count – High (3) had a fine homogenous microstructure unlike other parts. These findings support the hypothesis of the separate DSC peaks relating to the particle cores and background material and that the amount of energy input directly affects the size of the cores and the corresponding DSC peak.

All 'high' values resulted in markedly increased EaB and tensile strength, and marginally higher E-modulus. Comparison of mechanical properties with DSC results is discussed in subsequent sections.

9.2 Qualitative description of variation in DPM

Section 8.2 presented results for experiments where numerous parameters were varied, repeat measurements were taken for DSC analysis, and all findings were compared with microscopy results. This confirmed that DPM can be varied by changing build parameters and that the right-hand-side peak does relate to un-melted particle cores. Since the left-hand side peak exists due to SLS processing the two
peaks (left and right) are subsequently referred to as the ‘processing-peak’ and the ‘core-peak’ respectively.

Figure 70 showed that higher energy input results in a smaller core-peak for each parameter. Figure 104 is similar to Figure 70 but only shows the core-peaks for three specimens. These are for Fill Laser Power – Low (which showed the largest core-peak), Fill Scan Count – High (3) (which showed no core-peak), and Part Heater Set Point – High (which showed a core-peak approximately half the size of that for Fill Laser Power – Low). The line colouring in Figure 104 is the same as that used in Figure 70 and therefore is only used for identification purposes in Figure 104 (rather than indicating relative energy input).

![Figure 104 Variation of DSC core-peaks](image)

Figure 105 shows micrographs (previously presented in section 8.2) for the two extremes and middle value specimen shown in Figure 104. Shown sequentially, these illustrate how the size of particle cores decreases with variation in parameters and that this sequence matches the sequence of decreasing core-peak size.
9.3 Relationship between DSC readings and mechanical properties

9.3.1 Selection of DSC readings to quantify relationships

Figure 106 - Figure 108 show readings from the DSC melt peaks plotted against mechanical properties. For each mechanical property, % crystallinity, Core Peak Height, Processing Peak Height, Core Peak temperature and Processing Peak Temperature are plotted. The objective is to determine which DSC readings can be used to quantify DPM as a factor of mechanical properties. Charts are plotted at this stage in order to determine if there are any relationships apparent.

For each data series a linear regression line is plotted and the Coefficient of Determination (R² value) annotated. The R² value is a measure of how well a regression line represents the data and relates to the gradient and the average deviation of values from the regression line [Hinton, 2004]. The R² value varies from 0 – 1. The higher the value, the stronger the linear relationship between 2 variables. It should be noted that this is not a measurement of the statistical significance of the relationship and so the word ‘importance’ is used instead. Although the R² value can be determined without plotting the data on charts, it is important to plot the data so that individual examination of the data can also be performed.

For Figure 106 (EaB) % crystallinity, Core Peak Height and Processing Peak Height show apparently strong correlation with EaB (represented by high R² values) but
Processing Peak Temperature and Core Peak Temperature do not. As would be expected, as EaB increases % crystallinity decreases. Also related to increasing EaB is increasing Processing Peak Height and decreasing Core Peak height. There was no strong relationship apparent for Peak Temperatures.

Figure 107 (tensile strength) appears to show less strong correlation for all DSC characteristics though this may be due to outlying data points for Fill Scan Count - High (2) and Fill Scan Count - High (3) highlighted in Figure 107. This is addressed later. As with EaB, the strongest relationship was for % crystallinity, followed by Core Peak height, then Processing Peak height and finally by Peak Temperatures again for which there was particularly low correlation.

Figure 108 shows the data points for E-modulus. This shows no strong correlation as represented by low $R^2$ values. The highest $R^2$ values are for the Peak Temperatures but are still relatively low compared with the values for EaB and tensile strength. In this present study spherulite size was not measured. Spherulite size can affect mechanical properties of semi-crystalline polymers, particularly toughness and stiffness [Bessell et al, 1975; Deshmane, 2007] and so future study could investigate the effect of other factors (such as spherulite size) on mechanical properties, particularly E-modulus.
Figure 106 DSC readings and EaB
Figure 107 DSC readings and tensile strength
Figure 108 DSC readings and E-modulus
Table 10 lists the $R^2$ values from Figure 106 - Figure 108. Values higher than 0.9 are shaded dark green and values between 0.8 and 0.9 are shaded light green to give a basic indication of the most important relationships. The description of these limits is that an $R^2$ value of 0.9 – 1 (dark green) is of ‘primary importance’, a value from 0.8 – 0.9 (light green) is of ‘secondary importance’ and any other value is ‘unimportant’. These values show that the DSC characteristics % crystallinity, Core Peak Height and Processing Peak Height are the only ones to show important relationships with mechanical properties. Furthermore, these relationships are for EaB but not tensile strength and E-modulus.

<table>
<thead>
<tr>
<th>R$^2$ value</th>
<th>% crystallinity</th>
<th>Processing Peak Height</th>
<th>Core Peak Height</th>
<th>Processing Peak Temperature</th>
<th>Core Peak Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>EaB</td>
<td>0.942</td>
<td>0.817</td>
<td>0.934</td>
<td>0.238</td>
<td>0.368</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>0.733</td>
<td>0.536</td>
<td>0.683</td>
<td>0.034</td>
<td>0.293</td>
</tr>
<tr>
<td>E-modulus</td>
<td>0.105</td>
<td>0.059</td>
<td>0.106</td>
<td>0.555</td>
<td>0.223</td>
</tr>
</tbody>
</table>

Table 10 Importance of $R^2$ values

It was observed in Figure 107 that data points for Fill Scan Count - High may be outliers. The specimens produced with Fill Scan Count - High (2) and Fill Scan Count - High (3) have already been shown as unique compared to all other specimens with respect to their lack of particle cores and thus single melt peak. It is therefore considered feasible that they may not follow the same trends as parts containing cores. It should be noted that building parts with Fill Scan Count set to above 1 is not common standard practice and so it would be useful to analyse the data considering the data points as residual and therefore excluding them from the charts.

Figure 109 - Figure 111 show the same charts as Figure 106 - Figure 108 but with Fill Scan Count - High data points excluded.
Figure 111 DSC readings and E-modulus (Fill Scan Count values excluded)
The charts show considerably stronger correlation and the $R^2$ values are listed in Table 11 using the same colour coding as Table 10 to give a basic relative measure of importance. The exclusion of Fill Scan Count – High values lead to markedly strong correlation between EaB and tensile strength and % crystallinity and Core Peak Height. As before, there is insignificant correlation for E-modulus.

<table>
<thead>
<tr>
<th></th>
<th>% crystallinity</th>
<th>Processing Peak Height</th>
<th>Core Peak Height</th>
<th>Processing Peak Temperature</th>
<th>Core Peak Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>EaB</td>
<td>0.983</td>
<td>0.815</td>
<td>0.949</td>
<td>0.380</td>
<td>0.368</td>
</tr>
<tr>
<td>Tensile strength</td>
<td>0.995</td>
<td>0.749</td>
<td>0.942</td>
<td>0.407</td>
<td>0.293</td>
</tr>
<tr>
<td>E-modulus</td>
<td>0.332</td>
<td>0.255</td>
<td>0.252</td>
<td>0.223</td>
<td>0.022</td>
</tr>
</tbody>
</table>

Table 11 Importance of $R^2$ values (Fill Scan Count - High excluded)

The analysis in this section shows that if all parameters are considered then EaB correlates strongly with the % crystallinity and Core Peak Height but that there is no strong correlation for tensile strength and E-modulus. If Fill Scan Count - High values are excluded, and thus all specimens contain particle cores, there is particularly strong correlation between EaB and tensile strength and % crystallinity and Core Peak Height. However, it is important to note that at this point % crystallinity cannot be considered a measure of DPM because no theory has been presented explaining how DPM relates to % crystallinity. This is discussed later in Section 9.4.2.

### 9.3.2 Further analysis of selected DSC readings

Section 9.3.1 established that % crystallinity and Core Peak Height measured by DSC closely related to EaB and tensile strength values. EaB was shown to correlate strongly with % crystallinity and Core Peak Height when all data points are included. When Fill Scan - High values are excluded tensile strength also correlates strongly with % crystallinity and Core Peak Height. Figure 112 - Figure 117 show these values on separate charts with error bars displaying ±1 standard deviation in the X and Y axes.

The purpose of these charts is to consider the conclusions regarding correlation with respect to random error (i.e. uncertainty). They represent all data points (i.e. the
spread), whereas the $R^2$ values are only based upon the average values. They therefore indicate whether deviation from the trend line can be attributed to random error. A true value has a 68.3% chance of falling within error bars of ±1 standard deviation [Mathiesen and Pawl, 2003]. Therefore when the trend line intersects the perpendicular of an average data point between the error bars a statistically stronger relationship exists between the two factors (for example % crystallinity and EaB) than if the trend line passes outside the error bars.

Figure 112 and Figure 113 show EaB plotted against % crystallinity and Core Peak Height respectively with data points for Fill Scan Count - High included. In Figure 112 (EaB and % crystallinity) both X and Y standard deviation error bars for 6 of the 9 data points overlap the regression line. 1 data point only overlaps in the X-axis and 2 data points’ error bars miss the regression line. In Figure 113 (EaB and Core Peak Height) both X and Y error bars for only 2 of the 9 data points overlap the regression line. 4 data points only overlaps in the X-axis and 3 data points’ error bars miss the regression line though it should be noted that 2 of these data points had an X-axis standard deviation of 0. The relatively low number of data points overlapping the trend line in both X and Y in Figure 113 can be attributed to the much smaller standard deviation values for Core Peak Height than % crystallinity.
**Figure 112** % crystallinity, EaB (Fill Scan Count included)

**Figure 113** EaB, Core Peak Height (Fill Scan Count included)
Figure 114 and Figure 115 show % crystallinity and Core Peak Height plotted against EaB with data points for Fill Scan Count - High excluded. These are the same as Figure 112 and Figure 113 but have Fill Scan Count - High data points excluded. In Figure 114 (EaB and % crystallinity) both X and Y error bars for 5 of the 7 data points overlap the regression line, 1 in the X axis only and 1 in the Y axis only. It should be noted that these two data points only marginally miss the trend line.
In Figure 115 (EaB and Core Peak Height) both X and Y error bars for 3 of the 7 data points overlap the regression line, 2 in the X axis only and 2 miss the trend line completely.
Figure 116 and Figure 117 show % crystallinity and Core Peak Height plotted against tensile strength with data points for Fill Scan Count - High excluded. In Figure 116 (tensile strength and % crystallinity) both X and Y error bars for all 7 data points overlap the regression line.
In Figure 117 (tensile strength and Core Peak Height) both X and Y error bars for 3 of the 7 data points overlap the regression line, none in the X axis only, 1 in the Y axis only and 3 miss the trend line completely.
Figure 118 and Figure 119 summarise the results of the analysis conducted on the relationships decided as important in section 9.3.1. The $R^2$ values, which measure the strength of the relationships between the selected DSC parameters and mechanical properties, are presented in Figure 118. As described, these are all considered strong relationships ($R^2 > 0.9$) though the relationships between % crystallinity and EaB and tensile strength, with Fill Scan Count values excluded, are strongest.

![Figure 118 R² values from Section 9.3.1](image)

Figure 119 presents data showing the uncertainty of the trend line. For each relationship the number of data points for which the trend line passes between the standard deviation error bars in both X and Y are shown (green). The number of data points for which the trend line only passes between 1 set of error bars ('X or Y', yellow) or neither ('none', pink) are also shown. These are expressed as percentages so that, for example, for the relationship between % crystallinity and EaB with Fill Scan Count values included 5 of the 9 data points have the trend line pass between the error bars in both X and Y which leads to a value of 56% in Figure 119. These results also show that the strongest relationships are between % crystallinity and EaB and tensile strength with Fill Scan Count excluded. A very similar pattern is apparent between Figure 118 and Figure 119 in that the green bars in Figure 119 follow a similar pattern to the blue bars in Figure 118. This provides validation of the
relationships between mechanical properties (EaB and tensile strength) and % crystallinity and Core Peak Height described in Section 9.3.1. In particular the strength of the relationship between % crystallinity and mechanical properties is confirmed.

![Figure 119 Uncertainty of trend line](image)

### 9.4 Effect of DPM on selected DSC readings

Section 9.3 established that there is strong correlation between certain DSC readings (% crystallinity and Core Peak Height) and mechanical properties (EaB and tensile strength). This section (9.4) presents a theory to explain how variation of DPM can affect % crystallinity and Core Peak Height.

#### 9.4.1 Effect of DPM on Core Peak Height

As described previously in Section 7.2, and confirmed in Chapter 8 and Section 9.2, the right-hand side peak (Core Peak) on a DSC trace of an SLS produced part relates to the material that has not been melted by the laser. The size of this peak therefore relates to the total amount of this material in the specimen. Since the Core Peak and the Processing peak overlap, the peak height (rather than the peak area) is used to
indicate the peak size. DPM therefore directly affects Core Peak Height since Core Peak Height is a measure of the amount of material un-melted due to the DPM.

9.4.2 Effect of DPM on Crystallinity

In the context of traditional homogenous materials which are fully melted such as in injection moulding there is no reported necessary link between increased energy input and decreased % crystallinity. It is only in the context of a material consisting of semi-melted particles where the un-melted phase and the melted and crystallised phase have significantly different properties that this behaviour can be explained.

As mentioned in section 4.4.4, the production process of the Nylon-12 powder used in SLS results in a relatively very high % crystallinity. This value is roughly twice that of the material which has been melted and crystallised in the SLS process. The % crystallinity of the 3D Systems supplied virgin Nylon-12 powder used in the 'principal investigation' stage of this study was calculated to be 47%. Figure 106 shows that the % crystallinity of material processed with Fill Scan Count - High (2), consisting entirely of material that has melted and crystallised during the SLS process, is 25%. The reduced crystallinity of the melted and crystallised material may be due to factors such as higher cooling rate and/or the higher molecular weight of the material due to SLS processing [Zarringhalam et al, 2006].

The % crystallinity measured in all specimens in this investigation is the sum of the % crystallinity of the un-melted cores and the melted and crystallised (processed) material as shown in Figure 120. Figure 120 shows 4 bar charts representing 4 specimens with different ratios of (un-melted) core to melted and crystallised material (MCM) phase volume. The y-axes correspond to the volume fraction of each phase. The x-axes correspond to the % crystallinity of each phase. In these schematic illustrations the core phase has a crystallinity of 47% while the melted and crystallised phase has a crystallinity of 25%. By multiplying the volume fraction of each phase by the % crystallinity of each phase and summing the values the total % crystallinity of the specimen is determined. The microstructure associated with each bar chart is schematically illustrated above each one. This shows the core size decreasing due to the increasing DPM. The first example, for '100% core', represents the un-processed powder but the particles are considered as cores to simplify the model.
Based on this model it is suggested that the maximum theoretical % crystallinity of the part is that of the powder used and so by measuring the % crystallinity of the powder used, a 'crystallinity potential' can be determined. Such a model of the crystallisation must be considered alongside other SLS factors to be of use. For example, an extremely low degree of particle melt where the particles are only melted sufficiently enough to join by point contact would result in a relatively high total % crystallinity however this part would be highly porous and presumably quite weak. Potential benefits of high % crystallinity have to be considered along with the potential for inadequate consolidation.
Many factors invariably affect crystallisation (notably including cooling rates and nucleation behaviour) however the above described phenomenon is suggested as a crucial factor in determining properties of SLS processed material. Further work would be required to analyse the roles of different factors, such as those mentioned above.

9.5 Quantification of DPM by DSC

Section 9.1 and Section 9.2 showed that varied energy input due to build parameters affects DPM (as observed by optical microscopy), mechanical properties (EaB and tensile strength), and DSC readings (% crystallinity and Core Peak Height). Section 9.4 presented a theory to explain how DPM affects % crystallinity and Core Peak Height. DSC % crystallinity and Core Peak Height therefore theoretically can be used to measure DPM. Section 9.3 showed that DSC % crystallinity and Core Peak Height correlate strongly with mechanical properties (EaB and tensile strength). Since DSC % crystallinity and Core Peak Height theoretically measure DPM and also correlate strongly with mechanical properties it can be stated that ‘DPM, as measured by DSC, correlates with mechanical properties’. This validates the principal hypothesis of this investigation given in Section 7.5 that:

“DSC can be used to quantify variability in the degree that particles melt in SLS processed material’. This ‘degree of particle melt’ (DPM) as measured by DSC should correlate with mechanical properties including EaB.”

9.6 Double phase/single phase transition and the nature of crystallinity in SLS

As shown in Chapter 6, for parts built with varied post build cooling rate, higher EaB (and lower % crystallinity) was associated with lower tensile strength whereas for parts built with different build parameters higher EaB (and lower % crystallinity) correlated with higher tensile strength. This increase in tensile strength with increased EaB and lower % crystallinity is unusual behaviour. Figure 36 presented in section 6.1 showed how reduced % crystallinity normally reduces tensile strength. Lower % crystallinity is the actual cause of the changed properties.
The results of this investigation show that, in SLS, increased particle melt causes higher EaB and higher tensile strength which correlates with lower % crystallinity. This unusual behaviour may relate to the presence of un-melted cores. Figure 121 - Figure 126 show EaB, tensile strength and E-modulus plotted against % crystallinity and Core Peak Height. The X axes for these charts are in reverse order to show DPM increasing from left to right. Figure 121 - Figure 126 show the same data points as Figure 112 - Figure 117 but indicate those data points where cores were present (double phase) and those where no cores were present (single phase) which were the data points for Fill Scan Count - High. Independent trend lines are plotted for each (red). The blue dashed line does not represent the actual boundary between the double phase and single phase regions. The actual boundary could lie anywhere between the last data point in the double phase region and the first data point in the single phase region. Therefore for each region the trend line is extrapolated into the neighbouring region. These charts show a striking difference in mechanical properties between the double phase material (cores) and single phase material (no cores) which is subsequently discussed.

Figure 121 - Figure 123 show mechanical properties plotted against % crystallinity. Figure 121 (EaB) shows no major change for the single phase specimens except possibly for an upwards shift of the trend line with no major change in gradient.
Figure 121 Double phase / single phase transition for % crystallinity, EaB

Figure 122 (tensile strength) shows an apparent instantaneous tipping point at the transition from double phase to single phase specimens where the gradient changes from negative to positive (in real terms since the x-axis is in reverse order).
Figure 123 (E-modulus) showed no discernable trend except that the data point for Fill Scan Count - High (3) (which is single phase and received the highest energy input of all specimens) had the lowest E-modulus value by a considerable amount. Also while the standard deviation of most other specimens for E-modulus was comparably large, that for Fill Scan Count - High (3) was significantly smaller.

Figure 123 Double phase / single phase transition for % crystallinity, E-modulus

Figure 124 - Figure 126 show mechanical properties plotted against Core Peak Height. As would be expected, given the relationship between % crystallinity and Core Peak Height, the charts for Core Peak Height show similar patterns as those for % crystallinity. Figure 124 (EaB) shows little change for the double phase specimens except for a possible shift upwards as also observed in Figure 121 for % crystallinity and EaB. Similar to Figure 122, Figure 125 (tensile strength) also shows an apparent tipping point at the transition from double-phase to single phase specimens where the gradient changes from negative to positive. However this may potentially be a gradual change since a third order polynomial trend line appears to fit the double phase data points well and the extrapolated part of this line passes through the first of the single phase data points even though it has a relatively small spread. More data points would be required to prove this, as discussed later in Chapter 11. Since the
mechanical property values are the same, the Fill Scan Count – High (3) data point in Figure 126 (E-modulus) automatically had the same lowest E-modulus and standard deviation as in Figure 123.

Figure 124 Double phase / single phase transition for Core Peak Height, EaB

Figure 125 Double phase / single phase transition for Core Peak Height, tensile strength
The major observations from Figure 121 - Figure 126 considered unusual in typical polymer processing were:

- Increasing strength and EaB with decreasing % crystallinity for most data points.
- Sharp change in trend of increasing strength to decreasing strength at double phase/single phase transition.
- Lowest E-modulus (and low associated standard deviation) for single phase data point.

Decreasing % crystallinity usually results in decreased tensile strength which is not the case for double phase material (cores). Section 9.4.2 described why % crystallinity reduces with increased energy input and DPM. Since the % crystallinity itself is determined by the numerical fraction of melted core rather than levels of crystallisation of the bulk material, its effect on material properties may have to be considered secondary to and dependant on DPM. DPM would therefore be considered responsible for levels of % crystallinity and mechanical properties which then correlate with each other as a result of this common dependency rather than an actual dependency on each other. In other words it is mechanism/s associated with
DPM other than the total % crystallinity associated with DPM causing the unusual trend of increasing tensile strength.

Although the actual mechanism is not determined, and beyond the remit of this investigation, it is possible that the presence of particle cores hinders tensile strength and so the reduction in core size (through increased DPM) results in increased tensile strength. Additionally, increased energy input and DPM may affect the nature of particle consolidation in a manner that improves the tensile strength. This analysis of the nature of crystallinity and the double phase / single phase transition lead to specific recommendations for further work detailed later in Section 11.2.
10 Conclusions

10.1 Summary of conclusions

The title of this thesis is 'Investigation into Crystallinity and Degree of Particle Melt in Selective Laser Sintering'. Crystallinity relates to and determines mechanical properties in traditionally processed polymers. The nature of crystallinity in SLS processed Nylon-12 has been examined in this study and shown to be fundamentally different to that of traditionally processed polymers. Rather than depending primarily upon crystallisation factors such as cooling rate, it was shown to depend on the degree of particle melt (DPM). DPM was shown to be quantifiable by DSC measurements (by the % crystallinity and Core Peak Height) and distinct relationships between the quantified DPM and mechanical properties were found.

With regard to traditionally processed polymers, one would describe the effects of processing characteristics (such as machine configuration) on % crystallinity and then the effects of % crystallinity on mechanical properties. This study has shown that in SLS it is more appropriate to describe the effects of processing characteristics on DPM and then the effects of DPM on mechanical properties (at least partly due to the effects of DPM on % crystallinity). These alternative sequences of cause and effect are illustrated in Figure 127. Whether it would be more appropriate to sequentially describe the effects of DPM on % crystallinity and then the effects of % crystallinity on mechanical properties or to describe the effects of DPM and % crystallinity on mechanical properties concurrently could be addressed in further study.

![Figure 127 Cause and effect in traditional polymer processing and SLS](image)

It is important to differentiate between the % crystallinity as a reading from a DSC trace exclusively to quantify DPM, and the actual crystallinity itself and its effects on material properties.
10.2 Specific conclusions

10.2.1 Post build cooling

1. Temperature logging showed that parts do not cool below the crystallisation onset temperature during build showing that control of post build cooling rate can indeed directly affect part crystallisation.

2. Increased cooling rate in the post build stage of the SLS process is feasible and results in a marked increase in EaB.

3. It seems unlikely that EaB of SLS parts can be increased by an order of magnitude via changes in cooling rate.

4. Percentage crystallinity did not correlate significantly with cooling rate and mechanical properties.

10.2.2 Degree of particle melt

1. Un-melted particle cores and the surrounding material which has melted and crystallised have been shown to relate to separate peaks on a DSC trace. The peaks relate to the total volume fraction of the different phases. ‘Degree of particle melt’ (DPM) was introduced as the term to describe the amount that particles have melted. The context of the DPM as a ‘missing link’ between build characteristics and mechanical properties of parts produced is illustrated in Figure 128.

2. DPM was varied in numerous specimens by varying machine parameters. Variation of the DPM was verified by optical microscopy.

3. Total % crystallinity and the height of the DSC peak associated with the unmelted particle core (Core Peak Height) were used to quantify DPM.

4. Quantified DPM (% crystallinity and Core Peak Height) correlated strongly with changes to mechanical properties.
10.2.3 Nature of crystallinity in SLS

1. Reduction in total % crystallinity with increasing DPM was associated with a 'crystallinity potential' which is the maximum theoretical % crystallinity based on the % crystallinity of the un-melted powder. The % crystallinity decreases as the ratio of core to background material in a specimen decreases.

2. Material was identified as 'double phase' and 'single phase' depending on whether it consisted of un-melted cores and melted and crystallised material (double phase) or entirely melted and crystallised material (single phase). This characteristic of a material resulted in contrasting trends between DPM and mechanical properties. For double phase material, increasing energy input and DPM resulted in increasing EaB and increasing tensile strength with no apparent trend in E-modulus. For single phase material, increasing energy input resulted in increasing EaB but decreasing tensile strength and decreasing E-modulus.

10.2.4 Practical implications of research findings

1. It was shown that post build part cool down procedure can theoretically effect part properties and was seen to do so. The post build procedure could therefore become a controlled aspect of the build procedure to improve reproducibility of properties.

2. The research findings could help with the development of new materials. The understanding of the importance of DPM and the fact that it can be easily quantified means that small scale laboratory tests could be performed at the early stage of material development focussing on the effects of various factors on DPM.

3. The factors mentioned in 2 above could relate to energy input but could also relate to other aspects such as particle size, particle geometry and particle crystallinity for which it may be far more practical and economical to prepare or obtain small amounts (in the order of grams) rather than larger amounts for building (in the order of kilograms).

4. The understanding of DPM could help with the development of SLS machines. The effect of energy input on mechanical properties due to DPM means that the development of machines should focus on achieving controlled DPM. Since DPM can be easily quantified, experimental rigs could be constructed to test effects of various factors (e.g. machine insulation) on DPM.
before redesigning or modifying existing machines or even constructing new entire machine prototypes.

5. As with 4 above, the understanding of DPM could help with the development of build strategies used in SLS. Factors such as laser scan path, laser parameters (e.g. power), layer thickness and powder heating could all be developed with a focus on DPM.

6. Further to 5 above, the build strategy (particularly laser parameters) could be adapted to purposefully vary the DPM throughout parts. This would effectively result in a Functionally Graded Material (FGM). FGMs have been described as a ‘form of composite where the properties change gradually with position’ and that ‘the change in the property of the material is caused by a position-dependent chemical composition, microstructure or atomic order’ [Erasenthiran and Beal, 2006]. With regard to varied DPM it is the microstructure that would cause the change in properties.

7. The above points describe the potential importance of DPM for development of materials and process development. DPM could therefore be used to develop new models of the SLS process which would model the process of particle melt as a function of energy input.

8. Measurement of DPM could be implemented into quality control procedures. Parts that have failed within their intended operating conditions could be analysed for DPM at or near the point of failure to determine if this was the responsible factor. Machine setup could then be initially investigated before attempting to redesign a part.

9. Coupons for measuring DPM could be placed within the build volume as is sometimes performed with tensile dog bone specimens to check repeatability of builds. This could be advantageous over the use of dog bones since the parts could be much smaller and could therefore be dispersed throughout the build volume. Automated DSC specimen handling robots are typically offered for use with DSC machines which would result in more efficient testing.
11 Recommendations for further study

This chapter is comprised of two sections. Section 11.1 lists general recommendations for further study and section 11.2 presents further analysis which leads to a specific hypothesis for further study.

11.1 General recommendations

1. Work should be directed towards characterising the individual phases present in SLS parts more precisely. DSC could be used with variation of parameters such as heating rate and sample mass to attempt to separate the melt peaks. Modulated DSC could also possibly help in this respect due to the removal of any potential recrystallisation activity during melting. Other methods could also be used such as X-ray diffraction. X-ray diffraction would confirm the type of crystal forms present in the different phases (α and/or γ).

2. Unusually high peak melt temperatures were observed for SLS Nylon-12 material so it would be interesting to analyse the crystal structure of this material in more depth using techniques such as X-ray diffraction.

3. In process cooling rates and crystallisation should be investigated to see if these can be controlled and whether material properties are affected. Sintering is a time dependent process so factors affecting melting and crystallisation time during the build process could be critical. Such factors include the speed of the laser beam, the roller speed and more generally the entire individual layer build time.

4. The double phase/single phase transition should be investigated by gradually varying one parameter only e.g. laser power. A higher number of data points would show the nature of the transition i.e. whether it is an instantaneous tipping point or a more gradual change.

5. DPM should be varied by looking at variations to individual parameters (as in 4 above) so that the specific influence of different parameters on DPM can be determined.

6. Numerous factors affect mechanical properties including porosity. Further work is required to understand further the relative influence of the various factors including DPM and porosity.
7. It would be useful to employ image analysis techniques to quantify the amount of visible cores in the micrographs obtained. These results could be compared against DPM values as described in this thesis.

8. The model shown in Figure 120 (describing the total % crystallinity as the sum of the % crystallinities of the two phases) could be used to predict the total % volume of cores using micrographs and tested using DSC % crystallinity values.

11.2 Specific hypothesis for further work

Of particular interest is the change in trends at the double phase/single phase transition described in the last discussion section of this thesis, section 9.6. The presence of cores will affect the nucleation and crystallisation behaviour of the material resulting in variations to microstructure. Differences in microstructure can be directly responsible for variations in mechanical properties.

Figure 129 illustrates the possible difference between the microstructure of double phase and single phase material, even when the cores in the double phase material are relatively small.

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![Figure 129 Crystallisation of double-phase and single phase material](image-url)

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162
For both materials in Figure 129 the melting and crystallisation are described in 4 stages. Stage 1 shows the un-melted powder which is the same for both materials. Stage 2 shows the melted particles at the instant before crystallisation commences. The double phase material contains un-melted particle cores surrounded by the melt while the single-phase has received extra energy and so consists only of melted material.

Stage 3 shows nucleation and crystallisation. For the double phase material nucleation is heterogeneous with the surface of the particle cores as the predominant nuclei. For the single phase material, in the absence of particle cores which act as predominant nucleation sites, nuclei may consist of a combination of, for example, residual nuclei from the fully molten particles, additives and dust, with none dominating in the manner of the particle cores. Depending on the degree of melt and the melt’s composition it is feasible that homogenous nucleation (that can be observed in, for example, injection moulding) may also occur. The difference between the specimens as a result of the different nucleation behaviour is that for the double phase material the material crystallises easily from the particle cores so that crystallisation from other nuclei (as listed for single phase material) is inhibited. Due to the volume occupied by the particle cores, primary crystallisation completes faster which also reduces the chance of other nucleation occurring. For the single phase material nucleation occurs from a higher number of nuclei (considering each particle core of the double phase material as one nucleus).

Stage 4 shows the crystallised material. The microstructure of the double phase material consists of relatively large spherulites containing particle cores. The microstructure of the single phase material consists of smaller spherulites, in larger numbers, without particle cores.

The behaviour illustrated in Figure 129 would depend upon the crystallisation rate of the molten Nylon-12. The described behaviour would be more likely with relatively slower crystallisation rates whereas it may be less pronounced with faster cooling rates. Future work investigating this would therefore have to consider the crystallisation rates involved. The crystallisation rate of a given material varies with temperature [Michaeli, 1995] so experiments involving DSC using isothermal
crystallisation at different temperatures could be performed and the resulting microstructure compared.

Figure 130 and Figure 131 show micrographs of specimens built with Fill Laser Power – High (13.5W) and Fill Scan Count - High (3) respectively. Figure 130 (Fill Laser Power – High) is the specimen which received the highest energy input while still maintaining a double phase composition. Figure 131 (Fill Scan Count - High) received the highest energy input of all specimens and is single phase. Half of each micrograph has particle cores annotated in green and spherulite boundaries annotated blue. The annotation is not complete as it is not always possible to differentiate optically between the different regions/phases.

Figure 130 shows large spherulites crystallised from the un-melted particle cores. Figure 131 shows no cores and a larger number of smaller spherulites which supports the concept of the crystallisation behaviour illustrated in Figure 129. This shift in the nature of the microstructure with the transition from double-phase to single-phase material may be responsible for the observed shift in trend of changing tensile properties at the double phase / single phase transition described previously in Section 9.6.
Figure 130 Microstructure for Fill Laser Power - High (double phase)

Figure 131 Microstructure for Fill Scan Count - High (single phase)
The low E-modulus found with the single phase material, or rather the high E-modulus associated with double phase material could be attributed to high total % crystallinity but also possibly to typical large-particle composite behaviour. A typical large-particle composite contains a particulate phase (filler) which is harder and stiffer than the matrix. These are generally different materials such as the use of glass beads with various Nylons. These particles restrain movement of the matrix phase surrounding each particle thus causing increased stiffness and E-modulus [Callister, 2003]. The SLS material analysed in this investigation is chemically not a different material but considering the un-melted powder's significantly higher % crystallinity (which would theoretically result in increased stiffness and hardness) it could be considered analogous to a large particle composite as described above. This would explain why the transition to the single phase state (i.e. no cores) results in reduced E-modulus.

A hypothesis for further study is therefore that single phase material behaves as a traditionally processed polymer whereas double phase material behaves as a particle filled composite and must therefore be treated as a quasi-composite, obeying the associated laws of composite theory.
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171


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13 Appendices
Appendix 1. Blackbody calibration of pyrometer

The pyrometers used in the 3D Systems Vanguard SLS machine are not calibrated to give correct values and these values can also ‘drift’ over time. However, the IR sensors can be calibrated using a black body source, as described in the 2004 SLSSLAUG Conference presentation ‘Calibration of Sinterstation IR sensor’ [Allison and Alexander, 2004]. This is shown in Figure 132. The blackbody source is essentially a hotplate with high temperature epoxy coating. This is placed on the part piston in the SLS machine level with the normal powder bed surface. A thermocouple is attached to measure close to the target region of the pyrometer. The hotplate is set to different temperatures and the temperatures from the pyrometer and thermocouple recorded and plotted against each other on a characteristic curve as shown in Figure 133. This curve and the equation of the line is used to correct the readings from the IR sensors.

Figure 132 Blackbody calibration of pyrometer
Figure 133 Pyrometer characteristic curve

\[ y = 1.4468x - 29.579 \]
Appendix 2. Thermocouple calibration

The thermocouples used were K-type wire with exposed tips for fast response. These were fabricated and then checked at 3 temperatures against another UKAS laboratory calibrated thermocouple. The required working range was between approximately 20°C and 200°C and so the thermocouples were checked at approximately 0, 100 and 250°C. For additional certainty and to confirm correct operation of the data logger the 100 °C test was performed to check readings against the boiling point of water.

Figure 134 shows the thermocouples being calibrated at the boiling point of distilled water. Distilled water was placed in a conical beaker. The thermocouples were attached together so that their tips were located together. They were placed in the beaker 2cm from the surface of the water. The entrance to the beaker was then packed with cotton wool. As the water boiled the thermocouples measured the temperature of the steam as this should be exactly 100°C. Figure 135 shows that once boiling was achieved all temperatures were well within +/- 0.5 deg of 100°C and so no correction was required. The maximum deviation from the laboratory calibrated thermocouple was 0.5°C which is acceptable for the purpose of this investigation.

Figure 134 Thermocouple calibration at boiling point
Figure 136 shows the thermocouples being checked in crushed ice at approximately 0°C. This method requires measuring water at the point of melting. The conditions of the experiment did not provide for a dependable source at 0°C however the results, shown in Figure 137, do show again that at this temperature the maximum deviation from the laboratory calibrated thermocouple is under 0.5°C.
The thermocouples were finally tested against the laboratory calibrated thermocouple in a conventional oven at approximately 250°C as shown in Figure 138. Again the maximum deviation from the laboratory calibrated thermocouple was under 0.5°C and so no correction was required.
Appendix 3. Preparatory schematic cool down curves

Figure 139 Preparatory schematic cool down curves
Appendix 4. Cool down profiles used to calculate cooling rates

Figure 140 Cool down profile for T1 IR sensor, powder surface

Figure 141 Cool down profile for T3 thermocouple, specimen centre
Figure 142 Cool down profile for T4 thermocouple, specimen centre

Figure 143 Cool down profile for T6 thermocouple, specimen centre
Appendix 5. Original stress strain plots for Chapter 6
Figure 144 Original stress-strain plots for Ti, tested at 1mm/min.
Figure 145 Original stress-strain plots for T2, tested at 1mm/min
Figure 146 Original stress-strain plots for T3, tested at 1mm/min
Figure 147 Original stress-strain plots for T4, tested at 1mm/min
Figure 148 Original stress-strain plots for T5, tested at 1mm/min
Figure 149 Original stress-strain plots for T6, tested at 1mm/min
Figure 150 Original stress-strain plots for T7, tested at 1mm/min
Figure 151 Original stress-strain plots for T1, tested at 5mm/min
Figure 152 Original stress-strain plots for T2, tested at 5mm/min
Figure 153 Original stress-strain plots for T3, tested at 5mm/min
Figure 154 Original stress-strain plots for T4, tested at 5mm/min
Figure 155 Original stress-strain plots for T5, tested at 5mm/min
Figure 156: Original stress-strain plots for T6, tested at 5mm/min

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Figure 157 Original stress-strain plots for T7, tested at 5mm/min
Appendix 6. Published Journal paper
Effects of processing on microstructure and properties of SLS Nylon 12

H. Zarringhalam* , N. Hopkinson , N.F. Kamperman, J.J. de Vlieger

* Rapid Manufacturing Research Group, School of Mechanical and Manufacturing Engineering, Wolfson Building, Loughborough University, Loughborough LE11 3TU, United Kingdom
b TNO Science and Industry, De Rondom 1, P.O. Box 6235, 5600 HE Eindhoven, The Netherlands

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Abstract

There currently exists the requirement to improve reproducibility and mechanical properties of SLS Nylon parts for rapid manufacturing (RM). In order to achieve this, further fundamental research is needed and this paper addresses this need by investigating effects of potential sources of the lack of reproducibility and reports effects in relation to crystal structure, microstructure, chemical structure (molecular weight) and mechanical properties. Different crystal forms were identified and related to the unmolten particle cores and the melted/crystallised regions of the microstructure. The melt point of the γ-form varied depending on processing conditions. Observable differences were also present when comparing the microstructure of the parts. Molecular weight of parts was significantly higher than virgin powder but used powder also showed an increase in molecular weight. This was related to improved elongation at break of parts built from the used powder, consistent with previous studies. Tensile strength showed some increase with machine parameters selected for improved strength but Young’s modulus values were broadly similar.

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Keywords: Selective laser sintering; Nylon 12; Crystal structure; Microstructure; Molecular weight

1. Introduction

Rapid manufacturing (RM) is a family of technologies where products are made in an additive way directly from 3D CAD data, without the need for tooling. The technology was originally known as rapid prototyping (RP) since the properties of parts produced were generally only suitable for prototype parts. However, the technology has evolved to the point where RM is a viable manufacturing technique in numerous application areas [1,2].

Selective laser sintering (SLS) is a commonly used technique in RM [3] and has proved to be suitable for various applications including the creation of bespoke hearing aids [4] and parts for Formula 1 racing cars [5]. The aerospace industry in particular has recognised the advantages of SLS for RM where it is currently the most widely used technique [6]. Some aircraft already have numerous SLS production parts as standard [3,7] however the applications are still limited, partly due to the mechanical properties of parts produced.

Selective laser sintering produces parts by using a laser to selectively sinter individual layers of a material in a powder form (polymers, metals, ceramics). SLS systems are currently available commercially from two different manufacturers which are 3D Systems of the United States (previously DTM) and EOS of Germany. Prior to build a CAD model must be created and then processed which includes ‘slicing’ the CAD model into 0.1-0.15 mm thick 2D layers. After this the data is sent to the machine for part building which is described in Table I. Following build the part is removed from the unsintered powder and loose particles brushed and/or sprayed off gently using compressed air.

Semi-crystalline polymers (predominantly Nylon 12 and 11) can be successfully sintered with superior mechanical properties than amorphous polymers [8,9]. However, shrinkage during crystallisation hinders production of accurate parts [10]. For this reason it is essential that for materials to be processed by SLS the melt temperature be considerably higher than the crystallisation temperature so that crystallisation can be delayed and reduced during the build process [11] to allow new layers to bond to previous layers with a more homogenous microstructure. A high enthalpy of fusion is also preferable to prevent melting of powder particles local to the particles targeted by the laser due to conduction of heat. In addition, during laser sintering, a narrow
melt temperature range in combination with a low melt viscosity is required to achieve the necessary level of fluidity very quickly without inputting excess energy [11].

Molecular weight is well known to be a critical characteristic when describing polymers in general [12] and the weight average molecular weight ($M_w$) directly affects the melt viscosity [10]. The melt flow procedure is used to characterise melt viscosity by the melt flow index (MFI). Low MFI is associated with high melt viscosity and high molecular weight. Gornet et al. [13] and Shi et al. [10] investigated the effects of powder melt viscosity and related lower MFI (and therefore higher melt viscosity and $M_w$) to improved mechanical properties particularly elongation at break (EaB). It is standard practice in industry to blend virgin powder with used to maintain acceptable part properties which deteriorate with continued use of used powder [13]. The thermal load during the build process is presumed responsible for the increase in molecular weight and thus increased melt viscosity. Virgin powder is normally not used on its own in order to reduce associated costs. For RM consistency in mechanical properties is particularly important and so it is important to tackle the existing potential for lack of reproducibility of properties.

Nylon 12, as with other aliphatic Nylons, has been widely shown to form stable crystal structures of either the α- or γ-form [14,15]. For Nylon 12 the γ-form, which is more stable, always melts at a higher temperature than the α-form [16]. It has been demonstrated that under the majority of processing condition the liquid phase will crystallise to the γ-form, which is therefore the most commonly found crystal form in Nylon 12. However, certain conditions do result in the α-form. These have been reported as solution casting (at atmospheric or reduced pressure, below 90 °C) [16], drawing just below the melt point and high pressure crystallisation [21]. It has been demonstrated that the proportions of α- and γ-form can be altered (from 0% to 100% for each) by controlling the thermal history [16,17]. Different variations of the basic α- and γ-crystal forms have been created depending on processing conditions and these can be transformed from one to another by numerous methods depending from which and to which crystal form the material will be transformed [18–21].

Studies reporting melting points for the γ-form were reviewed by Aharoni [15] and values ranged from 172 to 185 °C with most data points close to 179 °C. The melt point of the less common α-form has been reported as ca. 173 °C [16]. SLS Nylon is obtained by dissolving polyamide-12 in ethanol under pressure at elevated temperatures followed by slow crystallization thereby forming crystals with a relatively high melting point of ca. 190 °C and a relatively high heat of melting [9,11]. The crystal structure of SLS Nylon powder or parts has not been reported on however the slow cooling rate during production would likely result in the virgin powder being comprised of relatively large crystals. The production process for SLS Nylon 12 does not exactly meet the requirements for formation of a crystal form and the high melt temperatures measured indicate the γ-form.

Published information relating to alternative methods for manufacture of SLS powder describes how standard Nylon 12 can be modified to increase the melt temperature with insignificant increase to the crystallisation temperature [22]. The process described involves heating powder or granules of the material in steam for extended time duration (up to 100 h). It is claimed that this increases the melt temperature by allowing the molecular chains to be rearranged. It is known that 'even numbered' nylons such as Nylon 12 can only achieve full inter-molecular hydrogen bonding and thus crystallisation by the molecular chains aligning in an anti-parallel arrangement [14] and it is thought that this is how the chains are 'rearranged'.

Young's modulus and tensile strength of selective laser sintered Nylon 12 are comparable with values for standard injection moulded samples [23]. However EaB (which indicates ductility) is at least an order of magnitude lower. Gornet et al. [13] demonstrated how mechanical properties can vary between different machines and even for the same machine in different builds. Saleh et al. [24] and Gibson and Doungpin [25] showed considerable variability for different part orientation and parts built in different locations in the build volume within the same build. Tong and Childs [26] investigated the effect of powder bed temperature (ambient build powder surface temperature) on density and showed that small variations in temperature have a marked effect on part density which can affect mechanical properties.

The SLS machine manufacturers supply powder and their key published mechanical (and other) properties, for their respective SLS Nylon 12 powders, are summarised in Table 2. Since the machine parameters used to generate the data are not given by both manufacturers and because the data is generated using different standards, this cannot be compared directly. It should therefore only be used to roughly gauge the potential of SLS Nylon 12. Where manufactures quoted a range of values, the average has been given.

From the application of SLS as a production process, the requirement to improve reproducibility and mechanical properties of SLS Nylon parts for RM exists. In order to achieve this, further fundamental knowledge of the underlying mechanisms is needed. This paper addresses this need by investigating effects

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Manufacturers' published materials properties for SLS Nylon 12 [27,28]</th>
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<tbody>
<tr>
<td>JDS Systems</td>
<td>EOS</td>
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<td>Tensile strength (MPa)</td>
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<td>Tensile elongation at break (%)</td>
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<td>Part melting point (°C)</td>
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of build procedure, parameters and powder blend and reports effects in relation to crystal structure, microstructure, chemical structure (molecular weight) and mechanical properties.

2. Methodology

Different specimens of SLS Nylon 12 powder and parts were analysed. Powders with different thermal histories were analysed and parts were produced from these. These are summarised in Table 3 and explained further in Section 2.1. Parts and powder were obtained from TNO Science and Industry and the Rapid Manufacturing Research Group, Loughborough University. These are referred to as TNO and Lboro, respectively. Different machines were used which were already configured with contrasting parameters. This was intended to provide a wider range of data. Each machine was used with SLS Nylon 12 powder supplied by the respective machine manufacturers. The differences are explained further in Section 2.2.

The powder specimens were analysed for molecular weight distribution by gel permeation chromatography (GPC), thermal properties and crystal structure by differential scanning calorimetry (DSC), and microstructure by optical microscopy. Part specimens were also tensile tested for mechanical properties.

2.1. Preparation of powder

Powder was prepared in different ways prior to building, as follows:
1. Virgin: Powder that has never been processed in a laser sintering machine.
2. Used: Part cake and overflow powder that has been through a complete SLS run.
3. Refreshed: A mix of 67% used and 33% virgin powder.

2.2. Part production

Standard tensile test specimens (as shown in Fig. 1) were produced according to ISO 527-2. The parameters of the TNO machine were set for optimized mechanical properties while those for the Lboro machine were configured for optimized accuracy which was anticipated to give reduced mechanical properties. Both machines can be configured for either improved mechanical properties or improved accuracy and so the choice of configuration for this research was simply based upon the existing configurations already in use by the different operators. The powder bed temperature of the Lboro machine was adjusted for each type of powder while the powder bed temperature of the TNO machine was kept constant for all powder types. Differences between the two different machines and their particular build setups are listed in Table 4. In order to ensure thermally stable conditions a base layer of two centimetres and a top layer of one centimetre were used for each run. Parts were built flat, laid parallel to the machine x-axis, at fixed places in the middle of the build area as shown in Fig. 1.

2.3. Molecular weight

The molecular weight was determined by GPC by drying 25 mg samples at 120 °C for 1 h. The samples were then dissolved at room temperature in 5 ml chloroform (stabilized with amylene) and 0.5 ml trifluoroacetic acid anhydride (TFA). After 2 h dissolving the solution was diluted with 20 ml chloroform. This solution was filtered without heating and analysed using two Waters™ Styrage™ HT6E 7.8 mm × 300 mm columns in combination with a differential refractive index detector (Waters™ 410) and a tuneable absorbance detector (Waters™ 486) at wavelength 264 nm. Polystyrene was used as the reference material.

Table 3: Specimen history

<table>
<thead>
<tr>
<th>Source</th>
<th>Specifics</th>
<th>Specimens</th>
<th>Powder</th>
<th>Parts from</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNO</td>
<td>EOS PA2200 powder, EOS P380 machine (tuned for mechanical properties)</td>
<td>Virgin</td>
<td>Virgin</td>
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<tr>
<td>Lboro</td>
<td>3D Systems Duraform PA powder, 3D Systems Vanguard machine (tuned for accuracy)</td>
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<td>Used</td>
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<td></td>
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<td>Refreshed</td>
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Table 4: Machine differences

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<th>Mechanical properties</th>
<th>Accuracy</th>
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</thead>
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<td>3D Systems Vantage</td>
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<tr>
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<td>PA2200 Nylon 12</td>
<td>Duraform PA Nylon 12</td>
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<td>Roller</td>
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<tr>
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<td>Heated (+100°C)</td>
</tr>
<tr>
<td>Build platform</td>
<td>Heated</td>
<td>Unheated</td>
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<td>Laser power (fill)</td>
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<td>Laser power (outline)</td>
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<tr>
<td>Scan spacing</td>
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</table>
2.4. Thermal properties

Differential scanning calorimetry (DSC) was used to determine thermal properties in order to study melting and crystallization behaviour and to identify crystal forms. Samples of mass ca. 10 mg were analysed in a "Thermal Analysis" DSC machine under nitrogen flow. Samples were heated from room temperature at 10 °C/min to 200 °C and then immediately cooled at 10 °C/min.

2.5. Microstructure

The microstructure of the processed materials was analyzed via optical microscopy. Samples of 3–5 μm thickness were cut at room temperature by microtome. Images were taken in bright field polarized illumination.

2.6. Mechanical properties

Tensile data was recorded using a clip-on extensometer. Each tensile test was executed with five individual specimens and results for tensile elongation at break, ultimate tensile strength and Young's modulus were recorded.

3. Results and discussion

3.1. Powder

3.1.1. Virgin powder: comparison of Lboro and TNO powder by thermal analysis and molecular weight analysis

Fig. 2 shows DSC results for Lboro and TNO virgin powder. Both show relatively sharp single endotherms with melting peaks at 189 ºC for TNO virgin powder and 188 ºC for Lboro virgin powder. These correspond with known values for virgin powder [29,11] however they are at least 3 ºC higher than the previously reported values for crystal forms of non-SLS processed Nylon 12 (172–185 ºC).

As mentioned previously, the conditions in the production of SLS Nylon 12 powder differ from those required to form α-form crystal structure and this suggests that the endotherms obtained from the virgin powder relate to the common γ-form. On the basis that prolonged molecular mobility increases the melt temperature it can therefore be inferred that the endotherms relate to the γ-form with far larger and more perfect crystal structure (due to increased hydrogen bonding) than previously analysed Nylon 12 specimens. Additionally, Ishikawa and Nagai [16] demonstrated that a single endotherm in a DSC test on Nylon 12 is only characteristic of a sample containing 100% γ crystal form since samples consisting of 100% α crystal form invariably develop a second melt peak during the DSC run due to recrystallisation of a portion of the specimen to the γ crystal form. The test parameters were the same as those used in the present investigation supporting the view that the crystal structure present in virgin SLS Nylon 12 material is of the γ crystal form.

Fig. 3 shows GPC results for Lboro and TNO virgin powder. The relative weight average molecular weight is 90,000 g/mol for Lboro virgin powder and 70,000 g/mol for TNO virgin powder. The polydispersity index is 2.26 for Lboro virgin powder and 2.34 for TNO virgin powder. The small peaks on the positive tail of each curve are possibly characteristic of anti-oxidants, which are known to be blended with the virgin Nylon 12 powder from EOS [28] and therefore presumed to be the same with 3D Systems supplied powder. Higher molecular weight of the Lboro powder could theoretically hinder processing and thus properties [30] however the difference is too small to be significant.

3.1.2. Sub-melt temperature heated powder: comparison of refreshed and virgin powder by thermal analysis and molecular weight analysis

Fig. 4 shows DSC results for virgin and refreshed TNO powder. The refreshed powder shows a very slight increase in melt temperature (<1 ºC) indicating more perfect crystals due to crystalline reorganisation. Crystallinity of the virgin and refreshed
Powder was measured as 55% and 51%, respectively with melt enthalpies of 115.7 and 106.6 J/g, respectively. The melt enthalpy for 100% crystalline material was taken as 209.3 J/g [31]. The slight decrease in crystallinity with the refreshed powder instead of an increase supports the view that the increase in melt temperature is due to crystalline rearrangement rather than increased crystallinity. The endotherm for the refreshed powder shows a slight 'bulge' to its left indicative of a polymorph likely due to the 1/3 virgin fraction of the blend.

Fig. 5 shows GPC results for virgin and used TNO powder. The relative weight average molecular weight is 170,000 g/mol for used TNO powder and 70,000 g/mol for virgin TNO powder. The polydispersity index is 2.84 for used TNO powder and 2.34 for virgin TNO powder. This increase in average molecular weight and molecular weight distribution indicates that polymerization occurs in the solid state powder. This may be one of the mechanisms leading to modified sintering characteristics with the reuse of SILS powder. For example, reduced molecular motion due to increased molecular weight could hinder crystallisation [18]. Since the objective of this analysis was to determine effects of heating the powder without melting, only the TNO material was analysed. This was because it was expected that any change would be more pronounced than with the Lboro material due to the increased thermal load on the material.

3.2. Parts

3.2.1. Optical analysis of part microstructure

Fig. 6 shows a micrograph of the cross-section of a Lboro part with annotations on the right hand side. The annotated features are also found on TNO specimens. The top of the image shows the edge of the part to which unmolten particles have fused. Moeskops et al. [32] have demonstrated how the part microstructure is composed of particle cores surrounded by spherulites. These cores were described as the unmolten central regions of particles occurring when particles do not receive enough heat to fully melt. Fig. 6 shows this and also shows spherulites without cores which formed from particles which were small enough to fully melt. Moeskops et al. [32] stated that the presence of these cores is believed to be critical to the properties and mechanical response of SLS processed materials.

3.2.2. Comparison of virgin powder and parts by thermal analysis and molecular weight analysis

Fig. 7 shows three superimposed sets of DSC results for TNO material. The results are for virgin powder, a part built from the virgin powder and a part built from virgin powder which was exposed twice (a second exposure of the same area prior
to deposition of the next layer) and which therefore received increased energy input. The curve for virgin powder is the same as in Fig. 4 and shows one melt peak at 189 °C. The curve for the normal part shows two peaks, smaller than the single peak for virgin powder. The larger of these two is at 185 °C and the smaller at 190 °C. The curve for the double exposed part only shows one peak which is at 185 °C.

The interpretation of Fig. 7 is that for parts the peaks at 185 °C relate to a poly-crystalline form, arising from the melting and crystallisation of virgin powder. The small peak at 190 °C for the parts represents a reduced total fraction of the initial γ-form of the virgin material and demonstrates a shift of 190-189 °C, similar to that shown in Fig. 4 (comparing virgin and used powder).

Fig. 8 shows a DSC curve for a Lboro part built from virgin powder and an optical image of one particle core with surrounding spherulite. This illustrates the concept that the DSC peak at 190 °C directly represents the unmolten particle core (which is essentially therefore used powder material) and that the surrounding spherulitic region relates to the material which has been melted and then crystallised.

Fig. 9 shows GPC results for TNO virgin powder and a part built from TNO virgin powder. A distinct increase of relative molecular weight and molecular weight distribution due to polymerization is observed as quantified by an increase from 70,000 to 230,000 g/mol weight average molecular weight and an increase from 2.34 to 3.32 for the polydispersity index. This increase in molecular weight with sintering might be desirable since higher molecular weight generally results in improved mechanical properties. Comparing Fig. 9 with Fig. 5 the molecular weight of the used powder falls in between those for virgin powder and the part built from virgin powder due to the nature of the polymerisation (i.e. solid state and liquid state for used powder and part, respectively).

3.2.3. Comparison of Lboro and TNO parts built from virgin powder by thermal analysis and optical microscopy

Fig. 10 shows DSC results for TNO and Lboro parts built from virgin powder. The curve for the TNO part is the same curve for the 'Normal part' in Fig. 7 showing two peaks, one at 185 and a smaller peak at 190 °C. The curve for the Lboro part also shows two peaks, at 189 and 181 °C. Both of the smaller peaks are ca. 1 °C higher than their respective peaks for virgin materials as shown in Fig. 2 demonstrating that the unmolten fraction in the part modifies in a similar manner to how the unmelted virgin powder modifies to its 'used' state. The difference between the larger peaks indicates significant difference in crystal size of the material melted and crystallised for the Lboro and TNO setups. This difference could arise from the different parameters chosen for this study (such as heated/unheated build platform) and/or inherent differences between the machine setup.

Fig. 11 shows microtomed sections of parts built from TNO virgin powder (a), Lboro virgin powder (b) and parts injection moulded from virgin TNO powder (c). Comparing the images for TNO and Lboro virgin material the Lboro specimen shows unmolten cores clearly contrasted against the surrounding material which consists of an evenly distributed spherulitic structure. These cores are also present in the TNO specimen but are less clearly defined. There is a clear step change between the core and the surrounding phase for the Lboro specimen compared with a more continuous change from one to the other for the
TNO specimen. The Lboro specimen also has larger cores and therefore the increased volume fraction of crystals (with a predominant 189 °C melting peak) within the material may also contribute to variations in mechanical properties.

The presence of cores may be inherent to SLS processed material but higher energy input (for example TNO specimen) reduces the core size. A higher 'degree of melting' occurring in the TNO specimen (Fig. 11a) could indicate better fusion/sintering of particles and hence superior mechanical properties. The injection moulded specimen clearly shows no particle cores and a much more even and fine microstructure due to the feedstock being fully melted (and presumably more fluid) and followed by faster cooling.

3.2.4. Mechanical properties

Fig. 12 shows the results for elongation at break (EaB) for parts made with different powders on the different machines. Fig. 12 shows (for both TNO and Lboro parts) a significant increase in EaB (an indicator of ductility) for refreshed and used powder compared with virgin powder. Distinct trends can be observed relating increased EaB to higher proportions of used powder and parameters selected for improved strength. These results match those of previous studies [13].

The increased molecular weight of the used powder may be responsible for the improved ductility since it would directly relate to the molecular weight of the particle cores and may have hindered crystallisation of the surrounding melted and crystallised regions. The increase in EaB of Lboro refreshed parts from Lboro virgin parts is 94% of the virgin-part value. The increase for the TNO parts is only 36%. This may be due to the increased powder bed temperature for Lboro parts due to the adjustment for each powder type. However it could also relate to the larger cores and hence building with more used powder (i.e. refreshed) would have a more significant effect on mechanical properties. To reiterate, the larger the core the greater the significance of the pre-melting powder history (e.g. powder blend). Likewise, the smaller the core (i.e. greater fraction of melted and crystallised region) the greater the significance of build related factors (e.g. build parameters).

Fig. 13 shows the results for ultimate tensile strength of parts made with different powders on the different machines. Fig. 13 indicates a difference in mechanical stress response between parts built from virgin, refreshed and used powder. The variation in ultimate tensile strength between virgin and refreshed material is small however there is a marked increase in tensile strength for used powder. Tensile strength values are higher for the TNO parts reflecting the parameters used (see Table 4).

Fig. 14 shows the results for Young's modulus for parts made with different powders on the different machines. Fig. 14 shows parts from refreshed powder having almost the same Young's modulus as parts from virgin powder for TNO parts but with Lboro parts the parts built with refreshed powder show a lower Young's modulus. Young's modulus values are slightly higher for the TNO parts.
4. Conclusions and recommendations

Materials research in the context of improving reproducibility of properties in SLS was conducted by building parts using different machines, with contrasting build parameters and different powders with varying blends. This study cannot be used to directly compare the two machines since different parameters and powder were used. To compare the machines against each other a study could be performed using identical powder (from the same batch), building parts on each machine using their complete range of parameters, i.e. 'strong parts' and 'accurate parts' could be built on each machine and compared.

Effects of the various factors on the microstructure of SLS parts were analysed. Parameters chosen for improved accuracy built on a 3D Systems machine (Lboro) resulted in well defined unmelted particle cores (virgin material) and parameters chosen for improved mechanical properties built on an EOS machine (TNO) gave a smoother transition between the unmelted particle cores and the melted/crystallised region. These differences may be due to the processing conditions, but could also be affected by inherent thermal conditions unique to each machine or to the specific powder material properties.

The crystal structure of the material was investigated using DSC to identify the crystal forms. Unmelted particle cores were matched to used powder material and have, most likely, the γ crystal form. The melting point was measured between 188 and 190 °C which is higher than commonly reported values for non-SLS processed Nylon 12 indicating particularly large crystals. The melted/crystallised regions were observed with lower melting points (181 and 185 °C) than virgin powder which lie within the known range for the γ-form. Both γ crystal forms were matched to distinct regions within the material’s observable microstructure. The difference between the melting points for the melted/crystallised regions are presumably due to different thermal processing conditions. Slower cooling for the TNO parts (due to parameters and/or inherent machine behaviour) likely resulted in larger crystals hence the higher melt point. Analysis by X-ray diffraction would allow detailed characterisation of the crystal structure.

Relative molecular weight of powder and parts was reported on. A significant increase in molecular weight was observed with building parts and it was also shown to increase with heating of the powder below the melt point (used powder) due to solid state polymerisation. Lboro virgin powder had a slightly higher molecular weight than TNO virgin powder though its significance is uncertain. It should be noted that batch to batch variation in ostensibly identical powder (e.g. different batches of Duraform) has not been considered and so the significance of the variation between the Lboro and TNO powder observed is currently unknown.

The most significant trends observed with mechanical properties were the changes to EaB. TNO parts showed higher EaB than Lboro parts and, within each group, building with used powder resulted in improved EaB. It is important to note that other important mechanical properties of SLS parts such as tensile strength and Young's modulus are similar to those obtained for traditionally processed samples such as injection moulding while EaB of SLS parts, however, lags far behind. This highlights the importance of investigating SLS material characteristics in relation to EaB. In this study increased molecular weight of used powder was related potentially to improved EaB of parts. Other factors could also be considered however. This paper demonstrated the variability typically encountered in SLS of Nylon 12 material and provided commentary and analysis. Molecular weight had been considered indirectly in other studies using the melt flow procedure to determine melt viscosity. This present study provided average molecular weight values for the first time however further study is required to understand properly the relationship between molecular weight and the variability observed in mechanical properties. In depth study in this specific area should comment on such aspects as changes in lamellae thickness distribution, chain entanglement density and tie-molecule density.

The porous nature of SLS parts is understood to be at least partly responsible for the low EaB relative to that of conventionally produced parts [33]. Another potential issue is that of various boundaries and interfaces within the part. The presence of unmelted particle cores leads to a composite-like structure. As such, inter-crystal-form and perhaps, inter-spherulite interfaces may have varying influence on mechanical properties. A strong inter-crystal-form interface (between particle core and surrounding melted/crystallised region) could lead to the highly crystalline γ-form being locked in a γ-form matrix of the melted/crystallised region with the micro-level mechanical properties of each γ-form particle core having a strong positive effect at the macro-level, i.e. the mechanical properties of the SLS part. A weak inter-crystal-form interface however could lead to rupture of the core from the matrix under relatively weak stress resulting in rapid crack formation and propagation and thus inferior mechanical properties such as low EaB, i.e. brittleness.

Further work could focus on in depth characterisation of the crystal forms present in SLS processed material and the precise effects of different processing and other parameters on these.

It would be interesting to investigate methods to quantify the amount of particle cores in specimens. Material interfaces, particularly that between the particle core and melted/crystallised region, could also be investigated. Effects of molecular weight on melt viscosity and their effects on processing and mechanical properties have not been discussed in this report and would also be a useful topic to pursue. This paper considered reproducibil-
ity of mechanical properties however further work could also investigate geometry and accuracy issues since this is also important to control. Research such as the current paper, focuswd in the various avenues can lead to improvements in reproducibility using existing material and equipment and will also be useful for developing new materials and hardware.

Acknowledgements

The work carried out at Loughborough University was supported by Solid Concepts and 3D Systems.

References


Appendix 7. Comparison of micrographs in polarised and un-polarised mode

Figure 158 Un-polarised x40 magnification (Fill Laser Power – Low)

Figure 159 Polarised x40 magnification (Fill Laser Power – Low)
Figure 160 Un-polarised x10 magnification (Fill Laser Power - Low)

Figure 161 Polarised x10 magnification (Fill Laser Power - Low)
Appendix 8. Original DSC traces for Chapter 8

Shown below are the original DSC traces used to generate the ‘averaged’ traces in Chapter 8. For each test the 5 DSC runs performed are superimposed on single charts.

Figure 162 Original DSC traces for ‘Default’

Figure 163 Original DSC traces for ‘Part Heater Set Point – High (150)’
Figure 164 Original DSC traces for 'Part Heater Set Point – Low (146)'

Figure 165 Original DSC traces for 'Slicer Fill Scan Spacing – High (0.13mm)'

Figure 166 Original DSC traces for ‘Slicer Fill Scan Spacing – Low (0.17mm)’

Figure 167 Original DSC traces for ‘Fill Laser Power – High (13.5W)’
Figure 168 Original DSC traces for 'Fill Laser Power – Low (9.5W)

Figure 169 Original DSC traces for 'Fill Scan Count – High (2)
Figure 170 Figure 156 Original DSC traces for 'Fill Scan Count – High (3)
## Appendix 9. DSC readings

<table>
<thead>
<tr>
<th></th>
<th>Specimen mass (mg)</th>
<th>Heat (J/g)</th>
<th>Core Peak Temp</th>
<th>Core Peak Height</th>
<th>Background Peak Temp</th>
<th>Background Peak Height</th>
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<tbody>
<tr>
<td>DEF</td>
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<td>1.15</td>
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Figure 171 DSC readings